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REPORT AND PRELIMINARY RESULTS OF
POSEIDON CRUISE 333
LAS PALMAS (SPAIN) – LAS PALMAS (SPAIN)
March 1st – March 10th, 2006
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<td>Ruhland, Götz</td>
<td>Marine Geology</td>
<td>MARUM</td>
</tr>
<tr>
<td></td>
<td>(Chief Scientist)</td>
<td></td>
</tr>
<tr>
<td>Alamo, Nauzet</td>
<td>Marine Chemistry</td>
<td>ICCM</td>
</tr>
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<td>Belokon, Walentin</td>
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<td>Gonzalez, Esther</td>
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<td>Hüttich, Daniel</td>
<td>Technician</td>
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<td>Kalweit, Holger</td>
<td>Technician</td>
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<td>Kopiske, Eberhard</td>
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<td>Rodriguez, Ivan</td>
<td>Scientist</td>
<td>ULP</td>
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<tr>
<td>Villagarcia, Marimar, Dr.</td>
<td>Marine Chemistry</td>
<td>ICCM</td>
</tr>
</tbody>
</table>

Institutions

MARUM  Zentrum für Marine Umweltwissenschaften der Universität Bremen, Leobener Str, 28359 Bremen, Germany

ICCM  Instituto Canario de Ciencias Marinas, Apto. Correos 55, 35200 Telde de Gran Canaria, Spain

ULP  Universidad de Las Palmas
Las Palmas de Gran Canaria
2. Research Objectives

The area off NW-Africa is one of the most important upwelling systems of the global ocean. High amounts of Sahara dust influence the transport of nutrients into and their concentration in the ocean and therefore play a major role for the particle production in the ocean influencing the processes of the biological carbon pump system. Hence they are controlling factors of the global atmospheric CO₂-budget. Despite the main driving force for climatic variability located in the North Atlantic, the upwelling area off NW-Africa is suitable to reconstruct the past climatic variability by monitoring present in-situ environmental changes and variations.

The research topics were carried out in correlation with the following project:

2.1 MERSEA (Marine EnviRonment and Security for the European Area – Integrated Project)

The main task will concentrate on the MERSEA EU project. The main aim of MERSEA is the data management and processing to take aim to the needs of scientific end-users.

The participating institutions during R/V POSEIDON cruise 333, MARUM/University of Bremen and ICCM, are involved in work package 3. They will ensure the availability of real time and delayed-mode and regional in-situ data and products in the form required by the MERSEA modelling, data assimilation and validation systems. The activities are partly research and development, innovation, and partly demonstration. The served research sites, continued from the preceding ANIMATE and DOLAN projects, are DOLAN/ESTOC, Canary Islands; PAP, Porcupine Abyssal Plain; CIS, Central Irminger Sea. The main task during POS 333 cruise will be the work on the DOLAN site. The DOLAN station is located 25 nm west of ESTOC and comprises technical devices for transmission of scientific data sets via satellite into the research institutes which collect the data in a database and make them available in the internet.
3. **Narrative of the Cruise**

R/V Poseidon left the port of Las Palmas on March 1\textsuperscript{st}, 2006 with heading to the DOLAN position. Due to the stormy weather conditions RV “Poseidon” could not continue to steam to the mooring position. Instead the ship went east of the island of Gran Canaria to the southernmost planned CTD station. The wind speed of Bft. 8 avoid to operate the CTD and the ship stayed overnight in the shelter south of Gran Canaria.

The next day (March 2\textsuperscript{nd}) the scientific work could be started at the second but southernmost station (#2) with a CTD cast. A second CTD station (#3) could be done later in the afternoon.

In the morning of March 3\textsuperscript{rd} the recovery of the mooring CI-19 had been done. In the afternoon the recovery of the DOLAN buoy and the belonging mooring followed. In the evening a post-calibration cast for the Microcats occurred.

![Figure 1: Trackline of the RV “Poseidon” cruise 333](image)

On March 4\textsuperscript{th}, the monthly monitoring on the ESTOC position could be carried out. Afterwards the ship steamed to the next CTD position to continue the CTD transect between the islands of Gran Canaria and Tenerife. The CTD station #4 had been made in the afternoon.
The day of March 5th was used to carry out the CTD stations #1 and #6. On the way to the next planned CTD station the wind speed increased rapidly to Bft. 8 which led to an interruption of the scientific work. The ship steamed again close to the southern coast of Gran Canaria to get shelter.

On March 6th the weather conditions were too bad to work outside the shelter of Gran Canaria. The time was used to maintain the DOLAN buoy and to prepare the new buoy mooring equipment.

In the morning of March 7th a new attempt had been done to steam onto the next CTD station. But wind speeds up to 42 kts. were too strong to continue scientific work. At noon the weather conditions became slightly better. Due to decreasing time all CTD activities were skipped to steam to the DOLAN buoy position north of the islands.

On March 8th the pre-calibration casts for the Microcats and the fluorometer were made. Afterwards the buoy mooring could be deployed successfully. In the afternoon the DOLAN buoy was connected to its mooring without any problems. In the time after deployment the direct wireless communication and the satellite communication had been tested both successfully.

On the next day, March 9th, the mooring CI-20 was deployed close to the ESTOC position. In the late afternoon RV “Poseidon” took course towards Las Palmas.

In the morning of March 10th RV “Poseidon” arrived in the port of Las Palmas.
4. **Scientific Report**

4.1 **Equipment Development and Tests**

4.1.1 **DOLAN Surface Buoy (SBU)**

The Surface Buoy Unit (SBU) operates since 1997 and was formerly part of the DOMEST and DOLAN projects. The unit carries several meteorological sensors, satellite telemetry links and sub sea telemetry links like ORCA acoustic modem and now a cable telemetry down to 100m. The DOLAN mooring was recovered at the evening of March 3rd, 2006 on its location at 29°10,40’N 15°55,30’W. The water depth on this position is about 3630 m.

The last routine maintenance has been carried out during R/V POSEIDON cruise 330 in December 2005. The redeployment took place on March 8th, 5 days later.

The complete mooring has been recovered during this cruise after a deployment period of approx. one year. The biofouling on the sensors and the buoy was at a medium level compared to previous cruises but more than in December 2005. This seasonal change has been seen on all cruises. The sensors and the buoy have been cleaned before reading all the data from the sensors.

There were no major damages visible on the buoy, all antennas, solar panels and cables on deck were in a good shape. Some minor damages like the bearings of the wind generator and some damages on the body of the buoy have been detected.
Status of the DOLAN Buoy before maintenance

The visual inspection of the buoys body shows cracks and damages at 5 different locations. The visible damage has been repaired. Some more serious repairs can be expected for the next cruises.

- The INMARSAT tracking system installed in December 2004 worked perfectly until the recovery. The battery capacity installed on the PO330 cruise has been doubled compared to previous deployments.

![INMARSAT Battery Voltage](chart)

**Figure 4:** Voltage log of the Inmarsat Battery

- The wind sensor and the compass were working fine during the tests.
- The air pressure sensor has been working well all the time and the data were transmitted using the online telemetry during the whole past mooring period. This sensor has not been replaced.
- The sensors of relative humidity and air temperature were damaged. We suppose that they were in contact with sea water during the cyclone on November 27th, 2005. They have been replaced. The readings have been successfully compared the ships weather sensors (DWD system).
- The DOLIX GPS including antenna was working well.
- There was no SAMI CO$_2$ sensor installed at 10m, only one Microcat. The Orbcomm telemetry worked very well during this mooring period with GPS and air pressure as well as the new measurement of the battery voltages. The data from the Microcat in 0m and 10m had not been transmitted. They have been integrated into the telemetry and they are transferring data now. The biofouling on the microcats was acceptable. The recorded data could be retrieved completely.
There were four microcats installed between 10m and 100m. They have been recovered and the data have been downloaded successfully. The antifouling of all Microcats except the ones at 0m and the 100m serial Microcat have been replaced.

- The data of the ADCP at 150m has been downloaded completely and the battery has been renewed.
- The fluorometer and the nutrient analyser in 100 m water depth were only very slightly affected by biofouling. The biowhipper of the fluorometer worked well, so that it’s optical system has been found without a biofouling film. The intake of the nutrient analyser was not effected by biofouling as well.

The fluorometer was connected to the telemetrie, but no data were transmitted due to software problems in the DOLIX computer.

The NAS-2E nutrient sensor has not been connected to the telemetrie due to problems with the sensor software.

The maintenance of the buoy electronics showed that the buoy was in a good shape. Both, 12V and 24V power supply were working well. No corrosion was found in the junction box of the solar panels.

![Figure 5: Plot of the 12V power supply during the deployment period.](image-url)
The voltage of the 24V power supply is shown below. No problems have been detected in the 24V power supply.

![Plot of the 24V power supply during the deployment period.](image)

The inspection of the 24V wind generator showed that the mast bearings had become loose. The wind generator has been replaced by the spare generator.

After the analysis of the status of the DOLAN Buoy we started the maintenance of the DOLAN electronics. The DOLIX computer has been replaced by the tested spare unit.

**New cable telemetry**
A new technique for the telemetry of data from the sensors at 100m depth was installed during the last cruise PO330. This new telemetry has been installed the first time on the DOLAN buoy. The 4 wire cable is a new design with a robust stainless steal amour. The very robust cable was in a good shape, but it was torn at the connector. This happened during the cyclone one day after the deployment on the 28’st of November 2005.

The cable has been repaired; the parts of the cable with water ingress have been replaced. The connector has been secured by fixing the cable to a shackle right above and right below the connector.

**WLAN link**
The old satel RF modems have been replaced by a new WLAN link for controlling the system from the ship. The according antenna has been installed on this cruise. The test of the WLAN system shows a very good and reliable performance. The maximum distance for the ship to communicate with the DOLAN Buoy via WLAN is ¾ nm. We operated the WLAN at a safe distance of ½ nm without any problems and at a datarate of 10MBit/sec.

An external switch for the WLAN by the use of an 4pin Subconn connector has been implemented to enable WLAN without opening the deck box on the buoy even if the Iridium link is not working.
For testing purposes several messages have been automatically generated and sent via the Iridium and the Orbcomm satellite link after the redeployment of the DOLAN buoy.

The wind speed and wind direction data have been compared with the ships wind data (DWD system). The results were reasonable but due to the fact that the buoy was standing on the aft deck the readings were not exact the same as the ships wind data.

**Table 1: Overview on the installed sensors / telemetry since March 2006**

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Telemetry</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaisala PTU200</td>
<td>ORBCOMM</td>
<td>ONLINE</td>
</tr>
<tr>
<td>- air temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- relative humidity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- barometric pressure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vaisala WS245</td>
<td>IRIDIUM</td>
<td>ONLINE</td>
</tr>
<tr>
<td>- windspeed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- winddirection</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TCM2</td>
<td>Working, delivers data for wind speed calculation</td>
<td>(ONLINE)</td>
</tr>
<tr>
<td>- buoy heading</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- pitch and roll for the buoy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thrane &amp; Thrane</td>
<td>INMARSAT</td>
<td>ONLINE</td>
</tr>
<tr>
<td>- GPS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microcat @0.5m</td>
<td>ORBCOMM</td>
<td>ONLINE</td>
</tr>
<tr>
<td>Microcat @10m</td>
<td>ORBCOMM</td>
<td>ONLINE</td>
</tr>
<tr>
<td>Microcat @100m</td>
<td>IRIDIUM</td>
<td>Status unclear</td>
</tr>
<tr>
<td>Fluorometer</td>
<td>IRIDIUM</td>
<td>(ONLINE)</td>
</tr>
<tr>
<td>Nutrient Analyser NAS-3E</td>
<td>Not in telemetry</td>
<td></td>
</tr>
<tr>
<td>DOLIX GPS</td>
<td>IRIDIUM</td>
<td>ONLINE</td>
</tr>
</tbody>
</table>

*Results of the tests before and after deployment*

All tested sensors and systems were working well during the tests prior to the deployment. The tests after the deployment were successful as well. Successful logins were performed on the DOLIX computer via Iridium several times.
No new sensors have been implemented on the DOLAN Buoy on this cruise. The focus was on the maintenance and improvement of the installed system. Several problems in the software have been corrected.

The test on the buoy shows a very good performance and a stable system. The main improvement was the renewed login process for a dial in via Iridium. Before the maintenance a runlevel change was necessary to enable the Iridium dial-in. This is not longer necessary, one can dial in via Iridium every time except during a short burst data session.

The redeployment of the mooring took place on March 8th, 2006. Tests of all sensors on the DOLIX took place after the deployment of the DOLAN buoy. All sensors were working fine. Only the data from the 100m Microcat could not be received. These tests have been performed via the new WLAN link on the buoy at a distance of ½ nm.

Status of the tasks from the POS330 cruise

- The power switching concept has to be redesigned
  - The redesigned power supply board has been installed and tested successfully
- A magnetic switch should be applied to switch on the WLAN link without opening the electronics box.
  - An external switch was installed by the use of a Subconn connector.
- The scheduler of the DOLIX need to be checked, it seams not to be reliable
  - The scheduler has been tested and works fine with more reliable applications
- The body of the buoy needs to be repaired on the next cruise
  - The damage of the DOLAN body have been repaired
- The power supply concept for the different sensors need to be redesigned
The new power supply and switching board has been installed. It shows a very good performance. The trigger of the switching has been redesigned in the software by the use of shell scripts. This leads to a more transparent and easy configuration of the switching concept.

Tasks for the next cruise

- connection of CanSor modules on the cable via Subconn connectors
- check of the CanSor telemetry for the 100m Microcat
- new revision of the CanSor software with bidirectional telemetry
4.2 Collection with Particle Traps

The particulate material collected will be analysed to determine total flux, particulate flux, particulate organic carbon, particulate nitrogen, biogenic opal, carbonate and stable isotopes of organic matter, and lithogenic material. The trapped material also will be investigated for species composition of the planktonic organisms (pteropods, foraminifera, coccolithophorides and diatoms). The objective of these studies is to identify signals of seasonal variations in those components, which play an important role in the sediment formation process. The result of these investigations will form a basis for the reconstruction of paleocurrent systems and paleoproduct from the sediments.

4.2.1 CI-19 (ESTOC)

The CI-19 mooring array was deployed on November 26th 2005 at 29°04.20’N and 015°15.36’W at a water depth of 3590 m. It had been recovered on March 3rd, 2006. Attached to this array were three particle traps at water depths of 699 m, 1025 m and 3052 m. All traps delivered the whole sets of 20 samples.

The mooring was redeployed on March 9th, 2006 as CI-20, with a comparable configuration. It is planned to recover this array in March 2006 with R/V MERIAN or R/V POSEIDON.

Figure 8: Drawing of CI-19 mooring.
Table 2: Mooring data for recoveries and redeployments during R/V POSEIDON cruise 333.

<table>
<thead>
<tr>
<th>Mooring</th>
<th>Position</th>
<th>Water depth (m)</th>
<th>Interval</th>
<th>Instr.</th>
<th>Depth (m)</th>
<th>Intervals (no x days)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mooring recoveries</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ESTOC</td>
<td>29°04,20`N</td>
<td>3590</td>
<td>16.03.05</td>
<td>S/MT 234</td>
<td>699</td>
<td>20 x 15</td>
</tr>
<tr>
<td>CI-19</td>
<td>15°15,36`W</td>
<td></td>
<td>10.01.06</td>
<td>S/MT 234</td>
<td>1025</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>S/MT 234</td>
<td>3052</td>
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<table>
<thead>
<tr>
<th>Mooring deployments</th>
<th>Position</th>
<th>Water depth (m)</th>
<th>Interval</th>
<th>Instr.</th>
<th>Depth (m)</th>
<th>Intervals (no x days)</th>
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<tbody>
<tr>
<td>ESTOC</td>
<td>29°04,10`N</td>
<td>3590</td>
<td>10.03.06</td>
<td>S/MT 234</td>
<td>699</td>
<td>20 x 22</td>
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<tr>
<td>CI-20</td>
<td>15°15`05W</td>
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<td>24.05.07</td>
<td>S/MT 234</td>
<td>1025</td>
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<td>S/MT 234</td>
<td>3052</td>
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</tbody>
</table>

Instruments used:
S/MT 234 = Particle sediment trap S/MT 234 KUM, Kiel
4.3 Marine Chemistry

4.3.1 Objectives and scientific questions

Along P333 the ANIMATE/ESTOC mooring was recovered and redeployed for the eighth time. It had been put in place in November 2005 during P330 and the sensors had been in the water for about 9 months and needed to be replaced. The ICCM took care of the nitrate sensor collected from the mooring extracting the data; it was also in charge of deploying a refurbished and calibrated NAS-2E # nitrate sensor in the mooring to be deployed.

At the same time it was necessary to do the biogeochemical monthly samplings at the ESTOC station (European Station for Time series in the Ocean Canary islands) and surrounded areas, that it has been continuously done since 1994. Calibration casts with CTD/Rosette were also made to accomplish the requirements of the sensors being recovered/deployed.

It was planned to sample different stations around Gran Canaria Island, but due to bad weather conditions only could be made some in the way from ESTOC to the passage between Tenerife and Gran Canaria Islands. The passage circulation of water masses has been studied in several cruises in the past too, with the aim to track the presence of the intermediate waters found in the area, i.e. Antarctic Intermediate Water (AAIW) and Mediterranean Water (MW).

![Figure 9: Position of the CTD stations (red crosses and numbers) made along Poseidon P333.](image)

4.3.2 Data

At the beginning of the cruise the meteorological conditions were not adequate to collect the DOLAN/ANIMATE mooring and, since better conditions were found in the channel between Gran Canaria and Tenerife Islands, two stations were made (st. #54 and 55, sampled to 2000m). When the weather improved, the DOLAN/ANIMATE mooring could be recovered, hence a rosette/CTD cast to 500m was made in order to have a calibration of the chemical sensors (st. #58). Then, after the DOLAN mooring with the physical and biogeochemical sensors from the MERSEA was recovered, the ESTOC station monthly sampling took place (st. 59, sampled to the bottom). As part of the monthly sampling at ESTOC since 1994, a NOAA buoy #54683 was deployed at 29°10.05'N, 15°19.58'W.

After this, the remaining stations from the transect between Tenerife and Gran Canaria islands were made starting from ESTOC and going diagonally south (st. #60, #61 and #62 down to
2000m), and finally a calibration was made prior to the mooring deployment (st. 63 profile 1 with microcats mounted, st. #63 profile 2 to 300m for fluorometer restrictions since it was mounted on the rosette).

The nitrate sensor was exchanged, collecting NAS-3X #2404 and deploying it again changing the battery. Refurbishing and calibration of the sensor were made on board using the standards that were maintained refrigerated on board, which had been checked and measured with the laboratory analyser Skalar® at the ICCM. Data obtained for the mooring period from the nitrate sensor was quite satisfactory, except for the last few days when the standards did not remain stable.

Table 3: List of stations sampled along the cruise P333, Las Palmas-DOLAN-Las Palmas (0=oxygen, N=nutrients, S=salinity, C=chlorophyll “a”, Ak=alkalinity, pH, TIC= Total Inorganic Carbon, Inc= Incidences).

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>St. #</th>
<th>CTD Cast</th>
<th>Depth sta, (m)</th>
<th>Lat. N</th>
<th>Long. W</th>
<th>Depth Ross. (m)</th>
<th>Nis kin Bot</th>
<th>Nom. Dep. samp, (m)</th>
<th>PARAMETERS</th>
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<td></td>
<td>54, 02</td>
<td>2710</td>
<td>27°53.11’</td>
<td>16°10.09’</td>
<td>2000</td>
<td>1 2000</td>
<td>√</td>
<td>√</td>
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<td>02.03</td>
<td>2006</td>
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<td>10:05</td>
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Physical (CTD, salinity) and biogeochemical parameters (oxygen, nutrients, chlorophyll, alkalinity, total inorganic carbon (TIC) and pH) were measured by sampling the Niskin bottles in order to characterize the water masses present in the water column (Table 1). Oxygen was analysed and calculated on board, samples for chlorophyll “a” were filtrated immediately after collection, taking the frozen filters to the ICCM. Nutrient samples were frozen and taken to the ICCM to be analysed there, whereas the salinity bottles were also analysed at the ICCM. Some of the parameters of the carbon system were analysed on board and other were done ashore.

### 4.3.3 Methods

#### 4.3.3.1 Water Sampling

Samples were collected immediately after the Niskin bottles were on board from each depth. The sampling sequence was as follows:

1.) Oxygen: was taken in glass bottles of about 125 ml of volume which were previously cleaned and washed with HCl acid and was fixed at once; then it was kept for at least six hours according to WOCE regulations and finally it was analysed at the laboratory on board the ship.

2.) Carbon system measurements: in this case pH, TIC and alkalinity: samples were taken in glass bottles and were fixed immediately on board.

2.) Nutrients: were taken in polypropylene bottles which were previously cleaned and washed with HCl acid and were completely dry. Samples were immediately frozen at -20ºC, analysing them as soon as possible after arrival at the laboratory. Freezing the samples is a
It does not or only in a non-significant way affect the nitrate+nitrite and the phosphate values (by a slight decrease) and is not noticeable in the silicate values (Kremling and Wenck, 1986; McDonald and McLunghlin, 1982).

3.) Salinity: samples were taken in dark glass bottles which were previously cleaned and washed with HCl acid. Then, they were kept in boxes to protect them from light till analysis on land.

4.) Chlorophyll: samples of one liter of water were taken. The chlorophyll samples were filtered immediately and the filters were frozen subsequently at -20°C. Their analyses take place at the ICCM laboratory in land.

All samples were taken using the procedures established in the WOCE Operations Manual, WHP Office Report WHPO 91-1/WOCE Report No.68/91.

4.3.3.2 Analysis

4.3.3.2.1 Dissolved Oxygen

The samples were analysed using the method described in the WOCE Operations Manual, WHP Office Report No. 68/91; the final titration point was detected using a Metrohm 665 Dosimat Oxygen Auto-Titrator Analyser.

Carbonate system measurements

The pHt in total scale (mol (kg-SW)^{-1}) was measured following the spectrophotometric technique of Clayton and Byrne (1993) using the m-cresol purple indicator (DOE, 1994). 0.0047 pH units were added to the pH experimental values in order to take into consideration the recommendations by Lee et al. (2000). A system similar to that described by Bellerby et al. (1995) was developed in our lab. The pHt measurements were carried out using a Hewlett Packard Diode Array spectrophotometer in a 25°C-thermostated 1-cm flow-cell using a Peltier system. A stopped-flow protocol was used to analyse seawater previously thermostated to 25°C for a blank determination at 730, 578 and 434 nm. The flow was restarted, and the indicator injection valve switched on to inject 10 μl dye through a mixing coil (2 m). Three photometric measurements were carried out for each injection in order to remove all dye effect on the seawater pHt measurement. Repeatedly, seawater measurements of the different Certified Reference Materials (CRM provided by Dr. Dickson, Scripps Institution of Oceanography) samples gave a standard deviation of ± 0.0015 (n = 54).

The total alkalinity of seawater (A_T) was determined by titration with HCl to the carbonic acid end point using two similar potentiometric systems, as described in more detail by Mintrop et al. (2000). In order to yield an ionic strength similar to open ocean seawater, the HCl solution (25 l, 0.25 M) was made from concentrated analytical grade HCl (Merck®, Darmstadt, Germany) in 0.45 M NaCl. The acid was standardised by titrating weighed amounts of Na_2CO_3 dissolved in 0.7 M NaCl solutions. The total alkalinity of seawater was evaluated from the proton balance at the alkalinity equivalence point, pH_{equiv} = 4.5, according to the exact definition of total alkalinity (Dickson, 1981). The performance of the titration systems was monitored by titrating different samples of certified reference material (CRM, batch 42) with known inorganic carbon and A_T values. The agreement between our data and CRM values was within ±1.5 μmol kg^{-1}. Total inorganic carbon (C_T) is computed from experimental values of pHt and total alkalinity, using the carbonic acid dissociation constants of Mehrbach after Dickson and Millero (1987). This set of constants presented the best agreement between C_T(pH, A_T) calculations and certified C_T values for CRM, batch 42, with a C_T residual of ± 3 μmol kg^{-1}, n=54 (Millero, 1995, Lee et al., 1997).
4.3.3.2 Nutrients

The nutrients determination was performed with a segmented continuous-flow autoanalyser, a Skalar® San Plus System (ICCM).

Nitrate+Nitrite: The automated procedure for the determination of nitrate and nitrite is based on the cadmium reduction method; the sample is passed through a column containing granulated copper-cadmium to reduce the nitrate to nitrite (Wood et al., 1967), using ammonium chloride as pH controller and complexer of the cadmium cations formed (Strickland and Parsons, 1972). The optimal column preparation conditions are described by several authors (Nydahl, 1976; Garside, 1993).

Phosphate: Orthophosphate concentration is understood as the concentration of reactive phosphate (Riley and Skippow, 1975) and according to Koroleff (1983a) is a synonym of “dissolved inorganic phosphate”. The automated procedure for the determination of phosphate is based on the following reaction: ammonium molybdate and potassium antimony tartrate react in an acidic medium with diluted solution of phosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-coloured complex, ascorbic acid. The complex is measured at 880nm. The basic methodology for this anion determination is given by Murphy and Riley (1962); the used methodology is the one adapted by Strickland and Parsons (1972).

Silicate: The determination of the soluble silicon compounds in natural waters is based on the formation of the yellow coloured silicic acid; the sample is acidified and mixed with an ammonium molybdate solution forming molybdenic acid. This acid is reduced with ascorbic acid to a blue dye, which is measured at 810nm. Oxalic acid is added to avoid phosphate interference. The used method is described in Koroleff (1983b).

Phytoplankton pigments

Pigments were measured using fluorimetric analysis, following the methodology described by Welschmeyer (1994). The determination was achieved using a fluorometer TURNER 10-AU-000.

Salinity

Samples were measured with a salinometer, model Autosal 8400a, whose measurement range was between 0.005-42 (psu), with an accuracy of ±0.003, according to the manufacturer. It was calibrated following the manufacturer’s information and standardizing it with IAPSO Standard Seawater. Salinity values were calculated as practical salinity according to Unesco (1978, 1984).

4.3.4 Preliminary Results

Preliminary raw values (27 November 2005 to 06 February 2006) extracted from the nitrate sensor collected from the mooring are shown in Figure 2a. There was data in the sensor until the mooring recovery but the values could not be accepted due to the incorrect standards values obtained for the last period (06.02.06 to 03.03.06). These raw values need to undergo a quality-controlled checking comparing them with the microcat data put below just below the sensors frame, since mooring movements may have introduced a variability not inherent to the system.

Samples of salinity were taken from all the Niskin bottles for the ESTOC station and from 3 bottles at each cast made in the other stations (except for station #63, cast 1, because the
Niskin bottles were removed to put the microcats. Figure 2b shows the station ESTOC as an example of the agreement between the CTD salinity values of the bottles closure and the results obtained with the Autosal© salinometer analyses of the samples taken, values for the other stations were also coherent with the CTD closing bottles results.

The temperature/salinity diagrams made from the CTD casts to 200db taken along this cruise (Figure 3b), shows that the mixed layer is quite developed for most of the stations. Below the surface (figure 3 to the left), it is found the characteristic straight segment of the

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**Figure 10:** a) Raw nitrate data obtained from the two standards (2 and 5 nitrate) put in sensor #2404 NAS-2E (Envirotech LLC©) during the mooring period. b) detail of ESTOC salinity data from the Niskin bottles, in black values measured by the 2 profiles of CTD and in red the results of the samples taken by the ICCM.

**Figure 11:** a) T/S plots to 2000m of depth from the stations made during P333, showing in the ellipse the area of intermediate waters. b) temperature versus pressure (to 200 db) of the same stations to show the mixed layer depth.
North Atlantic Central Water and, at intermediate waters, the stations show the different mixing states of the mingling of AAIW (Antarctic Intermediate Water) and MW (Mediterranean Water).

The passages between the islands are always controversial, due to the complex mixing –both vertical and horizontally- produced by the bulk process induced by the channelling of the water masses. At these depths, the stations located towards the north of the Canary Islands (#55, 59 and 60) are more influenced by the presence of MW and the values are greater in salinity and temperature. Stations #61 and 62 were made to the south of the islands and they have at intermediate level lower temperature and salinity values, i.e. they are mainly composed of only AAIW. Station #54 seems to be in between the two trends, i.e. shows mixing of both AAIW and MW.

At intermediate depths both the Antarctic Intermediate Water (AAIW) and the Mediterranean Water (MW) masses are found at different stages to the north of the Canary Islands (ellipse Figure 3a). Ranges of temperature and salinity at depths of 800-1200m in the Canary Islands environment are in the order of 5-12°C with salinity ranging between 35.2 and 35.5 (Llinás et al., 2002).

The oxygen results obtained during P333 down to 2000m (Figure 4a) show approximately the same trend, having the southern stations the lower values down the water column except in the surface. Calibration stations by DOLAN (st. 58 and 63) were only made to 500m and 300m due to sensors depth restrictions. The presence of AAIW is also pointed out by the relative minima, which is lower at the south and found at depths 600-800m. Values of oxygen minimum in the stations north of the Canary Islands were found to be around 3.6ml/l whereas at the south are of the order of 2.9ml/l.

Figure 12: a) Oxygen (2000m depth) for the stations measured during P333, ESTOC 03/06 is depicted in green. b) ESTOC station values of oxygen from CTD (in red) and from water samples taken by ICCM (in black).

The CTD/rosette had an oxygen sensor included and therefore it has been possible to compare the values measured for each Niskin bottle closure with those obtained by analyses of the water samples taken from each bottles for each station. Figure 4b depicts the results for the ESTOC station as an example, showing that the oxygen measured by the sensor was in the
order of between 0.5-1.0 ml/l lower than the values obtained by analysis on board of the samples taken. The difference between the values changes with the depth in the water column, being greater at the surface and lower at the oxygen minimum.

The chlorophyll “a” and oxygen for the surface layer down to 200m are plotted in Figure 5a and 5b respectively. Oxygen relative maxima were found at the surface having values of about 5.4 ml/l for all the stations sampled; the lower values both for the oxygen to 200m and the chlorophyll „a“ coincide with the southermost stations (#61 and 62).

Values for chlorophyll range were greater for station #54 ranging from 0.002 µg/l at 200m to 0.5 µg/l at 25m in this case. The rest of the stations made along P333 have the same trend in chlorophyll „a“ values, having the maximum at the range of 25-50m nominal depth with values of 0.50-0.31 µg/l.
### 5. List of Stations

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<th>Time UTC</th>
<th>Description</th>
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<td>16:49</td>
<td>Microcat IM-P 206 i/w</td>
<td>29° 11.24' N</td>
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<td>16:49</td>
<td>Fluorometer i/w</td>
<td>29° 11.24' N</td>
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<td>3629.0</td>
</tr>
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<td>3628.0</td>
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<td>17:05</td>
<td>Microcat IM-P 2269 i/w</td>
<td>29° 11.31' N</td>
<td>015° 55.65' W</td>
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<td>17:28</td>
<td>Microcat IM-P 1287 i/w</td>
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<td>65</td>
<td>09.03.2006</td>
<td>12:00</td>
<td>Station CI-20</td>
<td>29° 03.00' N</td>
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<td>12:15</td>
<td>Top Buoy (2 yellow) i/w</td>
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<td>12:15</td>
<td>10x Benthos (orange) i/w</td>
<td>29° 02.91' N</td>
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<td>6x Benthos (orange) i/w</td>
<td>29° 02.93' N</td>
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<td>14:05</td>
<td>Releaser i/w</td>
<td>29° 03.98' N</td>
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<td>Anchor weight i/w</td>
<td>29° 04.23' N</td>
<td>015° 14.97' W</td>
<td>3588.0</td>
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6. Acknowledgements

All scientific cruise participants thank Captain Michael Schneider and his entire crew for the flexible and friendly assistance during the R/V POSEIDON cruise 333. As on the previous cruises it was a good example of professional support and handling. The teamwork among the crew and scientists was friendly and relaxed as known from several other cruises on R/V POSEIDON. The cruise could be realized successfully.
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