

ACSOE

Atmospheric Chemistry Studies in the Oceanic Environment

Achievements and Scientific Highlights

Report of the ACSOE Panel on the Occasion of its 25th Anniversary

Atmospheric Chemistry Studies in the Oceanic Environment

Achievements and Scientific Highlights

Final report of the Natural Environment Research Council (NERC) Thematic Programme ACSOE, summarising the major activities and findings of the Programme over the period 1995 to 2000.

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A full list of ACSOE participants is available via the ACSOE web pages

It is now undisputed that human influences are causing the chemical composition of the Earth's atmosphere to change on a global scale. These changes may have a significant impact on the atmosphere in several ways, including climatic change due to the "greenhouse effect", depletion of stratospheric ozone, and enhanced concentrations of acidic compounds, ozone, and other harmful substances in the lower atmosphere (the "troposphere"). It has also become increasingly apparent over the last two decades that natural processes and biogeochemical cycles, notably those linking the atmosphere and ocean, are extremely important in the regulation of atmospheric chemistry and composition. The key to predicting the impact of human activity is first to understand how the natural system works, and then how it is perturbed by human activities. This is the theme underlying the International Geosphere-Biosphere Programme (IGBP) and its investigation into the chemistry of the atmosphere (the International Global Atmospheric Chemistry project, IGAC).

The NERC Atmospheric Chemistry Studies in the Oceanic Environment (ACSOE) Thematic Programme, with a budget of £3.9M, was instigated as a major UK contribution to this international scientific effort between 1995 and 2000. The overarching aim of ACSOE was to investigate the processes that control the production and fate of trace gases and particles (condensation nuclei and aerosols) in the atmosphere over the oceans. For convenience it was divided into three separate but linked activities; one studying air-sea exchange especially of atmospherically-important gases produced by marine microorganisms, one a study of the tropospheric ozone budget and underlying chemistry, and a third the development of aerosols and clouds in European air spreading out into the Atlantic Ocean. It was able to make use of world-class facilities based in the UK such as the NERC fleet of research vessels, the Meteorological Office C-130 aircraft, as well as comprehensively instrumented ground stations in Ireland, Tenerife, and the Alps.

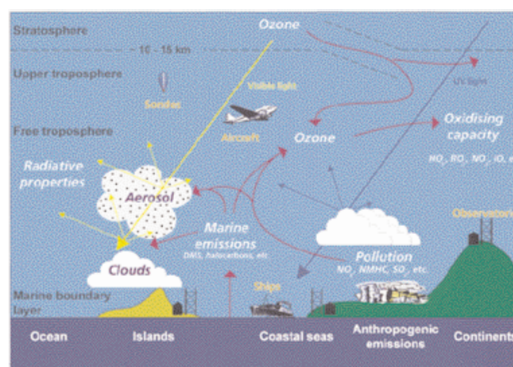
Over 100 ACSOE scientists have enjoyed much success, finding new chemical species and observing new processes, studying natural phenomena in the ocean and the atmosphere, and detecting the presence of pollutants thousands of miles from their sources. The science of atmospheric chemistry has definitely moved on as a result of all this effort. An extensive and publicly accessible database has been assembled and placed on-line via the World Wide Web, whilst numerous publications have been printed in leading science journals. The results have begun to enter international scientific assessments, and so lead on to policy development. They have also acted as springboards for other national and international research programmes. Another result of ACSOE is the cadre of young and enthusiastic scientists who are now entering careers that will surely move the science still further. ACSOE was directly responsible for creating a lively UK research community equipped with new instruments and innovative systems for studying the complexities of chemistry in the highly non-uniform fluid that is the troposphere. These will be of great benefit in the future when applied along with the new facilities now becoming available within the UK atmospheric research community.

Stuart A Penkett ACSOE Project Leader



Location of the major ACSOE field campaigns. Aircraft campaigns are in red lettering, ship cruises in blue, and ground stations in orange.

Schematic representation of the scientific arena studied by ACSOE. The mixture of pollutant gases from the continents, and natural emissions from the ocean, undergo chemical transformations in the troposphere. This leads to important potential changes to incoming solar radiation and outgoing terrestrial radiation - and hence climate - through the modification of cloud properties, haze particles (aerosol), greenhouse gases such as ozone, and chemical oxidising capacity.



Aims and Achievements of ACSOE

Objectives

Determine the ozone budget of the background lower atmosphere (i.e. the troposphere)

Study the sunlight-initiated chemistry of gases and particles (aerosol) in the background atmosphere

Determine the importance of nighttime chemistry

Seek evidence for extensive halogen atom chemistry

Measure air-sea gas transfer rates



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Assess the role of coastal and open ocean waters as sources of reactive gases

Observe the effects of atmospheric deposition on oceanic biogeochemistry

Investigate how clouds are affected by the chemistry of the inflowing air

Identify within-cloud processes affecting particle size and chemistry

Objectives

Outcomes

- transport of pollution over hundreds or thousands of kilometres identified
- natural chemical state of the lower atmosphere can easily be 'flipped' from ozone loss to ozone production by the presence of nitrogen oxides from long-range transported pollution
- measurements of elusive but highly reactive molecules such as hydroxyl and peroxy radicals
- modelling of the oxidation of man-made hydrocarbon gases and natural biological gases such as dimethyl sulphide (DMS) and isoprene, and their influence on ozone and particles
- discovery of a coastal 'particle burst' phenomenon linked to the state of the tide
- first vertical profile measurements of nitrate radicals (NO_3) in the lower atmosphere
- NO_3 radicals shown to be the major agent of DMS oxidation over the oceans, and an important loss mechanism for NO_2
- discovery of IO and OIO radicals in the lower atmosphere, and their origins from natural organic iodine gases
- iodine chemistry predicted to deplete ozone over the oceans and to account for the long-known, but previously unexplained, aerosol iodine enrichment
- innovative multiple tracer release experiments
- improved air-sea flux estimates for carbon dioxide and other gases, and their relationships with molecular properties



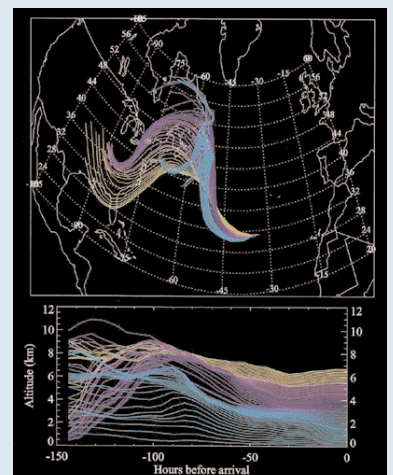
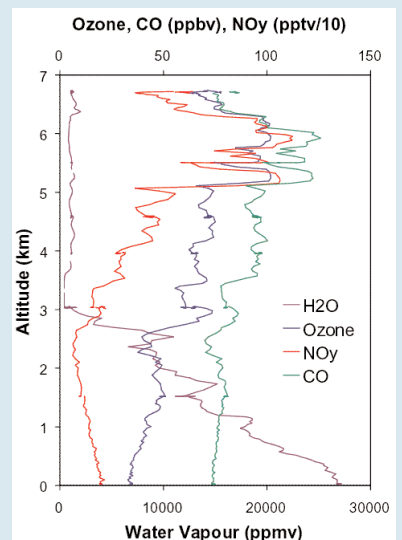
- seaweeds shown to be significant sources of halocarbons and volatile organic gases
- phytoplankton and photochemical sources of numerous gases identified in the open ocean
- detailed budget of DMS and hydrocarbons in a 'marked' water patch determined
- volatile selenium from the ocean found to balance its global budget
- easterly winds deposit pollution to a wide area west of Ireland, potentially enhancing phytoplankton growth and trace gas cycling
- first comprehensive measurements upwind, in and downwind of a sub-tropical cap cloud
- unexpectedly large numbers of cloud droplets reported, attributed to long range transport of aerosol pollution over the ocean
- out-gassing of nitric and hydrochloric acids from aerosols and subsequent uptake by cloud droplets identified
- cloud droplet acidity regulated by uptake of ammonia from land and ocean sources
- sulphur dioxide, from the degradation of DMS, transformed into aerosol sulphate in clouds by high levels of hydrogen peroxide

Outcomes



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Known affectionately as "Snoopy", the C-130 research aircraft is a former transport aircraft operated by the Meteorological Research Flight (MRF), with a Royal Air Force crew. It has a range of 5,000 km and an endurance of up to 12 hours. It can reach a ceiling of 10 km, or can skim the wave-tops at fifty feet. During ACSOE it flew missions over the North Sea and North Atlantic from its home base at Boscombe Down, Wiltshire, and was also detached to the Azores, mainland Portugal, and Tenerife for experiments further afield. It was instrumented in a number of different configurations, depending on the experiment in progress, including a new fit of fast *in situ* trace gas photochemistry instruments developed specifically for ACSOE. The aircraft has a central data acquisition system that logs data from all of the instruments and an on-board computer system called HORACE. The latter was configured to run various algorithms based on the real-time measurements.



Data from the Hurricane Erika flight including profiles of trace gases (above) and trajectories (below).

6 Throughout this report the concentrations of gases are frequently given as their 'volume mixing ratios', expressed as parts per million by volume (ppmv), parts per billion by volume (ppbv), or parts per trillion by volume (pptv). One pptv is equivalent to one volume of the gas in one trillion (10^{12}) volumes of air.

Atmospheric transport of pollutants and natural constituents

Data collected during the ACSOE programme have shown that long-range transport of pollutants and naturally emitted trace gases is a ubiquitous feature of the troposphere.

Air masses of very different origin have been observed, in aircraft and ozonesonde data, with layers interleaved with one another. Surface trace gas data collected at Mace Head, Ireland during the EASE'96 and EASE'97 campaigns (see page 10) also showed that, from one day to the next, air masses with very different origins and chemical composition were arriving at this site.

Back trajectory analysis was successfully used to diagnose the origin of different air masses, sometimes over extraordinarily long distances. The most dramatic example was found in ozonesonde data over Wales, when near-zero ozone conditions appeared to have been transported all the way from the Pacific Ocean.

ACSOE has contributed considerably to our increased knowledge of how trace gases are transported in the troposphere. It is now known, for example, that uplift of pollutants by frontal systems along the northeast coast of North America is an important mechanism for transporting pollutants into the mid and upper troposphere over the North Atlantic, and even as far as Europe.

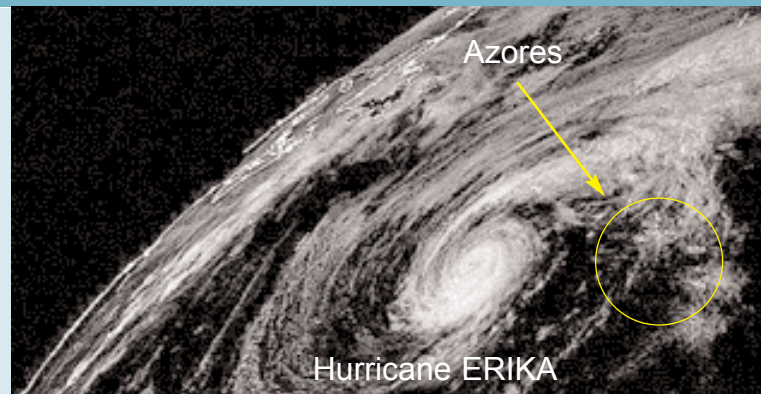
Global chemistry transport models were successfully used in ACSOE to reproduce the broad features seen in the observations (as further detailed in *The Northern Hemisphere ozone budget*), but they were unable to reproduce the finest-scale structures and layers that were observed. As part of ACSOE, however, a novel model technique, RATCATCHR, has been developed and is proving a powerful new tool for examining the relative roles of photochemistry and mixing between air masses.

The "Hurricane Flight"

SA Penkett, PS Monks, CE Reeves, KS Law,
MJ Evans, S Bauguitte, S Schmitgen

A major objective of the ACSOE aircraft experiment in September 1997 was to study air that had been transported around the Azores High from North America to the Eastern Atlantic. In the event the weather over the Atlantic that September was dominated by the presence of Hurricane Erika. This produced some spectacular effects including the transport of polluted air from the southeast USA out into the mid Atlantic free troposphere.

The aircraft track from Santa Maria in the Azores initially went south, then turned west into the cloud streamers emanating from the eye of the hurricane (see picture), before returning to Santa Maria through air that had been uplifted. The aircraft also cut vertically through the outflowing air, and a profile of ozone (O_3), carbon monoxide (CO) and total reactive nitrogen compounds (NO_y) is shown in the figure (left, top panel). High concentrations of these pollutants were clearly visible in layers at altitudes between 5 and 7 km. The ozone concentration in the layers reached 100 ppbv while NO_y exceeded 1 ppbv. Both were highly correlated with CO, indicating a boundary layer rather than a stratospheric source. Such concentrations of ozone and NO_y would, if widespread, be sufficient to influence the radiative properties of the mid and upper troposphere, and affect nitrate deposition in remote areas.



Satellite picture of Hurricane Erika on 14 September 1997.

Trajectory analysis (left, bottom panel) revealed how the polluted layers found by the aircraft had been uplifted from the boundary layer over the southeastern USA. The air was initially uplifted to about 9 km, then slowly subsided before being intercepted by the aircraft. Lower down in the profile the air had been slowly subsiding over several days, or had travelled in the marine boundary layer, where ozone is efficiently destroyed by sunlight and high water vapour concentrations.

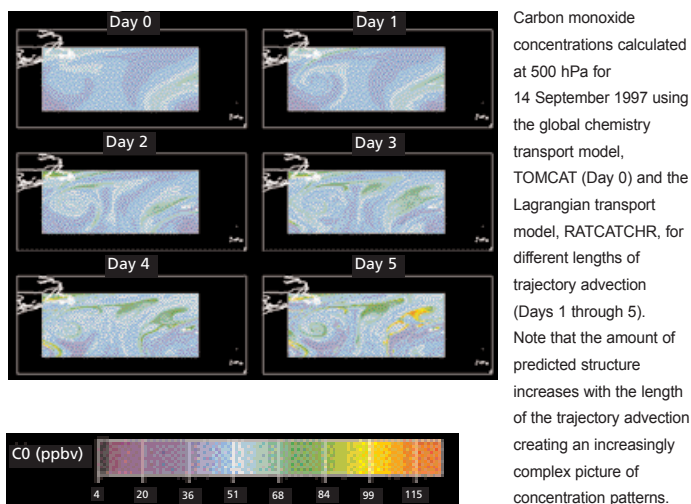
Uplift of pollution from continents does, therefore, provide an efficient mechanism for transporting pollution far from sources and into the free troposphere. When it descends to the surface it will add significantly to the background ozone levels experienced at the receptor site. This has important ramifications for the control of intercontinental transport of pollution.

Modelling small-scale atmospheric structure

MJ Evans, J Methven, S Arnold, KS Law, JA Pyle

ACSOE aircraft flights have shown that the atmosphere is composed of numerous intertwining layers, rather like a marble cake. Air masses of different composition swirl around each other in a complex three-dimensional pattern. Modelling these structures is a major challenge for the atmospheric chemistry community.

The RATCATCHR (Regional Atmospheric Trajectory model of Chemistry and Transport Calculated at High-Resolution) model uses back trajectories ending over a very fine grid across the region of interest to produce high-resolution concentration fields of trace gases. The starting points of the trajectories are initialised with concentrations calculated using the TOMCAT 3-D atmospheric chemistry model. The figure below shows an example of a sequence of carbon monoxide (CO) fields predicted using this technique.



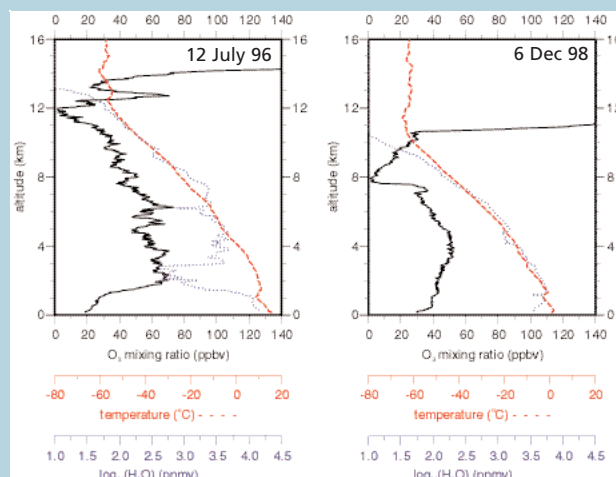
Day 0 shows the CO concentration field calculated by TOMCAT over a region of the North Atlantic for the day of the Hurricane Flight (see previous page). Days 1 to 5 show how RATCATCHR uses trajectories to advect TOMCAT fields from a number of days prior forward to the day of the Hurricane Flight. As the period of trajectory advection lengthens, features that are barely resolved in TOMCAT, such as Hurricane Erika itself, become much better defined. Advances in computing power should enable very large numbers of trajectories to be run including both chemical and mixing processes to study this type of event. This new approach will lead to improvements in our understanding of the importance of fine-scale structure for the chemical budgets of trace gases like ozone, and the broader implications for the oxidising capacity of the troposphere.

Ozone-poor layers in the upper troposphere

G Vaughan, WE Davies

During the course of ACSOE a number of ozonesondes were launched from Aberystwyth, Wales. On some occasions, layers with almost no ozone were observed in the upper troposphere. This is remarkable since ozone concentrations are normally observed to be relatively high in this region of the atmosphere.

On 12 July 1996, an ozonesonde was launched ahead of a warm front into a clear sky (see figure below, left panel). It encountered a layer about 1 km deep between 11 km and 12 km altitude where ozone concentrations reached values too low to be measured by the sonde (i.e. less than 3 ppbv). Three-dimensional kinetic back trajectories were calculated using winds extracted from ECMWF (European Centre for Medium-range Weather Forecasting) analyses. These clearly showed that the ozone-poor air had originated from near the surface of the equatorial Pacific (approximately 15°N, 180°W)



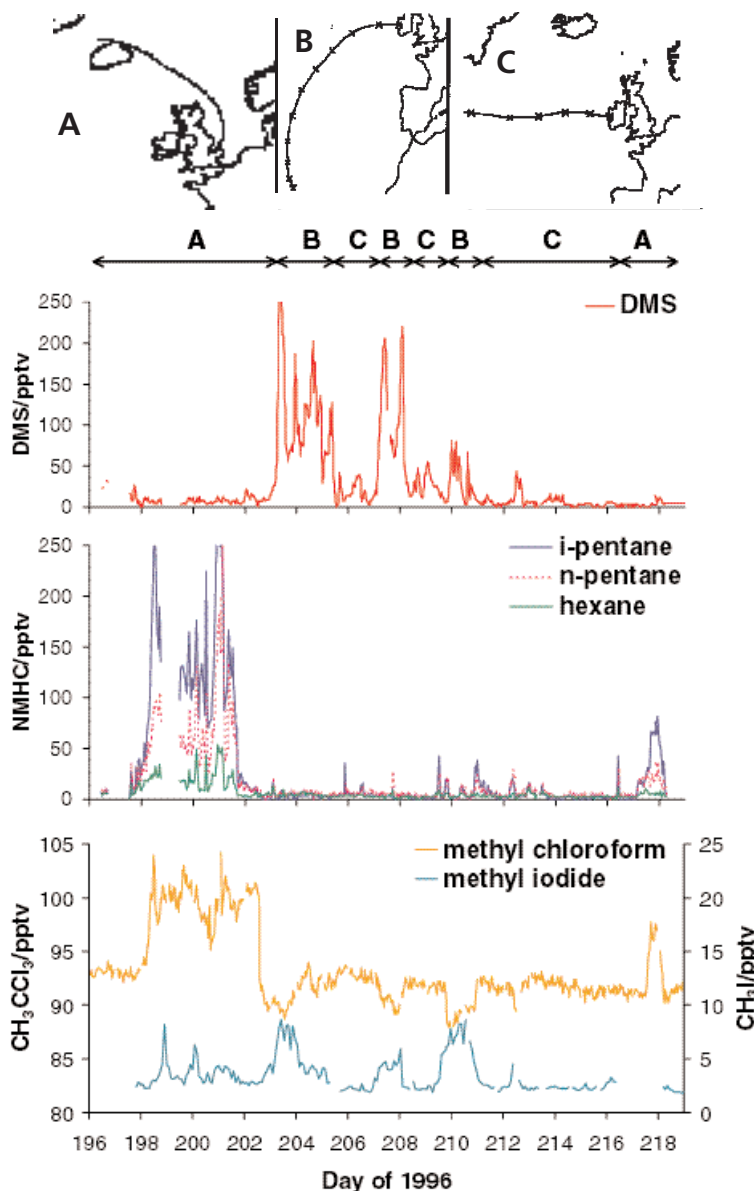
Ozonesonde data from balloon ascents over Aberystwyth on 12 July 1996 (left hand panel) and 6 December 1998 (right hand panel). Near-zero ozone levels were observed at about 12 km in the first case, and about 8 km in the second. The position of the tropopause (the boundary with the stratosphere) can be seen by the change in slope of the temperature profile and low water vapour content (i.e. at about 13 and 10 km respectively).

several days earlier. Near-zero ozone has previously been observed overlying the Pacific Ocean, possibly related to heterogeneous chemistry in the marine boundary layer. We think that this ozone-poor Pacific air was uplifted by deep convection, before being carried half way round the world to Aberystwyth.

A similar case of low ozone at high altitude was observed on 6 December 1998 (see right panel above), but this time the origins appeared to be very different. The trajectories showed polluted continental boundary layer air from the USA being uplifted by a frontal system near the North American coast. What is not clear on this occasion is how near-zero ozone conditions were maintained over a period of several days, as the polluted air was transported across the North Atlantic.

Continuous hourly measurements of non-methane hydrocarbons (NMHC), halocarbons, and dimethyl sulphide (DMS) were made using automated gas chromatography systems during the EASE'96 and EASE'97 campaigns (see over) at Mace Head, Ireland. The NMHC and halocarbon data have been classified into various air mass types, using a combination of observed concentrations and back-trajectories.

The figures (below) show time series of some man-made and natural ocean-derived gases during EASE'96, together with five-day back trajectories for three distinctly different types of air masses experienced during this period. During Days 198 to 202 an anticyclone dominated with easterly flows bringing in polluted air with high concentrations of pollutant gases such as hexane, pentane and methyl chloroform.



At the same time, high concentrations of methyl iodide (CH₃I) were observed, but low concentrations of DMS. High CH₃I was also coincident with elevated methyl chloride and methyl bromide during low wind speeds, suggesting that all three methyl halides have a common local source, possibly from coastal marine biological activity.

On Day 202, the situation reversed as sub-tropical air reached the site with high and strongly correlated concentrations of DMS and CH₃I, but much lower concentrations of the man-made gases. In fact, during these sub-tropical transport events, methyl chloroform concentrations were lower and were anti-correlated with methyl iodide. The concurrent elevated concentrations of DMS and CH₃I, coupled with modelled back trajectories, indicated that these two gases share common open-ocean source regions located broadly in an area of the North Atlantic Ocean between 30 and 40°N, and 20 and 50°W. Later, on Day 217, the concentration of the three NMHCs and methyl chloroform increased again associated with another pollution event. Tracers of anthropogenic pollution, such as acetylene, were also found to correlate extremely well with a range of chlorofluorocarbons (CFCs) and related compounds, whereas DMS correlated well with other trace gases of marine biological origin.

The different chemical reactivities of benzene and toluene with hydroxyl radical (OH), the major loss pathway for these gases, enabled a qualitative estimate of the chemical "age" of air masses reaching Mace Head to be made from the measured concentrations, using an estimated average OH concentration and known emission ratios. During continental easterly flow, a mean age of 17 hours was estimated, whereas during south-westerly tropical air flow this value increased to 104 hours. Finally, observations of acetylene/ethane ratios in polar air masses of different origin (Iceland or Greenland), suggest a possible influence of bromine chemistry as an additional loss mechanism.

Various trace organic gases measured between 14 June and 6 July 1996 (Days 196 to 219) during the EASE'96 campaign at Mace Head, Ireland. Dimethyl sulphide (DMS) and methyl iodide (CH₃I) derive from marine sources, whereas i- and n-pentane, hexane and methyl chloroform (CH₃CCl₃) are of man-made origin. Also shown are representative five-day back trajectories for each air mass (A = anticyclonic easterly; B = subtropical southwesterly; C = cyclonic westerly).

Mace Head 'EASE' campaigns

Some of the major ground-based ACSOE experiments were carried out at the Mace Head Atmospheric Research Station (53° 19' N, 9° 53' W). This facility, on the west coast of Ireland, is owned and operated by the Physics Department of the National University of Ireland, Galway. It benefits from westerly exposure to the North Atlantic Ocean, with a "clean" sector reaching from 180 degrees through west to 300 degrees, and the opportunity to study atmospheric composition under Northern Hemispheric background conditions, as well as European continental emissions during easterly winds.

The facility consists of two shore laboratories that are just 5 m above mean sea level, a 22 m walk-up tower, and a larger building (the "cottage") 200 m from the shore and 17 m above sea level. For the ACSOE campaigns, additional walk-up

towers were erected, extra laboratories and computing facilities set up in portacabins, shipping containers, and vans, and additional power and communication facilities installed across the site.

Two campaigns were undertaken; the Eastern Atlantic Summer Experiment 1996 (EASE'96) from June through August 1996, and the Eastern Atlantic Spring Experiment 1997 (EASE'97) from April to June 1997. Both campaigns were co-ordinated with ACSOE cruises of the RRS Challenger operating offshore, and with flights of the Cranfield Jetstream aircraft, which flew transit flights between the ship and shore. Vertical soundings above Mace Head were also provided by the Jetstream, as well as by tethered and free-flying radiosondes. These, along with satellite images and trajectories, proved crucial for positioning the ship and the aircraft, and in planning intensive measurement phases.



Mace Head Atmospheric Research Station. Left to right: Shore instrument tower; shore and 'cottage' laboratories photographed from the Jetstream; launching the balloon tethered radiosonde.

Gas transfer across the sea surface

PD Nightingale, R Upstill-Goddard, G Malin, D Ho, P Schlosser

Tracers being released from the aft of the RRS Challenger during the southern North Sea air-sea exchange experiment. A purple tinge from the rhodamine dyes can be seen in the water.



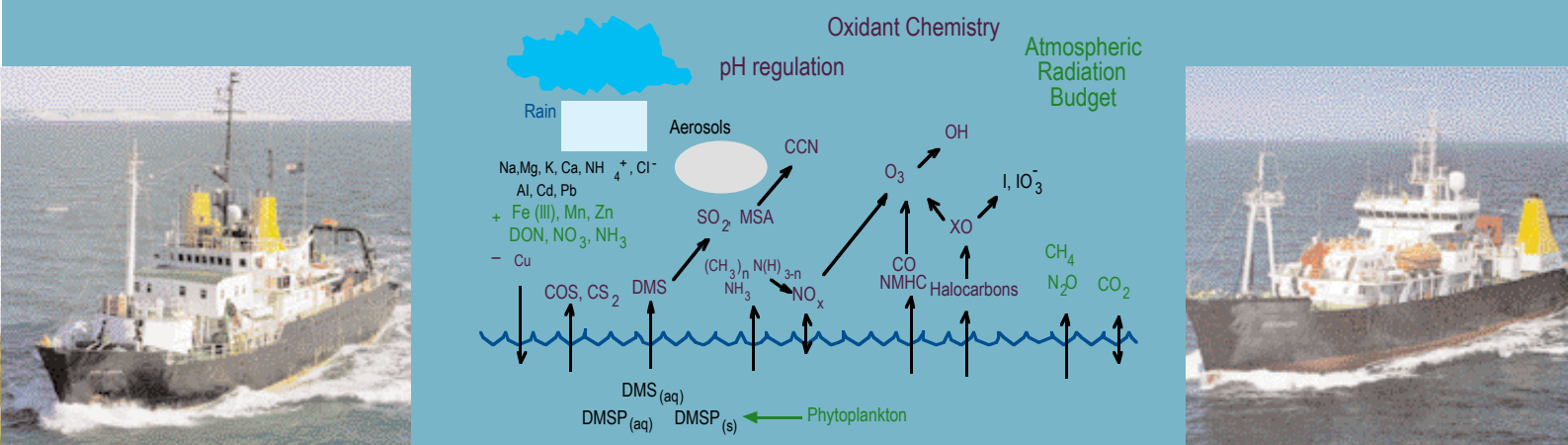
Air-sea fluxes of gases and aerosols are usually determined from a knowledge of the concentration gradient at the sea surface and a factor "k", known as the gas transfer velocity. A major uncertainty in present estimates of air-sea fluxes for most gases arises from the different empirical methods used to determine the gas transfer velocity at different wind speeds. The most widely used methods give values of k differing by up to a factor of 2.

As part of ACSOE, a deliberate release of five oceanic tracers (helium-3, sulphur hexafluoride, spores of *Bacillus globigii* var. *Niger*, and two rhodamines, WT and Sulpho-G) was made in the southern North Sea in order to measure gas exchange rates.

Air-sea interactions

Exchange of gases and particles across the air-sea interface has important implications for both atmospheric and oceanic chemistry. Trace gases produced in seawater can affect the acid/base balance of rain and aerosols and the oxidising capacity of the atmosphere (through breakdown of non-methane hydrocarbons and natural halocarbons). They can also affect the atmospheric radiation balance by uptake or release of carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4), and by the formation of cloud condensation nuclei (CCN) from the oxidation of dimethyl sulphide (DMS). The acidity-alkalinity (pH) of aerosols and precipitation is largely controlled by the balance between acids coming from fossil fuel burning and the oxidation of natural DMS (producing methane sulphonic acid (MSA), sulphur dioxide (SO_2) and sulphate (SO_4)), and bases (alkalis) provided by natural and man made sources of ammonia (NH_3) and methylamines. On the other hand, deposition of particles and precipitation provides a source of essential nutrients (such as iron and fixed nitrogen) to the euphotic (sunlit) zone of the oceans, and the organisms living therein. Since many of the above mentioned gases emitted to the atmosphere are biologically formed in the oceans, the up and down fluxes are, in reality, closely coupled and so logically studied together.

Exchanges of a wide range of substances across the sea surface, with their roles in the atmosphere and ocean biogeochemistry.

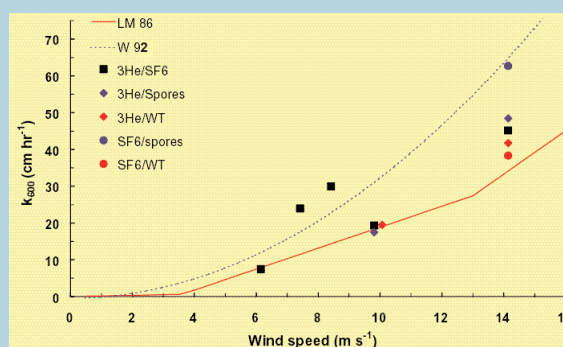


Two of NERC's research vessels were employed during ACSOE cruises. The RRS Challenger (left) sailed in the eastern Atlantic off the west coast of Ireland, and in the southern North Sea for the air-sea gas exchange experiment. The RRS Discovery (right) was used to conduct the ACSOE cruise further north in the mid-Atlantic south of Iceland. The Challenger has facilities for 14 scientists and technicians, depth casting, and on-board computer logging of underway oceanographic and meteorological parameters. The Discovery has berths for 28 scientists, bow-mounted meteorological package, and extensive ocean depth casting capabilities. (Photos Crown Copyright.)

These tracers can be tracked over many days thanks to the sensitivity with which they can be detected. Changes in the ratio of volatile and non-volatile tracers were used to derive estimates of gas exchange rates at approximately twelve-hourly intervals over a ten-day period. A number of estimates of the transfer velocity were obtained over a wide range of wind speeds and these fell within the range of the published predictions (see figure). The rhodamine study was particularly successful and indicated that these compounds should make useful oceanographic tracers in future field experiments. Using three non-volatile tracers allowed an over-determination of the system and gave an insight into the relationship between transfer velocity and the molecular properties of gases.

This project has improved confidence in air-sea flux calculations of carbon dioxide and a multitude of other biogeochemically and atmospherically important gases.

Gas transfer velocity (k) as a function of wind speed measured using a variety of purposefully added tracers in the southern North Sea. Two widely used k versus wind speed relationships are also shown (LM86 and W92).



Although representing only about 18% of the total ocean surface area, coastal seas are extremely bioactive, often significantly contributing to, or even dominating, trace gas emissions. Nutrient levels and temperatures tend to be higher in coastal areas, providing more favourable conditions for bacteria and phytoplankton growth and metabolism. Rocky shores dominate the coastlines of much of Northern Europe and allow seaweeds to proliferate there. All these marine organisms may contribute to oceanic trace gas release.

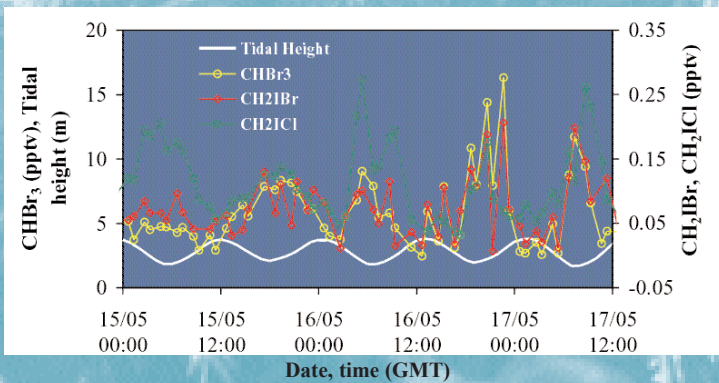
Distinct diurnal cycles in the atmospheric concentrations of alkenes were observed in westerly marine air during both EASE'96 and EASE'97 at Mace Head, Ireland. Daytime concentrations of ethene, propene, and iso and 1-butene were about twice as high as levels at night, supporting a photochemical mechanism of marine alkene formation.

The action of ultraviolet sunlight on dissolved organic carbon in the surface ocean is thought to initiate the formation of these volatile alkenes, which subsequently degas into the atmosphere. To be present at the relatively high concentrations measured at Mace Head, it can be inferred that these short-lived species must have very significant emissions in the surrounding coastal waters. The distinct diurnal cycle further dictates that the sources are located predominantly in near-surface waters. In the open ocean, and in waters off Mace Head, dissolved ethene concentrations were observed to decrease with depth from 2 to 50 m, also consistent with photochemical production near the sea surface.

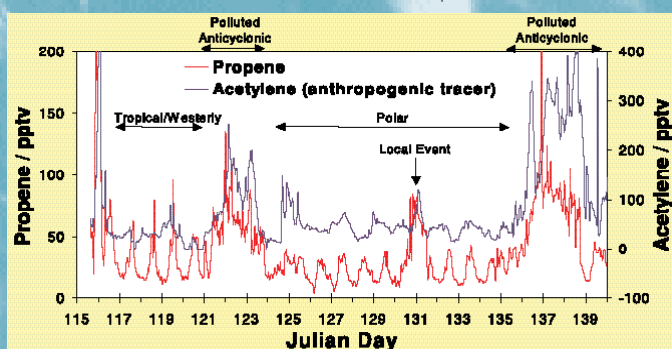
Dissolved salts of the halogens chlorine, bromine and iodine are, of course, found ubiquitously in seawater, and are accumulated by seaweeds as a vital part of their biochemistry. In the process, organic halogens are formed and released into the surrounding seawater. The clear influence of seaweeds on atmospheric halocarbons was observed during EASE'97. Highest concentrations occurred at low tide, when seaweeds were directly exposed to the air, and were lowest at high water when the seaweeds were mostly submerged. The influence of these biogenic halocarbons on the surrounding environment was found to be significant. Photolysis of iodine-containing halocarbons initiates a chain of reactions involving iodine oxide (IO) radicals, and potentially culminating in surface ozone destruction (see *Reactive inorganic iodine in the marine atmosphere*).



Algal beds off Mace Head, Ireland (Frithjof Küpper)



Pronounced increases in iodinated and brominated halocarbons in the atmosphere observed at low tide at Mace Head.



Clear diurnal cycles in propene were observed during EASE'97 except during polluted episodes (indicated by high acetylene) when propene levels were also generally elevated, suggesting that propene has both natural and pollution sources.

The budget of dimethyl sulphide (DMS)

DMS is emitted from surface seawater into the atmosphere where it oxidises and produces sulphate particles and acidic compounds. Sulphate particles have a cooling effect on climate since they reduce the amount of sunlight reaching the Earth's surface. By acting as light scattering surfaces and nuclei for condensation of water vapour and cloud formation, a portion of incoming solar radiation is reflected back into space. To understand and model these processes we need to know how much DMS enters the atmosphere and what controls its emission.

During ACSOE several research cruises took place in the NE Atlantic with the central aim of examining the production of atmospherically important gases in seawater, and their fluxes to the atmosphere.

In May 1997 in the eastern Atlantic a range of trace gases was measured from the RRS Challenger, including DMS, methyl iodide and a large number of non-methane hydrocarbons including isoprene. Concentrations in the water were found to have different distributions in space and time for each of the gases, showing that distinct sources dominate their production in this region. For example, the distribution of DMS was found to be related to the occurrence in the water of specific species of phytoplankton, whereas isoprene was related to the total mass of phytoplankton (i.e. it was not

related to any particular species), and ethene was formed by the reaction of light with dissolved organic matter in the water.

Sea-to-air fluxes were calculated from the product of these concentration fields and an appropriate transfer velocity (as discussed earlier). A photochemical box model was then used to assess the contribution of these fluxes to the concentrations of the gases measured at the Mace Head sampling site. This showed that the open Atlantic Ocean area studied was a substantial source of the DMS observed at Mace Head, a weak source of methyl iodide compared with emissions from the coastal zone (see facing page), a small source of ethene at night (when atmospheric photochemical loss is minimised), and a small source of isoprene (although insignificant compared to terrestrial sources).



WJ Broadgate

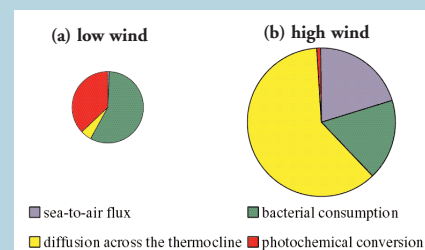
Discovery runs into high seas.

SM Turner, R Simo, M Steinke, A Thompson, LM Cardenas, PS Liss

Quantification, however, is not straightforward. Data from laboratory experiments provide some information, but large uncertainties are inherent in extrapolating the results to the real environment. Further, since ocean waters are in continual motion, it is extremely difficult to study the biological and chemical evolution of a small patch of seawater from a ship. It was not until the development of the SF₆ tracer technique that temporal changes could be distinguished from spatial variations with confidence.

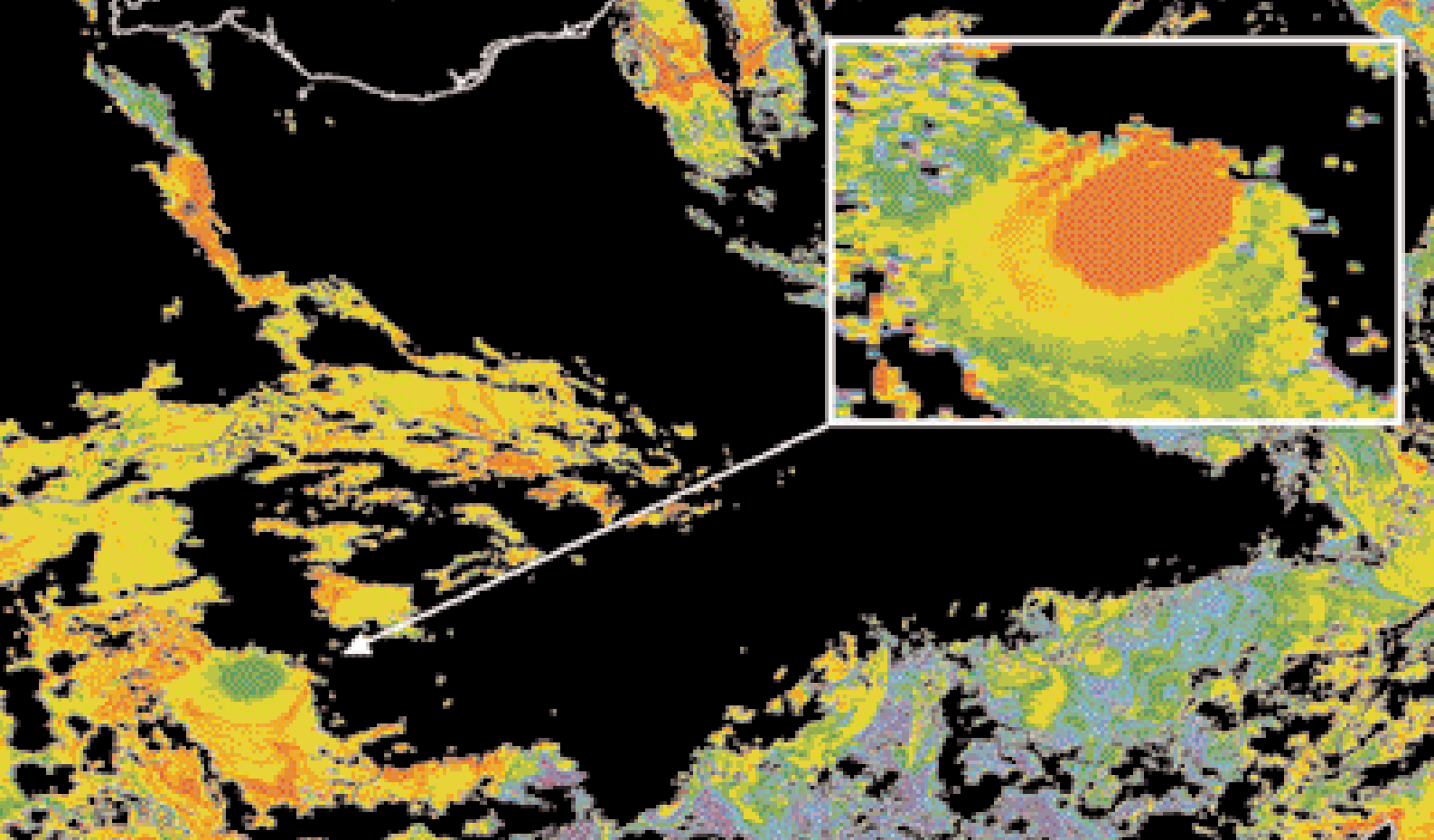
The ACSOE North Atlantic Experiment (1998) was the first *in situ*, comprehensive study of DMS and its major transformations in seawater. It was conducted in a rotating eddy south of Iceland (see picture over).

Comparison of the losses of DMS from the mixed layer for 2 different days: (a) calm and (b) stormy. The different sizes of the pies reflect the four-fold increase in DMS production over the four day period between (a) and (b), during which the bloom evolved.



Rates of production and consumption were determined and have enabled us to quantify the budget of DMS for an algal bloom of *Emiliana huxleyi* (a single celled plant of the group Coccolithophoridae, responsible for the formation of limestone on geological time scales).

Increased wind speed was found to alter the pattern of DMS loss mechanisms significantly. The sea-to-air emission of DMS increased from 1% to 15% of the total daily budget (a 100-fold increase in real terms) and the major loss pathway changed from bacterial consumption to downward mixing. It is clear that the amount of DMS which enters the atmosphere is only a small bleed from a large recycling reservoir, and is the result of a delicate balance of biological and physical forces. Any longer term perturbation could increase or decrease DMS emissions significantly, providing a climate feedback mechanism.



Satellite image (SeaWiFS) of chlorophyll-a and light scattering by specific organisms (inset picture) for an eddy south of Iceland, studied in ACSOE in June 1998. (Courtesy NASA, Orbital Sciences Corporation, NERC Dundee Satellite Receiving Station, NERC Remote Sensing Data Analysis Service.)

Selenium emissions from the sea

PS Liss, M Hamren-Larsson, D Amouroux, E Tessier, OFX Donard

Selenium is known to be an essential element for most plants and animals, including man. Some areas of the Earth's surface, however, are depleted in selenium, presenting serious health problems for animals and humans (e.g. cancer and heart disease). A connection between the observed selenium distribution, and its bioavailability, and the global cycling of the element may explain these findings. The atmosphere represents the major natural input of selenium to the land surface via 'wet' and 'dry' deposition (i.e. washout in precipitation, or uptake on soil and vegetative surfaces). From global budget assessments, the oceans are presumed to be a major source of selenium to the atmosphere, accounting for between 45 and 77% of global emissions. The data available so far, however, are too sparse to establish a reliable flux estimate to balance the assumed deposition to land. It has been speculated that the marine selenium cycle is analogous to that of sulphur, with volatile organic selenium species (e.g. dimethyl selenide, DMSe) emitted from surface seawaters, scavenged by airborne aerosols, with some ultimately deposited on land.

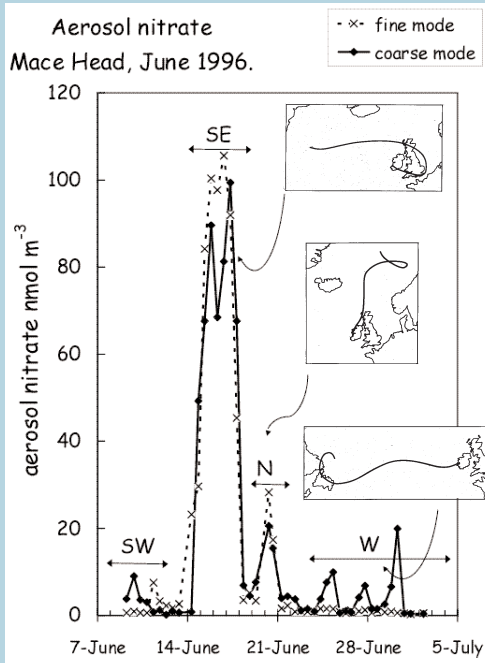


WJ Broadgate

LJ Spokes

During the ACSOE North Atlantic Experiment, we were able to measure volatile forms of selenium and DMS in seawater samples. The results showed that the dominant forms of volatile selenium are DMSe and the mixed sulphur-selenium compound dimethyl selenyl sulphide (DMSeS), in approximately equal amounts. They also showed a positive relationship between concentrations of DMS and DMSe (see figure right). Calculation of sea-to-air fluxes indicates that, provided the collected samples are representative, there is sufficient selenium emitted from the sea to balance the global budget of this element. Nevertheless, the flux from sea to land may not be sufficient to ensure that humans receive the selenium they need to protect against a variety of serious diseases. It has, for example, recently been shown that UK levels of selenium intake are, on average, more than a factor of two lower than that recommended for healthy living.

TD Jickells, LJ Spokes



Low concentrations of aerosol nitrate were seen during relatively clean westerly flow across the Atlantic Ocean. Near total conversion of fine mode (<1.0 μm diameter) to coarse mode (>1.0 μm diameter) aerosol was seen in these marine air masses due to reaction of nitric acid with coarse seasalt aerosol. Intermediate levels of nitrate were seen under northerly continental flow. The high concentration pulse of aerosol nitrate was associated with polluted anticyclonic flow from the UK and continental Europe. Even under these polluted conditions, coarse mode nitrate was prominent, suggesting rapid reactions with sea salt aerosols.



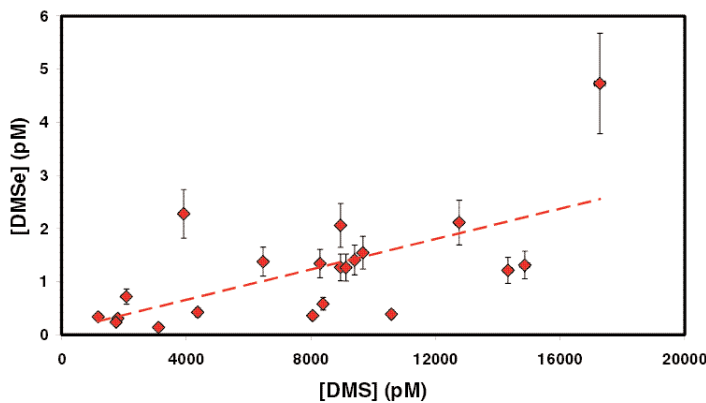
LJ Spokes

Left to right: North Atlantic Experiment participants; installing filter samplers on the mast; launching the water sampler rosette.

Mace Head normally receives 'clean' marine air off the North Atlantic Ocean. A striking feature observed during ACSOE, however, was the occurrence of pulses of highly polluted air arriving with easterly winds (see figure left). Over the whole year, easterly flow only occurs about 15% of the time, and represents air that has passed over highly populated, industrialised and farmed regions of Europe. Although uncommon, ACSOE results demonstrate that these pulses of polluted air dominate the input of material from the atmosphere into the oceans west of Ireland both in terms of rainfall and dustfall. Furthermore the interactions between this polluted air and sea salt in the marine atmosphere act to enhance deposition of nitrate and ammonium, thereby concentrating deposition into coastal waters. For instance, we calculate that for EASE'96, 55% of the total atmospheric nitrogen input to the surface waters west of Ireland arrived in polluted pulses representing only 18% of the time. Nitrogen is an essential nutrient for phytoplankton growing in these waters. These atmospheric inputs may enhance the growth of phytoplankton and have impacts on both the global carbon and climate systems through increasing the oceanic uptake of CO_2 , and the emission of gases such as DMS. In the area offshore of Mace Head we estimate that, during EASE'97, 30% of phytoplankton driven carbon export to deep ocean waters could have been supported by atmospheric nitrogen inputs.

We believe these pulses of polluted air can be carried hundreds of kilometres offshore and therefore have a significant effect over large areas of the North Atlantic. They deliver not only nitrogen, but also a range of other species including metals such as iron, lead and zinc. We estimate, for example, that atmospheric deposition - mostly from pollution pulses - is the major source of zinc, an important trace nutrient for phytoplankton, even 700 kilometres offshore.

The ACSOE programme was also responsible for one of the first comprehensive studies of nitrogen isotope ratios of aerosol nitrate and ammonium. The results clearly demonstrated that this new technique can distinguish between ammonia of marine and terrestrial origin, and may also be able to help quantify the relative importance of various sources of nitrate such as vehicles and coal combustion.



Dimethyl selenide (DMSe) and dimethyl sulphide (DMS) are correlated in water samples from the NE Atlantic, pointing to a common biological origin.

Chemical processes in the atmosphere

Oxidation processes are vitally important for maintaining the chemical composition of the lower atmosphere. Many important atmospheric gases, such as the oxides of nitrogen (NO_x), volatile organic compounds (VOCs), and methane are broken down this way into carbon dioxide, water and a variety of soluble inorganic and organic acids. These chemical changes are engineered by a variety of 'radicals' - highly reactive molecules in the atmosphere.

The ultimate source of atmospheric radicals is sunlight-driven photochemistry, which produces ozone (O_3) in an oxygen-rich atmosphere. Although ozone is not a radical species itself (although it is quite reactive towards certain VOCs) it can be photolysed by solar ultra violet (UV), resulting in excited oxygen atoms. These oxygen atoms can react with water vapour to form hydroxyl (OH) radicals. Hydroxyl is the most reactive radical in the atmosphere, and is able to break down and oxidise a wide range of compounds originating from both man-made and natural sources. Because OH is produced photochemically, it is mostly only present during the day. Ozone, however, can also oxidise nitrogen dioxide (NO_2) to form the nitrate (NO_3) radical. NO_3 is rapidly photolysed during the day, but can build up at night to become a significant oxidising agent for a number of organic molecules. Radical reactions with organic molecules almost always result in formation of peroxy radicals (RO_2 and HO_2), and observations of these provide 'smoking gun' evidence of radical-organic chemistry.

BJ Allan



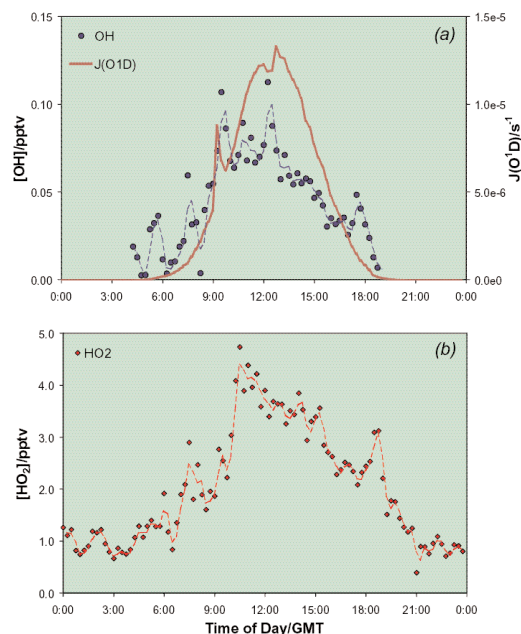
Chlorine, bromine and iodine oxides (ClO, BrO and IO) are produced by the reaction of halogen atoms with ozone. The source of chlorine and bromine atoms is airborne sea-salt particles, produced by wave breaking and bubble bursting. Iodine atoms, in contrast, result from photolysis of certain organic iodine gases released by marine organisms. The halogen atoms and oxides are important oxidants of many atmospheric organic gases. They also participate in ozone-depleting cycles, similar to those observed in the stratosphere.

During ACSOE, an unusually comprehensive suite of radicals (OH, NO_3 , BrO, IO, RO_2 and HO_2) was measured during the field campaigns, as were other relevant reactive compounds such as reactive nitrogen gases (known collectively as NO_y). A field study of dimethyl sulphide (DMS) oxidation was also carried out. DMS is oxidised in the atmosphere to form sulphuric and methane sulphonic acids. These acids have been proposed as sources of new particles in the marine boundary layer, and of cloud condensation nuclei, providing a potentially important feedback in the Earth's climate system.

The Differential Optical Absorption Spectroscopy (DOAS) light beam shining between the shore laboratory at Mace Head and the retroreflector on the North shore of the bay.

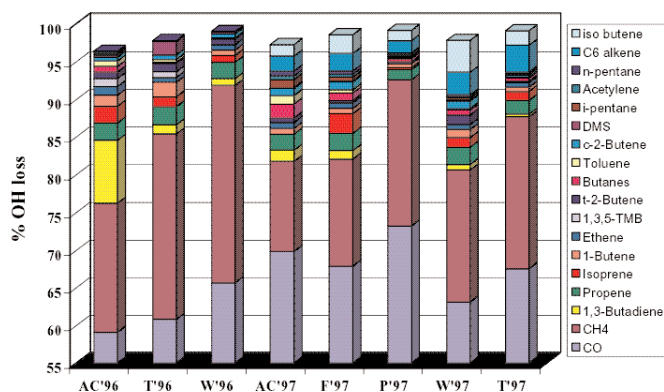
OH and HO₂ radicals (known collectively as HO_x) are central to the chemistry of the atmosphere. The OH abundance gives an indication of the oxidising capacity of the troposphere, which regulates the concentration of greenhouse gases, such as methane. Furthermore, the reaction of HO₂ with NO is an important source of tropospheric ozone. OH and HO₂ concentrations were measured using a FAGE (Fluorescence Assay by Gas Expansion) instrument, which uses laser-induced fluorescence at low pressure. The figure right shows average OH and HO₂ concentrations at Mace Head during EASE'97. Correlations were found between OH and the rate of photolysis of ozone, which is the primary source of OH (panel a).

Average diurnal variations at Mace Head during spring 1997 of (a) OH and ozone photolysis rate (J(O¹D)) and (b) HO₂. The data plotted are 15-minute averages of measurements made throughout EASE'97.



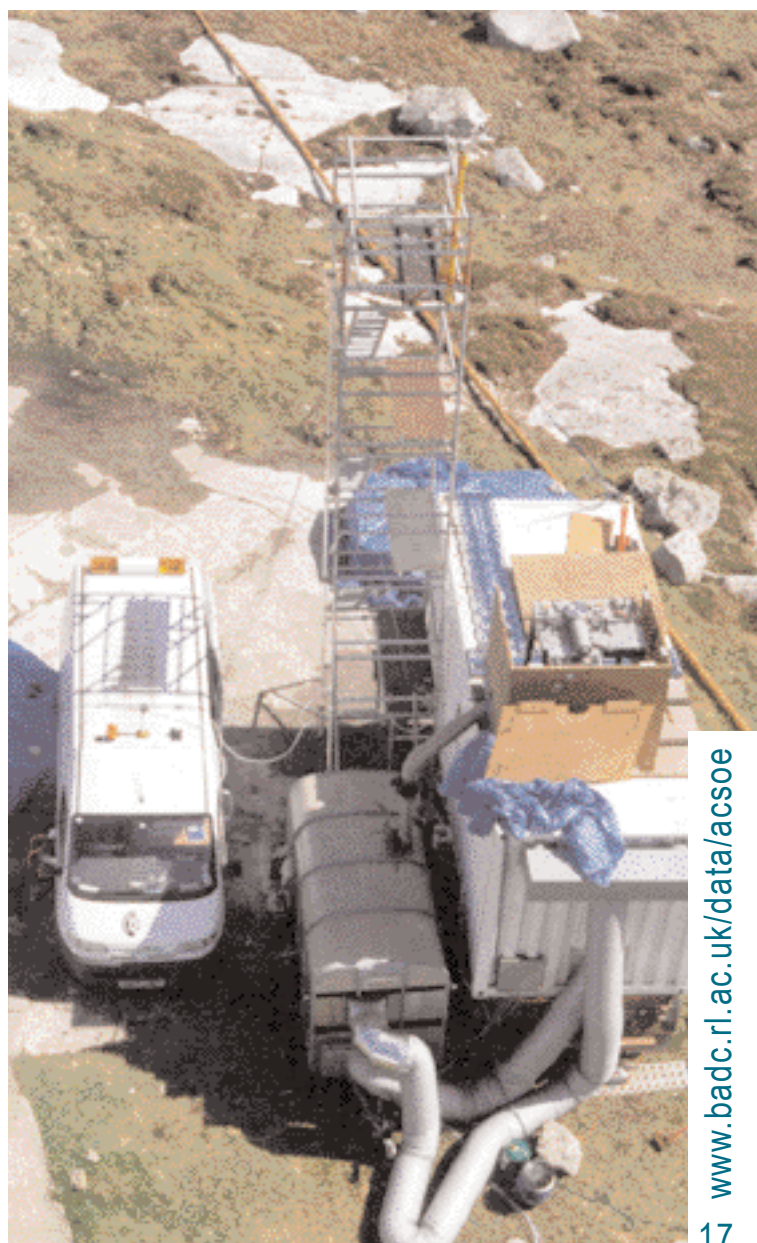
Measurements of VOCs and DMS were made using an automated gas chromatography system during both EASE campaigns. For each measured hydrocarbon, and also for carbon monoxide (CO), the product of the concentration of that compound and its rate coefficient for reaction with OH was calculated, and the hydrocarbons then ranked in order of importance (see figure below). Degradation schemes for the most important hydrocarbons were then taken from a detailed chemical mechanism, the Master Chemical Mechanism, to produce a zero-dimensional box model that was tailored specifically for the marine boundary layer.

In the clean air masses (T, W, P), most OH loss was due to reaction with CO and methane (CH₄), with a larger contribution from the other hydrocarbons in air masses subject to pollution (AC, F). The model was constrained by measurements of longer-lived species, and predicts the concentrations of short-lived radical species. Although there is good agreement under some conditions, the model consistently over predicts OH and HO₂. This suggests that other loss processes (including heterogeneous loss of OH or its precursors) are not adequately represented in the model.



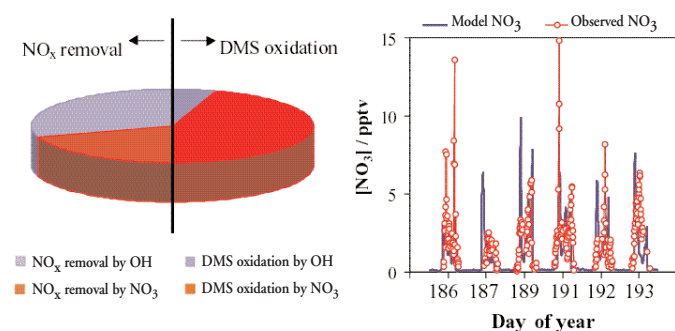
Percentage of OH reacting with various hydrocarbons, CO and CH₄ in the two EASE campaigns. The air masses are segregated into anticyclonic (AC), tropical (T), westerly (W), polar (P) and France (F), according to their origins.

The FAGE container (the 'HO_xBO_x') and VOC instrument van seen from the shore tower at Mace Head.



During the night, the main oxidants are NO_3 and ozone. Of particular interest in the marine boundary layer is the reaction of NO_3 with DMS. During ACSOE, NO_3 was observed by Differential Optical Absorption Spectroscopy (DOAS). This radical has a strong absorption band at 662 nm, and was measured with a detection limit of 0.5 pptv over a pathlength of about 8 km in the marine boundary layer. Peak nighttime concentrations averaged about 5 pptv in clean marine air, but reached 40 pptv in easterly continental air masses.

The rapid oxidation of DMS in air is the first step towards the formation of aerosol sulphate, thought to add a significant feedback mechanism in climate regulation. In background Atlantic air containing on average 50 pptv DMS, it was found that 80-90% of the available NO_3 initiated oxidation of DMS.



The pie chart illustrates the contribution NO_3 has to the oxidation of DMS and the removal of NO_x from the atmosphere, compared to that during the day by OH (data from the Tenerife campaign). Modelling the observed NO_3 has led to an improved understanding of the chemistry taking place and the significance of the role of NO_3 as an oxidant in the lower atmosphere (chart on right).

Box model studies indicated that if the concentration of NO_2 (which reacts with ozone to form NO_3) is more than 60% that of DMS, then DMS will be oxidised more rapidly at night by NO_3 than it is during the day by OH. This was indeed found to be the case for marine air arriving from the Atlantic.

The nitric acid (HNO_3) production rates, predominantly from the reaction of nitrate radical with DMS, are comparable with those calculated for the reaction of NO_2 and OH during the day for 100 - 300 pptv of NO_x . It is the subsequent deposition of nitric acid that provides a loss of NO_x from the system. In the case of polluted continental air masses containing little or no DMS, the nitrate radical mostly reacts with NO_2 to produce nitrogen pentoxide (N_2O_5), or it reacts with VOCs to form nitric acid. Nitrogen pentoxide is readily taken up onto the surface of aerosols, where it is hydrolysed, again forming nitric acid and so removing NO_x .

Vertical profile measurements of nitrate radical from the ground up to 20 km were obtained using a novel DOAS technique that observes zenith-scattered sunlight during sunrise. The measurements indicated the presence of significant and highly variable concentrations of NO_3 above the boundary layer in the free troposphere, adding to the oxidising capacity of the troposphere.

Peroxy radical measurements in the marine boundary layer

PS Monks, G Salisbury, SA Penkett

Peroxy radicals are key intermediates in the oxidation of many trace species in the atmosphere. They are important mediators in either the production or destruction of tropospheric ozone, and in the production of gas-phase peroxides. Peroxy radicals have atmospheric lifetimes of the order of 1-2 minutes, so their atmospheric concentrations rarely exceed a few tens of pptv at any given time. During the EASE campaigns at Mace Head a Peroxy Radical Chemical Amplifier (PERCA) was used to measure a composite of RO_2 and HO_2 , whilst the FAGE (see *HO_x measurements and modelling during ACSOE*) was used to measure HO_2 .

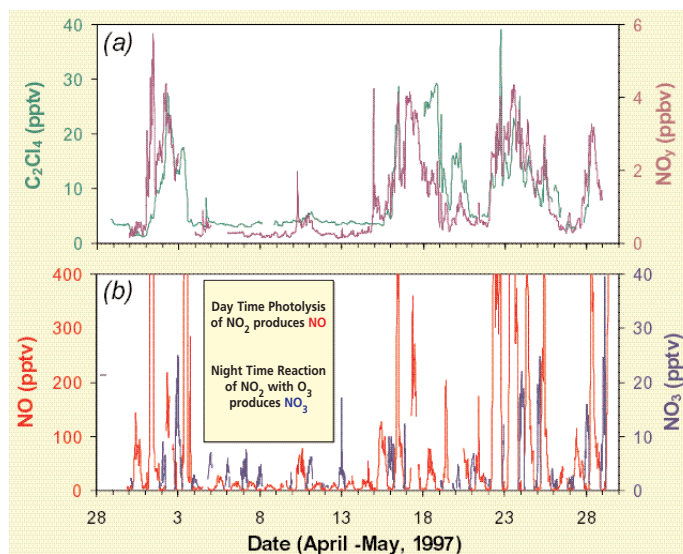
A number of interesting results emerged (see figure right). Firstly, concentrations of RO_2 and HO_2 were highly correlated with ozone photolysis rates ($J(\text{O}^1\text{D})$). Secondly, these radicals contributed significantly to the photochemical production of ozone throughout spring and summer (see *Making ozone in the marine boundary layer at Mace Head*). Thirdly, the time dependence of the measured peroxy radical diurnal cycle in different air masses agreed well with predictions from models. Finally, we were surprised to find substantial concentrations of both RO_2 and HO_2 at night. It is believed that these were produced primarily from reactions between ozone and alkenes, with a lesser contribution from NO_3 chemistry.

The presence of small amounts of reactive nitrogen compounds (NO_y) in the atmosphere has a huge impact on free radical chemistry both during the day and at night, and on the ozone budget. One of the prime objectives of ACSOE was to make measurements of the different forms of NO_y throughout the troposphere in both clean and moderately polluted air. This was achieved through the commissioning of a 4-channel NO_x/NO_y instrument from the US National Oceanic and Atmospheric Administration. This instrument (dubbed “ NO_{xy} ”) is capable of simultaneously measuring NO , NO_2 , NO_y and NO_y minus HNO_3 at concentrations below 10 pptv, such as may be encountered in clean marine air. Peroxy acetyl nitrate (PAN), another important component of NO_y , was measured separately by gas chromatography.



The 4-channel NO_{xy} instrument used in many of the ACSOE experiments.

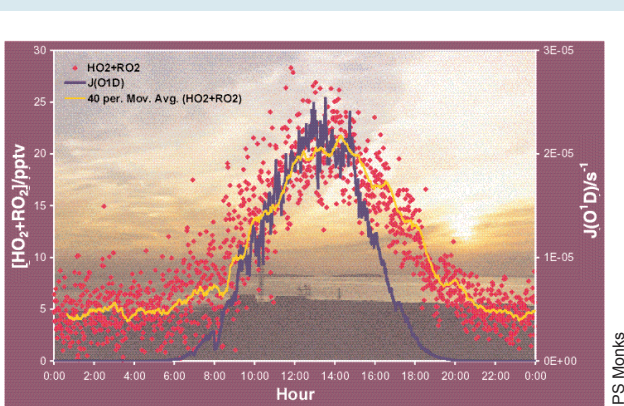
SA Penkett



Time series of (a) C_2Cl_4 and NO_y and (b) NO and NO_3 during the EASE'97 campaign at Mace Head, Ireland.

With the exception of minor forms such as methyl nitrate, almost all the NO_y in the atmosphere measured at the surface is associated with human activities. This was clearly seen in the close correspondence of NO_y and C_2Cl_4 (a perfect anthropogenic tracer) measurements at Mace Head during EASE'97 (see figure above, panel a). This was true for periods when the air had a polluted origin in early May, and from 15 May onwards, and also in the window between 5 and 14 May when the air was mainly from the Arctic.

A small contribution of NO and NO_2 to total NO_y was measured in the clean sector air, which almost certainly derived from decomposition of PAN, which accounted for the bulk of the NO_y . A time series of NO (see figure above, panel b) shows the variation of NO during EASE'97. Of special interest was the diurnal variation in the Arctic air, where up to 20 pptv of NO was present at midday. This NO would have reduced the net photochemical loss of ozone, and would have been important in maintaining the ozone concentration between 40 and 50 ppbv for most of this period (8-14 May). At night the NO , which is formed by the action of sunlight on NO_2 , disappears and some of the NO_2 is converted to NO_3 radicals, as discussed in the preceding section. This is clearly seen by the NO_3 trace in the figure. These are just a few aspects of the increased understanding of the NO_x in the background atmosphere of the Northern Hemisphere to come from ACSOE. NO_x is mostly man-made and it has perturbed both the ozone budget and free radical chemistry throughout the hemisphere.



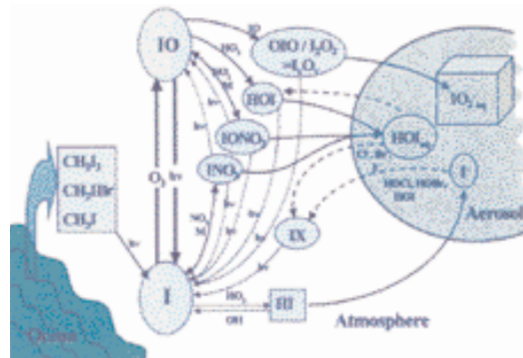
PS Monks

Measurements of peroxy radicals and $J(\text{O}'\text{D})$ in a westerly air stream during the summertime of 1997 at Mace Head, Ireland.

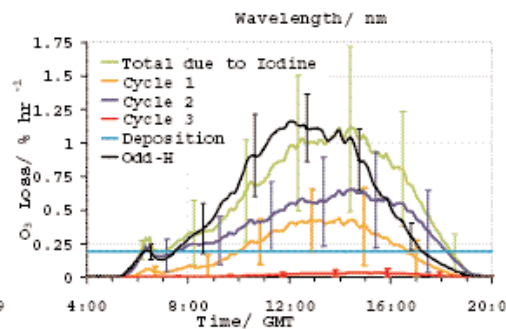
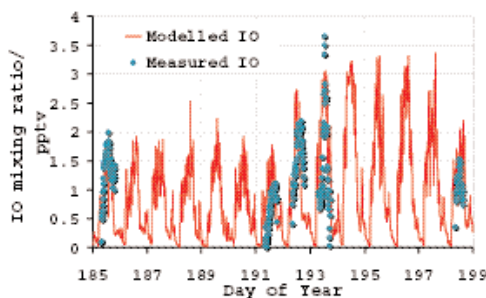
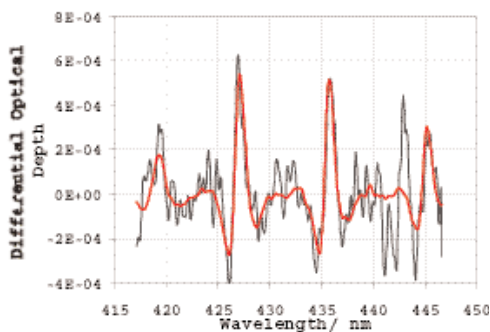
Chemical cycles involving reactive iodine species have the potential to significantly affect oxidative chemistry in the marine atmosphere. Prior to the ACSOE program, there was no direct evidence of the gas-phase cycling of reactive iodine in the atmosphere. Such evidence was provided during EASE'97 by DOAS observations of the iodine monoxide radical (IO). Spectra in the appropriate (415 to 450 nm) wavelength range were taken on five days, IO being present significantly above the detection limit on one of these.

The source of iodine in the Mace Head region is thought to be the local emission of iodocarbons from extensive seaweed beds there (see *Coastal ocean sources*). Subsequent observations of IO during the ACSOE experiments on the island of Tenerife (see figures below), where such coastal effects are largely absent, and

In addition, the prediction of huge iodine enrichments in marine aerosol is in good agreement with the numerous observations that have been made over many years of such enrichments, but which have never before been satisfactorily explained. Investigation of the possible subsequent activation of chlorine and bromine from sea salt as a result of this iodine chemistry is now underway.



Above: a simplified representation of the atmospheric iodine reaction scheme.



Left: differential optical density spectrum of IO from an observation on Tenerife.

Centre: observed and modelled IO for Tenerife.

Right: predicted diurnal profile of the average ozone destruction on Tenerife, comparing ozone removal by OH photochemistry, deposition to the surface, and iodine chemistry:

Cycle 1 involves HOI, Cycle 2 involves INO_3 and Cycle 3 involves OIO.

of both IO and the iodine dioxide radical (OIO) during a subsequent 'spin-off' experiment in Tasmania, all suggest that atmospheric iodine chemistry may not be confined to the coastal margins, but could be widespread over the oceans.

Implications of the observed iodine levels were investigated using a box model constrained by the observations of iodocarbon precursors and other relevant trace gases. Observed IO and OIO levels during each experiment were reproduced using a reaction scheme whereby reservoir species formed from IO (HOI, INO_3 , HI), are recycled through sea salt aerosol. It was found that iodine can destroy significant amounts of boundary layer ozone, and in the process convert NO_x into aerosol nitrate.

Chemical clues in ice

WT Sturges, R Mulvaney, JM Barnola, J Chappellaz

An historical perspective on atmospheric chemistry arose from measurements of trace gases in air extracted from deep polar snow (known as 'firn'). Although many of the reactive species that determine atmospheric oxidising capacity are not preserved in the firn, other gases are 'smoking guns' to past chemical behaviour. An example is the reaction of hydroxyl radical (OH) with man-made gases such as hydrochlorofluorocarbons (HCFCs). HCFCs are emitted in the Northern Hemisphere, and are broken

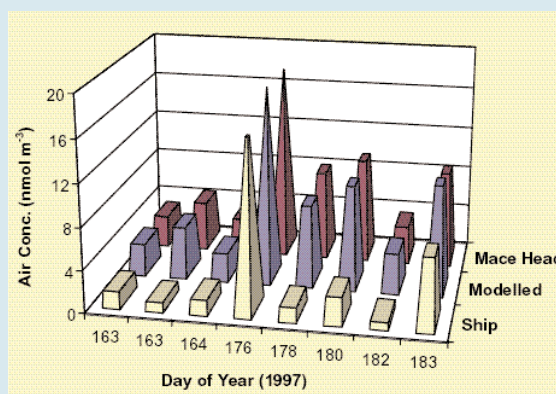
The oxidation of dimethyl sulphide (DMS)

RM Harrison, AG Allen, JD James, L Grenfell, NH Savage, CN Hewitt, B Davison, L Robertson

Oxidation of DMS is a process of great importance in the marine atmosphere, as it appears to be the main route to new particle formation. There are still major uncertainties in the precise chemical mechanisms by which DMS is oxidised, but the main oxidation products are recognised to be sulphuric acid and methane sulphonic acid (MSA). Sulphuric acid, in combination with water vapour and ammonia, is known to be able to condense from the vapour phase to form wholly new particles. This is the only known process of new particle formation in the marine atmosphere, and it is believed to be responsible for the formation of new particles in remote marine atmospheres that subsequently grow in size and act as cloud condensation nuclei.

During ACSOE, daytime measurements were made of DMS and its oxidation products both at Mace Head, and on board the RRS Challenger positioned some 160 km off the coast and directly upwind. Since the travel time of air between these sites is known, the rates of chemical conversion of DMS to products in westerly maritime air masses could be determined. This was then compared to predictions from a numerical model incorporating the best available knowledge of DMS chemistry obtained from laboratory investigations.

The results consistently demonstrated that DMS oxidation in the marine atmosphere proceeds at a rate several times faster than would be inferred from reaction with OH, which is expected to dominate daytime oxidation under such conditions. The figure below shows a comparison of measured and modelled oxidation product concentrations, which are seen to compare well when the rate of reaction of DMS with the hydroxyl radical was artificially increased by a factor of 3.3 in the model. The implication is that other reaction processes of DMS, possibly involving BrO, or oxidation in the liquid phase of suspended particles, are responsible for the majority of daytime DMS oxidation under clean air conditions. Furthermore, the results imply that new particle formation in the remote marine atmosphere can proceed more rapidly than had been assumed based on known chemical processes.



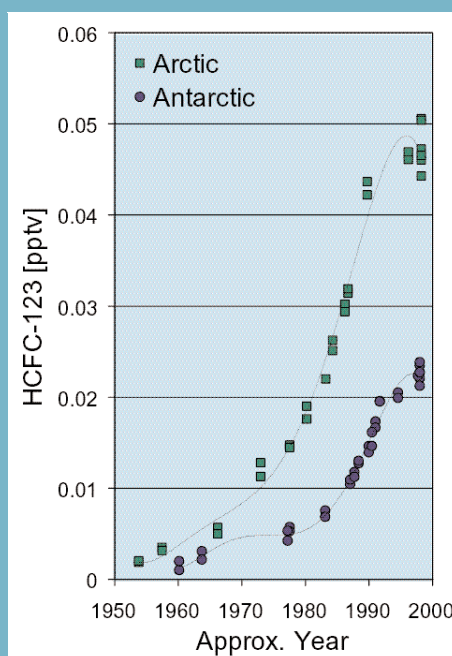
The molar concentration of oxidised sulphur species as measured at the ship and Mace Head, and as predicted by the model for Mace Head using an enhanced rate of DMS oxidation.

down in the atmosphere by OH.

Concentrations of the HCFCs in the Southern Hemisphere are, therefore, lower by an amount that depends on the global abundance of OH, the rate of reaction with OH, and the transport time.

The example here shows the results for HCFC-123 (CF₃CHCl₂). Southern Hemisphere concentrations can be seen to have closely tracked those in the north.

From studies of several such gases we are improving our knowledge of past atmospheric oxidising capacity. Oxidising capacity appears to have been relatively constant, at least over the last few decades, despite increased global air pollution.



Rising concentrations of HCFC-123 in the atmosphere deduced from measurements in polar firn. HCFC-123 has an average lifetime of 1.6 years in the atmosphere due to reaction with OH.

The Northern Hemisphere ozone budget

Many of the experiments carried out in ACSOE were designed to study ozone production and loss during spring and summer in relatively clean parts of the Northern Hemisphere, remote from large sources of pollution. Two ground-based campaigns were conducted at Mace Head, Ireland in the marine boundary layer, to follow the time development of free radicals and related compounds as the sun rises and sets. Aircraft experiments with the Met Office C-130 were based in the Azores to examine the potential for ozone production in the mid-Atlantic atmosphere from the surface up to 8 km, and to seek evidence for the presence of intercontinental transport of ozone. Additional information came from campaigns on the Jungfrauoch in the Swiss Alps, which allowed observations to be made of the diurnal cycle of ozone in the free troposphere.

Ozone in the troposphere has two main sources: the stratosphere and *in situ* production. The latter is strongly perturbed by emission of gases such as nitrogen oxides, hydrocarbons and carbon monoxide from human activities. ACSOE has helped to show that the ozone budget over the North Atlantic, and by inference throughout much of the Northern Hemisphere, is strongly impacted by pollution.

The measurements, no matter how extensive, only provide snapshots in time and space of the behaviour of ozone in the background atmosphere. Various model studies, however, have been conducted to calculate total ozone production and loss over larger regions of the Northern Hemisphere, and to understand the nature of the mixing processes between air from the surface and that injected from the stratosphere, which produce the observed ozone fields. The object of these model studies was therefore to produce a total ozone budget for these regions, and in doing so account for the concentration patterns actually observed.

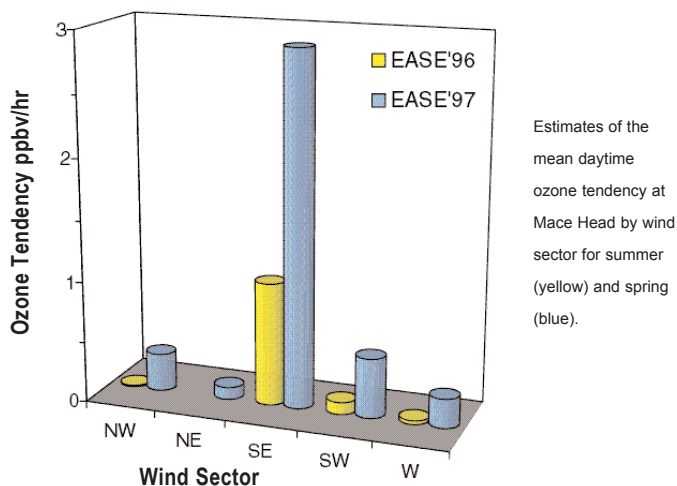
Making ozone in the marine boundary layer at Mace Head

PS Monks, G Salisbury, SA Penkett

A distinct annual cycle in ozone concentrations, with a broad maximum in the spring and a minimum in the summer, has been observed in a number of different locations in both the boundary layer and the free troposphere in the Northern Hemisphere. In contrast, winter maxima of many pollution tracers, including nitrogen oxides, carbon monoxide, methane and non-methane hydrocarbons, have been observed at remote sites in northern Europe. It is possible that the increase in photochemical activity in early spring, coupled with the build-up of relatively high levels of ozone precursors in the winter months, leads to high photochemical ozone production in spring, and hence makes an important contribution to the observed spring ozone maximum.

One of the objectives of ACSOE was to investigate the photochemical production of ozone in both spring and summer. Using a combination of free radical and trace-gas measurements at Mace Head, Ireland, estimates of the ability of the atmosphere to photochemically produce ozone (the "ozone tendency") were made. Incident air masses ranged from very clean air masses advected from the Arctic or the sub-tropical North Atlantic, to relatively polluted air masses originating over the British Isles and continental Europe.

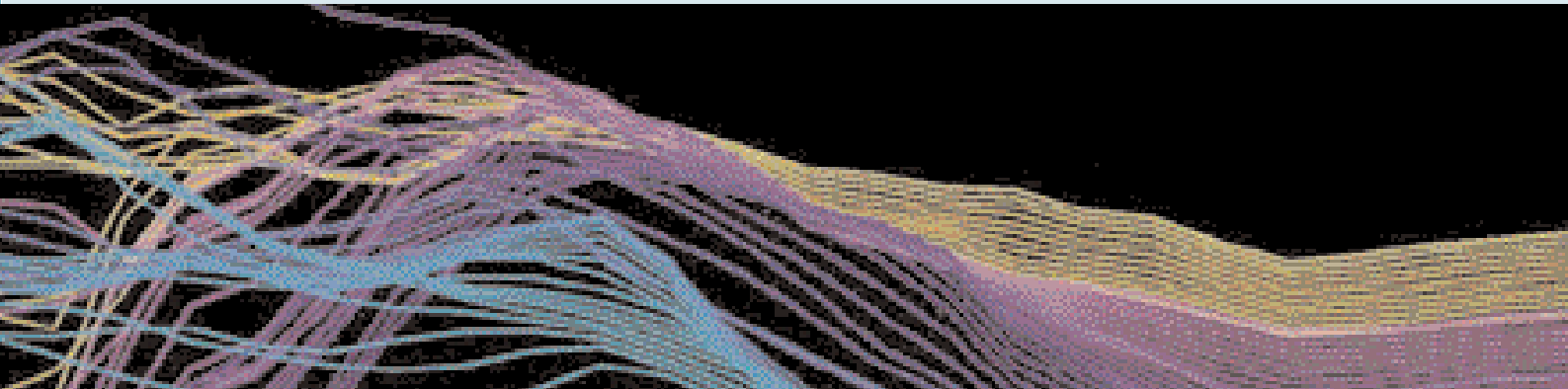
Analysis of ozone tendency by wind sector showed that polluted air masses dominated overall ozone production at Mace Head during both field experiments. The proportion of polluted air masses encountered at Mace Head was greater in the spring campaign than in the summer. In addition, the ozone tendency was greater for all wind sectors in the spring. Overall the average ozone production rate was almost three times higher in EASE'97 (spring) than in EASE'96 (summer). This demonstrates the importance of urban plumes to the ozone budget of remote locations, and suggests that the Northern Hemisphere spring ozone maximum is controlled, at least in part, by *in situ* photochemistry.



Meteorological models estimate the movement of air, allowing calculation of 'back-trajectories' that show the path of the air to a particular point. These were used in forecast mode for air-sea-ground experiment planning, as described in *Mace Head 'EASE' campaigns*, and also to plan flights of the C-130 aircraft such that it could sample particular air mass types. Back trajectories were also calculated from analysed meteorological data for an ensemble of points around and above Mace Head, along the flight tracks of the C-130, and for ascents of the Aberystwyth ozonesondes. This has proved extremely useful for determining the origin and history of air masses, both for case studies of particular episodes, such as identifying incidents of long-range pollution transport, and for air mass classification studies.

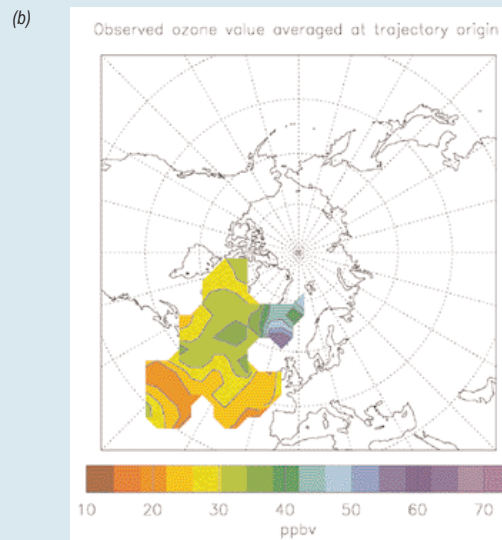
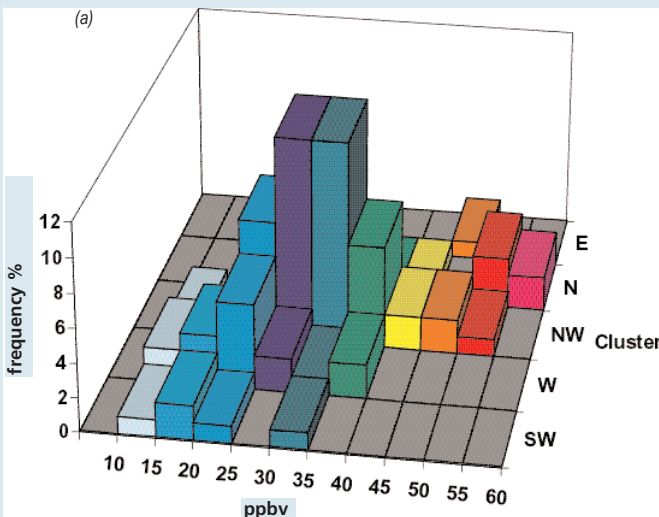
A statistical analysis technique has been used to create a climatology of air mass types arriving at Mace Head during the period 1995-97. Five distinct clusters of air mass trajectories exhibiting common origins were identified, as shown in panel a of the figure below. This allows an assessment of how typical conditions were during the two field campaigns, and enables the chemical observations to be considered in this context.

Furthermore, the relationships between the origin of the trajectories and the observed concentrations of various chemical species have been estimated using a new technique, which creates maps of average chemical concentration as a function of air mass origin ("origin averaged field": panel b). This technique has also been applied to the CiTTYCAT model (see p. 24) to estimate the origin averaged field of modelled ozone change along trajectories.



Panel a. Hourly average ozone concentrations measured at Mace Head during EASE'96, separated into the 5 main trajectory clusters. The frequency of occurrence of the different air mass types is shown along with the distribution of ozone concentrations associated with each. Air from the west and south-west, from over the Atlantic Ocean, can be seen to have had smaller ozone concentrations than air from the east and north, which had passed over Europe.

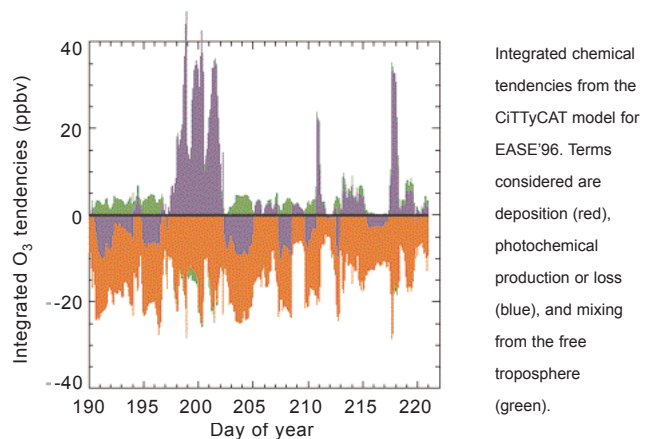
Panel b. Origin averaged observed ozone for Mace Head during EASE'96. Each 5 day back trajectory is labelled with the observed ozone at its arrival time at Mace Head, and then these values are used to calculate the origin averaged field. In agreement with panel a it shows lower ozone originating from the west and south-west, and higher ozone from the north. The high ozone shown apparently originating over Iceland relates to trajectories that had typically passed over north-west Europe earlier, picking up pollution and producing ozone (e.g. trajectory A on p. 9).



One of the aims of the ACSOE programme was to understand the processes controlling the concentration of ozone in the marine environment. The CiTTYCAT (Cambridge Tropospheric Trajectory model of Chemistry And Transport) model was developed to investigate the mechanisms leading to changes in ozone concentration on synoptic time scales (days to weeks). We have used it to study the ozone observed during the EASE'96 campaign at Mace Head, Ireland. The model uses the path taken by an air-parcel to arrive at the measurement site (its back trajectory) to infer the processes that change the concentration of ozone in an air mass from its climatological background state. In this way, the model can be used to investigate the relative importance of different processes in controlling the concentration of species observed at a site.

The figure (right) shows the cumulative effect on ozone of different processes occurring in the air masses arriving at Mace Head. The processes considered in the model are deposition to the surface, net photochemical production or loss, and mixing from the free troposphere. The important processes are the deposition and photochemistry, with mixing playing a minor role. There was, however, a large degree of

day to day variability. In clean conditions (e.g. Days 190 to 195), both photochemistry and deposition combined to remove ozone from the marine boundary layer, typically at a rate of a few ppbv per day. In these situations, the marine boundary layer acts to rapidly clean the atmosphere of pollutants. However, if the air arriving at the site originated from the UK (e.g. Days 196 to 200) pollution injected into the air mass resulted in photochemical ozone. In this event over 30 ppbv of ozone was produced as the air mass passed over the UK. By separating out the processes controlling ozone production, a model such as CiTTYCAT helps us to understand and quantify the role of the marine environment in cleansing the troposphere of pollutants.



Are trees that green?

DE Shallcross, PS Monks, N Carslaw, MJ Evans, AC Lewis, MJ Pilling, SA Penkett, PG Simmonds, JA Pyle

During the ACSOE campaign, high levels of ozone were observed on certain days, which were associated with urban pollution originating from mainland Britain. However, more detailed inspection using computer models has revealed that the levels of ozone predicted from the evolution of these urban plumes was somewhat less than that observed at Mace Head. Furthermore, when natural emissions of organic compounds from plants and trees, downwind of the urban source, were included (predominantly the molecule isoprene), the levels of ozone predicted rose significantly and were then in agreement

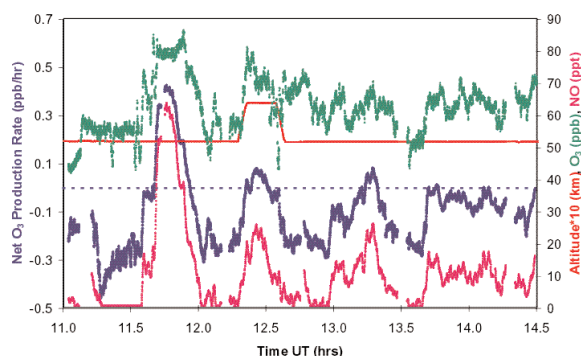
with the measurements made in Ireland. It should be stressed that these natural emissions alone cannot enhance levels of ozone. In concert with high levels of nitrogen oxides (NO_2 and NO), derived mainly from motor vehicles, natural emissions can, however, efficiently promote ozone formation. The figure illustrates the results of a computer simulation with and without these natural emissions, and it is clear that addition of these natural organic compounds makes a significant difference to the levels of ozone observed at remote sites, i.e. high ozone levels can be made a considerable distance away from the original pollution source. These findings have important ramifications for pollution control.

Calculated ozone, isoprene and NO_x along a single air mass trajectory arriving at 16:00 (GMT) on Day 199 at Mace Head, Ireland, showing the difference that the addition of the natural compound isoprene makes to ozone production.

An important quantity in the chemistry of the global background atmosphere is the NO “compensation point” (NO_{comp}). This is the concentration of nitrogen monoxide above which the atmospheric photochemical system switches from a state of net ozone loss to one of net ozone production, generally due to the presence of NO from pollution (notably vehicle emissions). Measurements made during two aircraft campaigns over the North Atlantic in April and September 1997 have been used to determine NO_{comp} and, for the spring flights (when NO measurements were available), net photochemical ozone production rates ($n\text{PO}_3$).

On average NO_{comp} showed no clear correlation with altitude in the lowest 4 km of the atmosphere with values mostly between 20 and 30 pptv, but above this height they decreased with increasing altitude to 10 - 15 pptv at 6 - 8 km. At the higher altitudes, the lower H_2O concentrations led to less ozone loss and hence lower values for NO_{comp} . The moist marine boundary layer (MBL) was found to provide an environment for rapid ozone loss but, once substantial ozone loss had taken place, only a small amount of NO was required to switch the system back into one of net photochemical ozone production.

The average calculated values of $n\text{PO}_3$ were mostly negative in the air masses sampled in April, ranging in altitude from about -0.4 ppbv/hr in the MBL to +0.05 ppbv/hr at about 7 km. This vertical trend was due to both lower values of NO_{comp} and higher concentrations of NO at the higher altitudes.



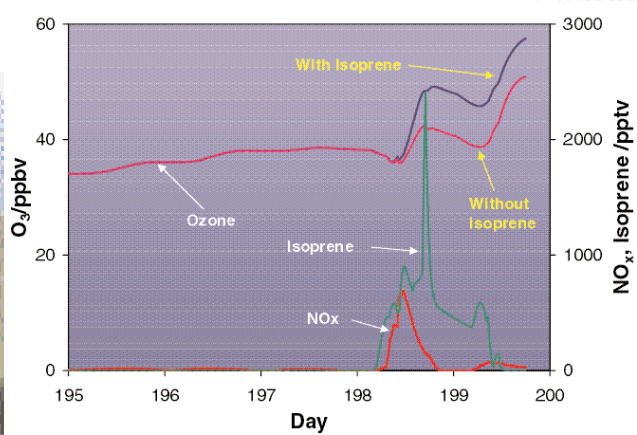
Net in-situ photochemical ozone production rates ($n\text{PO}_3$) calculated for flight A536 (10 April 1997) over the North Atlantic, along with observed ozone and NO concentrations and altitude of the aircraft.



CE Reeves

Some of the 'real-time' atmospheric chemistry instruments on board the C-130.

Policy makers must, for instance, balance the value of trees as carbon sinks against their potential role in ozone production. It is also noted that increasing global levels of CO_2 are expected to promote plant growth, and hence increase emissions of natural organic compounds, leading to an increased risk of high ozone episodes over wide regions of the Earth's surface.



SA Penkett

Much of the air sampled during the three April flights originated in the tropical MBL resulting in particularly low average NO concentrations and consequently low ozone production rates.

Departures from these average profiles were often observed. These appeared to be related to the specific origin and history of the sampled air mass.

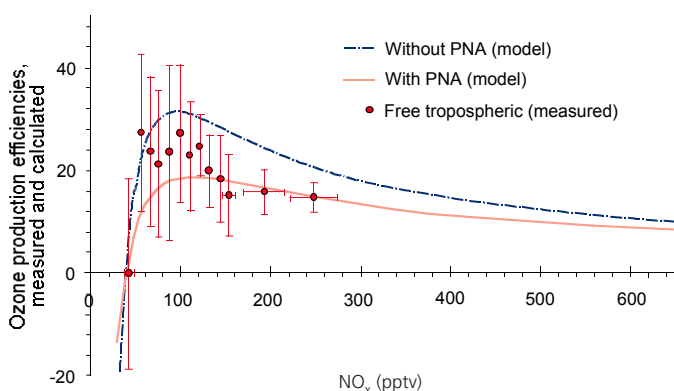
For example, on one flight a large air mass at 5 km altitude was found to contain elevated concentrations of NO and was calculated to have positive net ozone production rates (see figure above). Back trajectories suggested that this was due to long-range transport of pollution from over North America. On another flight a narrow plume with high NO concentrations, thought to have been emitted from a ship, was sampled over the mid-Atlantic within the MBL, and was found to have been rapidly producing ozone at a rate of 3 ppbv/hr.

Completing the ozone puzzle - from sea to the mountains

PS Monks, LJ Carpenter, E Schüpbach, P Zanis, SA Penkett, TJ Green, G Mills

The Jungfrauoch high alpine research station affords a rare opportunity to carry out prolonged atmospheric studies within the lower free troposphere - a region normally only accessible by aircraft. The free troposphere is removed from surface processes and localized emissions, and therefore offers a relatively simple chemical environment in which to study large-scale atmospheric processes. Such studies are vital for understanding atmospheric chemistry as a whole.

An important conclusion was that ozone is still being photochemically produced at altitudes high above ground in the continental free troposphere during spring. The cause of ozone production in this region is daytime nitric oxide (NO) levels of around 50 pptv, sufficient for the atmosphere to produce rather than destroy ozone.



The origins of the elevated NO concentrations are not well known. Degradation of potential NO_x reservoir species such as peroxy acetyl nitrate (PAN) was excluded by measurements and modelling studies. The so-called “ozone production efficiency” (defined as the number of molecules of ozone chemically produced per molecule of NO_x oxidised) was high at the Jungfrauoch at about 15 - 30 (see figure). High efficiencies at altitude due to reduced formation of nitric acid (HNO₃) were expected, but modelling the data indicated that another chemical process might be at work reducing the production efficiency.

At the cold temperatures of the free troposphere, peroxy nitric acid (PNA) is believed to be formed, which ties up some of the NO_x and HO₂ required for ozone production. These processes have important implications for understanding the way in which pollution impacts the remote atmosphere above the oceans and across the Northern Hemisphere.



Above: An extensive suite of instruments monitoring chemical species implicated in the control of ozone (O₃, NO_x, NO_y, HNO₃, PAN, CO, HO₂ + RO₂, HCHO, VOCs, etc.), were deployed at the Jungfrauoch High Alpine Research Station (3,580m above sea level) over a five-week period in 1996 and again in 1998. These constituted the FREETEX (Free Troposphere Experiment) campaigns.

Left: Comparison of measured and modelled ozone production efficiencies as a function of NO_x concentration. The model simulations were carried out with and without the formation of PNA. The measured values are the observed O₃/NO₂ ratios within a NO_x interval centred on the symbol - this ratio is a good approximation of the ozone production efficiency in the free troposphere.

A global perspective

JA Pyle, KS Law, MN Cobb

The 3-dimensional chemical transport model TOMCAT was used to study the budget of tropospheric ozone during the course of ACSOE. TOMCAT successfully reproduces the major chemical features of the troposphere so, by calculating a model ozone budget, we can gain an understanding of the true ozone budget. A budget scheme was developed to show how each chemical and physical process in the model contributes to the overall ozone budget. Globally, greatest net ozone production is seen in either hemisphere in the continental boundary layer during the summer, related to emissions into the boundary layer. Greatest photochemical loss of ozone occurs at the tropics all year round. In the Northern Hemisphere the largest production occurs over Asia and the USA with a smaller contribution from Europe.

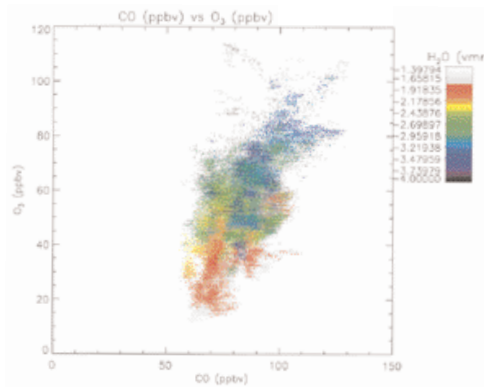
What can we learn from O₃:CO ratios?

KS Law, MJ Evans, JA Pyle, SA Penkett, S Schmitgen, the Met. Research Flight

The relationship between ozone and carbon monoxide (CO) has been used previously to estimate the amount of ozone (O₃) being exported from continents into the background troposphere. This is because CO is a major precursor to ozone and is emitted in large quantities in industrial regions. In this study, O₃:CO relationships were examined in air masses sampled during the 1997 summer C-130 flights, based in the Azores, to investigate factors affecting the concentration of summertime ozone in the troposphere between ~2 and 8 km.

The figure shows a composite of all ozone and CO from 5 flights coloured according to water vapour (H₂O) concentrations (as an indicator of air mass origin and availability of HO_x radicals). What is interesting is that different ozone, CO concentrations and ratios (varying from 0.3 to 0.8) exist for different abundances of

H₂O. In particular, larger ratios are evident in drier air masses. As well as higher CO, these air masses also had higher levels of condensation nuclei (CN), NO_y, and NO, indicating that they were more polluted, and generally they were sampled in the mid rather than the lower troposphere.



Air masses with lower ratios had lower ozone concentrations and higher H₂O, and originated largely over the North Atlantic. What is causing these differences? Is it photochemistry, or mixing with background air?

The CiTTYCAT model (see *Modelling short term changes in tropospheric ozone*) was run along typical 5 day, three-dimensional back trajectories, originating either from the polluted North American boundary layer, or from the relatively clean North Atlantic marine boundary layer.

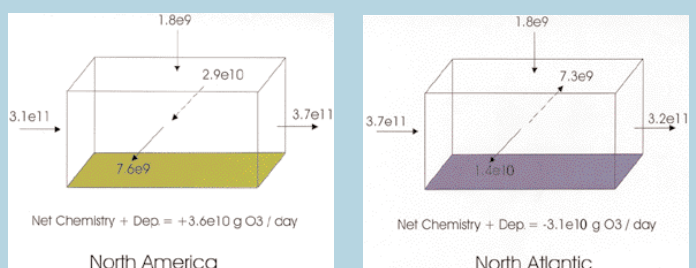
The most important result is that a combination of both photochemistry and mixing is required to reproduce the observed O₃:CO ratios and concentrations. In polluted air ozone can increase due to photochemical production, but also due to reduced photochemical loss resulting from lower water vapour in air that has been uplifted and dried. However CO concentrations, which are not really affected by photochemistry over a 5-day period, were calculated to be much higher than observed, suggesting that mixing with background air containing less CO must also have occurred.

Above: Ozone and CO measured during flights from the Azores over the central North Atlantic, colour coded according to water vapour concentration.

The net chemical budget was broken down into the key contributing reactions. The major source for ozone production is through the reaction of HO₂ and NO to form NO₂, which then leads to the formation of ozone. The tropics provide the major sink of ozone by photolysis followed by the reaction of O(¹D) with water vapour. This path for ozone destruction in the tropics is reasonably constant year round. The same reaction provides a small sink in the northern latitudes, where there is reduced solar radiation and water vapour.

Further studies were carried out to understand regional differences in the ozone budget. In particular, studies concentrated on the North Atlantic region. Two major areas were chosen for analysis. First, transport, chemistry and deposition over North America were analysed. Second, similar terms were calculated for the North Atlantic, as shown in the figure. The troposphere above North America sees net production of ozone in the TOMCAT model, with an enhanced flux of ozone to the North Atlantic compared with the flux into North America from the Pacific.

In contrast, the free troposphere above the North Atlantic is usually a sink for ozone, although on occasions heavily polluted air, in which ozone is produced, can reach Europe from North America. These findings are in broad agreement with the aircraft studies reported above. In one TOMCAT analysis, Asian emissions were identified as being a major contributor to ozone production in the Northern Hemispheric free troposphere.

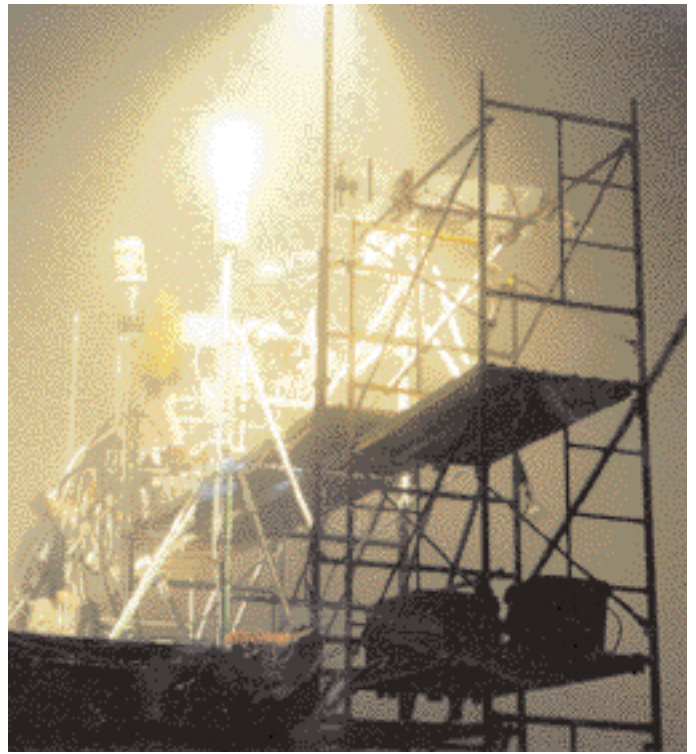


September average ozone fluxes calculated by TOMCAT over North America and the North Atlantic (in g O₃ per day averaged over the depth of the troposphere). Arrows show the horizontal (East - West and North - South) and vertical (from the stratosphere) ozone fluxes. The residual is the sum of the net chemistry and surface deposition terms.

Clouds and aerosols over the oceans

Clouds and aerosols have a profound affect on the radiation balance of the Earth's atmosphere, and hence on climate change. They are also mediums for a number of important chemical processes in the atmosphere. The cloud and aerosol studies performed under ACSOE were divided into two main components. One component was performed both in the sub-tropical North Atlantic between Portugal and the Canary Islands, and on the island of Tenerife itself in the Canaries. This component focussed on studies of the interactions of clouds and aerosols and, in particular, on an investigation of the processes controlling the evolution of aerosol properties between Europe and the Canaries in air advected off the continent by the NE Trades. The approach was to conduct both detailed "static" studies of processes in a hill cap cloud on a mountain ridge on Tenerife, and "Lagrangian" studies using the Met Office C-130 aircraft to revisit air masses at different stages of their evolution as they moved across the ocean. In the former studies, the cap cloud was used as a natural "flow through reactor" to study the response of clouds to in-flowing aerosol, and the subsequent processing of this aerosol by aqueous phase chemical processes.

The second component of the work was conducted at Mace Head, Ireland to investigate the formation of new particles in the coastal zone.



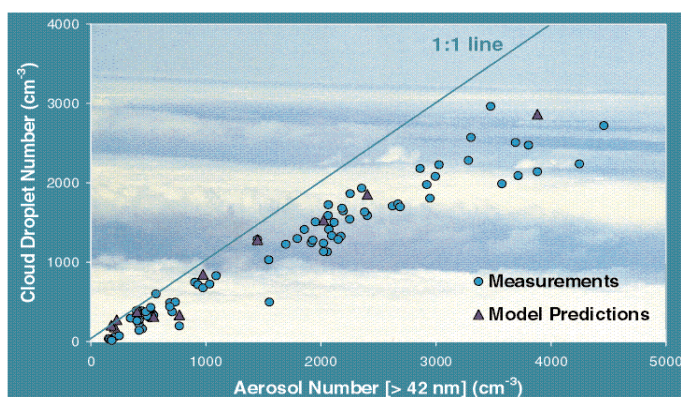
No time for sleep for scientists at Anaga ridge, making night and day measurements in the hill cap cloud.

Satellite image of the northeast of Tenerife. The main city of Santa Cruz is visible in the lower left. Marine altocumulus clouds are streaming in from the north, while a typical cap cloud formation can be seen sitting astride the main "Hillcloud" study area on the Anaga ridge (just above and right of centre).

Cloud droplet formation triggered by pollution

KN Bower, TW Choularton, MJ Flynn

Measurements were made on Tenerife within and in the vicinity of a cap cloud that was in contact with the ground along the Anaga ridge, to the northeast of the island. The origins of the aerosols arriving at the island during the campaign were varied, and ranged from being of clean oceanic origin to aged pollution aerosol originating over Western Europe. The aerosol size distribution and hygroscopic properties were measured at a site close to the shore upwind of the cloud, and then at sites leading up to, on the summit, and downwind of the cloud-capped ridge. Very large numbers of cloud droplets were detected during the polluted episodes, i.e. when the particle number concentrations were also very large (see figure below). It is unusual to see such high droplet numbers in clouds. In Global Circulation Models (GCMs) of the Earth's atmosphere, cloud droplet number is usually assumed to be less than about 600 particles per cubic



centimetre (cm^{-3}), irrespective of the number of aerosol particles present. As can be seen, in the Anaga hill cloud, droplet numbers were routinely higher than this, with peak values exceeding 2000 cm^{-3} . This has important implications for the modelling of cloud radiative properties: a key uncertainty in current climate models.

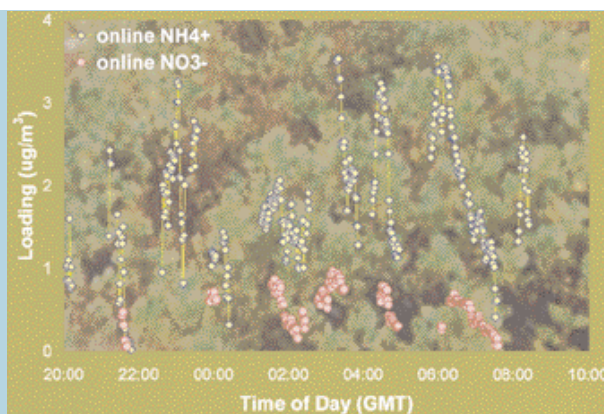
The explanation for these very large cloud droplet numbers is that during long range transport of pollution from Europe, aerosols evolve so that each particle becomes very hygroscopic (consisting mostly of ammonium sulphate and nitrate salts). This enables them to take up water vapour efficiently and to act as cloud condensation nuclei (CCN). Normally the numbers of such particles are controlled by loss mechanisms such as rainout. Between mainland Spain and Tenerife, however, very little precipitation occurs to remove particulate pollution, and so they remain in the air arriving at the island. As the air rises over the hills, it cools and water vapour condenses onto the particles to form large numbers of cloud droplets.

Left: Plot of cloud droplet number concentration against number concentration of aerosols in the size range larger than 42 nm (this is normally expected to include all CCN, i.e. the particles on which cloud droplets form). The solid 1:1 line shows the relationship that would exist if all the aerosols were to act as CCN. The model referred to here incorporates detailed cloud microphysics and aqueous phase chemistry, initialised by measured upwind aerosol properties. The close agreement with observations suggests that this model has successfully replicated the crucial processes occurring within the Tenerife aerosol-cloud system.

Enhanced nitrogen deposition

JN Cape, GG McFadyen

The Anaga ridge, at the north-east tip of Tenerife, receives much of its water as intercepted cloud water. This water supports a vigorous cloud forest of laurel and tree heather in an otherwise arid climate, and also provides sufficient moisture for small-scale agriculture. Pollution blown from Europe can, however, reach these islands, and be deposited with the cloud water. On one of the nights when we made measurements, the concentration of nitrogen (as both ammonium (NH_4^+) and nitrate (NO_3^-) ions) was found to vary with cloud cover. If the average deposition rate observed was applied to the whole year, it would be equivalent to $15 \text{ kg of nitrogen ha}^{-1}$ each year. While this is not large in agricultural terms, it represents a significant input of plant nutrients to an otherwise poorly fertilised ecosystem, and is similar to rates of nitrogen deposition observed in more polluted upland areas of England.



Above: Time history of nitrate and ammonium ion loadings in cloud water observed in the Tenerife hill cloud during long range transported pollution conditions.

Below: Cloud forest and subsistence agriculture on the Anaga ridge.



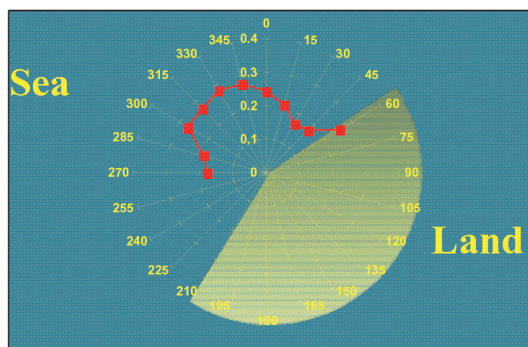
KN Bower

Ammonia from land and sea

C Milford, MA Sutton



Ammonia gas (NH_3) concentrations (below left) measured at the top of the Punta del Hidalgo lighthouse, Tenerife (top left). The red line shows the average concentration of ammonia in air, in $\mu\text{g m}^{-3}$, in relation to wind direction at the lighthouse, for all periods when the wind speed was more than 0.8 m s^{-1} (to avoid the influence of local sources).



Ammonia gas (NH_3) dissolves rapidly in cloud droplets to form ammonium ions (NH_4^+), and the cloud water acidity is reduced. When cloud droplets evaporate, the ammonium ions may be retained as solid ammonium-containing particles, or may be released back into the gas phase as ammonia. Many of the chemical reactions that occur in cloud droplets are strongly dependent on the acidity of cloud water, so ammonia plays an important role in determining cloud chemistry. There are many sources of ammonia from land-based activities. We identified large emissions from decaying potato haulms and from livestock on Tenerife. Less well understood are marine sources. By measuring ammonia concentrations from the top of the lighthouse at Punta del Hidalgo on Tenerife, in relation to the prevailing wind direction, we were able to show that even when the wind comes from the open Atlantic Ocean, the air contains significant concentrations of ammonia, up to $0.3 \mu\text{g m}^{-3}$. When the wind came off the island, ammonia concentrations were much greater, reflecting the various agricultural sources nearby.

Chemical processing in clouds

MJ Flynn, KN Bower, TW Choularton, GG McFadyen

Measurements of aerosol size distribution and chemical composition were made both upstream and downstream of the hill cap cloud. The measurements of chemical composition were made using Berner impactors, which enable aerosol chemistry as a function of size to be determined. It was found that passage through the cloud caused modification of both the aerosol size distribution and chemistry. The main causes of these changes were:

- Uptake of nitric and hydrochloric acid from the gas phase into the cloud droplets. These were then fixed in the aerosol phase by the uptake of ammonia gas to form ammonium salts. Out-gassing from large sea salt particles produced hydrochloric acid (HCl), which is important in the growth of small particles. Nitric acid (HNO_3) concentrations were higher in the polluted

episodes, and calculations implied that these were higher than could be accounted for by NO_2 oxidation alone. It is thought, therefore, that the nitric acid was mostly produced by out-gassing from nitrate-rich aerosol transported from Europe.

- Oxidation of sulphur dioxide (SO_2) by hydrogen peroxide (H_2O_2). The SO_2 was produced naturally from oxidation of dimethyl sulphide, and concentrations were low (typically only 30 pptv). H_2O_2 concentrations, in contrast, were in large excess (typically 0.3 to 1.0 ppbv).

Thermodynamic analyses (see figure) showed that entrainment into the boundary layer was very small as air flowed over the hill, so this did not affect the results. The analysis did show, however, that substantial entrainment had occurred upwind of the island, as was also shown in the aircraft studies described opposite.

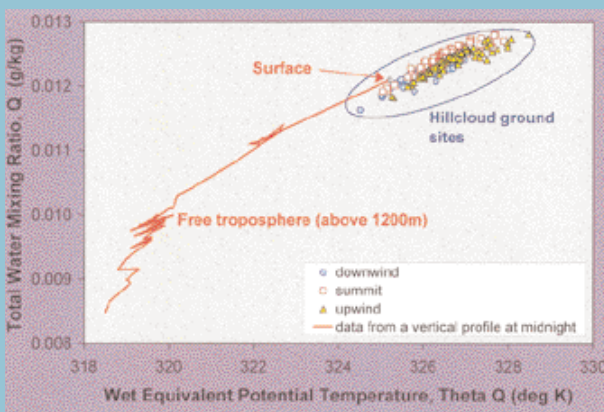
The aim of these experiments was to quantify the physical and chemical processes affecting the evolution of the major aerosol types observed over the sub-tropical North Atlantic. This was done in a Lagrangian framework in which air parcels were tagged, sampled, and followed over several tens of hours, during which the physical and chemical processes occurring were intensively measured. Three cloudy and three clear-air Lagrangian experiments were carried out within ACSOE using the Met Office C-130 aircraft flying between the SW tip of the Iberian Peninsula and the Canary Islands. The characteristics of the three cloudy Lagrangian experiments were very different, enabling a wide range of processes to be studied (see figure below).

In the first case, a clean marine air mass was studied in which sea salt production, due to increased wind speed, dominated the changes in accumulation mode aerosol concentrations. In the second Lagrangian, extensive cloud cover resulted in the processing of aerosol in a polluted air mass. Entrainment of air from the free troposphere was a major contribution to the decrease in aerosol concentrations over time observed in the boundary layer. The third cloudy flight showed little change in the aerosol characteristics, with aerosol in the boundary layer being constantly 'topped-up' by entrainment from a residual continental boundary layer above.

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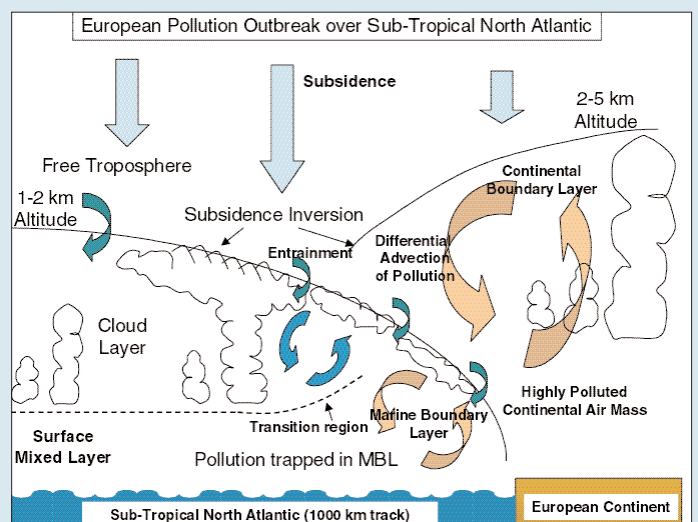


The C-130 prepares for a research flight.



A 'Paluch' thermodynamic diagram shows the parameters Q and Theta Q at the ground based sites, and also during a balloon launch. The scattering of points at the ground sites with time suggests that mixing was occurring upwind of Tenerife, while the close agreement between sites at any given time suggest little entrainment between sites.

Schematic diagram of the evolution of the polluted marine boundary layer during flow off the European continent and out over the sub-tropical North Atlantic.



Measurements of the number density of airborne particles at Mace Head during the ACSOE campaigns revealed frequent daytime occurrences of massively increased particle numbers. These were most marked in air coming off the Atlantic Ocean, when particle counts could change almost instantaneously from a background of just 200 cm⁻³ up to more than 100,000 cm⁻³. Such occurrences took place only during daytime, but did not appear to depend on any particular wind direction. To our surprise, the phenomenon was found to be strongly connected to the state of the tide. The figure below shows that the highest daytime concentrations of particles always occurred close to low tide. There was also evidence of corresponding elevations in OH concentrations, suggesting an intimate relationship with photochemistry.

No such particle bursts were observed from the RRS Challenger, sailing 160 km offshore of Mace Head. Neither were any recorded at the coastal site in Tenerife. The Tenerife coast has very low marine biological productivity. It is presently thought, therefore, that the particle bursts are related to emissions of biogenic gases, possibly sulphur or iodine-bearing gases, and possibly associated with seaweeds or other near-shore biota, as discussed elsewhere in this report (*Coastal ocean sources*).

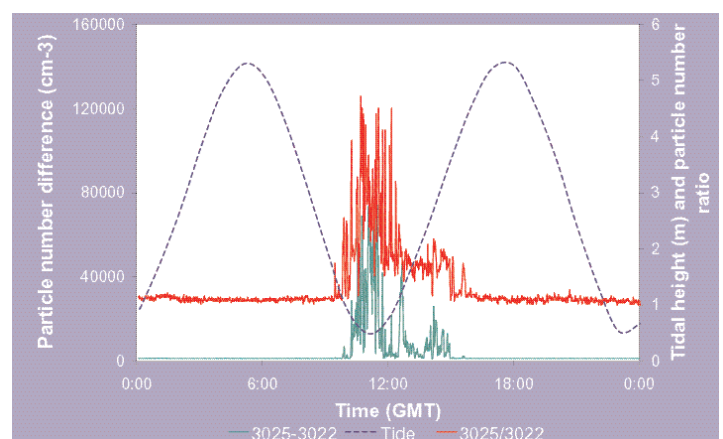
M. Geever



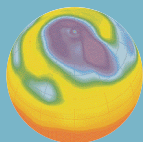
Studies using two particle counters in tandem, with different operational size ranges, showed that a large proportion of the particles measurable within a burst were in the range of just 3 - 7 nanometres diameter (a nanometre is one millionth of a millimetre, 10⁻⁹ m), clearly indicating that they had been very recently formed, i.e. they had not had an opportunity to grow into larger sizes.

The conclusion from these observations is that either

- some chemical species, as yet unknown, released from the coastal zone at low tide facilitates the formation of new particles from the condensation of sulphuric acid (H₂SO₄), or
- the coastal zone releases a gas that is rapidly oxidised to an involatile material, which then condenses onto newly formed sulphuric acid droplets that grow to the size measurable by the particle counting instruments, and subsequently continue to grow into cloud condensation nuclei.



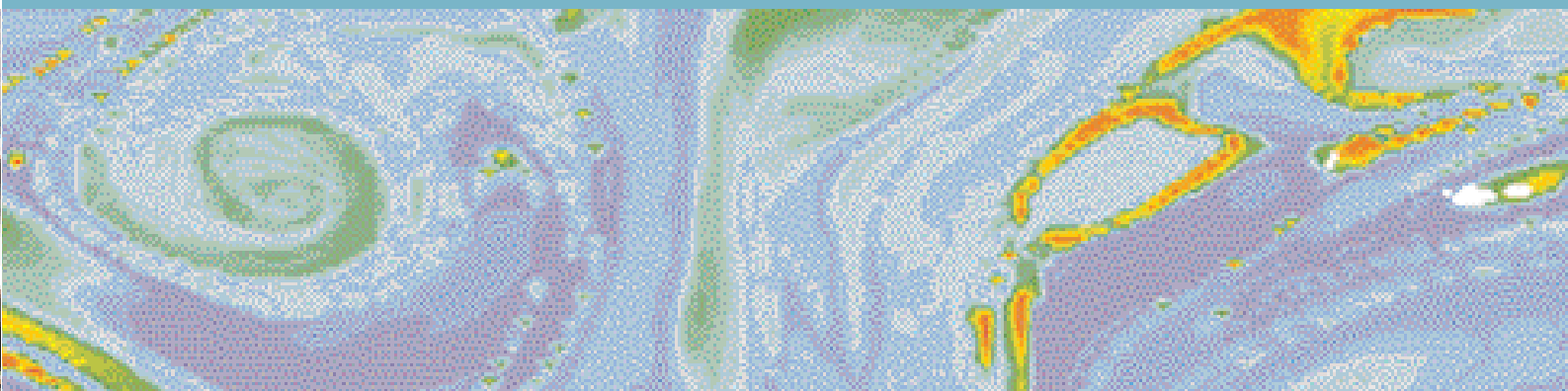
Plot of the difference between readings of two particle counters (TSI models 3025 and 3022, with lower size cut-offs at 3 and 7 nanometres respectively), the ratio between the two counters, and tidal height at Mace Head on 7 May, 1997.



Databases

ACSOE data are freely available to all through its two official NERC databases. Most of the data are available via the British Atmospheric Data Centre (BADC, <http://www.badc.rl.ac.uk/data/acsoe>), with the oceanographic data handled by the British Oceanographic Data Centre (<http://www.bodc.ac.uk/projects/acsoe.html>; enquiries to enquiries@bodc.ac.uk). ACSOE provided the first data set of its kind for the newly established BADC. This required the development of new automated data management procedures to ensure rapid dissemination and free flow of information within the ACSOE community, with intellectual property rights protected by a Data Protocol. All data were submitted to BADC in NASA Ames format, allowing automated error checking, cataloguing, and on-line query and data visualisation tools. This data management system has since been adopted as a model for other NERC Programmes utilising the BADC.

The BADC database for ACSOE lists seventy-two different measurement categories from ten separate 'campaigns'. Many of these measurement categories cover multiple chemical species such as non-methane hydrocarbons and halocarbons. Time scales of the measurements range from 'instantaneous' one second data, up to analyses of daily-integrated samples. BODC data covers multiple measurements collected during four separate ACSOE cruises. ACSOE has, therefore, left a lasting legacy of comprehensive, detailed and coordinated measurements in the ocean and in the background atmosphere across a wide area of the North Atlantic and its European seaboard.



Air mass trajectory prediction

An innovative and invaluable facility was the provision of regular three-dimensional air mass trajectories for the ACSOE field and aircraft campaigns (notably Mace Head and C-130 flights). These were provided by the University of Reading and BADC, based on data from the European Centre for Medium-range Weather Forecasting (ECMWF) model. During campaigns, trajectories based on meteorological forecasts were updated on a regular and frequent basis, and were accessed via FTP by investigators in the field. This proved crucial in planning experiments and in coordinating measurements between land, sea and airborne platforms. Trajectories based on analysed meteorological data (model runs constrained by observations) for the period of the field campaigns were also systematically calculated and archived on the ACSOE database and have been extensively used in many of the studies described here. An on-line version of this air mass trajectory computing system has since become available at the BADC, allowing registered users to retrieve sophisticated and customised trajectories for any specified location worldwide, via a simple and intuitive web interface.

Modelling capabilities

A number of modelling capabilities have been utilised in ACSOE, and in many cases have benefited from validation and development during the course of ACSOE. A number of these have been described in this report. Examples range from zero-dimensional models, in some cases based on the Master Chemical Mechanism, through to full 3-D chemical transport models such as TOMCAT. Certain trajectory models, such as CiTTYCAT and RATCATCHR, notably evolved as a result of ACSOE. Other products include chemical models of iodine chemistry, new particle formation, cloud microphysics-aqueous chemistry models, and a coupled ocean-atmosphere model of dimethyl sulphide cycling, amongst many others. Overall, a far more diverse and robust set of modelling tools than previously available have emerged from the Programme, to the benefit of the atmospheric and marine chemistry research community.

Dissemination of information

ACSOE research has resulted in over one hundred and fifty publications in peer reviewed journals, books, newsletters, and published reports, including papers in prestigious journals such as Nature, Science, Journal of Geophysical Research, Geophysical Research Letters, Faraday Transactions, Journal of Atmospheric Chemistry, Journal of Aerosol Science, Atmospheric Environment, Global Biogeochemical Cycles, and Limnology and Oceanography. A complete listing is available via the ACSOE web site.

International links

ACSOE was linked to a number of international programmes providing mutual benefit to both. The cloud and aerosol experiments, on and around the island of Tenerife, formed the UK component of the international Aerosol Characterization Experiment 2 (ACE-2). Likewise the Challenger cruise in the southern North Sea formed a crucial part of the air-sea gas exchange project ASGAMAGE, complementing work carried out on the Dutch research platform Meetpost Noordwijk. There was a good deal of time and data sharing with other projects on the C-130 aircraft, to derive maximum benefit from limited and costly flight hours. In many cases the same ACSOE investigators were involved in both, an example being the European Union (EU)-funded project Testing Atmospheric Chemistry in Anticyclones (TACIA). Coordinated flights were also made with research aircraft from other nations, including mid-Atlantic rendezvous with the US WP-3 aircraft and the German DLR Falcon. During EASE'97 ACSOE hosted the fieldwork component of the EU HALOTROP project, jointly leading to the discovery of reactive iodine chemistry in the marine atmosphere.

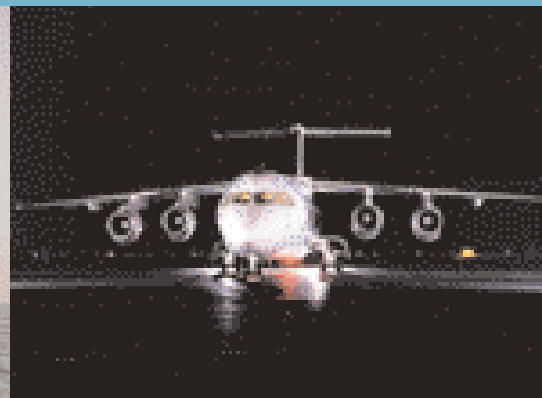
From left to right: The NOAA WP-3 seen from the C-130; the Meetpost Noordwijk, the 'new' BAe-146 research aircraft



SA Penkett



KNMI Royal Dutch Meteorological Institute



British Aerospace

Research activities emerging from ACSOE

Successful research activities frequently raise as many questions as they answer, and often lead on to further research. This is certainly true in the case of ACSOE. The discovery of particle bursts at Mace Head, for instance, led to the EU PARFORCE project (Particle Formation and Fate in the Coastal Environment) conducted at the same location in 1999. A return visit to Mace Head is also planned for 2002 to further investigate photochemical processes in the NERC-funded North Atlantic Marine Boundary Layer Experiment (NAMBLEX). This will use an updated version of the same instrument package deployed in the EASE campaigns. The same package has also been used to examine clean marine air chemistry on the other side of the world during the NERC Southern Ocean Atmospheric Processes Experiment (SOAPEX II) at Cape Grim, Tasmania. There has also been a follow-on campaign in the FREETEX series of campaigns on the Jungfraujoch.

The air-sea exchange cruise work has since led to the successful ANICE project (Atmospheric Nitrogen Inputs into the Coastal Ecosystem) and MEAD (Marine Effects of Atmospheric Deposition), both funded by the EU. ACSOE scientists have also been closely involved in the planning of SOLAS (Surface Ocean - Lower Atmosphere Study) – a major new IGBP initiative. Parts of ACSOE were in many ways prototypes of planned SOLAS experiments.

An important aspect of ACSOE was the development of a UK airborne atmospheric chemistry package - the first of its kind to fly on a UK aircraft, and the equal of counterparts in the US and elsewhere. This package has since been flown on the C-130 for projects such as the EU-funded MAXOX project (Maximum Oxidation Rates in the Free Troposphere), and the NERC-funded EXPORT (European Export of Precursors and Ozone by Long-range Transport) and UTLS (Upper Troposphere Lower Stratosphere) projects. This state-of-the-art instrument package will now be transferred on to the new NERC-MRF research aircraft, a four jet-engined British Aerospace 146, to further enhance the UK airborne research capability.

Summary

There are three overarching 'take-home' messages from ASCOE:

- Pollution spreads everywhere throughout the atmosphere - even more so than previously realised, impacting both global chemistry and climate. This has major repercussions given the projected rise in global air pollution resulting from dramatic increases in population and living standards in many parts of the world.
- Chemicals from the atmosphere have a profound effect on the oceanic web of life while, conversely, gases emitted from the oceans play vital roles in regulating atmospheric chemistry, particle production, and even the transport of essential elements. This calls for further assessment of the intricate feedbacks between air quality, ocean productivity, climate, and human health.
- Cloud chemistry and radiative properties - in the sub-tropical Atlantic at least - are far more affected by long-range transported pollution than present computer models necessarily allow for. It is vital to understand this effect given the important temperature regulation role played by clouds.

Overall, then, it is clear that the atmosphere exists in a delicately, if not precariously, balanced state with respect to natural chemical processes, interaction with the oceans, and the influence of pollutants swept off the continents. This makes the findings of ACSOE highly relevant to many policy issues. In particular it speaks to the 1979 Geneva Convention on Long-Range Transport of Air Pollution (CLRTAP) and subsidiary agreements, such as the 1999 Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone. It also speaks to the United Nations Framework Convention on Climate Change (UNFCCC, 1992), and to the revised Protocol that arose from the latter at the Kyoto Summit in 1997. Such studies are fundamental to the formulation and ratification process of these agreements. ACSOE is committed to making its findings public through international programmes and scientific assessments, such as those carried out by the Intergovernmental Panel on Climate Change (IPCC), the United Nations Environment Programme (UNEP), the International Geosphere-Biosphere Programme (IGBP), and through public accessibility to the entire project database.

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