Cruise report:

ACCACIA Arctic Spring Cruise

RV Lance
15 - 31 March 2013

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THE UNIVERSITY of York

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1. Overview and objectives of the cruise

The cruise took place as part of the larger NERC funded consortium project called Aerosol-Cloud Coupling And Climate Interactions in the Arctic (ACCACIA). The overarching objective of the project is to reduce uncertainty in the representation of Arctic cloud and aerosol processes in climate models. Airborne measurements of aerosol and cloud properties were made concurrent with the RV Lance research cruise, using the BAS MASIN and FAAM BAe146 aircraft, and a second research cruise on board the RRS James Clark Ross took place in July-August 2013.

The aims of the research cruise were to make surface based in-situ measurements of marine aerosol composition and properties, and aerosol precursor gases (DMS, VOCs, halocarbons). These measurements were supported by standard oceanographic measurements such as salinity, chlorophyll-a and nutrient concentrations. Bubble tank experiments were conducted, the results of which will be used to develop a primary multicomponent seaspray aerosol flux parameterisation.

The timing of the cruise was intended to capture the late winter/early spring period of sea-ice melt and the associated phytoplankton bloom has just begun. The cruise track is shown in figure 1. Stations were occupied alternately in open water and within the ice edge (mainly brash ice). Atmospheric measurements were made continuously, or semi-continuously, and a daily CTD cast was used to collect water samples. Some additional sampling of the pumped underway seawater supply also took place.

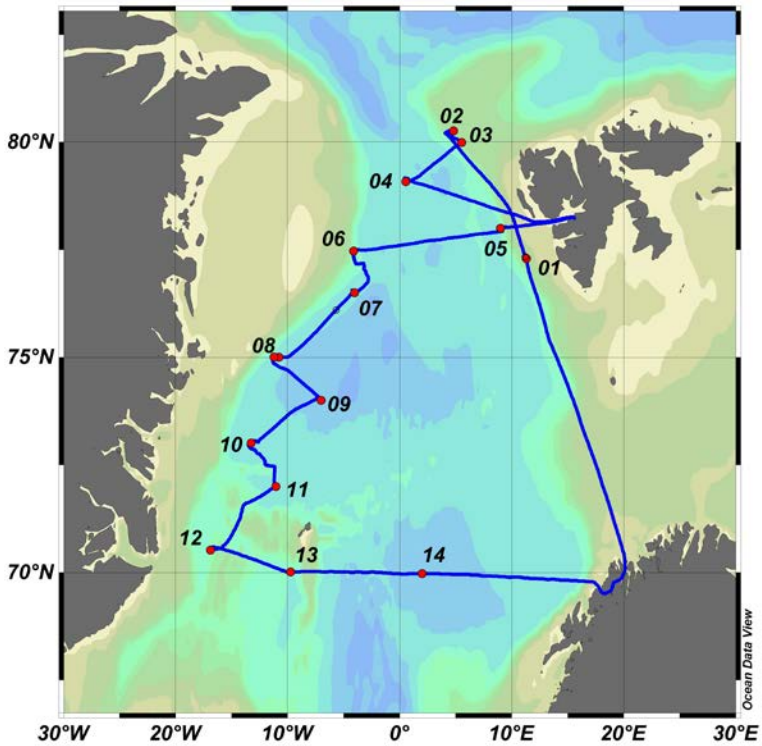


Figure 1.1 Cruise track and station positions for ACCACIA spring cruise. Map prepared using Ocean Data View: Schlitzer, R., 2013. Ocean Data View, http://odv.awi.de.

2. Scientific party

James Lee	University of York, UK
Rosie Chance	University of York, UK
Stephen Andrews	University of York, UK
William Manning	University of York, UK
Anna Dimond	University of York, UK
Juan Najera	University of Manchester, UK
Eoghan Darbyshire	University of Manchester, UK
James Whitehead	University of Manchester, UK
Marius Bratrein	Norwegian Polar Institute, Tromsø, Norway

Figure 2.1 Scientific party on board the RV Lance during the ACCACIA spring cruise.

3. CTD operations and underway sensors

3.1. CTD operations

The shipboard CTD was provided by NPI and operated onboard by Marius Bratrein, NPI. The CTD was fitted with temperature, salinity, two fluorescence (CDOM and chlorophyll-a), PAR and transmissivity sensors, plus a rosette of 12 x 10 L Niskin bottles. Sensors were maintained and calibrated by NPI. An oxygen sensor was also attached to the CTD, but the calibration on this was overdue so the data is not considered reliable.

A total of 16 shallow casts were made during the cruise, see Table 2. Sampling depths were selected by the scientific party.

CTD data has been processed by Rosie Chance (UoY) using Seabird SBE Data Processing software, following advice on suitable protocols from Dr Paul Dodd, physical oceanographer at NPI.

Station	Latitude, °N	Longitude, °E	Depths sampled	Notes
1	77.296	11.316	9,20,40,60,80,100,120,200,300	Open water
2	80.263	4.805	3,20,30,40,50,60,80,100,150,200	Ice edge
3	79.993	5.530	6,20,40,60,80,100,120,150	Open water
4	79.084	0.543	4, 20,40, 60, 80, 100	Open water
5A	78.002	9.000	3	Open water
5B	78.002	9.000	3, 20, 40, 60, 80, 100, 120, 150	Open water
6	77.467	-4.111	3,20, 40, 60, 80, 100, 120, 150	Ice edge
7	76.503	-4.018	3, 20, 40, 60, 80, 100, 120, 150	Open water
8A	75.002	-10.763	2,20, 40, 60, 80, 100, 120, 150	Open patch within sea ice
8B	75.007	-11.199	no bottles fired	Solar noon cast
9	73.998	-7.013	2, 20, 40, 60, 80, 100, 120, 150	Open water
10	73.009	-13.244	2, 20, 40, 60, 80, 100, 120, 150	Open patch within sea ice
11	71.998	-11.037	4, 20, 40, 60, 80, 100, 120, 150	Open water
12	70.518	-16.873	3, 20, 40, 60, 80, 100, 120, 150	Heavy ice
13	70.009	-9.725	3, 20, 40, 60, 80, 100, 120, 150	Open water
14	69.974	2.003	5, 20, 40, 60, 80, 100, 120, 150	Open water

Table 2. CTD station positions and nominal depths of bottle firing.

3.2 Underway seawater supply

In preparation for the ACCACIA cruise, a pumped underway seawater supply was installed on the RV Lance. As this was not fitted with any oceanographic sensors, all underway measurements were made using equipment provided by the scientific party. In addition to semi-continuous monitoring of the underway seawater supply, discrete samples were collected from the seawater tap. The pumped seawater was frequently orange in colour, and left an orange reside inside tubing and online instruments. This is assumed to have been due to iron contamination.

3.2.1 Salinity
A Seabird 45 TSG unit was kindly loaned by Margaret Yelland/Robin Pascal (National Oceanography Centre, UK) for the purposes of monitoring underway salinity. Data was logged every 10 minutes. Due to the iron contamination in the underway supply, the borrowed instrument requires cleaning and servicing, at additional cost to the ACCACIA project.

3.2.2 Fast Repetition Rate Fluorometry (FRRf)
A Chelsea Scientific Instruments FRRf (Mark I Fasttracka^{TM}) was provided for the cruise by National Marine Facilities (NMF), UK. This was set up in benchtop mode to make in line measurements on the underway seawater supply. The instrument and inlet tubing was covered with black plastic to minimise light exposure. The parameters were set according to NMF guidelines for underway in-line use; specifically the FRRf was set to an acquisition sequence of 100 saturation flashes, 20 decay flashes and 30,000 ms sleep time between acquisitions (i.e. measurements at 30 s intervals).

Unfortunately, high levels of noise mean it may not be possible to extract any meaningful information from the FRRf data. Possible causes of the high noise are: very low chlorophyll levels, contamination of the pumped underway supply, inappropriate choice of parameters for the conditions encountered.

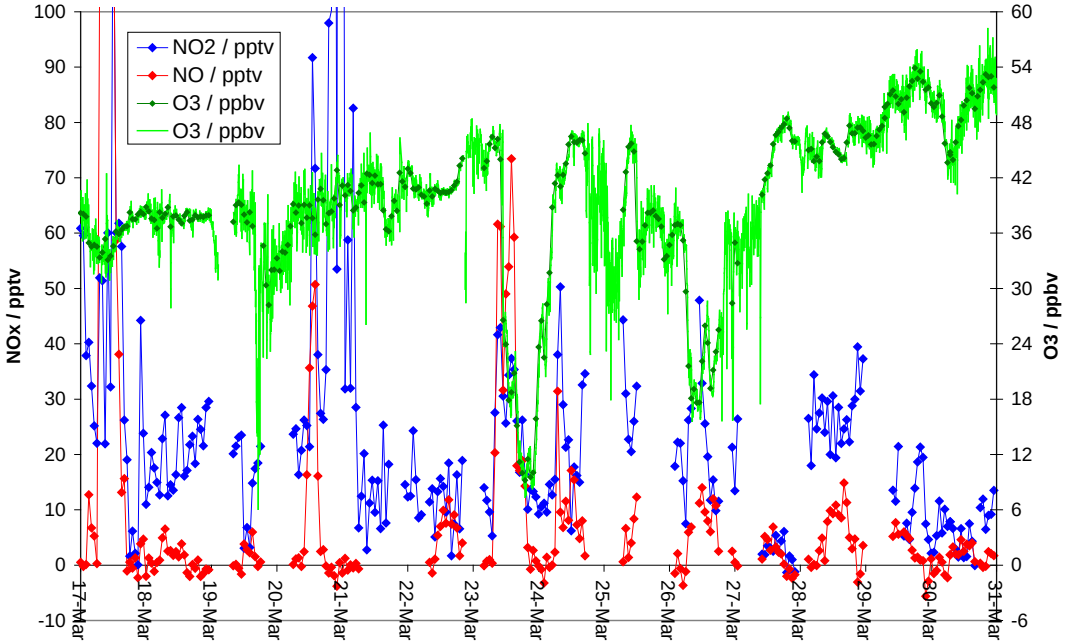
3.3 Ship position and meteorology
Latitude, longitude, ship heading and speed, air temperature, sea temperature, relative humidity and air pressure were logged by the ships systems. Ten minute averages of this data was downloaded by James Lee, UoY.

Relative wind direction and wind speed was measured using a 2D sonic anemometer on the monkey island deck (Rosie Chance, UoY) and a 3D sonic anemometer on a mast mounted to the scientific container on the forward deck (UoM team).

4. Atmospheric nitrogen oxides and ozone

James Lee and William Manning, UoY

Continuous measurements of NO_x and O_3 in air by chemiluminescence (with photolytic conversion for NO_2) and UV absorption respectively. Air samples were taken from an air intake line mounted on the forward mast. The plot below shows the data series (1 min and hourly averaged for O_3 and hourly averaged for NO_x). The detection limits for the NO_x measurements are around 3 and 5 pptv for NO and NO_2 respectively. Data is removed where the instruments were sampling the ship stack but this is available on request.



Typically NO shows a diurnal cycle peaking at 10-20 pptv at solar noon, with NO_2 levels of 15-30 pptv. The O_3 trend is of rising levels throughout the cruise (35 – 55 ppbv), which is typical of Northern hemisphere background concentrations from winter to the spring O_3 maximum. However two periods stand out in the data series. On 23rd – 24th March and 26th – 27th March there is a significant drop in O_3 levels (to 10 and 15 ppbv respectively), both coincident with small increases in NO_x. The NO_x increases are indicative of a change of air mass, possibly to air that is from Greenland or continental in origin. The levels of NO_x observed are not large enough for the O_3 drop to be due to titration with NO. The higher levels of NOx on 20th March are when we were sampling downwind of Svalbard island.

5. Trace gases (DMS, halocarbons) in air and water

Stephen Andrews, William Manning and Rosie Chance, UoY

5.1 Atmospheric trace gas measurements

A suite of trace gases (Dimethyl sulphide, DMS; halocarbons) were measured in ambient air using Thermal Desorption - Gas Chromatography-Mass Spectrometry (TD-GC-MS). Semi-continuous sampling (20 minutes sampling per data point) was conducted via an air intake line mounted on forward mast. Approximately 1440 air samples were analysed. The instrument was calibrated using preprepared gas standards, and instrument drift accounted for using ambient levels of atmospheric carbon tetrachloride.

5.2 Seawater trace gas measurements

A second TD-GC-MS instrument was used to measure the same suite of trace gases in underway and CTD seawater samples. Gases were extracted from the seawater samples using a semi-automated purge and trap system, which could either receive water direct from the pumped seawater supply, or draw up samples from a bottle, as required. All samples underwent gas tight filtration through a glass fibre filter (Whatman GF/F) prior to purging. Underway sampling from the surface water intake consisted of a discrete sample, taken approximately once every 45 minutes while the ship was underway. Discrete water samples from 8 depths (typically 150, 120, 100, 80, 60, 40, 20, 3 m) were collected using Niskin bottles during CTD casts. Approximately 500 underway and 112 CTD samples were analysed. Quantification was by the same methods as used for the air measurements.

Discrete water samples from 6 depths (typically 120, 80, 60, 40, 20, 3 m) were collected using Niskin bottles during CTD casts, acidifed and stored (-20^{o}C) for determination of DMSPt upon return to the UK. Analysis will be by purge and trap gas chromatography-mass spectrometry.

6. Organic matter in seawater and aerosol

Rosie Chance, UoY

6.1 Water sampling

Surface seawater samples (~10 L) were collected for extraction of dissolved organic matter using solid phase extraction (SPE-DOM). SPE extraction was carried out on board according to the method of Dittmar et al., 2008. 15 samples were collected with Niskin bottles during CTD casts. Extracted samples were stored frozen (-20^{o}C) for return to the UK. The SPE-DOM extracts will be characterised using liquid chromatography-mass spectrometry.

6.2 Aerosol sampling

High volume aerosol samples for characterization of organic were collected using Ecotech HiVol 3000 air sampler fitted with a PM2.5 size selective inlet (Ecotech). The sampler was mounted on the monkey island deck of the ship (figure 6.1). To avoid sampling contaminated air from the ships funnel, the collector was automatically controlled such that sampling only took place when the relative wind direction was between -110 and 70 degrees (with the bow set to 0 degrees), and the relative wind speed was greater than 2 m s^{-1}. This was achieved using a 2-dimensional sonic anemometer (Gill) coupled to a data logger (Campbell Scientific CR800), which sent a trigger voltage to the aerosol collector. When on, air flow through the collector was ~68 m^{3} hr^{-1}. Samples were collected onto precombusted (5 hours at 450^{o}C) Whatman QM-A quartz fibre filters deployed for periods of 24 hours each. A total of 15 samples, including two blanks, were collected. Samples were stored at -20^{o}C for return to the UK.

Aerosol extracts will be analysed by Liquid Chromatography - ion trap tandem Mass Spectrometry (LC-MS) and Fourier Transform - Ion Cyclotron Resonance -Mass Spectrometry (FT-ICR-MS). This analysis will provide structural information on functional groups, and determine molecular masses to sub-ppm resolution levels for unambiguous determination of molecular formulae, respectively. Prior to analysis, aqueous extracts of the aerosol samples will undergo solid phase extraction (as in section 6.1), for direct comparison with operationally defined seawater extracts.

sol sampler on the monkey island deck of the RV Lance during

References

Dittmar et al., 2008. A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. Limnol. Oceanogr: Methods, 6, 230-235.

7. Chlorophyll-a, nutrients and haloperoxidase activity

Claire Hughes and Anna Dimond, UoY

7.1 Chlorophyll-a and nutrient sampling

- Size segregated chlorophyll samples from surface water intake for analysis by fluorometry in the Environment Department at the University of York. Size fractions collected included >20, 2-20 and 0.2- 2 µm alongside a selection of GF/F samples. A total of 150 samples were collected from the underway seawater supply and CTD profiler.

- Filtered samples from surface water intake for determination of major nutrients (NO_3^-, NH_4^+, PO_4^{3-}, SiO_4) by autoanalyser at the University of East Anglia. A total of 150 samples were collected from the underway seawater supply and CTD profiler.

7.2 Haloperoxidase activity assay

The haloperoxidases (chloro-, bromo- and iodoperoxidases) are a group of vanadium or haem-containing enzymes which catalyse the breakdown of hydrogen peroxide through the two electron oxidation of halide ions (Butler & Walker, 1993). This leads to the formation of reactive hypohalous acids such as HOI and HOBr which can halogenate organic substrates. In some cases this can result in the production of halocarbon gases which can mediate the sea-to-air transfer of halogens with implications for atmospheric chemistry including ozone depletion and cloud formation (von Glasow *et al*., 2004). The haloperoxidases have been found in a range of marine organisms including seaweeds (Ohsawa *et al*., 2001), cyanobacteria (Johnson *et al*., 2011) and cold water diatoms (Hill & Manley, 2009) but major questions remain regarding the occurrence of the haloperoxidases in the pelagic marine environment and the reasons for their production.

A total of 12 haloperoxidase assays were performed during this cruise using the phenol red incubation method developed by Hill and Manley (2009). The assays were done on size fractionated (> 20, 2-20 and 0.2- 2 µm) plankton material concentrated onto membrane filters from 1L seawater samples.

References

Butler & Walker [1993] *Chem. Rev*., 93, 1937-1944
Hill & Manley [2009] *Limnol. Oceanogr*., 54, 812-822
Johnson *et al*. [2011] *J. Phycol*. **47**: 792-801
Ohsawa *et al*. [2001] *Phytochemistry*, 58, 683-692
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8. Aerosol properties and Bubble tank experiments

Eoghan Darbyshire, Juan Najera, Jamie Whitehead, James Allan & Gordon McFiggans

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8.1 Objectives

Our objectives in this spring cruise were to make *in situ* surface based measurements of marine aerosol sources, composition and properties, and provide comparison with the behavior of marine primary aerosol produced in the bubble tank experiments.
Aerosol measurements will be used to determine the biogenic and anthropogenic nature of aerosol sources within the Arctic boundary layer and how these aerosol sources changes with changing ice conditions. CCN (Cloud Condensation Nucleus) measurements, made as function of aerosol size and super-saturation, will be used as input in cloud microphysical models to investigate their influence on aerosol-cloud feedback sensitivity.
Bubble tank results obtained during the spring cruise (and from post-cruise experiments) will be used to provide a primary multi-component sea-spray aerosol flux parameterization for direct incorporation into the global aerosol modeling.

8.2 Methodology

8.2.1 Aerosol measurements

Atmospheric aerosol *in-situ* measurements were made continuously in a sea-container laboratory (Figure 8.1) from an aerosol inlet system mounted on a side mast using the following online instrumentation:

- *High Resolution Aerodyne Time of Flight Aerosol Mass Spectrometer (HR-TOF-AMS):* quantitative determination of mass concentrations of non-refractory chemical species present in sub-micrometric particles such as NH_4^+, NO_3^-, SO_4^{2-}, organics and Cl^- (non-sea salt).

- *Droplet Measurement Technologies-Cloud Condensation Nuclei Counter (DMT-CCN):* determination of size-resolved aerosol cloud condensation nuclei that can form into cloud droplets. Single sized particles (range 15-564 nm) were sampled at 5 different super-saturations (SS) allowing calculation of activated fraction as a function of super-saturation and dry sizes, particle critical super-saturation and ambient threshold dry diameter for activation.

- *Condensation Particle Counter (CPC):* measurements of total aerosol number concentration.

- *Hygroscopic Tandem Differential Mobility Analyser (HTDMA):* measurements of particle growth factors (<10% to 90% relative humidity) to assess the mixing state of aerosols, with dry particle size ranging 59-267 nm (after calibration) with a typical scan time of 10 minutes per dry size.

- *Differential Mobility Particle Sizer (DMPS)*: to measure ambient aerosol size distributions in the range from 15 nm to 564 nm during 15 minutes measurement period.

- *Particle size analyser/dust-monitor (GRIMM 1.108)*: to monitor aerosol number size distributions by optical particle counting. The GRIMM has a larger size cut than the DMPS and can measure coarse mode aerosol that the DMPS cannot.

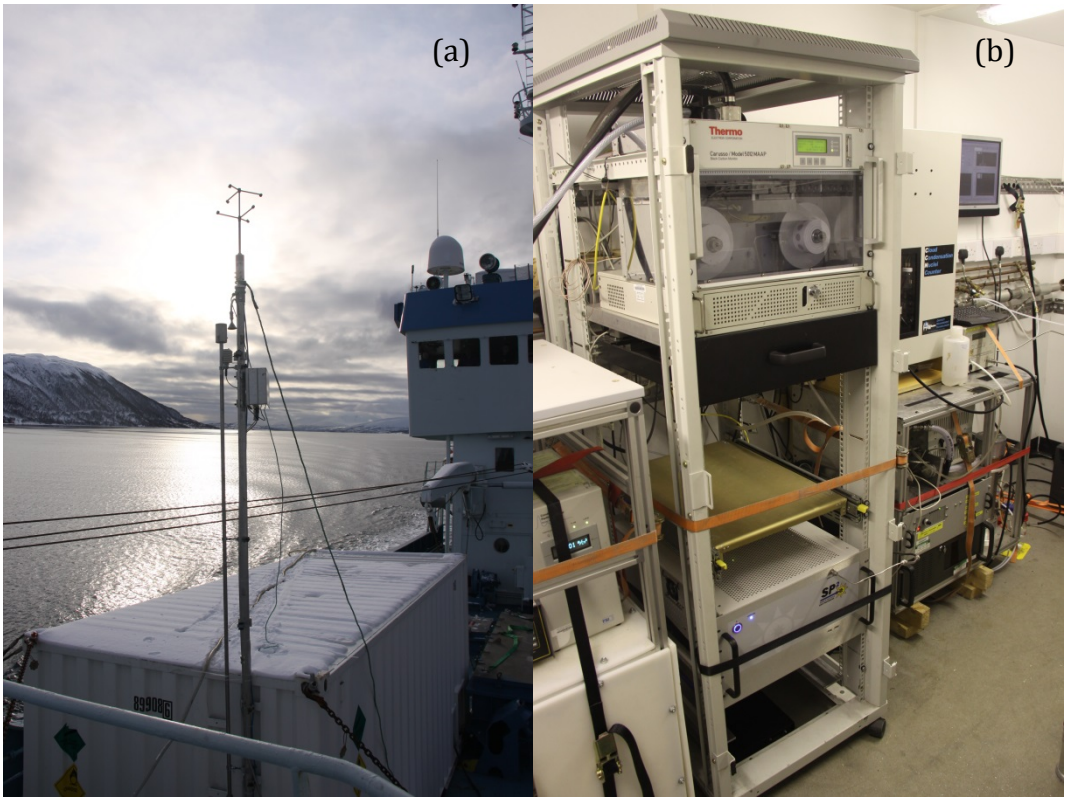

Figure 8.1: Sea-container lab located on the foredeck of RV Lance during spring cruise: (a) External view showing the aerosol inlet system mounted on a side mast; (b) Inside view showing part of measurement instrumentation used for monitoring ambient aerosol

- *Droplet Measurement Technologies Single Particle Soot Photometer (SP2)*: measurements of aerosol black carbon mass and number concentrations, size distribution and mixing stat, in individual airborne particles. Size range 200-1500 nm, soot mass range 1-300 femtograms (~10^{-15} g) per particle

- *Multi Angle Absorption Photometer (MAAP)*: for optical measurement of equivalent aerosol black carbon concentration and aerosol light absorption properties on particles collected on a filter substrate.

- *Meteorological conditions*: wind speed and direction, barometric pressure, ambient temperature and relative humidity were monitored using 3D apparent wind vector anemometer (Metek Sonic) and humidity probe (Hygroclip Rotronic), which were mounted in a box at the top side mast. Metereological measurements were made specific to the point of aerosol inlet sampling to screen for ship influences (*i.e.* ship stacks).

- *Compact Cascade Impactor (CCI):* to collect particles of different size ranges using an integrated system with a series of impactors with decreasing cut off diameters (6 size substrates). Aerosol samples were taken daily for off-line ICP-AES analysis of soluble aqueous ions (*i.e.* Na^+, K^+, Mg^{2+}, Ca^{2+}).

Table 1: list of CCI samples collected during spring cruise (B=blank, CB=cassette blank, S=Substrate)

Date	Samples	B	CB	S
Test	0	0, 1, 2, 3		0:1, 0:2, 0:3, 0:4, 0:5
15/03/13	1	1:1, 1:2, 1:3	1:1, 1:2, 1:3, 1:4, 1:5	
16/03/13	2			2:1, 2:2, 2:3, 2:4, 2:5, 2:6
17/03/13	3			3:1, 3:2, 3:3, 3:4, 3:5, 3:6
18/03/13	4	4:1, 4:2, 4:3		4:1, 4:2, 4:3, 4:4, 4:5, 4:6
19/03/13	5			5:1, 5:2, 5:3, 5:4, 5:5, 5:6
20/03/13	6			6:1, 6:2, 6:3, 6:4, 6:5, 6:6
21/03/13	7			7:1, 7:2, 7:3, 7:4, 7:5, 7:6
22/03/13	8	8:1, 8:2, 8:3		8:1, 8:2, 8:3, 8:4, 8:5, 8:6
23/03/13	9		9:1, 9:2, 9:3, 9:4, 9:5	9:1, 9:2, 9:3, 9:4, 9:5, 9:6
24/03/13	10			10:1, 10:2, 10:3, 10:4, 10:5, 10:6
25/03/13	11			11:1, 11:2, 11:3, 11:4, 11:5, 11:6
26/03/13	12			12:1, 12:2, 12:3, 12:4, 12:5, 12:6
27/03/13	13			13:1, 13:2, 13:3, 13:4, 13:5, 13:6
27/03/13	13b			13b:1, 13b:2, 13b:3, 13b:4, 13b:5, 13b:6
28/03/13	14			14:1, 14:2, 14:3, 14:4, 14:5, 14:6
29/03/13	15	15:1, 15:2, 15:3		15:1, 15:2, 15:3, 15:4, 15:5, 15:6

8.2.2 Bubble tank production

A bubble tank designed for the simulation of bubble bursting and breaking wave processes was employed as marine aerosol generator, which consist of a sealed PTFE tank with a water re-circulation pump which impulses water through a distribution system for the generation of four water jets.

Seawater samples collected daily by deploying a CTD (Conductivity, Temperature and Depth) were added in the bubble tank. Sea spray aerosols generated by bubble tank were measured as number size distributions (TSI 3080 SMPS) while air flow, temperature and relative humidity (RH%) conditions were recorded. Dry aerosol measurements (SMPS) in the size range from 15 nm to 700 nm were obtained during a 120 seconds measurement period.

Complementarily aerosol instrumentations were employed to sample these generated sea-spray aerosols to fully characterize their hygroscopic and cloud activation aerosol properties based on the variability in the sea-spray composition resulting from different seawater samples.

Table 2: location details at which seawater samples were collected from CTD during spring cruise

Date	CTD number	Latitude	Longitude	Depth/m
17/03/2013	1	77°17'N	11°E	9
18/03/2013	2	80°N	4°E	3
19/03/2013	3	80°N	5°E	6
19/03/2013	4	79°N	0°E	4
21/03/2013	5	78°N	9°E	3
22/03/2013	6	77°N	4°E	3
23/03/2013	7	76°N	4°E	3
24/03/2013	8	75°N	10°W	2
25/03/2013	9	74°N	7°W	2
26/03/2013	10	73°N	13°W	2
27/03/2013	11	72°N	11°W	3
28/03/2013	12	70°N	16°W	3

29/03/2013	13	70°N	9°W	3
30/03/2013	14	70°N	2°W	5

References

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- Fuentes, E., H. Coe, D. Green and G. McFiggans, On the impacts of phytoplankton-derived organic matter on the properties of the primary marine aerosol Part 2: composition, hygroscopicity and cloud condensation activity, *Atmos. Chem. Phys.* **10**, 26157-26205, 2010

Appendix I: Meteorological observations log

James Lee (UoY)

Date	Time UTC	Lat Deg	Lat Min	Long Deg	Long Min	Sea state	Course	Wind strength	Cloud	Air temp	Sea temp	Comments
16/03/2013	07:30	72	47.7	15	40.3	high	340	high	fully overcast	-0.5	5.5	largely sampling stack from front mast sample lines
16/03/2013	15:00	74	3.4	15	24.8	high	340	high	broken cloud	0	5.4	only occasional stack sampling
17/03/2013	09:00	77	17.2	11	19.5	med	355	high - med	mainly clear	-2.6	3.7	CTD1 taken
17/03/2013	18:00	78	37.2	9	19.9	low	330	low	clear	-2.6	3.1	
18/03/2013	07:30	80	16.4	4	34.6	low	stop	low	clear	-3.5	-2.6	full ice coverage - cant drop CTD
18/03/2013	09:00	80	0	5	0	low	stop	low	clear	-3.5	-2.6	edge of broken ice - CTD2
18/03/2013	09:40	80	15	4	30	low	stop	low	clear	-3.5	-2.6	stop in ice for day for Nox emission measurements
19/03/2013	08:00	80	0	5	30	high	stop	moderate	cloudy	-5.5	2.2	open water CTD 3
19/03/2013	15:00	79	30	2	50	med	220	moderate	cloudy	-6.2	2.2	underway in open water to CTD4 point
19/03/2013	20:00	79	0	0	37	med	stop	moderate	cloudy	-7.8	-0.4	CTD4 taken
20/03/2013	08:00	78	55.6	3	5.8	calm	115	low	some clouds	-3.7	-1.7	Heading for longyearbyen
21/03/2013	08:00	78	9	9	0	calm	stop	low	broken cloud	-3.2	3.5	CTD 5 in open water - FAAM overflight
22/03/2013	08:30	77	30	4	0	calm	stop	low	cloudy	-2.8	-1.5	CTD 6 on edge of ice then move into ice, more broken than ice station 1
23/03/2013	08:30	76	30	4	0	calm	stop	low	cloudy	-9	0.5	CTD7 in open water
24/03/2013	08:30	75	0	10	45	calm	stop	low	clear	-10.2	-1.5	CTD 8 in clear sport between the ice - then move into the ice. Large chunks of broken ice
24/03/2013	09:45	75	0	11	15	calm	stop	low	clear	-10	-1.8	Ice broken up - stop surrounded by chunks of broken ice. CTD8B put in water for PAR measurement at solar noon
25/03/2013	08:00	74	0	7	0	med	stop	moderate	mainly overcast	-9.9	1	CTD 9 in open water - remain in position until 15:00. Increasing wind around 12:00

26/03/2013	08:00	73	0	13	0	calm	stop	mod - high	mainly overcast	-15	-2.1	CTD10 on edge of ice (surrounded by it), then move into ice for day
27/03/2013	09:30	72	0	11	0	rough	stop	mod - high	mainly overcast	-11.2	-1.2	CTD11 in open water then move directly to next point - rough seas. Much calmer and sunny as we headed south
28/03/2013	08:00	70	30	11	50	calm	stop	low	mainly overcast	-9.1	-1.2	CTD12 sourounded by ice then stay until 18:00
29/03/2013	08:00	70	0	9	43	calm	stop	low	broken cloud	-5.6	1.1	CTD 13 in open water then carry on East
30/03/2013	07:45	70	0	2	0	rough	stop	mod	overcast - snowing	-1	4.9	CTD14 in open water ten carry on east