

STRIVE

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Advanced Aerosol Composition Measurements and Aerosol Radiative Properties

STRIVE

Environmental Protection
Agency Programme

2007-2013

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.

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EPA STRIVE Programme 2007–2013

Advanced Aerosol Composition Measurements and Aerosol Radiative Properties

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STRIVE Report

Prepared for the Environmental Protection Agency

by

National University of Ireland, Galway, Met Éireann and
University of Miami

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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 Professor S. Gerard Jennings (NUI Galway) assisted by Dr Darius Ceburnis (NUI Galway), Brendan M. Kelly (NUI Galway) and T. Gerard Spain (NUI Galway). Some of the earlier work was done in collaboration with members of the Rosenstiel School of Marine and Atmospheric Science, University of Miami, Florida, USA – Dr Dennis L. Savoie and his team. At a later stage of the project, chemical analysis of aerosol filter samples was continued through Met Éireann's analytical laboratory, led by Margaret Ryan. This arrangement was facilitated through the Head of the Instrumentation and Environmental Monitoring Division at Met Éireann, Liam Burke, and later by his successor, Eoin Moran. The project co-ordinator for the EPA was Dr Frank McGovern.

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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.

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Executive Summary

Aerosols affect the global radiation budget, directly through scattering of solar radiation and indirectly through the role of the aerosol component of cloud condensation nuclei in the activation of clouds, which leads to increased reflectivity (albedo) of solar radiation back to space and thus to increased cooling. Yet, despite the now recognised growing importance of atmospheric aerosols, there are insufficient data available on their microphysical, chemical and radiative properties in regions such as Western Europe and the North Atlantic. Marine aerosols provide a significant contribution to the global radiative budget, due to the 70% ocean surface coverage and the low albedo of the ocean surface. Ireland is located at the strategic region between the North Atlantic Ocean and the European continent, experiencing a vastly different atmospheric composition, which requires sustained monitoring.

This work describes physico-chemical and radiative measurements taken at the Mace Head Atmospheric Research Station during the period 2003–2006. The measurements are indicative of the medium- to long-term measurement programme at the site. These include mass concentration (mass per unit volume) of the total suspended particulates (TSP) of aerosol inorganic chemical species, the aerosol scattering coefficient, and the gradient measurements of aerosol chemical species. The relatively continuous nature of the measurement programme permitted both monthly and seasonal characteristics of aerosol parameters to be established.

Analytical method inter-comparison, which was required due to the change of the analytical laboratory from the University of Miami to Met Éireann, showed good agreement between the analytical methods, providing confidence and continuity in aerosol chemical data time series.

Chemical analysis of aerosol samples for the years 2003–2006 shows that the mass concentration of sea salt has a seasonal pattern, with minimum levels in the summer period of circa $9.0 \mu\text{g}/\text{m}^3$ and enhanced

values – by about a factor of 2 – in the winter period of the order of $14\text{--}16 \mu\text{g}/\text{m}^3$, due to the increase, with wind speed, in wintertime of super-micrometre coarse mode aerosol particles (diameter $>1.0 \mu\text{m}$) 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 remaining species is almost negligible.

Non-sea-salt sulphate (nssSO_4) TSP marine mass concentration shows lower values – by a factor of about 2 – during winter (with significant year-to-year variation) as compared with elevated values (mean levels up to $0.8 \mu\text{g}/\text{m}^3$) 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 (overall mean levels of circa $1.3 \mu\text{g}/\text{m}^3$) are a factor of about 3 higher than corresponding clean marine sectored levels.

Production mechanisms of aerosol chemical species, in terms of primary and secondary processes, were studied using vertical concentration gradient measurements at the coastal research station in Mace Head, Ireland. Total gravimetric PM1 mass, sea salt and water insoluble organic carbon (WIOC) concentration profiles showed a net production at the surface (i.e. primary production), while nssSO_4 and water soluble organic carbon (WSOC) concentration profiles showed a net removal at the surface. These observations indicate that WSOC was predominantly of secondary origin while WIOC was predominantly of primary origin.

The aerosol scattering coefficient was studied with respect to the shape of the particles. It was found that the size of the bins of the instruments to determine the number concentration of the particles in accordance with their diameter is critical in the comparison of measurements with modelling which can take into account particle shape.

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 with particle formation mechanisms, air quality and climatic effects. Continuous measurements are crucially valuable in order to determine seasonal patterns and longer-term trends.

Air quality is one of the major environmental issues facing Ireland due to the country's rapid development, particularly in the transport, energy and building/road construction sectors. Emissions from road traffic, such as nitrogen oxides, benzene and fine particulate matter have become the greatest potential threat to air quality, particularly in urban areas. At remote locations, only small spatial differences in chemical composition are found (although variations are found in total mass), showing the consistency of the regional background in the absence of strong local sources. These features are in contrast to the typical urban environment, where a multiplicity of sources lead to a heterogeneous aerosol population and chemical composition. Very limited available information shows that these pollutants will present a difficult challenge if the future EU limits are to be met. Receptor modelling techniques (Yin et al., 2005) have successfully discriminated major source categories, with unexplained materials accounting for about 7–28% of the particle mass. It has been shown that sea salt was a significant chemical component both in fine and coarse particles at all urban, coastal and rural sites in Ireland. It was shown that ammonium sulphate/ammonium nitrate and organic materials dominated fine particles.

This study reports the physico–chemical characteristics of North Atlantic aerosols, with a focus on clean marine aerosol. Aerosol physico–chemical characteristics and aerosol radiative parameters are measured for North Atlantic marine and modified marine air masses, and seasonal variations of these parameters are obtained. State-of-the art aerosol

measurement instrumentation is deployed at the Mace Head Atmospheric Research Station, which is in an ideal location for the observation of North Atlantic marine aerosol.

The composition of marine aerosol particles is closely related to the activities of marine biota, such as phytoplankton, whether they are formed through sulphur-induced gas-to-particle conversion or are injected directly into the marine boundary layer through the bubble-bursting process. These different particle formation processes affect the physical properties of marine aerosol, such as size and mass distributions and aerosol scattering (Yoon et al., 2007; Ceburnis et al., 2008; Krivacsy et al., 2008).

The project provided for aerosol chemical composition data and for aerosol radiative data. Research work was directed towards the measurement of aerosol chemical properties. Measurements of aerosol inorganic chemical species at Mace Head are presented for 2003–2006 for both sectorised and non-sectorised samples. In addition, aerosol radiative parameters measured at the Mace Head Atmospheric Research Station, near Carna, Co. Galway, have been reported. The project also provided measurements of concentration profiles of PM₁ mass, sea salt, non-sea-salt sulphate (nssSO₄), water insoluble organic carbon (WIOC) and water soluble organic carbon (WSOC). These profiles enabled an estimate for the first time of marine aerosol chemical fluxes.

The main results of the project can be summarised as follows:

- Aerosol chemical and physical properties were determined;
- Aerosol radiative parameters, i.e. aerosol scattering, absorption and optical depth, were measured;

Advanced aerosol composition measurements and aerosol radiative properties

- Gradient profiles and fluxes of aerosol mass and chemical components were also measured in clean marine air conditions;
- An aerosol database was created; and
- A national component of a future European aerosol observing system was enabled and sustained.

2 Analytical Method Inter-Comparison

The University of Miami, which had been doing inorganic sample analysis since 2001, was no longer able to carry on sample analysis from 2005 onward. An agreement was reached with Met Éireann, which committed to analyse samples using a similar methodology. An analytical method inter-comparison was organised in order to make analytical data compatible. The inter-comparison was made on 35 sectored and non-sectored samples, each from the 2004 sampling campaign. Non-sectored samples were obtained by sampling continuously, except when raining. Sectored samples were obtained when the wind direction was within the marine sector (190–300°) and there was no rain. The main difference between the laboratories in preparing samples for analysis was that the University of Miami used a quarter of the A4-size filter, while Met Éireann used only 1/24th. That may have implications for the results when uniformity of deposited matter is considered. It is worth noting that the samples represented total suspended particulates (TSP) and were not size controlled by using a PM10 inlet or a similar approach. Therefore, a few 'giant' particles deposited here and there on a large filter may have introduced an error when a relatively small portion of filter has been used for extraction. Another difference was that the University of Miami used a centrifuge to aid the extraction procedure, while Met Éireann just left filters for 24 h. This difference should have little if any impact on inorganic ions, which are highly soluble in water anyway. Both laboratories used

high-performance liquid chromatography (HPLC) as an analytical tool.

The results of the inter-comparison were split into sectored and non-sectored sample domains, as species concentrations in sectored samples tended to be generally lower. [Figures 2.1](#) and [2.2](#) present the results. Generally, the results agreed very well, except for a few outliers, which can be attributed to the non-uniformity of the material as outlined above. The outliers were mostly high-concentration samples, which would have a strong impact on regression parameters, but with a low statistical weight. It should be noted that there were few significant outliers of nssSO_4 due to its calculation methodology: nssSO_4 is calculated from total sulphate after subtracting sea-salt sulphate, which has a stable ratio of 1:4 with sodium. Therefore, analytical errors of total sulphate and sodium (both at high concentrations in the marine sector) can be superimposed in calculation, which is particularly problematic in the case of low concentrations of nssSO_4 . Therefore, the regression graph of nssSO_4 in sectored samples should be considered with caution. Overall, correlation or variance (presented in the figures as R^2 values) was highly statistically significant for all species in both sectored and non-sectored samples. The inter-comparison exercise led to the conclusion that the change of analytical laboratory did not have significant implications for reliability and continuity of the data.

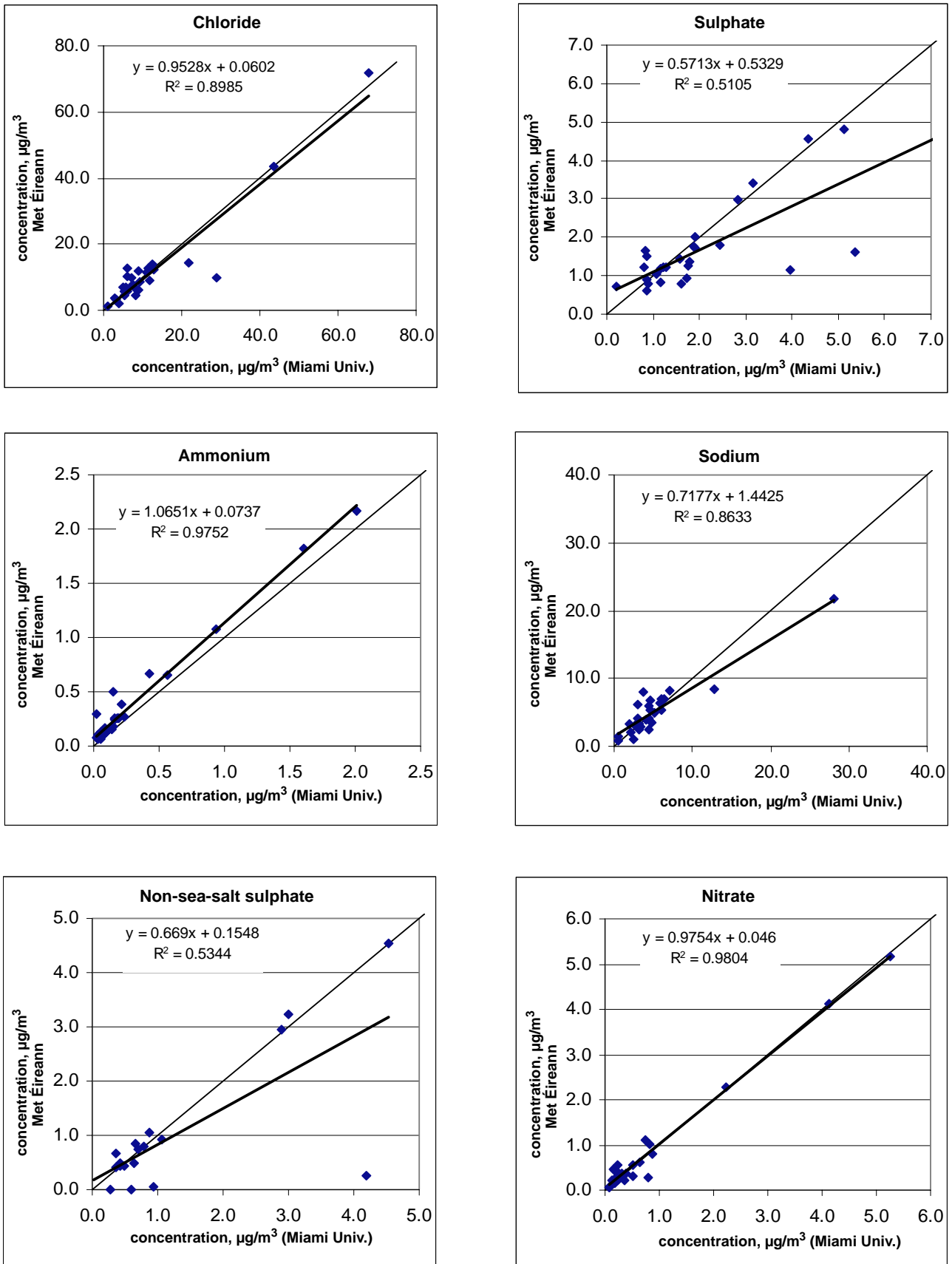


Figure 2.1. Analytical method inter-comparison of sectored samples between University of Miami and Met Éireann laboratories.

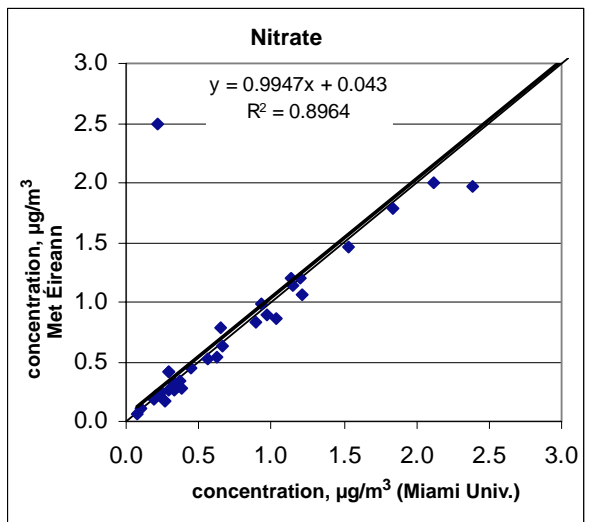
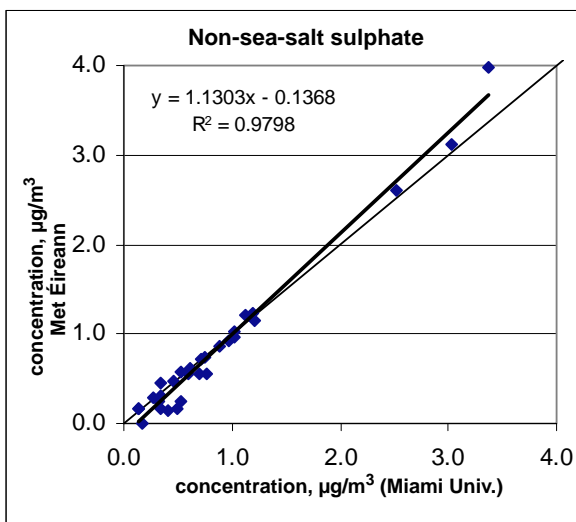
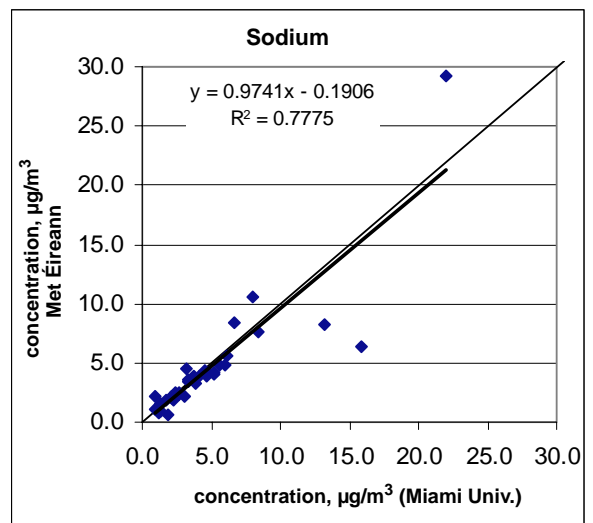
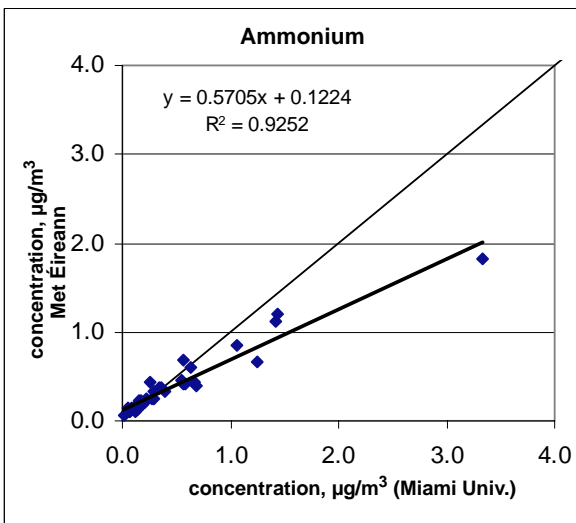
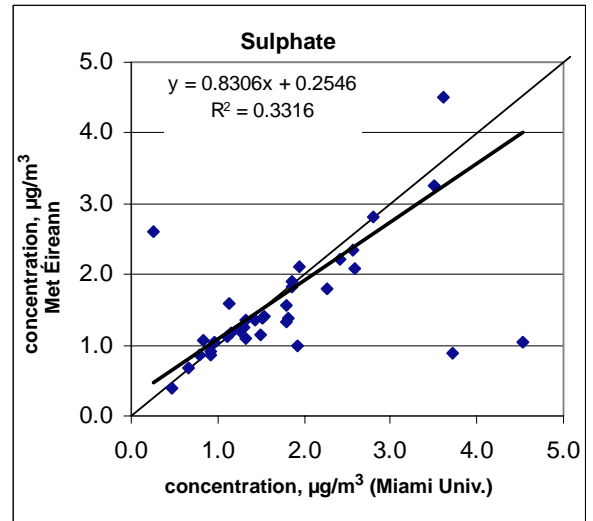
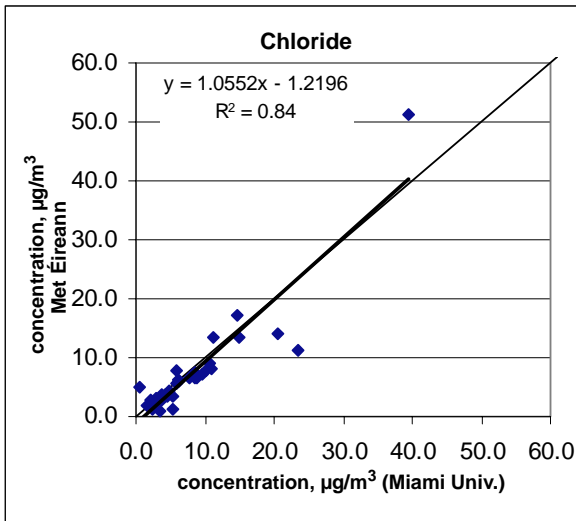


Figure 2.2. Analytical method inter-comparison of non-sectored samples between University of Miami and Met Éireann laboratories.

3 Aerosol Chemical Composition

During the time of the project (2004–2006), aerosol samples were collected on a 22-m tower which was constructed at the Mace Head site. Filter sampling on the 22-m tower used strict sampling sector control procedures. Two samples, one sectorised and one non-sectorised, were collected in parallel. Collaborative work with the University of Miami finished after analysis of the 2004 samples. A new agreement was reached with the Met Éireann to analyse the 2005 and 2006 samples. However, the 2005 sample record was poor due to a change in personnel at Mace Head. Only 67 samples were collected in 2005, which resulted in 34

samples after the validation procedure. Even fewer sectorised samples remained after the validation procedure (16 samples) due to insufficient sampling time, system malfunction and personnel shortage. In 2006, 130 non-sectorised samples were collected and all were validated as reliable.

Results from other experiments revealed that mass concentrations of selected ions for clean air are in reasonable agreement with clean marine samples measured by impactors at the site (e.g. Yoon et al., 2007). [Table 3.1](#) summarises the results from the

Table 3.1. Summary of aerosol chemical composition ($\mu\text{g}/\text{m}^3$) during 2003, 2004, 2005¹ and 2006.

	Chloride	Sodium	Sea-salt sulphate	Nitrate	Non-sea-salt sulphate	Ammonium
Non-sectorised samples						
Average 2003	6.198	3.438	0.865	1.970	1.464	0.951
October–April	8.352	4.656	1.172	3.328	1.962	1.635
May–September	4.550	2.506	0.631	0.931	1.084	0.428
Average 2004	7.890	4.391	1.077	0.943	0.939	0.467
October–April	9.151	4.957	1.215	1.100	0.892	0.533
May–September	5.723	3.323	0.825	0.675	0.988	0.349
Average 2005¹	7.121	3.871	0.842	1.491	1.305	0.789
Average 2006	5.624	3.223	0.806	1.457	1.149	0.610
October–April	7.932	4.473	1.118	1.761	1.406	0.797
May–September	5.308	3.041	0.760	1.056	0.906	0.436
Sectorised samples (clean marine)						
Average 2003	8.262	4.552	1.162	0.305	0.509	0.124
October–April	13.289	7.302	1.778	0.183	0.226	0.098
May–September	5.939	3.265	0.822	0.356	0.629	0.135
Average 2004	11.547	6.345	1.889	0.235	0.400	0.111
October–April	14.412	7.898	2.034	0.208	0.287	0.099
May–September	8.730	4.819	1.709	0.280	0.548	0.127
Average 2006	6.273	3.613	1.173	0.282	0.486	0.138
October–April	11.03	6.27	1.503	0.375	0.504	0.125
May–September	5.417	3.111	1.032	0.316	0.491	0.152

¹The 2005 data set is incomplete and so statistics are relatively poor.

2003, 2004, 2005 and 2006 samples, which consistently covered an entire year. It is evident that yearly averages are quite consistent from year to year, going up and down in concentration with no apparent trend.

Air masses at Mace Head differ dramatically in their origin, ranging from pristine North Atlantic air masses to relatively polluted easterly ones. Depending on how many samples are collected in each of those air masses, average mass concentrations of inorganic ions could be quite different from year to year. Regular sample coverage started in 2007, which will help to provide better statistics. Compared with other European Monitoring and Evaluation Programme (EMEP) stations in Europe, nssSO_4 , nitrate (NO_3), and ammonium (NH_4) concentrations at Mace Head are among the lowest. Certainly, long-range transported pollutants significantly contribute to air pollution levels in Ireland. Sectored sample concentrations at Mace Head are markedly lower: nssSO_4 two to three times

lower, NO_3 five to six times lower, NH_4 five to eight times lower than non-sectored samples. Only sea-salt concentrations are significantly higher in sectored samples due to the contribution from the marine sector.

The seasonal pattern of inorganic species was generally stable from year to year, but significantly different in sectored versus non-sectored samples. [Figures 3.1](#) and [3.2](#) show monthly variation in aerosol acidifying species concentrations in 2004 and 2006.

Non-sectored samples showed lower concentrations in summer, while sectored samples showed an opposite pattern, with higher concentrations during summer due to the contribution of natural sources (especially that of dimethylsulphide (DMS)). The sea-salt seasonal pattern was different with higher concentrations in winter in both sectored and non-sectored samples due to higher wind speeds during winter ([Fig. 3.3](#)).

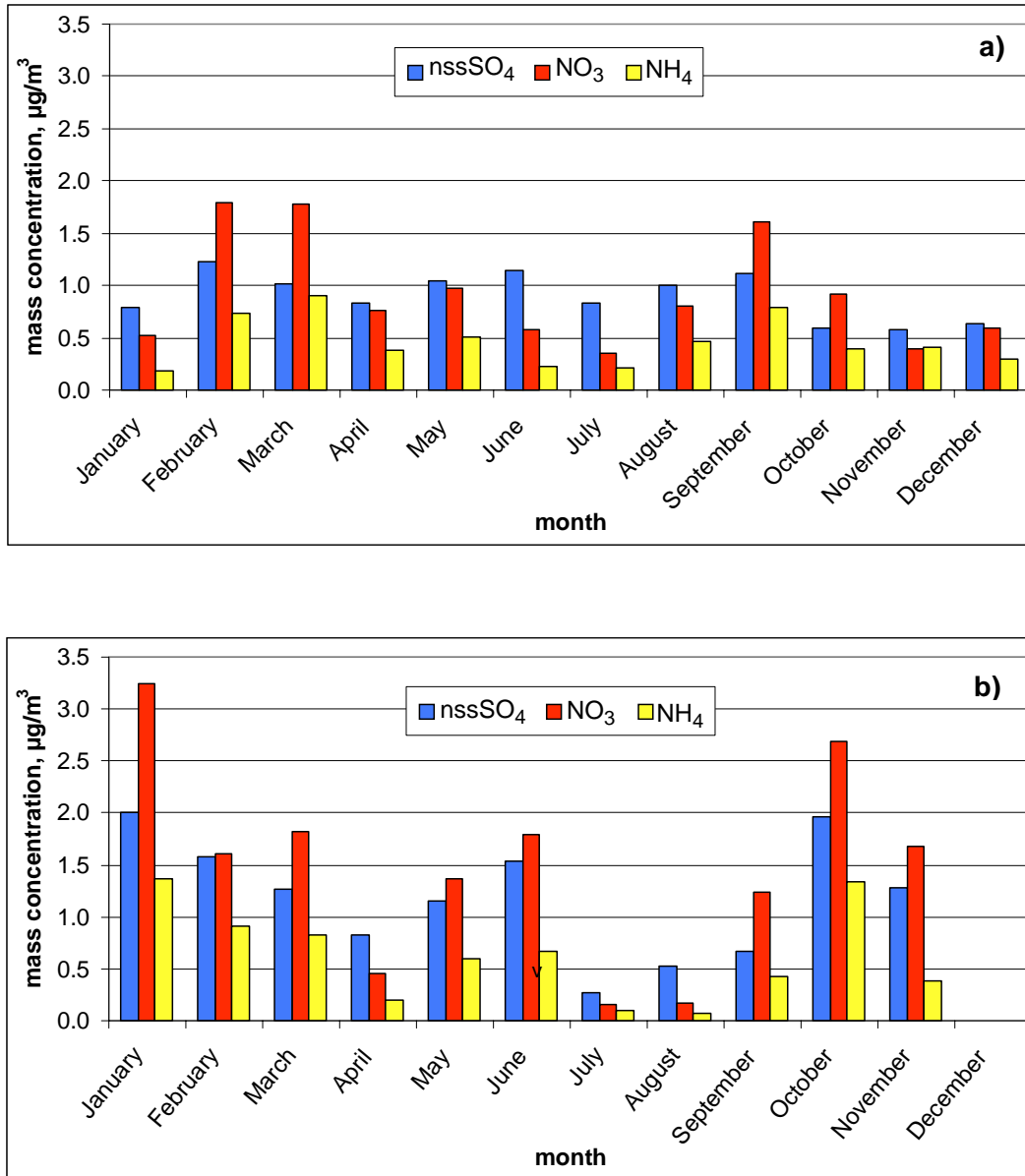


Figure 3.1. Monthly variation of mass concentration ($\mu\text{g}/\text{m}^3$) of aerosol acidifying species (nssSO₄, non-sea-salt sulphate; NO₃, nitrate; NH₄, ammonium) in non-sectored samples at Mace Head in 2004 (a) and 2006 (b).

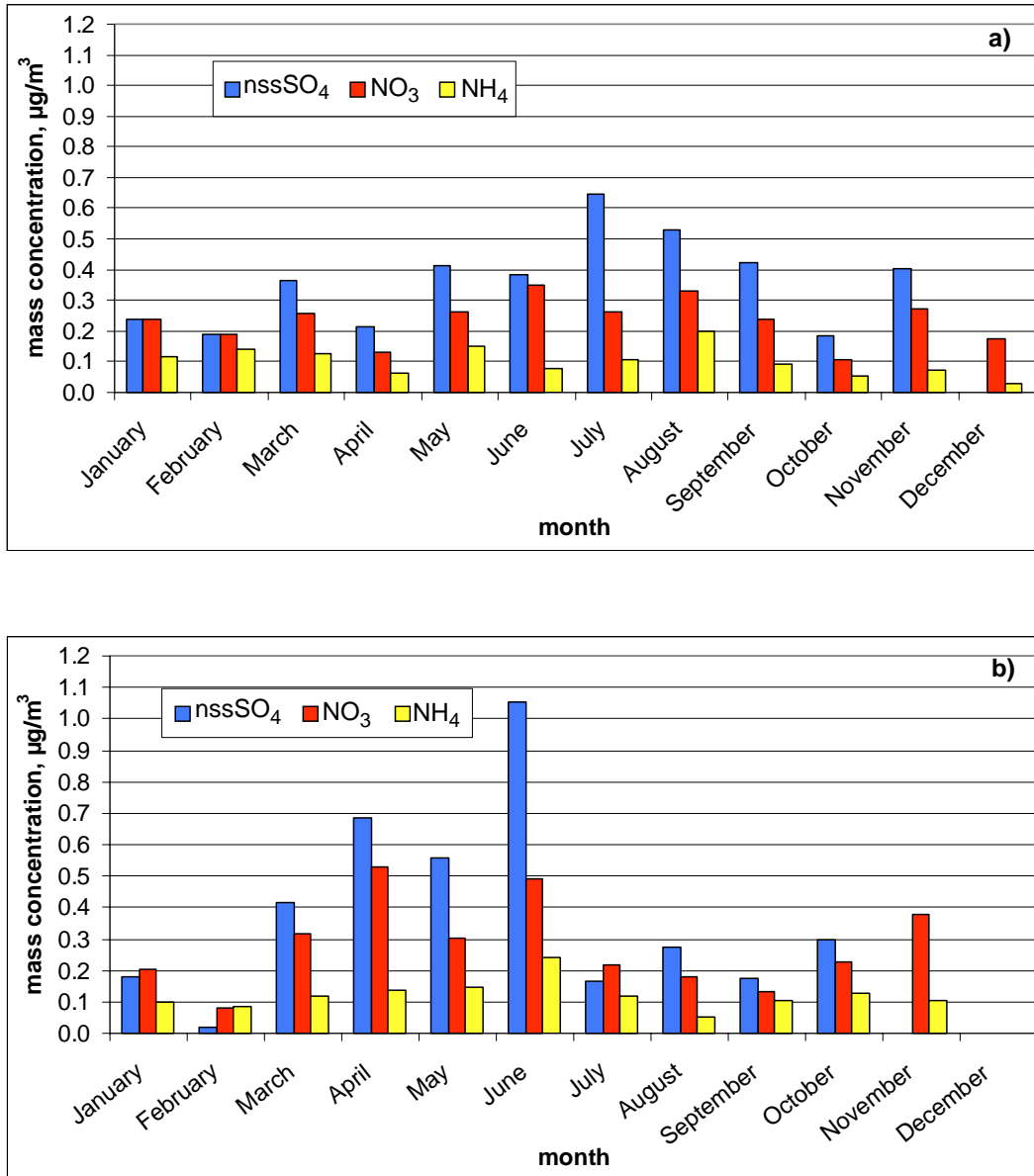


Figure 3.2. Monthly variation of mass concentration ($\mu\text{g}/\text{m}^3$) of aerosol acidifying species (nssSO₄, non-sea-salt sulphate; NO₃, nitrate; NH₄, ammonium) in sectored samples at Mace Head in 2004 (a) and 2006 (b).

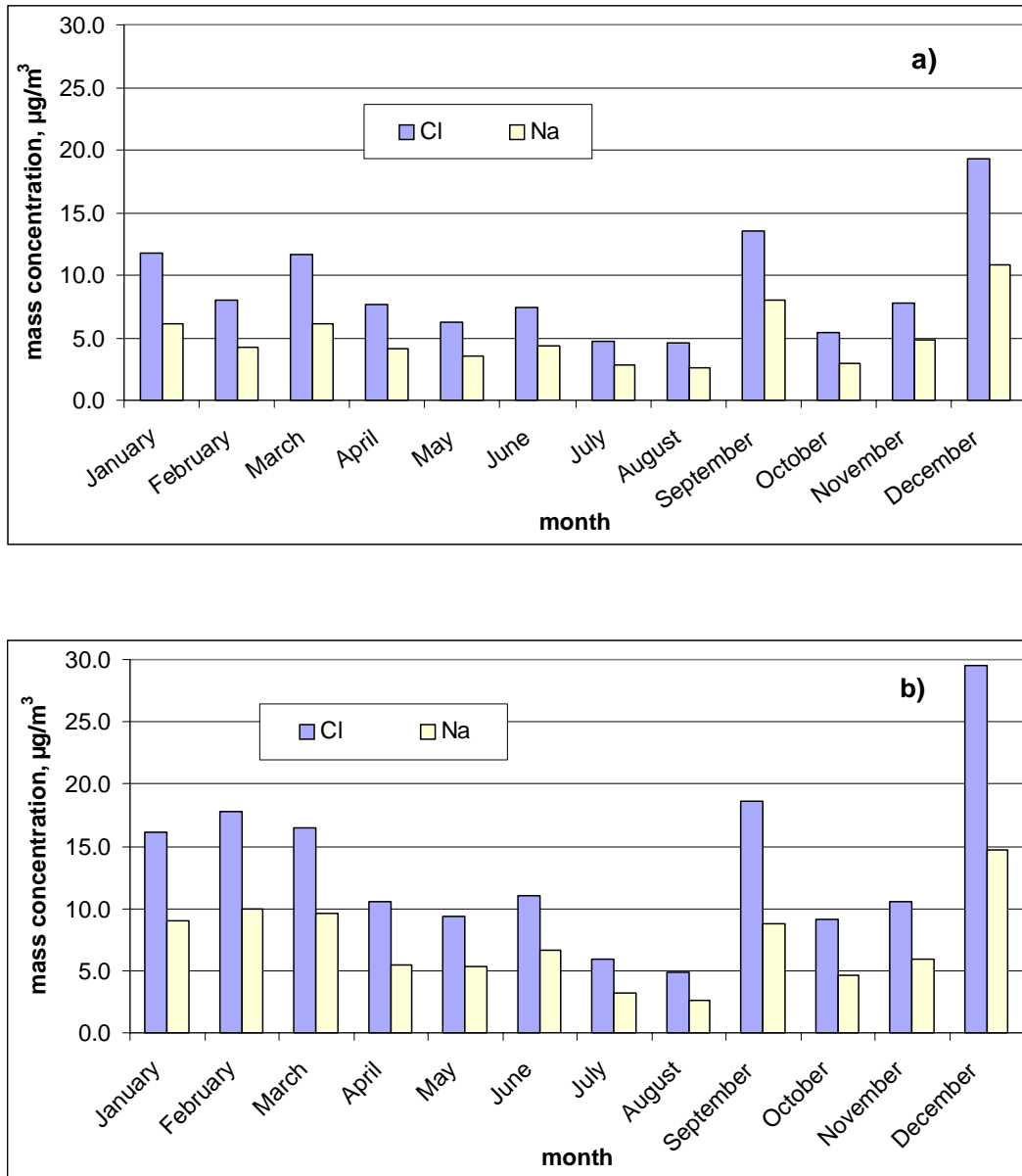


Figure 3.3. Monthly variation of mass concentration ($\mu\text{g}/\text{m}^3$) of sea salt (Cl, chloride; Na, sodium) at Mace Head in non-sectored samples (a) and sectored samples (b) in 2004.

4 Gradient Fluxes

Previous flux measurements in North Atlantic marine air using an eddy covariance (EC) technique (Geever et al., 2005) have found a strong dependency of primary sea-spray flux on the wind speed (flux $>10^6$ m^2/s at wind speeds of >10 m/s) and that approximately 50% of the number flux was attributed to the Aitken mode (10–100 nm) and 50% to the accumulation mode (100–500 nm). These measurements represented the first pseudo-size-segregated aerosol flux measurements in a marine environment, indicating a significant contribution of primary marine particles to the sub-micron Aitken and accumulation modes. However, the EC technique, including its modifications (relaxed eddy accumulation or disjunct eddy covariance) with near real-time measurement techniques, does not produce unambiguous results for aerosol chemical fluxes.

Given that off-line chemical analysis requires relatively long sampling times (of several days) to obtain sufficient particulate matter in clean marine air, alternative approaches to micro-meteorological flux techniques are required. This study adapted an experimental set-up used by Valiulis et al. (2002) to determine near-surface chemical gradients and resultant fluxes of north-east Atlantic marine air.

Vertical concentration profiles of sub-micron aerosol chemistry were taken in clean marine air at the Mace Head north-east Atlantic research station. The sampling was conducted on a 22-m tower approximately 80 m from the shoreline at 3-, 10- and 30-m heights (the highest sampling point was installed on an extended pole) relative to the ground which was approximately 5 m above mean sea level (MSL). The tower was located upwind of the station buildings relative to the ocean. The tower location relative to the sampling sector ensured minimal, if any, contamination from building-induced turbulence (de Leeuw et al., 2002).

PM1 size selective inlets (PMX inlet, Sven Leckel Ingenieurburo GmbH, Germany) were used to collect aerosols on quartz filters. An automated clean sector

sampling system ensured sampling only of air (1) reaching the site from a controlled sector between 190° and 300° , and (2) with a total particle number concentration ($d_{50\%} = 14$ nm) below 700 cm^3 . The system monitored both parameters at a time and activated sampling when both conditions were met. The sampling criteria ensured that air mass was of clean marine origin. Post-analysis also confirmed air mass cleanliness with black carbon concentrations of less than 50 ng/m^3 and a transit time of backward trajectories of 4–5 days over the ocean. Eighteen 7-day samples were obtained, with the actual accumulated sampling times ranging from 20 to 98 h (10–58% of the time), depending on the above conditions. Quality control resulted in 50% of the sample sets being discarded due to too short sampling times, and nine profile sets were retained for this analysis.

Samples were collected from April to October 2005, which covered the period of high biological activity over the north-east Atlantic. Samples were analysed for gravimetric mass, sodium, sulphate, WSOC and WIOC.

In order to deal with the wide range of concentrations encountered in each profile, concentrations were normalised to the sum of the total gradient concentration of individual chemical species mass. Such normalisation gives equal weight to each individual profile. After normalisation, the profiles of each mass category were averaged, resulting in statistically meaningful variances around the mean value. [Figure 4.1a](#) shows the averaged normalised concentration profiles of different species for the whole sampling period. Differences between concentrations at all three heights were generally statistically significant. PM1 mass, sea salt and WIOC exhibited a decreasing concentration profile with height, while nssSO_4 and WSOC showed the opposite pattern. The decreasing profile represents an upward mass flux and, therefore, respective chemical species are produced at the sea surface, while species exhibiting an increasing vertical profile (with height) point to a

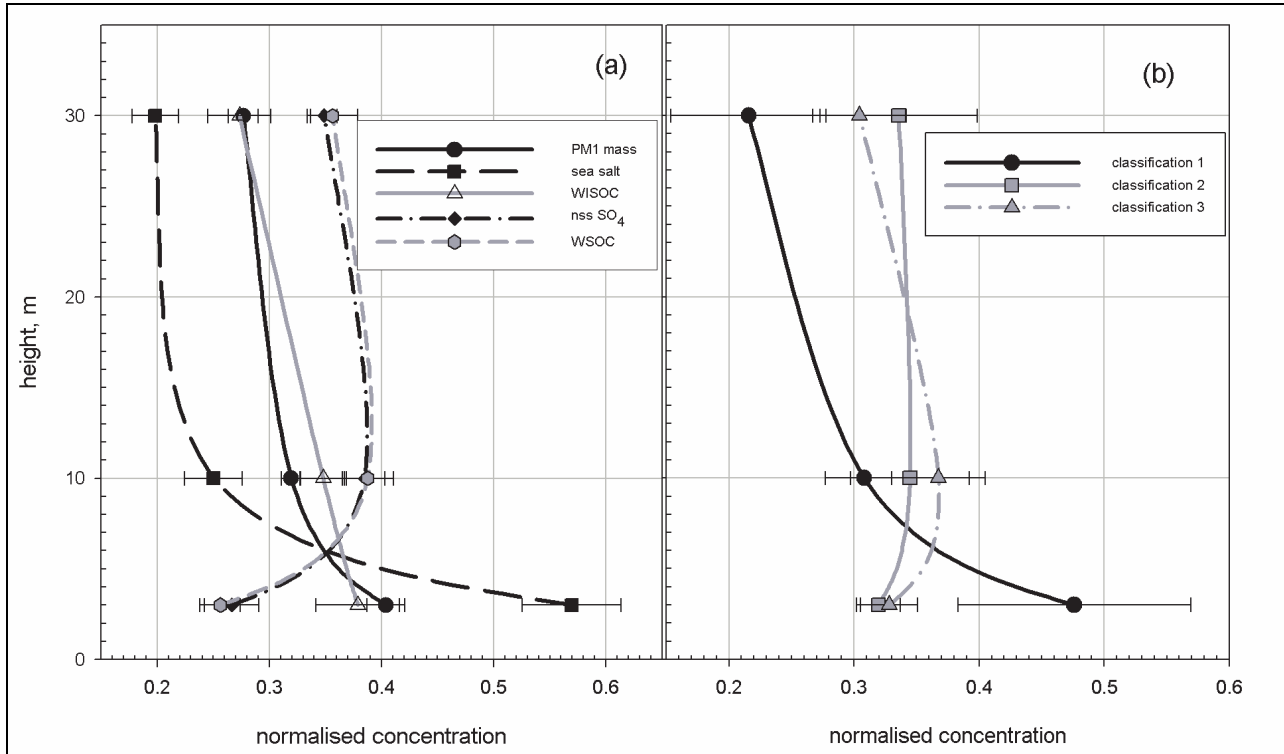


Figure 4.1 (a) Normalised vertical concentration profiles of PM1 mass, sea salt, nssSO₄ water soluble organic carbon (WSOC) and water insoluble organic carbon (WIOC) at Mace Head (WIOC = WISOC in the figure). (b) Normalised vertical concentration profiles of WIOC depicting three different classification types (1–3). Each profile is an average of two to four individual profiles representing the same gradient classification type. Error bars represent standard deviation of the normalised concentration average.

source either produced homogeneously in the boundary layer or from aloft (for example, cloud processing or entrainment from the free troposphere). Thus, it can be concluded that sea salt and WIOC are produced at the ocean surface via a primary or bubble-mediated production mechanism while nssSO₄ and WSOC must be produced via secondary (or gas-to-particle) aerosol formation processes. It should be noted that the removal of certain species at the surface is caused by dry deposition only, as wet scavenging below the cloud evenly removes aerosol particles.

While it is well known that sea salt is a primary aerosol and nssSO₄ is a secondary one, the distinct new finding in this study is that WSOC and WIOC species exhibited contrasting profiles and thus different formation mechanisms. The WSOC showed consistently increasing concentration profiles, while the individual WIOC profiles showed variable gradients that warrant further exploration. In fact, the WIOC

gradients were found to fit into three distinct classifications as shown in [Fig. 4.1b](#). The first classification exhibited a clear and strong negative gradient, corresponding to a significant primary surface source (net production) within the flux footprint; the second exhibits net removal through a positive gradient between 3 and 10 m and an almost zero gradient between 10 and 30 m; and the third classification exhibits a deposition flux gradient (positive) between 3 and 10 m and a source flux gradient (negative) between 10 and 30 m. Given that enrichment of the organic component in primary aerosol is related to enrichment of organic matter at the ocean surface, this range of behaviour can be interpreted in terms of the location of a biologically active region relative to the flux footprint. If this region is within the flux footprint (5 km from the coastline), a strong negative gradient as in Classification 1 will result. However, if the oceanic organic matter or primary organic aerosol production region is

significantly and exclusively upwind of the flux footprint (say ~20 km), the aerosol will have become well mixed throughout the boundary layer, and a clear deposition (positive) gradient will be observed as in Classification 2. Classification 3 can result from a combination of both scenarios. The classifications above are consistent with satellite analysis of the spatial and temporal development of chlorophyll-*a* distributions (Yoon et al., 2007).

These results are the first experimental evidence of different production mechanisms of the WSOC and WIOC in marine aerosol, indicating that WSOC is predominantly of secondary origin, while WIOC is predominantly of primary origin (Ceburnis et al., 2008).

The averaged profiles presented in [Fig. 4.1a](#) effectively show the mean concentration gradient and, hence, the direction of the flux over a period of a few months. While the direction of the flux was the main motivation for the study, an attempt was made to calculate the mass flux from individual gradients over each of the sampling periods using detailed meteorological measurements performed in 2005 in similar marine conditions.

First-order closure turbulent flux parameterisation, often known as a *gradient transport theory* or *K-theory*, can be expressed as follows:

$$F = -K_z \left. \frac{dc}{dz} \right|_z \quad \text{Eqn 1}$$

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

Therefore, knowing K_z and the measured concentration gradient, it is possible to calculate the mass flux of any chemical species. The approach, however, does not allow distinguishing between upward and downward fluxes, but rather enables estimation of the net fluxes. The uncertainty of the estimated flux would largely depend on the gradient function being fitted to the measured profile and the variability of the turbulent-transfer coefficient at any given wind speed.

The turbulent-transfer coefficient was derived from its relationship with the horizontal wind speed using the 2005 data set obtained under similar marine conditions and the same ensemble range. The relationship

followed a power law ($K_z = 0.00117U^{2.067}$, $r^2 = 0.62$, $P \ll 0.01$). The turbulent-transfer coefficient representing each individual sampling period of this study was derived from 30-min averages of the horizontal wind speed measured during that period. Then the K_z values were averaged to obtain the resultant turbulent-transfer coefficient corresponding to each sampling period of this study. The authors admit that such an approach introduced a certain degree of variability, but the long sampling time required for off-line chemical analysis necessitated averaging of environmental conditions. They believe that the magnitude of the flux error would largely depend on the variability of K_z value at any given wind speed.

It was mentioned above that the uncertainty of the calculated flux will depend on the gradient fitting procedure. The concentration profiles in [Fig. 4.1a](#) suggest a power function. However, due to the potential contribution of surf-zone emissions to the magnitude of the concentration at the 3-m level and, hence, to the shape of the gradient, a linear gradient profile was considered too, ignoring the lowest 3-m level concentration. Three different fitting exercises are presented in [Fig. 4.2a](#), using linear and two different power functions: $f = a + bx$, $f = a + bx^c$ and $f = ax^b$. PM1 mass concentration profiles were fitted with three different functions seeking the best correlation with the measurements and the fluxes calculated at the 22-m level using [Eqn 1](#). The linear gradient approach yielded a constant gradient. The gradient fitting procedure can be considered as a sensitivity analysis of the calculated flux. Then the calculated flux data were fitted with the power function to reveal the flux relationship to the wind speed and this is presented in [Fig. 4.2b](#). The impact of the fitting procedure is small up to wind speed values of about 9 m/s; however, the curves start to diverge at higher wind speeds. The area between the dashed curves can be considered as the uncertainty range of the calculated flux. Calculated fluxes of WIOM for cases with clear primary production ranged from 0.16 to 1.02 ng/m²/s at wind speeds of 8.4 and 7.9 m/s, respectively. Note that at similar wind speeds WIOM fluxes can differ by a factor of 6, which indicates the importance of seasonal biological activity in the flux footprint area. Further details are given by Ceburnis et al. (2008).

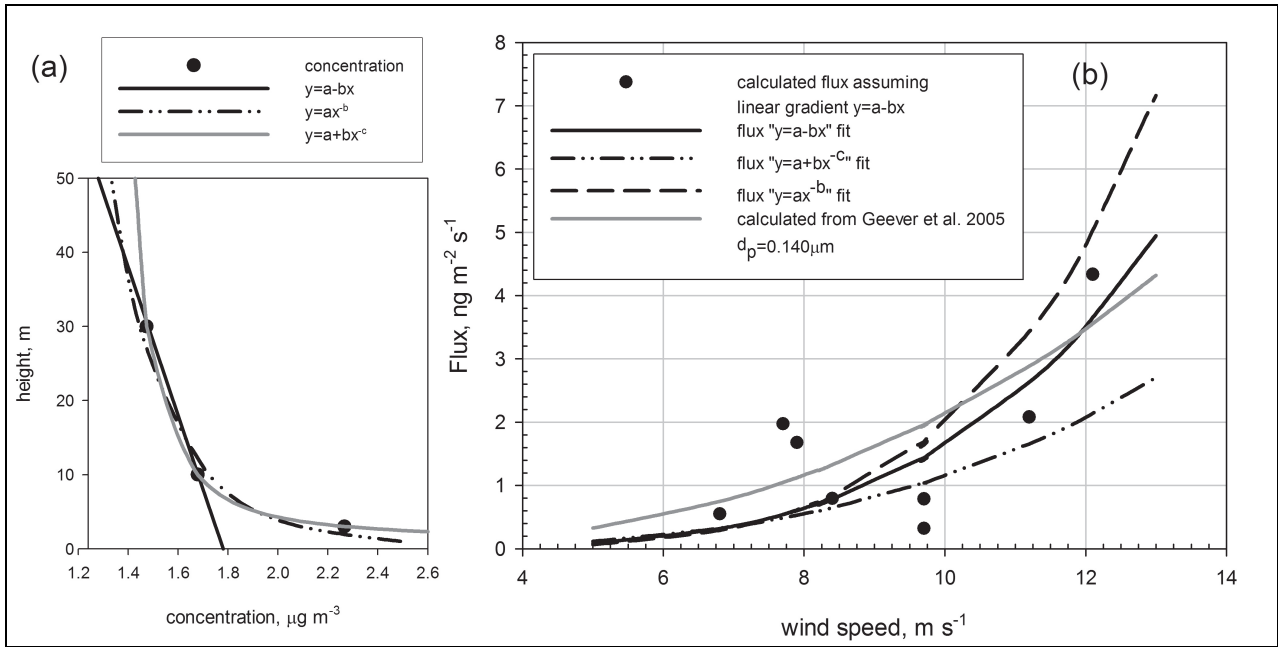


Figure 4.2 (a) Concentration gradient fitting procedure using linear and power functions. (b) PM1 flux relationship with the wind speed at the 22-m level. The calculated fluxes were obtained from Geever et al. (2005) using an accumulation mode diameter of $0.140\ \mu\text{m}$ and a particle density of $1.56\ \text{g/cm}^3$.

5 Aerosol Radiative Parameters

Aerosol radiative parameters (aerosol scattering coefficient, aerosol absorption coefficient and aerosol optical depth) are being reliably measured, with quality control procedures (in accordance with the Global Atmosphere Watch (GAW) protocols of the World Meteorological Organization (WMO)) strictly in place. Seasonal variations in aerosol radiative parameters along with microphysical aerosol parameters are being established. The seasonal variation with higher levels in the winter to early-spring periods is due to the higher contribution of sea salt in the marine boundary layer during the North Atlantic winter. By contrast, aerosols during late spring and summer exhibit larger Ångström parameters than winter, indicating a larger contribution of the biogenically driven fine or accumulation modes. Further details are given by Yoon et al. (2007).

High-resolution black carbon measurements are being taken using a new instrument, a multi-angle absorption photometer, alongside the existing aethalometer (AE-16) in order to carry out parallel and inter-comparison measurements of aerosol absorption coefficients.

Sea-salt aerosol particles in the maritime environment are usually modelled with a spherical shape due to their hygroscopic nature. However, in dry conditions, as encountered during aerosol sampling, sea-salt aerosols can exhibit a cubic shape or can be found as agglomerates of cubic particles.

Models using non-spherical particles are usually applied only to dust-like aerosols while only a few studies have investigated non-spherical sea-salt aerosols (e.g. Murayama et al., 1999). Moreover, ellipsoidal-shaped particles are usually considered for these non-spherical particles and T-matrix calculations are applied. Ground-based measurements of the

scattering and backscattering coefficients together with size distribution measurements give insights into the physical and optical properties of marine aerosols. The experimental set-up of all the measurements is indoors, allowing consideration of drier particles inside the nephelometer whose relative humidity rarely exceeds 50% due to internal heating of the instrument. This occurrence offers a possibility of studying optical properties of dried sea-salt aerosols through the work of Chamaillard et al. (2006).

Measurements of the aerosol scattering σ_{sp} and backscattering σ_{bsp} coefficients, using a nephelometer, were compared with Mie calculations (Bohren and Huffman, 1983) and discrete dipole approximation (DDA) (Draine, 1988) cubic calculations estimated for a size distribution of particles obtained from the electrical low pressure impactor (ELPI, Dekati Ltd) and for a particle diameter not greater than 2 μm . The calculations were performed at a wavelength of 0.55 μm and for the marine sector wind direction. The Mie model and DDA cubic calculations both overestimated the measured σ_{sp} and σ_{bsp} results by more than a factor of 2. Differences between the two models were more pronounced for σ_{bsp} , by as much as 40% for the cubic calculations compared with the spherical calculations. The differences in the scattering coefficient between the cubic model and the spherical model did not exceed 10% on average. The best fit of modelling to measured σ_{sp} and σ_{bsp} was obtained by decreasing the upper value D_{max} of the ELPI. [Figure 5.1](#) represents the result of the best fit to the measurements obtained with an upper diameter $D_{max} = 0.8 \mu\text{m}$ irrespective of the model used. Unfortunately, there was no possible distinction of particle shape with diameter less than 0.8 μm , using the two models.

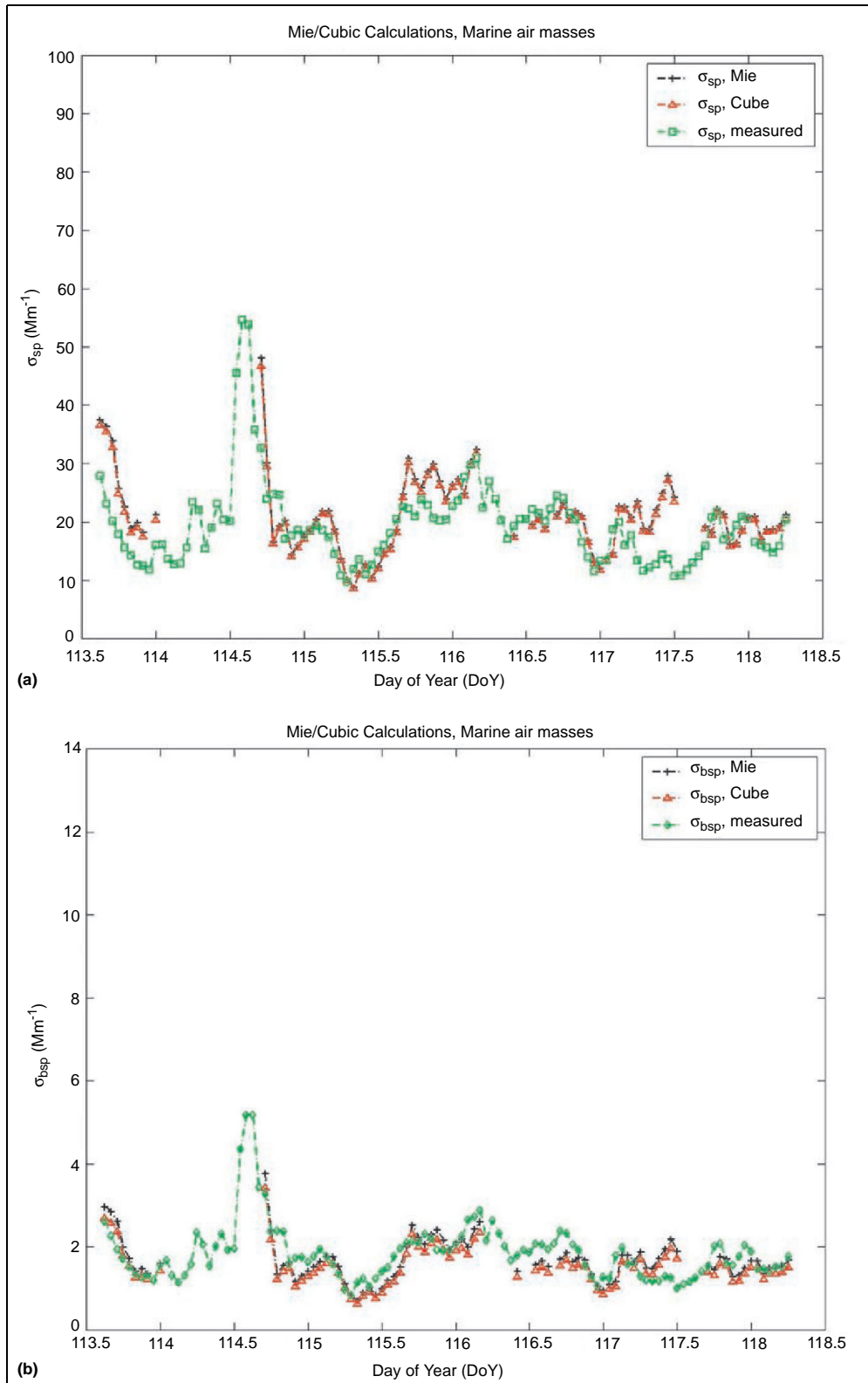


Figure 5.1. (a) Scattering coefficient at $\lambda = 0.55 \mu m$ measured by the nephelometer (square symbol), calculated for a cubic shape of particles (triangle symbol) and for a spherical shape of particles (plus sign) based on a size distribution of particles of diameters varying from 0.04 to 0.8 μm as measured by the ELPI instrument, and (b) the same as (a) for the backscattering coefficient. Backscattering nephelometer measurements are represented by diamond symbols.

6 Aerosol Database

The aerosol data measured at Mace Head are converted to the National Aeronautics and Space Administration (NASA) AMES 1000 format, used by the EMEP. Mean hourly data of the following aerosol parameters, using the NASA AMES 1000 format, are sent to the European Aerosol Database hosted by the Norwegian Institute for Air Research (NILU) (<http://www.nilu.no/projects/ccc/create>):

- Total condensation particle number concentration;
- Aerosol scattering coefficient;
- PM_{2.5} mass (TEOM, tapered element oscillating

microbalance); and

- Aerosol size distribution (SMPS, scanning mobility particle spectrometer).

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

7 Summary and Conclusions

An analytical method inter-comparison, which was required due to the change in analytical laboratory, showed good agreement between the analytical methods, thus providing confidence and continuity in aerosol chemical data time series. The time series of major inorganic aerosol chemical species during 2003–2006 were consistent with previous measurements, thus providing a reliable continuing database for model validation studies to be performed in the future (e.g. O'Dowd et al., 2008).

Production mechanisms and gradient fluxes of aerosol mass and inorganic and organic components in marine air over the north-east Atlantic were studied using vertical concentration profiles measured at Mace Head. Total gravimetric mass, sea salt and WIOC exhibited a net upward flux, pointing to a primary source at the sea surface. Non-sea-salt sulphate and WSOC showed an opposite profile, indicating a net downward flux, pointing to the removal of the species, which also indicates that they are produced via secondary processes. The difference in WSOC and

WIOC concentration gradients in clean marine air masses is the first experimental evidence of the different formation mechanisms of these species, namely, secondary and primary, respectively. Calculated fluxes depend significantly on the gradient fitting procedure, but consistently demonstrated a power law relationship with the wind speed. The estimated gradient fluxes are the first experimental estimates of the primary production rates for WIOC in the marine atmosphere. The total sub-micron aerosol mass flux relationship as a function of wind speed, described by a power law ($\text{flux PM}_{10} = 0.000096 U^{4.23}$), agreed well with previous EC measurements performed under similar conditions.

Comparisons of the cubic and spherical particle scattering models show an increased effect of the cubic particles of diameter larger than 1 μm to these coefficients. An increase of 70% in the backscattering coefficient and of 10% for the scattering coefficient was found for cubic particles compared with spherical particles of diameter less than 2 μm .

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Acronyms

CCN	Cloud condensation nuclei
DDA	Discrete dipole approximation
DMS	Dimethylsulphide
EC	Eddy covariance
ELPI	Electrical low pressure impactor
EMEP	European Monitoring and Evaluation Programme
GAW	Global Atmosphere Watch
HPLC	High-performance liquid chromatography
MSL	Mean sea level
NASA	National Aeronautics and Space Administration
NH₄	Ammonium
NILU	Norwegian Institute for Air Research
NO₃	Nitrate
nssSO₄	Non-sea-salt sulphate
SMPS	Scanning mobility particle spectrometer
TEOM	Tapered element oscillating microbalance
TSP	Total suspended particulate
WDCA	World Data Centre for Aerosols
WIOC	Water insoluble organic carbon
WMO	World Meteorological Organization
WSOC	Water soluble organic carbon

An Gníomhaireacht 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 déanaímid 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 Gníomhaireacht 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 peitreal.
- Scardadh dramhuisce

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 chomhordú 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 gníomhaíochtaí.

MONATÓIREACHT, ANAILÍS AGUS TUAIRISCIÚ AR AN GCOMHSHAOL

- Monatóireacht ar chaighdeán aeir agus caighdeán aibhneacha, locha, uiscí taoide agus uiscí talaimh; leibhéil agus sruth aibhneacha a thomhas.
- Tuairiscíú neamhspleách chun cabhrú le rialtais náisiúnta agus áitiúla cinntiú 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 caighdeán 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 Gníomhaireacht i 1993 chun comhshaol na hÉireann a chosaint. Tá an eagraíocht á bhainistiú ag Bord lánaimseartha, ar a bhfuil Príomhstíúrthóir agus ceithre Stíúrthóir.

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.

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.