NDP
National Development Plan 2007 - 2013

epa
Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

STRIVE
Report Series No. 4

Climate Change – An Analysis of Aerosol Properties at Mace Head

STRIVE
Environmental Protection Agency Programme
2007-2013

SSTI

Comhshaol, Oidhreacht agus Rialtas Áitiúil
Environment, Heritage and Local Government

Environmental Protection Agency

The Environmental Protection Agency (EPA) is a statutory body responsible for protecting the environment in Ireland. We regulate and police activities that might otherwise cause pollution. We ensure there is solid information on environmental trends so that necessary actions are taken. Our priorities are protecting the Irish environment and ensuring that development is sustainable.

The EPA is an independent public body established in July 1993 under the Environmental Protection Agency Act, 1992. Its sponsor in Government is the Department of the Environment, Heritage and Local Government.

OUR RESPONSIBILITIES

LICENSING

We license the following to ensure that their emissions do not endanger human health or harm the environment:

- waste facilities (e.g., landfills, incinerators, waste transfer stations);
- large scale industrial activities (e.g., pharmaceutical manufacturing, cement manufacturing, power plants);
- intensive agriculture;
- the contained use and controlled release of Genetically Modified Organisms (GMOs);
- large petrol storage facilities.

NATIONAL ENVIRONMENTAL ENFORCEMENT

- Conducting over 2,000 audits and inspections of EPA licensed facilities every year.
- Overseeing local authorities' environmental protection responsibilities in the areas of - air, noise, waste, waste-water and water quality.
- Working with local authorities and the Gardaí to stamp out illegal waste activity by co-ordinating a national enforcement network, targeting offenders, conducting investigations and overseeing remediation.
- Prosecuting those who flout environmental law and damage the environment as a result of their actions.

MONITORING, ANALYSING AND REPORTING ON THE ENVIRONMENT

- Monitoring air quality and the quality of rivers, lakes, tidal waters and ground waters; measuring water levels and river flows.
- Independent reporting to inform decision making by national and local government.

REGULATING IRELAND'S GREENHOUSE GAS EMISSIONS

- Quantifying Ireland's emissions of greenhouse gases in the context of our Kyoto commitments.
- Implementing the Emissions Trading Directive, involving over 100 companies who are major generators of carbon dioxide in Ireland.

ENVIRONMENTAL RESEARCH AND DEVELOPMENT

- Co-ordinating research on environmental issues (including air and water quality, climate change, biodiversity, environmental technologies).

STRATEGIC ENVIRONMENTAL ASSESSMENT

- Assessing the impact of plans and programmes on the Irish environment (such as waste management and development plans).

ENVIRONMENTAL PLANNING, EDUCATION AND GUIDANCE

- Providing guidance to the public and to industry on various environmental topics (including licence applications, waste prevention and environmental regulations).
- Generating greater environmental awareness (through environmental television programmes and primary and secondary schools' resource packs).

PROACTIVE WASTE MANAGEMENT

- Promoting waste prevention and minimisation projects through the co-ordination of the National Waste Prevention Programme, including input into the implementation of Producer Responsibility Initiatives.
- Enforcing Regulations such as Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances (RoHS) and substances that deplete the ozone layer.
- Developing a National Hazardous Waste Management Plan to prevent and manage hazardous waste.

MANAGEMENT AND STRUCTURE OF THE EPA

The organisation is managed by a full time Board, consisting of a Director General and four Directors.

The work of the EPA is carried out across four offices:

- Office of Climate, Licensing and Resource Use
- Office of Environmental Enforcement
- Office of Environmental Assessment
- Office of Communications and Corporate Services

The EPA is assisted by an Advisory Committee of twelve members who meet several times a year to discuss issues of concern and offer advice to the Board.

An Ghníomhaireacht um Chaomhnú Comhshaoil

Is í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) comhlachta reachtúil a chosnaíonn an comhshaol do mhuintir na tíre go léir. Rialaímid agus déanaimid maoirsiú ar ghníomhaíochtaí a d'fhéadfadh truailliú a chruthú murach sin. Cinntímid go bhfuil eolas cruinn ann ar threochtaí comhshaoil ionas go nglactar aon chéim is gá. Is iad na príomh-nithe a bhfuilimid gníomhach leo ná comhshaol na hÉireann a chosaint agus cinntiú go bhfuil forbairt inbhuanaithe.

Is comhlacht poiblí neamhspleách í an Ghníomhaireacht um Chaomhnú Comhshaoil (EPA) a bunaíodh i mí Iúil 1993 faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil 1992. Ó thaobh an Rialtais, is í an Roinn Comhshaoil agus Rialtais Áitiúil a dhéanann urraíocht uirthi.

ÁR bhFREAGRACHTAÍ

CEADÚNÚ

Bíonn ceadúnais á n-eisiúint againn i gcomhair na nithe seo a leanas chun a chinntiú nach mbíonn astuithe uathu ag cur sláinte an phobail ná an comhshaol i mbaol:

- áiseanna dramhaíola (m.sh., líonadh talún, loisceoirí, stáisiúin aistrithe dramhaíola);
- gníomhaíochtaí tionsclaíocha ar scála mór (m.sh., déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta);
- diantalmhaíocht;
- úsáid faoi shrian agus scaoileadh smachtaithe Orgánach Géinathraithe (GMO);
- mór-áiseanna stórais peitreail.

FEIDHMIÚ COMHSHAOIL NÁISIÚNTA

- Stiúradh os cionn 2,000 iniúchadh agus cigireacht de áiseanna a fuair ceadúnas ón nGníomhaireacht gach bliain.
- Maoirsiú freagrachtaí cosanta comhshaoil údarás áitiúla thar sé earnáil - aer, fuaim, dramhaíl, dramhuisce agus caighdeán uisce.
- Obair le húdaráis áitiúla agus leis na Gardaí chun stop a chur le gníomhaíocht mhídhleathach dramhaíola trí comhordú a dhéanamh ar líonra forfheidhmithe náisiúnta, díriú isteach ar chiontóirí, stiúradh fiosrúcháin agus maoirsiú leigheas na bhfadhbanna.
- An dlí a chur orthu siúd a bhriseann dlí comhshaoil agus a dhéanann dochar don chomhshaol mar thoradh ar a ngníomhaíochtaí.

MONATÓIREACHT, ANAILÍS AGUS TUAIRISCIÚ AR AN GCOMHSHAOL

- Monatóireacht ar chaighdeán aeir agus caighdeáin aibhneacha, locha, uiscí taoide agus uiscí talaimh; leibhéil agus sruth aibhneacha a thomhas.
- Tuairisciú neamhspleách chun cabhrú le rialtais náisiúnta agus áitiúla cinntí a dhéanamh.

RIALÚ ASTUITHE GÁIS CEAPTHA TEASA NA HÉIREANN

- Cainníochtú astuithe gáis ceaptha teasa na hÉireann i gcomhthéacs ár dtiomantas Kyoto.
- Cur i bhfeidhm na Treorach um Thrádáil Astuithe, a bhfuil baint aige le hos cionn 100 cuideachta atá ina mór-ghineadóirí dé-ocsaíd charbóin in Éirinn.

TAIGHDE AGUS FORBAIRT COMHSHAOIL

- Taighde ar shaincheisteanna comhshaoil a chomhordú (cosúil le caighdéan aeir agus uisce, athrú aeráide, bithéagsúlacht, teicneolaíochtaí comhshaoil).

MEASÚNÚ STRAITÉISEACH COMHSHAOIL

- Ag déanamh measúnú ar thionchar phleananna agus chláracha ar chomhshaol na hÉireann (cosúil le pleananna bainistíochta dramhaíola agus forbartha).

PLEANÁIL, OIDEACHAS AGUS TREOIR CHOMHSHAOIL

- Treoir a thabhairt don phobal agus do thionscal ar cheisteanna comhshaoil éagsúla (m.sh., iarratais ar cheadúnais, seachaint dramhaíola agus rialacháin chomhshaoil).
- Eolas níos fearr ar an gcomhshaol a scaipeadh (trí cláracha teilifíse comhshaoil agus pacáistí acmhainne do bhunscoileanna agus do mheánscoileanna).

BAINISTÍOCHT DRAMHAÍOLA FHORGHNÍOMHACH

- Cur chun cinn seachaint agus laghdú dramhaíola trí chomhordú An Chláir Náisiúnta um Chosc Dramhaíola, lena n-áirítear cur i bhfeidhm na dTionscnamh Freagrachta Táirgeoirí.
- Cur i bhfeidhm Rialachán ar nós na treoracha maidir le Trealamh Leictreach agus Leictreonach Caite agus le Srianadh Substaintí Guaiseacha agus substaintí a dhéanann ídiú ar an gcrios ózóin.
- Plean Náisiúnta Bainistíochta um Dramhaíl Ghuaiseach a fhorbairt chun dramhaíl ghuaiseach a sheachaint agus a bhainistiú.

STRUCHTÚR NA GNÍOMHAIREACHTA

Bunaíodh an Ghníomhaireacht i 1993 chun comhshaol na hÉireann a chosaint. Tá an eagraíocht á bhainistiú ag Bord lánaimseartha, ar a bhfuil Príomhstiúrthóir agus ceithre Stiúrthóir.

Tá obair na Gníomhaireachta ar siúl trí ceithre Oifig:

- An Oifig Aeráide, Ceadúnaithe agus Úsáide Acmhainní
- An Oifig um Fhorfheidhmiúchán Comhshaoil
- An Oifig um Measúnacht Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáide

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag ball air agus tagann siad le chéile cúpla uair in aghaidh na bliana le plé a dhéanamh ar cheisteanna ar ábhar imní iad agus le comhairle a thabhairt don Bhord.

EPA STRIVE Programme 2007–2013

CLIMATE CHANGE – An Analysis of Aerosol Properties at Mace Head (2000-LS-5.3.2-M1)

STRIVE Report

(End of Project Report available for download on http://erc.epa.ie/safer/reports)

Prepared for the Environmental Protection Agency

by

Atmospheric Research Group/Environmental Change Institute,

Department of Experimental Physics, National University of Ireland, Galway

and

Rosenstiel School of Marine and Atmospheric Science, University of Miami, USA

Authors:

S. Gerard Jennings, Darius Ceburnis, Brendan M. Kelly,

T. Gerard Spain, Dennis L. Savoie and Hal Maring

ENVIRONMENTAL PROTECTION AGENCY

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

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

DISCLAIMER

The EPA STRIVE 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.

EPA STRIVE PROGRAMME 2007–2013

Published by the Environmental Protection Agency

ISBN: 1-84095-259-8

Price: Free **Online version**

ACKNOWLEDGEMENTS

This report is published as part of the Science, Technology, Research and Innovation for the Environment (STRIVE) Programme 2007–2013. The programme is financed by the Irish Government under the National Development Plan 2007–2013. It is administered on behalf of the Department of the Environment, Heritage and Local Government by the Environmental Protection Agency which has the statutory function of co-ordinating and promoting environmental research.

The project was undertaken by the Atmospheric Research Group within the Department of Experimental Physics and affiliated with the Environmental Change Institute (ECI) at the National University of Ireland, Galway (NUI, Galway). The project leader was Prof. S. Gerard Jennings (NUI, Galway) assisted by Dr Darius Ceburnis (NUI, Galway), Brendan M. Kelly (NUI, Galway) and T. Gerard Spain (NUI, Galway). The work was done in collaboration with members of the Rosenstiel School of Marine and Atmospheric Science, University of Miami, Florida: Dr Dennis L. Savoie, Dr Hal Maring and their team. The initial measurement methodology was set up by the University of Miami Group, which also carried out the chemical analysis of the aerosol filter samples. The project co-ordinator for the Agency was Dr Frank McGovern.

Details of Project Partners

S. Gerard Jennings
Department of Physics/Environmental Change Institute
National University of Ireland
Galway
Ireland

Tel.: +353 91 492704
Fax: +353 91 494584
E-mail: gerard.jennings@nuigalway.ie

Darius Ceburnis
Department of Physics/Environmental Change Institute
National University of Ireland
Galway
Ireland

Brendan M. Kelly
Department of Physics/Environmental Change Institute
National University of Ireland
Galway
Ireland

T. Gerard Spain
Department of Physics/Environmental Change Institute
National University of Ireland
Galway
Ireland

Dennis L. Savoie
Rosenstiel School of Marine and Atmospheric Science
University of Miami
FL 33149
USA

Hal Maring
Rosenstiel School of Marine and Atmospheric Science
University of Miami
FL 33149
USA

Table of Contents

Executive Summary

Here, we report the physico–chemical characteristics of North Atlantic aerosols, with a focus on clean marine aerosol. This work describes physico–chemical and radiative measurements taken at the Mace Head Atmospheric Research Station during the period from 2000 to 2003. The measurements are indicative of the medium- to long-term measurement programme at the site. These include mass concentration (mass per unit volume) of total suspended particulate (TSP), aerosol inorganic chemical species, aerosol scattering coefficient; aerosol absorption coefficient and aerosol optical depth. The relatively continuous nature of the measurement programme permitted both monthly and seasonal characteristics of aerosol parameters to be established.

Chemical analysis of aerosol samples for the year 2003 shows that the mass concentration of sea salt has a seasonal pattern, with minimum levels in the summer period of around 7.5 μg/m^3 and enhanced values – by about a factor of 3 – in the winter period of the order of 22.5 μg/m^3, due to the increase in wintertime of super-micrometre coarse-mode aerosol particles (diameter >1.0 μm) with wind speed, formed mainly by the bubble bursting process within breaking waves. During winter, sea salt contributes to over 95% of the marine TSP mass while the contribution of the remaining species is almost negligible.

Non-sea-salt sulphate (nssSO_4^{2-}) TSP marine mass concentration shows lower values – by a factor of about 3 – during winter (mean levels of order 0.2–0.25 μg/m^3) as compared to elevated values (mean levels of around 0.75 μg/m^3) during midsummer. The enhancement is attributed to the marine biota cycle which is active during the North Atlantic phytoplankton bloom season – from late spring through to early autumn. Non-sectored mass concentration levels of nssSO_4^{2-} (overall mean levels of around 1.3 μg/m^3) are a factor of about 3 higher than corresponding clean marine sectored levels.

Aerosol scattering coefficient values show a similar seasonal trend as aerosol inorganic chemical mass concentration, in that a seasonal 3- to 3.5-fold increase obtains in the winter season, with values in the range 25–35 Mm^{-1}, as compared to summer values of the order of 7–12 Mm^{-1}. The frequency of occurrence of hourly averaged aerosol absorption data is found to be bimodally distributed, one mode resulting from clean marine air and the second mode resulting from anthropogenically polluted continental air. The hourly averages of the marine portion of the aerosol light absorption are found to follow closely a lognormal distribution with a geometric mean attenuation coefficient of 0.310 Mm^{-1}, equivalent to a black carbon (BC) mass concentration of 16.3 ng/m^3, based on a BC mass attenuation efficiency of 19 m^2/g. The BC mass concentration for marine air at Mace Head is in reasonably good agreement with other marine and coastal sites. Annual mean values of aerosol optical depth (in the range 0.1–0.11) are in good agreement with other values over the Atlantic and North Atlantic ocean, and so the aerosol optical depth measurements at Mace Head can be taken to be representative of the North Atlantic region.

Evidence of the impact of hemispheric long-range transport of air pollution on levels at Mace Head is afforded through observations of elevated values, for example, of nssSO_4^{2-}, BC and CO, which are traceable to transport from the North American continent, as well as from the UK and continental Europe. The United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (CLRTAP) Task Force Report on Hemispheric Transport of Air Pollution considers that continuation of long-term monitoring is essential to assess trends and impacts from long-range transport, as well as providing input for development and testing of a wide variety of models being used to address aerosol transport.

1 Introduction

It is important to obtain information about atmospheric aerosols, not only to identify their physico–chemical characteristics, but also to relate their properties to air quality and climatic effects. Continuous measurements are crucially important in order to determine seasonal patterns and longer-term trends.

Aerosol chemical composition work in Ireland has been fairly intermittent up to now. Until the advent of this work, no aerosol chemistry measurements on a quasi-continuous basis have been carried out at the Mace Head Atmospheric Research Station since the Atmosphere–Ocean Chemistry Experiment (AEROCE) measurement programme (Prospero, 2001) ceased in 1994, although several intensive measurement campaigns have included aerosol chemical composition work.

Analysis of total suspended particulate (TSP) filter samples collected between August 2001 and December 2003 is reported in this work. In addition, aerosol radiative measurements are reported, which include the aerosol scattering coefficient for the years 2000, 2001 and 2002, as well as the aerosol absorption coefficient/equivalent black carbon (BC) mass concentration for the period 1989–2003, which are indicative of the medium- to long-term aerosol measurement programme at the site.

2 Objectives of the Work

There three main objectives of this work are outlined as follows:

1. To revive measurements of aerosol chemical properties at the Mace Head Atmospheric Research Station
2. To deploy instrumentation to provide aerosol radiative measurements, i.e. aerosol scattering and absorption coefficient, and aerosol optical depth
3. To enable a national component of a European aerosol observing system.

3 Meteorological and Air Mass Classification

3.1 Meteorological Parameters

Meteorological parameters of wind speed and direction have been measured at the site since 1989. The prevailing wind direction is from a designated clean marine sector and air masses arriving at the station are dominated by westerly winds from the Atlantic Ocean. Meteorological data from the station show that, on average, 52% of air masses arriving at Mace Head can be defined as clean marine air (Jennings *et al.*, 2003). Continental polluted sector winds prevail about 20% of the time.

A wind sector control strategy is adopted in filter sampling for aerosol chemical composition determination. The clean marine sector is prescribed by a wind direction sector from 190° to 300°, and is usually coupled with a combination of aerosol or condensation nuclei number concentration of *ca* <700/cm^3 and/or an aerosol absorption coefficient of <1.43 Mm^{-1}. The polluted air sector is defined by wind direction (WD) alone:

45° < WD < 135°.

4 Aerosol Chemical and Radiative Instrumentation

4.1 Sampling Location

The Mace Head Atmospheric Research Station is one of the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) global stations for both aerosol and gaseous species and is mainly representative of marine air. Mace Head was audited favourably by the WMO GAW in November 2004. Mace Head (as well as Valentia Observatory) has undergone a GAW review (Barrie & Puckett, 2005).

Mace Head (53° 20' N, 9° 54' W) is located on the west coast of Ireland, an ideal location to obtain quite detailed information on marine aerosols from the North Atlantic region because of prevailing westerly–south-westerly winds. Results from air mass trajectory models usually show that these air masses generally stay over the ocean for 4–5 days before arriving at Mace Head.

4.2 Chemical Analysis

Samples were analysed using ion chromatography for Na^+, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, and for ash content by the University of Miami. The concentration of SO_4^{2-} from sources other than the dissolved salts in sea water (non-sea-salt sulphate, $nssSO_4^{2-}$) was calculated as total SO_4^{2-} minus the Na^+ concentration times 0.2516, the SO_4^{2-}/Na^+ mass ratio in bulk sea water. Mass concentration of sea-salt aerosol was derived from the Na^+ concentration through the use of a relation (Yin *et al.*, 2005): sea-salt concentration = 2.54 Na^+ concentration, based on individual speciated inorganic mass values obtained from impactor data at Mace Head.

4.3 Sampling Methodology

Samples were taken on the 23-m tower at Mace Head using high-volume samplers with an open-face filter at a flow rate of 40 m^3/h. The sampling system is able to control aerosol sampling based on wind speed (sample only when wind speed >1 m/s), wind direction (sample when the wind direction is 190° to 300° for the clean sector sample and 0° to 360° for the non-sectored sample), relative humidity (sample only when the relative humidity <95%), and rain presence (sample only when it is not raining). The majority of reliable samples come from multi-day (2–3 days) sampling.

4.4 Aerosol Radiative Measurements

4.4.1 Aerosol scattering coefficient

Aerosol particle scattering measurements were performed by a TSI Inc. 3563 3-wavelength integrating nephelometer. The TSI Model 3563 nephelometer measures the total aerosol scattering coefficient at wavelengths λ = 450, 550, 700 nm. The nephelometer is calibrated on a regular basis. A detailed discussion of the performance characteristics of this instrument is given by Anderson *et al.* (1996).

The scattering coefficient is recorded as 5-min values which are integrated to give hourly arithmetic mean values. The nephelometer is connected via a 15-mm diameter duct to the community air-sampling system with a flow rate of 150 l/min to ensure laminar flow. Due to internal heating of the nephelometer, aerosols were sampled at an average relative humidity of 35 ± 5%, and the nephelometer measurements should be considered as representing dry aerosol particles only.

4.4.2 Aerosol absorption coefficient

The attenuation of light through aerosol-laden quartz fibre filters has been measured using Magee Scientific Aethalometer Models AE-8 and AE-9 with manual filter change. The AE-8 model was in use up to December 1993. The instrument operates by measuring the attenuation of white light through a quartz fibre filter whilst air is being drawn through the filter (Hansen *et al.*, 1984).

4.4.3 Aerosol optical depth

Measurements of column-integrated light extinction have been conducted at the Mace Head site since March 2000 in order to derive aerosol optical depth (AOD). The measurements are performed with a precision filter radiometer (PFR), developed at the Physikalisch-Meteorologisches Observatorium Davos/World Radiation Centre (PMOD/WRC), Switzerland. The PFR is mounted on an automated solar tracker and continuously records the columnar light extinction every 2 min. The instrument measures at four wavelengths centred at 862, 500, 412, and 368 nm with a 5-nm full width at half maximum (FWHM) bandwidth.

The radiometer is annually calibrated by field comparisons with a travelling standard through the WMO GAW programme. The comparison of the Mace Head radiometer with the reference instrument shows deviations of <0.5%, indicating that the PFR exhibits high stability in time. The precision of the PFR is estimated to be 0.01 optical depth.

5 Aerosol Mass Concentrations of Aerosol Inorganic Components

5.1 Aerosol Inorganic Chemical Mass Concentration

Average mass concentrations of marine aerosol chemical species as well as data from other studies are summarised in Table 5.1.

5.2 Monthly and Seasonal Trends of Aerosol Inorganic Chemical Components

Filter samples from the Mace Head site for the period 1 January 2003 to the end of December 2003 have been analysed. The year 2003 was chosen since it well represented samples throughout the entire year without major gaps. Monthly analysis of the aerosol chemical mass concentration data for 2003 is shown in Table 5.2 and in Fig. 5.1 for clean marine air masses (sectored) and in Table 5.3 for unsectored air masses, for the following aerosol species: Cl^-, NO_3^-, Na^+, $nssSO_4^{2-}$ and NH_4^+.

A seasonal cycle is observed in both sectored and unsectored (not shown) filter samples. Higher levels of sea salt are caused by stronger winds during winter, generating more primary sea-salt particles, and mass concentrations are higher than for non-sectored samples. For example, the winter Na^+ mass concentration of 8.87 µg/m^3 (equivalent to sea-salt mass concentration of 22.53 µg/m^3) is about a factor of 3 higher than the corresponding values (2.89 µg/m^3 for Na^+ and 7.34 µg/m^3 for sea salt) in the summer period for the year 2003.

The clean sector seasonal cycle is also very different from the unsectored seasonal cycle. Mass concentrations of NO_3^-, $nssSO_4^{2-}$, NH_4^+ are elevated during the summer season, which is linked to biological activity in oceanic surface waters. This is also found from other analyses at Mace Head (Yoon *et al.*, 2007). $nssSO_4^{2-}$ exhibited the most pronounced seasonal cycle with peak values during July. This is also reflected in the comparison between averaged 2003 summer $nssSO_4^{2-}$ mass concentration levels of around 0.75 µg/m^3 – an enhancement of about a factor of 3 – as compared to winter $nssSO_4^{2-}$ levels of between 0.2 and 0.25 µg/m^3. Yoon *et al.* (2007) have shown that $nssSO_4^{2-}$ is highly correlated with MSA (methanesulphonic acid), which is a precursor species leading to production of $nssSO_4^{2-}$ via a secondary marine aerosol process (Seinfeld and Pandis, 1998).

Unsectored (as compared to sectored) air masses yield elevated mass concentrations of major ions: NO_3^-, $nssSO_4^{2-}$, and NH_4^+ for all seasons, due to polluted air masses.

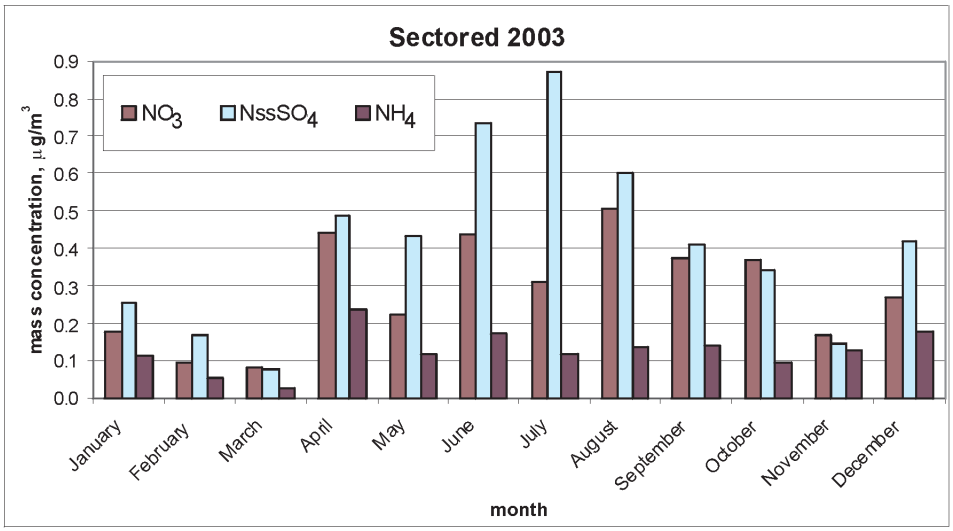
Table 5.1. Summary of marine aerosol inorganic mass concentrations (µg/m^3) of Na^+, Cl^-, $nssSO_4^{2-}$, NO_3^-, and NH_4^+ at Mace Head and in Tenerife, Canary Islands.

Sampling site	Sample type	Na^+	Cl^-	$nssSO_4^{2-}$	NO_3^-	NH_4^+
Mace Head (*this work*)	Sectored samples, TSP[1]	5.59	10.16	0.480	0.313	0.125
Mace Head	Clean marine samples, 1998–1999, TSP[2]			0.344	0.190	
Mace Head	Clean marine samples, Berner impactor[3]	3.64	6.22	0.233	0.185	0.072
Tenerife, ACE-2	Sub-micron fraction[4]			0.300		0.082
Mace Head (*this work*)	Unsectored samples, TSP[1]	3.66	6.51	1.340	1.776	0.891
Mace Head	1989–1990, unsectored samples, TSP[5]			1.290	0.743	

[1]TSP: total suspended particulate.
[2]Kleefeld *et al.* (2002).
[3]Cavalli *et al.* (2004).
[4]Sub-micron fraction – particles <1.26 µm in diameter.
[5]Savoie *et al.* (2002).

Table 5.2. Mass concentrations (µg/m^3) of aerosol chemical species for *sectored* (clean marine) samples in 2003.

	Cl^-	NO_3^-	Na^+	$nssSO_4^{2-}$	NH_4^+
January	15.714	0.179	8.395	0.254	0.113
February	22.384	0.096	12.355	0.168	0.055
March	10.328	0.079	5.836	0.075	0.024
April	5.221	0.443	3.301	0.488	0.236
May	9.569	0.222	5.323	0.430	0.117
June	6.699	0.434	3.852	0.731	0.172
July	5.045	0.307	2.811	0.873	0.118
August	3.775	0.503	2.002	0.602	0.137
September	6.471	0.371	3.344	0.410	0.138
October	12.857	0.368	7.100	0.342	0.092
November	7.498	0.166	3.898	0.144	0.124
December	10.495	0.270	5.874	0.416	0.178
Mean	**8.262**	**0.354**	**4.552**	**0.575**	**0.138**



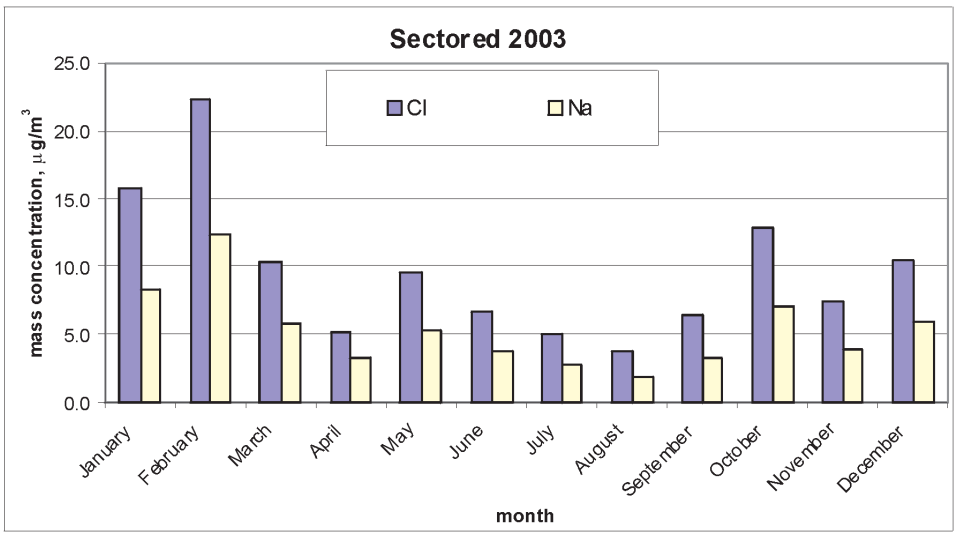


Figure 5.1. Sectored (clean marine) monthly mass concentrations (µg/m^3) of aerosol chemical species in 2003 at Mace Head.

Table 5.3. Mass concentrations (µg/m^3) of aerosol chemical species for *unsectored* samples in 2003.

	Cl^-	NO_3^-	Na^+	$nssSO_4^{2-}$	NH_4^+
January	10.761	0.719	5.791	0.502	0.278
February	12.947	4.837	7.000	2.224	2.618
March	8.419	5.486	4.812	2.069	3.122
April	4.173	5.739	2.464	2.650	3.040
May	5.816	0.705	3.209	0.684	0.358
June	5.226	0.776	2.874	1.226	0.392
July	4.025	0.695	2.236	1.328	0.352
August	2.942	1.230	1.675	1.114	0.570
September	6.198	1.038	3.345	0.861	0.426
October	4.309	3.704	2.494	3.764	1.435
November	8.303	1.457	4.967	0.872	0.589
December	7.517	1.595	4.176	1.988	0.314
Mean	**6.198**	**1.970**	**3.438**	**1.464**	**0.951**

5.3 Seasonal Levels of Aerosol Inorganic Chemical Components

For westerly air masses during winter, sea salt contributes to over 95% of TSP mass while the contribution of the remaining ionic species is almost negligible. However, the contribution of sea salt (Cl^-, Na^+ and sea-salt sulphate ($ssSO_4^{2-}$)) in summer is still high at about 80%. The remainder is mainly due to the increased contribution of NO_3^- and of $nssSO_4^{2-}$ originating from biological activity in oceanic surface waters. Interestingly, the concentration of $nssSO_4^{2-}$ during summer in westerly air masses is about 30% of the $nssSO_4^{2-}$ level in easterly air masses. This indicates that marine sources contribute fairly substantially to the total burden of $nssSO_4^{2-}$ at least over Ireland.

In order to characterise easterly air masses, backward air mass trajectories were studied and samples characterised by easterly air flow were attributed to the polluted or eastern sector (45–135°). A total of 27% of unsectored samples qualify as easterly polluted air masses. A comparison of the average mass concentrations in easterly and westerly sectors from August 2001 to December 2003 is summarised in Fig. 5.2.

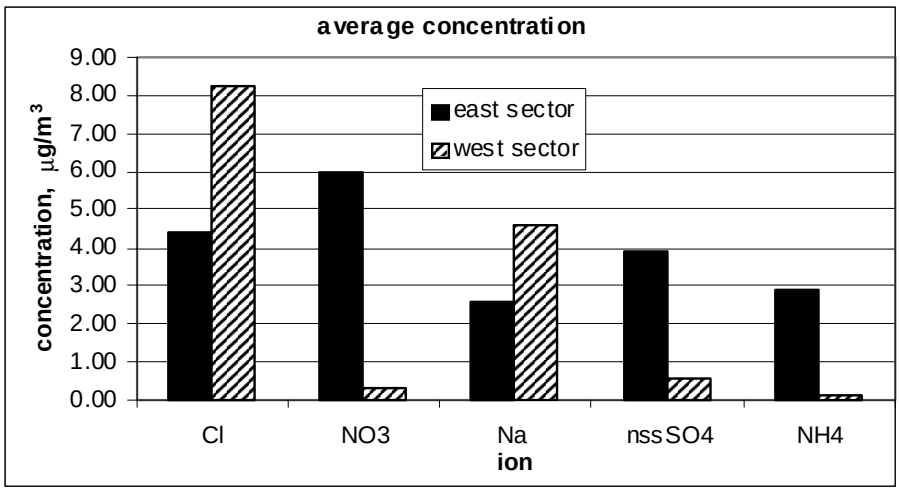


Figure 5.2. Average mass concentrations of major aerosol inorganic ions in total suspended particulate aerosol at Mace Head for air masses from an easterly and from a westerly direction.

The difference between inorganic ionic concentrations is large: a factor of about 20 for NO_3^- and NH_4^+, and a factor of about 8 for $nssSO_4^{2-}$.

Average sea salt mass concentration is still rather high for easterly air masses, with a contribution of around 40% (between about 6 and 7 µg/m^3) to the total mass. The rest of the mass is shared between NO_3^-, NH_4^+ and $nssSO_4^{2-}$ with the largest contribution from NO_3^-.

6 Atmospheric Aerosol Radiative Measurements

6.1 Aerosol Scattering Coefficient Measurements

The mean monthly total aerosol scattering coefficients (σ_{sp}) at a wavelength of 550 nm, calculated from the hourly values, have been determined. The overall mean aerosol scattering coefficient for 2001 amounts to 20.3 Mm^{-1} which is representative of the marine boundary layer (Quinn *et al.*, 2001). The seasonal cycle indicates values in winter that are a factor of 3 higher than those in summer, due to enhanced wind speeds.

6.2 Aerosol Absorption Coefficient Measurements

A distribution of occurrence of hourly averaged aerosol absorption measurements from 1989 to 2002 (Junker *et al.*, 2006) shows that two modes can be identified at approximately 0.4 Mm^{-1} and 4 Mm^{-1}, representing measurements of marine background aerosol and continental aerosol, respectively. One mode corresponds to marine sector conditions of absorption coefficient $\sigma_{abs} \approx 0.4$ Mm^{-1} (equivalent to a BC mass concentration of ≈21 ng/m^3 based on a BC mass attenuation efficiency of 19 m^2/g) and is within the range of mean concentrations found at other marine sites (in Panama, Junker *et al.* (2004) and in Korea, Kim *et al.* (2000)). The continental sector mode value of $\sigma_{att} \approx 3.4$ Mm^{-1} (equivalent to a BC mass concentration of ≈179 ng/m^3) is comparable to BC mass concentration levels reported for remote continental sites, for example by Junker *et al.* (2004) and by Echalar *et al.* (1998).

Both clean marine and polluted data show a general increase in levels from 1989 up to 1996/1997 and a slight decrease or levelling off thereafter (Junker *et al.*, 2006). The polluted sector shows an increasing trend of 10.9 ± 7.3% per annum for the years 1989 to 1997 and a slight decrease of –0.6 ± 9.8% per annum (not statistically significant) thereafter. The observed increase of continental BC is possibly related to increasing BC emissions over Ireland (UNSTAT, 2002). The marine sector shows an increasing trend of 7.7 ± 3.6% per annum for the years 1989 to 1997 and a slight decrease (–0.1 ± 6.0%) per annum thereafter.

The arithmetic means and the geometric means and modes of hourly averaged attenuation coefficients and BC mass concentrations for marine and continental air masses are listed in Table 6.1.

6.3 Aerosol Optical Depth Measurements

Mean monthly AOD values at $\lambda = 500$ nm are shown in Fig. 6.1 for the year 2001 and range from 0.06 to 0.16. About 8.6% of all daylight hours in 2001 are covered by

Table 6.1. Geometric and arithmetic means and modes for marine and continental sector hourly averaged aerosol attenuation coefficients at Mace Head for the period February 1989 to March 2003.

	Attenuation coefficient (Mm^{-1})	BC mass concentration[a] (ng/m^3)
Marine sector		
Geometric mean	0.310 ± 0.004	16.3 ± 0.2
Geometric mode	0.303 ± 0.005	15.9 ± 0.3
Arithmetic mean	0.709 ± 0.016	37.3 ± 0.8
Arithmetic mode	0.133 ± 0.020	7.0 ± 1.1
Continental sector		
Geometric mean	3.93 ± 0.08	207 ± 4
Geometric mode	6.49 ± 0.94	342 ± 49
Arithmetic mean	6.36 ± 0.11	335 ± 6
Arithmetic mode	2.00 ± 0.30	105 ± 16

[a]Based on BC mass attenuation efficiency of 19 m^2/g.

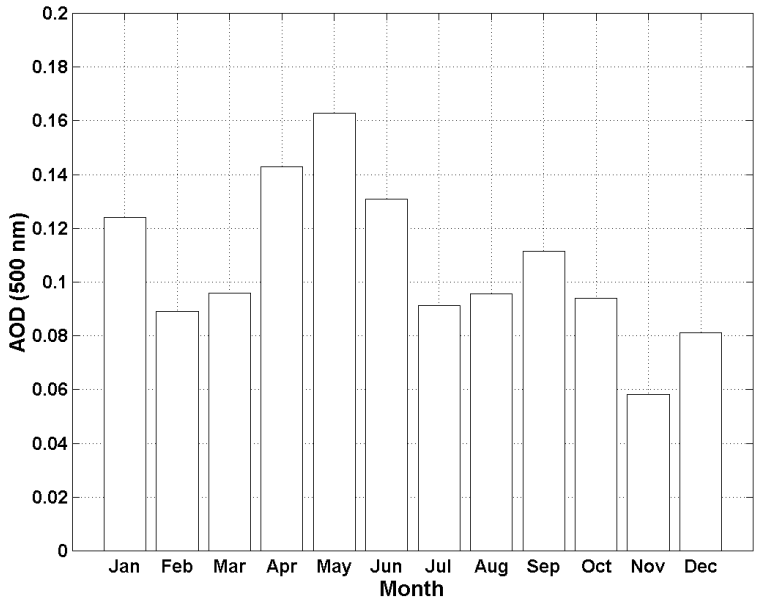


Figure 6.1. Mean monthly aerosol optical depth (AOD) at λ = 500 nm for the year 2001.

AOD measurements under clear sky conditions. The Mace Head site experiences high cloud coverage throughout the year because of its geographical location close to the path of Atlantic low-pressure systems. The resulting overall mean AOD (500 nm) for 2001 is 0.11 and is in good agreement with baseline AOD values of 0.07 over the Atlantic Ocean (Kaufman *et al.*, 2001) and of 0.11 over the North Atlantic Ocean as measured by Villevalde *et al.* (1994). Therefore, AOD measurements conducted at the Mace Head station can be regarded as being representative of the North Atlantic.

7 Hemispheric Transport of Air Pollution (HTAP)

7.1 Evidence of Hemispheric Transport of Aerosol to Mace Head

The outflow of aerosols from North America has been studied at the downwind site at Mace Head during the course of the AEROCE 6-year campaign (Prospero, 2001). Analysis of ~1- to 2-day aerosol samples during AEROCE shows that transport of sulphate aerosol from anthropogenic sources has had a major impact on the chemistry of the atmosphere over a large area of the North Atlantic, indicating that the aerosol arrived from across the ocean (Savoie *et al.*, 2002). For example, anthropogenic sulphate accounted for 85–90% of total $nssSO_4^{2-}$ at Mace Head over the period from 1988 to 1991 for marine sector data. Indeed, Mace Head $nssSO_4^{2-}$ mass concentration levels are several times higher than in the southern hemisphere (Barrie *et al.*, 2001), giving evidence of long-range transport from air pollution sources. Ongoing work, some of which is documented in this Synthesis Report, further supports the impact of long-range transport on aerosol inorganic compound levels at Mace Head.

Other evidence of the impact of long-range transport on levels at Mace Head is afforded through the observation of elevated levels of BC aerosol at Mace Head in 1998 which were traced to Canadian wildfires (Forster *et al.*, 2001), clearly demonstrating long-range transport of aerosols from North America.

Evidence of regional transport of polluted air from Europe to Mace Head has been observed for BC aerosol and CO (Jennings *et al.*, 1996; Derwent *et al.*, 2001). Covariance between the two species suggests a common source from incomplete combustion. Mean elevation of CO in European air masses above those of North Atlantic air masses is about 65–75 ppb.

7.2 UNECE CLRTAP Task Force on Hemispheric Transport of Air Pollution

The United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP) Task Force on Hemispheric Transport of Air Pollution (TF HTAP) has published the HTAP 2007 Interim Assessment Report (Keating and Zuber, 2007) which contains a chapter entitled *Observational Evidence & Capabilities Related to Hemispheric or Intercontinental Transport*.

8 Summary and Conclusions

Physico–chemical and radiative characteristics of North Atlantic marine and modified marine aerosol at Mace Head spanning a period from 2000 to 2003 are reported here.

Aerosol inorganic chemical analysis of North Atlantic TSP aerosol showed that the concentration of sea salt has a seasonal pattern, with a maximum in winter (22.5 µg/m^3). Even in an easterly air flow, sea-salt mass concentration is relatively high (6–7 µg/m^3). In contrast to sea salt, the nssSO_4^{2-} mass concentration showed an opposite seasonal pattern with lower values during winter and higher values during midsummer, which is attributed to active marine biota during the North Atlantic phytoplankton blooming seasons – from spring to autumn.

The overall mean aerosol scattering coefficient (at 0.55 µm wavelength) for 2001 amounts to 20.3 Mm^{-1}. A seasonal 3- to 3.5-fold winter increase in the aerosol scattering coefficient is due to the higher contribution of wind-generated sea salt to the super-micron particles in the marine boundary layer during the North Atlantic winter.

The work contains valuable data on light-absorbing aerosol properties, measured continuously over quite a long period of time (since 1989) at Mace Head. The work provides information for the 1989–2003 period on the absorption coefficient arithmetic mean (0.709 Mm^{-1}), equivalent to a mean BC mass concentration of 37.3 ng/m^3. Mode values are given in Table 6.1.

Monthly mean AOD values for 2001, at a wavelength of 0.5 µm, range between about 0.06 and 0.16 and are representative of baseline AOD values over the North Atlantic Ocean. The resulting annual mean AOD (500 nm) is 0.11 and is in good agreement with baseline AOD values over the North Atlantic Ocean. Therefore, AOD measurements conducted at the Mace Head station can be regarded as being representative of the North Atlantic Ocean.

Elevated values of nssSO_4^{2-}, BC and CO, for example at Mace Head, show that long-range transport of aerosol and gaseous species from both North America and the UK and continental Europe occurs. The UNECE CLRTAP Interim Assessment Report (Keating and Zuber, 2007) on Hemispheric Transport of Air Pollution 2007 considers that long -term monitoring is essential in order to assess impacts from long-range transport.

9 References

Anderson, T.L., Covert, D.S., Marshall, S.F., Laucks, M.L., Charlson, R.J., Waggoner, A.P., Ogren, J.A., Caldow, R., Holm, R.L., Quant, F.R., Sem, G.J., Wiedensohler, A., Ahlquist, N.A. and Bates, T.S., 1996. Performance characteristics of a high-sensitivity, three-wavelength, total scatter/backscatter nephelometer. *Journal of Atmospheric and Oceanic Technology* **13:** 967–986.

Barrie, L. and Puckett, K., 2005. *Report on the Review of the GAW Observatories Valentia and Mace Head, Ireland*. http://macehead.nuigalway.ie

Barrie, L.A., Yi, Y., Lohmann, U., Leaitch, W.R., Kasibhatla, P., Roelofs, G.-J., Wilson, J., McGovern, F.M., Benkovitz, C., Meliere, M.A., Law, K., Prospero, J., Kritz, M., Bergmann, D., Bridgemann, C., Chin, M., Christenen, J., Easter, R., Feichter, J., Jeuken, A., Kjellstrom, E., Koch, D., Land, C. and Rasch, P., 2001. A comparison of large scale atmospheric sulphate aerosol models (COSAM): overview and highlights. *Tellus* **53B:** 615–645.

Cavalli, F., Facchini, M.C., Decesari, S., Mircea, M., Emblico, L., Fuzzi, S., Ceburnis, D., Yoon, Y.J., O'Dowd, C. D., Putaud, J.P. and Dell'Acqua, A., 2004. Advances in characterization of size-resolved organic matter in marine aerosol over the North Atlantic. *Journal of Geophysical Research* **109:** D24215, doi:10.1029/2004JD005137.

Derwent, R.G., Ryall, D.B., Jennings, S.G., Spain, T.G. and Simmonds, P.G., 2001. Black carbon aerosol and carbon monoxide in European regionally polluted air masses at Mace Head, Ireland during 1995–1998. *Atmospheric Environment* **35:** 6371–6378.

Echalar, F., Artaxo, P., Martins, J.V., Yamasoe, M. and Gerab, F., 1998. Long-term monitoring of atmospheric aerosols in the Amazon Basin: Source identification and apportionment. *Journal of Geophysical Research* **103:** 31,849–31,864.

Forster, C., Wandinger, U., Wotawa, G., James, P., Mattis, I., Althausen, D., Simmonds, P., O'Doherty, S., Jennings, S.G., Kleefeld, C., Schneider, J., Trickl, T., Kreipl, S., Jager, H. and Stohl, A., 2001. Transport of boreal forest fire emissions from Canada to Europe. *Journal of Geophysical Research* **106:** 22,887–22,906.

Hansen, A.D.A., Rosen, H. and Novakov, T., 1984. The aethalometer, an instrument for the real time measurement of optical absorption by aerosol particles. *Science of the Total Environment* **36:** 191–196.

Jennings, S.G., Spain, T.G., Doddridge, B.G., Maring, H., Kelly, B.P. and Hansen, A.D.A., 1996. Concurrent measurements of black carbon aerosol and carbon monoxide at Mace Head. *Journal of Geophysical Research* **101:** 19,447–19,454.

Jennings, S. G., Kleefeld, C., O'Dowd, C. D., Junker, C., Spain, T.G., O'Brien, P., Roddy, A.F. and O'Connor, T.C., 2003. Mace Head atmospheric research station – characterization of aerosol radiative parameters. *Boreal Environmental Research* **8:** 303–314.

Junker, C., Sheahan, J.N., Jennings, S.G., O'Brien, P., Hinds, B.D., Martinez-Twary, E., Hansen, A.D.A., White, C., Garvey, D.M. and Pinnick, R.G., 2004. Measurement and analysis of aerosol and black carbon in the southwestern United States and Panama and their dependence on air mass origin. *Journal of Geophysical. Research* **109:** D13201,doi:10.1029/2003JD004066.

Junker, C., Jennings, S.G. and Cachier, H., 2006. Aerosol light absorption in the North Atlantic: trends and seasonal characteristics during the period 1989 to 2003. *Atmospheric Chemistry and Physics* **6:** 1913–1925.

Kaufman, Y.J, Smirnov, A., Holben, B.N. and Dubovik, O., 2001. Baseline maritime aerosol: methodology to derive the optical thickness and scattering properties. *Geophysical Research Letters* **28:** 3251–3254.

Keating, T. and Zuber, A., 2007. *The UNECE CLRTAP Interim Report on Hemispheric Transport of Air Pollution 2007*. Air Pollution Studies No. 16, United Nations, New York and Geneva, ISBN 978-92-1-116984-3.

Kim, Y.P, Lee, J.H., Kim, J.Y., Fung, K., Carmichael, G.R., Song, C.H., Kang, C.H., Kim, H-K., Lee, C.B., Moon, K.-C. and Shim, S.-G., 2000. Carbonaceous species in fine particles at the background sites in Korea between 1994 and 1999. *Atmospheric Environment* **34:** 5053–5060.

Kleefeld, S., Hoffer, A., Krivacsy and Jennings, S.G., 2002. Importance of organic and black carbon at Mace Head, on the west coast of Ireland (53 019'N, 9 054'W). *Atmospheric Environment* **36:** 4479–4490.

Prospero, J.M., 2001. The Atmosphere–Ocean Chemistry Experiment (AEROCE): Background and Major Accomplishments. *IGACtivities Newsletter* **24:** 3–5.

Quinn, P.K., Coffman, D.J., Bates, T.S., Miller, T.L., Johnson, J.E., Voss, K., Welton, E.J. and Neusüss, C., 2001. Dominant Aerosol Chemical Components and Their Contribution to Extinction During the Aerosols 99 Cruise Across the Atlantic. *Journal of Geophysical Research* **106**: 20,783–20,810.

Savoie, D., Arimoto, R., Keene, W.C., Prospero, J.M., Duce, R.A. and Galloway, J.N., 2002. Marine biogenic and anthropogenic contributions to non-sea-salt sulphate in the marine boundary layer over the North Atlantic Ocean. *Journal of Geophysical Research* **107**: 4356, doi:10.1029/2001JD000970.

Seinfeld, J.H. and Pandis, S.N., 1998. *Atmospheric Chemistry and Physics*, John Wiley & Sons, Inc., New York, USA, 1326 pp.

UNSTAT, 2002. The United Nations energy statistics database, Technical Report, Stat. Div., New York, USA.

Villevalde, Y.V., Smirnov, A., O'Neill, N.T., Smyshlyaev, S.P. and Yakovlev, V.V., 1994. Measurement of aerosol optical depth in the Pacific Ocean and the North Atlantic. *Journal of Geophysical Research* **99**: 20,983–20,988.

Yin, J., Allen, A.G., Harrison, R.M., Jennings, S.G., Wright, E., Fitzpatrick, M., Healy, T., Barry, E., Ceburnis, D. and McCusker, D., 2005. Major component composition of urban PM10 and PM2.5 in Ireland. *Atmospheric Research* **78:** 149–165.

Yoon, Y.J., Ceburnis, C., Cavalli, F., Putaud, J.P., Facchini, M.C., Decesari, S., Fuzzi, S., Jourdan, O., Jennings, S.G. and O'Dowd, C.D., 2007. Seasonal characteristics of the physico–chemical properties of North Atlantic marine atmospheric aerosols. *Journal of Geophysical Research* **112**, doi 10.1029/2005JD007044.

NDP
National Development Plan 2007 - 2013

Science, Technology, Research and Innovation for the Environment (STRIVE) 2007-2013

The Science, Technology, Research and Innovation for the Environment (STRIVE) programme covers the period 2007 to 2013.

The programme comprises three key measures: Sustainable Development, Cleaner Production and Environmental Technologies, and A Healthy Environment; together with two supporting measures: EPA Environmental Research Centre (ERC) and Capacity & Capability Building. The seven principal thematic areas for the programme are Climate Change; Waste, Resource Management and Chemicals; Water Quality and the Aquatic Environment; Air Quality, Atmospheric Deposition and Noise; Impacts on Biodiversity; Soils and Land-use; and Socio-economic Considerations. In addition, other emerging issues will be addressed as the need arises.

The funding for the programme (approximately €100 million) comes from the Environmental Research Sub-Programme of the National Development Plan (NDP), the Inter-Departmental Committee for the Strategy for Science, Technology and Innovation (IDC-SSTI); and EPA core funding and co-funding by economic sectors.

The EPA has a statutory role to co-ordinate environmental research in Ireland and is organising and administering the STRIVE programme on behalf of the Department of the Environment, Heritage and Local Government.

epa
Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

ENVIRONMENTAL PROTECTION AGENCY
PO Box 3000, Johnstown Castle Estate, Co. Wexford, Ireland
t 053 916 0600 f 053 916 0699
LoCall 1890 33 55 99
e info@epa.ie w http://www.epa.ie

SSTI

Comhshaol, Oidhreacht agus Rialtas Áitiúil
Environment, Heritage and Local Government