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# SOLAS–ANZ Dual Tracer Gas Exchange Experiment (Mar/Apr 2004):

# Science and Voyage Plan

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**Version 1.9 9 February 2004**

**Collated by Mike Harvey**

**SOLAS-ANZ Dual Tracer Gas Transfer Experiment**

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# C O N T E N T S

## C O N C E P T S

Phytoplankton blooms, either natural or stimulated, provide effective natural laboratories in which to study the pronounced biogeochemical fluxes and gradients associated with their evolution and decline. These phytoplankton-mediated signals are mainly expressed in the ocean, but also result in enhanced fluxes of $CO_2$, DMS and other biogenic gases across the air-sea interface. The use of a Lagrangian dual-labelling ($SF_6$, $^3He$) approach permits a number of questions pertinent to SOLAS, to be addressed.

The enhanced gas fluxes associated with a phytoplankton bloom provide optimal conditions for measuring the rate of gas exchange and the physical factors governing it. Few measurements have been made in the open ocean, particularly at high wind speeds. During the experiment the $SF_6$ tracer will serve not only to track the patch, but in conjunction with a second tracer with a different diffusion rate ($^3He$), it will allow gas transfer rates between the atmosphere and ocean to be determined. At the same time, key physical processes governing the exchange will be measured. These include near-surface turbulence (typically generated by breaking waves), temperature microstructure, stratification, wave field, wave breaking and wind speed. In conjunction with these process measurements, micrometeorological based techniques will be deployed to make direct atmospheric measurements of gas fluxes. This will allow a direct comparison with the exchange rates derived from the dual tracer technique.

## E X P E R I M E N T  G O A L S

Determine drivers and controls of ocean-atmosphere gas exchange quantifying:

*biological production and utilisation of climatic relevant gases in particular $CO_2$ and DMS) in the surface ocean*

*physical control of exchange across the interfaces of the surface mixed layer*

*production of aerosols resulting from interaction of biological and physical processes*

## O B J E C T I V E S

This experiment combines six main research objectives considering:

1. quantification of gas transfer fluxes and velocities
2. physical processes affecting gas transfer
3. ecosystem interactions controlling dissolved DMS concentration and $CO_2$ removal
4. the impact of iron availability upon phytoplankton productivity and its influence upon dissolved gas concentration

5. the impact of photochemistry in the surface ocean on dissolved gas concentration and air-sea exchange

6. the fate of DMS in the atmosphere and aerosol condensation nuclei production from chemical transformation in the atmospheric boundary-layer.

In order to assist with budget closure, a further sub-proposal of oceanic particulate aggregation and export is proposed:

7. Role of aggregation in the timing and magnitude of export processes

# Testing the CLAW hypothesis

The CLAW hypothesis (Charlson et al., 1987) is a series of linkages and interactions suggesting a climatic regulation by marine phytoplankton through dimethylsulfide emission at the ocean surface and atmospheric oxidation to sulfate aerosol which influence cloud albedo through the indirect aerosol effect.

The objectives of this experiment test 3 groupings of forward linkages (left hand side of Figure 1) of the CLAW hypothesis. The study is not limited to DMS and exchange of other climate relevant gases is also considered. (1) Objectives 1 & 2 will test methods and refine estimates air-sea exchange parameters. (2) Objectives 3,4 and 5 will examine factors controlling the seawater concentration of DMS. (3) Objective 6 will examine the early stages of atmospheric processing of DMS with the production of sulfur dioxide and sulfate in condensation nuclei (CN). Each of these three areas is elaborated on in diagrams below.

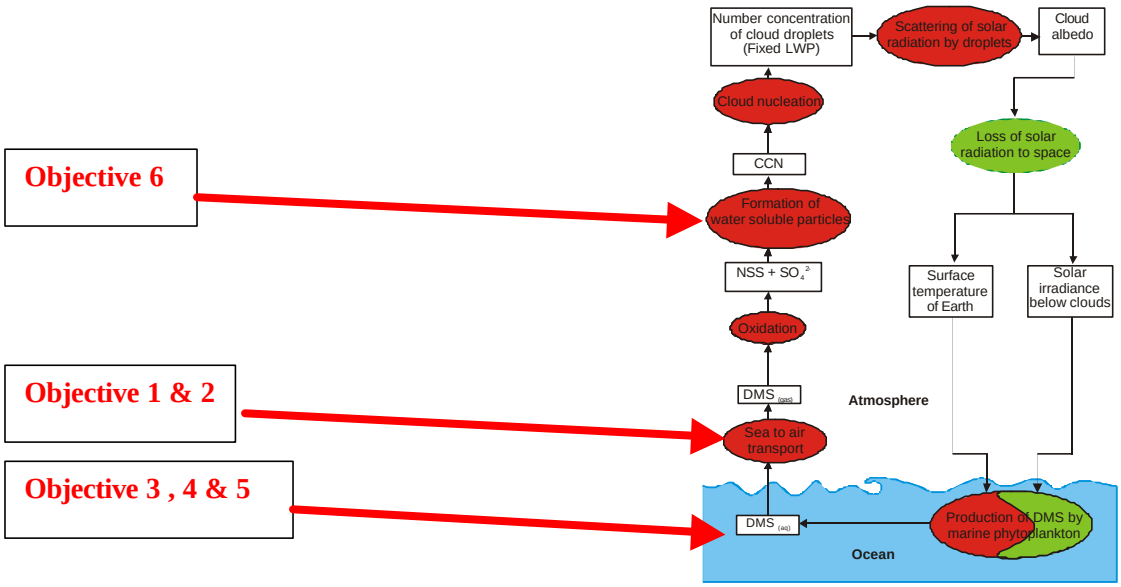


Figure 1. The CLAW hypothesis as presented by (Charlson et al, 1987).

# Physical processes governing air-sea exchange

For most gases of interest, the rate of gas exchange between the atmosphere and ocean is limited by transfer across a thin diffusive layer at the sea surface. The conceptual model of gas transfer shown in Figure 2 relates the transfer rate to both the thickness of the layer and the rate of renewal of the layer from below. These processes are largely controlled by near-surface turbulence derived from breaking waves. An additional effect of wave breaking is the direct injection of air bubbles into the water column.

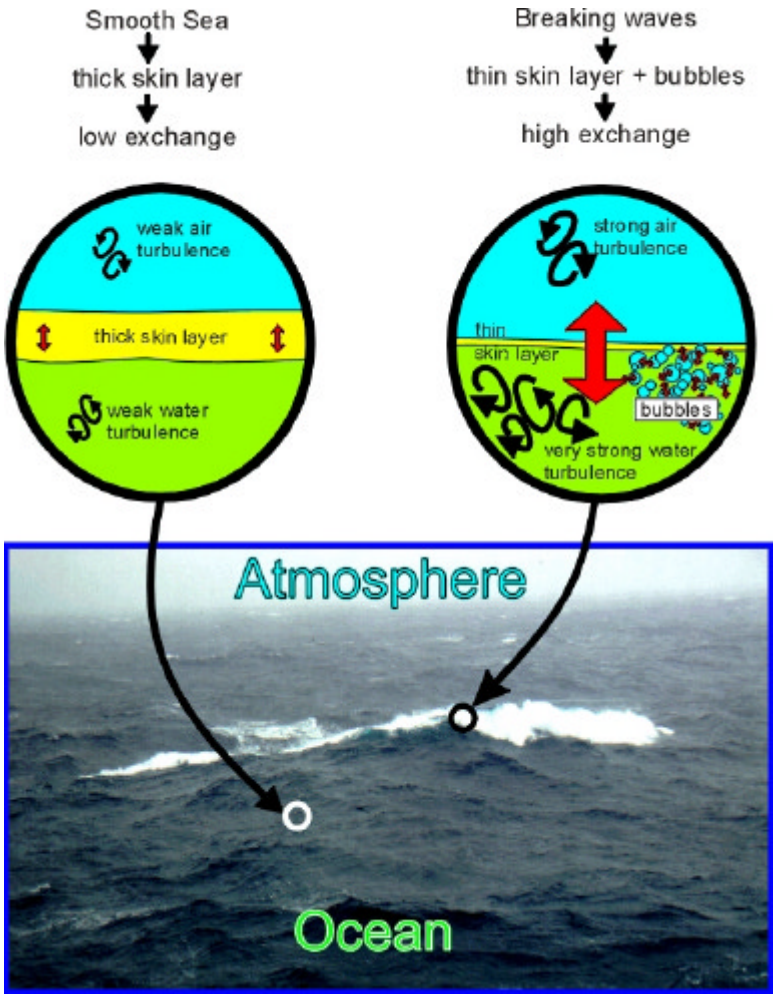


Figure 2. Physical processes at the air-sea interface.

# Complexities in the ocean sulfur cycle

Large fluxes can occur between the ocean organo-sulfur pools in a bloom with relatively small fluxes to and from the dissolved DMS pool and a small loss to the atmosphere. Using $SF_6$ tracer to define a control volume, exchange and mixing out of the control volume (Figure 3 red arrows) can be estimated. Within the volume the major factors governing the dissolved pool of DMS

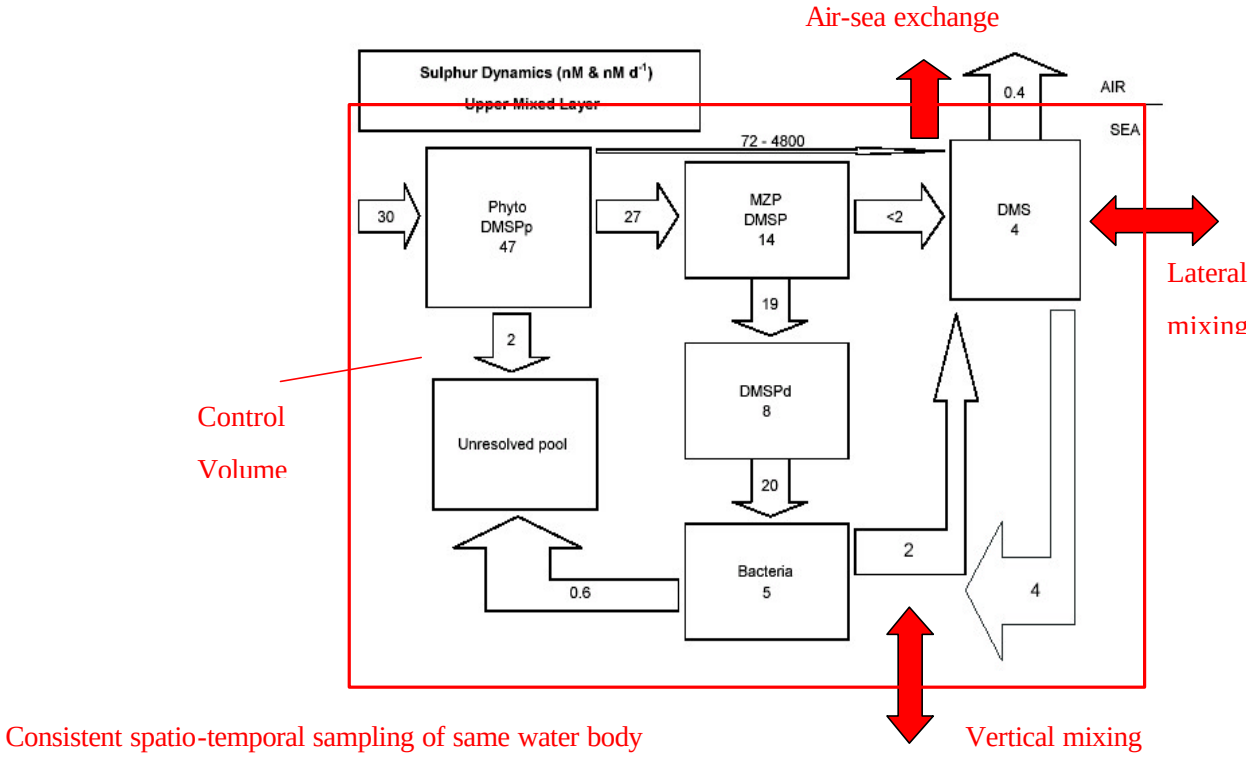


Figure 3. The ocean sulfur cycle adapted from Burkill et al, DSR II 49 (15) 2863-2885), 2002

will be quantified. Here the focus is on phytoplankton sulfur uptake, subsequent liberation to the dissolved pool through zooplankton grazing and the role of bacteria derived enzymes in the conversion of DMSP to DMS.

# Photochemical mechanisms in the surface ocean

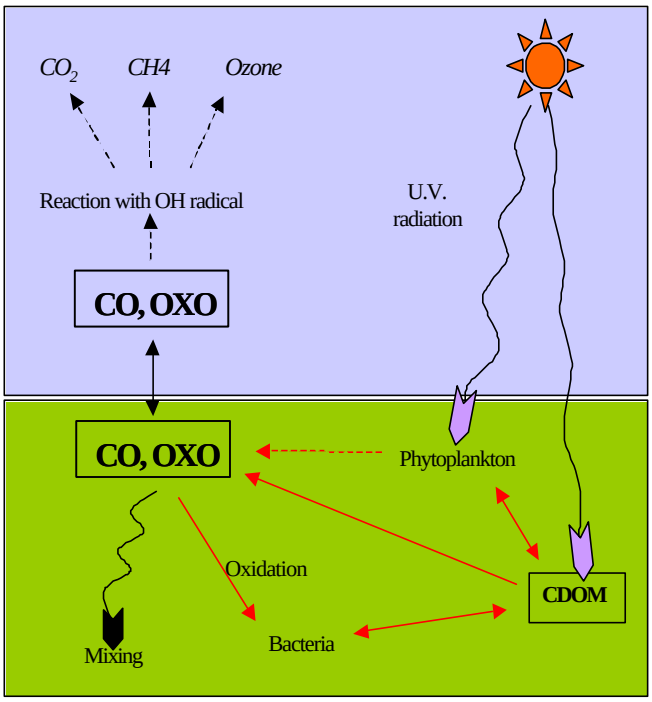


Figure 4: Oceanic source of carbon monoxide.

A growing body of research has highlighted the importance of the Southern Ocean in influencing the composition of the overlying troposphere. With reduced anthropogenic sources in the Southern hemisphere, photochemical reactions at the ocean surface represent a major source of radicals and volatiles that determine the tropospheric oxidising capacity, and so the residence times of other trace gases such as methane and the chlorofluorocarbons. Photochemistry may also play a significant role in biogeochemical cycling in the surface waters south of 45°S, with the elevated incident UV that results from reduced stratospheric ozone enhancing the photodegradation of Chromphoric Dissolved Organic Matter (CDOM) and inhibiting bacterial activity. Production and loss processes such as air-sea exchange, bacterial oxidation and mixing have not been studied for trace gases such as carbon monoxide (CO) and oxidised organics (OXO) such as acetone and acetaldehyde in this region. This will be redressed by measurements on the SOLAS-ANZ voyage, and complimented by the concurrent determinations of transfer velocity and vertical turbulent mixing.

# Complexities in the atmospheric sulfur cycle

Heterogeneous sinks for both gaseous and particulate precursors of CCN lead to non-linear and variable relationships between gaseous precursors and CCN. Sea-salt aerosol in the marine boundary-layer is possibly the most important sink for reactive gas precursors and new particles. Objective 6 will examine these relationships and sinks (Figure 5).

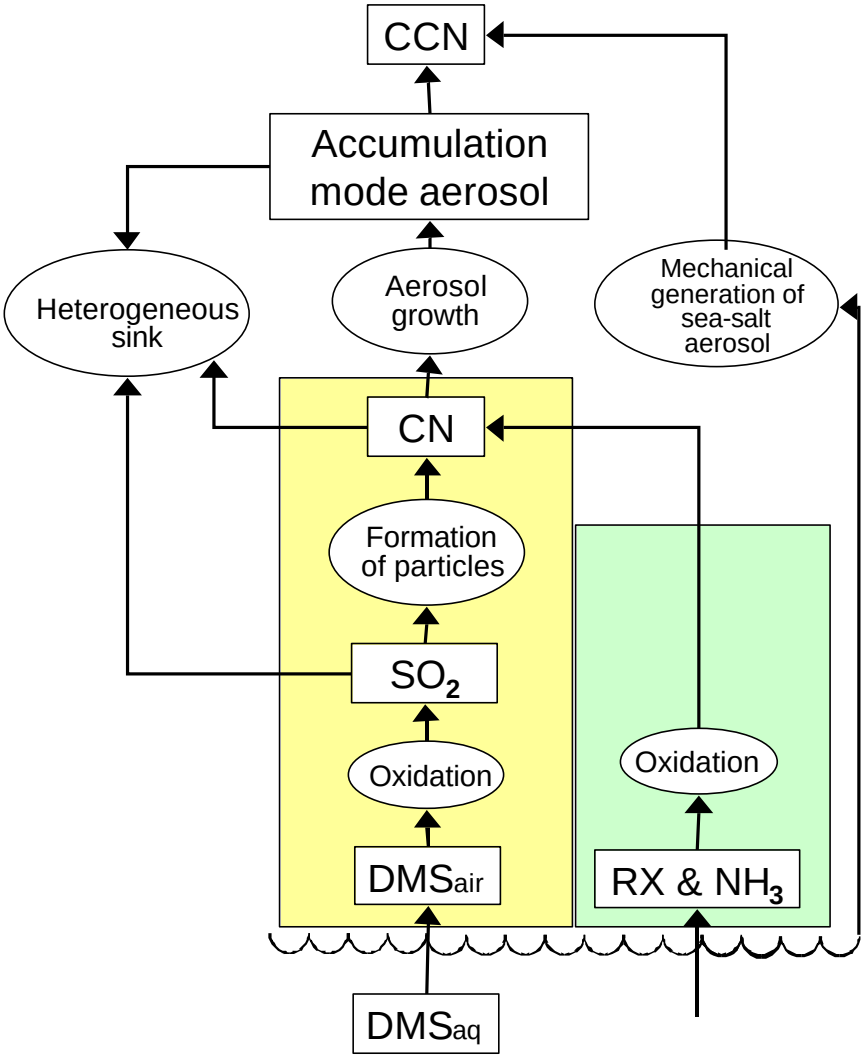


Figure 5. Aerosol formation processes

# S I T E  S E L E C T I O N

The experiment will be conducted as an open-ocean Lagrangian patch/dual-tracer study with the tracer $SF_6$ providing a control volume, vertical and lateral diffusion rates and estimates of air-sea exchange using a second tracer, $^3He$.

The voyage on the RV Tangaroa is scheduled for 30 days from 17 March to 15 April 2004.

The most likely location is in the S.W. Bounty Trough around 48°S, 172°E are in High-Nutrient-Low-Chlorophyll Sub-Antarctic waters. A desktop study has being undertaken to guide site selection. Selection criteria include:

PHYSICAL

- a relatively quiescent and homogeneous region allowing tracer labelled patch tracking for a month is one of the most difficult criteria to satisfy
- an optimal 30 to 60 m mixed layer depth for preservation of $SF_6$ and dilution of iron

ATMOSPHERIC

- a range of windspeed for the study of the gas exchange coefficient – windspeed relationship

BIOLOGICAL

- HNLC waters receptive to bloom development by iron fertilisation & non-limiting macro-nutrients

Gas fluxes ($CO_2$ and DMS) will be enhanced by artificially stimulated bloom (iron addition). Time permitting, this bloom will be followed through to the decline phase. Results from the recent SERIES experiment in the N.E. Pacific, at similar water temperatures, suggest a voyage length of 28 days minimum is required to adequately sample the bloom decline.

E X P E R I M E N T A L P L A N

# Experimental sequence

1/ A Pre-release survey conducted to find the optimal water mass characteristics in the chosen region.
2/ The initial iron fertilisation and tracer release to form a labelled patch is carried out over a day.
3/ Patch mapping, and bloom development: the focus in the early days is on continuous underway mapping of the patch as defined by $SF_6$ along with iron, nutrient status, phytoplankton health and productivity as a bloom hopefully evolves. Decisions need to be made on whether iron reinfusion is needed to maintain necessary concentrations. The combination of $^3He$, and $SF_6$ will be used to provide spatially and temporally integrated measurements of k, as well as to estimate vertical and horizontal eddy diffusion coefficients.
4/ A routine In and Out CTD station sampling programme is operated to obtain a biophysical and dissolved gas vertical profile time series for the experiment.
5/ Micrometeorological measurements are made continuously but optimal atmospheric flux measurement periods will be planned when ship motion is minimal and wind/ship orientation is optimised. Where possible, these periods will coincide with CTD stations.
6/ Downwind atmospheric sampling of airborne emissions and products will be attempted in the later stages of the experiment if emission fluxes from the patch are significantly elevated. The downwind atmospheric sampling will be within 10 km of the patch boundary and if possible combined with out station sampling. Of interest will be the mixing ratio of selected reactive gases and ultrafine condensation nuclei (3-10 nm dia.)

# Tracer release

Approximately 8000 L of seawater (in two 4000 L containers) will be injected with $SF_6$ and $^3He$ en route to the study site, and released into the surface mixed layer simultaneously to the release of iron sulfate fertiliser (approx 1.5 tonnes of $FeSO_47H_2O$ per infusion of 9000L) dissolved in seawater acidified to pH2 with Hydrochloric Acid. At the study site, the tracer release will be completed in a "lawnmower" pattern within a Lagrangian framework, achieved by following a central drifter buoy with GPS uplink to the ship, to correct the ships track for surface water advection during the release. After injection, the initial size of the patch will be ca. 50 $km^2$.

S C I E N C E P L A N

# 1. Gas fluxes and exchange velocities at the air-sea interface

## Hypothesis:

Uncertainty in exchange coefficient estimates, especially at high windspeed is due to physical factors that cannot be accounted for in a local windspeed parameterisation.

## Brief Methods:

*The gas transfer velocity (or exchange coefficient) k defines the rate of air-sea gas transfer for a given interface concentration gradient. Physical forcing through near-surface turbulence is thought to be the dominant mechanism. Windspeed plays a dominant role in turbulence generation, it is easy to measure and is therefore the basis of a number of parameterisations of k. However, the parameterisations based on windspeed alone diverge with increase in windspeed. We anticipate that improved accuracy of k prediction at high windspeed will involve more complex methods. In this experiment estimates of k will be made at two scales alongside detailed measurements of the interface physics (Objective 2).*

*Micrometeorological Scale:*

*These short timescale, small spatial scale (100 m to 1 km) measurements are important because they are made at an appropriate scale for quantifying the eddy transport/turbulence mechanisms that drive the gas exchange. Micrometeorlogical k estimates will be obtained from the relationship between vertical gas eddy diffusion flux F measured by the relaxed eddy accumulation method and the potential for flux due to the measured air-sea concentration difference:*

$$k = F/( [C]_{water} - [C]_{air}/H)$$

*where H is the Henrys Law constant of gas species C.*

*Patch Scale:*

*Patch scale dual tracer measurements provide estimates on larger spatial scales and integrated over longer temporal scales which are necessary to provide constraints for k. Using the dual tracer technique, the inert gases $SF_6$ and $^3He$ are artificially injected into the ocean, and the rates of decrease in their concentration are used to determine the exchange coefficients of the two gases [Wanninkhof et al., 1993].*

*Dispersion is distinguished from gas exchange using two tracers with different Schmidt numbers (Sc = kinematic viscosity of water, divided by diffusion coefficient of the gas in water). Following the dual tracer injection at a constant ratio into the mixed layer, their concentration decrease over time*

*monitored. Gas transfer velocities are determined from the change in ratio of $^3He$ and $SF_6$ over time with the assumption that the decrease in concentration over time due to advection and dispersion is a first order process. Under these conditions the ratio of k for $SF_6$ and $^3He$ can be expressed as:*

$$\frac{k_{SF_6}}{k_{^3He}} = \left(\frac{Sc_{SF_6}}{Sc_{^3He}}\right)^n \qquad (1)$$

*where $k_{SF_6}$ and $k_{^3He}$ are the gas transfer velocities and $Sc_{SF_6}$ and $Sc_{^3He}$ are the Schmidt numbers for $SF_6$ and $^3He$, respectively, and n is the Schmidt number exponent [Jähne et al., 1987]. For wavy, unbroken water surfaces without bubble entrainment, n has been shown to be -0.5 in both laboratory experiments [Jähne et al., 1987; Ledwell, 1984] and field measurements [Watson et al., 1991]. The gas exchange rate of $^3He$ can be determined by combining the advection-diffusion equation for $^3He$ and $SF_6$ in water and incorporating equation [Wanninkhof et al., 1993]:*

$$k_{^3He} = h\frac{d}{dt}\left(\ln\left(^3He_{exc}/SF_6\right)\Big/\left(1-\left(Sc_{SF_6}/Sc_{^3He}\right)^n\right)\right) \qquad (2)$$

*where h is the mixed layer depth, and $^3He_{exc}$ and $SF_6$ are the $SF_6$ and excess $^3He$ concentrations in the mixed layer. Conversely, $k_{SF_6}$ can be determined by substituting $SF_6$ for $^3He$ in Equation* 2.

## Objectives:

1. To obtain and compare multiple estimates of k under varying windspeeds, with the aim of producing more accurate transfer velocity parameterisations.

2. To obtain estimates of k in and outside of a phytoplankton bloom to determine whether biological activity significantly influences the kinetics of air-sea exchange through the production of surfactants.

3. To relate estimates of k to the variation in surface kinetic factors (Objective 2) with the aim of improving upon windspeed parameterisations of k by the inclusion of other parameters.

4. Determine the effect of spatial and temporal integration scales on calculated fluxes by comparing high temporal resolution micrometeorological flux measurements with larger scale, integrated tracer values.

5. To estimate evasive $SF_6$ loss in order to constrain the $SF_6$ budget, and obtain estimates of vertical diffusional losses from a 3-D model of the $SF_6$ patch evolution (Objective 2).

6. Determine the draw down of atmospheric $CO_2$ during a phytoplankton bloom by measuring surface $pCO_2$ both inside and outside the patch.

7. Determine the carbonate budget in near surface waters during a phytoplankton bloom.
8. Investigate anomalous ratios of atmospheric oxygen/carbon dioxide over the Southern Ocean. This ratio constrains estimates of the rate of oceanic uptake of $CO_2$.
9. Assist the large scale study of drivers of areal variability in ocean $CO_2$ exchange (Merlivat, LODYC).

These objectives will be met by measurements of:

- $SF_6$ in vertical profile samples and air (Law)
- Differential diffusion of $^3He$ and $SF_6$ in systematic sampling at the Lagrangian patch. (Ho/Schlosser/Smith/Law)
- $^3He$ in vertical profile samples (Ho/Schlosser)
- Micrometerological DMS flux measurements (Harvey/Smith)
- Micrometerological $CO_2$ flux measurements and aqueous and atmospheric $CO_2$ concentration using an automated underway $CO_2$ equilibriator system (Currie)
- High precision pH and total alkalinity (Macaskill/Currie).
- High precision measurements of atmospheric $O_2$ and $CO_2$ (Thompson).
- Micrometerological CO flux measurements (Law) (with Project 5)
- Micrometerological $SF_6$ flux measurements (Law)
- CFD modelling of airflow distortion (Popinet)
- $SF_6$ in surface waters (mapping) (Law/Abraham) to provide indirect estimates of air-sea exchange from the $SF_6$ budget
- Release “CARIOCA” drifters for in-situ measurement of pCO2 ,SST, SSS and fluorescence at the initiation of the patch (Merlivat, LODYC/Currie)

- **Analytical Equipment:**

| **Species** | **Technique** | **Scientist** |
|---|---|---|
| DMS/REA flux | FPD GC REA | Mike Harvey |
| Dissolved DMS | FPD GC sparger | Graham Jones, Steve Archer, Hilton Swan |
| $CO_2$ flux | Licor/REA bags, open path IRGA | Kim Currie, Murray Smith |
| $pCO_2$ | Licor /equilibrator | Kim Currie |
| Buoy $pCO_2$ | CARIOCA Buoy | Lilliane Merlivat, Jacqueline Etcheto |
| pH (discrete and continuous), alkalinity | Dye method | Burns Macaskill |
| $SF_6$ | ECD / sparger | Cliff Law |
| $^3He$ | He MS | David Ho |
| CO, $N_2O$ | | Cliff Law |
| Atmospheric $O_2/CO_2$ | | Rona Thompson |

# 2. Interface physics

*Determination of the factors that influence exchange at the air-sea interface and across the seasonal pycnocline*

## Hypotheses:

Prediction and parameterisation of the rate of exchange of climatically important gases (e.g. DMS, $CO_2$) between the atmosphere and ocean can be improved upon by the quantification and incorporation of physical processes governing turbulence.

Persistent stratification within the open ocean "mixed layer" during low to moderate winds during spring/summer retards homogeneity.

The exchange of nutrients across the seasonal pycnocline represents a major pathway for phytoplankton production.

## Brief Methods:

*Turbulence near the ocean surface plays a key role in exchange across the air-sea interface, and wave breaking is believed to be the dominant source of the surface turbulence. Current parameterisations of the transfer velocity depend on wind speed alone. The aim here is to improve upon that parameterisation by relating the transfer velocities obtained in Project 1 to the key physical processes of wave breaking, and near surface turbulence. Bubble mediated gas transfer may be a significant pathway at higher windspeeds. To assess the role of bubbles, additional noble gas Ne and Ar measurements will be made along with dissolved $N_2$ and $O_2$ concentrations and partial pressures determined using a combination of a gas tension device with dissolved $O_2$ measurements. Persistent gradient structure near the surface may also affect the exchange. Radiometer and microstructure profiler measurement of temperature will allow the temperature effect on solubility to be accounted for. The biological processes driving the drawdown of $CO_2$ or production of DMS are also dependent of the supply of nutrient. Thus the transport processes throughout the mixed layer and in particular across the pycnocline, will be determined using both tracers and measured physical parameters.*

## Objectives:

1. Determine the rate of wave breaking and dependence on wave properties.
2. Quantify the generation rate of turbulence near the ocean-atmosphere interface and its dependence on wave breaking and wind stress.
3. Determine the dependence of the gas transfer velocity (measured in Project 1) on the physical parameters of turbulent dissipation, wave breaking, sea-state, atmospheric stability, wind speed etc.

4. Establish the bubble contribution to gas transfer using a number of gas tracers with a range of solubility coefficients: He, Ne, Ar, $N_2$, $O_2$, $SF_6$.
5. Establish the role of temperature fine structure in retarding mixing in the surface mixed layer.
6. Determine the importance of near surface temperature structure on gas exchange, through the temperature dependence of gas solubility.
7. Quantify the vertical length-scales of upper ocean mixing derived from temperature and also from concurrent fluorescence fine-structure and relate to phytoplankton "health" (linked to FRRF profiling).
8. Determine exchange rates across the seasonal pycnocline using both tracer diffusion and temperature microstructure.
9. Improve upon existing $K_z$ parameterisations based upon buoyancy frequency (N) and the Richardson number; and compare estimates of $K_z$ obtained by different approaches.
10. Estimate the exchange of macro- and micronutrients across the seasonal pycnocline, and the contribution of this pathway to phytoplanktonic nutrient requirements (with Project 4).
11. Estimate mixing rates in the surface mixed layer using photochemical tracers (with Project 5).

These objectives will be met by measurements of:

- Microwave radar measurement of sea-state and wave breaking (Smith/Stevens).
- Micrometeorological measurement of wind stress, wind speed, atmospheric stability etc. (Smith)
- Deployment of autonomous temperature microstructure profilers in the near-surface ocean. (Stevens/Ward)
- Deployment of ADV in a similar repeat-profiling mode to directly measure turbulent energy dissipation in the open ocean. (Smith/Stevens)
- Ship-based profiling to below the pycnocline using TRAMP (heavy-duty version of SCAMP), including finescale fluorometry (10cm resolution) (Stevens).
- Radiometer measurement of skin temperature (Minnett/Ward)
- Processing of profile data, resolving energy dissipation rate as well as a range of other parameters associated with the turbulence.
- $SF_6$ in vertical profile samples (Law)
- $^3$He and Ne vertical profile samples (Ho)

- Ar vertical profiles (Bender)
- Gas tension device measurement of partial pressure of $N_2$. $O_2$ analysis (McNeil)
- ADCP shear (Abraham)
- Estimation of Kz in a 1-D diffusion model (Law/Abraham).
- $SF_6$ in surface waters (mapping) (Law/Abraham).
- Macronutrients and iron.

| **Measurement** | **Technique** | **Scientist** |
|---|---|---|
| Sea state, wave breaking | Microwave radar | Murray Smith, Craig Stevens, John McGregor |
| Infrared emission spectra from ocean and atmosphere | Marine-Atmospheric Emitted Radiance Interferometer (M-AERI) | Peter Minnett |
| Dissipation/temperature structure, thermal diffusivity | SCAMP, TRAMP autonomous temperature profilers | Craig Stevens |
| Temperature, conductivity, $O_2$ | SkinDeEP profiler | Brian Ward |
| Gas tension and dissolved oxygen | Gas tenson device, SBE43 and Aanderra Optprobe, Winkler coulometric | David Katz, Craig McNeill |
| Bubble processes | Nobel gas tracers | Bender |

# 3. Biology and dissolved gases

*Role of bacteria, phytoplankton and zooplankton in regulation of dissolved gases (including DMS, $CH_4$ and $N_2O$) in the surface ocean.*

## Hypothesis:

Dissolved DMS is a minor pool of organic sulfur resulting from plankton sulfate assimilation and ecosystem interaction. The size of this pool depends rates of release of pytoplankton DMSP through zooplankton grazing and through bacteria mediated DMS production and loss mechanisms.

*There are only a few open-ocean Lagrangian time-series studies where DMSP/DMS measurements have been made concurrently with detailed ecosystem data. Data gathered in this experiment will be used to examine the ocean ecosystem role in the production of DMS, in particular, mechanisms that regulate DMSP production, conversion of DMSP to DMS and DMS consumption and removal. Interpretation will be assisted by incubation/manipulation experiments in controlled environments and accompanying modelling in order to understand the role of bacterial processing and zooplankton grazing on the production of DMS.*

The production of long lived greenhouse gases, $CH_4$ and $N_2O$ is enhanced in biologically active waters. However, the key biophysical processes that govern their formation, concentration in the ocean and therefore potential source to the atmosphere are poorly understood.

## Objectives:

During the course of the iron-enrichment induced phytoplankton bloom and decay phase (if reached):

1. Measure changes in phytoplankton growth, size-fractionated primary production, DOC production and speciation.
2. Follow and quantify rates of DMS and particulate DMSP (DMSPp) production by phytoplankton.
3. Quantify rates of bacterial production, and bacterial utilisation of DMS and DMSP and production of DMS.
4. Follow and quantify the rates of DMS and DMSPp release resulting from microzooplankton, and mesozooplankton grazing.
5. Determine sulfur stable isotope ratios of size-fractionated phytoplankton to establish the marine biogenic sulfur source signature and establish relationships with phytoplankton physiology.
6. Examine the impact of photochemistry on DMS cycling (with Project 5).
7. Establish input and output fluxes affecting the concentration of dissolved DMS in the surface ocean.

8. Follow and quantify rates of $CH_4$ and $N_2O$ formation.

These objectives will be met by measurements of:

- Dissolved and particulate DMS and DMSP (Archer/Bury/Jones)
- Bacterial production using $^3$H-thymidine (Hall/Safi)
- Bacterial production and utilisation of DMS and DMSP during incubation experiments (Archer/Bury/Hall).
- Size-fractionated primary production, species-specific primary production, DOC release, and phytoplankton growth rates (Hall with Objective 4)
- DMS and DMSP production by phytoplankton using incubation experiments (Archer/Bury/Hall).
- Size-fractionated phytoplankton filter samples for subsequent laboratory $d^{34}S$ isotope analysis (Bury)
- DMS and DMSP release following microzooplankton grazing dilution experiments (also yielding direct phytoplankton growth estimates) and mesozooplankton grazing experiments (Archer/Hall/Safi/Bury).
- Water column nitrous oxide and methane concentration measurements (Law), with dissolved nutrients (Pickmere)
- Water column nitrous oxide isotope sample collection (Law/Popp)

## A comprehensive range of biological measurements are planned to include:

**1/ Biomass measurements**

- Chlorophyll a (Scott Nodder)
- Size fractionated chlorophyll (0.2-2, 2-5, 5-20, >20) (Scott Nodder/ Graham Jones)
- HPLC samples (Graham Jones for Simon Wright)
- Bacteria – flow cytometry including active/inactive (Jorma Kuparinen).
- Microzooplankton - flagellates & ciliates (Jorma Kuparinen)..
- Mesozooplankton – biomass (Julie Hall).
- Phytoplankton preserved samples for microscopy (Karl Safi)

**2/ Phytoplankton physiological status (Ed Abraham)**

- FRRF

**3/ Primary production** (Julie Hall)

- Stimulated in situ, 5 depths to bottom mixed layer
- Total production measured approx every second day
- Size fractionated measurements daily in conjunction with size fractionated chlorophyll a and dilution experiments.

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**4/Nutrient samples** (Stu Pickmere)

- Underway measurements
- Profile samples, collection and analysis

**5/ Water column chemistry samples (**Scott Nodder**)**

- DIC?
- DOC (LoriZ)
- POC, PON, PN?, PP?, PSi

**6/ In-situ underway and profile non-tracer dissolved gas measurements**

- DMS (Steve Archer, Graham Jones), $CO_2$ (Kim Currie) $O_2$ (David Katz) CO (Lori Ziolkowski), $N_2O$ (Cliff Law)

**7/ In-situ biogenic sulfur**

- DMSPd, DMSPp (Steve Archer), DMSO (Graham Jones)

**8/ On-board experiments: Biological production and utilization of DMSP/DMS.**

*Production DMSPp to be measured using dilution technique (Karl Safi/ Steve Archer)*

- Experiments to be conducted inside and outside patch.
    - Some size-fractionated experiments will be conducted (<2, 2-20 >20 and tot, in conjunction with primary production and chlorophyll a measurements).
    - Conduct some inhibitor experiments in conjunction with dilution experiments

*Microzooplankton DMSP utilization*

- Calculated by difference

*Bacterial production (Jorma Kuparinen).*

- Measured using both thymidine and leucine.

*Bacterial turnover of DMSP/DMS ( Steve Archer)*

- Two potential approaches:
- Inhibitor experiments,
- $^{35}S$ tracer experiments.

*Mesozooplankton grazing (Julie Hall)*

- Linked with Chlorophyll *a* and DMSPp consumption.

*Phytoplankton sulfur isotope measurements (Steve Archer)*

- Measure %S content and $d^{34}S$ signal in phytoplankton inside and outside patch
- Carry out some size fractionated sulfur isotope measurements (if analytical costs permit) in conjunction with primary production and chlorophyll a measurements possibly carry out $d^{34}S$ tracer experiments in conjunction with Steve's planned $^{35}S$ tracer experiments to measure bacterial turnover DMSP/DMS using $d^{34}S$ labelled DMSP (to be discussed with Steve and dependent on purchase cost of enriched $d^{34}S$ isotope and stable isotope analytical budget).

**9/ Sediment traps (**Scott Nodder**)**

Water column measurements to be co-ordinated with trap deployments

# 4. Iron and phytoplankton

*Iron Chemistry and Iron-Phytoplankton Interactions*

## Objectives:

1. A baseline survey of dissolved iron concentrations, phytoplankton physiological status (i.e. are the cells iron stressed) and identification of the main algal groups prior to the release of iron at the selected site.

2. Monitoring of changes in dissolved iron concentration, dissolved redox speciation and iron-binding ligands during the bloom. Concurrent monitoring of the timescales of changes in the physiological status of the algal cells (i.e. the alleviation of iron stress), size-fractionated chlorophyll (0.2-2, 2-5, 5-20 and > 20 microns) and rates of primary production (same size fractions) to provide a rapid assessment on board the vessels of changes in algal community structure. Sampling for algal pigments will also take place. Such monitoring in quasi-real-time will assist with decision-making regarding the need for further infusions of iron, and for intensive sampling of the bugs that may be responsible for DMSP production. Additionally, productivity will be assessed with vertical profiles of tracer ? $^{17}O$ (Bender).

3. Investigation of iron uptake kinetics during the bloom, and also of the impact of iron supply on silicic acid uptake kinetics to better elucidate the potential co-limitation of diatom growth by these factors. The ability of diatoms to alter their degree of silicification will also be studied in collaboration with materials chemists from Otago.

# 5. Marine Photochemistry

*To examine the cycling and flux of photochemical trace gases in the surface mixed layer.*

## Hypothesis:

Biological activity influences the production and rate of air-sea exchange of photochemical species.

*The oceans may play an important role in determining atmospheric composition in the southern hemisphere, where anthropogenic sources are less significant. This is particularly the case for photolytic gases such as carbon monoxide (CO) and non-methane hydrocarbons. We will use CO as a model photoltyic trace gas to establish the dominant processes influencing its cycling and emission, and determine whether the biota indirectly influence CO concentration. In addition, initial water column measurements of other oxidised organic volatiles will be made.*

## Objectives:

1. To determine the diel variation in dissolved CO in the water column.
2. To estimate the air-sea exchange rate of CO (with Objective 1).
3. To determine whether vertical concentration profiles, air-sea emissions and photochemical production rates of CO are significantly influenced by a phytoplankton bloom.
4. To examine CO cycling within a 1-D model with the aim of estimating vertical mixing rates in the surface mixed layer.
5. To measure changes in chromophoric dissolved organic matter (CDOM) and relate to changes in CO production.
6. To determine the apparent quantum yield for CO and how this changes with eth biological response to iron addition.

These objectives will be met by measurements of:

- CO in vertical profile samples and air (Ziolkowski /Law)
- Deck photo-irradiations for CO production and consumption (Ziolkowski /Law) and DMS loss (Archer)
- Controlled photo-irradiation of water samples using a solar simulator (Ziolkowski)
- Incident UV irradiation (Boyd) (with Objective 4)
- Water column light profiles (Boyd) (with Objective 4)

## Analytical equipment

| Species | Technique | Scientist |
|---|---|---|
| CO | Reduction Detector | Cliff Law |
| Deck irradiance | PAR and UV sensors | Cliff Law |
| CDOM | UV spectro-photometer | Law/Ziolkowski |
| CO - Photoproduction | Solar simulator | Ziolkowski |
| Water column UV profiles | PPMR | Phil Boyd |

# 6. Atmospheric aerosol production

*The role of biogenic gases in the generation of new particles.*

## Hypothesis:

Infrequent events of homogeneous nucleation can occur with high concentrations of gaseous precursors but opportunities are limited by the large heterogeneous sink magnitude of pre-existing marine aerosol.

*Downwind of the bloom biogenic gas source region, we will search for evidence in the atmosphere of aerosol (ultrafine condensation nuclei) products that have formed as a result of (photo)chemical interaction and nucleation of products. This is a first step in the production of cloud influencing nuclei (CCN) and we anticipate that a CN signal although not a CCN signal should be visible within practical time/space scales.*

## Objectives:

1. Assess the emission of dimethylsulfide and other volatile species in the region of an active and then decaying bloom (with Objective 1).
2. Assess the yield of key intermediate sulfur dioxide from dimethylsulfide.
3. Assess the formation of ultrafine condensation nuclei and ratio of ultrafine/total in the region of an active and then decaying bloom, considering relationship between reactive gas species concentrations and condensation nuclei number concentration.
4. Assess limitations on homogeneous nucleation due to aerosol surface area through laser aerosol spectrometer measurement.
5. Assess the chemistry of size resolved aerosol for quantifying heterogeneous conversion of $SO_2$.
6. Assess the role of UV radiation in the generation of new particles.

These objectives will be met by measurements of:

- Time series of dimethylsulfide and sulfur dioxide concentration in the air immediately over a bloom (DMS from Objective 1), $SO_2$ (Cainey).
- other volatile species, such as halogenated species and ammonia, in the air immediately over a bloom (Archer, Cainey).
- Monitor aerosol surface area in the air immediately over a bloom (Harvey).
- Measure size resolved aerosol chemistry by impactor (Sievering/DeVries)
- Measure changes in concentration of ultra fine condensation nuclei and condensation nuclei in the air immediately over a bloom (Harvey/Gras).
- Continuously monitor UV and visible radiation during the cruise (UV and PAR with Objective 4).

## Equipment:

| Species | Technique | Scientist |
|---|---|---|
| DMSa (combined with REA) | GC FPD | Harvey |
| $SO_2$ | HPLC fluorescence | Cainey |
| Trial of Iodocarbon, chloroform and maybe bromoform concentrations | Adsorbant trap / GC-MS | Archer |
| Ammonia | Unknown | Collaborator sought |
| Condensation Nuclei | TSI 3010 | Harvey |
| Ultra-fine condensation nuclei | TSI 30325A | Gras |
| Surface area | ASASP100X or Grimm | Harvey |
| Size resolved chemistry | Berner impactor | Sievering/DeVries |
| SW and PAR | Photometry | Boyd/Harvey/Law |
| Satellite ($AOD/r_{eff}$) | | Uddstrom / McGregor |

# 7. Oceanic particle aggregation and export

*Role of aggregation in the timing and magnitude of export processes at the end of a Fe-induced bloom cycle.*

## Hypothesis:

Export of organic material will occur upon nutrient limitation, consequent with increases in the rate of aggregation and grazing.

## Objectives:

1. Measure changes in aggregation potential (TEP, stickiness, repackaging, disaggregation) and processes (particle size, concentration) in a Fe-induced bloom/decay event.
2. Quantify the composition and magnitude of exported organic matter from a declining bloom.
3. Determine the time-scales of aggregation and export processes and linkages to temporal changes in physical, chemical and biological processes within a declining bloom.
4. Determine the transformation pathways of organic matter.
5. Provide information to derive elemental (C/N/S, maybe P and Si also) budgets from within the $SF_6$-defined patch.

Measurement strategies are still under consideration. The objectives could be met by measurements of:

- TEP, stickiness, aggregation/disaggregation rates using shipboard methods
- Stable isotopes (C/N/S) in dissolved and particulate phases
- Radio-chemical methods ($^{234}$Th, others)
- F-ratios: N uptake in nitrate, ammonium and urea
- Sediment traps: mass, C, N, S, gels [P, Si, biomarkers?]
- Phytoplankton sinking rates
- Faecal pellet production rates and chemical analyses
- Biomarkers and isotopic characterisation of organic compounds
- Camera and laser particle sizing
- Beam attenuation ($c_p$-POC calibrations)
- Marine snow collections and analyses

A P P E N D I C E S

# Planning Group

The NIWA planning and co-ordination group is made up of:

Edward Abraham, Mike Harvey, Philip Boyd, Sarah Bury, Mark Hadfield, Julie Hall, Cliff Law, Scott Nodder, Murray Smith, Craig Stevens

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Gas transfer: Murray Smith with Cliff Law and Mike Harvey

Surface Physics: Craig Stevens with Murray Smith

Ecosystem processes and dissolved gases: Julie Hall with Stephen Archer

Iron and phytoplankton: Philip Boyd

Photochemistry: Cliff Law

Atmospheric Chemistry: Mike Harvey

Export and Aggregation: Scott Nodder

Patch/tracer management and dynamics: Cliff Law

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