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An Integrated Source Apportionment and Climatic Implications of $PM_{2.5}$ and PM_{10} Particulate Matter

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Rialtas na hÉireann
Government of Ireland

ENVIRONMENTAL PROTECTION AGENCY

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- Office of Environmental Enforcement
- Office of Evidence and Assessment
- Office of Radiation Protection and Environmental Monitoring
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EPA RESEARCH PROGRAMME 2014–2020

An Integrated Source Apportionment and Climatic Implications of $PM_{2.5}$ and PM_{10} Particulate Matter

(2012-CCRP-FS.12)

EPA Research Report

Prepared for the Environmental Protection Agency

by

National University of Ireland Galway

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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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Executive Summary

Under the United Nations Economic Commission for Europe (UN-ECE) 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 in the northern hemisphere for a range of air pollution parameters, including fine particles and their precursors, ozone and its precursors and acidifying substances. There is still a lack of knowledge of particulate matter (PM) chemical composition and of sources of PM for Ireland. Long-term observations of $PM_{2.5}$ and $PM_{2.5–10}$ chemical composition have revealed significantly reducing trends in pollutants over the last 10 years, and an even longer, 35-year-long trend at Valentia Island (Co. Kerry). The trends were similar at stations at Mace Head and Valentia and consistent with decreasing emissions in Ireland and worldwide. Sulfate trends quantitatively matched the reduction in sulfur dioxide concentrations and the total sulfurous emissions in Ireland and Europe. The latest data suggest that sulfate concentrations are approaching hemispheric background concentrations of biogenic sulfate, demonstrating the success of pollution abatement strategies. However, a follow-up study that included a complete characterisation of ambient PM highlighted the efforts needed to address organic compounds that are not yet continuously monitored in regulatory networks across Europe.

An important intra-activity interaction was a combination of offline and online chemical composition measurements, i.e. aerosol mass spectrometry (AMS) and filter or impactor data. The use of both methods helps to validate the findings of each method and inform about their drawbacks. AMS is a powerful tool for aerosol studies, but its findings need to be verified and supported by other measurements. In addition, AMS measurements provide information only about non-refractory species (evaporating rapidly at 600°C) of PM and are limited to PM_1 size range. Although this range is thought to be the most crucial when considering air quality and human health interactions, the PM_1 category has not yet been incorporated into policy. The offline filter technique has major limitations, including time resolution, the need for a fully functioning analytical laboratory and, most importantly, the fact that data emerge only several months after actual sampling. The problem becomes particularly acute if unrecognised contamination affects the samples. AMS and the more user-friendly aerosol chemical speciation monitoring (ACSM) have been deployed on a 24/7 basis at Mace Head since 2008 and 2011, respectively, which has enabled comprehensive long-term comparison of near real-time data with offline data. The fellowship holder 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 of different complexity have been used in parallel to apportion various sources of organic matter. Several studies across the European continent as well as in Cork city have shown that both regional and local sources contribute to aerosol organic matter and have demonstrated the resolving power of positive matrix factorisation techniques. A study of pollution sources in Cork city has demonstrated the importance of regional and local pollution sources and their significant contribution to carbonaceous PM. Domestic solid fuel combustion is becoming a key source in Ireland, necessitating high-level focus and funding to quantitatively apportion the various sources. Clearly, a tighter control of the domestic fuel market would have a profound effect on pollution levels. Given their deployment flexibility and their ability to discriminate between different domestic solid fuel sources, high time resolution of real-time measurement techniques is highly recommended for air quality monitoring and addressing various local pollution problems.

Application of the carbonaceous matter source apportionment technique at the clean Southern Ocean environment at Amsterdam Island proved yet again the resolving power of isotope analysis. Carbon isotope analysis of aerosol samples revealed fundamental processes at the ocean surface and the atmosphere, where biological activity is playing a key role in organic matter enrichment of atmospheric particles. A dual-source model encompassing isotope fractionation

processes was proposed to inform an ongoing debate about the origin and the importance of marine biogenic organic matter.

Pollution abatement strategies aimed at improving air quality and, consequently, human health have resulted in reduced pollutant concentrations. However, reducing pollutant levels has significant climatic implications owing to aerosol cooling effects, which counteract global warming caused by greenhouse gases. The climatic implications of PM have been studied by looking at long-term surface global radiation trends alongside continuously reducing sulfate concentrations. It was found that over the last four decades global radiation has increased by approximately $5\,W\,m^{-2}$ while at the same time non-sea salt (nss) sulfate has decreased by approximately $2\,mg\,m^{-3}$. The results suggest that global brightening is occurring as pollution levels are decreasing, which is bad news for the global climate as it means that aerosols are reducing their cooling capacity. It is necessary to improve air quality at the same time as reducing greenhouse gas emissions if dangerous global warming is to be avoided.

The approach to this project implied close interaction with many researchers, including those from outside the country, during international field campaigns or collaborative projects. A comprehensive data set accumulated over the years of measurements at Mace Head is an excellent resource 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 significant effort was devoted to supporting national and international research campaigns at Mace Head and beyond: EMEP (European Monitoring and Evaluation Programme), PEGASO (Plankton-derived Emissions of trace Gases and Aerosols in the Southern Ocean), BACCHUS (Impact of Biogenic versus Anthropogenic emissions on Clouds and Climate: towards a Holistic UnderStanding) and MONET (Monitoring Network for Persistent Organic Pollutants). Twenty-six papers were submitted to peer-reviewed journals during the project, which demonstrates the significance of the research being supported at Mace Head research station and the efficient use of the expertise of the fellowship holder. Two intensive measurement campaigns co-ordinated by the EMEP programme were facilitated at Mace Head.

Overall, the research carried out at the Centre for Climate and Air Pollution Studies at National University of Ireland Galway, and at Mace Head Atmospheric Observatory in particular, is crucial in informing air quality policy in Ireland, by developing new approaches and tools to be used in the near future.

1 Introduction

1.1 Particulate Matter and Health Effects

Atmospheric particulate matter (PM) has been proved to adversely affect human health, ecosystems (through acidification and eutrophication) and visibility. Therefore, emission abatement measures have been implemented over the last few decades for PM_{10} and $PM_{2.5}$ (WHO, 2005). A clear association between mortality and urban air pollution in Ireland has been demonstrated by Kelly and Clancy (1984) and all over the world in numerous other studies. Dockery *et al*. (1993) convincingly demonstrated that there are clear health advantages of living in less polluted cities, suggesting that there is no limit to improving air quality with regard to continuing health benefits. Based on the hemispheric transport of air pollution multi-model experiments, the intercontinental transport of PM also influences human mortality rates. It is estimated that, of the total deaths associated with emissions in North America and Europe, 15% and 12%, respectively, are attributable to pollution originating outside these regions (TF HTAP, 2010). It must be acknowledged, however, that little is known yet about which PM properties (especially chemical composition) cause the health effects, although many epidemiological studies have highlighted a link between short- or long-term exposure to high levels of $PM_{2.5}$ mass concentration and adverse human health (Guo *et al.*, 2018). Puttaud *et al*. (2010) have demonstrated that aerosol characteristics can be different (or similar) at sites in different regions across Europe, even if PM mass concentrations are the same. These other characteristics are generally not available from regulatory monitoring networks, but are available from established infrastructures, such as that at Mace Head, where research projects are ongoing. As the implementation of emission reduction strategies and policies becomes more stringent, the issue of transboundary air pollution source apportionment is becoming increasingly relevant in evaluating national policy efforts to reduce air pollution levels. Ireland is mainly affected by transboundary pollution from Great Britain and Continental Europe, whereas the contribution of Ireland is a lot less significant because of associated westerly clean air masses advecting air over Ireland towards Europe, strong westerly winds facilitating mixing and efficient washout and the relatively small population of Ireland when compared with the populations of other European countries.

1.2 Climatic Implications of Particulate Matter

Atmospheric aerosols have very significant climate impacts as a result of both direct effects, by scattering and absorbing incoming solar radiation, and indirect effects, through cloud formation, cloud albedo and cloud lifetime (Intergovernmental Panel on Climate Change, 2014). All of the above effects result in global cooling that counteracts the global warming caused by greenhouse gases. Black carbon-containing particles can, on the other hand, contribute to global warming by reducing convection. Increases in aerosol concentration and changes in their composition, driven by industrialisation and an expanding population, may adversely affect water supply (Kaufman *et al.*, 2002). Most industrial nations (including developing countries) are trying to improve air quality, which will translate into a decrease in the cooling potential of atmospheric particulates in the future. It is, therefore, vital to understand the above effects, as the reduced cooling (increased warming) will have a negative impact on human health. To accurately study aerosol climate impacts requires continuous observations from satellites, networks of ground-based instruments and dedicated field experiments.

It has been demonstrated that Ireland, which is located on the western frontier of the European continent, receives plumes of North American forest fires (Forster *et al.*, 2001). Savoie *et al.* (2002) have shown that, during the late 1980s and early 1990s, the North-East Atlantic atmosphere was dominated by anthropogenic sulfate; however, particulate pollution, including sulfate-containing particulates, has decreased substantially in Europe since then (Torseth *et al.*, 2012). There is still a relative lack of knowledge of PM chemical composition and of sources of PM for Ireland. For example, measurements of the chemical composition of total suspended particulates (TSPs) or

of PM in Ireland, including in urban areas, have until recently been fairly intermittent. In the last decade only a few studies (Hellebust *et al*., 2010; Kourtchev *et al*., 2011) have been performed in Cork city, although an overview study by Yin *et al.* (2005) and Ceburnis *et al.* (2006) has also been published. Yin *et al*. (2005) reported PM_{10} and $PM_{2.5}$ data from four urban and rural locations and used a chemical mass balance method to show that the highest PM levels were often associated with polluted UK/European air masses, to which both local and long-range transported sources can be significant contributors. On the other hand, mainly local sources dominated higher levels of PM during advection of clean westerly air masses, as documented in a companion paper by Ceburnis *et al*. (2006), and suggested that Ireland is often a sink of airborne pollutants rather than a significant contributor or a regional source of pollution. Quantitative source apportionment is very difficult to address in a given country, but it is possible in Ireland owing to the exposure to contrasting air masses: clean marine air masses from the west (North Atlantic Ocean) and polluted air masses from the east (European continent).

1.3 Transboundary Air Pollution

A number of air pollutants, including PM, contribute to regional acidification, eutrophication and air pollution across Europe and in Ireland. Under the United Nations Economic Commission for Europe (UN-ECE) 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 in the northern hemisphere for a range of air pollution parameters, including fine particles and their precursors, ozone and its precursors and acidifying substances. The development and sustained support of an integrated system of observational data sources and of predictive models is required to address these important issues and related scientific questions, such as apportionment of sources to receptor regions. The Task Force on Hemispheric Transport of Air Pollution (TF HTAP) was created by the CLRTAP in December 2004 to improve our understanding of the intercontinental transport of air pollutants across the northern hemisphere. Under the leadership of the European Union (EU) and the USA, TF HTAP has organised a series of projects and collaborative experiments designed to advance scientific understanding of the hemispheric transport of air pollution (TF HTAP, 2010). The most tangible evidence for intercontinental transport of PM, often associated with biomass burning or windblown dust events, comes from satellite images, ground-based remote sensing networks and mountain-top records and long-term records of ground-based measurements in Europe, North America and Asia. PM deposition also damages a variety of different ecosystems, including forests and grasslands, through acidification. Similarly, eutrophication is damaging to biodiversity in sensitive ecosystems of low nutrient status. PM can benefit ecosystems by increasing the diffuse solar radiation; however, the contribution of long-range transport to these effects is very uncertain and largely based on poorly validated modelling efforts. The emission scenarios created by the TF HTAP, in 2010 projected a reduction in particulate sulfate levels of 30–70% and in black carbon of 15–50% by 2050. However, climate change is expected to have an impact on PM concentrations through changes in temperature, humidity, precipitation patterns and atmospheric chemistry and dynamics, as well as changing emissions from wind-blown dust, natural forest fires and biogenic hydrocarbons, all of which are not sufficiently studied. The TF HTAP (2010) has recommended that long-term observational systems be maintained and expanded, that intensive field studies be conducted to improve model validation, that innovative novel techniques be employed to quantify sources and that adjoint and other advanced modelling techniques be used to improve our understanding of current and future source–receptor relationships. An example of the use of such advanced techniques was published by Ceburnis *et al.* (2011), who demonstrated the potential of dual-carbon isotope analysis for source apportionment of carbonaceous PM.

The European Commission has proposed an ambitious strategy for achieving further significant improvements in air quality across Europe: “The Thematic Strategy on Air Pollution aims by 2020 to cut the annual number of premature deaths from air pollution-related diseases by almost 40% from the 2000 level. Under the Strategy, the Commission is proposing to start regulating fine airborne particulates, known as $PM_{2.5}$, which penetrate deep into human lungs” (URL: https://europa.eu/rapid/press-release_IP-05-1170_en.pdf).

The aim of CAFE (Clean Air for Europe Programme) is "to develop a long-term, strategic and integrated policy advice to protect against significant negative effects of air pollution on human health and the environment".

1.4 Mace Head Observatory and Its Impact

Ireland has established excellent regional and urban air quality monitoring networks in the last decade. Unified methodology has been key to the production of reliable medium- to long-term measurement series. The availability of air pollution data from sites such as Mace Head is deemed to be crucial in the framing of new air pollution legislation and its implementation thereafter. The data need to undergo quality assessment, which is resource demanding, before submission to a national or international database for archiving. The observational data are of paramount importance to the development of predictive models in order to validate them.

The aerosol measurement programme at the Mace Head Atmospheric Research Station started in late 1980s as part of the Atmospheric Ocean Chemistry Experiment (AEROCE) programme (1988–1994) co-ordinated by Prospero *et al.*, University of Miami, and permitted measurement of chemical (inorganic ion) mass concentrations of the main aerosol species in air pollutant TSPs. Measurements of aerosol TSP chemical composition, along with the collection of aerosol radiative data, resumed late in the year 2000, through funding support from the National Development Plan, administered by the Environmental Protection Agency (EPA). This work (Jennings *et al*., 2006) has provided useful natural background levels for sea salt mass concentration, albeit for a relatively short measurement period. Regional air pollution measurement networks had been established in Ireland in the 1980s and 1990s, but it was not until 2005 that reliable unified methodology was implemented in a reshuffled network. Numerous state-of-the-art instruments were acquired to expand the atmospheric research base at Mace Head and to maintain international recognition of atmospheric science in Ireland. The above efforts contributed to the longest reliable uncompromised and uninterrupted record of aerosol chemical composition measurements at Mace Head.

1.5 Objectives

The objectives of the project as outlined in the proposal were as follows:

- to facilitate sustained support for air pollution studies at Mace Head, maintaining high-quality monitoring of atmospheric pollutants;
- to provide continuing research support at Mace Head and for ongoing research programmes as agreed between the EPA and National University of Ireland Galway (NUIG);
- to produce a quantitative source apportionment for Ireland and an assessment of hemispheric and transboundary transport of pollutants using novel approaches;
- to evaluate climatic implications of fine and coarse PM.

To meet these objectives, the fellowship project implemented a process of collecting series of long-term measurements of aerosol chemicals, including inorganic, organic and persistent organic pollutant chemical species. It also facilitated research support efforts at Mace Head and for ongoing research programmes. The intensive European Monitoring and Evaluation Programme (EMEP) measurement campaigns focusing on carbonaceous PM and mineral dust and subsequent data analysis were central activities of the fellowship. A feasibility study was done using sulfur isotope analysis to unambiguously quantify sulfate sources: anthropogenic, biogenic and sea salt. The sulphur isotope study was aimed at building upon the success of carbon isotope analysis implemented by Ceburnis *et al.* (2011). An assessment of the climate effects of PM, relating PM to radiative parameters, was also undertaken. Climate impacts can be assessed only using long-term monitoring data of PM and radiative parameters, both of which have a decade-long data series. Preliminary work based on Mace Head data has shown great promise and the study was expanded into the wider European region.

The proposed work was essential in maintaining high-quality monitoring within the EMEP and Monitoring Network for Persistent Organic Pollutants (MONET) programme and is essential in producing data for modelling studies. The researcher involved in this project contributed to model validation work being undertaken in several other projects that were funded by the EPA. Real-time PM measurements at Mace

Head were used in the EU FP7 project Monitoring Atmospheric Composition and Climate and were transmitted in real time to the European Environmental Agency.

The fellowship project provided funding for a research fellow, taking advantage of the fully equipped research infrastructure at Mace Head. The fellowship project provides continuing and no-cost support to many research activities at Mace Head, but at the same time is pursuing specific tasks related to transboundary air pollution, in particular those related to the EMEP programme.

2 Measurements of Aerosol Chemical Composition and the Long-term Trends

Air pollution data from sites such as Mace Head are deemed to be a crucial input to national policy documents and to international convention task forces on air pollutant and climate change issues, and will have a direct impact on the framing of new policies and legislation and on their implementation thereafter here in Ireland. However, an international review (Barrie and Puckett, 2006) of Global Atmosphere Watch (GAW) sites in Ireland found that Mace Head was of unique importance to establishing a reliable national monitoring network. The uniqueness of the site is due to its geographical location on the west coast of Ireland facing prevailing westerlies that bring clean air into the European continent. On average, westerly clean air masses are established 50% of the time at Mace Head and the location of the site directly on the coast ensures unperturbed oceanic air flow.

The inorganic composition of fine and coarse PM has been monitored at Mace Head since 2001. While records at other locations in Ireland may go back further (e.g. at Valentia measurement started in the early 1980s), some chemical components were never reliably quantified. For instance, sulfate of sea salt origin may significantly contribute to total sulfate; therefore, quantification of non-sea salt (nss) sulfate is possible only by quantifying sea salt fractions, which requires quantification of sodium. Sodium measurements started at Valentia in 2004 and at Mace Head in 2001. Another specific example is ammonium, which can originate from agriculture, making the selection of the sampling location crucial for reliably quantifying ammonium. Higher ammonium concentrations at Valentia were the result of ammonia emissions from nearby pastures, as has been evidenced in a previous report (Ceburnis *et al.*, 2013).

Unfortunately, during the reporting period, a serious contamination issue was discovered with regard to nitrate and ammonium concentrations at Mace Head and Valentia. Pall polytetrafluroethylene (PTFE) filters were used at both stations. In 2012 and 2013, sporadic elevated concentrations of nitrate were detected, but despite serious investigation no reason for these were found. Blanks were measured on a monthly basis, but in the majority of cases the blank readings did not point towards a problem with the filters. As the measurements continued and the pattern of sporadic elevated concentrations did not go away, a detailed comparison with high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS) measurements was undertaken, which revealed more systematic elevated concentrations. In addition, both nitrate and ammonium concentrations closely followed each other, strongly pointing to an ammonium nitrate compound that is found only in polluted air masses along with nss sulfate. However, more often than not, elevated ammonium nitrate was not accompanied by elevated sulfate (e.g. 1–19 January 2014), which is environmentally inconceivable (Figure 2.1). During the period from 19 January to 29 February (JD 19–60), concentrations were correct and reliable, but not because of clean air advections, which are common throughout the year. Eventually, information received from the EMEP co-ordination centre revealed that the Pall company had indeed experienced contamination in the technological process; as a result, the EMEP network decided to replace the Pall PTFE filters with Whatman 40 filters. In Ireland sporadic contamination continued in 2016, although the frequency of episodes was significantly diminished. Unfortunately, nitrate and ammonium concentrations at both Mace Head and Valentia should be considered unreliable from 2011 until 2017, when Whatman 40 grade filters were reinstated. The changeover was undertaken concurrently at the Mace Head and Valentia stations.

This contamination was particularly damaging at very clean sites such as Mace Head, because at relatively polluted sites the problem could not easily be spotted.

2.1 Long-term Trends to Inform Clean Air Policies Required to Monitor Aerosol Organic Matter

The long-term measurement programme at Mace Head started in 2001 and was always supported by EPA projects or fellowships. Sampling intervals were irregular to begin with, from 2001 until 2006, then

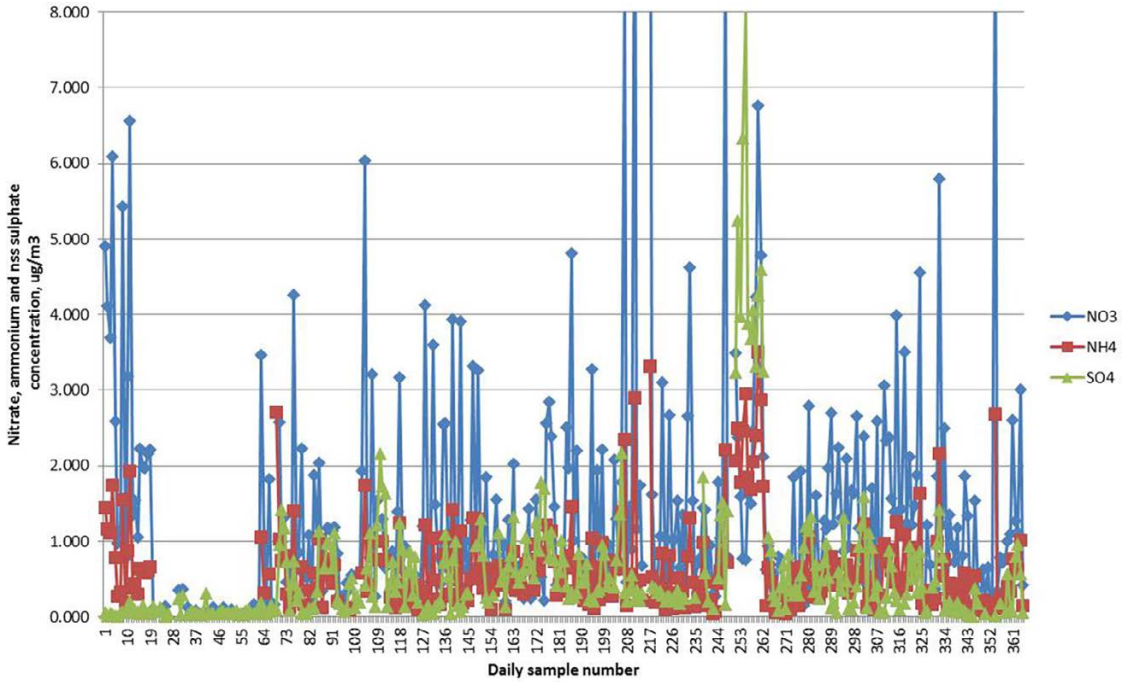

Figure 2.1. A time series of nitrate, ammonium and nss sulfate during 2014 at Mace Head.

continued on a 24-hour basis every second day from 2007 to 2012. In 2013, the sampling programme was updated to a daily sampling protocol, which has continued ever since. However, the longest record of air quality monitoring in Ireland is at Valentia, where it started in 1980. Unfortunately, until 2004 sulfate was measured as total sulfate, and without the measurement of sodium it was impossible to correct for the sea salt sulfate fraction. Figure 2.2 shows the combined time series of sulfur measurements at Valentia and Mace Head together with SO_x emissions in Europe. Yearly nss sulfate data at Valentia were corrected using sea salt sulfate concentrations measured in 2004–2005, assuming that the sea salt concentration remained stable over the years (at least on a yearly basis), allowing for the least biased correction. Notably, all concentration series follow each other closely, pointing at high accuracy of the measurements at both stations. It must be noted that sulfur concentrations derived from SO_2 and SO_4 measurements have been steadily declining since the mid-1980s, when concentrations reached their maximum. Worth noting is that concentrations of sulfur derived from SO_2 were slightly higher than concentrations of sulfur derived from SO_4, as the sulfur reduction during air mass advection is typically incomplete and limited by the oxidising capacity of the atmosphere and clouds. In about 2009, yearly sulfate concentrations started to level off and approached the biogenic background concentration, which is approximately 0.3 mg m^{-3}, which is only twice the hemispheric background concentration.

The pattern presented in Figure 2.2 clearly demonstrates the success of emission abatement strategies in Europe and worldwide.

Intensive measurement campaigns at Mace Head and in other parts of Europe, along with uninterrupted long-term near real-time measurements of complete aerosol chemical composition by HR-ToF-AMS at Mace Head, clearly point at organic matter as a major contributor to PM. Organic matter is not routinely monitored in air quality networks; hence, the measurements are missing a major fraction of PM. Low temporal resolution of filter measurement programmes and a multitude of various sources contributing to organic matter do not allow firm clean air policies to be established.

2.2 Intercontinental and Regional Transport of Air Pollution Monitored at Mace Head, Ireland, and over Europe

A number of air pollutants contribute to regional acidification, eutrophication and air pollution across Europe. Under the UN-ECE CLRTAP, member countries have an obligation to address scientific

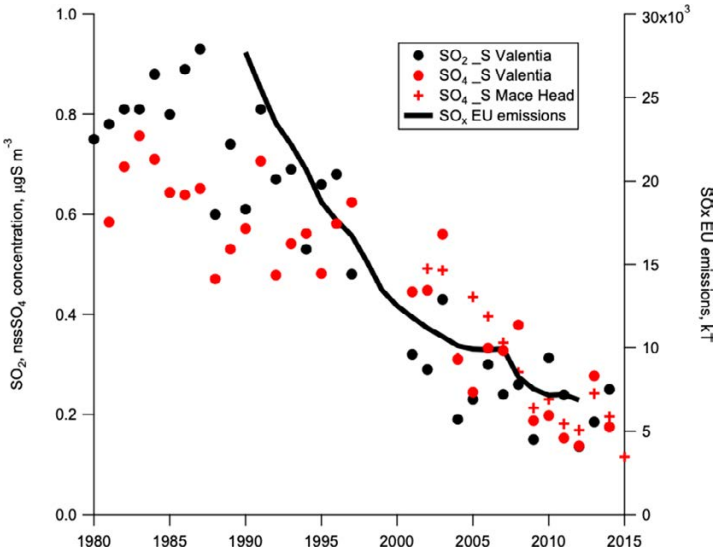

Figure 2.2. Sulfur concentrations at Valentia and Mace Head along with SO_x European emissions during the period 1980–2015. Concurrent linear rollback in reported emissions is observed in measured concentrations. Reproduced from Grigas *et al.* (2017). This is an Open Access article distributed in accordance with the terms of the Creative Commons Attribution (CC BY 4.0) 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/4.0/.

issues such as the effect of the hemispheric transport of air pollutants on air pollution concentration in the northern hemisphere for a range of air pollution parameters. This necessitates 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 AEROCE measurement programme (1988–1994) at the Mace Head Atmospheric Research Station permitted measurement of the chemical (inorganic ion) mass concentrations of air pollutant TSPs. Aerosol TSP chemical composition measurements resumed in late 2000, along with the collection of aerosol radiative data, through funding support from the National Development Plan administered by the EPA. This work has provided useful natural background levels for sea salt mass concentration as well as for nss sulfate (Jennings *et al.*, 2006; Ceburnis *et al.*, 2009). During the last decade a robust network of observations has been created in Ireland, and significant trends have recently emerged, manifesting the value of continued long-term measurements. The Mace Head Atmospheric Research Station has one of the longest uninterrupted and scientifically validated observational data records, not only in Ireland but worldwide.

The importance of the Mace Head site as a prime location for marine aerosol research is highlighted by its unique location, exposed to the North Atlantic Ocean. As a result, Mace Head has been used by several international research projects as well as for monitoring atmospheric composition. Figure 2.3 depicts 96-hour backward air mass trajectories over a 3-year period (2009–2011). Statistically, marine air masses arriving at Mace Head account for more than 50% of all air masses (Jennings *et al.*, 2003), during both winter and summer, and are consistent with Irish maritime climate features. It should be noted that over the 96-hour period maritime air masses have barely any contact with land and spend most of the time in the marine boundary layer. Dominant meteorological features make Mace Head an ideal location for observing northern hemispheric background air quality.

Non-sea salt sulfate, nitrate and ammonium concentrations have been decreasing rapidly in Ireland and over Europe in the last decade (Figure 2.4). The concentration decrease is of the order of 40–70% at all monitoring stations across Europe. A linear trend suggests that concentrations may reach northern hemisphere background levels in 2015–2030. The nss sulfate PM_{10} concentration at Mace Head (0.55 µg m^{-3}) is already close to the biogenic background level of around 0.35 µg m^{-3} (Yoon *et al.*, 2007).

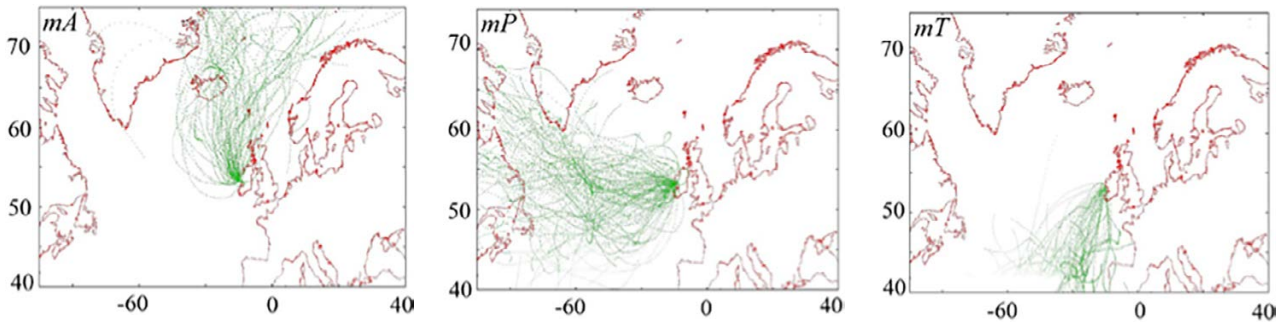

Figure 2.3. The 96-hour backward air mass trajectories at 500 m arriving at Mace Head, Ireland, from the North Atlantic Ocean during the 3-year period 2009–2011 and classified into maritime arctic (left), maritime polar (centre) and maritime tropical (right) air masses. Reproduced from Ovadnevaite *et al.* (2014a). 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/.

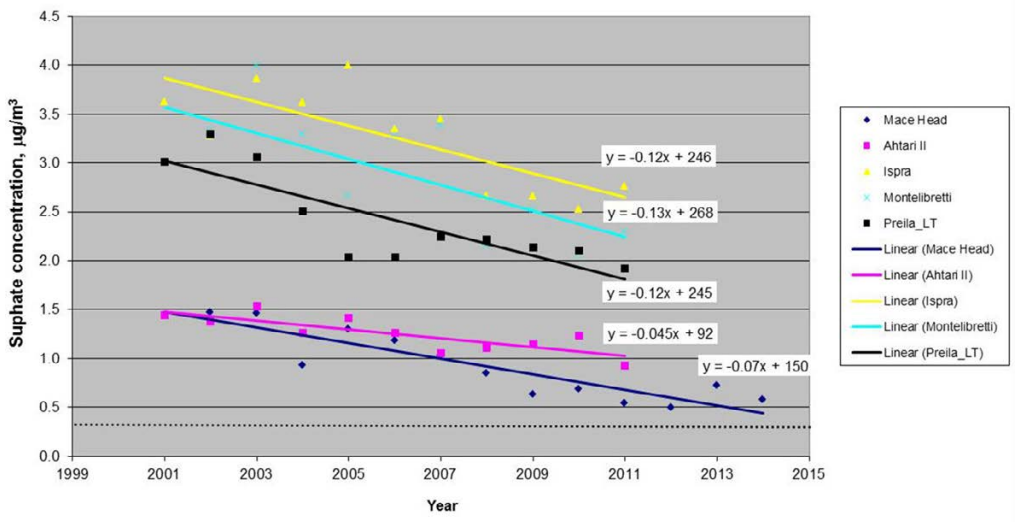

Figure 2.4. Trends in sulfate concentrations across Europe: Mace Head, Ireland; Ahtari II, Finland; Ispra, Italy; Montelibretti, Italy; and Preila, Lithuania. Data obtained from EMEP network database. The dotted horizontal line denotes the biogenic nss sulfate level (Yoon *et al.*, 2007).

Sea salt is a very significant component of $PM_{2.5}$ mass over Ireland, contributing ≥ 50% of the total mass excluding organic matter, which is expected to be a significant component, especially in polluted easterly air masses (Figure 2.5) and no less than 30% when organic matter is included. Chemical species concentrations are markedly higher in easterly air masses than in clean marine air masses.

The increasing availability and affordability of aerosol mass spectrometry (AMS) in the last decade have greatly improved the reliability of data because measurements are taken in near real-time and at high time resolution and contamination during sample collection, storage, handling and analysis can be avoided (Dall'Osto *et al.*, 2010). The latest advancement in AMS to quantitatively detect sea salt (Ovadnevaite *et al.*, 2012) has finally offered the possibility of routine, complete and rapid monitoring of atmospheric PM at high time resolution.

Atmospheric particulates have significant climatic implications through direct (scattering of incoming solar radiation) and indirect (cloud droplet formation and cloud lifetime) effects. As concentrations of atmospheric pollutants decrease, the amount of total

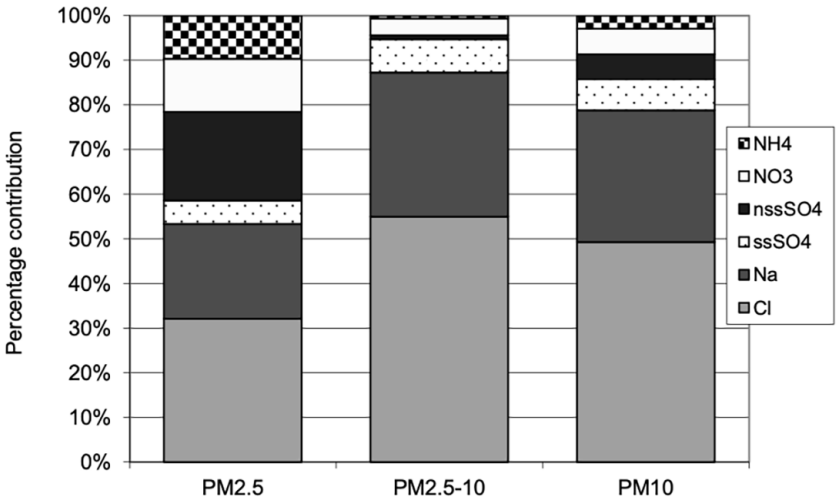

Figure 2.5. Percentage contribution of inorganic species to the aerosol mass in fine PM ($PM_{2.5}$), coarse PM ($PM_{2.5–10}$) and PM_{10} presented as a yearly average.

radiation reaching the ground increases, and this has been the case over the last decade at Mace Head. Clearly, the atmosphere has been brightening as the atmosphere has become cleaner, but it remains to be seen if the pattern is consistent over the larger European region. The Aerosol Robotic Network (AERONET) reports the same trend (Yoon *et al*., 2016), although cloudiness at Mace Head makes these types of measurements problematic.

3 Source Apportionment of Transboundary Air Pollution

It was envisaged in the original project proposal that transboundary air pollution would be studied using a Lagrangian approach, utilising backward air mass trajectories and long-term measurement data from the national EMEP network. With approximately 50% of air masses originating over the North Atlantic, there should have been plenty of trajectories connecting stations on the west coast of Ireland (Mace Head and Valentia) with Carnsore Point on the east coast. Statistical categorisation of the trajectories was indeed very promising, revealing dominant types: marine polar air masses from the west, tropical marine air masses from the south-south-west, Arctic air masses from the north-north-west and Continental air masses from the east (Figure 3.1). Note that Continental polluted air masses from the east constitute a relatively small fraction of all air masses, but a certain fraction of maritime Arctic and tropical air masses can also be slightly polluted after interaction with land. The trajectory analysis has been very revealing, but not explored to its full potential. The contamination detailed in Chapter 2 derailed the effort, casting doubt on nitrate and ammonium concentrations and preventing a robust statistical study.

Instead, several novel approaches utilising AMS measurements at Mace Head and Cork city produced exciting results that resulted in two peer-reviewed publications, as detailed in section 3.2.

3.1 Organic Aerosol Source Apportionment Based on 25 ACSM Datasets Across Europe Using a Consistent ME-2 Approach

Organic aerosols represent one of the major constituents of submicron PM (PM_1) and comprise a huge variety of compounds emitted by different sources. Currently, only a few studies concerning a broad spatial overview of organic aerosol sources are available in the literature. Three intensive measurement field campaigns to investigate the aerosol chemical composition all over Europe were carried out within the framework of the European

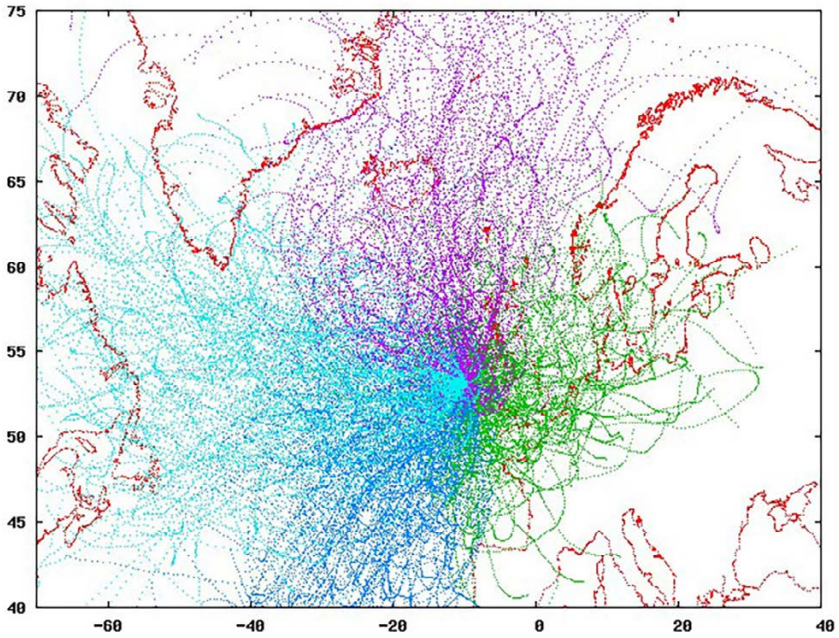

Figure 3.1. Clustered 96-hour air mass trajectories for the period 1990–2007 revealing four dominant types: marine polar air masses from the west, tropical marine air masses from the south-south-west, Arctic air masses from the north-north-west and Continental air masses from the east.

Integrated Project on Aerosol Cloud Climate and Air Quality Interactions (EUCAARI) and the intensive campaigns of EMEP during 2008 (May–June and September–October) and 2009 (February–March), as shown in Figure 3.2. The focus was on the identification of the main organic aerosol sources and the standardised methodology was defined to perform source apportionment using positive matrix factorisation (PMF) with the multilinear engine (ME-2) on AMS data. The source apportionment procedure was tested and applied on 25 datasets accounting for two urban sites, several rural and remote sites and two high-altitude sites; therefore, it was probably suitable for the treatment of AMS-related ambient datasets. At most of the sites, four organic components were retrieved, a significant improvement on previous source apportionment, in which only a separation in primary and secondary organic aerosol sources was possible. Generally, the solutions included two primary organic aerosol sources, i.e. hydrocarbon-like organic aerosols and biomass burning organic aerosols, and two secondary organic aerosol components, i.e. semi-volatile oxygenated organic aerosols (SV-OOAs) and low-volatility oxygenated organic aerosols (LV-OOAs) (Figure 3.3). For specific sites, cooking-related and marine-related sources were also separated. This study provided a large overview of organic aerosol sources in Europe and an interesting set of highly time-resolved data for modelling purposes.

On average, primary sources contributed less than 30% to the total organic aerosol mass concentration, while the predominant fraction of organic aerosols was associated with secondary formation (mainly SV-OOAs and LV-OOAs). The traffic contribution was season independent and accounted for 11 ± 6% of total organic aerosols in Europe as a whole. Biomass burning accounted for 12 ± 5% of the total organic aerosol mass and might have been associated with domestic heating during winter and with open fires, agricultural waste disposal and waste burning, etc., during the other seasons. Cooking was indeed a relevant source, mainly in urban locations (15%). Detailed studies across Europe will require learning about specific primary or secondary sources to limit particulate organic aerosols. In general, control of primary organic

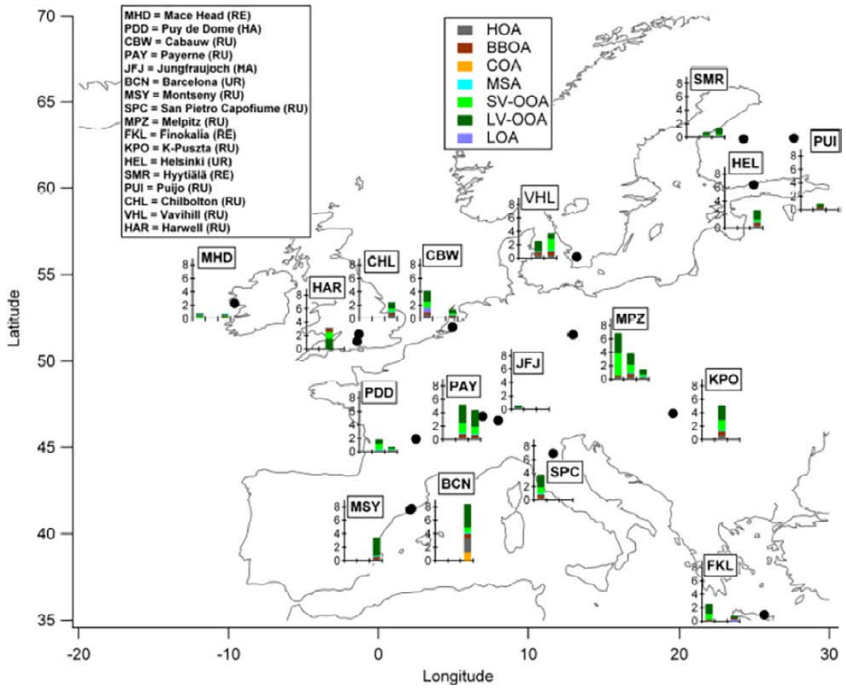

Figure 3.2. Measurement sites and average organic aerosol source contributions (bars). Measurement sites are classified according to their location as urban (UR), rural (RU), remote (RE) or high altitude (HA). The bar graphs report the average organic aerosol (OA) source concentrations (*y*-axis in mg m^{-3}) for the three measurement periods (in chronological order, from left to right, spring 2008, autumn 2008 and spring 2009 campaigns). The identified OA sources are HOAs (hydrocarbon-like OAs), BBOA (biomass burning OAs), COA (cooking OAs), SV-OOAs and LV-OOAs (semi-volatile and low-volatility oxygenated OAs), MSA (methane sulfonic acid) and LOAs (local OAs).

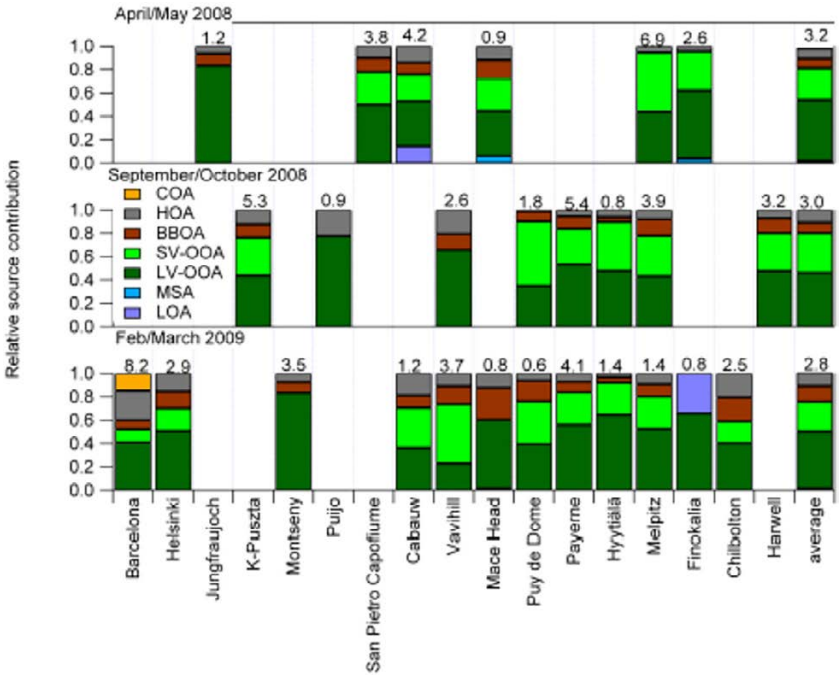

Figure 3.3. Relative organic source contributions (ME-2 results). On top of each bar the average organic concentration (in mg m^{-3}) is also reported. Site-specific sources are classified as LOAs (local organic aerosols) and include HULIS-related OAs (humic-like substances) in the case of Cabauw (Paglione *et al.*, 2014), and amines and local sources in the case of Finokalia (Hildebrandt *et al.*, 2011).

aerosol (POA) emissions should be accompanied by a reduction in the sources of secondary organic aerosols (SV- and LV-OOAs) in Europe as the latter constitute the dominant organic aerosol fraction, although the task will be quite challenging. Coupling Europe-wide measurements and source apportionment results with regional and global models will improve their prediction of POA and secondary organic aerosol (SOA) components.

3.2 Apportionment of Urban Aerosol Sources in Cork (Ireland) by Synergistic Measurement Techniques

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 aerosols at very high time resolution in the atmosphere. Until several years ago, most urban air quality studies were limited to mainly inorganic components of PM or at most including total organic carbon. Two different state-of-the-art online AMS methods 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, whereas AMS quantitatively measures mass concentrations of the non-refractory aerosol components as well as species-resolved size distributions. While ATOFMS does not have clear source apportionment capabilities owing to the difficulties in quantification of its outputs, AMS has proven itself to be a powerful tool for this purpose (Canagaratna *et al.*, 2007). Additionally, data from elemental carbon–organic carbon analysis (Sunset_EC-OC), offline gas chromatography/mass spectrometry and ion chromatography analysis of filter samples collected at 6-hour resolution were used to confirm the identification of the particle types obtained from the statistical analysis of the AMS datasets.

The first paper resulting from this study was published in *Atmospheric Chemistry and Physics* in 2013 (Dall'Osto *et al.*, 2013) and demonstrated the ability of HR-ToF-AMS to distinguish solid fuel types: peat, coal and wood. The second paper was published in *Science of the Total Environment* in 2014 (Dall'Osto *et al.*, 2014), further extending the source apportionment approach based on synergistic techniques and broadening source categories into regional sources.

PMF has been carried out to better elucidate aerosol sources not clearly identified when analysing results from individual aerosol techniques on their own. Two datasets have been considered: online measurements averaged over 2-hour periods, and both online and offline measurements averaged over 6-hour periods. Five aerosol sources were identified by PMF in both datasets (Figure 3.4), with excellent agreement between the two solutions: (1) regional domestic solid fuel burning – "DSF_Regional", 24–27%; (2) local urban domestic solid fuel burning – "DSF_Urban", 22–23%; (3) road vehicle emissions – "Traffic", 15–20%; (4) secondary aerosols from regional anthropogenic sources – "SA_Regional", 9–13%; and (5) secondary aged/processed aerosols related to urban anthropogenic sources – "SA_Urban", 21–26%. The results indicated that, despite regulations for restricting the use of smoky fuels, solid fuel burning is the major source (46–50%) of $PM_{2.5}$ in wintertime in Cork, and probably also in other areas of Ireland. Whereas wood combustion was strongly associated with organic carbon and elemental carbon, it was found that peat and coal combustion was linked mainly with organic carbon and the aerosol from these latter sources appeared to be more volatile than that produced by wood combustion. Ship emissions from the nearby port were found to be mixed with the SA_ Regional factor. The PMF analysis allowed us to link the AMS cooking organic aerosol factor (AMS_PMF_ COA) to oxidised organic aerosol, chloride and locally produced nitrate, indicating that AMS_PMF_COA cannot be attributed to primary cooking emissions only. Overall, there were clear benefits from factor analysis applied to results obtained from multiple techniques, which allowed better association of aerosols with sources and atmospheric processes.

3.3 Stable Isotope Measurements Reveal Dual-carbon Pools Contributing to Organic Matter Enrichment in Marine Aerosols

A sampling programme for carbon and sulfur isotope measurements was going very well, with about 30 weekly samples collected during the fellowship project, and it continued after the fellowship period. A revamped clean sector sampling system was used for sample collection in pristine North Atlantic air masses, enabling the sampling of two samples simultaneously and with independently selected parameters – wind direction, wind speed and black carbon concentration. A more conservative black carbon threshold of 15 ng m^{-3} was applied based on the paper of O'Dowd *et al.* (2014) on the representativeness of Mace Head station for marine aerosol studies. There was no additional funding available for sample analysis and this work was dependent on the voluntary efforts of researchers at the Center for Physical Sciences and Technology in Vilnius, Lithuania, under the research agreement. The sulfur isotope analytical method

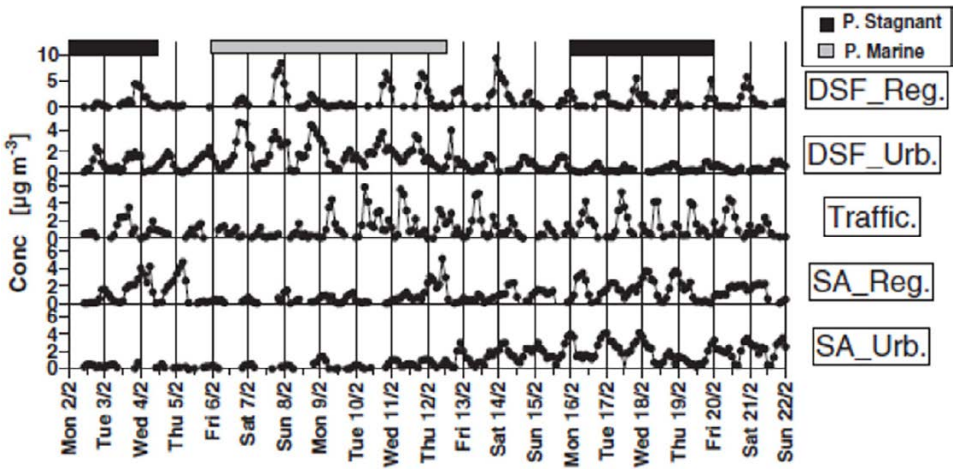

Figure 3.4. Temporal trends in the five PMF factors obtained at 2-hour resolution (Dall'Osto *et al.*, 2014). Reprinted from *Science of the Total Environment*, vol. 493, Dall'Osto, M., Hellebust, S., Healy, R.M., O'Connor, I.P., Kourtchev, I., Sodeau, J.R., Ovadnevaite, J., Ceburnis, D., O'Dowd, C.D., Wenger, J.C., Apportionment of urban aerosol sources in Cork (Ireland) by synergistic measurement techniques, pp. 197–208, copyright 2014, with permission from Elsevier.

development was halted owing to personnel changes at the Center for Physical Sciences and Technology in Vilnius and no samples have been analysed during the fellowship project.

Instead, a project on carbon isotope analysis of samples collected at Amsterdam Island (South Indian Ocean) was undertaken, which resulted in a major peer-reviewed publication in *Nature Scientific Reports*. The study revealed dual-carbon pools contributing to organic matter enrichment in marine aerosols, which will fundamentally advance the research field. The first carbon source or pool comprised fresh and largely insoluble organic matter associated with plankton blooms that was capable of aggregation into particulate organic matter and significant enrichment when transferred into sea spray particles. The second pool comprised old and processed organic matter that was mostly soluble and contributed only a minor but stable fraction of sea spray organic matter. Figure 3.5 is a conceptual diagram of organic matter cycling in the marine environment developed during the study.

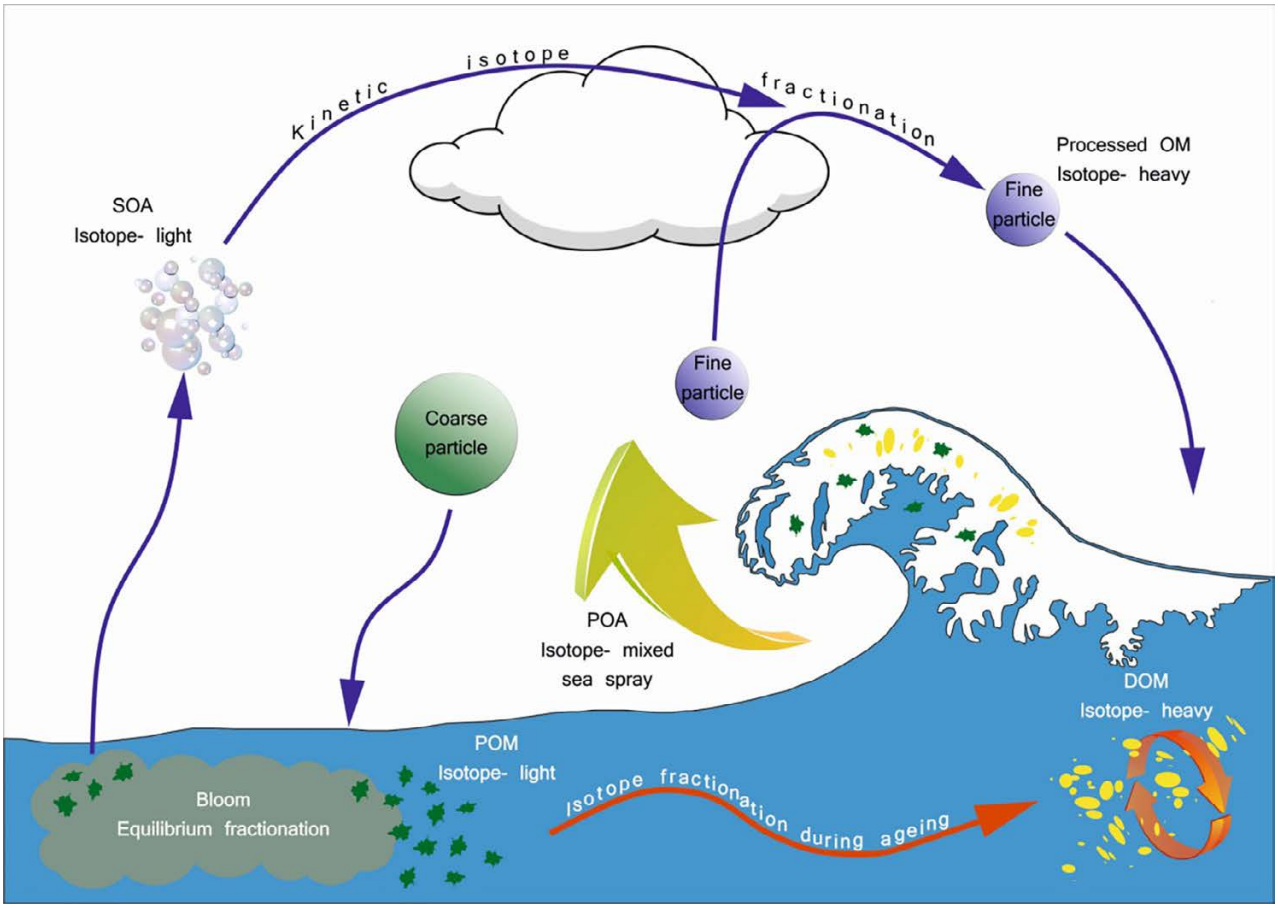

Figure 3.5. Marine organic matter cycling corroborated by a proposed model. Particulate organic matter (POM) in sea water is produced isotope-light by equilibrium fractionation during photosynthesis and is gradually processed by trophic-level interactions in the ocean (weeks to years timescale) to the isotope-heavy dissolved organic matter (DOM). Isotopically mixed sea spray organic matter (POA) undergoes kinetic fractionation by photochemistry and cloud processing in the atmosphere on a weekly timescale to isotope-heavy organic matter. The same scheme applies to SOA formed directly or condensed on primary particles. Aged, processed and isotope-heavy organic matter is returned to the ocean, contributing to the continuously recycled and replenished DOM pool. Ultimately, the two end-member pools emerge – sequestered, isotope-light and recycled, isotope-heavy organic matter. Reproduced from Ceburnis *et al*. (2016a). This is an Open Access article distributed in accordance with the terms of the Creative Commons Attribution (CC BY 4.0) 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/4.0/.

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 & Climate ImpactS) and at no additional cost to the fellowship project of Darius Ceburnis. This chapter constitutes a deliverable outlined in the fellowship proposal as “Analysis of key source/production mechanisms of aerosol pollutants”.

Aerosol principal sources and sinks over North-East Atlantic waters were studied through the deployment of an aerosol chemistry gradient sampling system. The chemical gradients of primary and secondary aerosol components, specifically sea salt, water-insoluble organic matter, water-soluble organic matter, nitrate, ammonium, oxalate, amines, methanesulfonic acid and water-soluble organic nitrogen were examined in great detail. Sea salt fluxes were estimated by the boundary layer box model and ranged from 0.3 to 3.5 $ng\,m^{-2}\,s^{-1}$ over the wind speed range of 5–12 $m\,s^{-1}$ and compared well with the derived fluxes from existing sea salt source parameterisations. The observed seasonal pattern of sea salt gradients was mainly driven by wind stress although marine organic matter also had an as yet unquantified effect on the fractional contributions of sea salt and organic matter in sea spray. Water-insoluble organic matter gradients were a complex combination of rising and waning biological activity, especially in the flux footprint area, and wind-driven primary sea spray production supported the coupling of recently developed sea spray and marine organic matter parameterisations.

Given the uncertainty of the estimated sea salt fluxes over the wind speed range it was necessary to compare estimated fluxes with the available sea spray source functions. Equally important was to cover a wide range of methods used to derive fluxes. Figure 4.1 presents the source functions for which submicron sea salt mass could have been calculated.

Although the gradient method provided parameterisation that was in good agreement with other, more up-to-date methods, the total uncertainty associated with the method did not allow for the establishment of trusted parameterisation and, therefore, the parameterisation based on physical

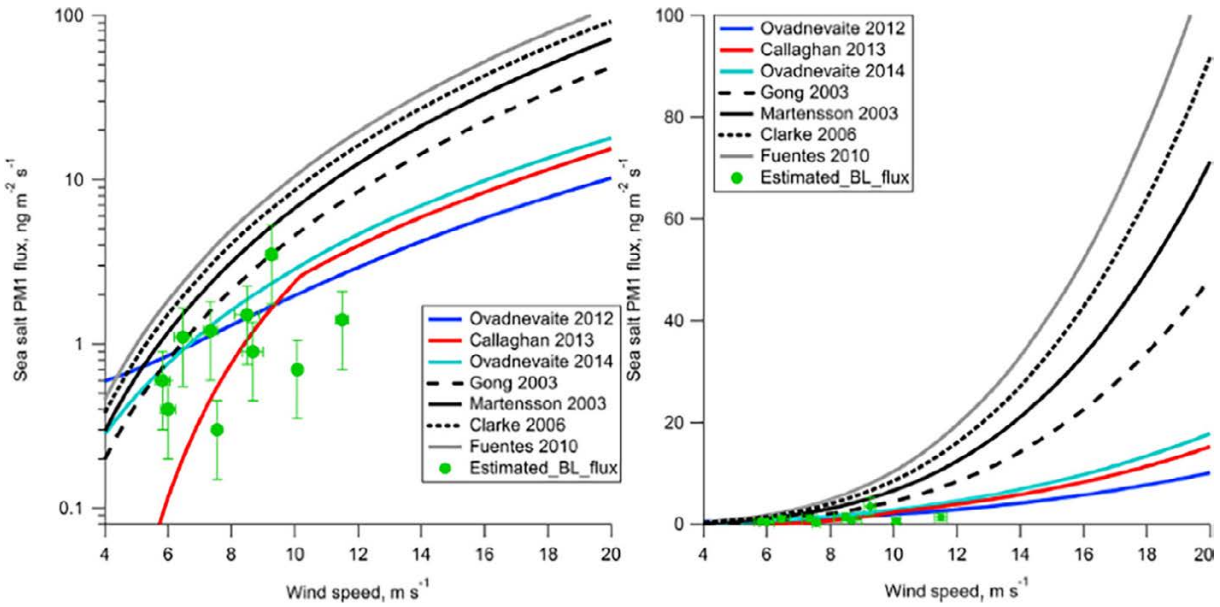

Figure 4.1. A comparison of the most often used and recently developed sea spray and wind speed parameterisations at log scale (left) and linear scale (right). The estimated boundary layer fluxes by the box model (green circles) were not fitted to the wind speed owing to the uncertainty related to the boundary layer filling time constant constituting the bulk of the total uncertainty.

real-time measurements of aerosol particles and utilising the sea state Reynolds parameter promised the most advanced physical sea spray parameterisation, “Ovadnevaite 2014” (Ovadnevaite *et al*., 2014b).

A paper reporting on this work was drafted during a previous fellowship period, prior to 2013, but the peer review process took 2.5 years. The paper was finally published in *Atmospheric Chemistry and Physics* journal (Ceburnis *et al*., 2016b).

5 Climatic Implications of Fine and Coarse Particulate Matter

Atmospheric aerosols have very significant climate impacts through direct effects, by scattering and absorbing incoming solar radiation, and indirect effects, through cloud formation and their lifetime in the cloud. All of the above effects result in overall global cooling (warming by absorption and other minor effects being small), counteracting the global warming caused by greenhouse gases. As air pollution control policies are projected to reduce particulate sulfate levels by 30–70% and black carbon by 15–50% by 2050, the cooling potential of atmospheric particulates will decrease as well. It is, therefore, vital to understand the above effects, as the reduced cooling (increased global warming) will have a negative impact on human health despite improving air quality. Long-term monitoring data revealed that the above projections hold, showing a 70% decrease in sulfate levels at Mace Head in the last decade alone (see Figure 2.2).

Atmospheric aerosols influence the Earth's radiative budget directly through the scattering of incoming solar radiation (insolation) back out to space via the formation of reflecting regional haze layers and, indirectly, through the formation and modification of reflecting cloud layers. Increased aerosol abundance and increased availability of cloud nuclei are predicted to increase atmospheric albedo and reduce surface insolation (incoming solar radiation), leading to a cooling effect. Indeed, it is believed that the high air pollution levels occurring in the third quarter of the 20th century significantly reduced the rate of global warming due to greenhouse gases.

In fact, over the past 40 years, there have been observed both global solar dimming and global solar brightening trends, which have been tentatively linked to an aerosol influence on climate. Solar dimming is a term associated with a decadal decrease in surface insolation, while solar brightening refers to an increase in surface insolation. Studies have shown that a widespread decrease in surface solar radiation occurred between 1960 and 1990, based on readings taken at a variety of locations worldwide. Increasing aerosol concentrations associated with increased air pollution over the period are considered responsible for the dimming, although the linkage is purely suggestive and circumstantial. Changes in cloud reflectance and cloud amount can also contribute to the dimming trend; however, in a particular study over Europe, it was concluded that changes in cloud coverage could not explain the dimming trend observed and that direct and indirect aerosol effects were most likely the predominant causes of the dimming trend (Wild *et al*., 2005). Strikingly, in the late 1980s the trend reversed into a brightening trend that seemingly continues to date.

As mentioned above, the dimming effect appeared to have been masking, or suppressing, greenhouse warming, with reduced or even negative trends on global temperatures over the period as greenhouse gases continued to accumulate. As the trend reversed from dimming to brightening, rapid temperature rises became evident. Since the mid-1980s, the decadal rise in temperature over the European area has been +0.38°C, significantly higher than in any other period since the pre-industrial era. The brightening has been associated with reduced aerosol pollution since the 1980s, when developed countries began to implement policies to clean up air pollution. Here we present a decade-long trend in PM_{10} nss sulfate aerosol mass concentrations at the World Meteorological Organization (WMO) GAW primary baseline site at Mace Head, located on the western boundary of Europe (specifically the west coast of Ireland) and on the interface with the North-East Atlantic. The station, on an annual basis, is exposed to approximately 50% clean marine air masses and 50% Continental or land-modified air masses. Previous studies have demonstrated that measurements spanning more than 2 or 3 days at the single Mace Head location are representative of the spatial scales associated with air masses in the region (that is, the larger regional spatial scale), as is to be expected for a location not subject to major local sources of pollution. The data include all sectors (i.e. both marine and Continental) and are, therefore, representative of regional-scale pollution over the North-East Atlantic and European

aerosol pollution exported to the North-East Atlantic. Annual European-scale emission trends for $PM_{2.5}$ mass, SO_x and NO_x all show sharp declines since the year 2000. Irish emissions for SO_x are seen to reduce from almost 140 Gg year^{-1} to 35 Gg year^{-1}. The Irish emissions are given simply because of the proximity to the measurements at Mace Head; however, it should be noted that the European-scale emission trends are also highly correlated with the Irish emission trends. The annual average sulfate PM_{10} mass concentration measured at Mace Head over a 10-year period from 2002 to 2011 also exhibits a rapidly declining trend as mass concentrations fall from 1.5 mg m^{-3} to less than 0.55 mg m^{-3} (Figure 5.1).

Concomitant with the decadal-scale reduction in nss sulfate mass is an increase in surface insolation (combined diffuse and direct) measured at Mace Head. The annual average insolation increases from 108 W m^{-2} in 2003 to 125 W m^{-2} in 2010, and this increase of ~20% is strongly correlated with the decrease in nss sulfate mass. Similar declining trends are seen in nitrate and ammonium aerosols, both of which are highly correlated with nss sulfate mass (r = 0.94), and ammonium was even more correlated with nitrate (r = 0.98), again reaffirming the anthropogenic nature of the sulfate aerosol. Surface insolation is also highly correlated with the combined sulfate, nitrate and ammonium PM_{10} mass concentration. This trend is not unique to Mace Head as a similar trend is seen in the Valentia Observatory GAW station located in the south-west of Ireland.

In order to understand the underlying effects, it was important to look at the wider European region. Data from the established monitoring stations in Europe were compiled and thoroughly examined for sulfate–radiation relationship. A dataset comprising data on global radiation and sulfate collected over approximately a decade from eight stations around Europe (one each in Finland, Lithuania, Ireland and Germany and two in each of Italy and Norway) has been compiled. Figure 5.2 shows sulfate–radiation trends at different stations. Two stations (Lithuania and Birkenes in Norway) show a similar pattern to the one found at Mace Head, albeit of a shallower slope. The other five stations exhibit an opposite trend, with sulfate concentrations reducing concurrently with reducing global radiation. Interestingly, Mace Head and the Lithuanian and Norwegian stations are all coastal, whereas the stations exhibiting the opposite trend to Mace Head are all Continental (stations in Italy, Germany and Finland). No clear pattern has been observed with regard to the magnitude of sulfate concentrations, disputing the findings and conclusions based on Mace Head data (Figure 5.1).

A second attempt was made to look at all available data from Ireland, including the longest data series from the Valentia station. There were only two stations in Ireland with long-term radiation and sulfate measurement data series: Mace Head and Valentia. The relationship between global radiation and sulfate presented in Figure 5.3 was similar to that presented in

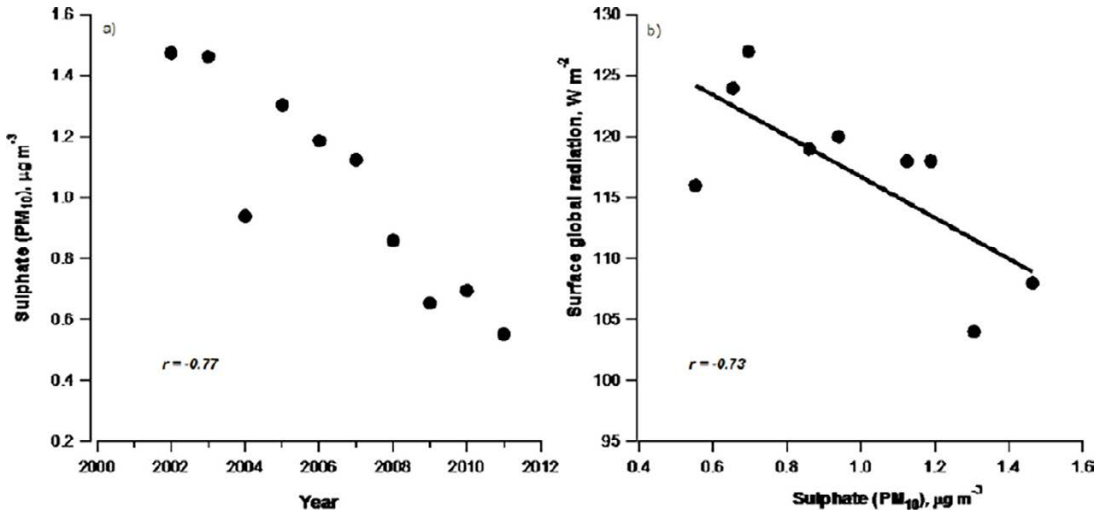

Figure 5.1. Left: nss sulfate PM_{10} mass concentrations measured at Mace Head from 2001 to 2011. Right: surface solar radiation versus nss sulfate mass at Mace Head, 2003–2011. Reproduced from O'Dowd *et al.* (2013) with the permission of AIP Publishing.

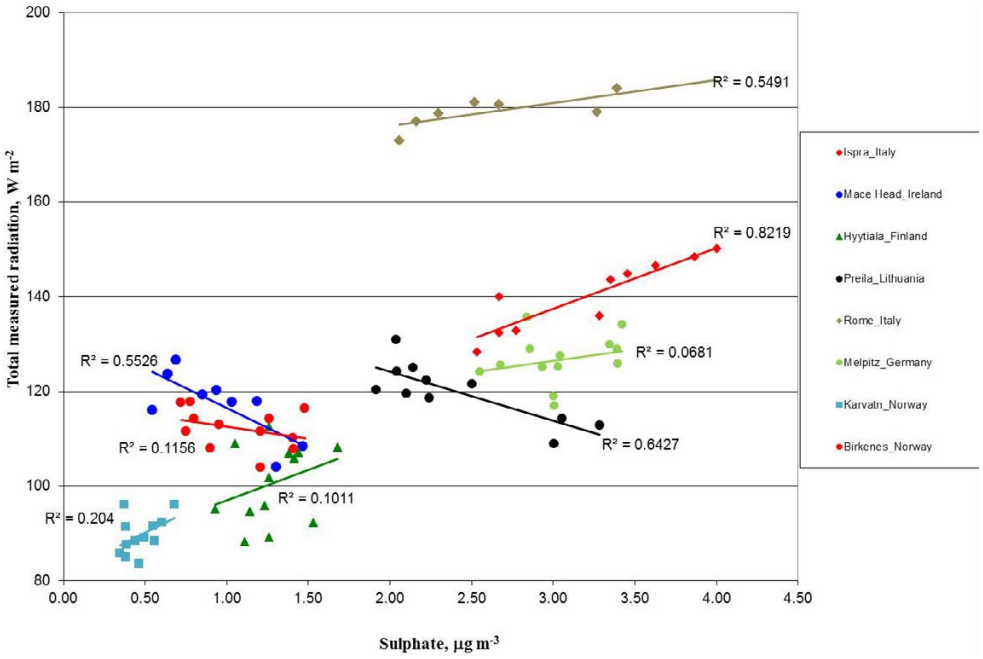

Figure 5.2. Sulfate–radiation relationships at different stations across Europe for the period 2001–2011. Correlation coefficients are indicated beside the regression lines.

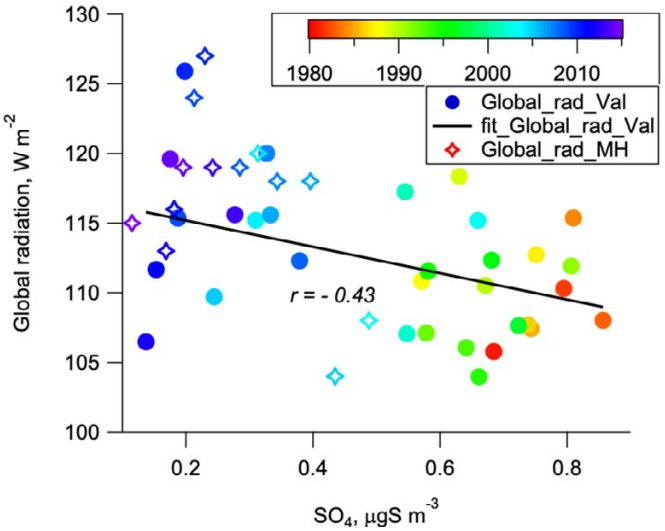

Figure 5.3. Sulfate–radiation relationship combining all Mace Head and Valentia data. Mace Head data are marked with diamonds and Valentia data with circles. Different colours represent different years.

Figure 5.1, albeit significantly shallower, approximately 7 W m^{-2} over the sulfate concentration of approximately 3 µg m^{-3}. The rate of change was similar to radiative forcing of PM. Consequently, the very rapid change presented in Figure 5.1 is most likely a combination of pollution-related brightening and changes in cloud cover due to a changing pattern of global circulation tentatively attributed to global warming.

The different patterns presented in Figure 5.2 can probably be attributed to atmosphere responses to pollution depending on the availability of water vapour. The marine atmosphere typically has a higher water content and, consequently, should respond faster to diminishing pollutant concentrations, brightening rapidly in the process. However, more research is needed to ascertain the reasons underlying the opposite patterns in Continental and marine regions.

6 European Monitoring and Evaluation Programme Intensive Observation Periods

The EMEP monitoring programme and its strategy (2010–2019) included intensive measurement periods (IMPs) at EMEP supersites to improve the scientific understanding of the relevant physico-chemical processes in relation to regional air pollution and its control. The EMEP Task Force on Measurements and Modelling had, therefore, recommended conducting these measurements during two contrasting measurement periods in 2012/2013. The focus of the intensive campaigns was on organic carbon and mineral dust, the important components in estimating hemispheric and long-range transport. The latest IMP facilitated during the fellowship period was devoted to mineral dust.

6.1 Geochemistry of PM_{10} over Europe during the EMEP Intensive Measurement Periods in Summer 2012 and Winter 2013

The third IMP organised by the EMEP under the UN-ECE CLTRAP took place in summer 2012 and winter 2013, with PM_{10} filter samples concurrently collected at 20 (16 EMEP) regional background sites across Europe (Figure 6.1) for subsequent analysis of their mineral dust content. All samples were analysed using the same or a similar methodology.

PM_{10} concentrations in summer were, in general, higher in the southern sites (Figure 6.2). Mean levels ranged from 8 to 40 $\mu g\,m^{-3}$. In winter, low PM_{10} levels were registered in northern and south-western Europe (3–9 $\mu g\,m^{-3}$) and the highest PM_{10} levels were

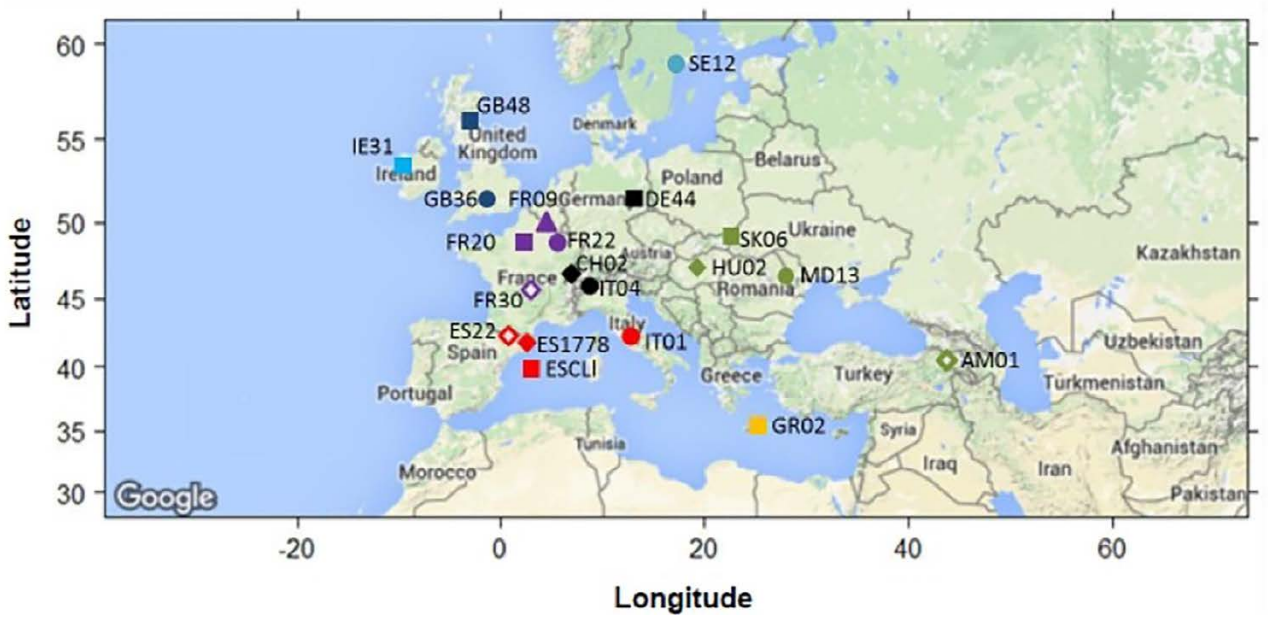

Figure 6.1. A network of intensive observation period in Europe during summer 2012 and winter 2013. Reproduced from Alastuey *et al*. (2016). This is an Open Access article distributed in accordance with the terms of the Creative Commons Attribution (CC BY 3.0) license, which permits others to distribute, 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/.

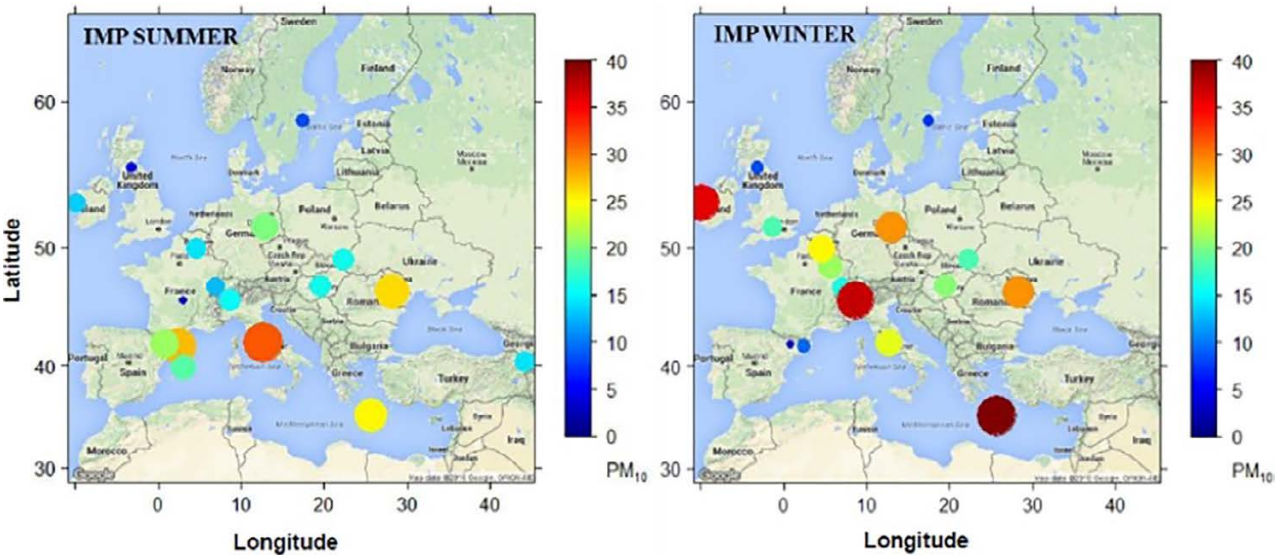

Figure 6.2. Mean PM_{10} concentrations (µg m^{-3}) recorded during the June/July 2012 and January/February 2013 EMEP IMPs. The diameter of the circles is proportional to the concentration. Reproduced from Alastuey *et al.* (2016). This is an Open Access article distributed in accordance with the terms of the Creative Commons Attribution (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/.

measured in southern, eastern and central Europe (20–40 µg m^{-3}). High PM_{10} levels were recorded along a north-west to south-east transect, ranging from 22 to 40 µg m^{-3}, with the highest concentrations observed for GR02 (Crete, Greece), CH02 (Jungfraujoch, Switzerland) and IE31 (Mace Head, Ireland) (40, 37 and 36 µg m^{-3}, respectively).

Sea salt accounts for a larger fraction of PM_{10} at coastal sites, around 10% on average, with important variations in winter (Figure 6.3). At the north-western sites, the sea salt load was up to 1 order of magnitude higher in winter than in summer, reaching an average concentration of 19 µg m^{-3} at the coastal Mace Head location (> 50% of PM_{10}) and more than 2 µg m^{-3} at GB48 (Scotland, UK) and GB36 (England, UK) (30% and 14% of PM_{10}, respectively). In the Mediterranean area, the average sea salt contribution was slightly higher at GR02 (Crete, Greece) (3.9 µg m^{-3}, 10% of PM_{10}) than at the other sites (< 1 µg m^{-3}).

Figure 6.4 shows the spatial variation of the average mineral dust load contribution determined for each site and IMP. In general, recorded concentrations of mineral dust were higher in summer than in winter. The exceptions were GR02, strongly affected by Saharan dust events in winter, and IE31, with very low concentrations of mineral dust. The summer maxima of mineral dust were more evident in the southern and eastern countries, showing a spatial distribution similar to that described for PM_{10}. Saharan dust outbreak events are relatively frequent in southern Europe during the summer, but rarely observed in northern Europe, including at Mace Head, where no Saharan event was detected during the IMP. However, individual Saharan dust events are regularly observed at Mace Head, but only very few over an entire year, i.e. during an observation period of 1 month only there was a low probability of a Saharan dust event because of only few observed during an entire year.

The third EMEP intensive monitoring period, conducted in summer 2012 and winter 2013, addressed the chemical speciation in PM_{10} with a particular emphasis on mineral dust and trace metals. For the first time, mineral dust was determined in filter samples (PM_{10}) collected concurrently at a substantial number (20) of regional background sites across Europe, using a similar methodology at 18 of the sites, i.e. particle-induced X-ray emission, conducted

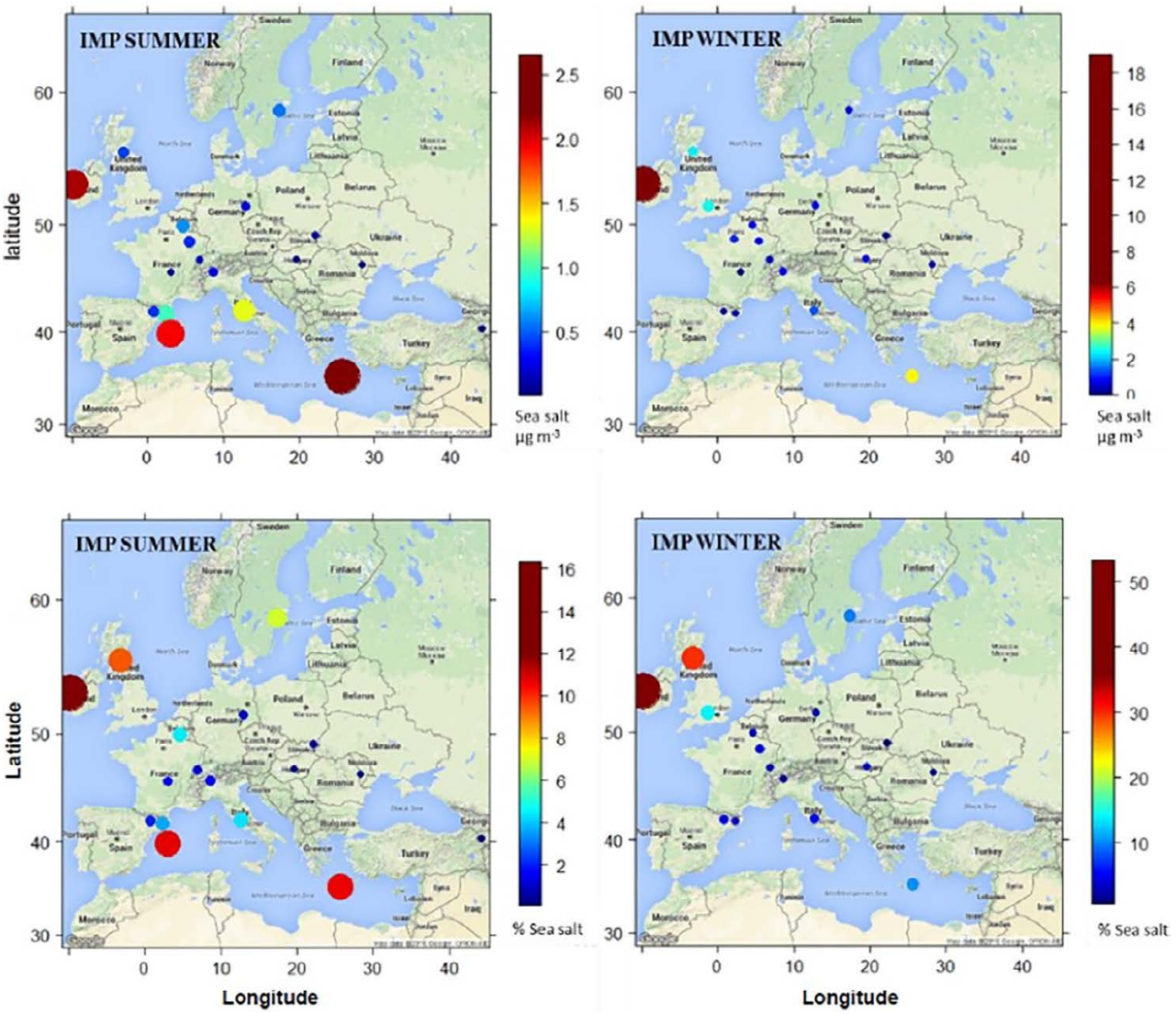

Figure 6.3. Spatial distribution of the mean sea salt aerosol concentration (µg m^{-3}) and its relative contribution (%) to PM_{10} during the EMEP IMPs in summer 2012 and winter 2013. The diameter of the circles is proportional to the concentration or percentage. Reproduced from Alastuey *et al.* (2016). This is an Open Access article distributed in accordance with the terms of the Creative Commons Attribution (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/.

at the Italian National Institute of Nuclear Physics Laboratory of Nuclear Techniques for Cultural Heritage (INFN LABEC) of Florence, Italy. Particle-induced X-ray emission analysis allowed for the simultaneous detection of most mineral elements (i.e. Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe, Sr, Zr) with high sensitivity. The PM_{10} mineral dust composition across Europe demonstrated the influence of both local (natural and anthropogenic) and external sources, as evidenced by ratios of different mineral components in the PM filter samples. In general, recorded concentrations of mineral dust were higher in summer than in winter, with the summer maxima of mineral dust being more evident in the southern and eastern European countries.

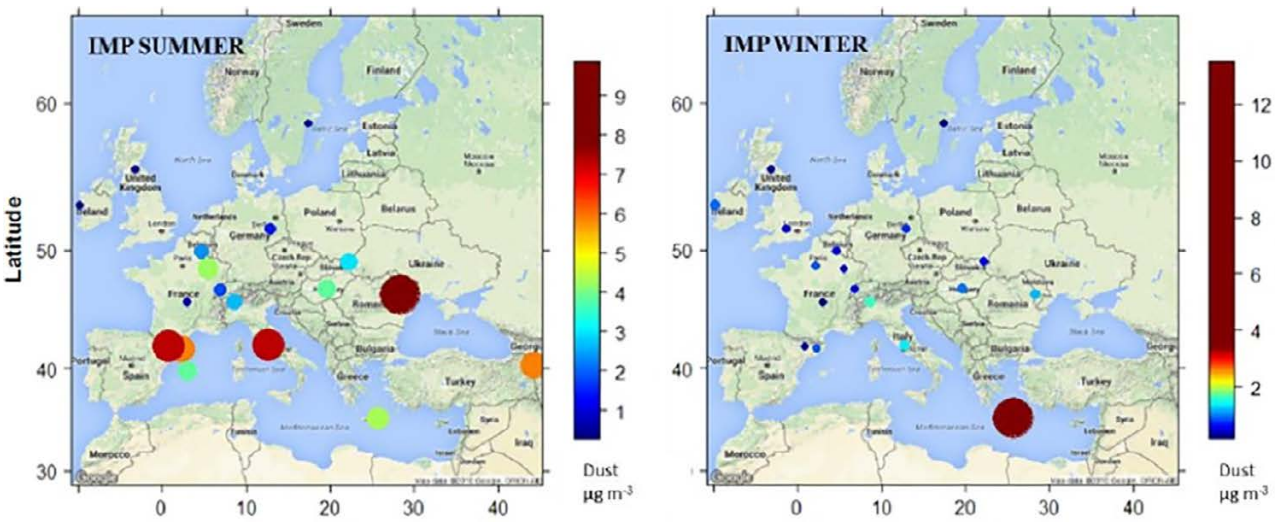

Figure 6.4. Spatial distribution of the average mineral dust concentration (µg m^{-3}) measured at each site in the summer 2012 and the winter 2013 IMPs. The diameter of the circles is proportional to the concentration or percentage. Reproduced from Alastuey *et al.* (2016). This is an Open Access article distributed in accordance with the terms of the Creative Commons Attribution (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/.

7 Support of Ongoing Research Programmes

During the project, significant effort was devoted to supporting national and international research campaigns at Mace Head and ongoing research programmes. Such research effort dominated the activities of this fellowship, sometimes at the expense of the original goals, e.g. WP3 activities with regard to Lagrangian studies. Nevertheless, all support effort was directed towards achieving the main objectives of the fellowship and intended to result in peer-reviewed publications, which were produced in significant numbers and are listed in Chapter 9. The following sub-sections outline contributions made during those activities and corresponding research papers published during the fellowship period.

7.1 PEGASO (Plankton-derived Emissions of trace Gases and Aerosols in the Southern Ocean)

Researchers from the Centre for Climate and Air Pollution Studies (C-CAPS) at NUIG were invited to join the research cruise PEGASO on board Spanish RV *Hesperides* in the Antarctic area to study biogenic marine aerosols (Figure 7.1). The aim of the cruise was to identify plankton-derived emissions of gases and aerosols in the Southern Ocean. It was intended that the cruise plan would visit strategic locations where phytoplankton blooms are a regular feature, with locations 1 and 2 in the Weddell Sea region, location 3 near South Georgia Island and location 4 around the South Shetland Islands. Significant effort went into mobilising the Spanish research vessel in October 2014, with the core scientific instruments relocated from Mace Head for 6 months during the winter period (Austral summer). The main scientific campaign was scheduled for 1 January–14 February 2015.

Two research papers were published in *Nature Scientific Reports* (Dall'Osto *et al*., 2017; Fossum *et al.*, 2018) after the end of the fellowship.

7.2 BACCHUS (Impact of Biogenic versus Anthropogenic emissions on Clouds and Climate: towards a Holistic UnderStanding)

BACCHUS is a European FP7 collaborative project under the lead of ETH Zurich, Switzerland. In the years 2013–2017, 21 research institutions from the

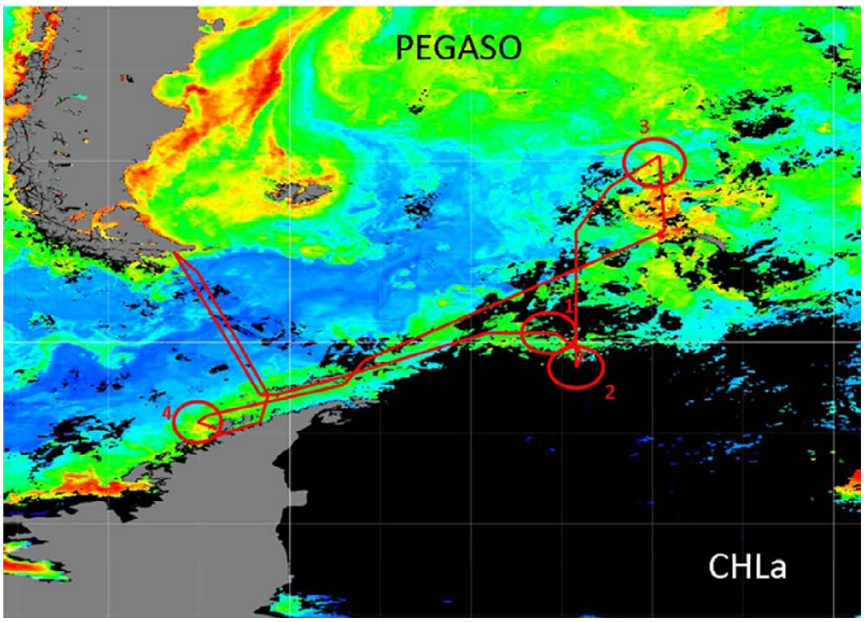

Figure 7.1 PEGASO cruise path overlaid on sea water chlorophyll *a* concentration in the Southern Atlantic Ocean and around Antarctica during January–February 2015.

EU, Switzerland, Norway and Israel worked closely together to better understand key processes in aerosol–cloud interactions (ACIs). BACCHUS is one of three research projects building the research cluster “Aerosols and Climate” that the EU initiated, recognising the importance of improving climate predictions to develop sustainable policies for Europe.

Clouds are a very important, yet not well understood, feedback factor in climate change (cloud formation and brightness and their lifetime effects) as they contribute to the effective radiative forcing from ACIs. The uncertainty of this radiative forcing is larger than for any other forcing agent (greenhouse gases, ozone, contrails, etc.). Additionally, feedback between the terrestrial and marine biosphere and the atmosphere involving ACIs may play an important role in regulating climate change, but the relevance of feedback remains poorly quantified.

BACCHUS aims to quantify key processes and feedback controlling ACIs by combining advanced measurements of cloud and aerosol properties with state-of-the-art numerical modelling. Analysing contrasting environments is the guiding strategy for BACCHUS. The project consortium investigated the importance of biogenic versus anthropogenic emissions for ACIs in regions that are key regulators of the Earth’s climate (Amazonian rainforest) or are regarded as tipping elements in the climate system (Arctic). A unique database linking long-term observations and field campaign data of aerosols, cloud condensation and ice nuclei, and cloud microphysical properties was obtained.

Ice phase transitions in mixed phase clouds are poorly represented in numerical models, leading to uncertainties associated with cloud phase (liquid/ice) partitioning, cloud precipitation rates and atmospheric radiative transfer. Atmospheric ice nucleating particles (INPs) play an important role within these complex aerosol–cloud–climate interactions, enabling heterogeneous ice formation. Sea spray aerosol, particles generated from wave breaking and bubble bursting, is a weak INP source in comparison with terrestrial sources. However, it has been hypothesised that marine organic aerosols arising from oceanic biological activity serve as a potentially important source of marine INPs in the high-latitude marine boundary layer and clouds forming over it.

Marine organic aerosol plumes, or periods of high marine organic aerosol concentrations associated with elevated offshore biological activity, are often observed at Mace Head. This location provides access to ambient pristine marine air, yet the composition and abundance of marine INPs have not been investigated at Mace Head.

In August 2015, two aerosol filters were collected daily at the top of the 10-metre mast; total sample collection periods ranged from 6 to 37 hours (20 hours on average). The pump for the “clean sector filter” was powered using the Mace Head Observatory (MHO) clean sector system, which collects particles only when the black carbon concentration is $< 15\,ng\,m^{-3}$ and wind direction is between 190 and 300°. The pump for the “all sector filter” was powered continuously during the total collection period. The clean sector filters represent aerosols from pristine marine air and the all-sector filters represent aerosols from both marine and terrestrial sources. Particles on filters were suspended in pure water for analysis using an ice spectrometer, providing INP number concentrations (nINP) as a function of temperature. Additionally, an offline heating test was performed on a portion of the collected aerosol suspension (heating to 98°C for 20 minutes) to determine the contribution of biological INPs within the different sectors. Future tests will include size filtering and hydrogen peroxide digestions (treatment to determine the role of organic carbon).

Total number concentrations of INPs active at −15°C (nINP, –15°C), shown in Figure 7.2, ranged from 0.0005 to $0.009\,L^{-1}$. The highest nINP at −15°C were often associated with elevated organics, and two specific events indicate important contributions of marine and terrestrial organic aerosols to the total INP population at MHO.

From these data it was concluded that future studies at coastal sites aimed towards quantifying ambient marine INP number concentrations should utilise a system similar to the clean sector sampler to isolate the marine INPs signal from non-marine INPs.

The above data have been published in *Journal of Geophysical Research – Atmospheres* (McCluskey *et al.*, 2018).

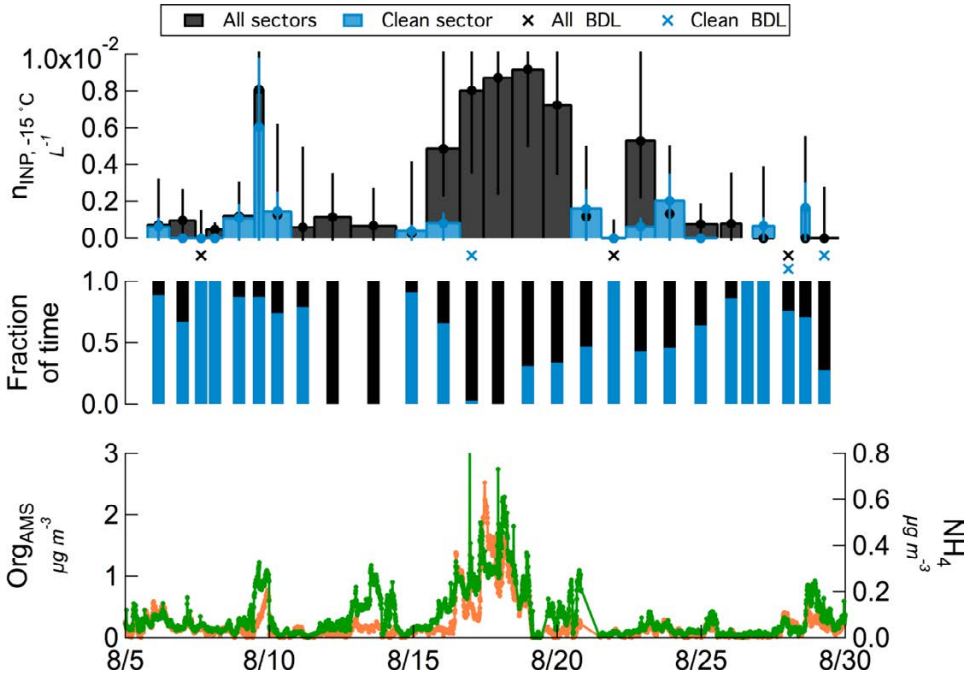

Figure 7.2. Timelines of (top) INP number concentrations active at –15°C, (middle) fraction of time spent in the clean sector and (bottom) organic aerosol mass concentrations at the MHO. Crosses indicate samples that were below the detection limit (BDL).

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 to protect human health and the environment from POPs by reducing or eliminating their releases into the environment. According to Article 16 of the Stockholm Convention, its effectiveness shall be evaluated starting 4 years after the date of its entry into force, and periodically thereafter at intervals to be decided by the Conference of the Parties. A Global Monitoring Plan has been developed with an objective of evaluating whether the POPs actually were reduced or eliminated on the global scale. Design of the continent-wide network has to address long-term needs for attaining appropriate representative data in all regions to achieve global coverage. Figure 7.3 shows an extended network of stations participating in the MONET European-wide network. A 12-weekly sampling protocol was followed during 2011–2016 and continued after the fellowship period. As sampling duration increased, the number of POP species also increased, as did the network, which expanded into Africa. Mace Head is considered crucial for the network because it provides the least perturbed background for POPs arriving into Europe by prevailing westerly air masses. At the same time, participation in the network gives access to the data and, most importantly, ensures the consistency of sample analysis that is performed at the centralised laboratories in the Czech Republic (Brno, RECETOX Centre).

7.4 A National Network to Monitor Ambient Atmospheric Ammonia Concentration in Ireland

The principal objective of this project was to set up and run a year-long national ambient atmospheric ammonia monitoring programme, which was undertaken by Dr B. Doyle, assisted by the fellowship holder with regard to sample collection at Mace Head. The programme assessed ambient atmospheric ammonia concentrations in rural and urban environments, away from large point sources, informing the design of an optimum national network for future routine ammonia monitoring.

This monitoring network utilised a network of volunteers throughout Ireland to collect samples (Figure 7.4), intended to contribute to the improvement of our knowledge of ambient atmospheric ammonia levels and their spatial and temporal variation within the country. The project built on a previous national ammonia study (de Kluizenaar and Farrell, 2000).

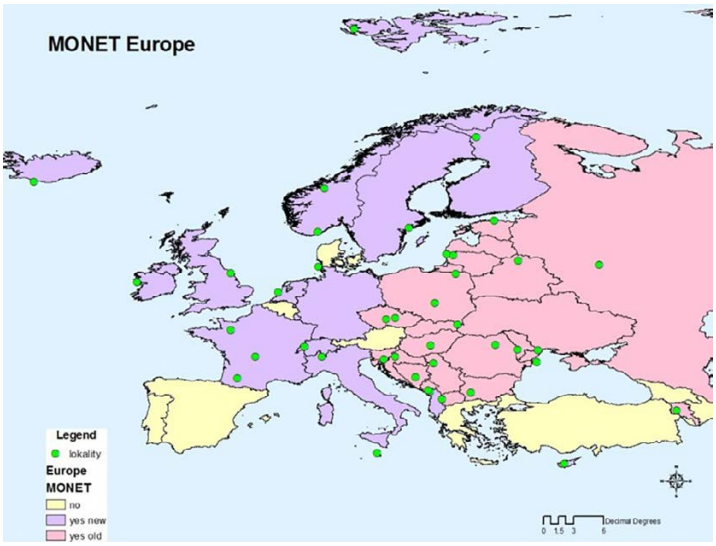

Figure 7.3. European-wide MONET network for sampling POPs.

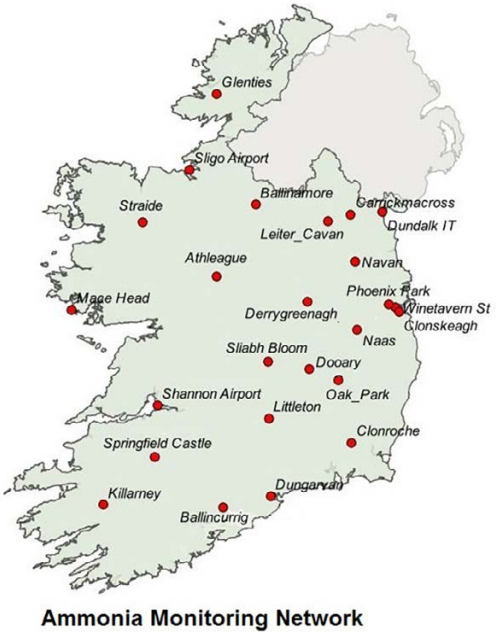

Figure 7.4. Ammonia monitoring network in Ireland (Doyle *et al.*, 2017).

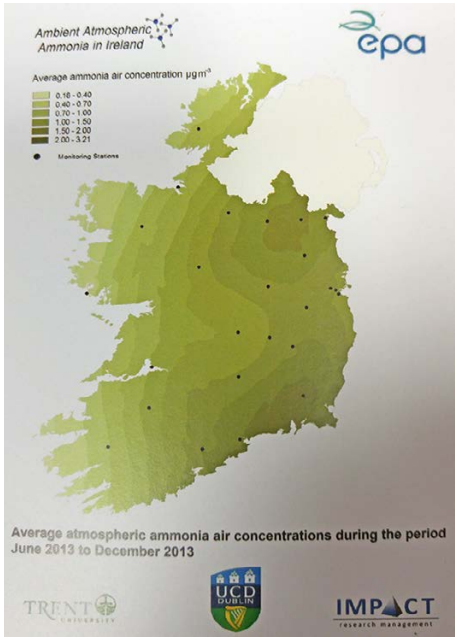

Figure 7.5. Average ammonia air concentrations during the period June 2013 to December 2014 (courtesy of B. Doyle).

The project was funded through the EPA's 2013 STRIVE programme (project reference Baseline Ammonia Deposition Rates in Ireland, 2012-CCRP-MS8).

The distribution of ammonia across Ireland is presented in Figure 7.5. It can be seen that ammonia concentrations are significantly lower over the western part of Ireland than over the eastern part of the country.

7.5 Molecular-scale Evidence of Aerosol Particle Formation via the Sequential Addition of HIO_3

A dedicated field campaign was performed at Mace Head coastal station on the Irish west coast from 1 August to 29 October 2013 to pursue identification of the molecular steps involved in new particle formation in an iodine-rich environment. A suite of novel instrumentation, and, in particular, nitrate ion-based chemical ionisation atmospheric pressure interface

time-of-flight (CI-APi-TOF) mass spectrometry capable of resolving the chemical composition of freshly formed electrically neutral clusters, was applied.

Homogeneous nucleation and subsequent cluster growth leads to the formation of new aerosol particles in the atmosphere. The nucleation of sulfuric acid and organic vapours is thought to be responsible for the formation of new particles over continents, whereas iodine oxide vapours have been implicated in particle formation over coastal regions. The molecular clustering pathways that are involved in atmospheric particle formation have been elucidated in controlled laboratory studies of chemically simple systems, but direct molecular-level observations of nucleation in atmospheric field conditions that involve sulfuric acid and organic or iodine oxide vapours have yet to be reported. The field data from Mace Head, Ireland, and supporting data from northern Greenland and Queen Maud Land, Antarctica, enabled the identification of the molecular steps involved in new particle formation in an iodine-rich, coastal atmospheric environment (Figure 7.6). It was found that the formation and initial growth process is almost exclusively driven by iodine oxoacids and iodine oxide vapours, with average oxygen–iodine ratios of 2.4 found in the clusters. On the basis of this high ratio, together with the high concentrations of iodic acid (HIO_3) observed, it was suggested that cluster formation primarily proceeded by sequential addition of HIO_3, followed by intracluster

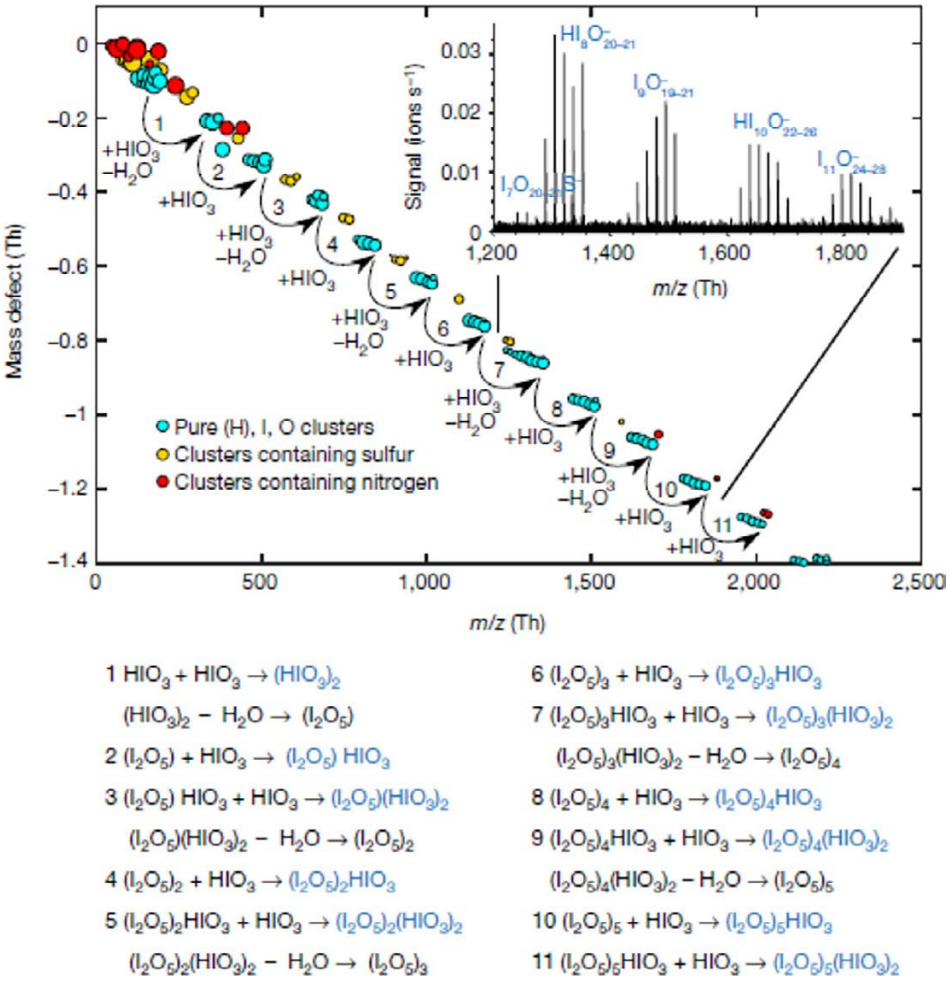

Figure 7.6. Plot of mass defect versus cluster mass depicting the abundance and atomic composition of nucleating neutral clusters during the event. The distribution of the clusters is dominated by iodine oxides (Sipilä *et al.*, 2016). Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature. *Nature*, Molecular-scale evidence of aerosol particle formation via sequential addition of HIO_3, Sipila, M., Sarnela, N., Jokinen, T., Henschel, H., Junninen, H., Kontkanene, J., Richters, S., Kangasluoma, J., Franchin, A., Perakyla, O., Rissanen, M.P., Ehn, M., Vehkamaki, H., Kurten, T., Berndt, T., Petaja, T., Worsnop, D., Ceburnis, D., Kerminen, V.M., Kulmala, M. and O'Dowd, C. © 2016.

restructuring to I_2O_5 and recycling of water either in the atmosphere or on dehydration. The study provided ambient atmospheric molecular-level observations of nucleation, supporting the previously suggested role of iodine-containing species in the formation of new aerosol particles, and identified the key nucleating compound.

The paper has been published in *Nature* (Sipilä *et al.*, 2016). The paper was the pinnacle of the research support efforts of the fellowship as it was conceived and executed at Mace Head station, again highlighting the unique status and research potential of the station, NUIG and Ireland in atmospheric science.

8 Data Collection, Quality Control and Archiving

Data collection and quality control routine for offline and online chemical measurements were the essential parts 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 are measured by a liquid chromatography method in which positive and negative ions are quantified separately. Positive and negative ions should be balanced as they constitute certain chemical compounds in the particles. The method had already been successfully applied by Ceburnis *et al*. (2006), who revealed certain deficiencies in PM samples. The ion balance method, which is the ratio of positive and negative ions, can give insight about missing chemical species or incomplete chemical analysis, e.g. carbonates are not normally measured by high-performance liquid chromatography (HPLC) 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 at analytical errors. The samples are routinely subjected to ion balance check during a validation procedure. Another quality control check is done by comparing HPLC analysis-derived inorganic component concentrations with AMS-derived concentrations. The above checks ensure comparability and consistency between different techniques, giving a high degree of confidence in the obtained results.

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

- total condensation particle number concentration;
- aerosol scattering coefficient;
- aerosol absorption coefficient and black carbon concentration;
- $PM_{2.5}$ mass [tapered element oscillating microbalance (TEOM)]
- aerosol size distribution (scanning mobility particle sizer).

Since 2014, the aerosol scattering coefficient and aerosol absorption coefficient have also been delivered in real time using an implemented real-time transfer algorithm provided by NILU. The delivery of other data has been significantly delayed by a change in the personnel observing instrument performance and validating instrument output (the Technical Officer left in late 2014 and was replaced in mid-2015). Significant effort went into training and transferring knowledge to the replacement, which delayed data delivery, but this is currently in progress and should be completed by the end of 2019.

The aerosol optical depth data were sent to the World Radiation Centre at Davos, Switzerland, under the auspices of WMO GAW, which transmits the data to the World Data Centre for Aerosols, run by WMO GAW, through Dr Julian Wilson, at the Institute for Environment and Sustainability, European Commission, DG JRC, Ispra (Va), Italy. However, as the result of a decision made at the World Data Centre for Aerosols, the aerosol optical depth instrument at Mace Head was removed and the measurements discontinued. The reason for this was diminished scientific interest in the measurements and the fact that overwhelming cloudiness at Mace Head meant that data were available for only 15% of the total time.

The fellowship project necessitated close interaction with many researchers, including some from outside Ireland during international field campaigns or collaborative projects. A 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 has ensured that such requests are managed efficiently and in a timely manner.

9 Peer-reviewed Publications Produced during the Project

1. Allastuey, A., Querol, X., Aas, W., Lucarelli, F., Pérez, N., Moreno, T., Cavalli, F., Areskoug, H., Balan, V., Catrambone, M., Ceburnis, D., Cerro, J.C., Conil, S., Gevorgyan, L., Hueglin, C., Imre, K., Jaffrezo, J.L., Leeson, S.R., Mihalopoulos, N., Mitosinkova, M., O'Dowd, C.D., Pey, J., Putaud, J.-P., Riffault, V., Ripo, A., Sciare, J., Sellegri, K., Spindler, G. and Yttri, K.-E., 2016. Geochemistry of PM_{10} over Europe during the EMEP intensive measurement periods in summer 2012 and winter 2013. *Atmospheric Chemistry and Physics* 16: 6107–6129.

2. Cavalli, F., Alastuey, A., Areskoug, H., Ceburnis, D., Čech, J., Genberg, J., Harrison, R.M., Jaffrezo, J.L., Kiss, G., Laj, P., Mihalopoulos, N., Perez, N., Quincey, P., Schwarz, J., Sellegri, K., Spindler, G., Swietlicki, E., Theodosi, C., Yttri, K.E., Aas, W. and Putaud, J.P., 2016. A European aerosol phenomenology-4: harmonised concentrations of carbonaceous aerosol at 10 regional background sites across Europe. *Atmospheric Environment* 144: 133–145.

3. Ceburnis, D., Jennings, S.G. and O'Dowd, C.D., 2013. Intercontinental and regional transport of air pollution monitored at Mace Head, Ireland and over Europe. Nucleation and Atmospheric Aerosols: 19th International Conference. *American Institute of Physics Conference Proceedings* 1527: 591–594.

4. Ceburnis, D., Masalaite, A., Ovadnevaite, J., Garbaras, A., Remeikis, V., Maenhaut, W., Claeys, M., Sciare, J., Baisnee, D. and O'Dowd, C.D., 2016. Stable isotope measurements reveal dual carbon pools contributing to organic matter enrichment in marine aerosol. *Scientific Reports* 6: 36675. https://doi.org/10.1038/srep36675

5. Ceburnis, D., Rinaldi, M., Ovadnevaite, J., Martucci, G., Guillianelli, L. and O'Dowd, C.D., 2016. Marine submicron aerosol gradients, sources and sinks. *Atmospheric Chemistry and Physics* 16: 12425–12439.

6. Crippa, M., Canonaco, F., Lanz, V.A., Äijälä, M., Allan, J.D., Carbone, S., *et al*., 2014. Organic aerosol components derived from 25 AMS data sets across Europe using a consistent ME-2 based source apportionment approach. *Atmospheric Chemistry and Physics* 14: 6159–6176.

7. Dall'Osto, M. Querol X., Alastuey, A., Minguillon, M.C., Alier, M., Amato, F., *et al*., 2013. Presenting SAPUSS: Solving Aerosol Problem by Using Synergistic Strategies in Barcelona, Spain. *Atmospheric Chemistry and Physics* 13: 8991–9019.

8. Dall'Osto, M., Hellebust, S., Healy, R.M., O'Connor, I.P., Kourtchev, I., Sodeau, J.R., Ovadnevaite, J., Ceburnis, D., O'Dowd, C.D. and Wenger J.C., 2014. Apportionment of urban aerosol sources in Cork (Ireland) by synergistic measurement techniques. *Science of the Total Environment* 493: 197–208.

9. Dall'Osto, M., Ovadnevaite, J., Ceburnis, D., Martin, D., Healy, R.M., O'Connor, I.P., Kourtchev, I., Sodeau, J.R., Wenger, J.C. and O'Dowd, C.D., 2013. Characterisation of urban aerosol in Cork city (Ireland) using aerosol mass spectrometry. *Atmospheric Chemistry and Physics* 13: 4997–5015.

10. Garbaras, A., Masalaite, A., Garbariene, I., Ceburnis, D., Krugly, E., Remeikis, V., Puida, E., Kvietkus, K. and Martuzevicius, D., 2015. Stable carbon fractionation in size-segregated aerosol particles produced by controlled biomass burning. *Journal of Aerosol Science* 79: 86–96.

11. Genberg, J., Denier van der Gon, H.A.C., Simpson, D., Swietlicki, E., Areskoug, H., Beddows, D., Ceburnis, D., Fiebig, M., Hansson, H.C., Harrison, R.M., Jennings, S.G., Saarikoski, S., Spindler, G., Visschedijk, A.J.H., Wiedensohler, A., Yttri, K.E. and Bergstrom, R., 2013. Light-absorbing carbon in Europe – measurement and modelling, with a focus on residential wood combustion emissions. *Atmospheric Chemistry Physics* 13: 8719–8738.

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10 Recommendations

- Long-term observations of $PM_{2.5}$ and $PM_{2.5–10}$ chemical composition have revealed significantly reducting trends in pollutants over the last 10 years at Mace Head, and the trend is following an even longer, 35-year long trend at Valentia Island (Co. Kerry). The trends were similar at stations at Mace Head and Valentia and consistent with decreasing emissions in Ireland and worldwide. Sulfate trends quantitatively matched the reduction in sulfur dioxide concentrations and the total sulfurous emissions in Ireland and the latest data suggest that sulfate concentrations are approaching hemispheric background concentrations of biogenic sulfate, demonstrating the success of pollution abatement strategies. However, a follow-up study that included a complete characterisation of ambient PM highlighted the efforts needed to address organic compounds that are not yet continuously monitored in regulatory networks across Europe.
- High time resolution measurements using AMS methods of different complexity have been used in parallel to apportion various sources of organic matter. Several studies across the European continent as well as in Cork city have shown that both regional and local sources contribute to aerosol organic matter and have demonstrated the resolving power of PMF techniques. Given their deployment flexibility and ability to discriminate between different domestic solid fuel sources, high time resolution of real-time measurement techniques are highly recommended for air quality monitoring and addressing various local pollution problems.
- Application of the carbonaceous matter source apportionment technique at the clean Southern Ocean environment at Amsterdam Island proved yet again the resolving power of isotope analysis. Carbon isotope analysis of aerosol samples revealed fundamental processes at the ocean surface and the atmosphere, where biological activity is playing a key role in organic matter enrichment of atmospheric particles. A dual-source model encompassing isotope fractionation processes was proposed to inform an ongoing debate about the origin and the importance of marine biogenic organic matter.
- The climatic implications of PM have been studied by looking at long-term surface global radiation trends alongside continuously reducing sulfate concentrations. The results suggest global brightening as pollution levels are decreasing, which is bad news for the global climate as aerosols are reducing their cooling power. The study has found that the efforts devoted to air quality improvement (and, therefore, reduced cooling effect) should be concurrent with the reduction of greenhouse gas emissions if dangerous global warming is to be avoided. If greenhouse gas emissions remain at their current pace, the reduced cooling will accelerate warming.
- The PM_{10} mineral dust composition across Europe during the EMEP intensive observation period demonstrated the influence of both local (natural and anthropogenic) and external sources, as evidenced by ratios of different mineral components in the PM filter samples. In general, recorded concentrations of mineral dust were higher in summer than in winter, with the summer maxima of mineral dust being more evident in the southern and eastern European countries.

The high-quality research done at C-CAPS, and the research support undertaken at Mace Head atmospheric observatory, has provided significant insights into air quality policy in Ireland while at the same time developing new approaches and tools to be used in the near future. The uniqueness of Mace Head's location is evident in the number of concerted observation campaigns conducted or facilitated at Mace Head and the number of worldwide networks supported. The expanded knowledge base will ensure that the policymakers will be able to make the best-informed decisions and keep up with international treaties and commitments.

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Abbreviations

ACI	Aerosol cloud interaction
ACSM	Aerosol chemical speciation monitoring
AEROCE	Atmospheric Ocean Chemistry Experiment
AERONET	Aerosol Robotic Network
AMS	Aerosol mass spectrometry
ATOFMS	(Single particle) aerosol time-of-flight mass spectrometry
BACCHUS	Impact of Biogenic versus Anthropogenic emissions on Clouds and Climate: towards a Holistic UnderStanding
CAFE	Clean Air for Europe Programme
C-CAPS	Centre for Climate and Air Pollution Studies at NUI Galway
CLRTAP	Convention on Long-range Transboundary Air Pollution
EMEP	European Monitoring and Evaluation Programme
EPA	Environmental Protection Agency
EU	European Union
EUCAARI	European Integrated Project on Aerosol Cloud Climate and Air Quality Interactions
GAW	Global Atmosphere Watch
HPLC	High-performance liquid chromatography
HR-ToF-AMS	High-resolution time-of-flight aerosol mass spectrometry
IMP	Intensive measurement period
INP	Ice nucleating particle
LV-OOA	Low-volatility oxygenated organic aerosol
MHO	Mace Head Observatory
MONET	Monitoring Network for Persistent Organic Pollutants
NILU	Norwegian Institute for Air Research
nss	Non-sea salt
NUIG	National University of Ireland Galway
PEGASO	Plankton-derived Emissions of trace Gases and Aerosols in the Southern Ocean
PM	Particulate matter
PMF	Positive matrix factorisation
POA	Primary organic aerosol
POP	Persistent organic pollutant
PTFE	Polytetrafluoethylene
SOA	Secondary organic aerosol
SV-OOA	Semi-volatile oxygenated organic aerosol
TF HTAP	Task Force on Hemispheric Transport of Air Pollution
TSPs	Total suspended particles
UN-ECE	United Nations Economic Commission for Europe
WMO	World Meteorological Organization

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.

EPA Research Report 298

An Integrated Source Apportionment and Climatic Implications of $PM_{2.5}$ and PM_{10} Particulate Matter

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

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. 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 emerging state-of-the-art techniques such as near-real-time aerosol mass spectrometry offer an immediate response to air pollution issues, but they need to be comprehensively tested and developed for public use. A number of international obligations towards established air quality networks (European Monitoring and Evaluation Programme – EMEP, European Research Infrastructure for the observation of Aerosol, Clouds and Trace Gases – SCTRIS) can and are readily supported at knowledge-based research infrastructures such as Mace Head.

Identifying Pressures

The largest environmental pressures of the late 20th and early 21st centuries have been air pollution, with its ensuing health effects, and global climate warming, firmly attributed to anthropogenic greenhouse gas emissions. The above two effects are closely related, because aerosols offset a significant fraction of global warming induced by greenhouse gasses. Therefore, reducing air pollution with the aim of improving human well-being will result in stronger, accelerated warming, which is now 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.

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 and those of regional governments. It was found that a dramatic reduction in pollution – a 70% reduction in anthropogenic sulfate over the North-East Atlantic – simultaneously caused an increase in atmosphere brightness, which is accelerating global warming. Synergistic deployment of state-of-the-art instrumentation revealed that air pollution episodes in cities are caused by solid fuel combustion. The facilitation of several international network activities (EMEP, ACTRIS, MONET Programme for persistent organic pollutants) would not have been possible without this fellowship and returned great value for money.

The 26 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 sophisticated methodology developed using aerosol mass spectrometry is enabling unambiguous determination of the cause of urban air pollution.

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