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Research Support for Integrated Atmospheric Studies at Mace Head

Authors: Darius Ceburnis, Colin D. O'Dowd, Stephen G. Jennings and Margaret Ryan

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National University of Ireland, Galway

Authors:

Darius Ceburnis, Colin D. O'Dowd, Stephen G. Jennings and Margaret Ryan

ENVIRONMENTAL PROTECTION AGENCY
An Ghníomhaireacht um Chaomhnú Comhshaoil
PO Box 3000, Johnstown Castle, Co. Wexford, Ireland

Telephone: +353 53 916 0600 Fax: +353 53 916 0699
Email: info@epa.ie Website: www.epa.ie

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The EPA Research Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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Project Partners

Dr Darius Ceburnis
School of Physics and Centre for Climate and Air Pollution Studies
Environmental Change Institute
National University of Ireland, Galway
Galway
Ireland
Tel.: +353 91 493 437
Email: darius.ceburnis@nuigalway.ie

Professor Colin D. O'Dowd
School of Physics and Centre for Climate and Air Pollution Studies
Environmental Change Institute
National University of Ireland, Galway
Galway
Ireland
Tel.: +353 91 493 306
Email: colin.odowd@nuigalway.ie

Professor Stephen G. Jennings
School of Physics and Centre for Climate and Air Pollution Studies
Environmental Change Institute
National University of Ireland, Galway
Galway
Ireland
Tel.: +353 91 492 704
Email: gerard.jennings@nuigalway.ie

Ms Margaret Ryan
Met Éireann Analytical Laboratory
Glasnevin Hill
Dublin 9
Ireland
Tel.: +353 1 806 4227
Email: lab@met.ie

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Executive Summary

Under the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (CLRTAP), member countries have an obligation to address scientific issues such as the effect of hemispheric transport of air pollutants on air pollution concentrations in the Northern Hemisphere for a range of air pollution parameters, including fine particles and their precursors, ozone and their precursors and acidifying substances.

This fellowship project was funded by the Environmental Protection Agency (EPA) Ireland to support extensive research efforts on particulate matter (PM) studies in Ireland and at Mace Head station, particularly for building a knowledge base and establishing and sustaining long-term measurement series at the station. The fellowship was devoted to supporting various research activities at Mace Head and providing a continuity element between the projects undertaken at Mace Head.

One of the key areas that this fellowship project addressed was PM chemical composition measurement series. There is still a relative lack of knowledge of PM chemical composition and of sources of PM in Ireland. Long-term observations of the chemical composition of $PM_{2.5}$ and $PM_{2.5–10}$ revealed significant reduction trends of pollutants over the last 10 years. The trends were consistent between stations at Mace Head and Valentia and concurrent with decreasing emissions in Ireland and worldwide. The sulfate trend quantitatively matched the reduction in sulfur dioxide concentrations and total sulfurous emissions in Ireland. This has important policy implications as it demonstrates the value of continuing long-term monitoring of PM and the success of the emissions reduction policy in Ireland and beyond.

One of the research support activities carried out during the fellowship period was an intensive observation campaign during the Eyjafjallajökull eruption in Iceland in 2010. During the 2-month eruption period, measurements at Mace Head, together with the rapidly developed forecast capability, facilitated numerous advisories given to the Irish Aviation Authority by Professor Colin O'Dowd. Mace Head station was strategically located with respect to advancing volcanic ash plumes from Iceland, enabling a reliable update of the situation in real time. Darius Ceburnis himself gave an introductory interview for the Irish television channel TG4 on the day of the first ash plume arrival over Ireland. Two public lectures were later given as an overview of the eruption impacts for Ireland with respect to air quality and flight safety. The intensive observation carried out during the Eyjafjallajökull eruption revealed that Mace Head is an ideal location, depending on meteorology, for observing volcanic ash advections from Iceland; it resulted in extensive efforts being made towards building volcanic ash detection and forecast capacity for the aviation industry.

The most advanced scientific topic explored during the fellowship period was devoted to carbonaceous matter source apportionment using a dual isotope technique performed for the first time at the European Monitoring and Evaluation Programme (EMEP) network station Mace Head. Carbon isotope analysis of aerosol samples demonstrated the benefits of the technique, suggesting that a proper carbon budget can be obtained, enabling more precise source apportionment of carbonaceous PM at a given location. It demonstrated the potential of the novel approach of combining stable carbon and radiocarbon measurements for unambiguous source apportionment of organic matter.

Another important intra-activity interaction was envisaged in combining offline and online chemical composition measurements, i.e. aerosol mass spectrometry (AMS) and filter or impactor data. AMS is a powerful tool for aerosol studies, but its findings need to be verified and supported by other measurements. AMS has been deployed on a 24/7 basis at Mace Head since 2008, which enabled a comprehensive long-term comparison of near real-time data with offline data. Such a comparison over a yearly or longer period of time has not been performed anywhere in the world because of the lack of continuous AMS measurements. Darius Ceburnis closely interacted and collaborated with researchers

directly responsible for AMS measurements, which resulted in numerous peer-reviewed publications. High time resolution measurements using aerosol mass spectrometers clearly showed their advantage in studying urban and marine environments in high detail. For example, the study of pollution sources in Cork city has demonstrated that wood burning in Ireland contributes significantly to carbonaceous PM, despite being a minor fuel type, with a similar conclusion attributed to the use of peat and coal as domestic fuel. Clearly, a tighter control of the domestic fuel market would have a profound effect on pollution levels. It was proven for the first that AMS can quantitatively measure sea salt unambiguously, demonstrating that all major chemical species can be reliably monitored by the online technique. It is recommended that offline chemical analysis techniques should be combined with near real-time analytical techniques such as AMS for studying pollution episodes and regional and intercontinental transport of aerosols.

The approach to the project resulted in close interactions with many researchers, including those from outside Ireland, during international field campaigns or collaborative projects. The comprehensive dataset accumulated over the years of measurements at Mace Head is an excellent source for various research studies, especially modelling studies. There have been numerous requests for the data from outside the research group and the fellowship project ensured that such requests were managed efficiently and on a timely basis. During the project a significant effort was devoted to supporting national and international research campaigns at Mace Head: EUSAAR (European Supersites for Atmospheric Aerosol Research), EUCAARI (European Integrated project on Aerosol Cloud Climate and Air Quality Interactions), ACTRIS (Aerosol, Clouds and Trace Gases Research Infrastructure) and MONET [Monitoring Network (for persistent organic pollutants)]. Thirty-one peer-reviewed papers were contributed during the project, which demonstrated the significance of the research being supported at Mace Head research station and the efficient use of the expertise of the fellowship holder. Three intensive measurement campaigns co-ordinated by EMEP were facilitated at Mace Head.

1 Introduction

A number of air pollutants including particulate matter (PM) contribute to regional acidification, eutrophication, and air pollution across Europe and here in Ireland. Under the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (CLRTAP), member countries have an obligation to address scientific issues such as the effect of hemispheric transport of air pollutants on air pollution concentration in the Northern Hemisphere for a range of air pollution parameters, including fine particles and their precursors, ozone and its precursors and acidifying substances. This will necessitate the development and sustained support of an integrated system of observational data sources and of predictive models in order to address these important issues and related scientific questions, such as the apportionment of sources to receptor regions. The observations require the quality assessment of data and its archiving, which is resource demanding, prior to submission to a national database.

There is still a relative lack of knowledge of the chemical composition of PM and of sources of PM in Ireland. For example, measurements of the chemical composition of total suspended particulate (TSP) matter or of PM in regions outside urban areas have been fairly intermittent in Ireland up to now, as summarised in Table 1.1. Ceburnis *et al*. (2006) have documented that Ireland is often a sink of airborne pollutants rather than a significant contributor or a source.

The AEROCE (Atmosphere/Ocean Chemistry Experiment) measurement programme (1988–1994) at the Mace Head Atmospheric Research Station (co-ordinated by Prospero *et al*., University of Miami) permitted measurements of the chemical (inorganic ion) mass concentration of the main aerosol species in TSP matter. Aerosol TSP chemical composition measurements resumed in late 2000, along with measurement of aerosol radiative data, through funding support from the National Development Plan, administered by the Environmental Protection Agency (EPA). This work provided useful natural background levels for sea salt mass concentration (Jennings *et al*., 2006b), albeit for a relatively short measurement period.

The Higher Education Authority (HEA), through the Programme for Research in Third Level Institutions (PRTLI) cycle IV, funded a very significant expansion of the research infrastructure at Mace Head in 2007–2008. Numerous state-of-the-art instruments were acquired to expand the atmospheric research base and to maintain international recognition of atmospheric science in Ireland. Such an expansion clearly needs sustained institutional support for research management at Mace Head.

The international importance of Mace Head station can be demonstrated by the number of peer-reviewed publications acknowledging the site, which is close to 300, far more than for any other research infrastructure worldwide (ISI Web of Science). The development of the Atmospheric Research Station

Table 1.1. Summary of PM and chemical composition measurements at Mace Head

Year	Measurement scope
1988–1994	AEROCE (Atmosphere/Ocean Chemistry Experiment) measurements of trace metals and major ions
1996–1997	ACSOE (Atmospheric Chemistry Studies in Oceanic Environment) project
1998–1999	PARFORCE (Particle Formation and Faith in Coastal Environment) European Union Framework Programme 5 (FP5) project and campaign-long sampling of PM
1998	2-month campaign for sampling total carbon (TC) and water-soluble carbon
1998–1999	14-month sampling of TC, WSOC (water-soluble organic carbon) and black carbon at Mace Head
2001–2005	TSP sampling and major ion analysis of sectored and unsectored samples in parallel
2007–	$PM_{2.5}$ and $PM_{2.5–10}$ sampling of daily samples for major ion analysis, which the fellowship is meant to facilitate
2008–	High-resolution time-of-flight aerosol mass spectrometer installed for continuous measurements at Mace Head

at Mace Head began in 1957 with the search for a suitable site to undertake research on air from the Atlantic Ocean that was not complicated by nearby sources of man-made pollutants. The site finally chosen was a disused coastal watch lookout post, constructed during World War II, on top of Mace Head, which is a low rocky promontory west of Carna, County Galway, close to the centre of the Atlantic coast of Ireland and of Europe. Winds from a direction between 180° and 300° from the north reach it without passing over any inhabited area, and the rest of the countryside around it is sparsely populated. Its situation on the interface between the land and the ocean is advantageous for the study of oceanic and continental air masses and for ocean–atmosphere exchange processes. It is located about 55 miles or 88 km west of Galway city.

1.1 Objectives

Some of the specific objectives of the fellowship project can be outlined as follows:

- enablement of new $PM_{2.5}$ and PM_{10} mass concentration measurements and of their chemical inorganic ion mass concentration measurements at the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) Mace Head Atmospheric Research Station, as recommended by the WMO GAW European Research Centre (ERC) review report of Barrie and Puckett (2006);
- operational support for instrumentation located at Mace Head;
- analysis of the hemispheric transport of pollutants, such as PM mass and chemical composition data;
- support of ongoing research programmes and projects at Mace Head, as agreed between EPA Ireland and the National University of Ireland, Galway, and of relevant upcoming programmes;
- develop and support data collection and archival data systems for reporting to national (e.g. EPA) and international (e.g. European Monitoring and Evaluation Programme – EMEP, WMO GAW) bodies;
- integration of various measurements performed at Mace Head into comprehensive research studies, resulting in a number of peer-reviewed publications.

The objectives of the fellowship project were diverse and sometimes not related to each other, given the research support nature of the fellowship. Therefore, some of the activities were planned and proposed whereas many others were not envisaged before the start of the project and were only established during the course of the project.

Additional objectives or activities can be outlined as follows:

- An intensive observation period during the Eyjafjallajökull eruption in Iceland in 2010. During the 2-month period, measurements at Mace Head, together with the rapidly developed forecast capability, facilitated numerous advisories given to the Irish Aviation Authority by Colin O'Dowd. Mace Head station was strategically located with respect to the advancing volcanic ash plumes from Iceland, enabling a reliable update of the situation in real time. Darius Ceburnis himself gave an introductory interview to the Irish television station TG4 on the day of the first ash plume arrival over Ireland. Two public lectures were later given as an overview of the eruption impacts for Ireland with respect to air quality and flight safety.
- The approach to the project resulted in close interactions with many researchers, including those from outside Ireland during international field campaigns or collaborative projects. The comprehensive dataset accumulated over the years of measurements at Mace Head is an excellent source for various research studies, especially modelling studies. There have been numerous requests for the data from outside the research group and the fellowship project ensured that such requests were managed efficiently and on a timely basis.
- An even more important interaction was envisaged in combining offline and online chemical composition measurements, i.e. aerosol mass spectrometry (AMS) and filter or impactor data. AMS, specifically high-resolution time-of-flight AMS (HR-ToF-AMS), is a powerful tool for aerosol studies, but it needs to be verified and supported by other measurements. AMS was deployed on a 24/7 basis at Mace Head, which enabled comprehensive long-term comparison of near real-time data with offline data. Such a

comparison has never been performed anywhere in the world because of the lack of continuous AMS measurements, specifically HR-ToF-AMS measurements. Therefore, the research fellow involved with this project closely interacted and collaborated with researchers who were directly responsible for AMS measurements, which resulted in a significant number of publications.

2 Measurements of Aerosol Chemical Composition and the Decadal Trends

This chapter summarises contributions of the current fellowship towards aerosol chemical composition measurements in Ireland. The contributions add an important component towards building up a long-term measurement strategy in which Mace Head station is considered a key monitoring site and part of the national network. The measurements were performed not only at Mace Head, but also at other locations nationally, where the instrument base moved sometimes for research campaigns. All those studies performed outside Mace Head contributed towards other research activities and projects and involved either traditional filter methods or state-of-the-art aerosol mass spectrometric techniques for studying the chemical composition of PM and its sources.

2.1 Decadal Trends in Particulate Matter Components

The availability of air pollution data from sites such as Mace Head was deemed to be crucial. The site had received regular research funding from EPA Ireland over the previous decades and, therefore, contributed towards providing input to national policy documents and to international convention task forces on air pollution and climate change issues, which will directly impact the framing of new policies and legislation and their implementation in Ireland. However, an international review – the WMO GAW ERC review report (Barrie and Puckett, 2006) – of GAW sites in Ireland found that Mace Head was of unique importance with regard to establishing a reliable national monitoring network.

An inorganic composition of fine and coarse PM has been monitored at Mace Head since 2001. Although other locations in Ireland may have a longer record (e.g. measurements at Valentia started in the early 1980s), some of the chemical components were not reliably quantified. For instance, sulfate of sea salt origin may significantly contribute to the total sulfate concentration; therefore, non-sea salt sulfate ($nssSO_4$) quantification is possible only by quantifying the sea salt fraction, which requires quantification of sodium. Ammonium (NH_4) is another ambiguous compound originating from agriculture.

Figure 2.1 shows the decadal trends of $nssSO_4$, nitrate (NO_3) and NH_4 at Mace Head and Valentia stations. The trends for NH_4 have a very similar slope, but different absolute concentrations, because of ammonia emissions from surrounding pastures around Valentia station; this issue is being addressed by the planned relocation of the sampling equipment. Nss sulfate, NO_3 and NH_4 concentrations have been decreasing in Ireland over the last decade, with a less significant trend observed at Valentia because of the availability of fewer data (see Figure 2.1).

The above two stations have the longest uninterrupted chemical composition measurement record in Ireland, with the Valentia record starting in 1980 and the Mace Head record starting in 2001, using the same methodology. Overall, decadal trends at Mace Head and Valentia compare very well.

Sulfate concentrations have been steadily decreasing all over Europe at a similar pace (Figure 2.2), with slightly faster rates at more polluted sites and slightly slower rates at cleaner locations. It can be estimated by extrapolating the established trends that $nssSO_4$ concentrations may reach the northern hemisphere background levels in 2015–2030, depending on the pollution level, as sulfate concentrations are becoming similar to the levels observed at other remote locations.

Despite the different inorganic components having different precursors, their decadal trends were remarkably similar, as depicted in Figure 2.3, and species such as sulfate and nitrate exhibited a significant correlation despite their different sources. Sulfate is mainly a product of SO_2 emissions from thermal power stations and sulfurous fuel combustion, whereas nitrate is mainly a product of emissions from traffic, with contributions from stationary sources similar to those for sulfate. It clearly suggests that the comprehensive effort to reduce all types of emissions

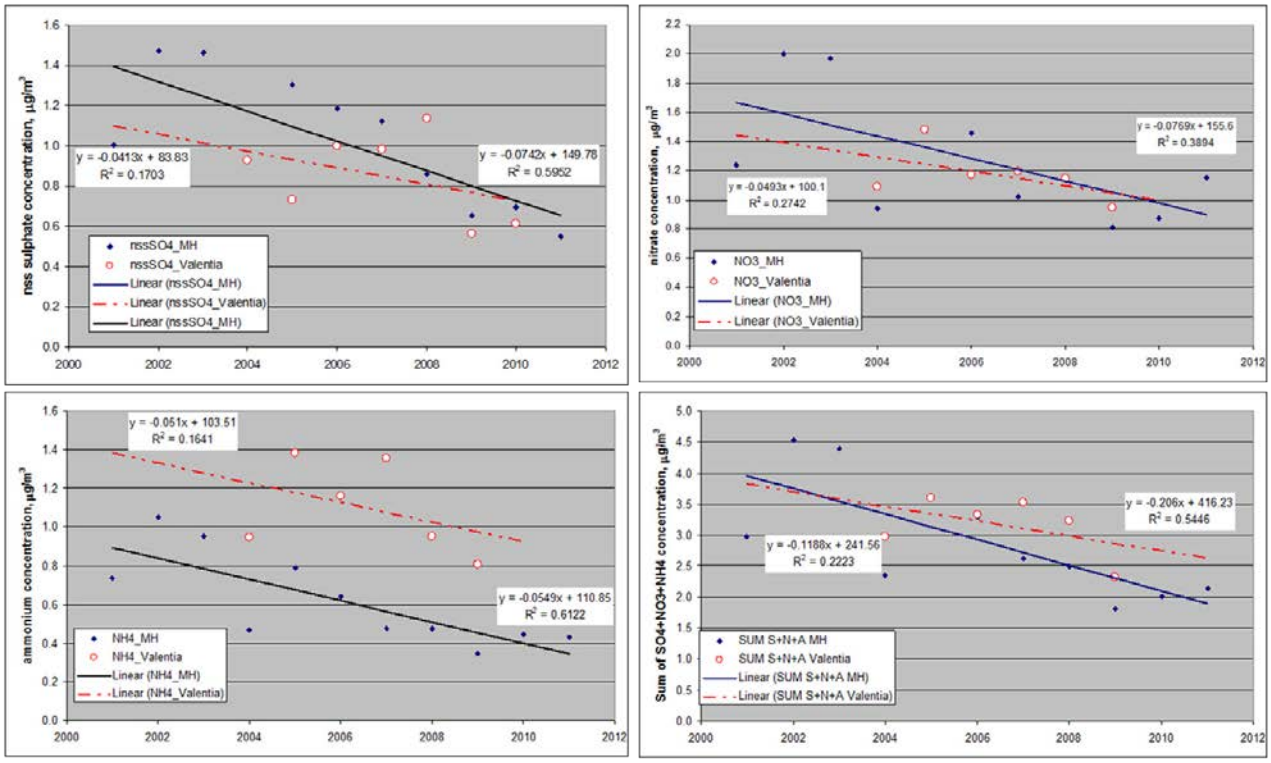


Figure 2.1. Nss sulfate, NO_3 and NH_4 concentrations in Ireland over the last decade at Mace Head and Valentia stations.

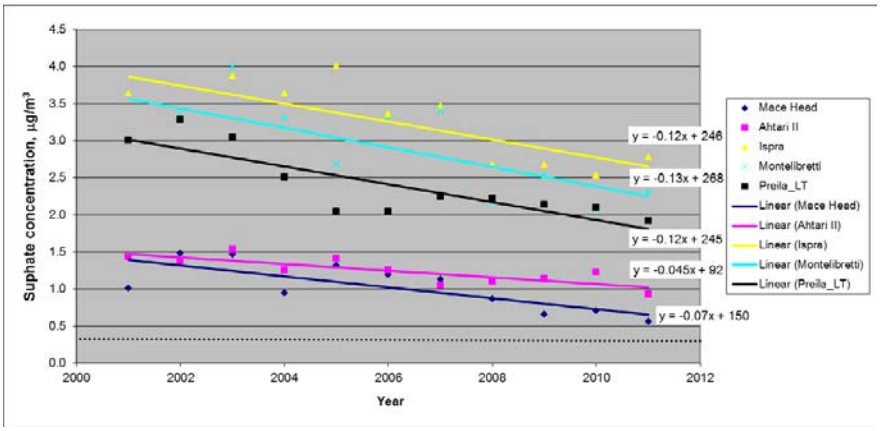


Figure 2.2. Sulfate concentration trends over Europe: Mace Head, Ahtari II (Finland), Ispra (northern Italy), Montelibretti (southern Italy) and Preila (Lithuania). The horizontal dotted line signifies the biogenic sulfate concentration over the North-East Atlantic.

was a success story over Europe, with Mace Head being a representative observational location almost equally affected by both European and North Atlantic air masses. Figure 2.4 (middle) shows a decadal trend of decreasing emissions in Ireland, accompanied by a corresponding trend for SO_2 at Valentia (left) and corresponding correlation of SO_x emissions in Ireland and the sulfate concentration at Mace Head (right).

2.2 Characterisation of Aerosol Chemical Composition in Cork City

The objective of this study was to characterise the fine PM component detected at an urban background site in Cork using an array of online and offline aerosol techniques, in order to improve the source identification of atmospheric aerosol particles at

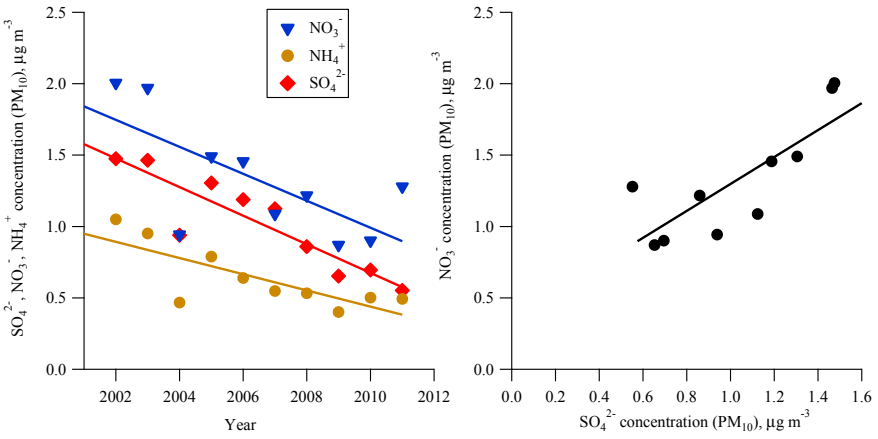


Figure 2.3. Decadal trends of inorganic components at Mace Head (left) and correlation between sulfate and nitrate (right).

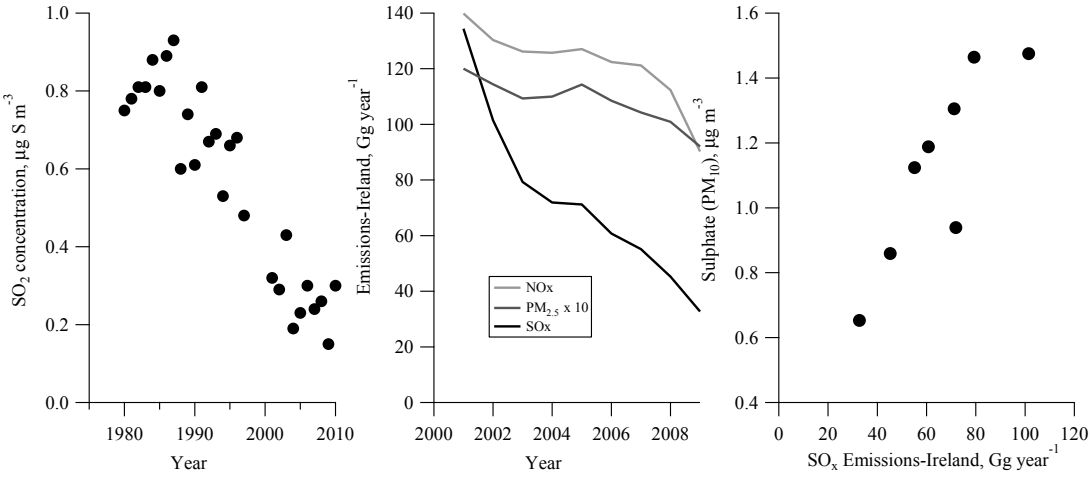


Figure 2.4. Long-term trend of SO_2 concentrations at Valentia (left); decadal trend in emissions of various pollutants in Ireland (middle); and the correlation between sulfate concentrations at Mace Head and sulfurous emissions in Ireland (right), which follows a similar trend to that in other developed countries.

very high time resolution. Until a few years ago, most urban air quality studies were limited to mainly inorganic components of PM or, at most, included total organic carbon. Two different state-of-the-art online AMS techniques were deployed in this study: ATOFMS (aerosol time-of-flight mass spectrometry) and HR-ToF-AMS. ATOFMS provides single particle information on the abundance of different types of aerosol particles as a function of particle size with high time resolution (Dall'Osto *et al*., 2004), whereas HR-ToF-AMS quantitatively measures mass concentrations of the non-refractory (flash evaporated at 600°C) aerosol components, as well as species-resolved size distributions (Canagaratna *et al*., 2007). Although the ATOFMS does not have clear source apportionment capabilities because of the difficulties in absolute quantification of its outputs, the AMS has proven itself to be a powerful tool for this purpose (Canagaratna *et al*., 2007). Additionally, we also used data from offline filter-based techniques to support the analysis of particle types obtained from the statistical analysis of the AMS datasets.

The ambient wintertime background urban aerosol particles in Cork city, Ireland, were characterised using AMS with two different instruments, which synergistically enhanced each other despite being somewhat different with respect to particle evaporation and subsequent ionisation. Single particles detected by ATOFMS were classified into five organic-rich particle types, internally mixed to different proportions with elemental carbon (EC), sulfate and nitrate, with the remaining 7% being predominantly inorganic in nature. Non-refractory PM_1 aerosol was characterised

using HR-ToF-AMS (Aerodyne) and was also found to comprise organic aerosol as the most abundant species (62%), followed by nitrate (15%), sulfate (9%), ammonium (9%) and chloride (5%). Positive matrix factorisation was applied to the HR-ToF-AMS organic matrix and five distinct aerosol sources were found to describe the variance in the data well. Specifically, "hydrocarbon (CH)-like" organic aerosol comprised 20% of the mass, "low-volatility" oxygenated organic aerosol (LV-OOA) comprised 18%, "biomass burning" organic aerosol (BBOA) comprised 23%, non-wood solid-fuel combustion "peat and coal" organic aerosol (PCOA) comprised 21% and, finally, a species type characterised by primary m/z peaks at 41 and 55, similar to previously reported "cooking" organic aerosol (COA), but possessing different diurnal variations from what would be expected for cooking activities, contributed 18%. The "cooking" aerosol type will require further analysis and experimental evidence to verify its origin. Moreover, controlled combustion experiments in the laboratory made it possible to separate peat and coal sources, as presented in Figure 2.5. Correlations between the different particle types obtained by the two aerosol mass spectrometers are also discussed (Dall'Osto *et al.*, 2013). Despite wood, coal and peat being minor fuel types used for domestic space heating in urban areas, their relatively low combustion efficiencies result in a significant contribution to the PM_1 aerosol mass (44% and 28% of the total organic aerosol mass and non-refractory total PM_1, respectively).

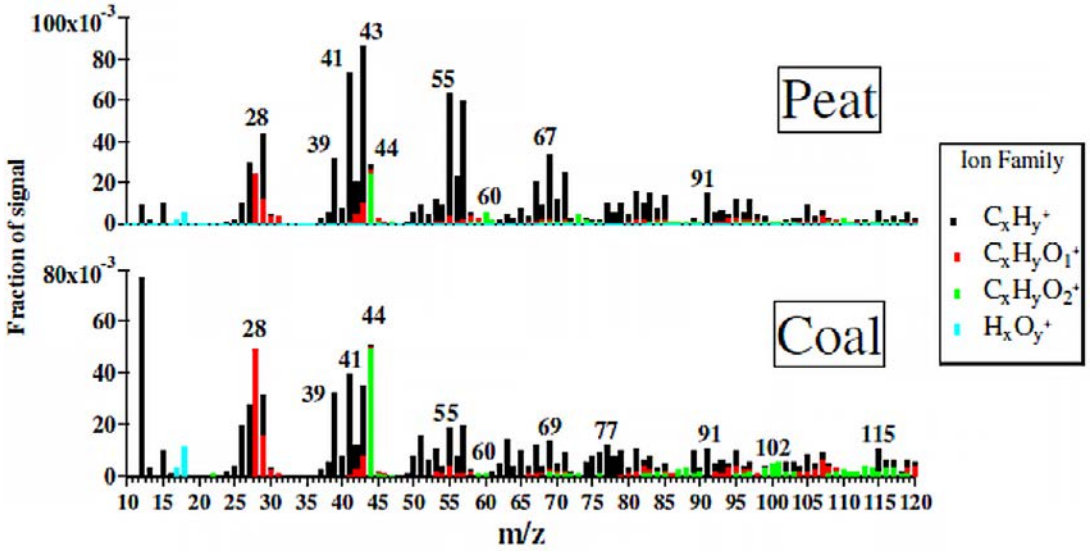


Figure 2.5. Mass spectra of the peat and coal combustion laboratory experiment. The ion families of the different factors are shown in the legend. Reproduced from Dall'Osto *et al.* (2013). This is an Open Access article distributed in accordance with the terms of the Creative Commons Attribution Unported (CC BY 3.0) license, which permits others to distribute, remix, adapt and build upon this work, for commercial use, provided the original work is properly cited. See http://creativecommons.org/licenses/by/3.0/.

3 Aerosol Mass Spectrometry Studies

This chapter summarises the activities of the fellowship project towards exploiting the full potential of HR-ToF-AMS for advanced chemical composition studies at Mace Head. The instrument's full potential was realised only by running it continuously, to be able to observe natural environmental phenomena often missed by traditional techniques because of time resolution issues or simply not running it continuously. A high-resolution time-of-flight mass spectrometer has been continuously deployed at Mace Head since 9 May 2008. The fellowship holder actively contributed towards exploitation and maintenance of the instrument, which required advanced knowledge, as well as time. The instrument deployment coincided with the field campaign of the Framework Programme 6 (FP6) EUCAARI project (European Integrated project on Aerosol Cloud Climate and Air Quality Interactions). An excellent AMS dataset was obtained during the 4 weeks of the campaign and the study was published in 2010 (Dall'Osto *et al.*, 2010a). Significant efforts were made to ensure that the instrument was running 24/7, obtaining the first long-term AMS dataset in the world. Some of the case studies using AMS measurements and complementary data for inorganic components are highlighted in the following sections. A seasonal analysis of a 3-year dataset has been completed (Ovadnevaiete *et al.*, 2014).

3.1 Organic Matter Plumes and the Dichotomous Behaviour of Primary Marine Organic Matter over the North Atlantic

It was long considered that the concentration levels and processes observed in the atmosphere were largely in steady state or were changing slowly from clean background levels to a polluted situation. However, deployment of HR-ToF-AMS at Mace Head revealed for the first time that evolution of organic matter (OM) concentrations and its composition are changing rapidly, especially in clean air. These events or plumes of OM in clean marine air were detected and documented for the first time, as previously a high time resolution instrument had not been run continuously. During one such event, submicron organic marine aerosol plume concentrations peaking at 3.8 mg m^{-3} were detected in clean maritime air masses. These concentrations were far greater than those previously determined by offline techniques and can exceed typical terrestrial concentrations of organic aerosol particles. The organic mass comprised 77% of the total submicron non-refractory mass and such plumes were associated with regions of high biological activity and moderately high wind speeds over the North-East Atlantic. High-resolution mass spectra analysis revealed a unique marine organic aerosol fingerprint (Figure 3.1) compared with anthropogenic organic aerosol and, in particular, anthropogenic CHs. In total,

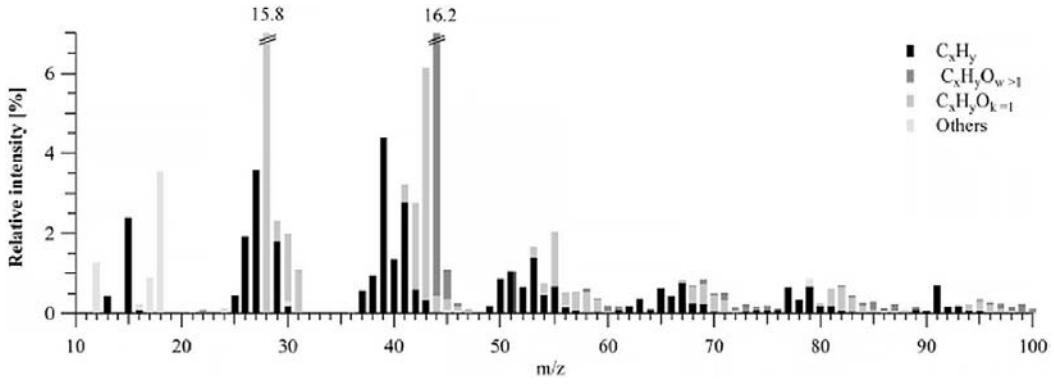


Figure 3.1. HR-ToF-AMS mass spectra [major organic family CH and CHO (oxygenated CH) only] of a marine organic plume detected on 15–16 August 2009 at Mace Head, Ireland. Reproduced with permission from Ovadnevaite *et al.* (2011a). Copyright 2011 by the American Geophysical Union.

37% CH and 63% oxygenated CH (CHO) speciation was observed for the organic mass, indicating that at least 37% of the organic mass is produced via primary sea spray. The CH and CHO species were highly correlated ($r > 0.99$), suggesting that a significant, if not dominant, fraction of the oxygenated component is also likely to be of sea spray in origin. The conclusions of this study were supported by $PM_{2.5}$ sea salt mass measurements, which, despite low time resolution, strongly supported the AMS findings, as depicted in Figure 3.2. The above findings have been published in *Geophysical Research Letters* by Ovadnevaite *et al*. (2011a).

A follow-up study by Ovadnevaite *et al*. (2011b) demonstrated that, in addition to the observed very high concentrations of OM in clean marine air masses, organic sea spray physico-chemical properties revealed an apparent dichotomous behaviour in terms of water uptake. Specifically, sea-spray aerosol enriched in OM possessed a low hygroscopic growth factor (GF, ~1.25) while simultaneously having a cloud condensation nuclei/condensation nuclei (CCN/CN) activation efficiency of between 83% at 0.25% supersaturation and 100% at 0.75% supersaturation (Figure 3.3). In contrast, the activation efficiency of particles dominated by $nssSO_4$ ranged between 48% and 100% over the supersaturation range 0.25%–1%. Simultaneous retrieval of the cloud droplet number concentration (CDNC) during primary organic aerosol plumes revealed CDNC concentrations of 350 cm^{-3} for organic mass concentrations of 3–4 mg m^{-3}. It was demonstrated that the retrieved high CDNCs under clean marine conditions can be explained only by organic sea spray, which corroborates the high CCN activation efficiency associated with primary organics. Figure 3.4a shows temporal evolution of CDNCs, which can be quantitatively tracked only if CCN were considered to be produced by sea spray – a combination of sea salt and primary OM. Figure 3.4b demonstrates excellent agreement between the composition-derived CDNC and the remotely retrieved CDNC. It is postulated that marine hydrogels are responsible for this dichotomous behaviour.

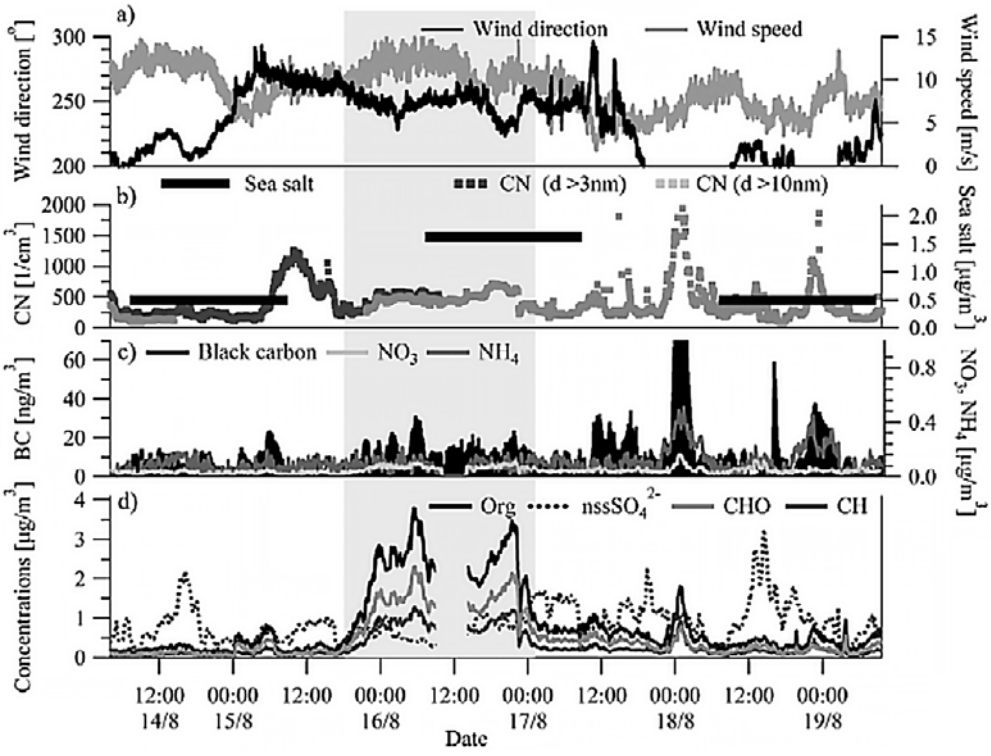


Figure 3.2. Temporal (UTC) trends of (a) wind speed, wind direction, (b) CN concentrations and $PM_{2.5}$ sea salt mass, (c) black carbon mass and AMS-derived NO_3 and NH_4 and (d) AMS-derived total organic, $nssSO_4$, CHO and CH mass loadings. The time period in the grey colour visually emphasises the marine primary organic aerosol plume detected (15–16 August 2009). The data gap around 12:00 on 16 August was due to routine AMS calibration. Reproduced with permission from Ovadnevaite *et al*. (2011a). Copyright 2011 by the American Geophysical Union.

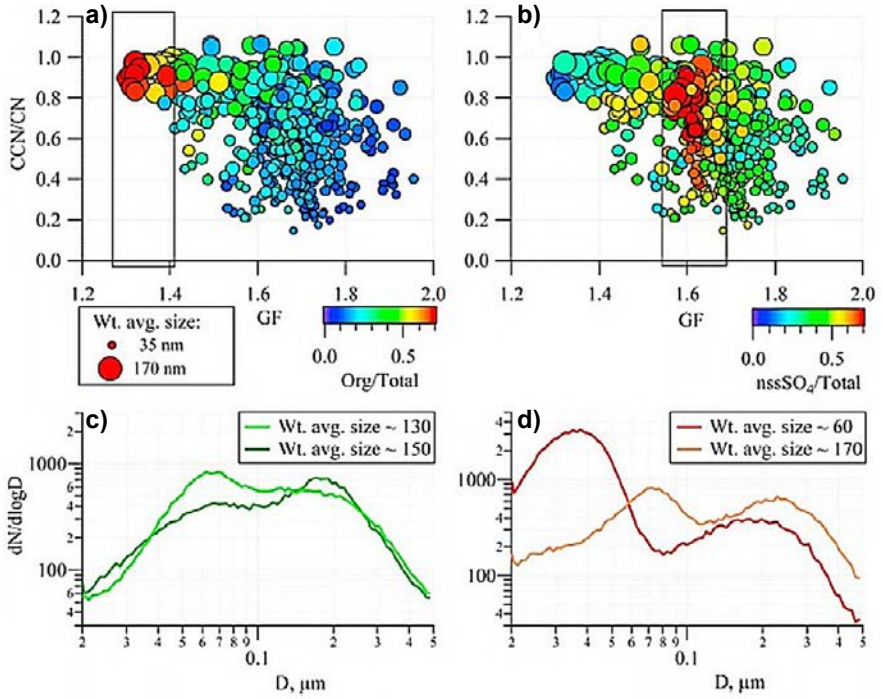


Figure 3.3. (a and b) CCN 0.75% activity (CCN/CN) as a function of GF [at 90% relative humidity (RH)], chemical composition (colour scale) and weighted average particle size (size of the circle). CN is the total particle number above 20 nm in diameter; the colour scale represents the dominance of a given chemical species. Measurement periods: 2–27 May 2009, 11–28 August 2009 and 14 July–12 August 2010. Note that the measurement periods cover periods much longer than individual plume events. In (a), the boxed region highlights particles dominated by primary OM whereas, in (b), the boxed region highlights the particles dominated by sulfate. Particles to the extreme right of both figures are dominated by sea salt mass. (c) Two organic-dominated size distributions (on 16 August 2009 from 00:00 UTC to 22:00 UTC and 5 August 2010 from 13:30 UTC to 16:30 UTC) and their resultant weighted diameters and (d) the same for sulfate-dominated distributions (on 2 August 2010 from 21:00 UTC to 22:00 UTC and 9 August 2010 from 06:00 UTC to 10:00 UTC). Reproduced with permission from Ovadnevaite *et al.* (2011b). Copyright 2011 by the American Geophysical Union.

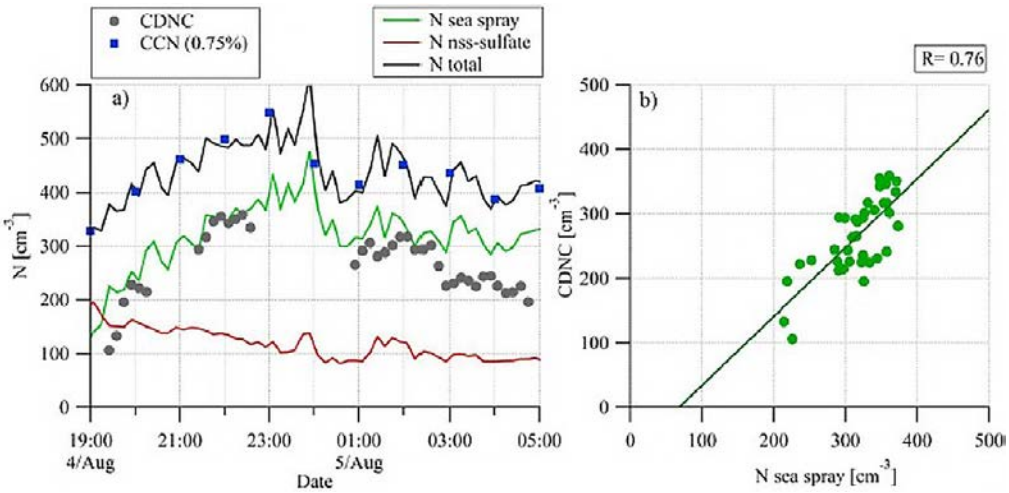


Figure 3.4. (a) CDNC, measured CCN 0.75% and calculated sea-spray, sulfate and total nuclei concentration. (b) CDNC as a function of sea-spray particle concentration. Reproduced with permission from Ovadnevaite *et al.* (2011b). Copyright 2011 by the American Geophysical Union.

3.2 Submicron Sea Salt Concentrations and Wind Speed-driven Source Fluxes Studied by HR-ToF-AMS

The HR-ToF-AMS technique was evaluated for its ability to quantify submicron sea salt mass concentrations. The evaluation, which has been published by Ovadnevaite *et al*. (2012), included both laboratory and field studies. Quantification of the sea salt signal by HR-ToF-AMS was achieved by taking the $^{23}Na^{35}Cl^{+}$ ion as a surrogate for sea salt and then identifying a calibration scaling factor through a comparison with mono-disperse laboratory-generated sea salt aerosol. Ambient sea salt concentrations calculated using this method agreed well with those obtained by ion chromatography of filter samples, as presented in Figure 3.5, following a 1:1 regression slope and a correlation coefficient of $R = 0.93$. Such a good agreement between two radically different measurement techniques was demonstrated for the first time. A key advantage of this AMS-based method is that it allows for high time resolution measurements of sea salt (5 minutes) along with the speciation of other chemical compounds, including primary organics contributing to sea spray. The high time resolution sea salt measurement capability enabled the quantification of sea salt mass in both increasing and decreasing wind speed regimes up to 26 m s^{-1}. A sea salt mass flux source function was also derived and was found to have a power law wind speed dependency with an exponent of 3.1 for increasing winds and 2.3 for decreasing winds (Figure 3.6). A source function is a dependence of sea salt mass (source) on the wind speed at a 10 m height; therefore, it is a true mathematical function. It is common practice in aerosol science and atmospheric models to use those parameterisations. Comparison of the mass flux relationship in this study suggests that previous schemes based on the Monahan whitecap–wind speed approach significantly over-estimate the submicron mass flux. Both the whitecap–wind speed component and the differential whitecap–aerosol productivity component of the source flux function contribute towards the over-estimation.

This study clearly demonstrated a synergetic advantage of multiple measurement techniques, advancing knowledge of the key properties of air–sea exchange.

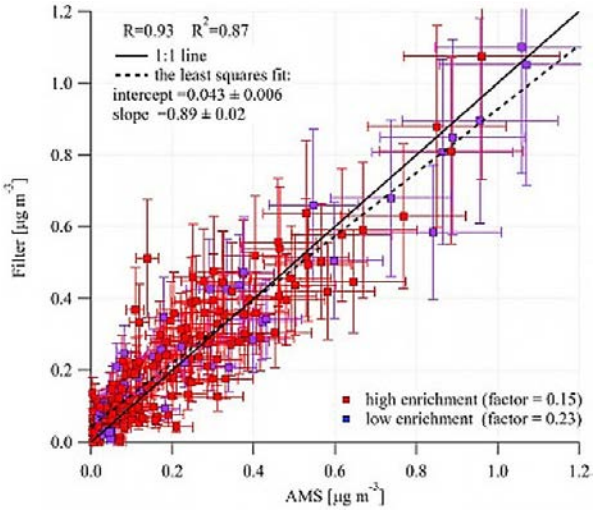


Figure 3.5. A comparison between HR-ToF-AMS and ion chromatography sea salt measurements. Colours represent different factors applied for the periods of low and high organic enrichment, when deriving the PM_1 sea salt concentration from $PM_{2.5}$ filter measurements. Error bars represent the ion chromatography and HR-ToF-AMS measurement Reproduced with permission from Ovadnevaite *et al*. (2012). Copyright 2012 by the American Geophysical Union.

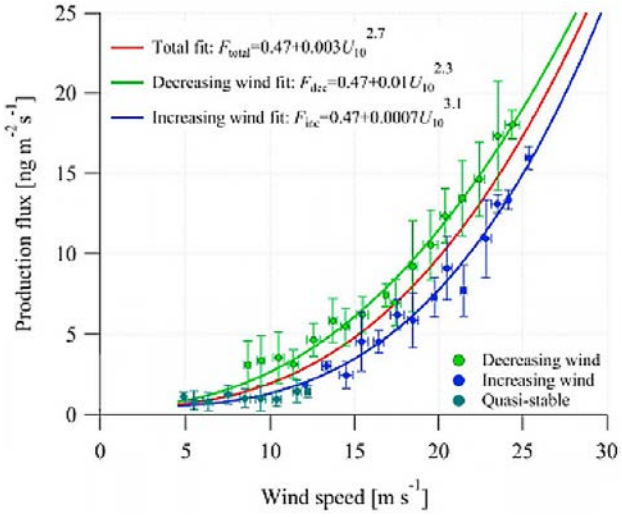


Figure 3.6. Sea spray production flux for increasing and decreasing wind speed history regimes. The intercept in the power function represents the starting aerosol flux at the onset of the whitecap, with the flux being 0 before the whitecap onset and making a step transition into the minimum value after the onset. Reproduced with permission from Ovadnevaite *et al*. (2012). Copyright 2012 by the American Geophysical Union.

4 Aerosol Chemical Fluxes

Aerosol chemical fluxes were studied as part of the EPA-funded project EASI-AQSIS (Exchange at the Air-Sea Interface: Air Quality and Climate Impacts), at no additional cost to the fellowship project of Darius Ceburnis. This chapter describes a deliverable outlined in the fellowship proposal as “Analysis of key source/production mechanisms of aerosol pollutants”. The work described in this chapter was conceived and fully realised by the fellowship holder in its entirety; therefore, more details are provided than for the various supported research activities, to demonstrate the extensive work undertaken during the fellowship project.

Marine aerosols contribute significantly to the global radiative budget and, consequently, changes in marine aerosol abundance and/or chemical composition have an impact on climate change through both direct and indirect effects. The North-East Atlantic region is of particular interest because of a combination of storminess, prevailing westerlies, bringing marine air masses into continental Europe, and biological activity in surface waters, which significantly affects the chemical composition of atmospheric PM (O’Dowd *et al*., 2004). OM has been observed in marine aerosol particles for many decades and has been linked to the enrichment of sea spray by biogenic matter transferring from the sea surface into the tropospheric boundary layer through bubble-mediated production processes (Blanchard, 1964; Hoffman and Duce, 1977; Middlebrook *et al*., 1998; Oppo *et al*., 1999; Russell *et al*., 2010). Significant progress has been made in understanding marine aerosol composition, which has been identified to consist of significant amounts of OM (Cavalli *et al*., 2004; Sciare *et al*., 2009), both water soluble and water insoluble. The understanding of marine aerosol chemical composition has historically progressed from it mainly consisting of sea salt and $nssSO_4$ (Charlson *et al*., 1987; O’Dowd *et al*., 1997) to it consisting of complex primary biogenic organic mixtures and states (Cavalli *et al*., 2004; Leck and Bigg, 2005; Russell *et al*., 2010; Decesari *et al*., 2011), as well as secondary organic compounds such as organic acids (Kawamura and Sakaguchi, 1999; Mochida *et al*., 2002; Turekian *et al*., 2003; Rinaldi *et al*., 2011) and recently discovered biogenic amines (Facchini *et al*., 2008a; Müller *et al*., 2009). The findings of Ceburnis *et al*. (2008) and Facchini *et al*. (2008b) independently confirmed that water-insoluble organic carbon (WIOC) in the marine atmosphere has a primary origin whereas water-soluble organic carbon (WSOC) is mainly of secondary or processed primary origin (Decesari *et al*., 2011); however, studies by Keene *et al*. (2007) and Russell *et al*. (2010) have provided evidence that even WSOC can largely be of primary origin.

The flux of sea spray aerosol has been studied previously as sea salt mass fluxes or aerosol size and number flux (O’Dowd and De Leeuw, 2007; de Leeuw *et al*., 2011). Apart from one or two studies, the flux experiments have typically focused on super-micron-sized particles. The eddy covariance method, introduced by Buzorius *et al*. (1998), allowed the study of submicron particle fluxes and sinks and has since been applied in a variety of environments: boreal and tropical forest (Buzorius *et al*., 1998; Ahlm *et al*., 2009), ocean (Nilsson *et al*., 2001; Geever *et al*., 2005; Norris *et al*., 2008; Brooks *et al*., 2009), desert (Fratini *et al*., 2007) and urban (Martensson *et al*., 2006; Martin *et al*., 2009). The eddy covariance method is typically used to study total particles fluxes. The technique has been modified to the relaxed eddy covariance method to allow the study of size-segregated particle fluxes (Gaman *et al*., 2004) or the disjunct eddy covariance method (Held *et al*., 2007). It should be noted, however, that, although the number of sea spray particles is dominated by submicron particles, mass is dominated by super-micron sizes and there is not a single method that is capable of measuring particles around the important boundary of 1 mm. None of the above techniques was suitable for studying chemically resolved fluxes, because chemical analysis typically requires a long sampling time (many hours for offline chemical analysis). Most recently, however, the eddy covariance system coupled with high-resolution AMS has been used to study chemically resolved fluxes (Nemitz *et al*., 2008; Farmer *et al*., 2011), but these were largely limited to areas with a relatively high concentration of species.

After the climatologically significant fraction of marine sea spray particles were found to contain biogenic OM compounds (O'Dowd *et al*., 2004), it became ever more important to determine the principal sources and sinks of marine OM. Tentatively, the source of biogenic marine OM has been linked to the ocean surface, being driven by biological activity in surface waters, based on a seasonality pattern of OM and chlorophyll *a* observed by satellites (Yoon *et al*., 2007; Sciare *et al*., 2009) or regression analysis (O'Dowd *et al*., 2008; Russell *et al*., 2010). Furthermore, the first quantitative estimate of submicron aerosol OM in the oceanic environment was performed by Ceburnis *et al*. (2011) using dual carbon isotope analysis, who found that over 80% of OM in clean marine air masses is of marine biogenic origin. A pilot study based on the concentration gradient method performed in the marine environment by Ceburnis *et al*. (2008) revealed that water-soluble OM (WSOM) is largely produced by secondary processes whereas water-insoluble OM (WIOM) is of primary origin. The latter study evaluated the first wind speed-dependent fluxes, but these were quite uncertain because of the absence of the parallel eddy covariance measurements. Considering a significant seasonal cycle of marine OM, it was important to study chemical fluxes on a full-year basis to capture the variability in sources and sinks.

This study was an extension to the study of Ceburnis *et al*. (2008), combining eddy covariance measurements with offline chemical analysis of samples for a wide range of chemical species during an entire year (from spring 2008 to spring 2009).

A new set-up was installed to study aerosol chemical fluxes at Mace Head Atmospheric Research Station on the west coast of Ireland (Jennings *et al*., 2003; O'Connor *et al*., 2008). Meteorological records demonstrate that, on average, marine westerly air masses occur for over 50% of calendar time at the station (Cooke *et al*., 1997; Jennings *et al*., 2003) and, therefore, the Mace Head location represents very well the entire North-East Atlantic region impacted by both oceanic air masses and polluted European air masses. The sampling system included three PM_1 samplers (Sven Leckel Ingenieurbüro GmbH) running in parallel at 3, 10 and 30 m heights, with a flow rate of 38 l.p.m. (litres per minute). Samples were collected on quartz filters in clean marine conditions (wind direction 190° < wind direction < 300° and condensation particle counts (CPC) < 700 particles cm^{-3}) using an automated sampling system for the analysis of both organic and inorganic components of marine aerosol. Active control of the sampling conditions excluded sampling during occasional short-term spikes of CN, because of either coastal nucleation events or occasional local ship traffic. Post-sampling analysis revealed that such air masses did not have contact with land for 4–5 days (as confirmed by air mass back trajectories) and the black carbon concentration, measured by an aethalometer (AE-16, Magee Scientific; single wavelength at 880 nm), did not exceed 50 ng m^{-3}. Such air masses have spent the previous 48 hours (at least) in the marine boundary layer, as documented by Cavalli *et al*. (2004) and Ceburnis *et al*. (2011). The latter study quantitatively demonstrated that, in clean marine air masses, anthropogenic carbon species typically contribute 8–20% of the total carbon mass, which should be applicable to other anthropogenic species because of internally mixed anthropogenic aerosol far from the source. It is important to note that clean marine samples collected at Mace Head are representative of the open ocean environment, considering chemical and physical similarities between the open ocean and the coastal (Mace Head) samples (Rinaldi *et al*., 2009). Fifteen PM_1 gradient samples were collected over a 13-month period in clean marine conditions. The sampling strategy aimed for two samples per month, providing that clean marine conditions were prevailing, to obtain a sampling duration of at least 50 hours per calendar week.

The samples were analysed for a wide range of chemical species, primary and secondary, present in aerosol particles: sodium (a marker for sea salt), $nssSO_4$, NO_3, NH_4, methanesulfonic acid (MSA), oxalate, WSOC, WIOC, TC, water-soluble organic nitrogen (WSON), total nitrogen (TN), dimethylamine (DMA) and diethylamine (DEA). WIOC was calculated as TC – WSOC, whereas WSON was calculated as TN – water-soluble inorganic nitrogen (WSIN). WSOM was calculated as WSOC × 1.8 and WIOM was calculated as WIOC × 1.4. Sea salt concentration was calculated as Na × 3.1.

Eddy covariance measurements of micrometerological parameters, water vapour (H_2O) and CO_2 fluxes were undertaken in parallel (Keane-Brennan, 2011), which provided micrometeorological measurement data for calculating gradient fluxes. The flux package consisted of a Solent sonic anemometer (Gill Windmaster Pro) to provide three-dimensional wind fields at 10 Hz.

The sonic anemometer was mounted 2 m out from the sea-facing side of the 22 m tower and a turbulent flow (Buzorius *et al*., 1998). Flux data were averaged for 30 minutes for further analysis; more details on the flux data can be found in Geever *et al*. (2005) and Keane-Brennan *et al*. (2011). Half-hourly flux data were averaged to match the periods of the gradient samples. The strategies undertaken allowed a complete analysis of the source and sink fluxes as a function of wind speed and oceanic biological activity and provided a quantification of both primary and secondary inorganic and organic aerosol species cycling in the marine boundary layer.

First-order closure turbulent flux parameterisation, often known as gradient transport theory or K-theory, can be expressed according to Stull (1988) as follows:

$$F = -K_z \left.\frac{dc}{dz}\right|_z \qquad (4.1)$$

where F is the flux, K_z is the turbulent transfer coefficient and dc/dz is the concentration gradient.

Thus, having the K_z value and the measured concentration gradient it is possible to calculate fluxes of chemical species. This approach, however, would allow calculation only of the net flux and does not allow upwards and downwards fluxes to be distinguished in high time resolution, as is typically done with the eddy covariance system. The K_z parameter can be calculated from eddy covariance measurements using high-frequency data on vertical wind velocity using the formula $\sigma = \sqrt{2Kt}$. K_z had to be averaged over about 40–140 hours to represent the sampling period of a particular concentration profile. The averaged K_z values were compared with eddy covariance data (Figure 4.1) to check whether the averaged K_z values were consistent with the high time resolution measurements. The dependence of K_z values on horizontal wind speed was very similar to wind speed, pointing to the fact that K_z values were normally distributed and the mean average representing the gradient samples was statistically meaningful. It is worth noting that the power law coefficient of the averaged K_z(wind speed) dependence was very similar to that provided by Ceburnis *et al*. (2008) (1.97 and 2.07, respectively), giving confidence that K_z values can be reliably derived from horizontal wind speed measurements if they cannot be estimated directly. However, in doing so, it must be ensured that only marine sector data are used. The scatter of K_z values over the short or long time period was mainly due to gustiness, as presented in Figure 4.2, in which the K_z and wind speed relationship is categorised according to the normalised standard deviation of the horizontal wind speed. All elevated values of K_z were accompanied by high values of the standard deviation of the horizontal wind speed. Therefore, K_z values were all meaningful and must be included in the mean average to represent fast turbulent eddies.

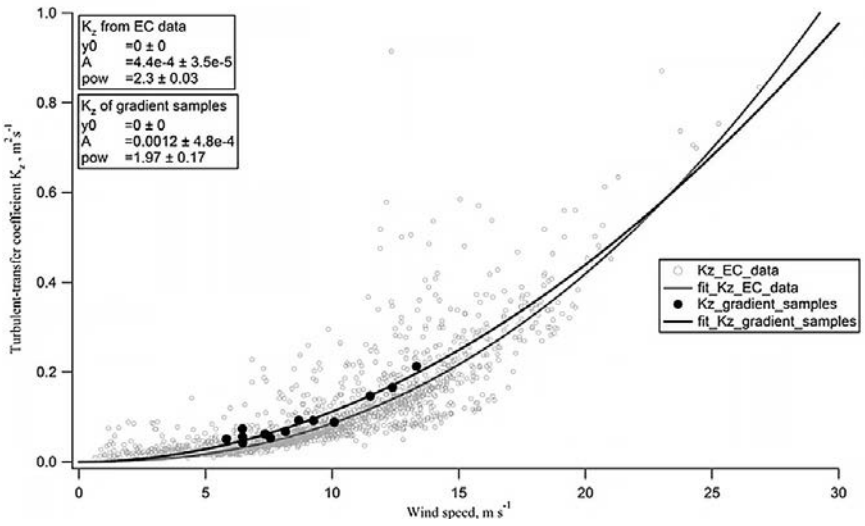


Figure 4.1. Relationship between the coefficient of the turbulent transfer K_z and horizontal wind speed in clean marine air over the whole sampling period. Grey open circles, 30-min data from the eddy covariance system; black circles, averaged K_z values for gradient samples.

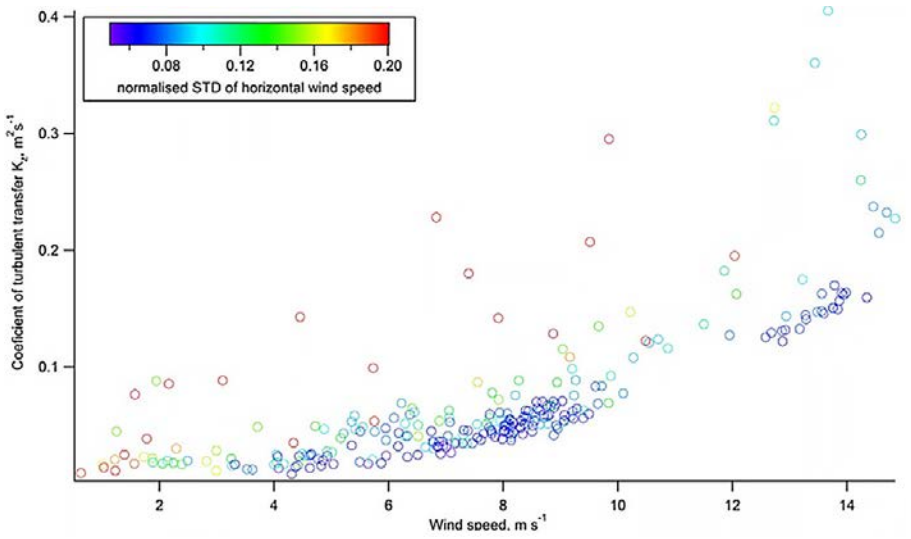


Figure 4.2. Dependence of the coefficient of turbulent transfer K_z on the horizontal wind speed and normalised standard deviation of the wind speed during April 2008.

It is important to know the thickness of the surface layer as it is in this layer that fluxes are considered constant and gradients adhere to similarity theory. Another caveat is the formation of internal boundary layers. Detailed measurements performed during the NAMBLEX (North Atlantic Marine Boundary Layer Experiment) campaign at Mace Head (Heard *et al*., 2006) provided strong evidence that the internal boundary layer had little impact on the measurements made on the main tower if they were conducted above 7–10 m (Coe *et al*., 2006; Norton *et al*., 2006), which would include two of our three sampling points. Norton *et al*. (2006) showed that the internal boundary layer was limited to below 10 m and never propagated to the top of the tower in marine sectors. Coe *et al*. (2006) concluded that over a wide range of aerosol sizes there was no impact of the inter-tidal zone or the surf zone on measurements made at 7 m above ground level or higher.

The measurements performed at three different heights allowed the vertical concentration profiles of different chemical species to be resolved. Different sources and sinks with corresponding fluxes can shape the profiles. Most were non-linear but well interpretable, having studied the concentration and flux footprints in detail in the previous pilot study by Ceburnis *et al*. (2008). It is important to note that the footprint of the measured absolute concentration was of many tens to hundreds of kilometres offshore, whereas the footprint of the concentration gradient or the flux was within about 10 km of the measurement location, i.e. coastal waters (Ceburnis *et al*., 2008).

The surf zone emissions may have had a certain influence on the concentrations of sea salt or sea spray at the lowest level of 3 m, but had little or no impact on secondary organic aerosol particles.

Normalised averaged concentration profiles of all measured chemical species are presented in Figure 4.3. Normalisation was carried out by dividing the concentration at every height by the sum of the concentrations at the three levels, thus giving the same weight to every profile for averaging purposes. After normalisation, the profiles of each mass category were averaged, resulting in statistically meaningful variances around the mean value. The main features were similar to those documented by Ceburnis *et al*. (2008): decreasing concentration with height was common for species produced at the surface by primary processes, whereas increasing concentration with height was common for species produced by secondary processes in the atmosphere aloft (boundary layer, clouds or free troposphere). The concentration profile of sea salt (top left in Figure 4.3) was unambiguously primary, i.e. the concentration decreases vertically. Individual sea salt concentration profiles are presented in Figure 4.4. Some of these profiles were sharper than others, but all were primary with only three exceptions, in which the profiles were distorted at lower heights possibly partly because of measurement errors and partly because of boundary layer dynamics and changes in sea state during the sampling period (ascending and descending wind regimes). However, as stated above, surf zone emissions could have had an influence

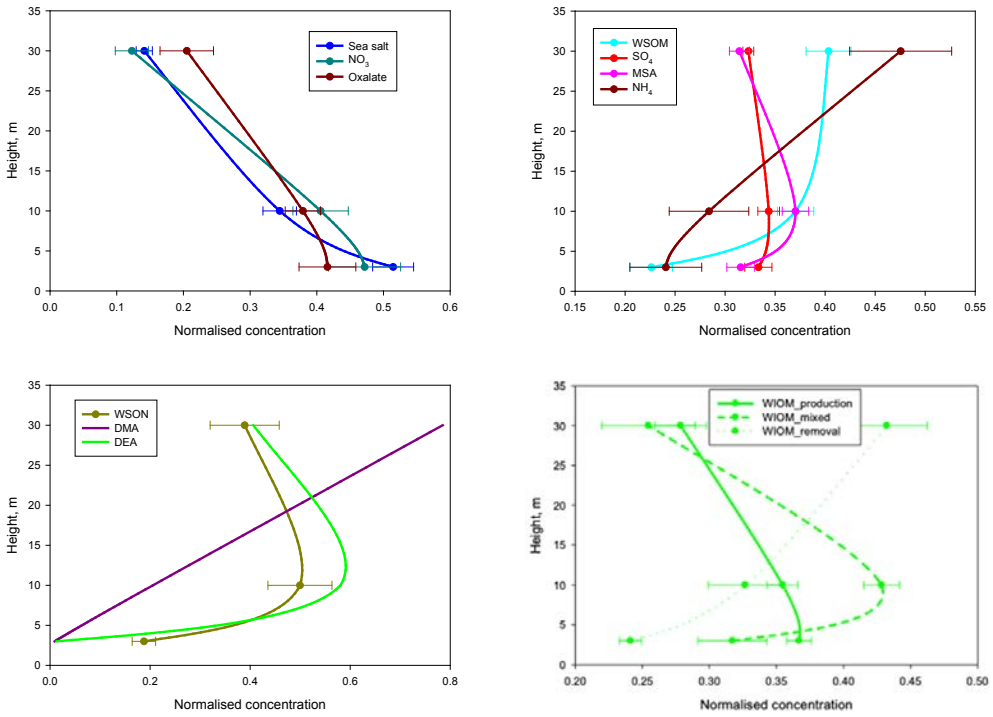


Figure 4.3. Gradient profiles of chemical species studied: species resembling primary production (top left); species resembling secondary production (top right); organic nitrogen species (bottom left); and WIOM split into production, removal and mixed profiles (bottom right).

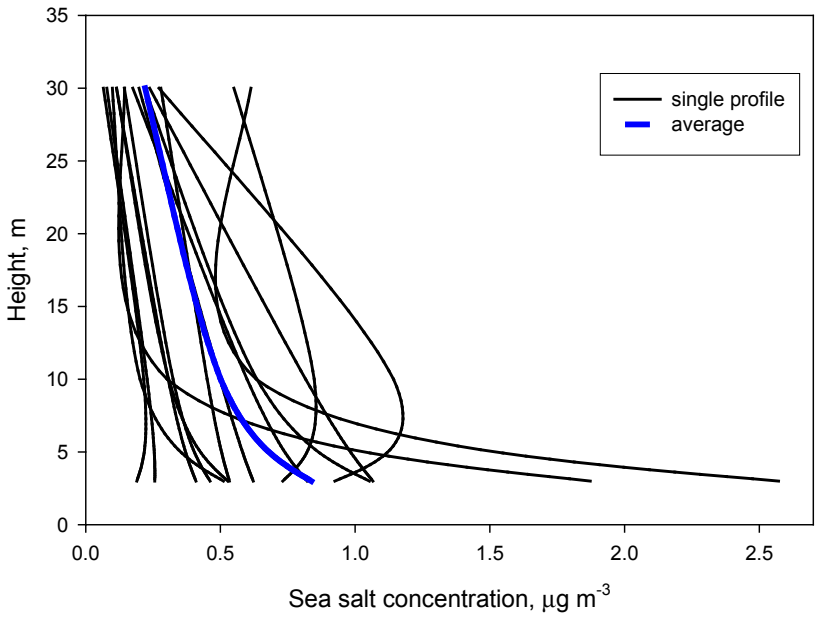


Figure 4.4. Individual and average sea salt concentration profiles.

on concentrations at the lowest level of 3 m and this level was not used in flux calculations of primary sea spray species.

Interestingly, similar "primary" concentration profiles were obtained for nitrate and oxalate. However, these profiles were slightly but systematically distorted.

It is fairly well known that nitrate is produced by secondary processes and mainly manifests itself through condensed nitric acid on pre-existing sea salt particles in the absence of anthropogenic ammonium nitrate. As the source of the secondarily produced chemical compounds is in the atmosphere aloft, the

concentration profile was distorted close to the ground by deposition. Similarly, oxalic acid could have been condensing on pre-existing sea salt particles – there was insufficient time for surf zone-generated particles to pick up nitric acid, but some of the oxalate could also be produced by oxidation of OM inside sea spray particles (Rinaldi *et al*., 2011) manifesting itself as "primary" species. This could indicate that the main source of oxalate is processed primary OM.

The main secondary species are presented in the top right and bottom left of Figure 4.3: $nssSO_4$, NH_4, MSA, WSOM and WSON. The profile of MSA was also affected by condensation of MSA on the pre-existing sea spray particles, but to a much lesser extent than, for example, nitrate. Interestingly, the concentration profile of ammonia was almost linear and decreasing, possibly because of the fact that ammonia is a neutralising agent produced to neutralise acidic species such as sulfuric acid and nitric acid. However, the degree of neutralisation is never constant, depending on how much sulfate and nitrate is present in the particle and the degree of external/internal mixture, as internally mixed particles (especially relatively fresh sea spray particles that have just picked up traces of acidic species) would be neutralised less than aged externally mixed sulfate particles. It must be noted that the concentration profile of $nssSO_4$ was systematically distorted. $NssSO_4$ was calculated as the difference between two relatively large numbers (total measured SO_4 minus sea salt SO_4, as inferred from a conservative tracer such as Na ions). As the sea salt concentration was changing quite dramatically with height, especially at moderate to high wind speeds, some ambiguity must be acknowledged before interpreting the $nssSO_4$ profile. In any event, $nssSO_4$ concentrations at the three different heights were not statistically significantly different, preventing any conclusions with respect to apparently secondary $nssSO_4$.

The WIOM concentration profiles were split between three main categories: production, removal and mixed profiles (bottom right of Figure 4.3). Given that enrichment of the organic component in primary aerosol is related to enrichment of OM at the ocean surface, this range of behaviour can be interpreted in terms of the location of the biologically active region relative to the flux footprint. The biologically active water patches within the flux footprint (~10 km from the measurement location) were responsible whether WIOM was produced or removed from the surface layer, or a combination of both processes occurred. Therefore, a mixed profile pointed to production at a longer distance from the coast and removal at the measurement location. Thus, the removal profile, although pointing at deposition within the flux footprint area, actually demonstrated the absence of biological activity in surface waters within the flux footprint area and not necessarily that WIOM was produced by secondary processes, which, however, cannot be excluded. It is worth noting that the production profiles were observed in early spring when biological activity is starting at the coast and during late summer when biological activity has its second maximum (Yoon *et al*., 2007). In contrast, the removal profiles were observed during late spring and early summer when biological activity is moving away from the coast into the open ocean. Despite the general pattern of the evolution of biological activity presented by Yoon *et al*. (2007), it should be stressed that biological activity is very patchy all over the ocean, including coastal areas, and phytoplankton blooms are generally governed by the availability of nutrients, which themselves are supplied by ocean currents and upwellings and become unpredictable on a day-to-week timescale.

The WSON concentration pattern and those of the selective amine species DMA and DEA are presented in the bottom left of Figure 4.3. The concentration profile of DMA was clearly secondary, but that of DEA was mixed; the concentration profile of WSON profile was also secondary. These profiles are presented for the first time and should be considered cautiously. First, WSON, DMA and DEA are minor constituents of marine aerosol, together typically accounting for 10% of secondary organic aerosol. However, the magnitude of their absolute concentrations may be misleading – amines can be important species facilitating new particle production in the marine atmosphere (Dall'Osto *et al*., 2012) – and quantification of their concentration by offline chemical analysis is always challenging. Mostly, concentrations of DMA and DEA at the lowest height were below the detection limit and, therefore, the profiles may be ambiguous. On the other hand, the mixed profile of DEA depicting production in the further footprint area can be explained by condensation of the less volatile DEA onto pre-existing sea spray particles. Such condensation is possible only if sea spray particles were already slightly acidic (amines are basic species), which they probably were,

with at least small amounts of nitrate, non-neutralised sulfate and MSA present. Taking into account average wind speeds of 5–10 m s^{-1}, a marine boundary layer of 500–1000 m, an updraft of 1 m s^{-1} and the gradient footprint area of 10 km from the coast (Ceburnis *et al*., 2008), one would get one to three cloud cycles within the gradient footprint, which is sufficient for freshly produced sea spray to pick up traces of $nssSO_4$ or nitric acid and become mildly acidic.

The well-established aerosol chemical compounds such as nitrate, oxalate and MSA, and the less-well-established WSON, were all studied for the first time using the gradient method. The gradient method has indeed demonstrated that the above species were secondary and, therefore, were produced in the atmosphere aloft. However, the gradient method also revealed important features, with the potential to quantify their production rates. Despite a strong similarity in the concentration pattern of nitrate and primary sea salt, it is obvious that nitrate is derived by condensation of nitric acid on pre-existing sea salt. Figure 4.5 (top left) presents the relationship between nitrate and sea salt, which is linear with the exception of two to three outliers. The outliers likely appeared because of the presence of trace amounts of ammonium nitrate. Ammonium nitrate is generally considered an anthropogenic species and can be present in trace amounts because of background pollution. The trace amount was very small, 20–30 ng m^{-3}, only re-affirming the cleanness of the marine atmosphere. A similar relationship was observed for oxalate (Figure 4.5, top right), but there were many more outliers from the linear pattern. Although oxalate can indeed condense on pre-existing sea salt particles, its chemical pathways of secondary production are different and more diverse than that of nitrate. Oxalate is usually present in sea spray particles as a result of oxidation of OM in sea spray and, therefore, is dependent on the biological activity of the ocean. In contrast to nitrate, oxalate was not enhanced in the presence of copious amounts of sea salt particles, suggesting that oxalic acid is not an ever-present species in the boundary layer that would readily condense on sea salt. The same was true for

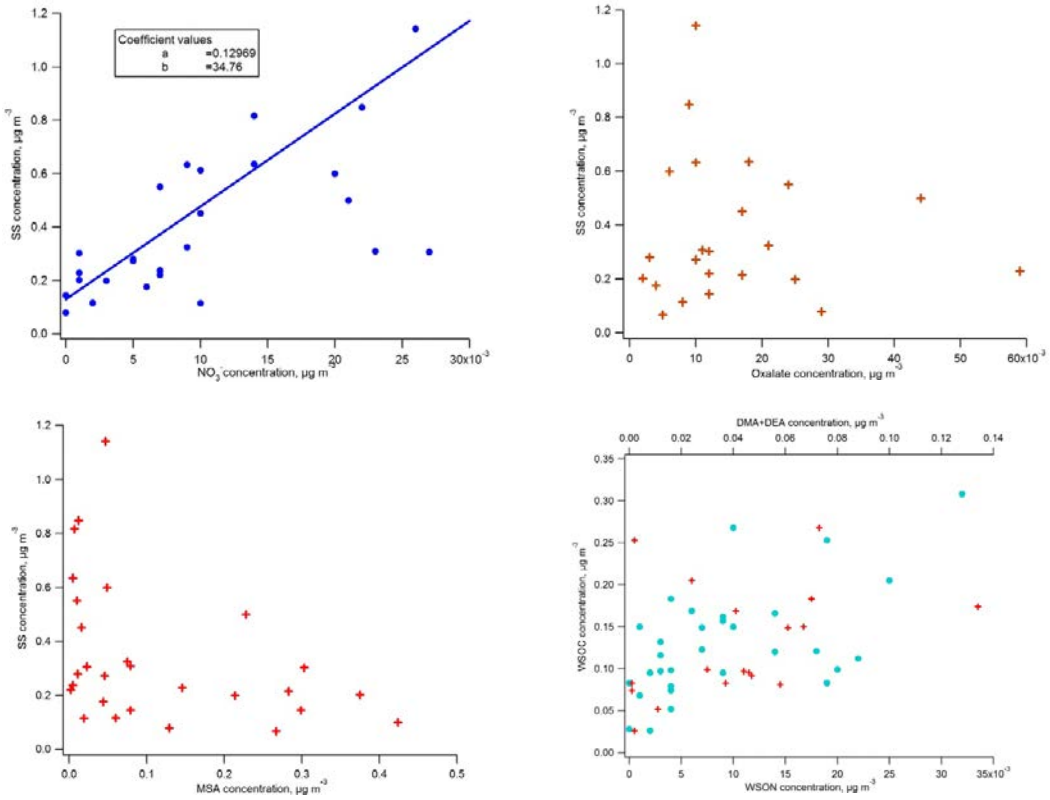


Figure 4.5. Plots of sea salt (SS) and secondary species which resembled primary production pattern: sea salt vs NO_3 (top left); sea salt vs oxalate (top right); sea salt vs MSA (bottom left). The relationship between WSOC and WSON (also plotted as the sum of DMA and DEA) is shown in the plot in the bottom right.

MSA, which showed even less of a relationship with sea salt mass (Figure 4.5, bottom left) as being truly secondary species mostly produced in subtropical humid air masses.

Water-soluble organic nitrogen is a relatively less studied class of chemical compounds, of which amines are the best known. Interestingly, both WSON and the sum of DMA and DEA correlated quite well with WSOM (Figure 4.5, bottom right). WSON concentrations were difficult to quantify – they were calculated as the difference between the concentration of TN and the concentration of WSIN; the comparison between the absolute amounts of WSON and the sum of the amines suggested that the amines are probably the dominant species of WSON.

The individual concentration profiles had to be fitted first in order to calculate gradients and then fluxes using equation 4.1. The concentration gradient is a derivative of the concentration change with height. The lowest level at which concentration was measured was 3 m; these measurements may have been affected by surf zone fluxes, as discussed in detail by Ceburnis *et al*. (2008). Therefore, only the concentrations measured at 10 and 30 m were used to calculate the primary fluxes in order to reduce surf zone-related uncertainty. This approach yielded "linear gradients" and constant fluxes, but as the fluxes were valid only at a particular height (in this study the height at which K_z values were measured), it did not affect the accuracy of the fluxes. Sea salt and sea spray (sea salt + WIOM) flux dependence on wind speed is presented in Figure 4.6. The obtained relationship was the power law, which was very similar to that obtained by Ceburnis *et al*. (2008), but this time it was quantified separately for sea salt and sea spray. The relationship for the sea spray flux was stronger; however, inherent uncertainty had to be considered. The K_z values were calculated explicitly and, therefore, the uncertainty in the flux was the result of the uncertainty of the gradient, which in turn was dependent on the accuracy of the chemical analysis. The accuracy of the sea salt chemical analysis was about 5%; however, such random uncertainty would propagate into 20–25% uncertainty in the gradient. The power law exponents of the sea salt and sea spray (2.53 and 2.73, respectively) source function were very similar to the sea salt source function obtained by Ovadnevaite *et al*. (2012), who obtained a power law exponent of 2.7 using high-resolution measurements by AMS.

The corresponding chemical flux of WIOM was calculated and is presented in Figure 4.7. All reasoning and uncertainty considerations are the same as for the sea salt and sea spray fluxes. There was one important difference, however. The WIOM fluxes turned out to be positive only at relatively strong wind speeds exceeding 7 m s^{-1}. All WIOM fluxes below this value were negative, pointing at the removal or deposition of WIOM. It suggested that WIOM fluxes in the gradient footprint zone at low wind speeds were lower than deposition fluxes and that WIOM was produced outside the gradient footprint zone. According to the discussion above,

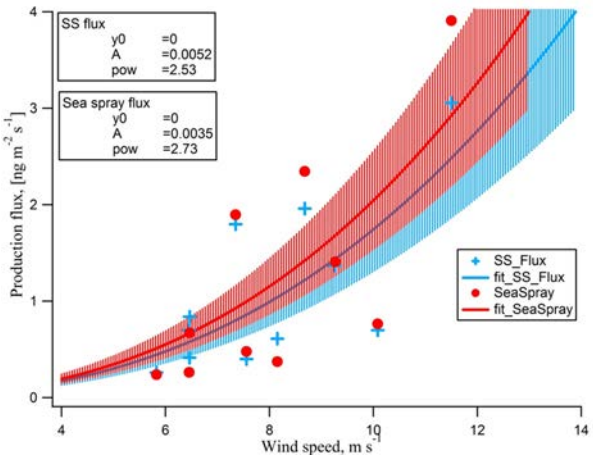


Figure 4.6. The sea salt (SS) net production flux vs relationship with wind speed. The area around the curve represents the uncertainty of the source function.

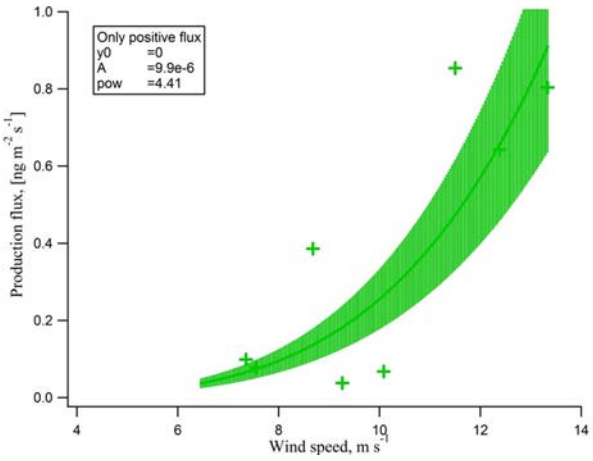


Figure 4.7. The WIOM net production flux vs relationship with wind speed. The area around the curve represents the uncertainty of the source function.

it is possible that the resulting negative WIOM flux at low wind speeds occurred because of the absence of biological activity in the flux footprint area (within ~10 km of the measurement location). Another possibility is that there is no measurable concentration increase in WIOM mass at wind speeds below 7 m s^{-1}, resulting in a negative flux as WIOM is being removed from the surface layer because of the absence of the source.

This could at least partly explain the much steeper power law coefficient of the WIOM flux (4.41) compared with the sea salt flux (2.53), if small fluxes were missing because of the absence of the source at the time of sampling. Indeed, considering the uncertainty ranges of the sea salt and WIOM flux functions, they do overlap (2.53 ± 0.85 and 4.41 ± 1.2, respectively).

The WSOM exhibited the clearest removal gradient throughout the study period, which allowed study of the seasonal pattern of sink and dependence on meteorological parameters. Individual WSOM concentration profiles were first fitted to the power law and then the resulting fluxes were calculated using equation 4.1 at the 22 m height. The dependence of the removal rate on wind speed is presented in Figure 4.8 and fitted to the power law. The WSOM removal rate or sink was strongly dependent on wind speed, with a power law coefficient of 5.4. However, the relationship suggests that the removal flux should also depend on the concentration of WSOM in the boundary layer.

The most significant limitation of the chemical gradient flux method is that it allows calculation of fluxes up to a medium wind speed only. It is extremely rare that an average wind speed above 15 m s^{-1} would be sustained over a week-long period. Therefore, the sea spray source function method proposed by Ovadnevaite *et al*. (2012) has to be considered to be more reliable, covering the wind speed range up to 26 m s^{-1}, as every proposed source function is reliable only over the wind speed range that it was derived from. An extension of the source function, albeit practical, may introduce significant error outside that range.

Gantt *et al*. (2011) suggested that OM enrichment in sea spray particles depends not only on biological activity in oceanic surface waters, but also on wind speed at the point of emission. The data in this study were examined according to the approach of Gantt *et al*. (2011). Figure 4.9 presents organic enrichment in sea spray (OM_{ss}) dependence on wind speed using the dataset in this study and that from the earlier study by Ceburnis *et al*. (2008), which were not part of a dataset used by Gantt *et al*. (2011). The relationship for the dataset from this study is very clear, and the data from Ceburnis *et al*. (2008) follow the same pattern (top left plot). However, when the same relationship is categorised according to chlorophyll *a* concentration

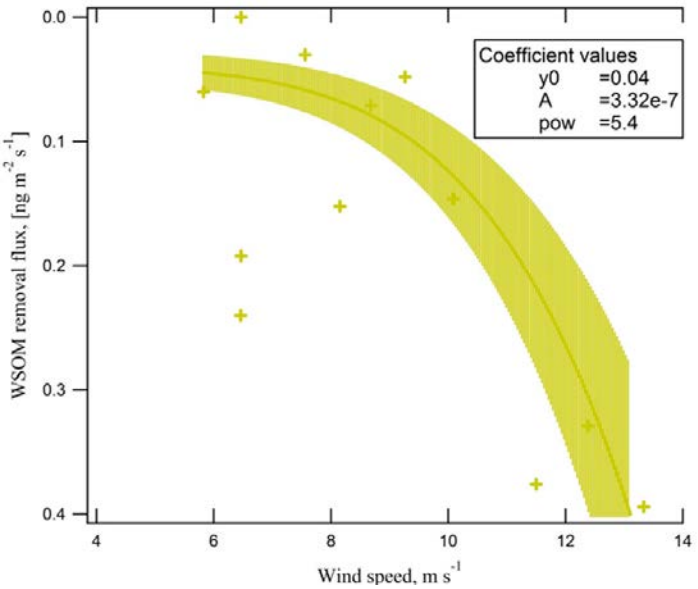


Figure 4.8. The dependence of the negative WSOM removal rate on wind speed at a height of 22 m. The shaded area represents the uncertainty of the flux.

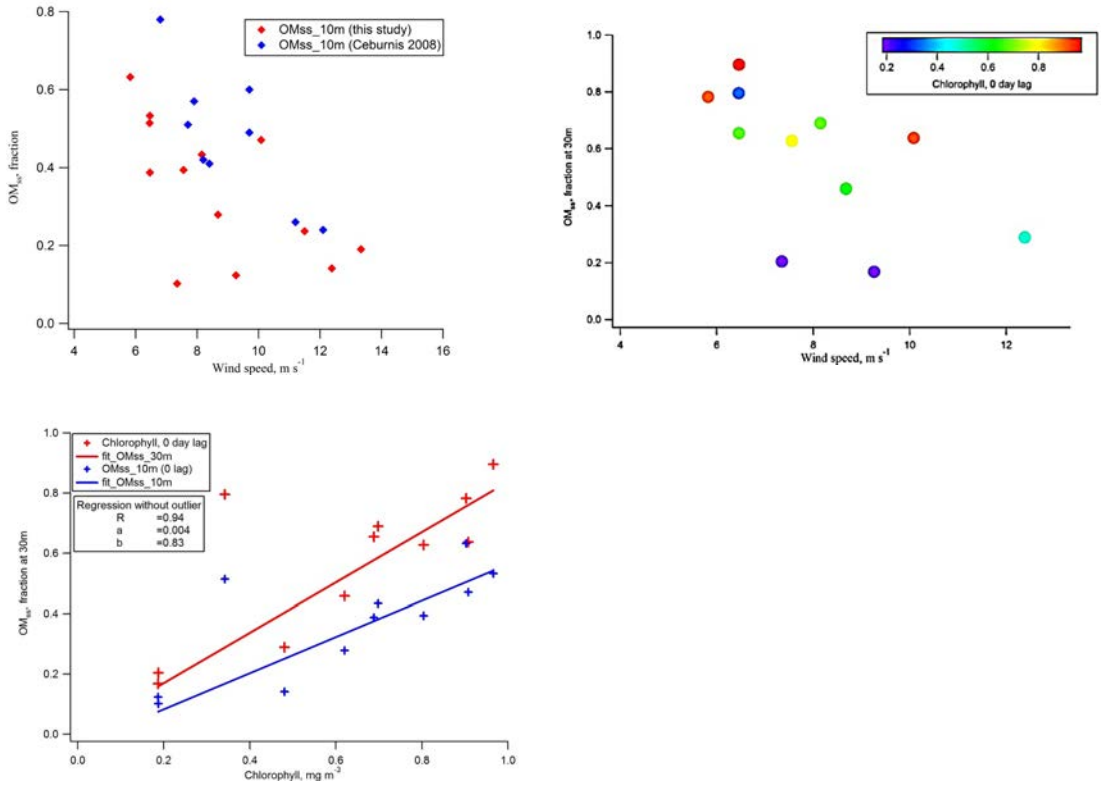


Figure 4.9. Effect of wind speed and chlorophyll *a* concentration on OM enrichment OM_{ss}: OM_{ss} vs wind speed (top left); OM_{ss} vs wind speed categorised by chlorophyll *a* concentration (top right); and OM_{ss} vs chlorophyll *a* concentration (bottom left).

in the oceanic region upfront of the measurement location at Mace Head, no apparent pattern can be discerned (top-right plot). Further, when OM_{ss} is plotted against chlorophyll *a* concentration, a well-defined linear dependence emerges (bottom-left plot), suggesting that the OM enrichment in sea spray can be largely explained by the chlorophyll *a* concentration alone, without invoking wind speed. It is, however, possible that OM_{ss} dependence on wind speed can be important over a much wider range of conditions and using larger datasets, as in Gantt *et al*. (2011). It can be concluded that, although OM_{ss} dependence on wind speed cannot be excluded, it should be weaker than OM_{ss} dependence on chlorophyll *a*, because of the interdependence of wind speed and chlorophyll *a* – wind speed is higher in winter when the chlorophyll *a* concentration is at its lowest and vice versa.

4.1 Boundary Layer Filling Time

The calculated fluxes allowed an estimation of an important parameter called boundary layer filling time, τ, according to the following equation:

$$F_{eff} = \frac{C \times H_{MBL}}{\tau} \qquad (4.2)$$

where F_{eff} is the effective flux; C is the concentration; and H_{MBL} is the height of the marine boundary layer.

The boundary layer filling time was calculated using only averaged values of the calculated sea salt flux (see Figure 4.6), measured average absolute sea salt concentration and boundary layer height. The averaged value of the boundary layer height is typically below 1000 m (boundary layer height 850 ± 350 m) in the marine environment (Dr Giovanni Martucci, NUI Galway, personal communication). Hence, the corresponding filling time value is 40 ± 17 hours, which is roughly 2 days, and the uncertainty range is 1–3 days. The same range for the boundary layer filling time was obtained by Ovadnevaite *et al*. (2012), based on considerations of Hoppel *et al*. (2002), low-pressure system development and precipitation data.

The average calculated WSOM removal flux at the surface (1 m height) was 3.5 ng m^{-2} s^{-1}, based on the non-linear concentration profile (equation 4.1). The average lifetime of WSOM was, therefore, approximately 1–2 days, considering an average

boundary layer height of 850 ± 350 m (equation 4.2). This is an important finding, suggesting that the anthropogenic pollutants are removed from the marine boundary layer half-way through a typical air mass passage from North America and are then replenished by biogenic material before advecting over Ireland, resulting in a largely unperturbed atmosphere. It is no coincidence that the lifetime of WSOM was approximately equal to the filling time, as the source flux matches the deposition flux once steady state is reached.

The marine aerosol sources, sinks and chemical fluxes were studied over the entire year using the gradient method. The chemical fluxes of primary species, such as sea salt, WIOM and sea spray, were found to show a strong power law relationship with wind speed. The power law exponent of the sea salt mass source function was 2.53, which was slightly lower than the generally considered cubic power law relationship. The flux versus wind speed relationship of WIOM (4.41) was found to be even stronger than that of sea salt (2.53), confirming a strong dependence on biological activity in oceanic waters, as supported by the strong OM enrichment dependence on chlorophyll *a* concentration. The study of certain secondary species (nitrate, oxalate, MSA and WSON) was performed for the first time, which showed the potential to estimate their production rate in the marine boundary layer. The boundary layer filling time was found to be approximately 2 days, which is the important parameter considering steady state conditions in the marine boundary layer. The removal rate of WSOM was estimated to be approximately 1–2 days, which suggests that aerosol lifetime in the vigorous North Atlantic marine boundary layer is relatively short.

5 Eyjafjallajökull Volcano Eruption and Chemical Characterisation of Volcanic Ash Plume Particles Detected at Mace Head

The Eyjafjallajökull volcano erupted explosively on 14 April 2010, ejecting an ash plume into the atmosphere at levels between 4 km and 9 km above mean sea level. Although the Eyjafjallajökull eruption was moderate and regarded as a mid-sized eruption, it had a severe impact on aviation over Europe. The eruption occurred under north-north-westerly air flow relative to continental Europe and under conditions of minimal precipitation, resulting in rapid dispersion of the ash cloud over Central Europe, Ireland and Britain. Based on plume mass estimates from the European Volcanic Ash Advisory Centres, European aviation authorities decided to close European airspace, impacting air traffic to 23 European countries, amounting to a 75% closure of the European aerodrome network. The net effect was that more than 100,000 flights were cancelled, affecting 10 million passenger journeys between 14 April and 20 April. Further incursions of the ash cloud over Western Europe caused sporadic additional airspace closures until 18 May 2010, leading to the cancellation of about 7000 further flights.

The Eyjafjallajökull ash plume was detected at the Mace Head Atmospheric Research Station numerous times from 19 April until 18 May 2010 following subsidence into, and dilution in, the boundary layer. The three strongest of these events, lasting 12–18 hours, were analysed in detail in terms of their physical, chemical and optical properties and were discussed by O'Dowd *et al*. (2012a). The influence of volcanic aerosols on cloud formation and microphysics was studied by Martucci *et al*. (2012) and showed that volcanic aerosol can be an efficient CCN. Forecast modelling capabilities were built using the REMOTE model and the validation of the model was discussed by O'Dowd *et al*. (2012b).

This chapter summarises the results of an inter-comparison exercise between different analytical techniques, with the emphasis on physico-chemical characterisation of volcanic ash plume particles detected at Mace Head during May 2010. Over 10 plumes of different magnitudes were detected during the entire month (more during April 2010), but all of the smaller plumes could be identified only with the HR-ToF-AMS technique because of its high temporal resolution. Significant plumes were detected during four periods on 2, 4, 17 and 19 May. The events on 4 and 17 May were the strongest of all of the observed plume events at Mace Head during the entire eruption phase of the Eyjafjallajökull volcano.

The whole operational suite of instruments at Mace Head was running uninterrupted during the eruption phase of the Eyjafjallajökull volcano. However, this report only discusses methods used for the chemical characterisation of particles. Scanning electron microscopy (SEM) was also applied to physically identify ash particles and to reveal their qualitative chemical composition to support established quantitative chemical methods.

An aerosol mass spectrometer is capable of measuring size-resolved PM_1 particle chemical composition (non-refractory) in near real time. High time resolution data were averaged to represent 24-hour averages to compare with X-ray fluorescence (XRF) and ion chromatography analysis.

The XRF method is designed to measure the elemental composition of aerosol particles irrespective of their chemical make-up. The following elements were analysed as a standard instrumental set using XRF: Al, Ca, Cl, Cu, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, Si, S, Ti, V and Zn. The analysis was carried out at the Consiglio Nazionale delle Ricerche (CNR), Rome, on six $PM_{2.5}$ samples and four $PM_{2.5–10}$ samples because of cost constraints. Four samples represented the four major plumes described above and two $PM_{2.5}$ samples represented clean marine conditions on 1 and 16 May.

Ion chromatography analysis was carried out on daily samples during the entire eruption period (16 April–31 May). Analysis was carried out at Met Éireann laboratory under the management of Ms Margaret Ryan. The ion chromatography method implies that only water-soluble material is analysed, which is a viable method for major aerosol chemical species:

sulfate, nitrate, ammonium, sodium, chloride and MSA. $PM_{2.5}$ and $PM_{2.5–10}$ samples were split in half for XRF and ion chromatography analyses.

Figures 5.1–5.3 represent time trends of $nssSO_4$, sodium and chloride concentrations, respectively, measured using three different methods (AMS, XRF and ion chromatography). AMS and ion chromatography $nssSO_4$ concentrations correlated very well (see Figure 5.1). There were small departures from an otherwise very good agreement, but the quantitative comparison between AMS and ion chromatography is ongoing. XRF $nssSO_4$ concentrations generally matched AMS or ion chromatography concentrations very well during non-plume days; however, there were significant departures from the general agreement on some of the days when significant volcanic plumes were detected.

Sodium and chloride concentrations generally agreed very well between ion chromatography and XRF, with the exception of 17 May, when a major volcanic plume was detected (see Figures 5.2 and 5.3).

It is important to emphasise that the high temporal resolution of AMS and its ability to provide measurements in near real time had major value in providing up-to-date information during the volcanic ash cloud observation period. The high time resolution trend in $nssSO_4$ concentrations measured by AMS is presented in Figure 5.4, where multiple plumes at significant concentrations were clearly identified as having a volcanic origin following the paper published by Ovadnevaite *et al.* (2009), which documented a volcanic outgassing event detected in 2007 that was different from the Eyjafjallajökull event discussed in this report, namely with high sulfate but very low nitrate, ammonium and organics in polar/arctic air masses.

The presence of significant sulfate concentrations that were not neutralised by ammonium implied the presence of sulfuric acid during the volcanic plume events, making aerosol particles extremely acidic. Consequently, it suggested the occurrence of certain chemical reactions in the particle phase because of the presence of naturally occurring sea salt, volcanic ash and sulfuric acid during plume events.

First, it is important to note that sea salt particles, primarily NaCl, can react with sulfuric or nitric acid, producing volatile hydrochloric acid according to equation 5.1. The result of this reaction is a soluble salt and depletion of chloride from particles. Chloride depletion can be observed in Figures 5.2 and 5.3 on 4 and 17 May (major volcanic ash events) or by a significant departure from a Cl/Na ratio of 1.8 during the other two events (2 and 19 May). By comparison, during the period of 14–16 May, no significant depletion occurred in clean marine air masses. Figure 5.2 shows that the Na concentration recovered very well according to the ion chromatography analysis, confirming the solubility of Na_2SO_4, with the exception of the major plume on 17 May.

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl \quad (5.1)$$

There were more chemical reactions at play as a result of the presence of volcanic ash, which was confirmed by the high elemental concentrations of Si and Zn and significant non-sea salt concentrations of Mg, Ca and K determined by XRF analysis. It has already been documented that the Eyjafjalljökull eruption produced ash with a dominant presence of SiO_2. The reported ash composition revealed the presence of several other major oxides, as they were presented by the Icelandic Meteorological Service during the eruption period: Al_2O_3, FeO, CaO, Na_2O, MgO and TiO_2. Accordingly, the following reactions were possible:

$$Ca(Na,K)O + H_2O \rightarrow Ca(OH)_2 + \text{heat (exothermic reaction)} \quad (5.2)$$

$$Ca(Na,Mg,K,Fe,Zn)O + H_2SO_4 \rightarrow Ca(Na,Mg,K,Fe,Zn)SO_4 + H_2O \quad (5.3)$$

$$Fe(Mg)O + 2HCl \rightarrow Fe(Mg)Cl_2 + H_2O \quad (5.4)$$

$$SiO_2 + Na_2O \rightarrow Na_2SiO_3 \quad (5.5)$$

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \quad (5.6)$$

In summary, all of the reactions suggest that mineralisation of ash was taking place, causing significant discrepancies between the different analytical methods. First, evaporation of sulfuric acid from particles already collected on the filter medium was taking place during all of the significant plumes. As AMS is a non-destructive, online, near real-time measurement technique, evaporation was not an issue. The other major discrepancy between the methods occurred on 17 May. When the possible error in ion chromatography was dismissed, it was clear that sulfate was largely missed by the ion chromatography method because of the formation of low-solubility $CaSO_4$ or moderate-solubility $ZnSO_4$ (equation 5.3). In addition, the ion chromatography method did not detect any calcium for the same reason, whereas the

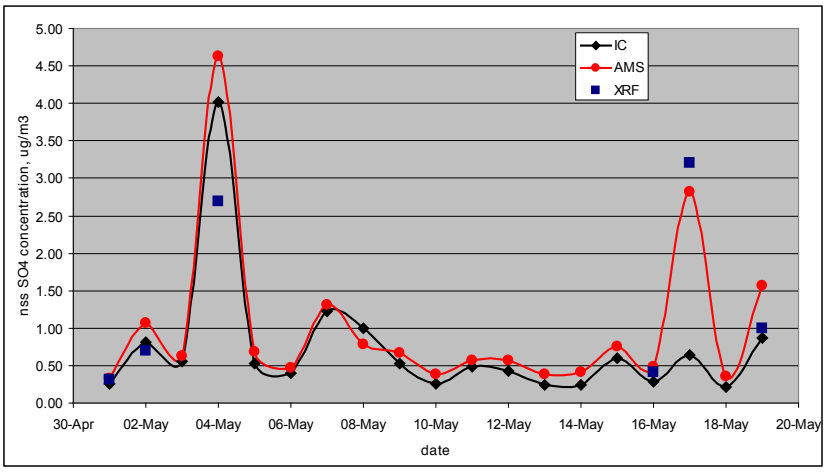


Figure 5.1. Time trend of the $PM_{2.5}$ $nssSO_4$ concentration during May 2010. Significant volcanic plumes were detected on 2, 4, 17 and 19 May (see Figure 5.4).

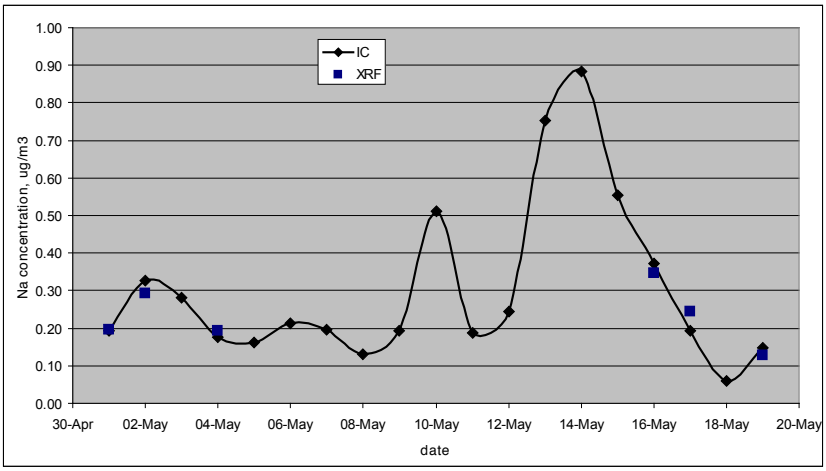


Figure 5.2. Time trend of the $PM_{2.5}$ sodium concentration during May 2010. Significant volcanic plumes were detected on 2, 4, 17 and 19 May (see Figure 5.4). Sodium is an element found in tephra emissions and, consequently, in volcanic plumes, as well as being a major ion of sea salt and would be picked up during air mass advection over the ocean before arriving at the Mace Head location.

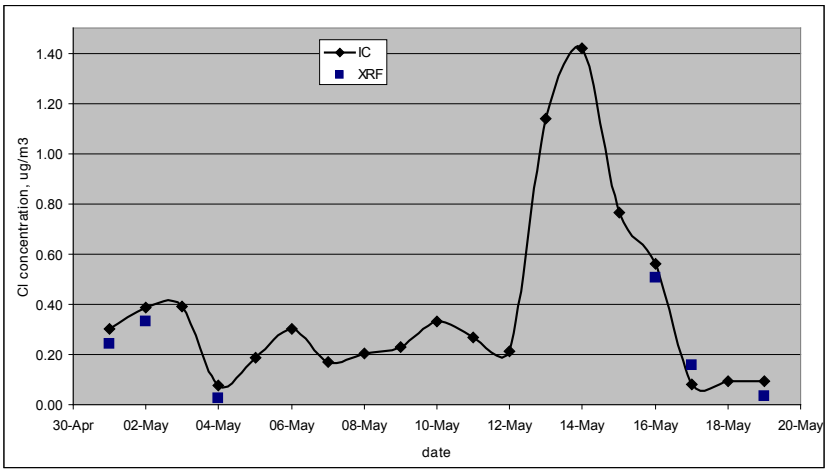


Figure 5.3. Time trend of the $PM_{2.5}$ chloride concentration during May 2010. Significant volcanic plumes were detected on 2, 4, 17 and 19 May (see Figure 5.4). Note the almost complete depletion of chloride on 4 and 19 May.

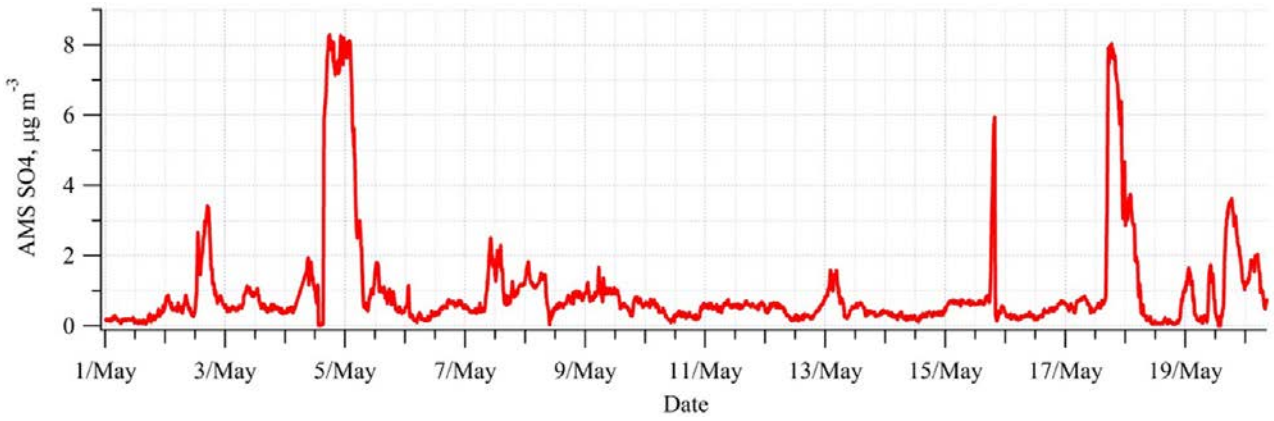


Figure 5.4. Time trend of the nssSO_4 concentration in high time resolution measured by AMS during May 2010. High sulfate peaks were a definite sign of volcanic plumes, as such high levels of sulfate were not observed even in the most polluted air masses.

XRF method quantitatively measured both sulfate and calcium (and zinc) during that event. The SEM analysis performed on 17 May revealed significant amounts of gypsum, which is a hydrated form of $CaSO_4$ ($CaSO_4 \cdot 2H_2O$) (see Figures 5.1 and 5.5). In fact, the missing sulfate mass could be quantitatively matched by a chemically equivalent mass of calcium and zinc, supporting the idea of the error caused by the lack of solubility of the reaction products.

The relatively smaller depletion of chloride during the 17 May event confirms the reaction in equation 5.4, whereas the relative overabundance of sodium during the same event confirms the reaction in equation 5.5. All of the aforementioned reactions were possible because of (1) the large amount of sulfuric acid present; (2) the production of hydrochloric acid (equation 5.1), which when mixed with sulfuric acid could have enhanced ash mineralisation; and (3) the dissolution of metal oxides in acid, which was even more effective in the dry free troposphere during atmospheric transport from Iceland or on the sampled filter at Mace Head because of the ultimate water loss, leading to an even more concentrated acid.

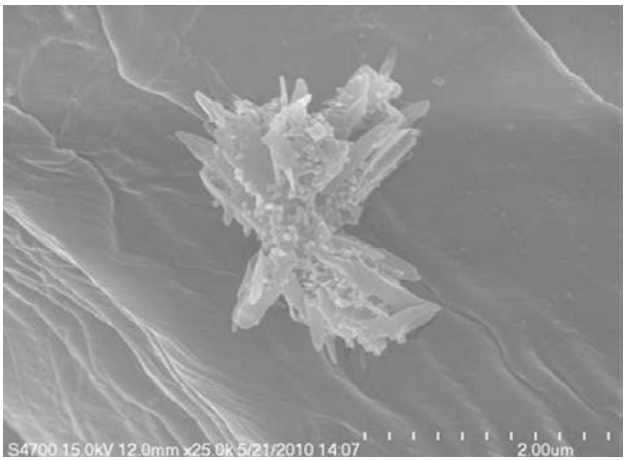
The entire reaction scheme has important environmental implications, because all of the reaction products (salts) are more soluble than the respective oxides, including partially reacted silica. Mineralisation of silica was limited by the availability of Na_2O, which was 10 times less abundant than SiO_2 (see Table 5.2). Silicon is an essential nutrient for phytoplankton growth (diatom species build their shells from silicic acid, e.g. H_4SiO_4, which can be produced by the acidification of the aforementioned sodium silicate, Na_2SiO_3). Concurrently, mineralisation of volcanic iron has well-known implications for ocean fertilisation (enhancing phytoplankton growth) and consequently carbon cycling (Langmann, 2013).

The percentage contribution of the major chemical species in PM_{10} during two of the major plumes is summarised in Table 5.1, as derived from XRF analysis. Note that the XRF analysis did not measure nitrate, ammonium, OM or water bound in chemical compounds, such as gypsum or sulfuric acid. Therefore, the total PM mass is underestimated.

One should also keep in mind that, because of dynamic evolution of the plumes, 24-hour-long samples could not detect peak events as demonstrated in Figure 5.4, giving a false impression of the magnitude of PM concentrations during volcanic ash observation days.

Three major compound classes had a roughly equal share of the PM mass: sulfate, ash and sea salt (see Table 5.1). When split into fine ($PM_{2.5}$) and coarse ($PM_{2.5–10}$) particles, fine particles consisted mostly of sulfate whereas coarse particles were made up of mainly ash and sea salt (likely externally mixed).

The last important result was the percentage contribution of major oxides in the volcanic ash fraction of the particles. The percentage contribution of oxides in volcanic ash was remarkably similar between the particles sampled at Mace Head and the ash fallout near the volcano (Table 5.2). Considering that the listed compounds are inert, their similar percentage contributions allow their Icelandic origin to be confidently asserted.



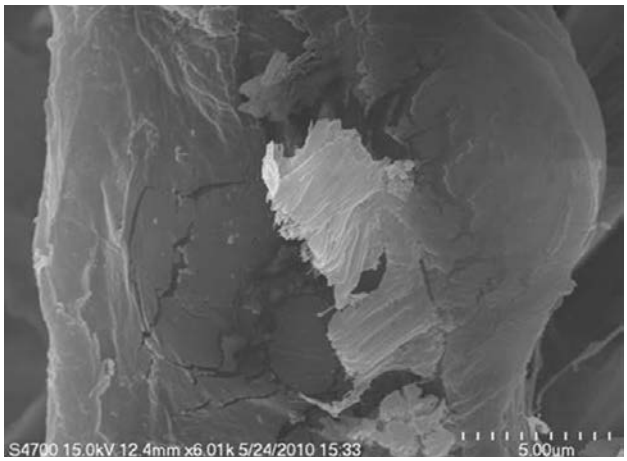


Figure 5.5. SEM images of the particles, resembling the morphology of gypsum (twinned crystal shape) and confirmed by their exclusive chemical composition of Ca, S and O.

Table 5.1. Percentage contributions of major compound classes to particulate mass concentrations (24-hour averages) derived from XRF analysis

Date	PM_{10}[a] (μg/m³)	$nssSO_4$ (%)	Ash (%)	Sea salt (%)
04/05/2010	9.23	35	24	40
17/05/2010	11.45	33	39	28
	$PM_{2.5}$[a] (μg/m³)	$nssSO_4$ (%)	Ash (%)	Sea salt (%)
04/05/2010	3.53	76	22	1
17/05/2010	5.03	64	30	7
	$PM_{2.5-10}$[a] (μg/m³)	$nssSO_4$ (%)	Ash (%)	Sea salt (%)
04/05/2010	5.70	10	26	64
17/05/2010	6.42	10	46	44

[a]PM concentrations exclude nitrate, ammonium, OM and compound-bound water (as in gypsum, sulfuric acid, etc.).

Table 5.2. Percentage contribution of major oxides in the volcanic ash fraction of coarse particles derived by XRF analysis

Date	SiO_2	Al_2O_3	FeO	CaO	Na_2O	MgO	TiO_2	Sum
17/05/10	57	11	3	10	6	0	1	88
Ash fallout[a]	59	14	9	5	5	3	1	96

[a]http://www.earthice.hi.is/page/IES-EY-CEMCOM (accessed 2013; this information was later removed from the website).

The multi-analytical approach used had a huge advantage in studying the complexity and evolution of the volcanic ash plume events. HR-ToF-AMS was able to provide evidence of volcanic sulfate plumes as a result of its high temporal resolution. It was also capable of measuring sulfuric acid as the aerosol was sampled and analysed in real time. Offline analytical techniques were compromised because of their low temporal resolution, but the XRF technique was capable of full elemental analysis, in contrast to ion chromatography and AMS, which are able to determine the composition of soluble and mostly non-refractory (not destructed at 600°C) matter. Each of the techniques had its strengths and weaknesses, but collectively produced evidence of the processes and chemical reactions taking place in the ash plumes. As well as providing useful scientific evidence, the analytical inter-comparison proved the high precision and accuracy of all of the methods applied.

6 European Monitoring and Evaluation Programme Intensive Observation Periods

The EMEP monitoring programme and its strategy (2004–2009) included intensive measurement periods. The first period occurred in 2006–2007, with Aas *et al*. (2012) summarising the efforts made and lessons learned during the campaigns, which helped in designing later studies. The EMEP Task Force on Measurements and Modelling (TFMM) recommended repeating these measurements during two contrasting measurement periods in 2008/2009. The dates (15 September–15 October 2008 and 25 February–25 March 2009) were chosen to (1) investigate two different meteorological conditions with strong temperature gradients across Europe (beginning of autumn and beginning of spring), (2) include periods during which large NO_3^- events were observed across Europe in previous years and (3) maximise synergies between the regular EMEP measurements and the intensive measurement year of the European Integrated Project EUCAARI (www.atm.helsinki.fi/eucaari), which ran from February 2008 to February 2009.

During the autumn 2008 campaign, daily samples were collected for inorganic chemical analysis and weekly samples were collected for analysis of organic carbon and elemental carbon, levoglucosan (a marker for biomass burning), mineral dust and the carbon isotopes ^{13}C and ^{14}C. The EPA provided additional funding to cover the costs of those analyses, which were performed in centralised laboratories in Norway, Denmark, Switzerland and Lithuania.

The overview paper of the entire campaign has been published. The next section describes the carbon isotope analysis.

6.1 Source Apportionment by Carbon Isotope Analysis and Contribution of Mineral Dust

Particulate carbonaceous matter (PCM) has been observed to contribute significantly to ambient PM concentrations in a wide range of environments, even over remote ocean regions. However, the inherent complexity of PCM has made it difficult to quantify and resolve to a compound level. In addition, secondary processes, along with chemical processing in the atmosphere, ensure an ever-changing nature of PCM, rendering quantitative source apportionment highly challenging. Carbon isotope analysis offers a method for quantitative source apportionment of three principal sources of PCM, because of their unique isotopic signatures, i.e. marine, continental (non-fossil) fuel and fossil fuel sources (Ceburnis *et al*., 2011).

The source characterisation was performed using isotope mixing equations applied to both stable carbon isotope $d^{13}C$ and radiocarbon $D^{14}C$ isotope ratios, according to Figure 6.1. The schematic presentation

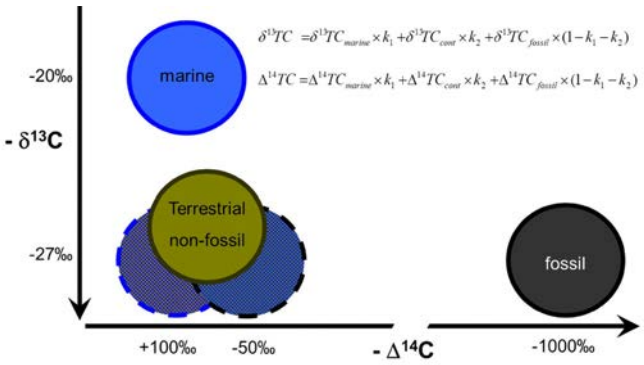


Figure 6.1. Schematic presentation of the dual carbon isotope method used for the apportionment of three principal sources of PCM: marine, continental non-fossil fuel and fossil fuel, where k_1, k_2, k_3 are contributions of the aforementioned sources and delta notations for each isotope accordingly.

reveals that the $d^{13}C$ method cannot distinguish terrestrial sources (continental non-fossil and fossil fuel) as their isotopic values overlap, whereas the $D^{14}C$ method cannot separate non-fossil sources. Combined together, dual carbon isotope analysis makes apportionment between three principal sources unambiguous.

The above equations are solved when the calculated isotopic ratios converge on the measured ratios. It is worth noting, however, that the solution is tightly constrained, with little degrees of freedom when selecting individual source ratios, primarily because the $d^{13}C$ equation clearly separates the marine source and the $D^{14}C$ equation clearly separates the fossil fuel source, because of distinctly different source ratios. For the marine, continental non-fossil fuel and fossil fuel sources, the respective $d^{13}C$ ratios are –20.5‰, –25‰ and –27‰ and the respective $\Delta^{14}C$ ratios are –50‰, 100‰ and –1000‰.

The EMEP monitoring programme, along with the EUCAARI project, conducted two intensive measurement periods in autumn 2008 and spring 2009, focusing on carbonaceous aerosol using both online and offline chemical analysis. In the present study, we report the results from the offline chemical analysis at Mace Head station, where ^{13}C, ^{14}C and ^{15}N were determined in $PM_{2.5}$ filter samples, collected according to the quartz-behind-quartz sampling approach, as well as organic carbon, elemental carbon and levoglucosan. Five weekly samples were collected in autumn 2008 and four weekly samples were collected in spring 2009. The contribution of marine, continental non-fossil fuel and fossil fuel sources to TCp (particulate TC) is presented in Figure 6.2, showing the dominance of the continental non-fossil fuel source. An attempt was made to separate continental non-fossil fuel sources into biomass burning and natural terrestrial sources using the biomass-burning tracer levoglucosan; however, a question remains whether levoglucosan can be an equally good tracer in fresh and aged carbonaceous aerosol for reliable biomass-burning source apportionment (Yttri *et al*., 2019).

Apart from the source apportionment, some new insights were obtained by the determination of stable nitrogen isotope (^{15}N) levels in spring 2009 samples and stable carbon isotope (^{13}C) levels on the sequentially stacked-up front and back quartz filters. The gaseous species would be adsorbed on both front and back filters, while PCM would be adsorbed on the front filter only, revealing a positive sampling artefact. A statistically significant difference in nitrogen isotope ratios was obtained between anthropogenically perturbed samples (4.82‰) and clean marine samples (–1.24‰), clearly showing that clean and polluted samples exhibit not only distinct stable carbon isotope ratios but also distinct nitrogen isotope ratios.

Stable carbon analysis of the sequentially stacked-up front and back quartz filters suggested that gas phase compounds adsorbed on the back filter, and considered to be responsible for the positive sampling artefact, are “lighter” in terms of the stable carbon isotope (~1‰). It cannot yet be concluded whether this finding is due to isotopic fractionation or is

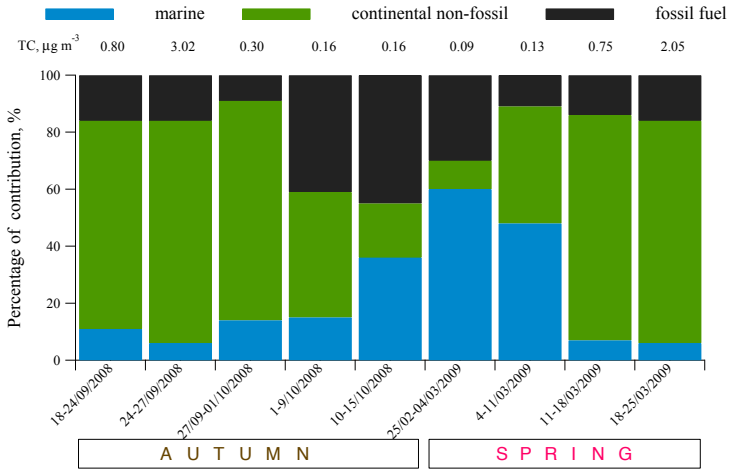


Figure 6.2. Contribution of three principal sources of PCM during the autumn and spring EMEP intensive observation periods. Individual weeks noted along the *x*-axis.

simply source dependent. Our findings suggest that continental non-fossil fuel sources are more significant than previously thought and thus should be adequately considered in models.

In addition to carbonaceous aerosol analysis, $PM_{2.5}$ samples were analysed for mineral dust, which in some regions may contribute significantly to or even dominate PM mass. However, the analysis of mineral dust in the Mace Head samples revealed that its contribution to the $PM_{2.5}$ mass was negligible – approximately 1–2% only. Mineral dust is very rarely transported to northern latitudes from the Sahara region in Africa, but this often remains above the boundary layer.

7 Support of Ongoing Research Programmes

During the project a significant effort was devoted to supporting national and international research campaigns at Mace Head and ongoing research programmes. The following sections outline contributions made during these activities and corresponding research papers published during the fellowship period.

7.1 MaCloud – Marine Aerosol–Cloud Interactions

The ad hoc transnational-access EUSAAR (European Supersites for Atmospheric Aerosol Research; 2010) and ACTRIS (Aerosol, Clouds and Trace Gases Research Infrastructure; 2011) campaigns were organised at Mace Head, with a 2-week winter (1–15 December 2010) and 4-week summer (1–30 May 2011) observation period.

The aims of this research were to:

- source apportionment of marine aerosol;
- quantify the formation and evolution characteristics;
- quantify the hygroscopic and CCN properties;
- quantify marine aerosol impacts on cloud microphysics.

The winter campaign focused on quantifying sea salt production and its impact on cloud physics whereas the summer campaign was organised to quantify primary, secondary and organic/biological impacts on cloud microphysics.

A suite of state-of-the-art instrumentation was deployed and facilitated at Mace Head:

- online aerosol mass spectrometric techniques and offline proton nuclear magnetic resonance (HNMR) techniques for aerosol chemical characterisation [e.g. HR-ToF-AMS, ATOFMS, micro-orifice volatilisation impactor–chemical ionisation mass spectrometer (MOVI-CIMS), thermal desoprtion chemical ionisation mass spectrometer (TD-CIMMS)];
- aerosol physics instrumentation for physical characterisation of the particles [neutral cluster and air ion spectrometer (NAIS), AIS, pulse height condensation nucleus counter (PH-CPC), nanoparticle scanning mobility particle spectrometer (SMPS)];
- a range of mass spectrometer techniques for gaseous characterisation [O_3, volatile organic compounds (VOC), OH, H_2SO_4, MSA, I_2, API-ToF-MS, particle size magnifier (PSM) and proton transfer reaction mass spectrometer (PTR-MS)];
- a range of hygroscopic uptake and CCN instruments for both air and laboratory studies [hygroscopicity tandem differential mobility analyser (HTDMA), volatility hygroscopicity tandem differential mobility analyser (VHTDMA), CCN, bubble tanks);
- ground-based remote sensing and *in situ* aircraft to determine cloud microphysics, e.g. CLOUDNET (study entitled ‘development of European pilot network of stations for observing cloud profiles’) and FAAM (Facility for Airborne Atmospheric Measurements study) cloud radar, lidar, microwave profiler and aircraft).

7.2 Laboratory Experiments to Study the Primary Production of Marine Aerosols

Laboratory experiments to study the primary production of marine aerosols were conducted and co-ordinated as part of the EPA-funded project EASI-AQSIS, at no additional cost to the fellowship project of Darius Ceburnis.

A stainless-steel tank was designed and built for the bubble-bursting experiments, to study the primary production of marine aerosols from phytoplankton exudates. Together with collaborators from the Martin Ryan Marine Institute, National University of Ireland, Galway, laboratory experiments using two different phytoplankton species – diatoms (*Leptocylindrus danicus* and *Cylindrotheca closterium*) and *Emiliania huxleyi* and their different densities – were carried out using a suite of instruments: AMS, HTDMA, SMPS and Berner impactors.

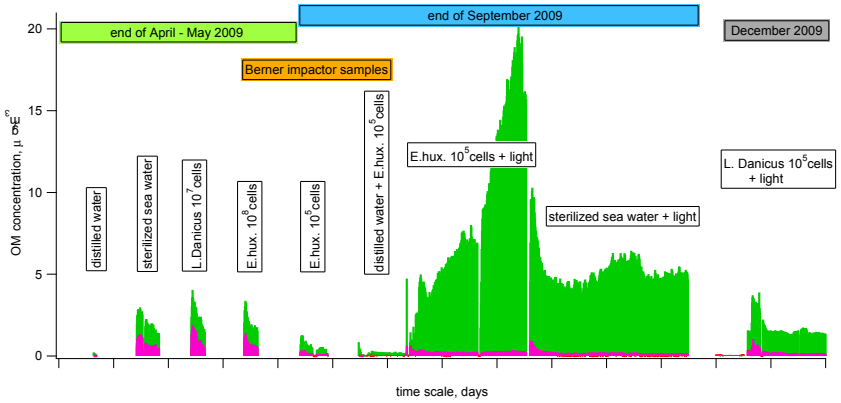


Figure 7.1. Bubble-bursting experiment time series during 2009. Only the concentrations of OM (green) and chloride (pink) measured by AMS are presented.

A summary of the evolution of sea spray OM during the experiments is presented in Figure 7.1. In all but one experiment in Figure 7.1 there was no significant OM released during the first 8 hours of experiments, regardless of the cell density used. However, during the experiment in September 2009 with *E. huxleyi* microalgae, a massive release of OM was observed about 24 hours after the start of the bubble-bursting experiment which lasted another 24 hours until the experiment was terminated to cross-check the sterilised sea water. The reasons for this significant release of OM remain unclear, but it was not related to external contamination or other external factors examined (temperature of the water, flow regime inside the bubble-bursting tank, age of the culture, light regime). In fact, the experiment was repeated six more times in 2010 and only once was a similarly large release of OM observed again (March 2010). This time more concurrent measurements were available, which included SMPS and HTDMA measurements. The SMPS spectrum is presented in Figure 7.2 and is classified into a low organic phase (initial 24-hour stage of the experiment) and a high organic phase (peak OM concentration). Notably, the total particle number concentration increased by about 25% whereas the total particle volume increased by over 60%, because of the significant increase in particle diameter, from a mode of about 100 nm to a mode of about 140 nm. However, the total OM mass increased by about five times, as revealed by AMS and offline chemical analysis. Consequently, considering the physical and chemical measurements together, OM enrichment in submicron sea spray particles must have increased from about 10% to about 50% on average during the peak OM concentration, in order to explain the tremendous increase in organic mass. The high enrichment and its increase with decreasing particle size was confirmed by offline chemical analysis of Berner impactor samples (Figure 7.3). Such an enrichment pattern was observed in ambient studies (O'Dowd *et al*. 2004) and laboratory studies (Facchini *et al*. 2008b). The released OM was very CH like, as presented in Figure 7.4, with most of the mass accounted for by CH ion fragments and the associated oxygen-to-carbon ration being as low as 1.05, suggesting the presence of long-chain aliphatic compounds.

The corresponding HTDMA measurements of selectively chosen particle sizes (50, 75, 110 and 165 nm) are presented in Figure 7.5, split into low and high OM phases. As the OM fraction increased, the particles became increasingly hydrophobic, which is consistent with their CH-dominated content. Moreover, hydrophobic properties (low hygroscopic GF) were significantly more pronounced for smaller particles (50 nm) than for larger particles (165 nm). This is consistent with the property of surface-active hydrophobic compounds (micelle type and aggregated hydrogels) to enrich more as the particle size decreases (above the size at which the Kelvin effect would be pronounced). Considering all of the spectra and all of the particle sizes in Figure 7.5 together, it is evident that OM enrichment must have been approximately 50%, consistent with the considerations above.

Considering multiple lines of evidence, the large amount of OM released by bubble bursting using *E. huxleyi* microalgae was very hydrophobic (exhibiting low GF), with its content being mainly

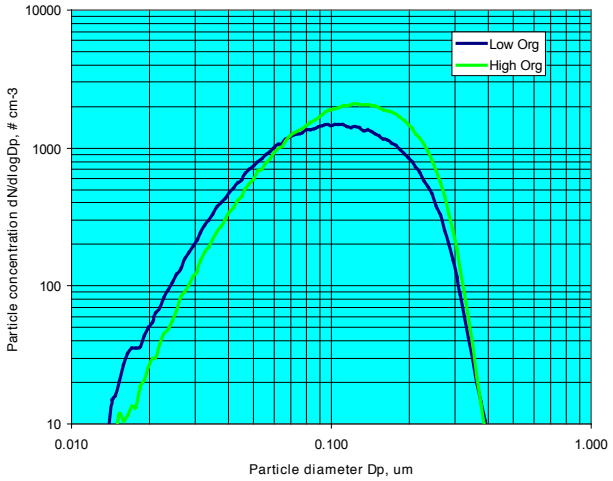


Figure 7.2. The SMPS spectrum during the successful experiment in March 2010. Low (blue) and high (green) OM phases are presented.

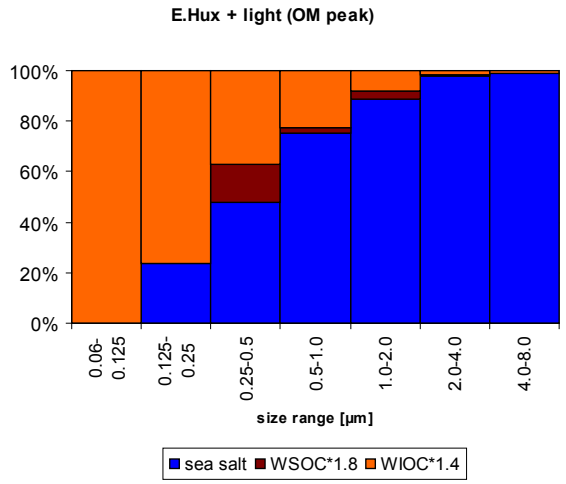


Figure 7.3. Size-segregated percentage composition of Berner impactor samples collected during the high OM release phase. Both of the carbon species, WSOC and WIOC, were multiplied by the coefficient to convert to OM mass to account for the average oxygen mass.

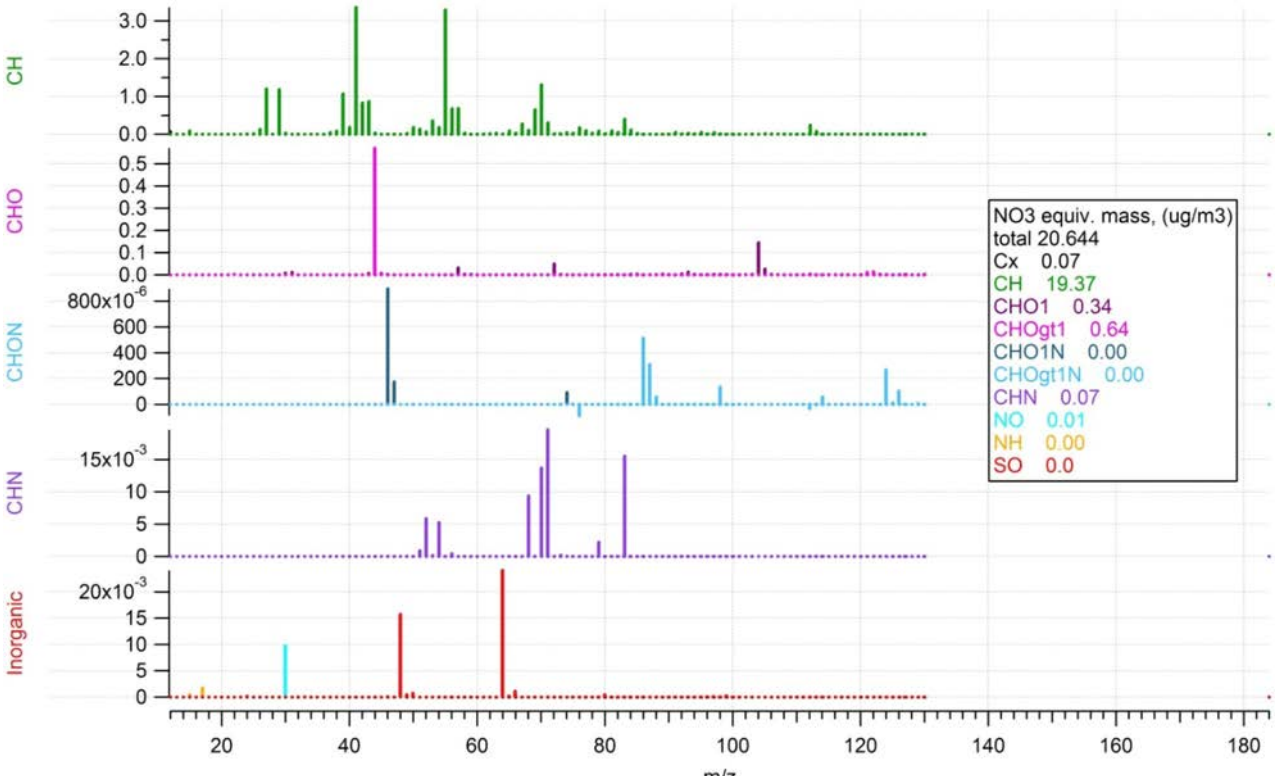


Figure 7.4. Organic mass in nitrate-equivalent organic mass split between CHs, CHOs, oxygenated hydrocarbons with nitrogen (CHONs), hydrocarbons without nitrogen (CHN) and inorganics.

CH dominated – most likely long-chain aliphatic compounds. In addition, the particles were significantly enriched in OM, with the enrichment increasing as the particle size decreased. The only common feature that was typical during two successful experiments with a significant release of OM was the rather high

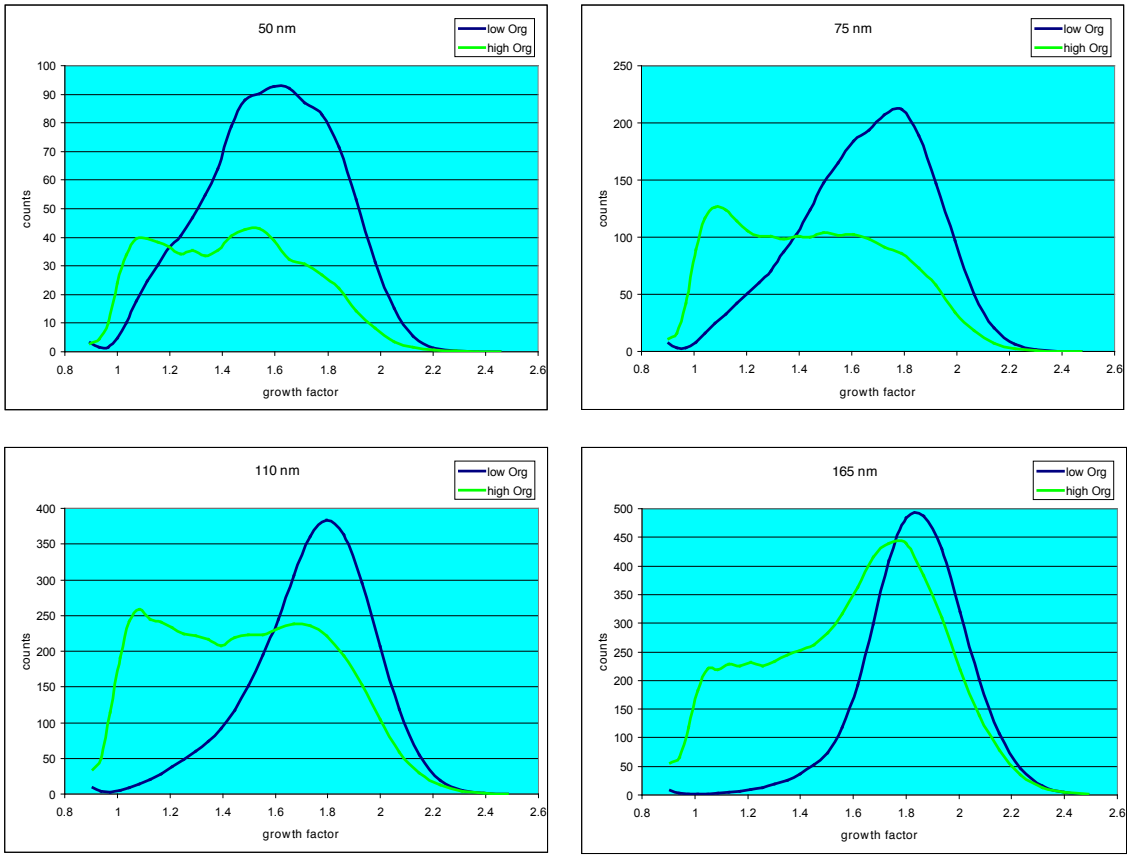


Figure 7.5. The HTDMA GF spectra of the 50, 75, 110 and 165 nm particles during the low and high OM phases.

OM content background in sterilised sea water before *E. huxleyi* was added; however, it is unclear how this related to the observed results.

7.3 European-wide MONET Project

The Stockholm Convention on Persistent Organic Pollutants (POPs) entered into force on 17 May 2004, with the main objective being to protect human health and the environment from POPs by reducing or eliminating their release into the environment. According to Article 16 of the Stockholm Convention, its effectiveness was to be evaluated 4 years after the date of its entry into force, and periodically thereafter at intervals to be decided by the Conference of the Parties (COP). A global monitoring plan was developed, with the objective of evaluating whether POPs actually had been reduced or eliminated on a global scale. The design of the continent-wide network had to address the long-term need to obtain appropriate representative data from all regions to achieve global coverage. The contribution of the fellowship holder was to facilitate the sampling programme at Mace Head, which was considered to be a key station in the network. Figure 7.6 shows the extended network of stations participating in the European-wide Monitoring Network (MONET). During 2009–2011, 4-weekly samples were collected at Mace Head and samples were analysed by the Research Centre for Environmental Chemistry and Toxicology at Masaryk University, Brno, Czech Republic. Sample collection is now complete. In total, 48 different POP species have been measured, with a selected few presented in Figure 7.7. The concentrations presented in Figure 7.7 represent analytical data that became available during the fellowship report preparation and were not analysed because of a lack of time and expertise. The POP sampling protocol is based on a passive sampling approach using impregnated polyurethane foam, but conversion factors are fairly well established to derive air concentrations accordingly.

A 12-weekly sampling protocol was followed during 2011–2013. Although the sampling duration increased, the number of POP species also increased, as the network expanded into the African continent.

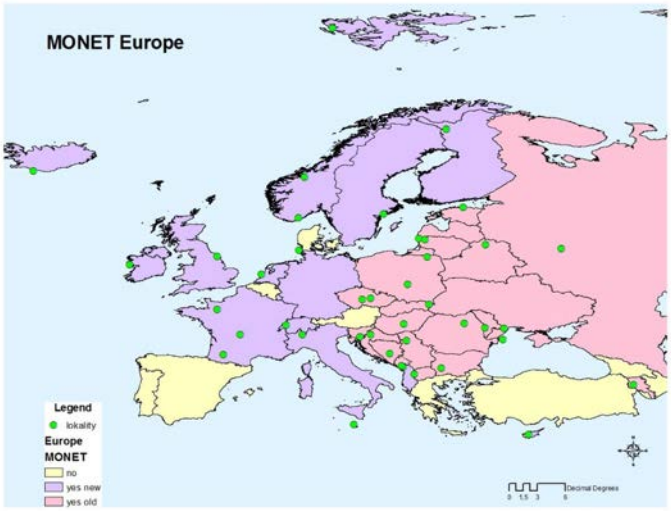


Figure 7.6. The European-wide MONET network for sampling POPs.

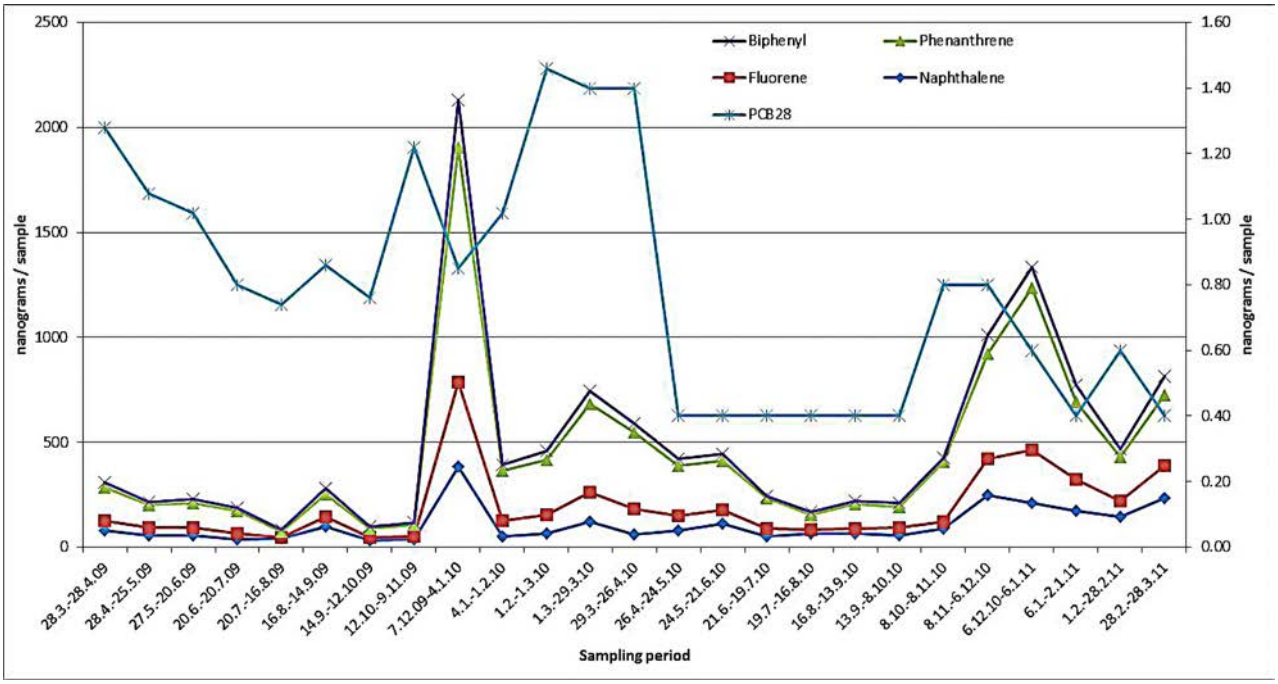


Figure 7.7. POP concentrations of selected species during 2009–2011 at Mace Head.

7.4 Fundamental Studies of Marine Aerosols

The fellowship holder was responsible not only for $PM_{2.5}$ and $PM_{2.5–10}$ inorganic composition data collection but also for numerous other instruments and collection of data: an aerosol particle counter for supermicron particle measurements; tapered element oscillating microbalance (TEOM) for particulate mass measurements; Berner impactors for size-segregated chemical composition measurements; collection of PM_1 size selective samples on quartz filters; co-responsible for AMS and black carbon measurements. Data from all of the above techniques have been published, contributing to the advancement of atmospheric science (Chamaillard *et al*., 2010; Coen *et al*., 2010; Rinaldi *et al*., 2010a,b, 2011; Dall'Osto *et al*., 2010a,b, 2011, 2012; Maninen *et al*., 2010; Lehtipalo *et al*., 2010; Ehn *et al*., 2010; Facchini *et al*., 2010, 2011; Thalman *et al*., 2011; Decesari *et al*., 2011). The fellowship holder significantly contributed to all of these publications, not only providing data but also working on the manuscripts and contributing to the post-review process.

7.5 Contribution of Data for Modelling Studies

The comprehensive PM chemical composition dataset accumulated over the years of measurements performed at Mace Head provides an excellent data source for various research studies, especially modelling studies. There have been numerous requests for the data from within and outside the research group. Vignati *et al*. (2010), Myriokefalitakis *et al*. (2010) and Gantt *et al*. (2011, 2012) have used Berner impactor data on the clean marine sector collected during 2002–2009. Mangold *et al*. (2011) and Varghese *et al*. (2011) validated model performances (REMOTE and European Centre for Medium Range Weather Forecast) using inorganic chemical data from 2003. O'Dowd *et al*. (2012) used AMS and TEOM high time resolution sulfate data obtained during the volcanic ash plume advections. In total, seven research papers have benefitted from data collected by the fellowship holder over several years.

8 Data Collection, Quality Control and Archiving

Data collection and quality control for offline and online chemical measurements were an essential part of the fellowship activities. Development of the quality control routine was outlined as a deliverable in the fellowship proposal. The inorganic components of PM samples were measured using liquid chromatography, with positive and negative ions quantified separately. Both positive and negative ions should be balanced as they constitute certain chemical compounds in the particles. The method was already successfully applied, as described by Ceburnis *et al*. (2006), with the method revealing certain deficiencies in the PM samples. The ion balance method, which is the ratio of positive and negative ions, can give insight into missing chemical species or incomplete chemical analysis, e.g. carbonates are not normally measured using high-performance liquid chromatography techniques. In other cases, when potentially missing species would constitute a minor fraction of PM, e.g. crustal dust in maritime air masses, the ion balance method will point to analytical errors. The samples were routinely subjected to an ion balance check during a validation procedure. Another quality control check was carried out by comparing high-performance liquid chromatography-derived inorganic component concentrations with aerosol mass spectrometer-derived concentrations. The above checks ensure comparability and consistency between different techniques, giving a high degree of confidence in the results obtained.

The aerosol data being measured at Mace Head are being converted to the NASA Ames 1000 format used by EMEP. Mean hourly data for the following aerosol parameters, using the NASA Ames 1000 format, are being sent to the European Aerosol Database hosted by the Norwegian Institute for Air Research (NILU), Norway (http://www.nilu.no/projects/ccc/create):

- total condensation particle number concentration;
- aerosol scattering coefficient;
- $PM_{2.5}$ mass (TEOM); and
- aerosol size distribution (SMPS).

The aerosol optical depth data are being sent to the World Radiation Centre at Davos, Switzerland, under the auspices of the WMO GAW, which is transmitting the data to the World Data Centre for Aerosols (WDCA), run by WMO GAW, through Dr Julian Wilson at the Institute for Environment and Sustainability, European Commission, DG Joint Research Centre, Ispra, Italy.

9 Peer-reviewed Publications Produced during the Project

1. Vignati, E., Facchini, M.C., Rinaldi, M., Scannell, C., Ceburnis, D., Sciare, J., Kanakidou, M., Myriokefalitakis, S., Dentener, F. and O'Dowd, C.D., 2010. Global scale emission and distribution of sea-spray aerosol: sea-salt and organic enrichment. *Atmospheric Environment* 44: 670–677.

2. Chamaillard, K., Jennings, S.G., Ceburnis, D., Yoon, Y.J. and O'Dowd, C.D., 2010. Effect of instrumental particle sizing resolution on the modelling of aerosol radiative parameters. *Journal of Quantitative Spectroscopy & Radiative Transfer* 111: 753–771.

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10 Conclusions

Long-term observations of the chemical composition of $PM_{2.5}$ and $PM_{2.5–10}$ revealed significant reduction trends of pollutants over the last 10 years. The trends were consistent between stations at Mace Head and Valentia and concurrent with decreasing emissions in Ireland and Europe. The sulfate trend quantitatively matched the reduction in sulfur dioxide concentrations and total sulfurous emissions in Ireland. A reduction in sulfurous emissions in Ireland is likely to be an indication of the emission trend in Europe or even worldwide, as atmospheric concentrations observed at Mace Head are not a direct consequence of emissions reductions in Ireland alone. This result has important policy implications as it demonstrates the value of continuous long-term measurements of PM and the success of the emissions reduction policy in Ireland and beyond.

High time resolution measurements using aerosol mass spectrometers clearly showed their advantages in studying urban and marine environments. A study of pollution sources in Cork city demonstrated that wood burning in Ireland contributes significantly to carbonaceous PM, despite it being a minor fuel type, with a similar conclusion attributed to the use of peat and coal as domestic fuel. It was proven for the first time that AMS can quantitatively measure sea salt unambiguously, demonstrating that all major chemical species can be reliably monitored using the online technique. It is recommended that offline chemical analysis techniques should be combined with near real-time analytical techniques such as AMS for studying pollution episodes and regional and intercontinental transport of aerosols. The concurrent use of different techniques is always beneficial for quality control, especially as near real-time AMS measurements are clearly the future of air quality observations. Near real-time measurements have great value in providing air quality guidance to the public.

The intensive observation period during the Eyjafjallajökull eruption revealed that the Mace Head location is an ideal spot for observing volcanic ash advections from Iceland and resulted in extensive efforts towards building volcanic ash detection and forecast capacity for the aviation industry. After the Eyjafjallajökull eruption, the Irish Aviation Authority became interested in investing in advanced measurements at stations such as Mace Head or at national airports.

Carbonaceous matter source apportionment using a dual isotope technique was performed for the first time at the EMEP network station Mace Head. Carbon isotope analysis of aerosol samples demonstrated the benefits of the technique, suggesting that a more accurate carbon budget can be obtained, enabling more precise source apportionment of carbonaceous PM at a given location.

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Abbreviations

AEROCE	Atmosphere/Ocean Chemistry Experiment
AMS	Aerosol mass spectrometry
ATOFMS	Aerosol time-of-flight mass spectrometry
CCN	Cloud condensation nuclei
CDNC	Cloud droplet number concentration
CH	Hydrocarbon
CHO	Oxygenated hydrocarbon
CN	Condensation nuclei
DEA	Diethylamine
DMA	Dimethylamine
EMEP	European Monitoring and Evaluation Programme
EPA	Environmental Protection Agency
ERC	European Research Centre
EUCAARI	European Integrated project on Aerosol Cloud Climate and Air Quality Interactions
GAW	Global Atmosphere Watch
GF	Growth factor
HTDMA	Hygroscopicity tandem differential mobility analyser
MONET	Monitoring Network (for persistent organic pollutants)
MSA	Methanesulfonic acid
NH_4	Ammonium/ammonia
NO_3	Nitrate
nssSO_4	Non-sea salt sulfate
OM	Organic matter
OM_{ss}	Organic enrichment in sea spray
PCM	Particulate carbonaceous matter
PM	Particulate matter
POP	Persistent organic pollutant
SEM	Scanning electron microscopy
SMPS	Scanning mobility particle spectrometer
TEOM	Tapered element oscillating microbalance
TN	Total nitrogen
TSP	Total suspended particulate
WIOC	Water-insoluble organic carbon
WIOM	Water-insoluble organic matter
WMO	World Meteorological Organization
WSIN	Water-soluble inorganic nitrogen
WSOC	Water-soluble organic carbon
WSOM	Water-soluble organic matter
WSON	Water-soluble organic nitrogen
XRF	X-ray fluorescence

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL
Tá an Ghníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaol a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaol a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: *Déanaimid córais éifeachtacha rialaithe agus comhlíonta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.*

Eolas: *Soláthraímid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírithe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.*

Tacaíocht: *Bímid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaol atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaol inbhuanaithe.*

Ár bhFreagrachtaí

Ceadúnú
Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaol:
- saoráidí dramhaíola *(m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistrithe dramhaíola)*;
- gníomhaíochtaí tionsclaíocha ar scála mór *(m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta)*;
- an diantalmhaíocht *(m.sh. muca, éanlaith)*;
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe *(OGM)*;
- foinsí radaíochta ianúcháin *(m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha)*;
- áiseanna móra stórála peitril;
- scardadh dramhuisce;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil
- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdaráis áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhíriú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídíonn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaol.

Bainistíocht Uisce
- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uiscí idirchriosacha agus cósta na hÉireann, agus screamhuiscí; leibhéil uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaol
- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil *(m.sh. tuairisciú tréimhsiúil ar staid Chomhshaol na hÉireann agus Tuarascálacha ar Tháscairí)*.

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn
- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis cheaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil
- Taighde comhshaoil a chistiú chun brúnna a shainaithint, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta
- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaol in Éirinn *(m.sh. mórphleananna forbartha)*.

Cosaint Raideolaíoch
- Monatóireacht a dhéanamh ar leibhéil radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas
- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaol ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaol *(m.sh. Timpeall an Tí, léarscáileanna radóin)*.
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chosc agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta
- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil
Tá an ghníomhaíocht á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:
- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- Oifig um Chosaint Radaíochta agus Monatóireachta Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltaí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair imní agus le comhairle a chur ar an mBord.

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Research Support for Integrated Atmospheric Studies at Mace Head

Authors: Darius Ceburnis, Colin D. O'Dowd, Stephen G. Jennings and Margaret Ryan

Under the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (CLRTAP), member countries have an obligation to address scientific issues such as the effect of hemispheric transport of air pollutants on air pollution concentrations in the Northern Hemisphere. The Mace Head Atmospheric Research Station is a renowned world-class facility lacking operational support. The support of established facilities offered a great return on investment from consolidated knowledge and the extent of synergistic observations. The ongoing observations at established national facilities such as the Mace Head and Valentia stations require coherent study of emerging trends to ensure data consistency. The value of continuous scientific operations can be highlighted by accidents such as the 2010 Eyjafjallajökull eruption in Iceland in 2010.

Identifying Pressures

Air pollution reduction measures aimed at improving human well-being may result in stronger, accelerated global warming; this is becoming evident, especially over the Polar regions. Consequently, air quality issues have to be looked at concurrently with climatic implications, both of which can be enabled by observations carried out at the developed world-class infrastructure at Mace Head. The highest uncertainty in air pollution studies comes from inaccurate source apportionment using traditional offline chemical analysis. New, more accurate and rapid methods need to be developed and applied to adequately respond to air quality pressures.

Informing Policy

This fellowship consolidated and facilitated research efforts and outcomes at the Mace Head facility, with specific research topics aimed at informing policies such as the Clean Air Act. Long-term measurements supported at Mace Head provided evidence that air pollution measures aimed at reducing sulfurous emissions have had great success, dramatically reducing sulfate levels in the entire North Atlantic region. Synergistic deployment of state-of-the-art instrumentation revealed that air pollution episodes in cities are caused by solid fuel combustion, with significant contributions from wood, peat and coal. The established and facilitated 24/7 near-real-time measurements of aerosol chemical composition by aerosol mass spectrometry offer a method of air pollution monitoring at reduced cost, as well as the ability to provide a rapid emergency response. This was demonstrated during the Icelandic volcano eruption in 2010.

The 31 research papers contributed by the fellowship holder demonstrate the scope and extent of the consolidated research efforts, leading to improved understanding of air quality and climate associations and better-informed policies at national and international level.

Developing Solutions

This fellowship enabled and sustained scientific operations at Mace Head Atmospheric Research Station. The advanced method of dual carbon isotope analysis will allow better identification of natural and anthropogenic source contributions, which is essential for quantifying human-induced global climate change. The emerging state-of-the-art methodology developed using near-real-time aerosol mass spectrometry will enable a rapid response during emergency situations.

EPA Research: McCumiskey House, Richiew, Clonskeagh, Dublin 14.

Phone: 01 268 0100
Twitter: @EPAResearchNews
Email: research@epa.ie

www.epa.ie

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