Short Cruise Report

Meteor Cruise 60-5 Fort-de-France to Lisbon 9 March 2004 – 15 April 2004



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# Background

#### **TTO Revisited and Water-Column Chemistry**

The main theme of Meteor 60-5 was to resample a set of hydrographic stations that had been occupied in 1981 during the US-led Transient Tracers in the Ocean program (TTO). We therefore gave Meteor 60-5 the nickname: 'TTO Revisited'. The TTO expedition was itself, partly a reoccupation of the famous GEOSECS expedition of the early 1970's. Both GEOSECS and TTO were concerned with the penetration into the ocean of tracers derived from nuclear fallout: particularly tritium (<sup>3</sup>H) and radiocarbon (<sup>14</sup>C). The atmospheric weapons testing of the early 1960's had initiated a global-scale tracer-labeling experiment that was monitored by worldwide expeditions such as GEOSECS and TTO. These expeditions and the tracers measured, returned major new insights, as well as some new questions, concerning the circulation of the deep ocean.

By the time of TTO however, concern was already shifting away from the decaying problem of man-made radioactivity towards the growing problem of man-made  $CO_2$ . Hence the TTO cruises included extensive measurements not only of fallout tracers but also of oceanic  $CO_2$ .

Twenty-three years on from TTO, there has still been no carbon equivalent of the Nuclear Test Ban Treaty, and the result is that the  $CO_2$  problem continues to grow. Human beings continue to release more and more  $CO_2$  into the atmosphere, with 30-40% of the amount released 'disappearing' into the ocean. The consequence of the ocean uptake is that ocean  $CO_2$  levels are rising. The major goal of the Meteor 60-5 cruise was to collect data to document and quantify this increase of oceanic  $CO_2$  over time. Comparison of our data with the high-quality data collected 23 years ago during TTO, gives us an unprecedented view into the magnitude of this change and its geographical distribution. This information in turn can be used to check and improve the models that try to predict how much  $CO_2$  the ocean will take up in the future.

During Meteor 60-5, we travelled along the long path trod by the RV Knorr, 23 years ago. The result is a strange looking cruise track (Figure 1) that zigs and zags across the mid-latitude Atlantic in order to reoccupy as many TTO stations as possible. The Meteor 60-5 cruise, combined with a northern North Atlantic cruise of Meteor and two related US-led cruises conducted in 2003, provide an almost complete 'snapshot' of the North Atlantic for the period 2003-2004. This can be compared directly with how the Atlantic looked in 1981. In addition to the expected CO<sub>2</sub> increase, we are looking for changes in temperature, salinity, oxygen, nutrients and tracers such as the Freons using the high-quality TTO data as a baseline.



Figure 0: Cruise track of Meteor 60/5

Our comparison with data collected in 1981 required chemical measurements of extremely high accuracy. The atmospheric pCO<sub>2</sub> has increased by about 35-36  $\mu$ atm since 1981: the time of the TTO expedition. This is an ~10% increase in the carbon content of the atmosphere but the equivalent increase in the surface ocean is 25  $\mu$ mol/kg: just over 1% of the background seawater carbon content. Obviously detecting anthropogenic changes of 1% or less over 23 years requires extremely accurate measurements. And the problem doesn't stop with carbon: ocean carbon is subject to natural variability associated with photosynthesis and respiration. To correct for variable amounts of carbon respired in subsurface waters we use dissolved oxygen: these data have to be accurate to about 1-2 parts in 300. To interpret any changes in oxygen we need the most accurate measurements of temperature and salinity, and so it goes on with the accuracy needs cascading down from one measurement to another.

The CO<sub>2</sub> measurements were made on board by a team of 5 IfM-GEOMAR analysts who



### Figure 0: The CO2 Laboratory during M60/5

worked shifts around the clock to keep up with the samples being collected (see Figure 2). Samples were also collected for shore-based analyses of <sup>13</sup>C at Kiel University's Leibniz Labor für Altersbestimmung. These analyses can provide an independent estimate of anthropogenic  $CO_2$ , by detecting the progressive dilution of the heavier isotope of carbon by 'lighter' carbon released into the environment with the burning of fossil fuel.

To complement the CO<sub>2</sub> measurements, we had a significant transient tracer measurement program on board, including measurements of CFCs 11 and 12, CH<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub>, and for the first time in this region, SF<sub>6</sub>. All of these compounds are man-made and have, like CO<sub>2</sub>, increased in the atmosphere and hence in the ocean over the past 40 (SF<sub>6</sub>), 60 (CFC11 and 12), to 80 (CCl<sub>4</sub>) years as a result of human emissions. Unlike CO<sub>2</sub>, these compounds have no natural background. In addition to these 'tracer' gases, we measured a range of naturally-produced gases. These include the important greenhouse gas, N<sub>2</sub>O, and a wide range of halocarbons including some 'exotic' brominated and iodinated compounds that play key roles for atmospheric chemistry.

#### **Biological Program and Bioassay Experiments**

Meteor 60-5 also had a biology program with two components: one small group from IFM-GEOMAR (Kiel) was catching particles and 'marine snow' with a custom large-volume water sampler ('Snow Catcher') deployed on a hydro-wire. There was also a larger 'Bioassay Group' comprised of scientists from IfM-GEOMAR, the University of Essex, the University of Plymouth and the Southampton Oceanography Centre. This group conducted on-board experiments to study nutrient limitation.

In some ways, Meteor 60-5 was two separate expeditions sharing the same vessel and cruise track. The program of physical and chemical measurements of the deep water column occupied the majority of the scientific staff on board. However the Bioassay group rarely went near the CTD/rosette system and their activity was almost completely out-of-phase with that of the rest of the scientific staff.

The Bioassay Group was seeking to determine the nutrient(s) (nitrogen, phosphorus, or iron) that limit the productivity and biomass of the phytoplankton, the fixation of nitrogen ( $N_2$ ) by the microbial community, as well as the bacterial productivity. They conducted a series of on-board experiments involving manipulations of surface seawater pumped from a towed 'fish'. Each experiment consisted of filling approximately 150 1-liter bottles under trace-metal clean conditions in an on-board clean laboratory container. Nutrient forms of nitrogen, phosphorus, iron are then added to these bottles in all possible combinations. The bottles were incubated on-deck for 48 hours. Parameters

such as phytoplankton productivity and chlorophyll, as well as nitrogen fixation, and bacterial productivity were measured both at the beginning and end of the incubations in order to determine the effects of the different nutrient additions. Samples were also collected for molecular analysis of DNA and RNA in order to identify and quantify organisms responsible for nitrogen fiaxation.

The Bioassay Group also examined how dust derived from the African continent might affect these biological processes. Atmospheric transport of dust from the Saharan desert is well known to be an important source of iron. During Meteor 55 to the tropical Atlantic, similar bioassay experiments had suggested that additions of Saharan Dust might stimulate nitrogen fixation by relieving both phosphorus and iron limitation. Similar experiments were conducted during M60-5 to determine the amount of N, P and Fe released when dust is added to seawater.

## **Cruise Narrative**

## Week 1 (9.3.2004 - 14.3.2004)

Meteor 60 Leg 5 departed Fort-de-France (Martinique) at 1330 (local) on March 9. Unpacking and laboratory set up had continued right up until the time of departure, but we were at that point able to relax a little and enjoy the view as we sailed along the western coast of Martinique.

During the first week, we sampled 6 of the old TTO stations. Overall the data quality looks very good, with our nutrient and oxygen data falling exactly on top of the older data. We could already see evidence for a significant increase of  $CO_2$  in the top 700-800m of the water column. After sampling at TTO station 22 (25° 47'N; 66°W) we made a right turn, and headed northeast towards a cluster of TTO stations located 750 nautical miles south of Newfoundland. As we traveled slowly north, we had warm and calm conditions.

#### Week 2 (15.3.2004 – 21.3.2004)

By the end of the second week we had made good progress and had occupied 17 stations. Eleven of these were re-occupations of stations occupied by the Transient Tracers in the Ocean expedition of 1981. Data collection had settled down to a more-or-less routine operation. The CTD/rosette operations were going well and Christopher Smarz managed to repair our fluorometer with some ingenious 'Bastelei'.

From a first look at our data from southern stations we can see a very clear signal of the post-1981 anthropogenic  $CO_2$  increase down to depths of about 700m, or to seawater potential densities of about 1027. Further north there were indications of the signal being found in deeper and denser waters.



**Figure 0: Preparing the Snowcatcher** 

During the 2<sup>nd</sup> week, we benefited from the route-planning assistance provided by the Bordwetterwarte of the Deutscher Wetterdienst. In particular, we were able to 'snatch' an extra, northern TTO station out of the jaws of two storm depressions thanks to insight into model predictions from our meteorologist.

### 3rd week (22.3.2004 - 28.3.2004)

During the third week, we retraced an old TTO cruise track and the even older GEOSECS-Atlantic track as far as 42°N 42°W, 350 miles east of the Tail of the Grand Banks. Along the way we sampled at a US CLIVAR-Carbon station of WOCE line A20 (29°34'N 52°20'W) that was occupied by our US colleagues during 2003. The intention had been to resample this station as a cross-check on data intercomparability. Unfortunately at this station we encountered a major technical difficulty when signal transmission to/from the CTD was interrupted during two separate attempts at a deep cast. Both times the connection was lost at depths of about 5000m. Eventually we left the station with complete CTD downcast profiles available for comparison, but only 7 water samples. While limited in scope, comparison of these 7 deep water samples with their CLIVAR equivalents was encouraging, with the chemical properties such as nutrients, oxygen and carbon agreeing to within the desired tolerances. In general, weather conditions were remarkably favorable, including sunny and warm conditions at our northernmost station. In general the region of the Atlantic covered by the cruise to this point had been filled with high pressure systems, both north of the Azores and SW of Newfoundland. Nevertheless, in the middle of the 3<sup>rd</sup> week we were located directly at the air mass boundary between the two Highs which gave us strong winds and swell and forced us to miss one planned station. The missed station was a shallow TTO station that had been occupied on top of a seamount with relatively few chemical measurements: our failure to 'collect' it, was therefore not too damaging to our program.



*Figure 4:* The Bioassay Group ready for a long night in the Clean Lab. Container. From left to right: Mark Mills, Rebecca Langlois (IfM-GEOMAR), Angie Milne and Eric Achterberg (Plymouth Univ., UK). Not shown are: Mark Moore (Southampton Oceanogr. Centre) who took the photo, Kerstin Nachtigall and Peter Fritsche (IfM-GEOMAR). Assistance with nutrient measurements is provided by Frank Malien (IfM-GEOMAR).

By the end of the 3<sup>rd</sup> week, the Bioassay Group had already successfully completed four experiments. The experiments benefited from the wide range of conditions that we encountered on the cruise, ranging from oligotrophic surface waters of the tropics to pre-bloom, 400-m deep mixed layers of the northern Atlantic. Initial results showed that nitrogen additions stimulated phytoplankton productivity and chlorophyll concentrations, whereas a combination of nitrogen and phosphorus was required to stimulate bacterial productivity. This result may run counter to some recent work suggesting a primary role for phosphorus in limiting productivity. Further conclusions have to await more detailed analysis of the results including analysis of stored samples in Kiel.

# 4<sup>th</sup> Week (29.3.2004 – 4.4.2004)

The fourth week of Meteor 60-5 saw fewer stations being occupied in part due to a long transit southwards in order to resume our eastward transect along about 33°N. This planned gap was followed later by an enforced ~24-hour halt to stations due to strong winds and high seas. The transit time was used by the various chemical measurement groups on board to make adjustments to their systems,

perform more extensive calibrations, and work up data. It also allowed our two CTD operators to take a much-needed break. Despite the bad weather, we managed to sample at, or close to, all planned TTO stations and so remained on schedule. By the end of the week, we had just completed a re-occupation of TTO station 49 at 33° 46'N 25° 8'W. Immediately after this we attempted a biological CTD and particle-catching station in about 280m of water on top of the nearby Atlantis Seamount. However wind and weather conditions on top of the Seamount were difficult and the station was abandoned. The 5th week of Meteor 60-5 started with an attempted biological station on top of the Atlantis Seamount (33 deg 59'N 30 deg 5 W). We found a good shallow location for the station and collected an interesting-looking fluorescence and oxygen profile with the CTD. Unfortunately difficult wind, current and wave conditions then forced us to cancel the particle catcher deployment.

We also took the opportunity of the long transit at the beginning of the week to hold our 'Bergfest'. This included the cultural highlight of the cruise with the awarding of prizes for the Meteor 60-5 photo contest. Twenty excellent entries were submitted in the categories: 'Science', 'Life on Board', and 'Art:



Figure 5: Warm and calm seas in the Canary Basin.

Hands or Feet'. Upon examination of the entries, the judges were forced to add an additional category: 'uncategorisable'. Later in the week, on April 1, the Chief Scientist was the victim of an extraordinarily elaborate hoax.

# 5<sup>th</sup> week (5.4.2004 – 11.4.2004)

The 5<sup>th</sup> week saw us following the footsteps of Larry Armi's TTO Leg 3 into the Canary Basin. The 'bioassay group' will start another of their experiments at our southernmost point. Then we made a

northwards transect, to the east of the Azores, and started the final transect eastwards towards Lisbon along 37°N, following the path of TTO Leg 4 (Chief Scientists: Wally Broecker and Claes Rooth).



As we headed southeast into the Canary Basin, we gradually encountered a progressively stronger influence of Salinity Maximum Water (SMW, sometimes known as the Subtropical Underwater). This water mass is formed convectively in the eastern Atlantic as a result of strong evaporation driven by dry winds leaving NW Africa. The salinity of this water mass has increased over the past several decades, perhaps reflecting large-scale changes in the hydrological cycle. However this water mass appears to be of significance not only for climate but also for biogeochemistry.

The same hot, dry winds that drive evaporation also deposit dust carried from the Sahara/Sahel onto the ocean surface. And our experimental and field results from Meteor 55 had strongly supported the hypothesis that dust addition can stimulate nitrogen fixation. During the first week of our cruise we had already sampled SMW as a subsurface layer off the Caribbean Islands, where it was marked by high levels of nitrate relative to phosphate. This 'excess nitrate' signal has been attributed to high rates of

oceanic nitrogen fixation in the source regions of this water mass. Our transit towards the SMW formation region provided a perfect opportunity for our biologists to start their 7th nutrient limitation bioassay experiment. Interestingly, along the transit, the on-board iron measurements revealed increased levels of Fe (II), perhaps a signal of increased dust deposition. We collected DNA samples in the region for characterization of nifH genes coding for the nitrogenase enzyme. This will help us to determine the type of organisms responsible for any enhanced nitrogen fixation measured there.

This part of the cruise was marked by flat calm conditions, sun and warm temperatures and was very, very pleasant.

The southernmost point on this part of the cruise was reached on the 6<sup>th</sup> of April at 30° 49'N 26° 44'W. We then returned along a line of TTO stations, in a northeasterly direction, towards the Azores. Upon approaching the Azores it was decided to make a detour to Ponta Delgada to offload a sick crewmember. Thanks to thorough preparations by Captain Jakobi and the other Officers, the entire operation consumed the absolute minimum of time. Only one station was cancelled and this, fortunately, was not a TTO station.

During this week, we were able to celebrate Easter Sunday in a relaxed manner, with an excellent lunch. Life on board Meteor had settled into a routine and we had been well cared for by the crew. But as the cruise drew to an end, we were increasingly thinking about the end of the voyage and looking forward to returning home.

6<sup>th</sup> Week (12.4.2004 – 17.4.2004)

The final days of the cruise saw us occupy 4 more TTO stations. After that, the final analyses were completed and then we moved closer to the coast in order dismantle equipment and pack before arriving in Lisbon on Thursday morning (15.4.2004). In Lisbon, the ship was unloaded on the Friday and most cruise participants departed for home. The Chief Scientist and crew remained aboard, and hosted a reception, lunch and information exchange for the German Ambassador, embassy staff, Portuguese foreign affairs specialists and scientists on the Saturday (17.4.2004).

## **Results and Initial Findings**

The circulation tracers that we measured include the chlorofluorocarbons 11 and 12 ( $CCl_3F$  and  $CCl_2F_2$ ), together with  $CCl_4$  and  $SF_6$ . CFC-11 and CFC-12 have been measured worldwide since the

1980's. We re-sampled some stations where the very first North Atlantic measurements of these compounds were made, during TTO, in 1981. Not surprisingly, our data revealed a large increase in the concentrations of these compounds, at all depths, since that time. Much less commonly measured are  $CCl_4$  and  $SF_6$ . Both compounds are also exclusively man-made, but have very different time-histories of input to the oceans compared to the CFCs.  $CCl_4$  has been used widely as a solvent since the early 1900's, and has had significant environmental concentrations since the late 1920's.  $SF_6$  in contrast has increased rapidly in the environment since the 1960's. Taken together, the suite of compounds covers input timescales of <80 years ( $CCl_4$ ), <60 years (CFCs 11 and 12) and <40 years ( $SF_6$ ). The distributions of the tracers in the western basin reveal the impact of ventilation of the interior ocean over these three distinct timescales.

In the deep waters of the western basin we saw some striking variations in the relative distributions of CFC11 and CCl<sub>4</sub>. On some density horizons we have found relatively high levels of CCl<sub>4</sub> in the near-absence of CFC11. This signals tracer associated with a water mass component that was ventilated at a time when CCl<sub>4</sub> was already present in surface waters but CFC levels were still low. At other density surfaces and locations we have found similar levels of CCl<sub>4</sub> associated with much higher CFC11 levels. This water therefore represents a component that was ventilated when both CCl<sub>4</sub> and F11 were present in surface waters. Only in the upper 1000-2000m and in North Atlantic-derived deep water masses along the boundaries do we find evidence of a 'young' component containing detectable SF<sub>6</sub>. The 'senior' water contains no detectable SF<sub>6</sub>. The deep water distribution of SF<sub>6</sub> shows some strong similarities with the distribution of CFC11 as it was at the time of TTO. One of our goals is to employ this diverse tracer information to help us interpret the patterns of increase of CO<sub>2</sub> that we measure through our comparison with TTO data.

We also measured a variety of biogenic gases ranging from the important greenhouse gas,  $N_2O$ , through to a variety of naturally produced halocarbons. The relation to dissolved oxygen dominated the sub-surface  $N_2O$  distribution. The Meteor 60-5 data can be compared to data from earlier zonal sections collected by the IFM-GEOMAR group at 42°N and along 10°N over the past 3 years. A strong correlation with  $O_2$  is present in all the data sets, but the regression slope and intercept varies with latitude and between the western and eastern basins for reasons that are not yet clear.

On a separate gas chromatograph, we measured the concentrations of a range of compounds including bromoform (CHBr<sub>3</sub>), chloroform (CHCl<sub>3</sub>), dichloromethane, dibromomethane, and methyl iodide. These compounds play potentially significant roles in atmospheric chemistry. We have been measuring their distributions in vertical profiles, surface water and air. The vertical profiles, in

particular, are quite different between western and eastern Atlantic basins and these differences likely contain clues to the underlying oceanic production and consumption processes. Of particular interest is the behavior and sea-to-air flux of CHCl<sub>3</sub>: an important trace gas that definitely has oceanic sources but about which very little is known.

## **Bioassay Experiments**

Initial results from the Bioassay group showed that at the five oligotrophic sites primary production and chlorophyll a production was nitrogen limited (Figure 8). Once nitrogen limitation was relieved CO2 fixation rates and chlorophyll a concentrations increased further with the addition of phosphate. Likewise the bacterial productivity was stimulated by the combined addition of nitrogen and phosphorus. Further additions of Fe did not generally enhance primary production, chlorophyll a concentrations, or bacterial production. The addition of glucose did not stimulate bacterial production on its own, but increased productivity approximately 100x when added to the combined N and P treatments.

In all experiments where surface nutrient concentrations were undetectable the addition of Saharan dust stimulated primary production, chlorophyll a biomass, and bacterial productivity.



Figure 7. Map showing sites of M60/5 (red) and M55 (blue) bioassay experiments.



Figure 8. Mean chlorophyll a response in at the five sites with undetectable levels of nutrients in the surface waters (oligotrophic). Responses are relative to control.

There is still considerable work to be carried in the laboratory. Samples for the nitrogen fixation rates will be analyzed in Kiel, and the DNA/RNA samples will also be analyzed. Additionally, flow cytometry samples collected for cell abundance and diversity, and low level phosphate measurements, will be made during this period,