

## PRECURSORS TO PARTICLES 2006 (P2P 2006)

### RELEVANCE OF CAMPAIGN TO SOLAS

This campaign will use the Cape Grim Baseline Air Pollution Station as the major measurement platform.

The Cape Grim Baseline Air Pollution Station is one of 23 Global Atmosphere Watch Stations and will have been in continuous operation for 30 years in April 2006. The campaign will build on the measurements currently made as part of the Cape Grim Program. This includes the following continuous relevant measurements:

### Routine Measurements

Radiation (PAR, direct, diffuse and global), carbon dioxide, methane, nitrous oxide, ozone, particle number concentration (CN), CCN, black carbon, radon and the non-CO<sub>2</sub> greenhouse gases, which including the ozone depleting gases, with methyl bromide and methyl iodide being of special relevance to this campaign.

Standard meteorological measurements are made continuously, with wind data available at 10m, 30m and 50m. A ceilometer and visometer will be installed prior to the campaign and will provide additional information on cloud cover, augmenting the measurements made by the Radiation Program.

Other non-continuous routine relevant measurements include the collection of discrete air samples (flasks) for halocarbons, oxygen/nitrogen, PM10 aerosol and PM2.5 aerosol (organic and soluble) and precipitation in clean air. A new program monitoring aerosol chemistry at 144m above sea level (at the 50m level on the tower at Cape Grim, to ensure sampling is free from the influence of the cliff bluff) commenced in July. The focus of this program is non-sea-salt sulfate and the role biogenic calcium plays in buffering the reactions in aerosol.

We also have a regular program of small boat work focusing on methyl bromide and iodide in the surface waters and air at a site 50km south of Cape Grim. This work includes biological measurements (secchi depth, Chl-a, nutrients (P, N and Si), species composition and cell counts) at 4 depths to 20m. During the 2005 forerunner to the 2006 campaign we started a 5km transect off Cape Grim, along 270°. This transect comprises of 5 stations, with biology at 4 depths and methyl halide concentrations in surface water at each station. Air samples are taken at the 100m and 5km stations.

### Campaign Measurements

In addition to the routine measurements above we will add the following:

Name	Institution	Activity	Frequency	Funding
Melita Keywood	CMAR	DMA particle size distribution	continuous	CGBAPS
		APS particle size distribution	continuous	CGBAPS
		P-Track (beach measurements)	targeted	CGBAPS
		Flow tube Experiment	targeted	CGBAPS
		2 stage Impactor at 50m	2-weekly	CGBAPS
John Gras	CMAR	Nephelometer, particle scattering coefficient	continuous	CGBAPS
Brailsford	NIWA	CO <sub>2</sub> /O <sub>2</sub> continuous	continuous	CGBAPS
Galbally/Meyer	CMAR	NO <sub>x</sub>	continuous	CGBAPS
Ian Galbally	CMAR	VOCs PTRMS and passive	continuous	CGBAPS
Rob Gillett	CMAR	Formaldehyde	Passive	CGBAPS
Mike Harvey	NIWA	ASASP, DMS(air), TSI 3010, thermal preconditioning	continuous	NIWA
Zoran Ristovski	QUT	VHTDMA	continuous	ARC?

Roland Von Glasow	UHberg	1D modelling atmospheric chemistry	After expt	?
*Uli Platt	UHberg	MAX-DOAS	?	?
*Karin Kerher	NIWA	MAX-DOAS	?	?
*Keith Bigg	Independ	Single particle analysis	Targeted	?

\* Not yet confirmed as being involved in the campaign.

The aims of the campaign are as follows:

Identify and quantify the gaseous precursors involved in new particle formation at Cape Grim.

This would be achieved by:

1. Identifying new particle formation by measuring microphysical properties of the aerosol such as particle number concentration, particle size distribution, the hygroscopic growth and volatility of nano-particles, and size-resolved chemical composition of particles
2. Continuous measurement of implicated precursor gaseous species for new particle formation.
3. Using precursor gaseous and new particle data in model of atmospheric chemistry to assess likely impacts of various gases in particle formation at Cape Grim and compare with observations of new particle formation.
4. Measurement of particle number concentrations and a limited number of gaseous species (using flask sampling) on the beach below Cape Grim and compare these data with the measurements made 94m above the beach at the Cape Grim Station.
5. Making regular sampling trips along the new 5km, 270° transect at Cape Grim to monitor biology and surface concentrations of methyl halides and DMS in surface waters and the immediately above the surface water.

The campaign aims to focus on the region from the top of the marine boundary layer (~1000m) to 20m below the ocean surface.

#### SOLAS Activities directly addressed by campaign

##### Focus 1: Biogeochemical Interactions and Feedbacks Between Ocean and Atmosphere

The measurements obtained during the campaign will be used in a 1D model to understand the role that biogenic gas emissions and aerosol have in cloud formation (see below for more detail).

##### Activity 1.1: Sea-salt Particle Formation and Transformations

The aerosol samples collected at 144m above sea level will contribute to an understanding of the role of sea salt and biogenic material in the atmospheric sulfur cycle, with a particular focus on non-sea-salt sulfate and the alkalinity of the aerosol, which is critical in determining how much gaseous sulfur dioxide is incorporated into the sea salt aerosol, rather than forming new particles.

Single particle analysis will assess the role of organic material in particle nucleation.

This work has been and will continue to be incorporated into models to gain a better understanding of sea salt aerosol processing.

The campaign will contribute to Specific Goal IV.

#### Activity 1.2: Trace Gas Emissions and Photochemical Feedbacks

Our routine Phytoplankton Program fits this activity, monitoring methyl bromide and methyl iodide (and alkyl nitrates) in surface waters and in the air immediately above the surface (2m). In addition to these measurements, biological measurements are made at 0, 10, 15 and 20m and one tow is completed at each station, plus secchi depth. The aim of this program is to determine the biological parameters that influence methyl halide production in the waters off Cape Grim. While this program has been running at Couta Rocks, at a single station, for 5 years, we have now added the 5km transect directly off Cape Grim, providing more detailed information at 5 stations (100m, 1km, 2km, 3km and 5km) along 270°.

The Non-CO<sub>2</sub> Greenhouse Gases Program (part of AGAGE) at Cape Grim provides the long term background measurements of methyl halides in clean air and this program provided the impetus for the Phytoplankton Program, since the fluxes of methyl bromide in this region are poorly understood.

The entire Cape Grim program fits well within Activity 1.2, including measurements as given above.

The campaign will assess VOCs, using a PTRMS and passive gas samplers.

Measurements on the beach below Cape Grim will assess the role of radiation and tides in particle formation. Measurements to be made include CN and ultra-fine CN number concentrations, radiation and discrete seawater and air samples for DMS and methyl halides.

Two experimental techniques will be utilised to assess particle formation. Thermal preconditioning will be used to determine size-resolved aerosol chemistry (limited to four components), at a high time resolution. A flow tube will be used to assess the ability of particle-free ambient air to generate particles when exposed to UV radiation.

The campaign will contribute to Specific Goals I, III and V. While not a focus of the campaign measurements would also provide information that could be used to address Specific Goal II.

#### Activity 1.3: Dimethylsulfide and Climate

While DMS has not been measured continuously at Cape Grim since 1998, the now ceased Sulfur Program provided a great deal of information on the atmospheric sulfur cycle at Cape Grim, with measurements of DMS, sulfur dioxide and size-resolved aerosol chemistry.

During the campaign continuous atmospheric DMS measurements will be made at the station, with the possible addition of discrete seawater and air samples for DMS, collected on the 5km transect and from the beach 94m below the Cape Grim Station.

Sulfur dioxide measurements will be provided by a MAX-DOAS during the campaign.

As indicated above the sulfur cycle and the role of halogenated species in new particle formation or particle transformation will be modelled.

The campaign will contribute to Specific Goals II and III and in a limited way to Specific Goal I.

## Focus 2: Exchange Processes at the Air-Sea Interface and the Role of Transport and Transformation in the Atmospheric and Oceanic Boundary Layers

### Activity 2.1 Exchange Across the Air-Sea Interface

This activity will only be addressed in a limited way through the measurement of trace gases (methyl bromide, methyl iodide and DMS) in both surface waters and the lower atmosphere.

The campaign will contribute to Specific Goal I.

### Activity 2.3 Processes in the Atmospheric Boundary Layer

The campaign focuses on this area – on the processes that occur in the marine boundary layer which affect particle formation. Measurements of precursors gases, reactive gases, aerosol chemistry and particle number concentrations, will be used to assess correlations and used in a model for further assess the links between gases and particles.

In addition to the chemistry and the surface biology, the routine radiation and meteorological measurements will be essential in the modelling. Boundary layer height will be determined through daily radiosonde flights. The ceilometer will provided limited additional information.

The campaign would be enhanced if we could obtain a sounder to perform continuous assessments of boundary layer height. However we have not been able to locate one in NZ or Australia.

The campaign will contribute to Specific Goals II and IV.

## Focus 3: Air-Sea Flux of CO<sub>2</sub> and Other Long-Lived Radiatively Active Gases

### Activity 3.1 Geographic and Sub-Decadal Variability of Air-Sea CO<sub>2</sub> Fluxes

This is not a major focus of the campaign, but a continuous CO<sub>2</sub>/O<sub>2</sub> instrument will be added to the routine CO<sub>2</sub> measurements at Cape Grim during the campaign.

The instrument will be used at Cape Grim to assess the differences between the ocean flux from the oceans west of Cape Grim, when compared to the measurements made at Baring Head (NZ) in air derived from the ocean to the east of NZ, as there are anecdotal differences.

The campaign will contribute to Specific Goals I and III,

## Model Details:

The model to be used with the data generated from this campaign is a 1D model, with 150 levels in the atmosphere. Heterogeneous processes are included in the model with two aerosol and two cloud droplet chemistry size classes. Microphysics is calculated in 4900 bins and there is a 2-way feedback between microphysics and chemistry nucleation parameterisation. Aerosols are sized from 10 nm to 10  $\mu$ m and from the nucleation parameterization it is possible to determine an apparent nucleation rate to estimate new particle formation.

The model will be run by Roland von Glasow. For further information see the following references:

S. Pechtl, E. R. Lovejoy, J. B. Burkholder, R. von Glasow, Modeling the possible role of iodine oxides in atmospheric new particle formation, *Atmos. Chem. Phys. Disc.*, 5, 9907-9952, 2005

von Glasow, R. and P. J. Crutzen, Model study of multiphase DMS oxidation with a focus on halogens, *Atmos. Chem. Phys.*, 4, 589 - 608, 2004

von Glasow, R., R. Sander, A. Bott, and P. J. Crutzen, Modeling halogen chemistry in the marine boundary layer. 1. Cloud-free MBL, *J. Geophys. Res.*, 107, 4341, doi: 10.1029/2001JD000942, 2002

von Glasow, R., R. Sander, A. Bott, and P. J. Crutzen, Modeling halogen chemistry in the marine boundary layer. 2. Interactions with sulfur and cloud-covered MBL, *J. Geophys. Res.*, 107, 4323, doi: 10.1029/2001JD000943, 2002.

#### Data Management:

A Precursors to Particles 2006 (P2P 2006) database will be set up. All raw and QA/QC data from all participants is to be provided to the database within 3 months of the end of the experiment (end of May 2006).

There will be a post-campaign meeting to coincide with the mid-July 2006 Cape Grim Working Group Meeting, held in Melbourne, where the data will be assessed and discussed.

After this meeting a CD-ROM of all data (raw, QA/QC and meta) will be provided to all participants.

Data will also be presented at the Cape Grim Annual Science Meeting in October/November 2006.

Participants also hope that they will be able to present the results of this campaign at the joint CACGP/IGAC Meeting in Cape Town, South Africa, 17-23 September 2006.

Data will be embargoed for 2-3 years (earliest release date will be 1 March 2008, latest release date will be 1 March 2009) to allow participants to publish their own results. After this period the data will be made publicly available on the Cape Grim Data Website.