Institut für Meereskunde an der Universität Kiel

Cruise Report

F.S. "POSEIDON"
Cruise 211

31.8. - 11.9. 1995
Reykjavik (IS) - Lisbon (P)

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Marine Chemistry Department
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CONTENTS

1. Purpose of the cruise

On the cruise 211 of R. V. POSEIDON leading from Reykjavik, Iceland, to Lisbon, Portugal, several investigations concerning the air-sea exchange of trace gases should be carried out, most of the participating groups beeing tied to the OMEX-air-sea exchange group.

2. List of participants

Dr. Ludger Mintrop	chief scientist	UBG, Bremen and IfM, Kiel, D
Dr. Robin Keir	scientist	GEOMAR, Kiel, D
Gregor Rehder	scientist	GEOMAR, Kiel, D
Dr. Stuart W. Gibb	scientist	PML, Plymouth, GB
Angela Hatton	scientist	UEA, Norwich, GB
Jonathan M. Baker	scientist	UEA, Norwich, GB
Cyril Szakolczai	scientist	CNRS, Gif-sur-Yvette, F
Finn Hansen	technician	RISO, Roskilde, DK
Marcel Moerman	technician	TNO, Den Haag, NL
Jorge Pérez Juste	student	IIM, Vigo, ES
Marcus Busse	student	IfM, Kiel, D

abbreviations:

UBG	*Universität Bremen, Fachbereich Geowissenschaften*
IfM	*Institut für Meereskunde an der Univ. Kiel*
GEOMAR	*Forschungszentrum für marine Geowissenschaften*
PML	*Plymouth Marine Laboratory*
UEA	*University of East Anglia, School of Environmental Sciences*
CNRS	*Centre National de Recherche Scientifique*
RISO	*Riso National Laboratory, Meteorol. Department*
TNO	*TNO Physics and Electronics Laboratory*
IIM	*Insituto de Investigaciones Marinas*

3. Research program

The planned cruise track is shown in Figure 1a with the stations indicated where CTD-casts should be taken. After leaving Reykjavik a station situated in the Denmark Strait shall be approached, using the time to fully install all systems and start first underway measurements. A hydrocast is planned at the first station mainly to characterize the different water masses expected along the depth profile and their concentrations of the different compounds listed below, which will be analysed during this cruise. The second station will be the Goban Spur near the Irish shelf, a central region of OMEX. The last station off the Portuguese coast is planned as a pilote to future OMEX-activities in this area. However, main emphasis is laid on underway investigations to measure the variables listed in the following:

Carbon dioxide and oceanic carbon system variables:

Emission of anthropogenic carbon strongly disturbs the natural carbon cycle. The ocean with its largest accessible carbon reservoir on earth will ultimately control carbon concentrations in the atmosphere, but the short term reaction on the anthropogenic pertubation is most important for the development of climate in the near future. The flux at the air-sea interface is regulated by the difference of partial pressure of CO_2 in the two phases. Partial pressure of CO_2 in surface seawater and air shall be followed during the whole cruise by a continuously measuring IR-system (IfM Kiel) and a GC-system, which allows for the analysis of a sample approx. every 10 minutes (GEOMAR Kiel). The flux of CO_2 between ocean and atmosphere should be measured directly by a dissipation method with two instruments installed in parallel in the ship´s mast. From surface samples taken at certain time intervals (ranging from 30 minutes to 4 hours) pH will be measured on board ship and samples shall be taken to determine alkalinity (IIM Vigo, IfM Kiel) and total carbonate (IfM Kiel). This will allow for the analysis of the oceanic carbonate speciation. The internal consistency of the carbon parameter (pH, pCO_2, alkalinity, total carbon) shall be checked as well as the comparability of results from different labs.

Methane:

Methane is a trace gas in the atmosphere which has a variety of natural and anthropogenic sources. In shallow seas, methane concentration will be controlled by the intensity of in-situ sources such as gas seeps, and the rates of oxidation and gas exchange with the atmosphere. To learn more about the natural pathways of methane also for the interpretation of continental margin and deep-sea data (OMEX), the opportunity of this cruise shall be used. Samples from hydrocasts as well as from surface sea water shall be analyzed for dissolved methane concentrations.

Sulfur compounds:

Volatile sulfur compounds like dimethylsulfide (DMS) are produced by biological processes in the sea surface and emitted into the atmosphere. DMS is generated from the breakdown of dimethylsulphoniopropionate (DMSP), an osmoregulatory compound of phytoplanktón. Once in the atmosphere it formes the bases for cloud nuclei, contributing to the acidity of rainwater. DMS can also be oxidized to dimethylsulphoxide (DMSO) via photooxidation or bacterial oxidation. Atmospheric concentrations are approximately two orders of magnitude lower than those in seawater, so there is effectively a net one-way flux of DMS from the ocean to the atmosphere. Investigations about this flux should be determined from measurements of DMS concentrations in air and surface seawater during the cruise.

Nitrogen compounds:

Nitrogen compounds in oxic seawater range from the thermodynamically most stable species, nitrate, to reduced compounds such as ammonia and its methyl derivatives, the methylamines (monomethylamine, MMA; dimethylamine, DMA and trimethylamine, TMA). These are biogenic compounds widely distributed in the marine environment and intimately involved in oceanic nitrogen fertility. By virtue of their volatility they are capable of evasion across the air-sea interface and may be an important source alkali to the troposphere and so subsequently play a significant role in the regulation of atmospheric and rainwater pH. Analysis of methylamines and ammonia were to be carried out during the cruise in order to help answer these questions.

Halocarbons:

The halocarbon methyl bromide (CH_3Br) is the major source of bromine ions to the stratosphere. Bromine has an ozone depletion potential of up to six times that of chlorine, so is a very effective ozone destroyer. The sources of CH_3Br are both anthropogenic (structural and agricultural fumigants, gasoline) and natural (the ocean and biomass burning). Very little is known about the fluxes to the atmosphere from any of the sources, especially from the ocean; some scientific groups believe the ocean to be a source and some a sink. On the cruise, the concentrations of CH_3Br, CH_3Cl and CH_3I were to be determined in surface water and air samples to answer this question.

Nutrients:

Since nutrients are essential for any build up of organic carbon by organisms their concentrations can serve as indicator for biological processes and to trace the biological history of a water parcel and its potential for further development. Since the trace gases under investigation on this cruise are more or less coupled to biological processes, nutrient analysis from surface samples should be carried out to support the other investigations.

Chlorophyll and carotenoid pigments:

In biological oceanography the photosynthetic pigments, in particular Chlorophyll a, have long been recognised as unique and convenient markers of phytoplankton biomass. Although spectrophotometric and fluorimetric techniques have been widely used to determine biomass, the utilisation of high performance liquid chromatography HPLC not only permits a more accurate measurement of Chlorophyll a, but also allows simultaneous separation and quantification of a range of other chloropigments and carotinoids in marine phytoplankton. Many of these compounds have strong chemotaxonomic associations, through which it is possible to obtain an understanding of the taxonomic composition of the overall phytoplankton biomass. It might be possible that pigments are potential proxy biomarkers for biogas fluxes. However, as far as methylated biogases are concerned, particularly the MA's and halocarbons, correlation data is extremly sparse. So analysis of chlorophyll and carotenoids on this cruise in parallel to the biogas measurements should serve to close this gap.

4. Narrative of the cruise

leaving Reykjavik ...

The cruise POSEIDON 210 ended in Reykjavik, Iceland, on August 28. The following day was filled with activities to unload the ship, while a lot of logistic problems had to be solved to get all the equipment of the various groups together for the next cruise. After the members of the last cruise had left the ship in the morning of August 30, hectic activities began to convert the ship into the place with the highest instrument density except Spacelab, not without provoking questions like "how many months are you going to stay here?". The last delivery of equipment arrived few minutes before the POSEIDON left the pier on August 31 at 10:00 for its 211th cruise to sail west towards the first planned station in the Denmark Strait.

The setup of instruments continued the first day and a seawater pump was mounted in the moon pool of the ship to supply seawater for sampling and continuous measurements. The CTD, that had been successfully used on the last cruise, had been mounted into a 24 x 10L-bottle rosette.

starting the measurements ...

The continuous determination of methane started on September 1, using an equilibrator feed by the seawater supply. Unfortunately, the transport had killed the computer for continuous pCO_2 measurement, so the system had to be converted to a manual mode, thus allowing to start the measurements in the afternoon at the location where the first station was planned.

the stationwork ...

After a first test of the CTD-rosette with the instrument standing on deck was positive, a test station was inserted into the scedule. The rosette was lowered to about 200m and bottles were triggered to close. Data transmission worked well, but when the rosette was recovered, no bottle had closed. While approaching the first station, all connection and the release system were checked and the rosette tested while standing on deck, with mixed success. The ship´s electrical engineer did a brave job to localize problems in the wire and fix them. However, problems in the release trigger system persisted. A further test after stopping the ship lowering the rosette to 100m failed again as did any attempts when the location of the first station was reached. When there was no hope left for the problem to be fixed, the first station had to be left without sampling. The next days, a lot of effort was undertaken to solve the rosette problem, consulting the experts in Kiel by fax and telephone endlessly. The weather forecast solved the problem, unfortunately not in a positive way: due to reported bad weather in the target region the course was altered, even partly going back, to avoid getting in close contact with the storm. This made the expected time of arrival in Lisbon questionable, so the course had to be changed again to head directly to Lisbon as soon as the weather would allow, thus omitting the Goban Spur station and leaving no ship time left for the third station.

underway sampling ...

Since no deep samples could be expected any more, the surface measurement program was intensified to get an optimal data coverage and also to include some processes off the Spanish and Portuguese coast. No coastal upwelling was observed at the Portuguese coast, although this is reported to be a regularily observable feature at this time of the year. After passing the estuary of the Tejo river the seawater pump was switched off and the remainig instruments were packed.

arriving Lisbon ...

The pier was reached at 14:00 hrs on Sept. 11. All hands were needed to pack all the equipment as quickly as possible to get the container from board and give the crew the opportunity to wash the ship from top to bottom for the following day. On Sept. 12 a press conference and a reception was held at the beginning of the next cruise, when Prof. G. Siedler took over as chief scientist for the next cruise, # 212.

at last ...

The scientific question about upwelling was solved later by GEOMAR: Gregor Rehder, relaxing from the cruise, stepped into the water of the Algarve coast two weeks after the cruise where he could feel a very effective upwelling by getting ice-cold feet but learned at the same time from fellow-holidaymakers that this has not occured but very recently. This findings lead to the conclusion that obviously the seasonal upwelling occured late this year and started well after the cruise had been terminated.

5. Preliminary results

5.1. Hydrography (M. Busse, L. Mintrop)

Along the transect (see Fig. 1b), temperature and salinity were registered continuously by the thermosalinograph and stored as 1-minute mean values. The cruise track is divided into two parts, the first from Reykjavik (A) to the location where the first station was planned (B), and the second part from there to Lisbon (C). Figure 2a shows the measured water temperature and the salinity along track A-B and figure 2b shows the values along track B-C.

While there is little variation in salinity (34.9-34.95) and temperature (9.5-10.0°C) on part A-B after leaving the harbour of Reykjavik, temperature and salinity rise steadily to 20°C and 35.3, respectively, along part B-C until reaching the estuary of river Tejo.

5.2. The carbonate system

5.2.1. Total carbonate and alkalinity in surface waters (L. Mintrop, A. Körtzinger and S. Schweinsberg)

Around 80 surface samples were collected for the determination of total carbonate and alkalinity. During the time of the cruise, the instruments were about to return from an Indian Ocean expedition. They were installed on the R.V. POLARSTERN in November, therefore the samples were taken on that cruise and were measured on board POLARSTERN. Total carbonate (C_T) was measured by coulometric titration using the SOMMA-system, alkalinity by potentiometric titration with the VINDTA-system. Total carbonate values are also necessary for the interpretation of the results from the ^{13}C-measurements and alkalinity values will be compared to those obtained by the Vigo-group. This intercomparison is in progress now but is not terminated yet to be included in this report. Preliminary values are listed in the data section.

5.2.2. Determination of pH and alkalinity in surface waters (F. Fernandez Pérez and J. Pérez Juste)

Samples of surface seawater were collected at approx. 30 min. intervals during daytime. The pH was measured using a Metrohm pH meter and combination glass electrode standardisized with NBS pH 7.413 and pH 4.008 buffers. The electrode was adapted to the ionic strength of seawater by means of a synthetic seawater buffer of pH 4.4. Temperature was measured and the pH values normalized to 15°C. In order to determine the systematic errors produced by variations of residual liquid-junction potential by estimating the apparent activity coefficient of hydrogen ions, titration curves for seawater were made at the end of the cruise. The curves were linearized and the mean value obtained from the inverse slope has been used to correct the pH_{15} results. The pH_{is} is the pH recorded at zero potential. This pH_{is} can vary because of the real variations of the electrode, changes in the buffer or an error during the calibration. The anomalies from each calibration and the linear regressions have been used to correct the pH_{15} results obtained (Fig. 3a). The pH_{15} measured during the cruise is plotted vs. the Julian day in Fig. 3b.

Selected seawater samples for alkalinity were collected and stored until analysis in the land laboratory. Alkalinity was measured using an automatic potentiometric titrator (Metrohm) with a separate glass electrode and a reference electrode. Potentiometric titrations were carried out with hydrochloric acid to a final pH of 4.44. Fig. 3c shows the relationship between alkalinity and salinity. From this relationship the alkalinity for the samples not measured has been calculated.

5.2.3. pCO_2 in surface waters (L. Mintrop)

Due to the damage of the computer during transport the automatic determination of surface pCO_2 had to be converted into a manual mode. Fortunately, the data from the IR-system could be read out by a labtop found on board. The switching of the valves to measure calibration gases and atmosphere had to be done manually. Besides some more work later to the data, data quality did not suffer. Nevertheless, some corrections (moisture and temperature) still have to be incorporated into the calculation to convert the molar fraction measured into the fugacity of CO_2 in dry air at in situ temperature. However, this will not change the observed pattern, since this will likely result only in an offset correction for all data by some few micromoles. A comparison between the continuous method (IfM Kiel) and the discontinuously measuring GC-system (Geomar, Kiel) is done at the moment and not yet included in this report. Data were collected in one minute intervals, however, Fig. 4 shows the molar fraction of CO_2 from 10 minute values along the track (B-C, see above). Along the track, values are increasing from a pronounced undersaturation of the seawater in respect to the atmosphere (up to 60 ppm) to slight oversaturation in the last part, approching the Portuguese coast, until values increase dramatically in the river Tejo estuary to more than 500 ppm.

5.3. Methane and pCO_2 (R. Keir, G. Rehder)

The concentrations of CO_2 and methane in the atmosphere have both risen due to human activities, from 280 to 360 ppmV for CO_2 and from 700 to 1750 ppbV in the case of methane. Since there is an influence of these trace gases on the earth´s radiation budget, it is important to know the role of the ocean in the biochemical cycles and the ocean´s response to the changing atmospheric mixing ratios.

The importance of the ocean system to the cycle of the two gases is quite different. The ocean is believed to act as the major sink for the burden of CO_2 produced from anthropogenic sources, but in the case of methane the ocean acts as a minor source to the atmosphere.

The marine environment is believed to contribute about 2-5% to the global source strength of methane, mainly from the shelf regions. The estimate of the open ocean source has recently been reduced by one order of magnitude, based on studies in the pacific between 1987 and 1994.

A fully automated device for the detection of methane and pCO_2 was run throughout the cruise, with only short periods in which the instrument was shut down for maintainance.

Seawater concentrations are measured by the detection of the mole fraction of the gases in a sample of air that has been equilibrated with a continuous flow of seawater. The air is dried with Sicapent™, separated by gas chromatography and measured with an FID. The CO_2 is reduced by H_2 on an activated Ni-catalyst before detection.

In addition to the air sampled from the equilibrator, two calibration gases and clean, uncontaminated air pumped from the ship´s bow are measured. The whole sequence of 8 measurements (Calib.Gas1 - Equil.air - Air - Equil.air - Calib.Gas2 - Equil.air - Air - Equil.air) is run during an 80 minutes period, with a time interval of 20 minutes between 2 seawater measurements. A scheme of the device is shown in Fig. 5a.

Methane concentrations were in general in equilibrium with the atmosphere. Over Iceland shelf, the surface waters were oversaturated by ~4%. Strong oversaturations were detected in the River Tejo estuary, indicating very high methane content (Fig. 5b). The end of our investigations was unfortunately too early to give an estimate of the freshwater concentration.

The pCO_2 profiles show that the Atlantic Ocean is a strong sink for atmospheric CO_2 in the area of investigation during summer, with a partial pressure difference of nearly 100 ppmV west of Iceland. CO_2-undersaturation decreased from the North to the South (Fig. 5c), which is in agreement with previous measurements in this region. CO_2-oversaturation was only found at the end of the survey in waters influenced by the freshwater supply from the River Tejo.

5.4. Methylamines and ammonia in atmosphere and surface waters (S. Gibb)

Nitrogen, a biologically essential element in the marine environment, is found in a variety of inorganic and organic forms in oxic seawater ranging from the thermodynamically most stable species, nitrate, to reduced compounds such as ammonia and its methyl derivatives, the methylamines (monomethylamine, MMA; dimethylamine, DMA and trimethylamine, TMA). These are biogenic compounds widely distributed in the marine environment and intimately involved in oceanic nitrogen fertility. By virtue of their volatility they are capable of evasion across the air-sea interface and may be an important source alkali to the troposphere and so subsequently play a significant role in the regulation of atmospheric and rainwater pH.

An understanding of the marine distribution and biogeochemical cycling of these compounds has largely been restricted through the absence of a sensitive and selective analytical technique capable of their individual quantification at the nano-molar levels characteristically found in the marine environment. Only recently has it been possible to reliably analyse ammonia and the methylamines at these concentrations in natural waters.

The objective was to characterise the spatial distribution of the methylamines (MA's) and ammonia in the surface waters and overlying atmospheric phases of the N.E. Atlantic and to establish the magnitude and direction of their air-sea gas exchange fluxes and interpret the results of these studies within the context of the biogeochemical cycle of nitrogen. Further the distribution and fluxes of MA's were to correlate with those of their sulphur cycle analogue DMS and also the phytoplankton biomass and taxonomic composition.

Surface seawater samples were collected from an on line supply either in gas-tight polyethylene bottles (250 ml) or in glass syringes (100 ml). Methylamines and ammonia were determined by *Flow Injection Gas Diffusion coupled to Ion Chromatography* (FIGD-IC). This novel technique, recently automated for shipboard deployment, permits the simultaneous measurement of MA's and ammonia at the nano-molar concentrations typical of oceanic waters. (l.o.d. 1-3 nM; co. of variation 2-6% at 20nM for methylamines). It should be noted that FIGD-IC gives a measure of the total dissolved species present in an aqueous sample and it is these values which are reported i.e. dissolved gas+solvated cation e.g. in the case of ammonia $[NH_3]_{total} = [NH_{3(g)} + NH_4^+{}_{(s)}]$.

For atmospheric samples, tandem filter systems, equipped with cyclone separators in series with Teflon and acid impregnated paper filters, were employed in the collection of particulate and gaseous atmospheric methylamines and ammonia. Filters were frozen for subsequent laboratory extraction and FIGD-IC analysis.

Event only rainwater samples were collected using a series of polyethylene funnel-bottle combinations. Assay of MA's and ammonia were ferformed on unfiltered samples and thus reflect total (wet + dry) deposition during a rain event. methylamines and ammonia were measured in rainwater samples using FIGD-IC operated under the same conditions as for seawater analysis.

Methylamines were observed to be relatively ubiquitous in surface waters but generally at concentrations of 1-2 orders of magnitude lower than that of ammonia (see the data tables and sample chromatogram Fig. 6). MMA was consistently the most abundant methylamine, followed by DMA and TMA. The trend of decreasing concentrations with increasing methylation of the parent ammonia compound is consistent with observations made of other surface waters in both coastal and open ocean regimes (e.g. English Channel, N.W. Indian Ocean) and may be a reflection on their biogenic production and microbial transformation.

Whilst concentrations of DMA and TMA determined in the N.E. Atlantic were comparable to those recorded offshore in the Mediterranean Sea (1-9 and 0-7 nM respectively) levels of MMA exceeded even those measured recorded in the coastal euthrophic waters of the Gulf of Lions (4-38 nM). Comparable seawater concentrations of MMA have only been found previously in the monsoon driven, coastal upwelling system of the N.W. Indian Ocean.

Although the presence of ethylamine (EA), a primary alkylamine and structural isomer of DMA, has been reported by other workers it has not previously been quantified in seawater using FIGD-IC. However, during the Poseidon N.E. Atlantic transect, the occurrence of EA was indeed confirmed.

Due to the currently absence of chlorophyll and carotenoid pigments it has not been possible to determine the relationship between MA distribution or air-sea interfacial fluxes with either phytoplankton biomass or specific taxonomic algae groups. Nor has it yet been possible to correlate the spatial distribution of MA´s with DMS/DMSP.

Since atmospheric aerosols and gas samples have not yet been analysed (see also the data tables), it is not possible to describe the atmospheric distribution and speciation of MA´s and ammonia nor the magnitude and direction of their air sea exchange fluxes. However, given that some of the highest open ocean concentrations of MA´s were observed in the region between LAT 60°N LON 26°W and LAT 55°N LON 19°W it would be surprising if the ocean was not acting as a local source of atmospheric MA´s and ammonia.

Rainwater concentrations of ammonia would appear to be consistent with those previously reported for the N. Atlantic (0.1 - 23.3µM and 0 - 8.9µM). The only reported concentrations of individually resolved MA´s in rainwater of 11 - 29, 6.7 - 11 and 5.8 - 17 for MMA, DMA and TMA respectively would also appear to be in reasonable agreement.

In addition to ammonia and the MA´s, EA and one other, as yet unidentified, alkylamine were found in the rainwater samples collected.

5.5. Halocarbon analysis (J. Baker)

Methyl bromide (CH_3Br) is the major source of bromine ions to the stratosphere. Bromine has an ozone depletion potential of up to six times that of chlorine, so is a very effective ozone destroyer. It is for this reason, that the production of CH_3Br may be banned. The sources of CH_3Br are both anthropogenic (structural and agricultural fumigants, gasoline) and natural (the ocean and biomass burning). Very little is known about the fluxes to the atmosphere from any of the sources, especially from the ocean; some scientific groups believe the ocean to be a source and some a sink. The processes leading to the formation of CH_3Br are as yet unknown.

To analyse the halocarbon concentrations in the atmosphere and ocean gas chromatography was used. The air sample or stripped gas is preconcentrated on a trap at -180°C and then injected onto a column to separate the components and detected by an electron capture detector.

The concentrations of CH_3Br, CH_3Cl and CH_3I varied very little along the cruise track, maybe a slight decrease in concentrations if any change. The results will be analysed in full in the near future.

I will be collecting a large data set of CH_3Br (and various other halocarbon) concentrations in the atmosphere and ocean to be able to produce a computer model otf the global concentrations. I will be also looking into greater detail at the oceanic source.

5.6. Sulfur compounds

Dimethylsulfide (DMS) is a biogenic sulfur compound generated from the breakdown of dimethylsulphoniopropionate (DMSP), an osmoregulatory compound of phytoplankton. DMS is a volatile compound which passes readily over the sea-air interface into the atmosphere. Once in the atmosphere it formes the bases for cloud nuclei, contributing to the acidity of rainwater. DMS can also be oxidized to dimethylsulphoxide (DMSO) via photooxidation or bacterial oxidation. Atmospheric concentrations are approximately two orders of magnitude lower than those in seawater, so there is effectively a net one-way flux of DMS from the ocean to the atmosphere.

Two independent groups were measuring DMS on the cruise. Results will be compared to serve as an intercalibration.

5.6.1. Dimethylsulfide and related compounds (A. Hattón)

The objective of the cruise was to measure concentrations of DMS, DMSO and DMSP dissolved and particulate and use these to investigate the relationship between the three compounds in surface waters.

DMS was measured using a gas chromatograph fitted with a flame photometric detector. Samples were preconcentrated in a Tenax TA loop prior to analysis. DMSP samples were broken down to DMS using NaOH and DMSO was broken down using the enzyme DMSO-reductase, these were then measured as DMS samples.

Preliminary results indicated that DMS concentrations were low throughout the cruise. Concentrations ranged from <0.5-2.1 nM for DMS, <0.5-3.1 nM for DMSO, 6.8-55 nM for DMSPd and 22-80 nM for DMSPp.

5.6.2. Dimethylsulfide in surface waters (C. Szakolczai)

During the cruise, the concentrations of dimethylsulfide in seawater were measure every two hours between 7:00 and 21:00 UTC using gas chromatography with flame detection.

In total 71 DMS analyses were performed, 45 samples collected for DMSP and 45 others for DMSO. DMSP and DMSO analysis will be performed in the laboratory by the same method. In addition, the DMS detector response will be calibrated with respect to a primary standard tube.

Decreasing DMS concentrations were recorded from the North to the South of the transect. In addition, a large DMS peak was observed between 55 and 56°N, 19-20°W (Sept. 4).

A full data set will be compiled and correlated with other oceanographic and meteorological measurements.

5.7. Direct measurements of air-sea fluxes (M. Moerman and F. Hansen)

The objective of the TNO Physics and Electronics Laboratory (TNO-FEL) to participate in the gas-exchange experiments of the Poseidon is to collect experimental data for the interpretation of the flux measurements of chemical reactive gases, and participate in the analysis and interpretation of the flux data to gain better understanding of processes in the marine atmospheric surface layer and air-sea exchange.

CO_2 fluxes are measured as an independant determination of the flux of a chemically inert species, to improve the data collection and processing methods including the development of an dissipation method with the TNO/Riso system consisting of two CO_2 samplers and a sonic, and because CO_2 fluxes are interesting in itself.

As an example, Fig. 7 shows the spectrum and the cospectrum of the CO_2 absorption line from the two instruments.

5.8. $^{12}C/^{13}C$ - isotope relation in dissolved inorganic carbon (G. Rehder, R. Keir, H. Erlenkeuser)

In parallel to the other surface samples also samples were taken for the analysis of carbon- and oxygen isotopes. The samples were brought to the Leibniz-Labor für Altersbestimmung und Isotopenforschung (Kiel University) and will be analyzed by masspectrometry.

Although North Atlantic Deep Water shows a linear correlation between $\delta^{13}C\Sigma CO_2$ and phosphate because of the uptake of isotopic light carbon during photosysnthesis and its remineralization in the water column, the mixed layer water differs from this relationship due to air-sea exchange of CO_2. In the North Atlantic, surface water $\delta^{13}C$ is shifted to lower values. The isotopic fractionation during air-sea exchange is temperature dependent, and as a result, the slope of the $\delta^{13}C\Sigma CO_2$ to phosphate becomes less steep.

The data collected during POS 211 can give new information in the $\delta^{13}C\Sigma CO_2$ - Nutrient relation in the North Atlantic surface waters and hence, the relative importance of the biological pump and air-sea exchange on the carbon cycle.

5.9. Nutrients (H. Johannsen)

Samples for the determination of the nutrients phosphate, silicate, nitrite and nitrate were collected during the cruise and stored deep frozen. After the ship returned to Germany, the samples were brought to the POLARSTERN to be measured on a cruise in November by standard photometrical methods using a four channel autoanalyzer (IfM Kiel). Results are included in the data tables.

5.10. Chlorophyll and carotenoid pigments (S. Gibb)

In biological oceanography the photosynthetic pigments, in particular Chlorophyll a, have long been recognised as unique and convenient markers of phytoplankton biomass. Although spectrophotometric and fluorimetric techniques have been widely used to determine biomass, the utilisation of high performance liquid chromatography HPLC not only permits a more accurate measurement of Chlorophyll a, but also allows simultaneous separation and quantification of a range of other chloropigments and carotinoids in marine phytoplankton. Many of these compounds have strong chemotaxonomic associations, through which it is possible to obtain an understanding of the taxonomic composition of the overall phytoplankton biomass e.g. measurement of the carotenoid fucoxanthin is used to infer the presence of diatoms, whilst the presence of 19´-hexanoyloxyfucoxanthin is used as a biomarker of prymnesiophytes.

There is growing evidence that the various classes of phytoplankton exhibit a unique impact on ocean chemistry and this has important implications for biogeochemical cycling. Since various pigments are biomarkers for specific groups, there is often a correlation between pigments and biogeochemical features e.g. chlorophyll a with pCO_2 and of 19´-hexanoylfucoxanthin with DMS. It would thus appear that pigments are potential proxy biomarkers for biogas fluxes. However, as far as methylated biogases are concerned, particularly the MA´s and halocarbons, correlation data is extremly sparse.

The objective of the cruise was to use the chlorophylls and carotenoids to map the spatial distribution of phytoplankton biomass and taxonomic composition along the cruise transect and to attempt to elucidate the spatial relationship between these biomarkers and the respective distribution of methylated biogases.

Algal cells were collected from 2L water samples on 47 mm (GF/F) fibre filters and snap frozen in liquid nitrogen (a total of 63 samples were obtained). Pigments will be extracted from filters by ultrasonication in cold buffered methanol. Chlorphyll and carotenoids will be separated by reversed phase binary HPLC equipped with absorbance and fluorescence detectors.

No analysis has yet been performed of filters collected during the cruise. However, storage of filters in liquid nitrogen has been shown to arrest pigment degradation for up to one year. It is envisaged that samples collected for the analysis of pigments will be analysed January-February 1996.

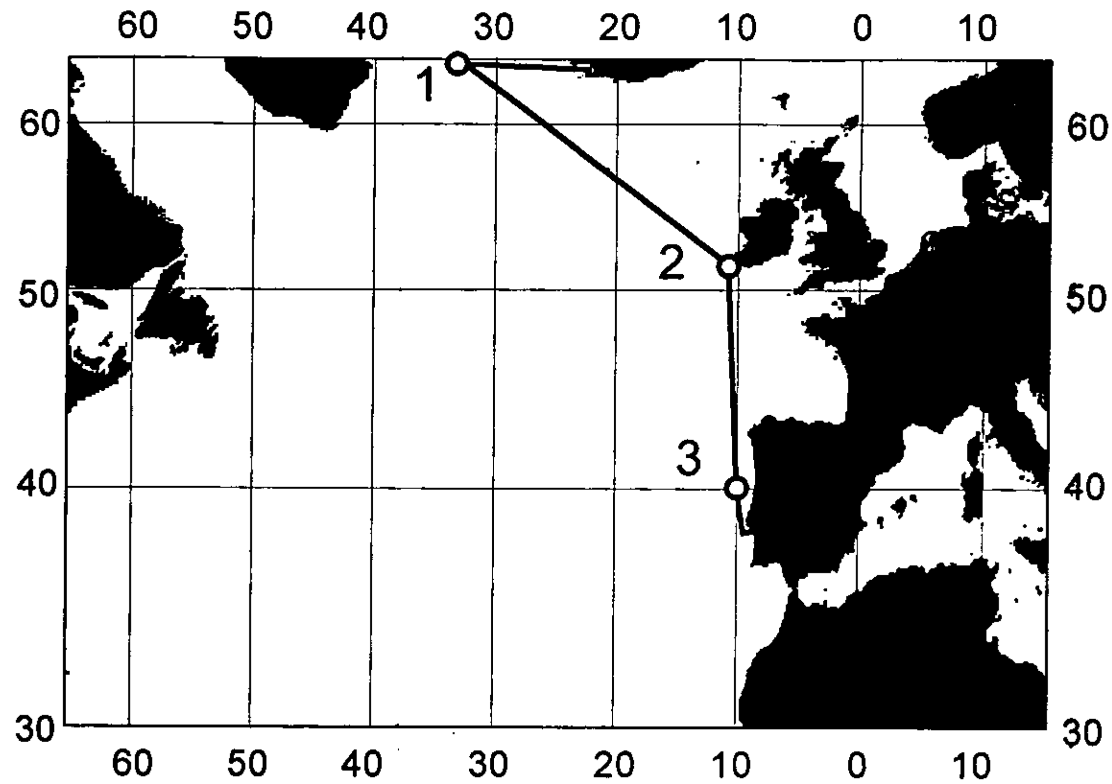
6. Figures
(starting on following page)

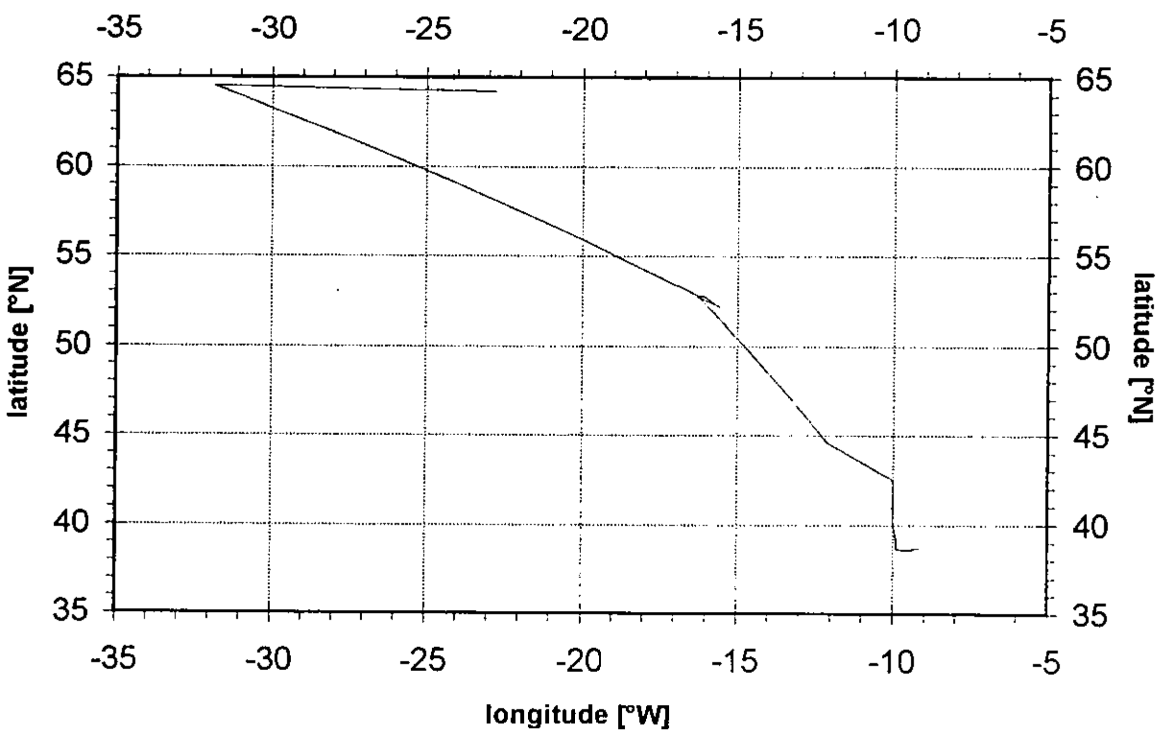
7. Data tables
(appending after the figure section)

8. Concluding remarks

The scientists wish to thank the crew of F.S. POSEIDON for excellent cooperation. Many people in addition to those on board helped with analyses of samples in the land laboratory and working on the data. Their effort is greatly acknowledged. Hopefully their enthusiasm will persist to turn the preliminary data presented here into jointly elaborated scientific results.

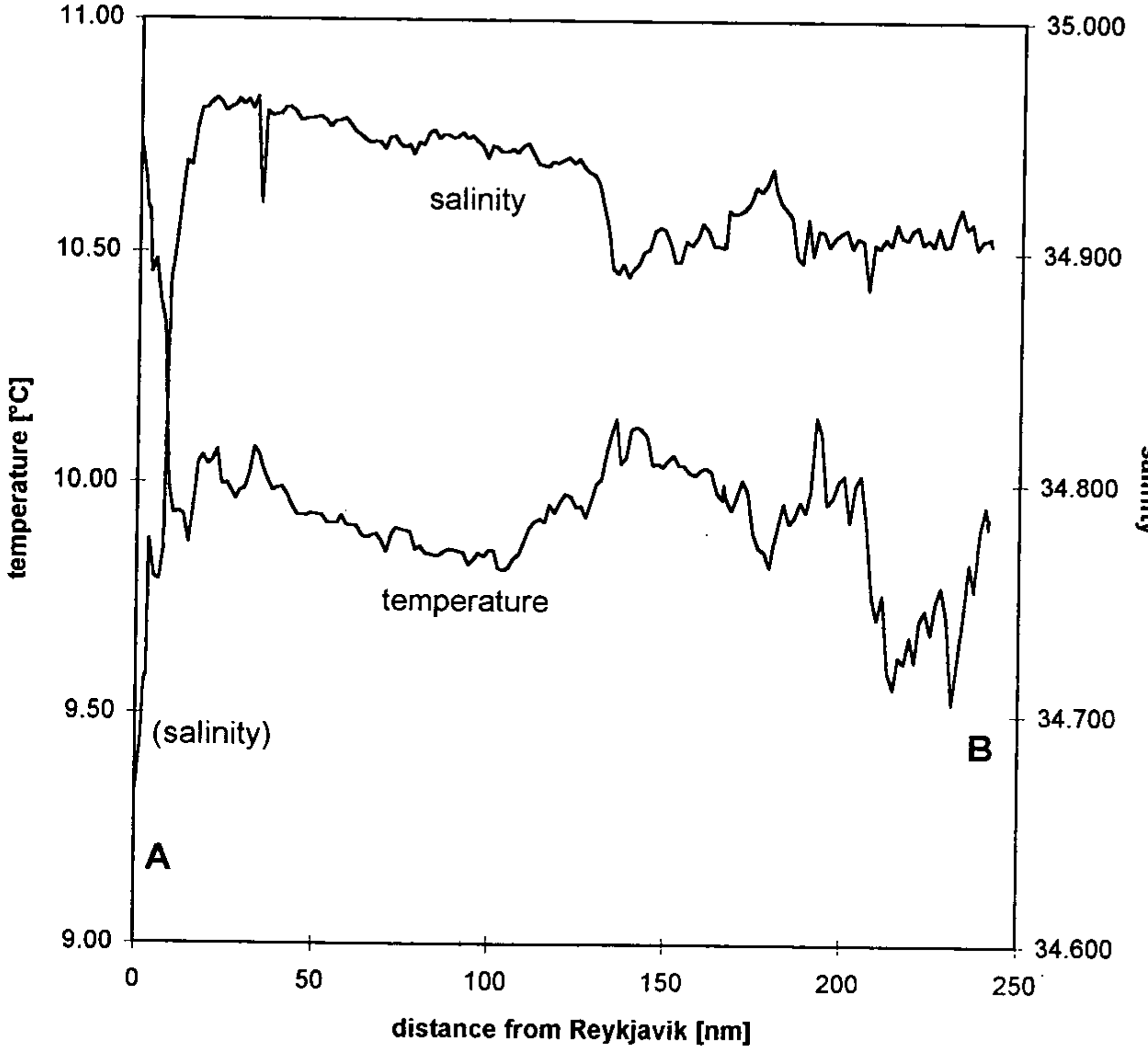
cruise track as planned





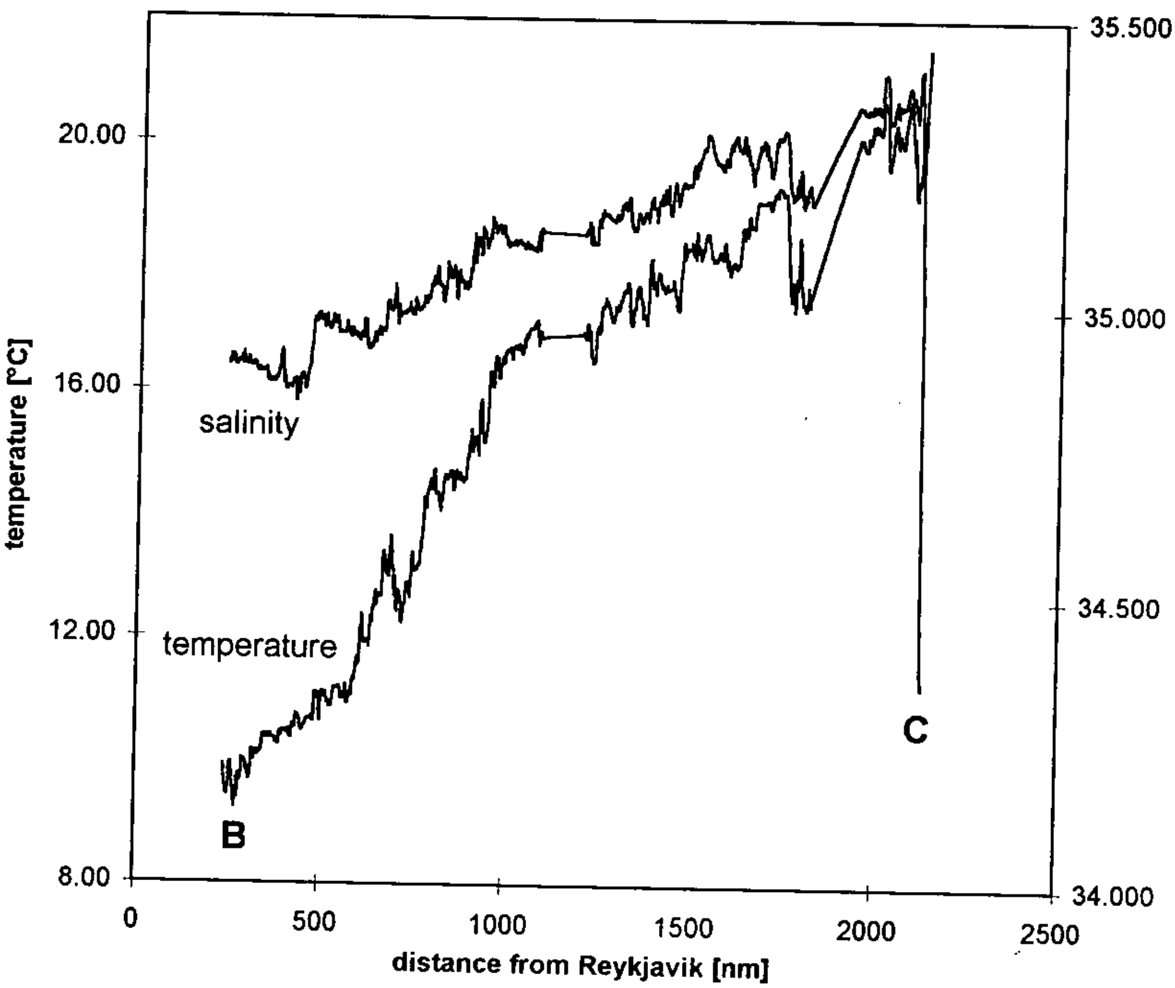
cruise track from ship´s data

FIG 1



salinity and temperature

FIG 2a



salinity and temperature

FIG 2b

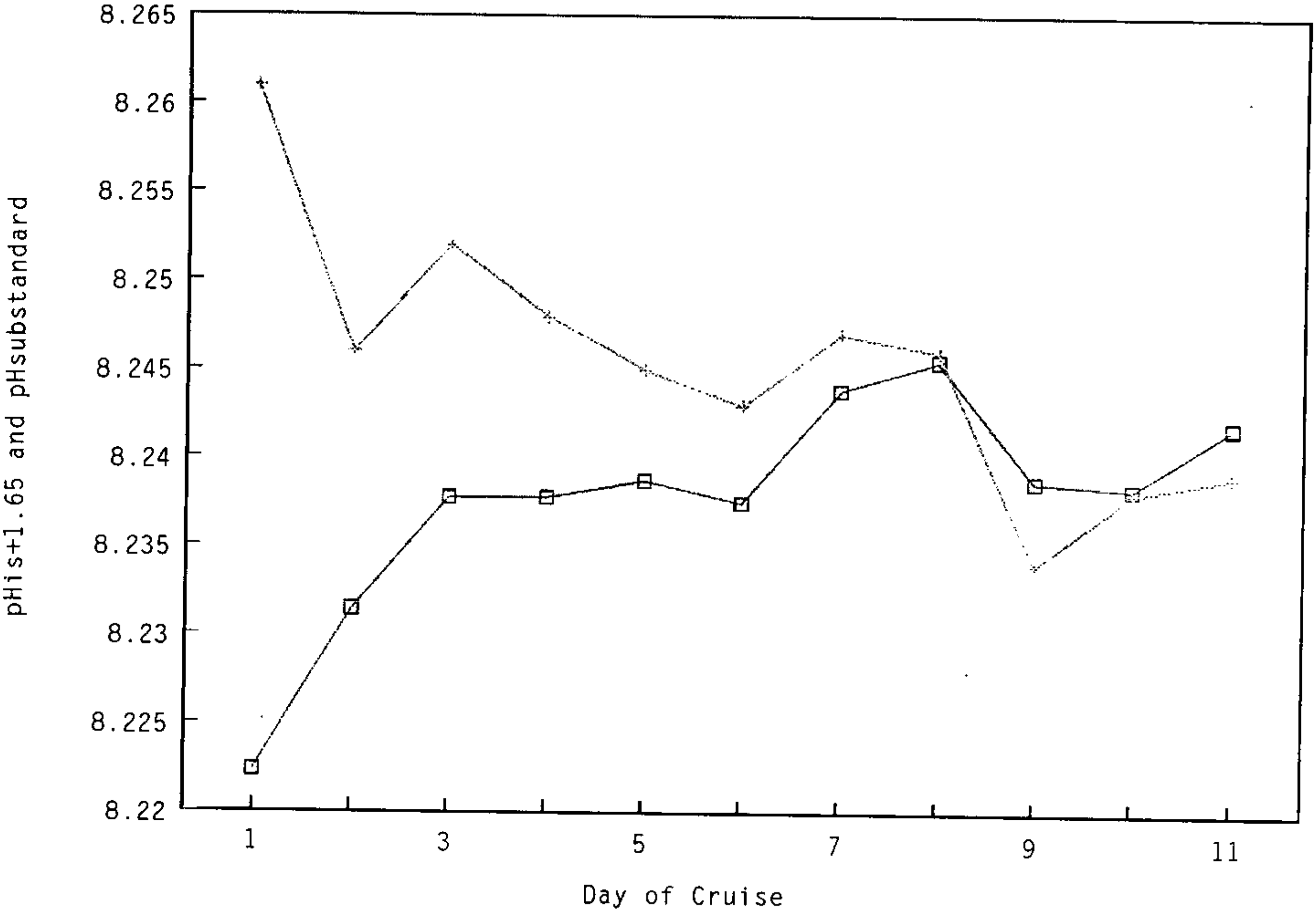


FIG 3a: variation of pH(isoelectric)

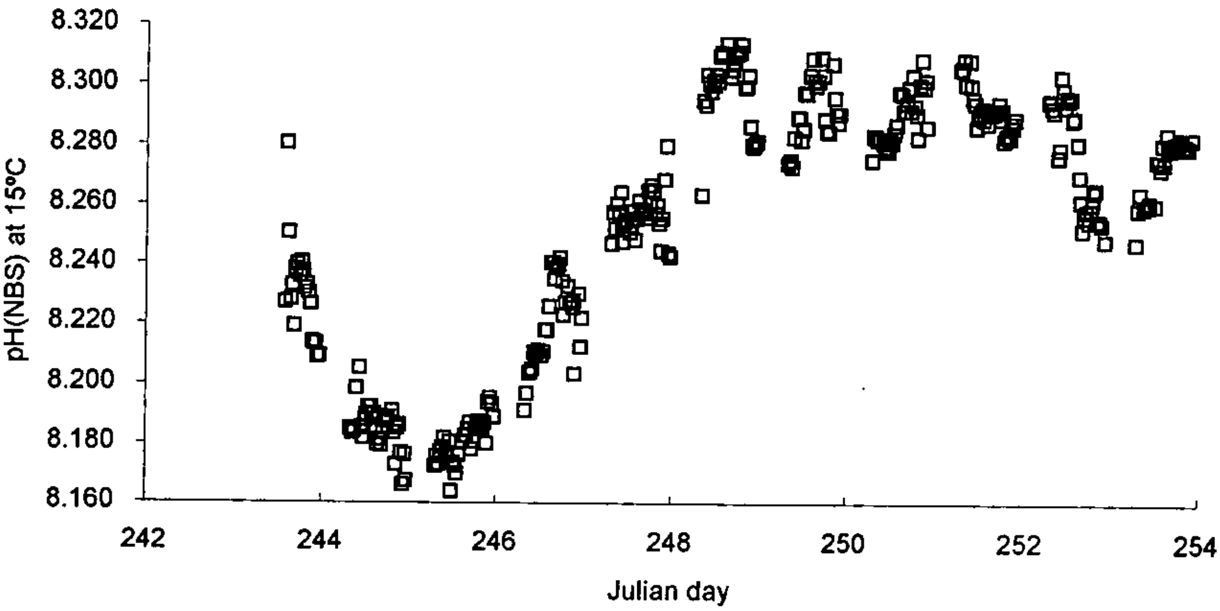


FIG. 3b: pH (NBS) at 15°C vs. Julian day

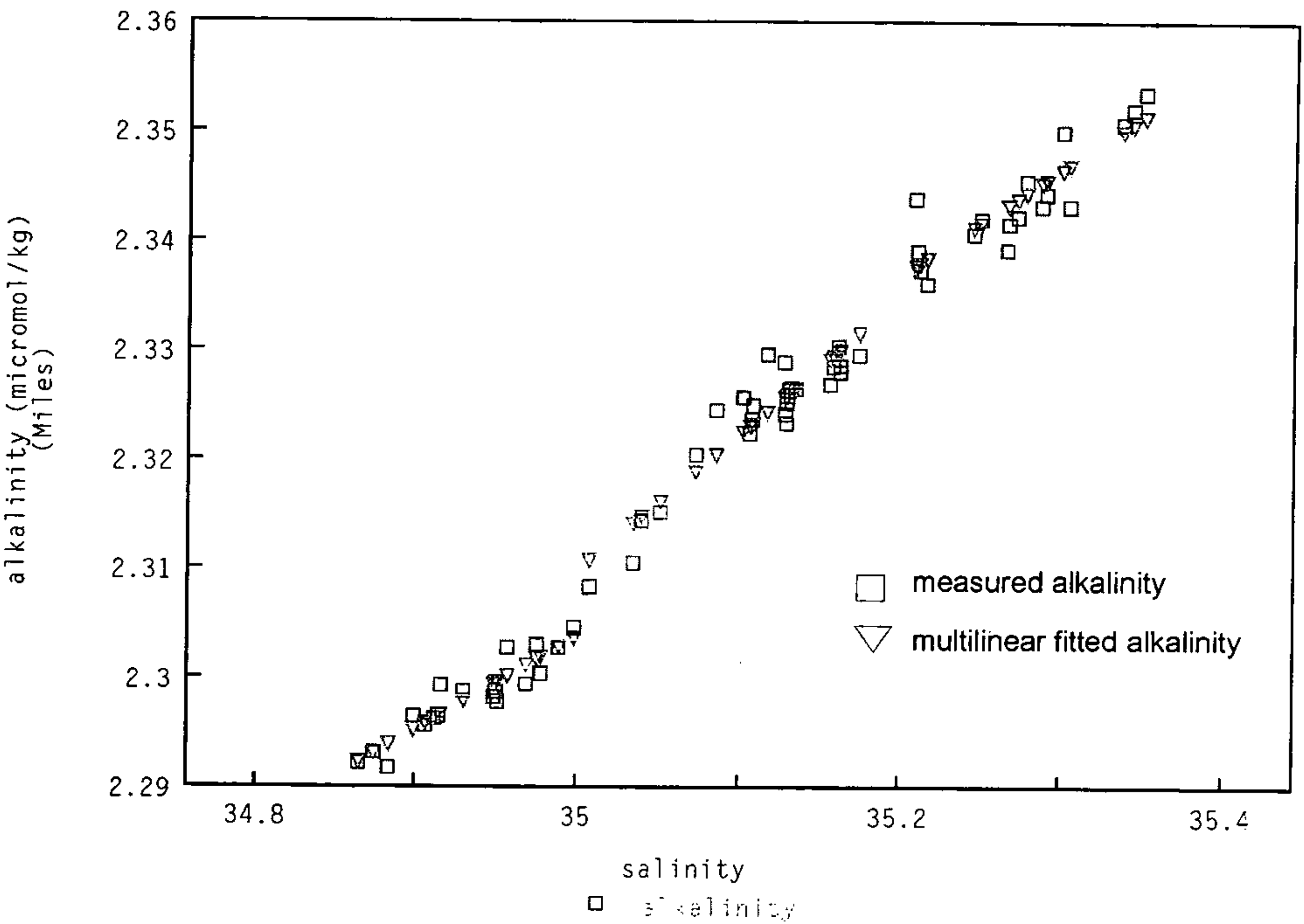
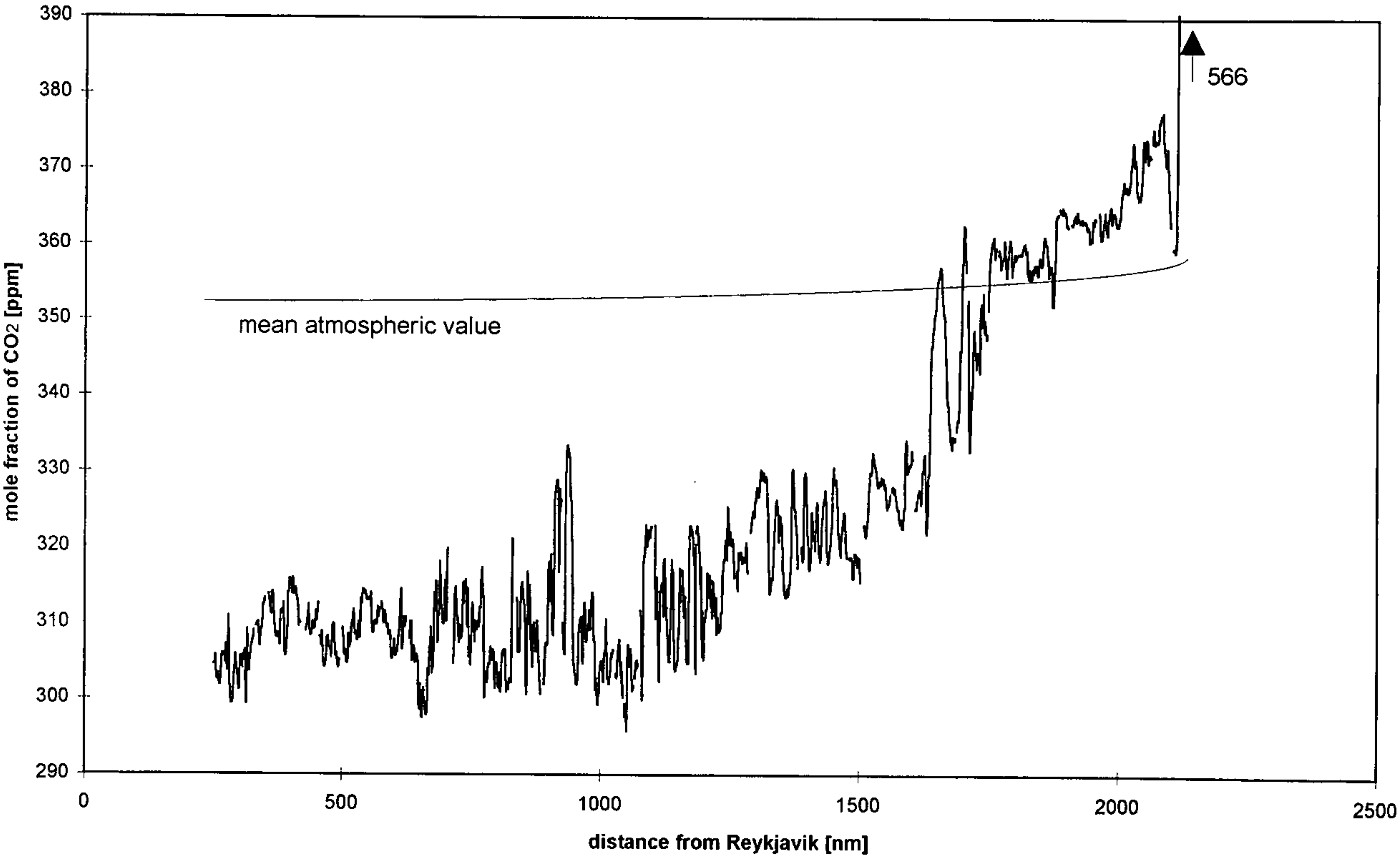
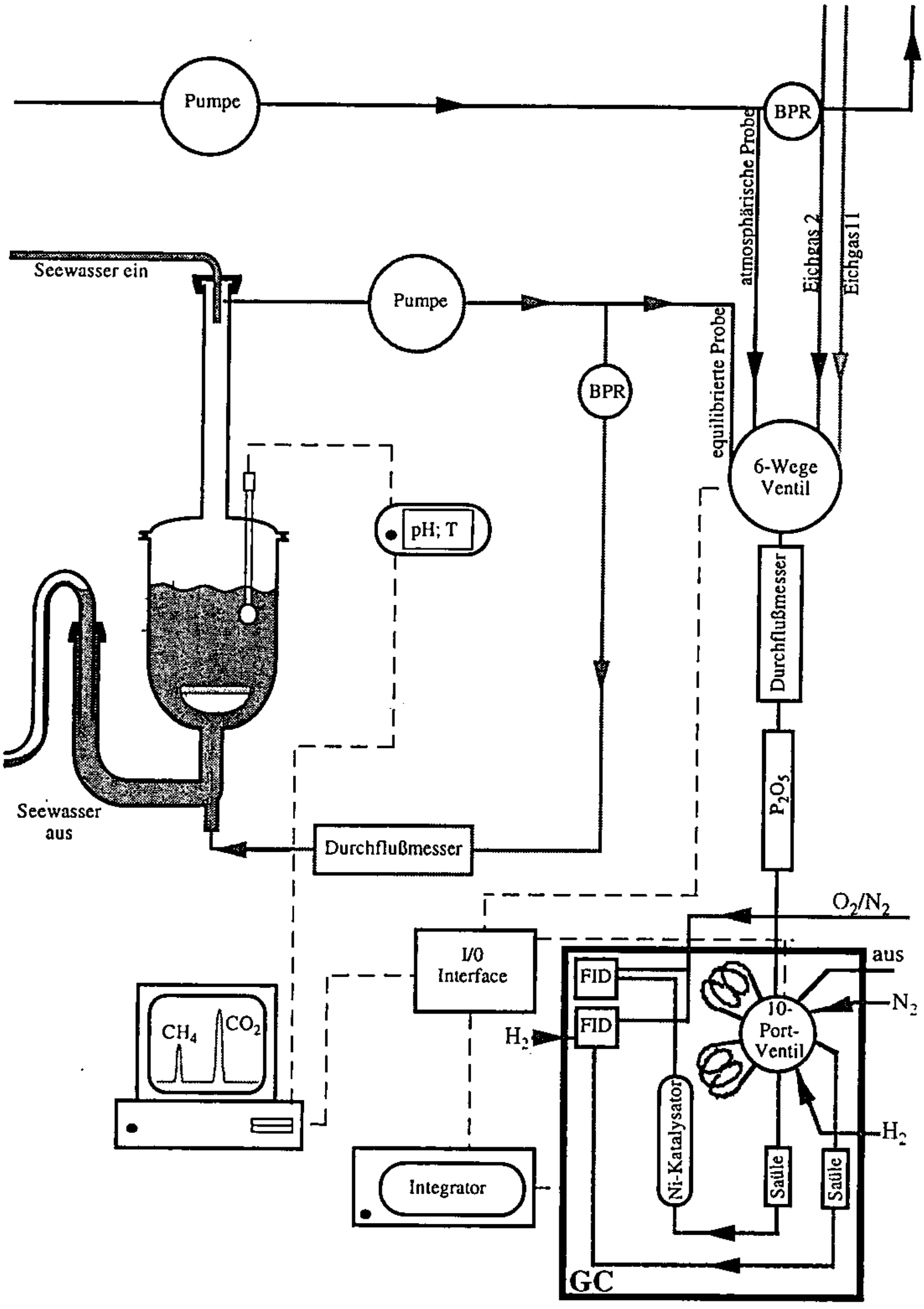


FIG. 3c: alkalinity-salinity correlation



molar fraction of carbon dioxide along the cruise track (prelim. values)

FIG 4



Schematic of the automated underway system for the determination of surface water pCO_2 and methane

FIG. 5a

CH_4 mole fraction of gas in equilibrium with surface water

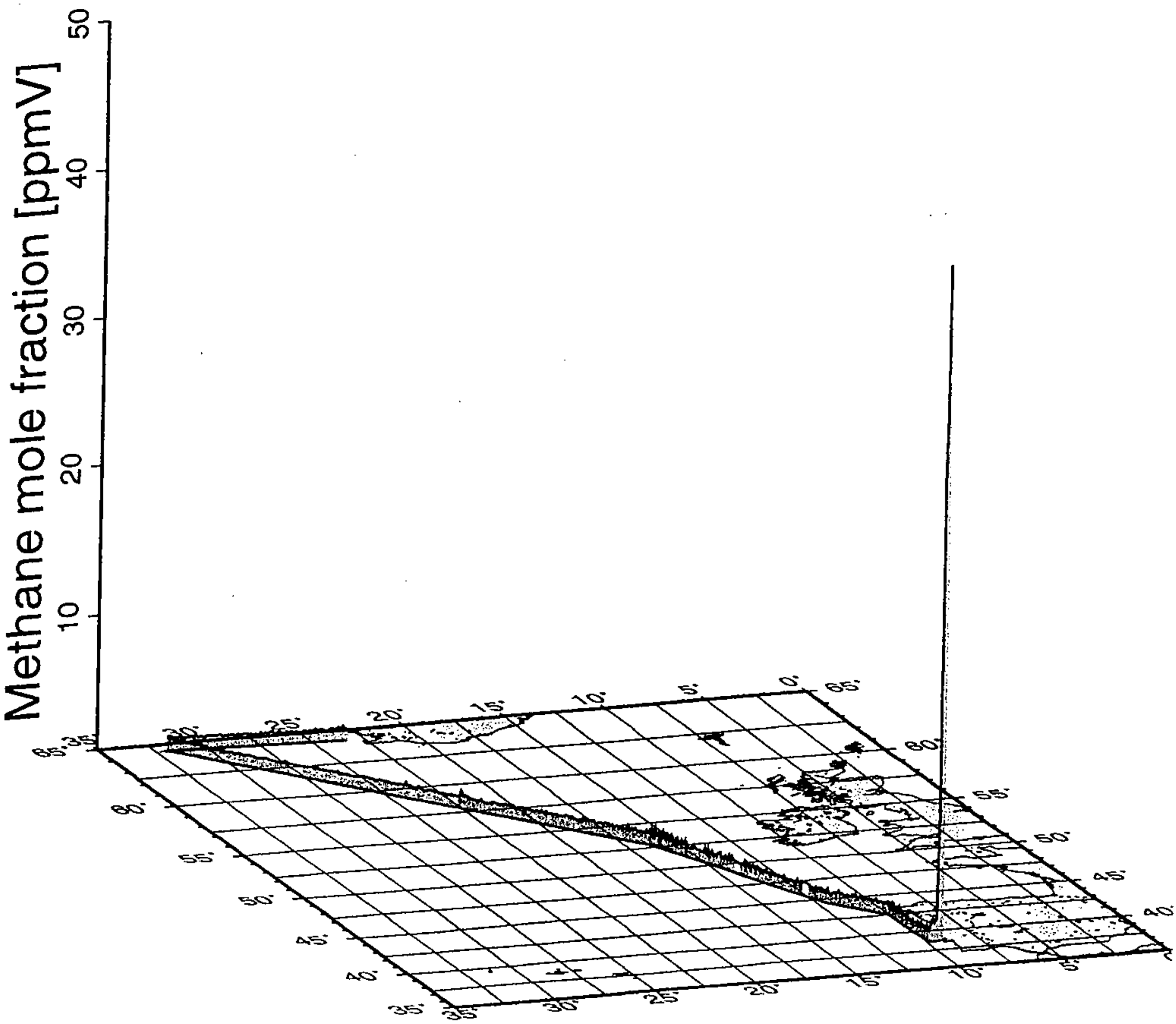


FIG. 5b

CO_2 saturation during Pos 211/ (raw data)

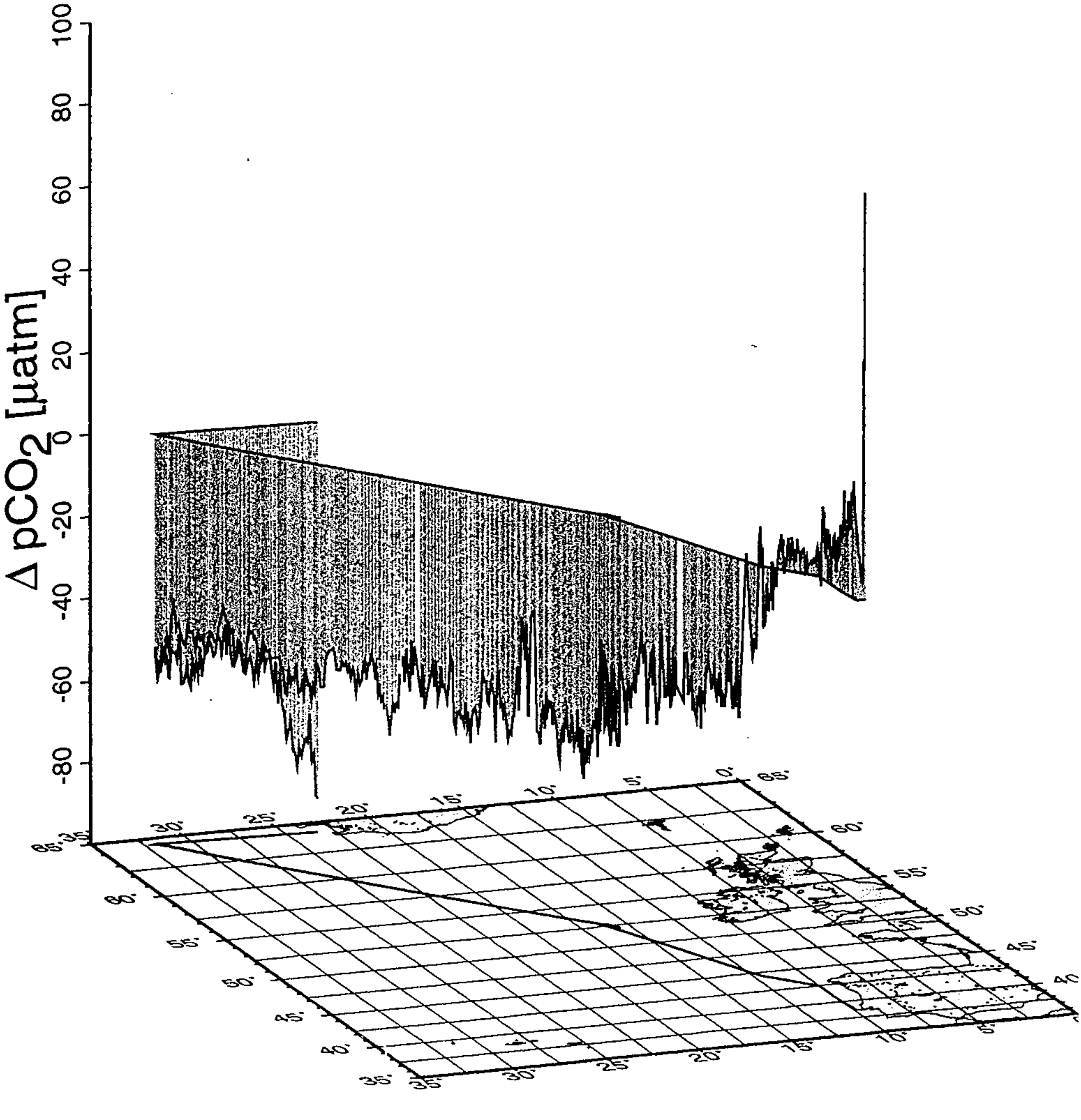


FIG. 5c

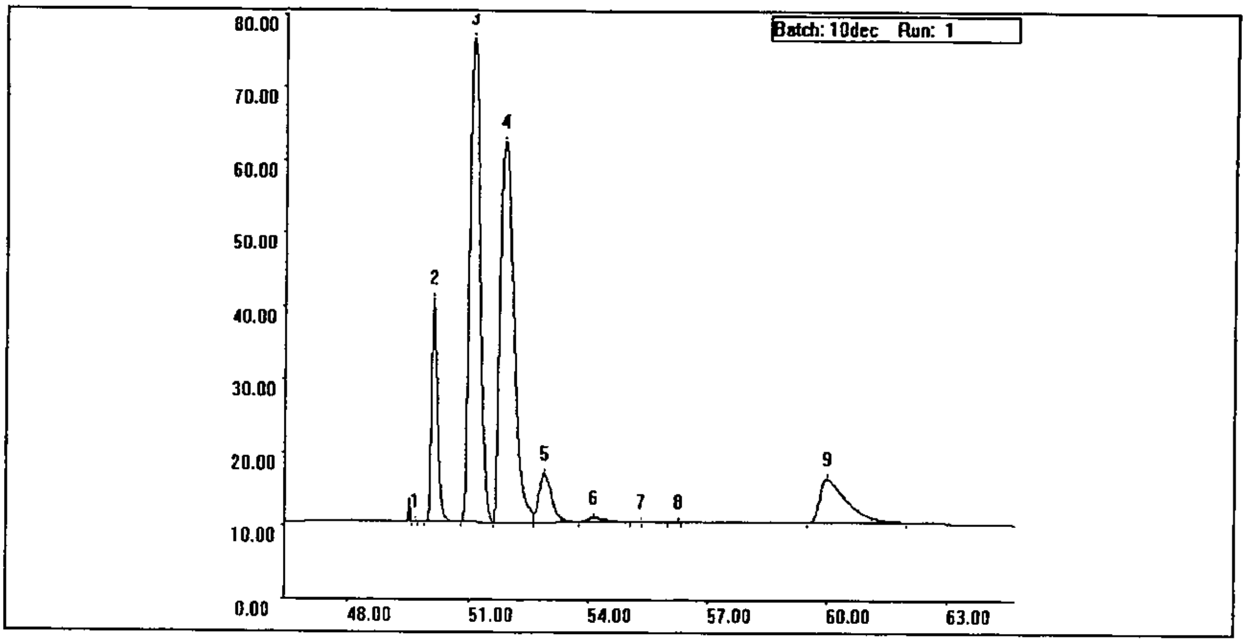


Fig. 6: Typical FIGD-IC Conductivity (8µS fsd) vs. time (mins) Chromatogram for surface seawater. Peaks of interest: 4. NH_4^+, 5. MMA, 6. DMA, 8. TMA, 9. sec-butylamine (int. std.). Other peaks: 1. injection, 2. H^+, 3. Na^+, 7. unidentified.

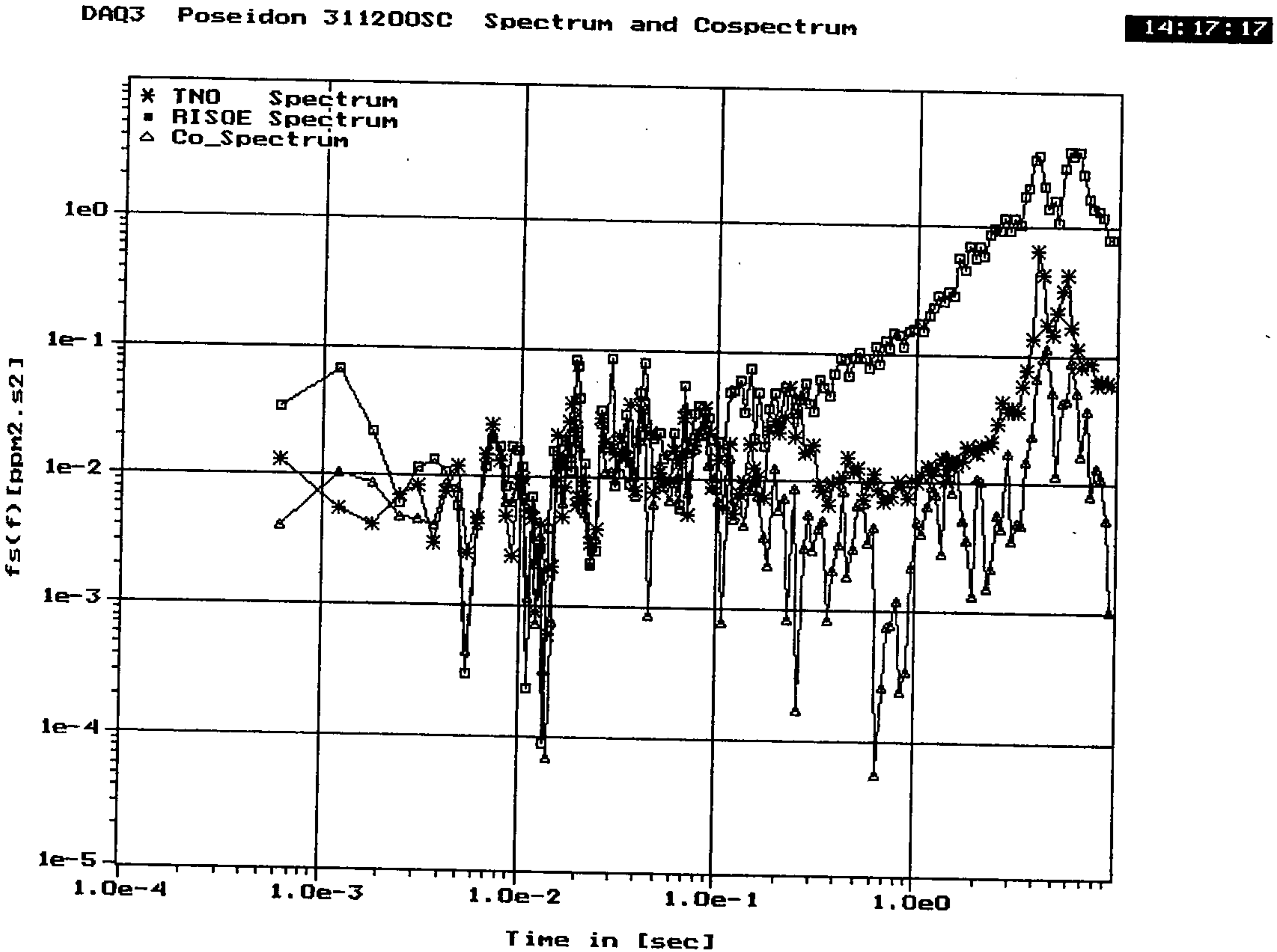

DAQ3 Poseidon 311200SC Spectrum and Cospectrum
14:17:17
* TNO Spectrum
▪ RISOE Spectrum
△ Co_Spectrum
fs(f) [ppm2.s2]
1e0
1e-1
1e-2
1e-3
1e-4
1e-5
1.0e-4
1.0e-3
1.0e-2
1.0e-1
1.0e0
Time in [sec]

FIG. 7

TABLE 7.1.

bottle #	date UTC	time UTC	temp. TSB 2	sal. TSB	C_T [µmol/kg]	nC_T [µmol/kg]	NO_2 [µmol/L]	NO_3 [µmol/L]	PO_4 [µmol/L]	SiO_4 [µmol/L]
POS043	31.08.95	19:02	9.92	34.958	2058.3	2060.8	no	sample		
POS034	31.08.95	23:00	9.85	34.947	2066.2	2069.3	0.05	2.28	0.78	0.21
POS059	01.09.95	07:00	10.05	34.904	2067.4	2073.1	0.13	3.42	1.29	1.27
POS042	01.09.95	13:06	10.13	34.909	2069.9	2075.3	0.13	5.18	1.25	0.92
POS047	01.09.95	19:30	9.92	34.899	2062.6	2068.5	0.14	5.09	1.43	0.93
POS055	01.09.95	21:00	9.87	34.905	2068.2	2073.9	0.18	5.24	1.27	0.97
POS031	01.09.95	23:03	9.60	34.919	2095.5	2100.4	0.16	3.53	1.42	0.90
POS016	02.09.95	01:00	9.97	34.912	2068.0	2073.2	0.07	3.57	1.28	0.41
POS039	02.09.95	03:00	9.76	34.900	2063.2	2069.1	0.20	4.76	1.37	1.16
POS015	02.09.95	05:00	10.08	34.888	2069.3	2075.9	0.22	6.20	1.34	1.54
POS051	02.09.95	07:00	10.40	34.872	2063.7	2071.3	0.14	5.54	1.45	1.61
POS001	02.09.95	09:05	10.42	34.879	2060.8	2067.9	0.10	2.60	1.26	0.77
POS018	02.09.95	11:06	10.31	34.879	2064.0	2071.1	0.08	5.21	1.23	1.08
POS044	02.09.95	13:00	10.47	34.863	2062.0	2070.1	0.34	3.97	1.43	1.63
POS052	02.09.95	15:00	10.36	34.867	2062.6	2070.5	0.21	4.13	1.42	0.94
POS026	02.09.95	17:10	10.70	34.886	2062.1	2068.9	0.31	3.25	1.09	1.38
POS035	02.09.95	19:00	10.59	34.895	2063.0	2069.2	0.12	4.94	1.27	2.28
POS036	02.09.95	21:00	10.71	34.974	2065.9	2067.4	0.22	3.42	1.03	0.97
POS019	02.09.95	23:02	10.96	34.978	2072.7	2074.0	0.13	1.62	0.96	0.47
POS027	03.09.95	01:00	11.08	34.963	2061.3	2063.5	0.07	3.66	1.19	0.83
POS060	03.09.95	03:00	11.11	34.967	2065.8	2067.7	0.14	3.32	1.07	0.79
POS061	03.09.95	05:00	11.14	34.956	2066.5	2069.1	0.07	1.63	1.16	0.44
POS021	03.09.95	07:00	10.94	34.962	2068.7	2070.9	0.15	3.30	1.04	0.92
POS062	03.09.95	09:00	11.35	34.942	2060.4	2063.8	0.22	2.27	1.21	0.49
POS038	03.09.95	11:05	12.39	34.973	2057.6	2059.2	0.07	1.82	0.85	0.21
POS030	03.09.95	13:04	11.88	34.941	2056.4	2059.9	0.06	1.09	0.95	0.12
POS029	03.09.95	15:05	12.67	34.956	2066.2	2068.8	0.06	0.84	0.69	0.00
POS046	03.09.95	17:01	13.15	34.985	2043.0	2043.8	0.19	0.58	0.64	0.03
POS025	03.09.95	19:08	13.34	35.015	2051.6	2050.7	0.11	0.55	0.98	0.17
POS022	03.09.95	23:01	12.32	34.900	2073.3	2079.2	0.12	2.22	0.80	0.72
POS041	04.09.95	03:00	13.09	34.997	2048.6	2048.8	0.14	1.46	0.66	0.00
POS049	04.09.95	07:00	14.31	35.037	2054.4	2052.3	0.09	0.15	0.65	0.09
POS017	04.09.95	11:05	14.08	35.009	2041.5	2040.9	0.36	0.30	0.54	0.30
POS048	04.09.95	15:00	14.45	35.021	2057.6	2056.3	0.15	0.61	0.52	0.22
POS033	04.09.95	19:00	14.91	35.062	2044.5	2040.9	0.05	0.00	0.54	0.29
POS053	04.09.95	23:04	15.29	35.113	2094.6	2087.8	0.22	0.48	0.50	0.05
POS020	05.09.95	02:56	16.45	35.134	2034.8	2027.1	0.00	0.00	0.36	0.27
POS058	05.09.95	07:00	16.65	35.112	2032.8	2026.3	0.11	0.10	0.38	0.14
POS028	05.09.95	11:05	16.62	35.111	2027.9	2021.5	0.06	0.07	0.60	0.10

Contamination
Si looks irregular
NO_3 - Si
worst aff

POS054	05.09.95	19:05	17.07	35.104	2026.1	2020.1	0.09	0.05	0.45	0.31	
POS037	05.09.95	23:05	16.95	35.135	2042.3	2034.4	bottle	empty			
POS056	06.09.95	11:00	16.88	35.130	2032.6	2025.0	0.18	0.19	0.73	0.39	
POS024	06.09.95	15:05	16.90	35.129	2029.5	2022.0	0.10	0.12	0.35	0.06	
POS040	06.09.95	19:00	16.91	35.128	2039.0	2031.5	0.00	0.00	0.30	0.00	
POS050	06.09.95	23:00	16.92	35.127	2034.0	2026.6	0.01	0.01	0.24	0.09	
POS045	07.09.95	03:00	16.49	35.114	2036.9	2030.3	0.03	0.07	0.36	0.10	
POS032	07.09.95	07:05	17.43	35.162	2047.6	2038.2	0.61	0.51	0.50	0.43	
POS023	07.09.95	11:05	17.44	35.177	2047.4	2037.1	0.01	0.02	0.26	0.19	
POS057	07.09.95	15:05	17.28	35.138	2047.2	2039.2	0.22	0.22	0.36	0.15	
POS006	07.09.95	19:05	17.15	35.156	2047.0	2037.9	0.11	0.14	0.42	0.21	
POS004	07.09.95	23:00	17.91	35.200	2034.0	2022.4	0.09	0.12	0.32	0.12	
POS011	08.09.95	03:01	17.74	35.213	2048.5	2036.1	0.12	0.16	0.37	0.16	
POS005	08.09.95	07:00	18.32	35.216	2056.8	2044.2	0.01	0.06	0.30	2.93	208800
POS012	08.09.95	11:10	18.23	35.276	2045.5	2029.5	0.15	0.17	0.37	0.19	
POS003	08.09.95	15:09	18.13	35.254	2039.3	2024.6	0.00	0.04	0.27	0.46	
POS002	08.09.95	19:10	17.94	35.280	2047.6	2031.3	0.06	0.11	0.32	0.32	
POS007	08.09.95	23:00	18.59	35.298	2041.3	2024.1	0.01	0.06	0.33	0.32	
POS008	09.09.95	03:00	18.89	35.259	2046.7	2031.6	0.01	0.12	0.21	0.00	
POS013	09.09.95	07:00	19.05	35.287	2042.3	2025.7	0.27	0.20	0.32	0.12	
POS010	09.09.95	11:12	19.18	35.296	2041.1	2024.0	0.05	0.04	0.30	0.03	
POS009	09.09.95	15:10	18.78	35.252	2067.9	2053.1	0.62	0.50	0.32	0.60	208772
POS014	09.09.95	19:06	17.83	35.210	2075.5	2063.1	0.06	0.08	0.28	0.30	
POS079	09.09.95	23:00	17.71	35.217	2063.5	2050.8	0.05	0.11	0.29	1.66	208807
POS081	10.09.95	01:00	17.74	35.195	2063.7	2052.3	0:12	0.07	0.25	0.10	
POS080	10.09.95	04:00	18.25	35.231	2061.6	2048.1	0.04	0.05	0.45	0.24	
POS074	10.09.95	05:05	18.44	35.244	2061.3	2047.1	0.05	0.02	0.25	0.07	
POS070	10.09.95	07:00	18.76	35.266	2066.9	2051.3	0.03	0.04	0.57	7.14	208774
POS075	10.09.95	09:00	19.11	35.290	2064.7	2047.7	0.55	0.42	0.41	1.67	208810
POS068	10.09.95	09:05	19.12	35.291	2061.8	2044.8	0.03	0.04	0.34	0.16	
POS076	10.09.95	11:00	19.45	35.314	2065.6	2047.2	0.00	0.00	0.29	1.96	208775
POS071	10.09.95	13:01	19.79	35.338	2061.4	2041.6	0.03	0.06	0.31	2.56	208812
POS069	10.09.95	15:05	20.10	35.359	2058.0	2037.1	0.00	0.00	0.21	0.31	
POS064	10.09.95	17:00	20.12	35.348	2058.4	2038.1	0.87	0.85	0.27	3.44	208814
POS065	10.09.95	19:08	20.33	35.352	2058.0	2037.5	0.01	0.05	0.23	2.43	208776
POS063	10.09.95	22:58	19.61	35.327	2067.2	2048.1	0.03	0.10	0.27	0.17	
POS066	11.09.95	01:00	20.20	35.346	2062.9	2042.7	0.32	1.77	1.88	2.37	208816
POS067	11.09.95	03:05	19.92	35.353	2066.4	2045.8	0.23	0.28	0.31	0.20	
POS072	11.09.95	05:05	20.70	35.384	2065.3	2042.9	0.01	0.05	0.31	0.00	
POS078	11.09.95	07:00	19.18	35.335	2064.2	2044.7	bottle	empty			
POS073	11.09.95	07:25	19.27	35.374	2066.2	2044.3	0.48	0.44	0.70	2.70	208778
POS077	11.09.95	09:00	19.52	35.249	2083.9	2069.2	0.08	0.08	0.30	1.70	208766

TABLE 7.2.

dia	hora	juliano	lat	long	temp	sal	ph15	Calculated Alk	Calculated TIC	Calculated pCO2
8,31	14,04	243,59	64,211	-23,043	10,371	34,906	8,227	2296	2039	274
8,31	14,30	243,60	64,215	-23,178	9,955	34,916	8,280	2297	2010	232
8,31	15,00	243,63	64,220	-23,330	9,883	34,938	8,250	2298	2028	252
8,31	15,38	243,65	64,227	-23,521	10,039	34,964	8,228	2301	2042	270
8,31	16,04	243,67	64,232	-23,651	10,053	34,961	8,233	2300	2040	267
8,31	16,30	243,69	64,238	-23,781	9,973	34,964	8,219	2301	2047	276
8,31	17,00	243,71	64,242	-23,928	9,995	34,964	8,238	2301	2037	262
8,31	17,33	243,73	64,248	-24,095	10,048	34,959	8,240	2300	2036	262
8,31	18,10	243,76	64,255	-24,282	9,990	34,960	8,236	2300	2038	264
8,31	18,30	243,77	64,259	-24,388	9,975	34,961	8,241	2300	2035	260
8,31	19,07	243,80	64,265	-24,586	9,931	34,957	8,237	2300	2037	262
8,31	19,30	243,81	64,270	-24,709	9,930	34,956	8,232	2300	2040	266
8,31	20,00	243,83	64,274	-24,871	9,915	34,956	8,233	2300	2039	265
8,31	20,30	243,85	64,280	-25,031	9,913	34,953	8,230	2300	2040	267
8,31	21,00	243,88	64,285	-25,194	9,885	34,948	8,226	2299	2042	269
8,31	21,30	243,90	64,291	-25,355	9,886	34,947	8,214	2299	2049	279
8,31	22,00	243,92	64,297	-25,516	9,890	34,949	8,213	2299	2049	279
8,31	22,30	243,94	64,302	-25,675	9,901	34,944	8,213	2299	2049	279
8,31	23,02	243,96	64,309	-25,846	9,849	34,949	8,209	2299	2051	282
8,31	23,28	243,98	64,314	-25,983	9,843	34,949	8,209	2299	2051	282
9,01	8,01	244,33	64,411	-28,823	10,030	34,912	8,185	2296	2061	304
9,01	8,31	244,35	64,414	-28,999	9,979	34,902	8,183	2295	2061	304
9,01	9,00	244,38	64,417	-29,008	9,966	34,904	8,184	2296	2061	303
9,01	9,32	244,40	64,418	-29,007	9,980	34,903	8,198	2296	2054	292
9,01	10,30	244,44	64,423	-29,188	9,976	34,918	8,205	2297	2051	286
9,01	11,02	244,46	64,431	-29,379	9,876	34,930	8,185	2298	2062	301
9,01	11,30	244,48	64,435	-29,540	9,820	34,936	8,182	2298	2064	303
9,01	12,08	244,51	64,442	-29,762	9,926	34,917	8,188	2297	2060	300
9,01	12,30	244,52	64,448	-29,891	9,962	34,896	8,189	2295	2058	299
9,01	13,02	244,54	64,456	-30,083	10,148	34,908	8,192	2296	2057	299
9,01	13,37	244,57	64,463	-30,291	10,014	34,910	8,192	2296	2057	297
9,01	14,00	244,58	64,468	-30,428	9,918	34,902	8,188	2295	2059	299
9,01	14,30	244,60	64,475	-30,603	9,915	34,884	8,190	2294	2057	298
9,01	15,01	244,63	64,479	-30,786	9,769	34,907	8,185	2296	2060	300
9,01	15,30	244,65	64,484	-30,952	9,627	34,907	8,179	2296	2063	303
9,01	16,00	244,67	64,490	-31,123	9,616	34,912	8,181	2296	2063	301
9,01	16,30	244,69	64,496	-31,298	9,676	34,903	8,179	2296	2063	303
9,01	17,02	244,71	64,503	-31,489	9,699	34,904	8,183	2296	2061	300
9,01	17,30	244,73	64,507	-31,655	9,713	34,911	8,188	2296	2059	297
9,01	18,03	244,75	64,516	-31,848	9,947	34,901	8,187	2295	2059	300
9,01	18,30	244,77	64,517	-31,881	9,915	34,905	8,189	2296	2059	299
9,01	19,30	244,81	64,497	-31,853	9,918	34,899	8,191	2295	2057	297
9,01	20,00	244,83	64,433	-31,750	9,574	34,917	8,183	2297	2062	299
9,01	20,31	244,85	64,366	-31,646	9,434	34,914	8,172	2296	2067	306
9,01	21,01	244,88	64,301	-31,544	9,883	34,904	8,185	2296	2060	301
9,01	21,30	244,90	64,239	-31,441	9,961	34,899	8,186	2295	2059	301
9,01	22,01	244,92	64,169	-31,338	9,540	34,903	8,177	2295	2064	304
9,01	22,30	244,94	64,104	-31,237	9,218	34,907	8,166	2296	2070	308
9,01	23,00	244,96	64,038	-31,134	9,498	34,915	8,176	2297	2066	304
9,01	23,30	244,98	63,975	-31,030	9,389	34,921	8,167	2297	2070	310
9,02	7,35	245,32	62,916	-29,511	10,364	34,871	8,172	2293	2064	318
9,02	8,00	245,33	62,866	-29,429	10,405	34,875	8,175	2293	2063	316
9,02	8,30	245,35	62,805	-29,338	10,395	34,872	8,173	2293	2064	318
9,02	9,00	245,38	62,744	-29,247	10,418	34,879	8,177	2293	2062	315
9,02	9,31	245,40	62,679	-29,153	10,367	34,879	8,178	2293	2062	313
9,02	10,00	245,42	62,618	-29,063	10,356	34,890	8,182	2294	2061	310
9,02	10,31	245,44	62,551	-28,972	10,307	34,919	8,176	2297	2066	314
9,02	11,00	245,46	62,492	-28,884	10,294	34,916	8,175	2297	2066	315
9,02	11,30	245,48	62,435	-28,782	10,365	34,884	8,180	2294	2061	311
9,02	12,01	245,50	62,372	-28,691	10,380	34,858	8,164	2292	2068	326
9,02	12,30	245,52	62,312	-28,601	10,473	34,864	8,173	2292	2063	319
9,02	13,00	245,54	62,249	-28,508	10,471	34,863	8,172	2292	2064	320
9,02	13,30	245,56	62,187	-28,414	10,469	34,861	8,170	2292	2065	322
9,02	14,01	245,58	62,121	-28,318	10,463	34,865	8,176	2292	2062	316
9,02	14,58	245,62	62,003	-28,142	10,374	34,869	8,180	2293	2060	312
9,02	15,39	245,65	61,917	-28,021	10,574	34,867	8,182	2292	2059	312
9,02	16,00	245,67	61,873	-27,957	10,591	34,875	8,182	2293	2059	313

9,02	16,30	245,69	61,812	-27,864	10,749	34,880	8,184	2294	2059	313
9,02	17,00	245,71	61,750	-27,772	10,726	34,884	8,187	2294	2058	311
9,02	17,30	245,73	61,686	-27,682	10,642	34,872	8,178	2293	2062	317
9,02	18,02	245,75	61,615	-27,581	10,540	34,866	8,180	2292	2060	314
9,02	18,30	245,77	61,554	-27,493	10,551	34,886	8,184	2294	2059	311
9,02	19,02	245,79	61,486	-27,393	10,595	34,897	8,186	2295	2059	310
9,02	19,30	245,81	61,427	-27,305	10,636	34,926	8,187	2297	2061	310
9,02	20,00	245,83	61,362	-27,218	10,687	34,969	8,185	2301	2065	312
9,02	20,31	245,85	61,295	-27,120	10,668	34,982	8,184	2302	2066	313
9,02	21,00	245,88	61,232	-27,028	10,713	34,974	8,187	2302	2064	311
9,02	21,30	245,90	61,165	-26,937	10,642	34,987	8,180	2303	2069	317
9,02	22,00	245,92	61,096	-26,845	11,083	34,976	8,194	2302	2061	311
9,02	22,30	245,94	61,030	-26,744	11,097	34,977	8,195	2302	2060	310
9,02	23,00	245,96	60,963	-26,646	10,996	34,978	8,193	2302	2062	310
9,02	23,30	245,98	60,897	-26,557	10,736	34,977	8,189	2302	2064	310
9,03	8,00	246,33	59,780	-25,024	11,130	34,951	8,191	2300	2061	314
9,03	8,30	246,35	59,717	-24,931	11,299	34,948	8,196	2299	2058	311
9,03	9,05	246,38	59,645	-24,820	11,477	34,951	8,203	2300	2054	308
9,03	9,30	246,40	59,592	-24,748	11,538	34,956	8,204	2300	2054	308
9,03	10,00	246,42	59,528	-24,662	11,643	34,951	8,205	2300	2054	309
9,03	10,34	246,44	59,458	-24,561	12,171	34,953	8,210	2300	2051	311
9,03	11,02	246,46	59,399	-24,486	12,396	34,975	8,210	2302	2053	315
9,03	11,30	246,48	59,341	-24,407	11,920	34,929	8,211	2298	2049	307
9,03	12,30	246,52	59,218	-24,244	11,945	34,936	8,209	2298	2050	309
9,03	13,00	246,54	59,157	-24,158	11,851	34,943	8,211	2299	2050	306
9,03	13,30	246,56	59,095	-24,077	12,299	34,955	8,218	2300	2047	307
9,03	14,01	246,58	59,032	-23,994	12,319	34,950	8,218	2300	2047	307
9,03	14,31	246,60	58,971	-23,914	12,507	34,955	8,226	2300	2043	303
9,03	15,03	246,63	58,903	-23,827	12,722	34,958	8,240	2300	2035	293
9,03	15,44	246,66	58,817	-23,715	12,719	34,963	8,240	2301	2036	293
9,03	16,00	246,67	58,783	-23,671	12,662	34,963	8,234	2301	2039	297
9,03	16,30	246,69	58,719	-23,589	12,690	34,962	8,238	2301	2037	294
9,03	17,07	246,71	58,641	-23,488	13,141	35,008	8,239	2311	2045	301
9,03	17,30	246,73	58,592	-23,425	13,412	35,004	8,242	2310	2043	302
9,03	18,03	246,75	58,522	-23,335	13,150	34,996	8,234	2303	2041	305
9,03	18,30	246,77	58,465	-23,261	13,045	34,995	8,223	2303	2047	313
9,03	19,01	246,79	58,399	-23,176	13,038	35,009	8,227	2311	2052	310
9,03	19,30	246,81	58,338	-23,097	13,292	35,005	8,232	2310	2049	309
9,03	20,01	246,83	58,272	-23,012	13,164	34,999	8,227	2304	2046	311
9,03	20,21	246,85	58,230	-22,958	13,155	35,000	8,227	2304	2046	311
9,03	21,00	246,88	58,147	-22,851	12,993	34,997	8,225	2303	2046	310
9,03	21,30	246,90	58,083	-22,769	12,441	34,988	8,203	2303	2057	321
9,03	21,07	246,88	58,132	-22,832	12,925	34,994	8,228	2303	2045	307
9,03	22,30	246,94	57,956	-22,605	12,687	34,991	8,230	2303	2043	302
9,03	23,04	246,96	57,884	-22,512	12,314	34,989	8,212	2303	2053	312
9,03	23,30	246,98	57,829	-22,441	12,491	34,995	8,222	2303	2048	306
9,04	7,38	247,32	56,795	-21,107	14,425	35,039	8,247	2315	2045	312
9,04	8,00	247,33	56,748	-21,047	14,560	35,051	8,257	2316	2040	306
9,04	8,30	247,35	56,685	-20,965	14,421	35,044	8,252	2315	2042	308
9,04	9,00	247,38	56,621	-20,883	14,708	35,072	8,260	2319	2041	305
9,04	9,30	247,40	56,558	-20,801	14,479	35,045	8,256	2315	2040	305
9,04	10,00	247,42	56,494	-20,720	14,373	35,038	8,264	2314	2035	297
9,04	10,29	247,44	56,437	-20,649	14,370	35,038	8,247	2314	2044	311
9,04	10,31	247,44	56,433	-20,645	14,354	35,035	8,253	2314	2041	306
9,04	11,03	247,46	56,369	-20,563	14,088	35,008	8,254	2311	2037	301
9,04	11,33	247,48	56,305	-20,486	14,308	35,028	8,255	2313	2039	304
9,04	12,30	247,52	56,186	-20,334	14,646	35,062	8,250	2317	2045	313
9,04	13,00	247,54	56,123	-20,257	14,580	35,053	8,252	2316	2043	310
9,04	13,30	247,56	56,057	-20,183	14,626	35,055	8,258	2317	2040	306
9,04	14,00	247,58	55,993	-20,102	14,668	35,073	8,248	2319	2047	315
9,04	14,30	247,60	55,929	-20,024	14,680	35,061	8,255	2317	2042	309
9,04	15,00	247,63	55,864	-19,947	14,448	35,021	8,261	2312	2035	300
9,04	15,30	247,65	55,802	-19,867	14,645	35,066	8,258	2318	2041	306
9,04	16,08	247,67	55,720	-19,769	14,674	35,048	8,257	2316	2040	307
9,04	16,30	247,69	55,672	-19,714	14,674	35,046	8,257	2315	2040	307
9,04	17,00	247,71	55,608	-19,634	14,628	35,040	8,255	2315	2040	308
9,04	17,31	247,73	55,543	-19,553	14,602	35,043	8,264	2315	2035	300
9,04	18,00	247,75	55,481	-19,477	14,598	35,043	8,260	2315	2038	303
9,04	18,30	247,77	55,416	-19,398	14,609	35,037	8,266	2314	2034	298

9,07	10,30	250,44	51,067	-15,349	17,404	35,164	8,278	2330	2040	328
9,07	11,09	250,46	50,975	-15,304	17,475	35,180	8,279	2332	2041	328
9,07	11,31	250,48	50,924	-15,278	17,462	35,174	8,277	2331	2042	329
9,07	12,00	250,50	50,857	-15,240	17,596	35,184	8,281	2333	2041	328
9,07	12,30	250,52	50,786	-15,201	17,607	35,171	8,280	2331	2040	329
9,07	13,00	250,54	50,716	-15,165	17,654	35,174	8,283	2331	2038	327
9,07	13,30	250,56	50,645	-15,128	17,751	35,190	8,286	2333	2038	326
9,07	14,30	250,60	50,505	-15,045	17,121	35,144	8,297	2328	2027	307
9,07	15,00	250,63	50,434	-15,007	17,224	35,137	8,297	2327	2027	309
9,07	15,31	250,65	50,360	-14,970	17,360	35,136	8,291	2327	2030	315
9,07	16,00	250,67	50,292	-14,936	17,637	35,162	8,291	2330	2033	320
9,07	16,30	250,69	50,224	-14,897	17,675	35,166	8,294	2330	2032	318
9,07	17,00	250,71	50,154	-14,857	17,643	35,155	8,299	2329	2027	313
9,07	17,30	250,73	50,083	-14,816	17,512	35,152	8,291	2329	2032	318
9,07	18,00	250,75	50,009	-14,785	17,344	35,158	8,303	2329	2025	305
9,07	18,31	250,77	49,935	-14,749	17,228	35,161	8,293	2330	2032	313
9,07	19,00	250,79	49,867	-14,710	17,235	35,163	8,290	2330	2033	315
9,07	19,30	250,81	49,796	-14,674	17,278	35,162	8,282	2330	2038	323
9,07	20,00	250,83	49,725	-14,635	18,000	35,186	8,300	2333	2030	317
9,07	20,30	250,85	49,654	-14,600	18,143	35,195	8,308	2334	2026	312
9,07	21,00	250,88	49,582	-14,562	17,708	35,174	8,299	2331	2029	314
9,07	21,30	250,90	49,512	-14,525	17,790	35,176	8,301	2332	2028	313
9,07	22,00	250,92	49,440	-14,487	17,583	35,156	8,285	2329	2035	324
9,08	7,05	251,30	48,145	-13,836	18,325	35,216	8,305	2338	2032	318
9,08	7,30	251,31	48,083	-13,813	18,308	35,215	8,305	2338	2032	317
9,08	8,00	251,33	48,011	-13,774	18,420	35,238	8,308	2340	2032	317
9,08	8,30	251,35	47,937	-13,734	18,209	35,248	8,300	2341	2037	321
9,08	9,34	251,40	47,778	-13,661	18,570	35,246	8,308	2341	2032	319
9,08	10,03	251,42	47,709	-13,623	18,365	35,261	8,299	2343	2038	324
9,08	10,31	251,44	47,642	-13,596	18,163	35,267	8,295	2343	2041	325
9,08	11,05	251,46	47,563	-13,553	18,220	35,278	8,294	2344	2043	327
9,08	11,30	251,48	47,503	-13,522	18,344	35,277	8,285	2344	2048	336
9,08	12,00	251,50	47,434	-13,488	18,509	35,301	8,289	2346	2048	336
9,08	12,30	251,52	47,364	-13,453	18,566	35,302	8,290	2346	2047	336
9,08	13,05	251,55	47,278	-13,409	18,470	35,290	8,292	2345	2045	332
9,08	13,30	251,56	47,214	-13,379	18,355	35,283	8,288	2345	2047	334
9,08	14,31	251,60	47,056	-13,304	18,142	35,261	8,287	2343	2046	332
9,08	15,01	251,63	46,977	-13,265	18,150	35,252	8,291	2342	2042	328
9,08	15,31	251,65	46,898	-13,229	18,219	35,251	8,290	2342	2043	330
9,08	16,05	251,67	46,809	-13,189	18,264	35,250	8,291	2342	2042	330
9,08	16,31	251,69	46,742	-13,156	18,165	35,243	8,290	2341	2042	329
9,08	17,00	251,71	46,667	-13,118	18,305	35,259	8,291	2342	2043	331
9,08	17,31	251,73	46,588	-13,080	18,340	35,258	8,294	2342	2042	329
9,08	18,00	251,75	46,516	-13,042	18,014	35,258	8,288	2342	2045	329
9,08	18,30	251,77	46,439	-13,007	18,144	35,278	8,291	2344	2045	328
9,08	19,03	251,79	46,359	-12,967	17,906	35,278	8,281	2344	2051	334
9,08	19,30	251,81	46,295	-12,936	18,046	35,292	8,283	2346	2051	335
9,08	20,00	251,83	46,228	-12,898	18,089	35,299	8,283	2346	2051	335
9,08	20,31	251,85	46,152	-12,866	18,073	35,296	8,282	2346	2051	336
9,08	21,00	251,88	46,084	-12,831	18,014	35,278	8,287	2344	2047	330
9,08	21,30	251,90	46,015	-12,800	18,056	35,279	8,286	2344	2048	332
9,08	22,00	251,92	45,949	-12,766	18,122	35,273	8,288	2344	2046	331
9,09	7,00	252,29	44,870	-12,244	19,055	35,288	8,294	2345	2044	339
9,09	7,30	252,31	44,820	-12,220	19,073	35,271	8,294	2344	2042	339
9,09	8,00	252,33	44,760	-12,192	19,104	35,266	8,292	2343	2043	341
9,09	8,30	252,35	44,701	-12,163	19,105	35,256	8,291	2342	2043	342
9,09	9,40	252,40	44,562	-12,082	19,035	35,245	8,276	2341	2051	356
9,09	10,00	252,42	44,527	-12,044	19,114	35,246	8,278	2341	2049	354
9,09	10,30	252,44	44,474	-11,991	19,201	35,288	8,302	2345	2039	333
9,09	11,00	252,46	44,421	-11,936	19,188	35,286	8,298	2345	2041	337
9,09	11,30	252,48	44,367	-11,882	19,246	35,299	8,292	2346	2046	343
9,09	12,00	252,50	44,312	-11,827	19,305	35,294	8,295	2346	2043	341
9,09	12,36	252,53	44,249	-11,763	19,288	35,295	8,295	2346	2044	342
9,09	13,00	252,54	44,208	-11,720	19,281	35,300	8,295	2346	2044	341
9,09	13,40	252,57	44,136	-11,647	19,198	35,310	8,288	2347	2049	347
9,09	14,00	252,58	44,102	-11,613	19,220	35,309	8,289	2347	2049	347
9,09	15,00	252,63	44,000	-11,515	18,958	35,275	8,280	2344	2051	351
9,09	15,33	252,65	43,948	-11,462	18,497	35,227	8,269	2339	2053	354
9,09	16,00	252,67	43,905	-11,420	17,995	35,210	8,261	2338	2057	354

9,09	16,30	252,69	43,861	-11,375	17,637	35,203	8,251	2337	2061	358
9,09	17,00	252,71	43,813	-11,326	17,641	35,197	8,256	2334	2056	353
9,09	17,35	252,73	43,755	-11,266	17,713	35,195	8,258	2334	2055	352
9,09	18,08	252,76	43,699	-11,208	17,452	35,189	8,254	2333	2056	352
9,09	18,30	252,77	43,661	-11,173	17,497	35,210	8,258	2338	2058	349
9,09	19,07	252,80	43,598	-11,110	17,807	35,209	8,260	2338	2057	352
9,09	19,33	252,81	43,555	-11,063	18,235	35,238	8,264	2340	2057	355
9,09	20,05	252,84	43,500	-11,011	18,265	35,221	8,265	2339	2055	354
9,09	20,33	252,86	43,452	-10,959	17,586	35,195	8,254	2334	2057	354
9,09	21,00	252,88	43,404	-10,911	17,444	35,178	8,254	2332	2055	351
9,09	21,35	252,90	43,344	-10,851	17,452	35,191	8,253	2334	2057	353
9,09	22,35	252,94	43,237	-10,744	17,482	35,212	8,248	2338	2064	359
9,1	7,00	253,29	42,265	-9,999	18,765	35,266	8,247	2343	2069	381
9,1	7,31	253,31	42,187	-10,000	18,853	35,273	8,258	2344	2063	371
9,1	8,00	253,33	42,113	-10,000	18,935	35,278	8,263	2344	2061	367
9,1	9,06	253,38	41,950	-10,000	19,122	35,291	8,259	2345	2064	375
9,1	9,30	253,40	41,891	-10,001	19,191	35,296	8,259	2346	2064	375
9,1	10,15	253,43	41,778	-9,999	19,318	35,305	8,259	2347	2065	377
9,1	10,30	253,44	41,740	-9,999	19,361	35,308	8,260	2347	2065	377
9,1	12,04	253,50	41,495	-10,003	19,628	35,327	8,260	2349	2067	383
9,1	12,30	253,52	41,428	-10,001	19,701	35,332	8,274	2349	2059	369
9,1	13,00	253,54	41,349	-9,999	19,787	35,338	8,274	2350	2059	370
9,1	13,30	253,56	41,272	-9,998	19,872	35,344	8,272	2350	2061	374
9,1	14,00	253,58	41,195	-9,999	19,957	35,350	8,280	2351	2057	367
9,1	14,30	253,60	41,118	-10,003	20,075	35,351	8,273	2351	2061	376
9,1	15,03	253,63	41,034	-10,004	20,103	35,350	8,283	2351	2055	366
9,1	15,30	253,65	40,965	-10,003	20,025	35,346	8,279	2351	2057	369
9,1	16,05	253,67	40,874	-10,001	19,934	35,343	8,278	2350	2057	369
9,1	16,30	253,69	40,807	-9,999	19,914	35,340	8,279	2350	2057	367
9,1	17,30	253,73	40,648	-10,001	20,042	35,346	8,280	2351	2056	368
9,1	18,09	253,76	40,546	-9,999	20,278	35,354	8,280	2351	2057	372
9,1	18,30	253,77	40,491	-10,002	20,299	35,348	8,282	2351	2056	371
9,1	19,00	253,79	40,416	-10,002	20,329	35,351	8,281	2351	2056	372
9,1	19,30	253,81	40,338	-9,999	20,297	35,355	8,280	2352	2057	373
9,1	20,05	253,84	40,243	-10,000	20,225	35,344	8,279	2351	2057	372
9,1	20,33	253,86	40,167	-10,003	20,208	35,343	8,279	2350	2057	372
9,1	21,00	253,88	40,095	-10,002	20,474	35,386	8,279	2355	2060	377
9,1	22,00	253,92	39,934	-9,991	20,640	35,407	8,282	2357	2060	377

Table 7.3.: status and summary of MA and ammonia data

Table 7.3. medium	species concentration					
	ammonia [µM]	MMA [nM]	EA⁺ [nM]	DMA⁺ [nM]	EA+DMA⁺ [nM]	TMA [nM]
surface seawater	#	6.8-117	0-5.8	0.4-8.0	0-30	0-6.0
rain water	2.1-9.5	29-102	0-3.8	10-101	12.4-101	1.1-25
atmospheric aerosol	NA	NA	NA	NA	NA	NA
atmospheric gas	NA	NA	NA	NA	NA	NA

+: where EA and DMA were quantifiably resolved, individual concentrations are given, in cases in which this was not possible, their summed concentrations are presented; #: data requires intercalibration; NA: not yet analysed

Table 7.4.: list of samples collected for MA and ammonia analysis in atmospheric aerosols and gases

Table 7.4. filter set	sequence	date	time [GMT]	filters collected -aerosols	filters collected -gases
1	start stop	31/8/95 1/9/95	13:57 18:00	1 blank + 3 replicates	1 pair blanks + 3 pair replicates
2	start stop	1/9/95 3/9/95	20:00 18:00	1 blank + 3 replicates	1 pair blanks + 3 pair replicates
3	start stop	3/9/95 5/9/95	18:57 18:23	1 blank + 3 replicates	1 pair blanks + 3 pair replicates
4	start stop	6/9/95 8/9/95	08:15 07:27	1 blank + 3 replicates	1 pair blanks + 3 pair replicates
5	start stop	8/9/95 10/9/95	08:48 13:00	1 blank + 3 replicates	1 pair blanks + 3 pair replicates