# Merian-Expedition MSM 01/01-a February 16 to 22, 2006 Warnemünde – Stockholm Chief scientist: Prof. Dr. K. Jürgens

## **Preliminary Report**

Emphasis of this first leg of Maria S. Merian Cruise 001 leg was on the oxygen-depleted deep water and on the redox-controlled biogeochemistry in relation to external matter supply to the central basins of the Baltic Sea. Other focal points were the investigation of microbial communities in oxic-anoxic boundary layers and the distributions of harmful substances and elementary mercury.

Figure 1 shows the investigation area, with the main work carried out in the Gotland Sea (Gotland and Faroer Deep). Stations were also sampled in the Arkona- and Bornholm Sea and in the Landsort Deep. Investigations comprised water column sampling with a CTD-Rosette and IOWs Pump-CTD, *in situ* pumps as well as multi-corer and box-corer sampling of surface sediments.

After short stations in the Arkona- und Bornholm Basins, on which CTD-profiles and water samples were obtained, the vessel steamed to the Gotland Sea, where work proceeded at 57° 0,01 N 20° 10,07 E. A comprehensive sampling programme (water column and surface sediments was conducted within 5 days thereafter in the vicinity of the central monitoring station TF0271 at 57° 19,98 N 20° 9,88 E. Here, water column profiles were obtained by Rosette-CTD as well as IOW-Pump-CTD with a particular focus on the oxic-anoxic boundary layer at ~120 m depth (for the first time comparing these alternative techniques). For sediment investigations, and as a basis for subsequent multi-corer deployments, a sediment echo sounder (type SES-2000, Innomar) was deployed. This system is able to produce particularly deep frequencies of 2-7 kHz and provides a high lateral resolution. Several transects were mapped within the Gotland and Landsort Deep (200 nm and 60 nm, respectively).

Multi-corer samples were taken in the central basin as well as at the fringes. Stations with anoxic bottom water obviously had experienced prolonged periods of anoxia as evidenced by laminated sediments. Sediment pore water samples were taken under anaerobic conditions for later analyses of nutrients, sulphur, metals and dissolved inorganic carbon analyses. Further sediment samples were stored frozen for determinations of main and trace elements and stable isotope rations (S, O, C). Sediment cores were incubated under *in situ* conditions to assess the release of anaerobic mineralisation products, and the vertical distribution of sulphate, sulphide, pH and  $O_2$  within cores were measured with micro-sensors.

One highlight of the work were video documentations of the sea floor on 3 transects in the Gotland Basin with a camera attached to the IOW-Pump-CTD. The system was deployed only few cm above the sea floor and thus provided information about the sediment texture and the colonisation by microorganisms. Between 90 m and 120 m water depth dense mats of microorganisms were found and sampled with a multi-corer at 57° 22.70 N, 20° 34.95 E. These mats of filamentous bacteria (probably *Beggiatoa* sp.) play an important role in oxydizing sulphide leaching from the sediment. Video mappings give precise pictures of the small-scale patchiness and the larger-scale distribution distribution at the basin fringes, and provide information about the development of anoxic bottom waters. Cores with *Beggiatoa*-maths were investigated with micro-sensors, and samples were stored for later lab-based analyses.

Under water video camera deployments further enabled us to visualise of those milky turbid layers at the oxic-anoxic boundary layer in the water column. Measured dark fixation of  $CO_2$  by microbial communities located there showed a maximum in the upper sulphidic zone, confirming the high activity of chemolithoauutotrophic bacteria. On-board flow cytometry evidenced new bacterial clusters with specific size and DNA-content in this layer which could be sampled by the cytometer for later DNA- and RNA-based analyses.

The same investigations as in the central Gotland Sea were performed at a station in the Faroe Deep and in the Landsort Deep. Both stations are permanent monitoring sites and exhibited similar chemical profiles, with an oxic-anoxic boundary layer and sulphidic bottom water as in the Gotland Deep.

Surface and deep water were sampled to assess the distribution of organic harmful substances (PCBs, DDT, PAKs etc.) in the Bornholm Basin, the Gotland, Faroe and Landsort Deep. Samples were taken with the vessels sea water flow-through system and *in situ* pumps, concentrating particulate and dissolved matter from 300 – 400 liters of water for later landbased analyses.

Further marine-chemical measurements focussed on the exchange of elementary mercury (Hg<sup>o</sup>) between atmosphere and water ind the Arkona, Bornholm and Gotland Sea. Sampling was done quasi-continuously during steaming between stations (water / atmosphere sampled every hour /every 5 minutes, respectively). Vertical profiles of Hg<sup>o</sup> were taken on 2 stations (Gotland- und Landsort Deep), and sampled were taken to determine total mercury and dissolved and particulate organic carbon.

Finally, on February 20, 2006 a sediment trap mooring was retrieved at the station in the Gotland Deep and re-deployed again one day later.



Figure 1: Track plot of cruise MSM 01/01-a

# Merian-Expedition MSM 01/01-b February 22 – March 15, 2006 Stockholm - Helsinki Chief scientist: Prof. Dr. D. Schulz-Bull

# **Preliminary Report**

During the cruise watercolumn and surficial sediments at central stations in each of the two northern basins of the Baltic, in the transition areas between them and on transects towards the outer estuaries of the rivers Thorne and Kemi were sampled. Analyses of 14 water-columns, 10 ice-cores and 9 porewater-profiles for the whole suite of plant nutrients (NH4, NO3, NO2, PO4, SiO4) and O2/H2S for watercolumn profiles were carried out.

By means of a video-camera mounted to the CTD, video sequences of sediment surfaces at all stations were obtained.

Pore water analyses for dissolved organic carbon of 9 profiles were performed on board. Water column particulates were filtered at the same 14 stations for the later analysis of particulate carbon/nitrogen, isotopic composition of N and C, particulate phosphorus, particulate silica and electron microscopic mineralogical analyses

On 13 stations the multicorer was employed to gain up to 8 sediment samples of 40 cm depth. One or two cores were stored away for later sedimentological/mineralogical analyses, one core was sliced for organic contaminant analysis, one for pore water processing and two more for sulfur and carbon analyses of the swedish group.

On 5 stations experiments of in-situ sinking speed with a new sampler-mounted video device were obtained and the observed and collected particles were filtered and stored for later analysis of variables decribed above.

A sediment trap array with 3 traps for bulk element, metal and organic contaminant flux estimates was succesfully launched at the central basin of the Bothnian bay. The retrieval is planned for summer 2007.

A 12 m gravity core was obtained in the central part of the Landsort deep at 450 m water depth. The core was sectioned in 10 parts and stored away for analysis in the Warnemünde labs.

First results show, that the nutrient and oxygen concentrations in the northern basins were high troughout the water column except for phosphorus, which was constantly at the detection limit. A gradient towards the northern rivers could be seen by increased values of silica and nitrate. Higher P concentrations concomittant with lower oxgygen and elevated ammonia values were found in bottom water of the deep basins in the Bothnian Sea. The higher salinity suggests the lateral import of this water mass and its reduced compounds from the Gotland area.

The ice core nutrient concentrations showed a reduced silica content compared to the water below, comparable nitrate and phosphate concentrations but much higher ammonia values. It could not be decided, whether the samples were contaminated by the drilling procedure, but the extremely high ammonia and particle content of molten snow from the ice surface points towards high atmospheric input in winter.

The pore water nutrient concentrations increased according to depth in the sediment and the redox state of the sediment strata. Pore water DOC showed a clear increasing gradient towards the river mouths and therefore reflected the long term riverine carbon input better than the open water measurements.

The sedimentation speed measurement of single particles showed distinct differences in size and sinking speed between particles of different water layers. A detailed analyses of the video-sequences and the quality of the sampled material has still to be performed in the lab.

Another objective of the cruise was to sample organic carbon from the water column and the surficial sediments in order to make a source apportionment of marine and terrestrial organic carbon. We determined on board DOC by means of catalytic carbon combustion (SHIMADSU TOC-VCPH). Ultrafiltrated DOM was obtained from all major stations by means of tangential flow filtration with a cut off 1000 Da. The gathered UDOM (ultrafiltrated dissolved organic matter) samples as well as the sediment cores will be corner stones for a carbon budget of the Bothnian Bay and Bothnian Sea that will be formed with the other participants of the RV MARIA S. MERIAN cruise. The quantification of organic matter and biogenic element sources and sinks within estuaries such as the Gulf of Bothnia is challenging, and is often hindered by a large number of complex and overlapping interactions between organic matter sources and sinks. As a consequence, simple mass balance approaches, i.e. box models or two end member mixing curves alone do not often constrain potential sources and sinks within estuaries. Therefore stable isotopes of  $\delta$ 13CDOC determinations from the UDOM samples and the sediment samples will be performed to quantify various sources of organic matter in te Bothnia Bay and Bothnian Sea: terrestrial, estuarine and marine organic matter showed  $\delta$  13CDOC values of -27‰, -23- to -25‰ and -21‰, respectively. We will use additionally the  $\delta$  34S isotope composition of estuarine organic matter (water column and sediment), since  $\delta$  34S has a broader range from +21‰ in marine to approximately +6‰ in terrestrial organic matter. This makes  $\delta$  34SDOS a much more powerful tracer to estimate estuarine retention of dissolved organic matter in the Gulf of Bothnia. Since there are not many labs worldwide that can measure  $\delta$  34SDOS, we will be the first to our knowledge applying this technique to the Baltic Sea. The molecular composition of terrestrial organic matter reflects the prevailing watershed vegetation. Using lignin-derived phenols as chemotaxonomic tracers, one is able to distinguish between TOC derived from taiga and tundra ecoregions. In particular, the ratio between syringyl to vanillyl phenols correlates significantly with the proportion of tundra in the watersheds. These and other proxies on organic carbon (amino acids, carbohydrates etc.) will be measured during the RV MERIAN cruises by a group from the Baltic Sea Research Institute and will compliment our data nicely. Whereas our isotope studies on DOM will allow a more quantitative description how much of the overall DOM in the BB is of terrestrial origin, the chemotaxonomic tracer will allow a source apportionment from which areas (forest, wetlands etc.) in the watersheds most DOM is arrived. It is planed that these measurements will be also performed on the river samples.

As yet another objective, continuous surface water CO2 partial pressure measurements were performed during the entire cruise and data are available for the latitudinal pCO2 distribution in the entire Gulf of Bothnia. The pCO2 records were complemented by the determination of the total CO2 (CT) in samples taken from the ship's pumping system at intervals of 10 miles during steaming from the most northern station to the Landsort Deep.

Depth profiles for  $C_T$  and pCO<sub>2</sub> were determined at 12 stations with varying depth resolution (70 samples for each  $C_T$  and pCO<sub>2</sub>). For the determination of the below-surface pCO<sub>2</sub> the pump CTD was used in order to provide the flow-through pCO<sub>2</sub> measurement system with water from varying depths.



Figure 2: Track plot of cruise MSM 01/01-b.

## Merian-Expedition MSM 01/01-c March 16 - 20, 2006 Helsinki - Warnemünde Chief scientist: Prof. Dr. B. von Bodungen

#### **Preliminary Report**

The short 3rd leg of Maria S. Merian Cruise 001 was dedicated to bottom-near particle dynamics and conditions of particle incorporation into the sediment in the boundary layer between oxygenated and oxygen-free bottom water. This leg had members of the media (camera teams from German television channels) on board to gather and distribute information about the vessel and the scientific programmes conducted.

Figure 3 shows the cruise track and positions of sampled stations. Investigations primarily took place on a transect perpendicular to the slope of the eastern Gotland Deep (rectangle on cruise track in fig. 3) which was repeatedly sampled. Here the sedimentary structure was surveyed first by means of Parasound to select sampling positions. This was followed by sampling 6 stations to investigate the structure of the bottom-near water column by means of IOWs profiling *in situ* pump-CTD. Video-mapping of the sediment surface on all stations put emphasis on documenting microbial structures at the water-sediment interface. Water samples from 20 - 100 cm above the sea floor were pumped on board the ship and treated for later laboratory analyses of the particulate and dissolved fractions. Finally at all transect stations a multicorer was deployed to sample the upper sediment layers.

On the central part of the transect at about 120 m water depth, in the transition zone from oxygenated to  $H_2S$ -containing bottom waters, a 6 m long gravity corer was successfully deployed. Results will enable us to trace changes of bottom water conditions back into the geological past.

Two more stations were sampled in the central Gotland Sea to obtain material for laboratory experimental work after the cruise. All work could be carried out free of any instrumental or logistical problem.



Figure 3: Track plot of cruise MSM 01/01-c.