MARATHON

Marine Atmosphere Oxidation Capacity Experiment

MARATHON

ENV4-CT95-0004

Leading scientist:

Dr. Hans-Peter Dorn
Forschungszentrum Jülich GmbH (FZJ), Institut für Atmosphärische Chemie, 52425 Jülich, Germany
Tel.: +49-2461-61-6768
FAX: +49-2461-61-8188
e-mail: ✉ h.p.dorn@fz-juelich.de

Description of the project:

One of the most important issues in global tropospheric chemistry is the quantification of the oxidation capacity ("self-cleansing ability") of the troposphere and their sensitivity to changing human influence. The oxidising power is predominantly determined by the concentration of hydroxyl radicals (OH) because oxidation by OH is the dominant sink for most trace gases in the troposphere. As a consequence of the high reactivity of OH the photochemical system controlling OH is complex with many intricate feedback loops; its analysis requires rather complicated numerical models. In order to test these models, it is necessary to have measurements of tropospheric OH concentrations along with measurements of those parameters which are known to determine the concentration of OH in a given air mass.However, OH measurements are extremely difficult because of the very low concentration which hardly exceeds summertime maxima of $1x10^7$ radicals per cm^3. Although the first indication of the importance of OH radicals was already given by Levy II in 1971, even until today only few direct tropospheric in situ OH measurements were successful.Predominantly these measurements were performed at locations in the continental boundary layer with the exception of campaigns carried out at the Mauna Loa Observatory which, however, were made partially in the free troposphere. So far no experimental OH data exist for the remote marine boundary layer over the oceans which constitutes about 25% of the mass of the global atmosphere. The ***Marine Atmosphere Oxidation Capacity Experiment, MARATHON***, was a ship-based measurement campaign carried out with two major topics:The first was the investigation of the latitudinal distribution of hydroxyl radical concentrations in the marine boundary layer (MBL) over the Atlantic Ocean and the factors controlling this distribution. We measured the concentration of OH radicals onboard the German research vessel RV POLARSTERN using differential UV-laser absorption spectroscopy.Simultaneously to OH we measured baseline data of parameters important in controlling the local OH concentration including meteorological parameters, aerosol data, O_3, H_2O, NO*, NO_2*, CO, CH_4, H_2O_2*, HCHO*, NMHC, and photolysis rates of O_3, NO_2, H_2O_2, and HCHO. Most of the OH measurements during MARATHON were carried out in the southern hemisphere in the anthropogenically unperturbed marine troposphere.The second topic of MARATHON was the investigation of the photochemistry of dimethyl sulfide (DMS). DMS is the dominant sulfur gas in surface marine waters, where it is formed by phytoplancton. The sea is supersaturated with DMS resulting in a net flux from the ocean to the atmosphere where DMS is readily oxidized by OH radicals forming SO_2 and methanesulphonic acid (MSA). SO_2 can undergo further gas phase oxidation by OH or liquid phase oxidation by H_2O_2 to form H_2SO_4. MSA undergoes gas-to-particle conversion to form submicrometer aerosol particles or is absorbed into cloud water were it becomes rapidly oxidized to non-sea-salt sulfate (nss-SO_4). Submicrometer sulfate aerosol particles affect the Earth's radiation budget and thus the climate.

---

*data by Rolf Weller, AWI Bremerhaven

Objectives of MARATHON:

- Measurement of the latitudinal distribution of OH radical concentrations in the marine boundary layer (MBL) over the Atlantic Ocean during a ship cruise using long-path laser absorption spectroscopy.
- Simultaneous measurements of parameters important in controlling the OH concentration, including O_3, H_2O, photolysis rates, condensation nuclei (CN), aerosol surface, and meteorological parameters.
- Measurement of the concentration of dimethylsulfide (DMS) and its precursor dimethylsulfoniumpropionate (DMSP) in ocean water and in the atmosphere.
- Determination of the oceanic source strength of DMS and the OH-radical controlled lifetime of DMS in the MBL.
- Measurement of DMS oxidation products (MSA, DMSO, SO_2, nss-SO_4^{-2}) in the atmosphere and in the heterogeneous phase on aerosols.
- Assessment of the role of DMS oxidation products in the formation of sub-micrometer aerosol particles and cloud condensation nuclei.
- Development and test of a box model used for the description of the OH/DMS photochemistry.

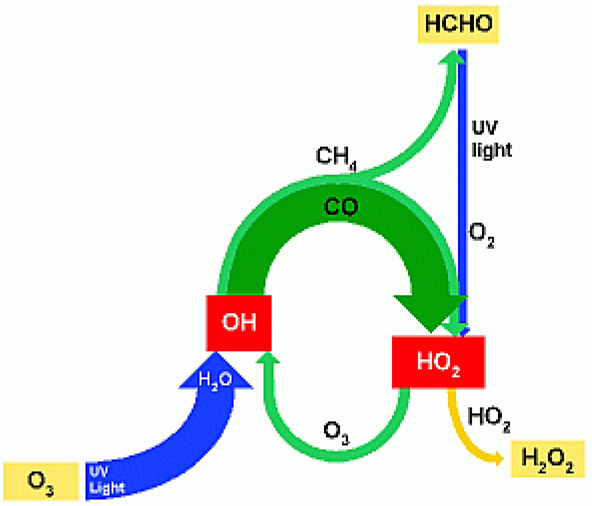
RESULTS

I) Photochemistry of OH Radicals

a) Measurements of ancillary data

During the entire campaign the photolysis frequencies of ozone and nitrogen dioxide were recorded by filter radiometers with seconds time resolution. Together with the available ozone data and the water vapour measurements the primary production rate of OH from ozone photolysis was calculated for all days.From October 6 to November 4 we continuously recorded meteorological parameters, condensation nuclei, aerosol scattering coefficient, and solar radiation data on the compass deck (details see individual report). Ozone mixing ratios were measured with two UV photometers which sampled the air on the port and starboard side of the compass deck. During the cruise we observed episodes with significant differences in the ozone readings of both instruments. This effect is attributed to local pollution by the ship exhaust and is also reflected in the CO data set. Non-contaminated ozone concentrations ranged from 15 ppb at the equator, 25 ppb in the southern hemisphere, and 30 ppb in mid-northern latitudes.The latitudinal variation of CO was measured by an in-situ gas chromatograph with a detection limit of 1 ppb and a time resolution of 2 minutes. During the cruise CO was measured from 68°N to 45°S (in total more than 7800 samples). The CO mixing ratio steadily decreased from (95 - 110) ppb in the northern hemisphere to (50 - 75) ppb in the southern mid-latitudes. Short periods of highly increased CO can be attributed to contamination by ship exhaust. Additionally we collected 107 whole air samples which were analysed for methane, hydrocarbons, and halogenated hydrocarbons in the lab.

b) OH radical measurements and photochemistry



For the first time direct and absolutely calibrated measurements of the OH radical concentration in the marine boundary layer were performed. The long-path laser absorption instrument was set up on the compass deck of RV POLARSTERN about 25 m above sea level. In total we performed about 600 OH radical measurements within the latitudinal range 5°N to 35°S. The time resolution for a single OH measurement was 5-10 minutes. Simplified OH photochemistry for low-NOx conditions. Under these conditions photochemical ozone loss is observed during the day. Most of the OH measurements were performed under very low (<3-25 ppt) concentrations of nitric oxides ('low-NOx conditions'). In contrast to all OH measurements carried out so far at continental sites the MARATHON cruise offered the unique opportunity to observe OH radicals in a regime where net photochemical ozone destruction is observed. Such conditions can only be found far from anthropogenic sources, i.e., on the oceans. During the measurements in the tropics and subtropics NO_x concentrations were often below the detection limit of 3ppt. The observed noontime maximum OH concentrations were around $8x10^6$ OH/cm^3. From the days with full coverage by OH measurements we calculated a 24 hours mean OH concentration of $(1.5\pm0.3)\times10^6$ OH/cm^3 in the latitudinal range 1°N 30°S along the 30°W meridian (October 24 - November 02, 1996).As predicted by the theory for low-NOx conditions we found a linear correlation of the measured OH concentrations with the primary production rate of OH (which is photolysis of ozone, P(OH)). The statistical analysis shows that 72% of the observed OH variability is explained by the variability of P(OH). The steady state OH concentration during MARATHON was theoretically estimated for low-NOx conditions under the assumption that secondary OH production from the HO_2 pool was negligible. Taking into account only the measurements of ozone, water vapour, ozone photolysis frequency, carbon monoxide, and methane (see figure above but ignoring the reaction of HO_2 with O_3) the calculated OH exceeds the measured concentrations twofold (on the average). When additional first order losses of OH via H_2, HCHO, H_2O_2, and O_3 are added the overprediction of the 'model' is reduced to less than 20% on the average.On the basis of our trace gas measurements we calculated an OH radical lifetime of one second for the remote marine boundary.The OH concentration data together with the set of ancillary measurements allow the first direct characterisation of the self cleansing ability (oxidation capacity) of the background marine troposphere. The measurements of a variety of trace gases, photolysis frequencies, and OH radicals represent a unique data set for testing and initialisation of various models of tropospheric photochemistry (box models and 3d-models) as well as of radiation transport models.

II) Investigation of the DMS photochemistry

Between October 10 and November 4, 931 sea water and 130 atmospheric samples of dimethylsulfide (DMS) have been collected and immediately processed onboard using two Varian gas-chromatographs.
Sea water DMS concentrations were measured continuously from 67°N to 45°S and ranged from 5-210 ngS/l. The lowest values were observed close to Iceland and the highest within the subtropical convergence zone at 40°S to 45°S. High DMS values were also observed within the north and south equatorial currents. Atmospheric DMS concentrations were measured from 58°N-38°S and ranged from 20 to 400 ppt (mean 120 ppt). The lowest atmospheric concentrations of DMS observed around 55°N and 38°S are in line with the low DMS values measured in sea water in the same areas.
Wind speed and air-masses origin seem to be other important factors controlling the atmospheric DMS concentrations. Pronounced diurnal variations have been observed for atmospheric DMS with the lowest concentrations between 12-18h. This is a clear indication that photochemical degradation via oxidation by OH is the main process controlling the fate of DMS in the marine atmosphere. On these days the noon time average OH concentration varied between $(6\text{-}8)\times10_6$ OH/cm$_3$. The corresponding DMS lifetime thus varied between 8 and 6 hours, respectively.Aerosol methane sulfonic acid (MSA) concentrations found on aerosols correlate quite well with the observed atmospheric DMS concentrations and air-sea flux of DMS. The size distribution of MSA in particles was calculated from the analysis of all cascade impactor filters sampled along the cruise. About 54% was found in the particles with diameter lower than 1mm. Thus, almost half of the MSA was present on the sea salt aerosol and had not involved in new particle production.
Dimethyl sulfoxide (DMSO) concentrations in the sub-micronic particles compare very well with DMS flux, better than the MSA indicating that the measured DMSO concentrations better reflect the variability of the local source of DMS.
Although the box model of the DMS photochemistry describes qualitatively quite well the variability of the observed atmospheric DMS concentrations, it calculates a day to night amplitude smaller by about a factor of 2.5 compared to measurements. In addition during night the model underestimates the atmospheric DMS concentrations. From these first model calculations a number of open questions result:
I: What is the accuracy of the sea-to-air DMS flux? Models employed for calculating the DMS sea-air transfer are difficult to test and may not be accurate to better than a factor of two [Ayers et al., 1995].
II: What is the accuracy of the DMS oxidation rate coefficients? Is there any unaccounted DMS oxidant or oxidation pathway, such as reactions with Cl, Br or BrO?
III. Can the impact of dynamics (i.e., vertical mixing) in the marine boundary layer be ignored a priori in the model of DMS?During MARATHON simultaneous measurements of DMS in sea water and in the atmosphere were carried out with high time resolution over a latitudinal range of 112 degrees which is one of the largest data sets ever measured in the Atlantic region. These measurements fulfil the central need of representative ocean surface water data against which the atmospheric data can be more rigorously compared. This will help to get a more detailed insight into the atmospheric sources and sinks of dimethyl sulfide.

Interaction with other EU Projects

During the ship campaign OH radicals were simultaneously measured by another laser spectroscopic technique, ***Laser Induced Fluorescence spectroscopy (LIF)***. These measurements were carried out within the EC funded project DCHOR, ENV4-CT95-0003 (Co-ordinator: Dr. A. Hofzumahaus, Forschungszentrum Jülich).

The temporally overlapping measurements of both OH instruments allowed for the first time an intercomparison of two in-situ OH instruments under low-NOx conditions where the OH photochemistry is less complex than under continental conditions.
In the view of potential calibration and sensitivity problems and possibly systematic errors of any OH measurement technique it is very important (and actually a demand of the scientific community) to compare different OH instruments in the field in order to assess the reliability of the OH detection and the accuracy of its calibration.
The long-path absorption spectroscopy is an absolutely calibrated technique of high accuracy (error less than 7%) and is therefore ideally suited to test the calibration technique developed for the LIF instrument.
The comparison of both OH data sets shows a very good agreement. Details are presented in the final report of the DCHOR project.

Acknowledgement

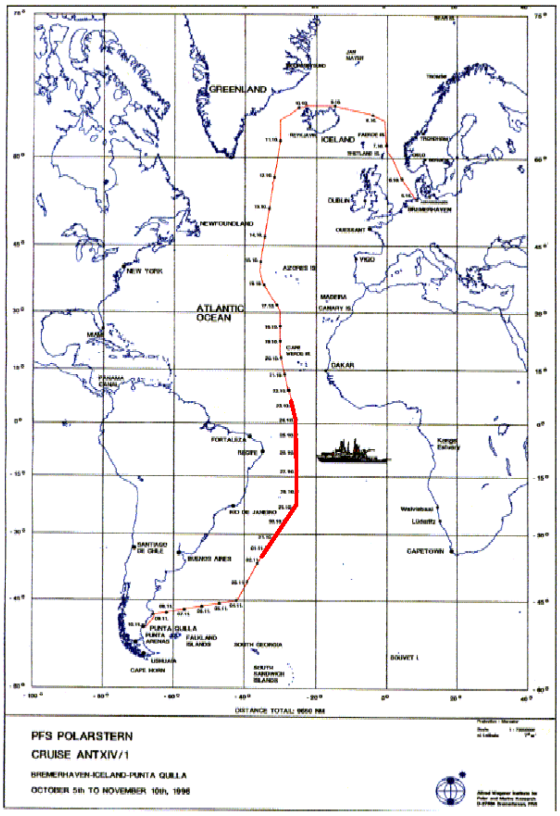
All participants of MARATHON want to express their thanks to the crew of RV POLARSTERN, in particular we are grateful to captain Jürgen Keil and chief engineer Volker Schulz for their continuous interest in our work and their always friendly and more than generous support prior and during the cruise.
We also thank all participants of the ALBATROSS science team for their good co-operation and for providing their data prior to publication, particularly to the DCHOR team (EU grant ENV4-CT95-0003).
The "MARATHON crew" is very grateful to the **European Commission** for the financial support under grant **ENV4-CT95-0004**.

The results are published in:

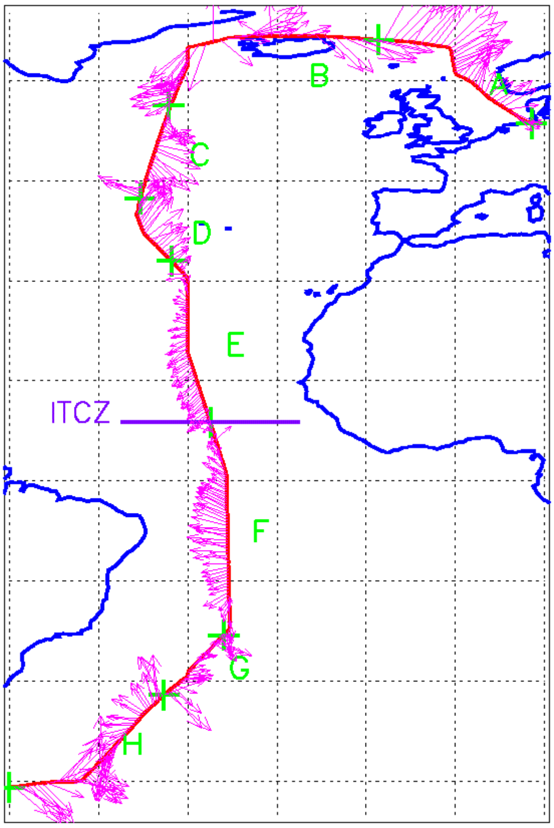
Brauers, T., Hausmann, M., Bister, A., Kraus, A., Dorn, H.-P.
OH radicals in the boundary layer of the Atlantic Ocean. First measurements by long-path laser absorption spectroscopy.
J. Geophys. Res., 106, 7399-7414, 2001.

PICTURES

The Scientists

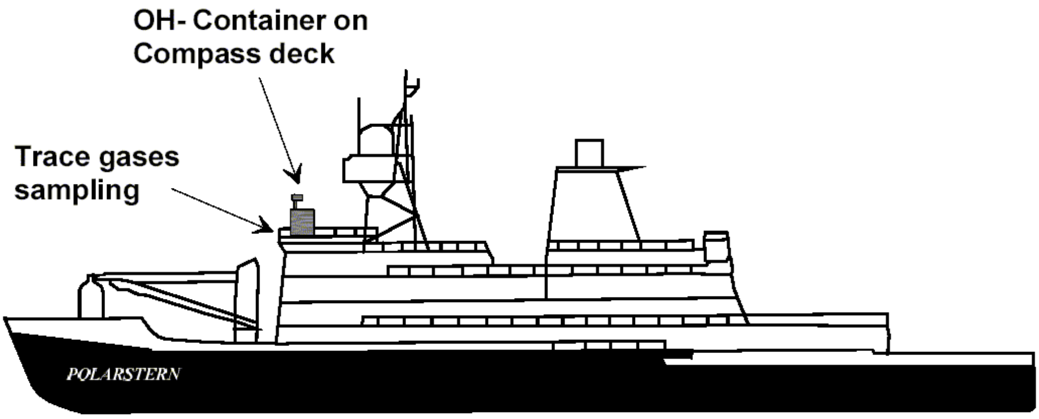


The Cruisetrack

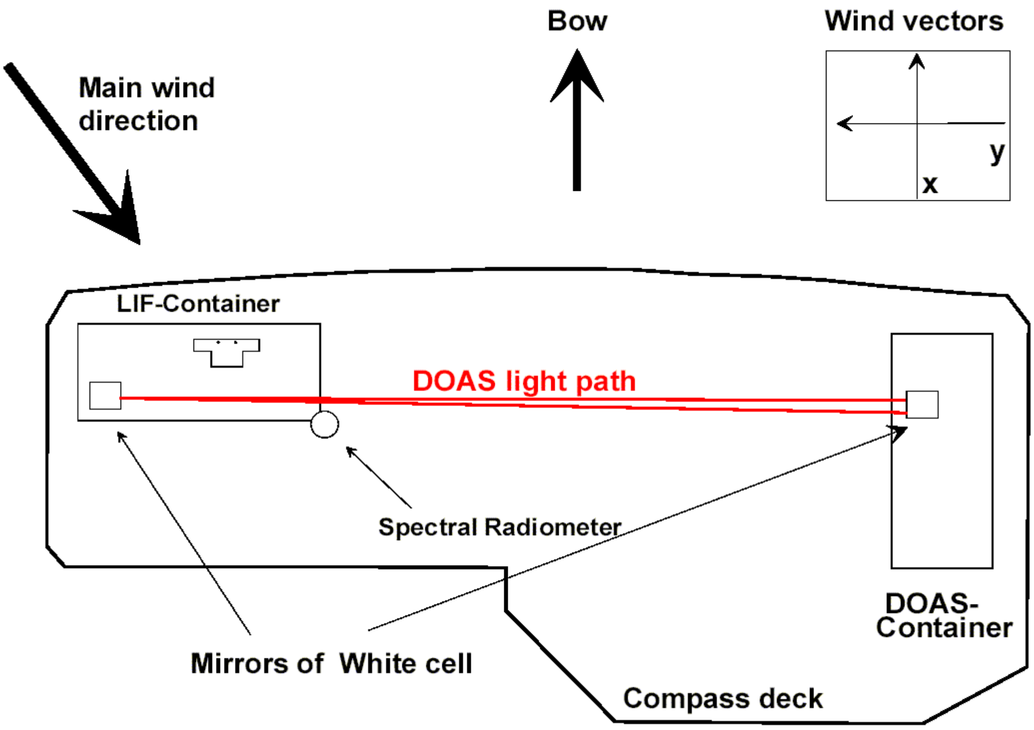


The Cruise winds

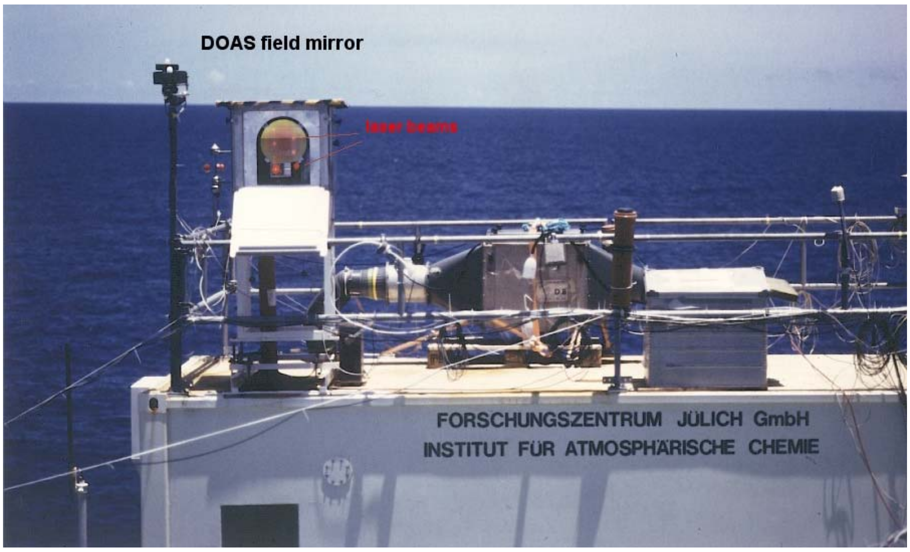
The DOAS Container



POLARSTERN side view

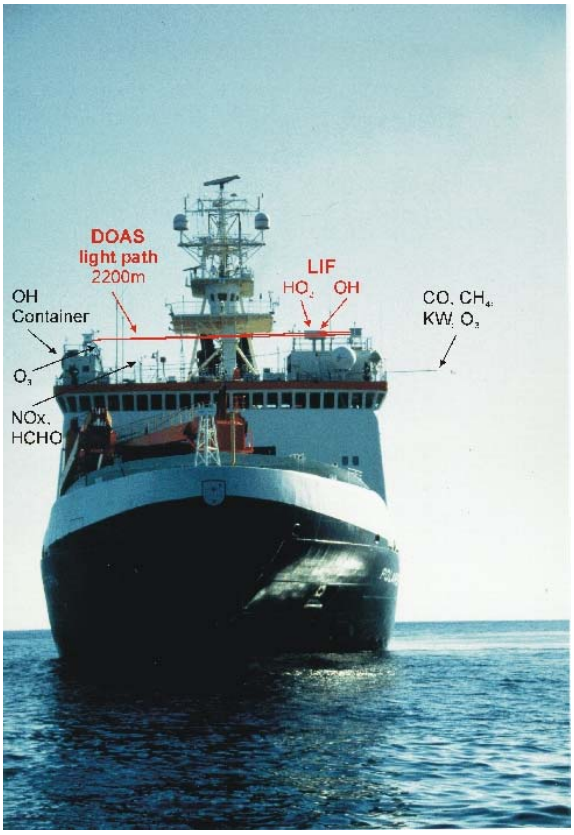


POLARSTERN top view

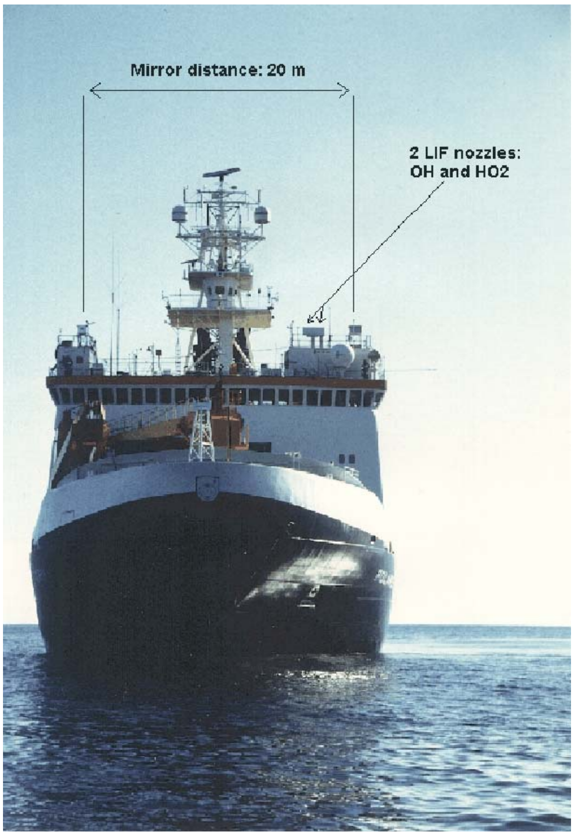


DOAS Container Description

LIF Container Description



Instrumental Setup



POLARSTERN Bow Description

Sunset

Sunset from the brigde