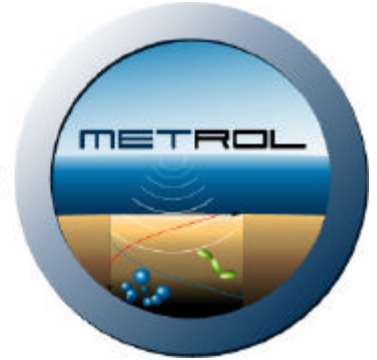


Thematic Programme: Environment and Sustainable Development



Fifth Framework Programme
1998 - 2002

METROL
METHANE FLUX CONTROL IN OCEAN MARGIN SEDIMENTS



**Methane fluxes in ocean margin sediments: microbiological and
geochemical control - contract no. EVK3-CT-2002-00080**

First Periodic Report

**SECTION 2: EXECUTIVE PUBLISHABLE SUMMARY, RELATED TO THE FIRST
REPORTING PERIOD (12 MONTHS)**

Period covered: 1. November 2002 – 31. October 2003

Date of submission 09.01.2004

SECTION 2: Executive publishable summary, related to the first reporting period (12 months)

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|-------------|---|-------------------|------------|
| Contract n° | "CT -"2002-00080 | Reporting period: | First year |
| Title | Methane fluxes in ocean margin sediments: microbiological and geochemical control | | |

Objectives:

The main scientific objectives of METROL in the first 12 months were:

- To start establishing methods to study transport and oxidation of methane in selected European margin sediments.
- To determine the position of the sub-surface methane barrier at selected locations in the Aarhus Bay, Kattegat, and Skagerrak.
- To obtain samples in order to later identify, through 16S rDNA-based techniques and isotopic biomarker analyses, the microbial populations responsible for methane oxidation.
- To develop initial analytical and predictive models on the complex processes determining methane fluxes in the sea floor and their regulation by environmental change.
- To acoustically map the accumulation of methane gas in selected ocean margin sediments.
- To establish a METROL section within the Pangaea data base on biogeochemical key parameters determining the methane flux and retention in marine sediments, based on the new data and on existing data and literature.
- To establish a web site which includes an interactive access to the data base, to informative GIS-based maps and graphs of the data, and to a practical modeling tool for calculating the controls on methane fluxes in ocean margin sediments.

Scientific achievements:

WP1

Cruises:

In the first year, five research cruises have been organised and carried out successfully to Aarhus Bay, to the Northern Kattegat and to the Skagerrak. Goals of these cruises were:

- to produce high resolution seismic data on the distribution of subsurface gas plumes in Aarhus Bay, which served as a basis for the establishment of five “type” localities for seasonal sediment sampling; to sample the type localities.
- To seismically locate subsurface gas plumes in the northern Kattegat and to sample sediments for the analyses of various geochemical and microbiological parameters and process rates.
- To perform seismic surveys and sediment sampling over an extended depth gradient across the southern Skagerrak trench slope and, on a more detailed scale, across pockmarks.

Two cruises performed in 2002 had already been dedicated to gas seeps and pockmarks located in the North Sea Oil fields. Both cruises addressed to similar biochemical and microbiological key processes for methane cycling in marine sediments, and METROL will considerably benefit from their results.

Web site, GIS and Data management:

The newly established project web site www.METROL.org serves for public information on the scientific objectives, background and current state of the project, announcements of METROL related news, and as a gateway to the PANGAEA data base and to interactive GIS and modelling applications. A password secured METROL Members Area serves as a platform for internal exchange of information.

High resolution GIS maps for bathymetry and various sediment parameters have been established for large parts of the target areas. Data on bottom water chemistry and benthic organisms were also incorporated into the GIS system, which is coupled with the PANGAEA database. For the distribution of maps via the internet, the ArcIMS Internet Map Server allows an interactive selection of maps and retrieval of data for the partners of the project as well as for the general public. The WDC-MARE/PANGAEA database is ready to store all data, documents and data web page files utilisable within the METROL project. Newly generated data will only be accessible to project members, while published data will be available for the scientific community world-wide.

Reaction Transport Model:

The Biogeochemical Reaction Network Simulator (BRNS) provides a simulation environment in which transport processes are interfaced with relevant biogeochemical reactions. The BRNS has been expanded to include processes and parameters corresponding to anaerobic oxidation of methane (AOM). The AOM model is currently being tested using literature data, and will be included into a fully diagenetic model when these processes have been verified. By remotely accessing the server, users can construct a biogeochemical reaction network or update an existing one by for example, exploring fluctuations in environmental boundary conditions and microbial activity.

WP2

Seismics and geochemistry:

The depth of methane gas accumulation was measured acoustically by high resolution seismics with various instruments (X-Star, Geo spark, boomer and multi-channel seismics). Based on these measurements sediment sampling stations were chosen to represent various depths of free methane gas. In Aarhus Bay, Kattegat, Skagerrak and North Sea pockmark sites, 3-6-m long cores obtained by gravity or vibro corers were used for the analyses of depth profiles for SO_4^{2-} and CH_4 concentrations in pore water in order to estimate the position of the sulphate-methane transition zone (SMTZ) which is an effective sub-surface methane barrier. The loss of sediment in the gravity cores was estimated by aligning the pore water profiles for SO_4^{2-} with those measured in Rumohr Lot cores from the same stations. Further work focuses on the high resolution analyses of other METROL relevant pore water-dissolved compounds and solid state constituents (e.g. concentrations of H_2S , HCO_3^- , organic C and N, diffusion coefficients for CH_4 and SO_4^{2-} , CH_4 -carbon isotopy, a.o.). Aarhus Bay and Kattegat data on concentrations of SO_4^{2-} and CH_4 have been delivered to the PANGAEA-data base. They are used to illustrate how the sub-surface methane barrier can be related to the accumulation of methane gas. Stable carbon-isotope data indicate that CH_4 from all sites sampled in the Kattegat, Skagerrak has a microbial origin.

The seismic survey in the Aarhus Bay revealed that the subsurface gas plumes almost reach the sediment surface in some locations. According to these results, stations along a NW-SE transect were chosen for seasonal sediment sampling which covered depth ranges of free gas from >4 m below seafloor (bsf) to <1 m bsf. The pore water profiles revealed considerable differences for the SMTZ: 2 stations SE on the transect showed rather wide and shallow SMT zones, an intermediate station displayed a narrow SMTZ in 2 m depth bsf, and the

station in the NW did not show any SMTZ at all.

WP3

Methanogenesis, acetogenesis, AOM and SRR:

Rates of methane turnover in Northern Kattegat and Skagerrak sediments were determined by direct measurement through the sulphate-reduction zone, the SMT- and the methanogenic zone. In two cores from the Kattegat elevated rates of methanogenic activity at the transition zone depths were related to high rates of anaerobic oxidation of methane. This is indicative of substantial methane cycling in this zone. The process of anaerobic oxidation of methane (AOM) is investigated in sediments from the Kattegat, Skagerrak and selected North Sea pockmarks. While most analyses are still in progress, first results from North Sea pockmarks indicate that an AOM community is situated in distinct sediment layers at the interface of carbonate crusts and fine sand. Areal sulphate reduction rates (SRR_A) were analysed in sediments from all working areas. Calculations of total SRR_A at stations with different sediment composition in the Kattegat indicated 3-8 fold higher rates in fine sand compared to silt. The major difference was caused by much higher SRR_A in surface-near sediment layers of the sandy station. In both sediment types, only a minor proportion of the SRR_A took place in the SMTZ.

Modelling:

Modelling methane turnover has taken a two-pronged approach.

1. A detailed investigation into how kinetics and thermodynamics can be combined to effectively quantify methane turnover in sediments by anaerobic oxidation. With this Thermodynamic-Kinetic Model (TKM), thermodynamic constraints on syntrophic consortia of sulphate reducers and methane oxidisers in marine sediments are explored.
2. A diagenetic reactive transport model of AOM incorporating the principal diagenetic reactions of redox-sensitive species. It is based on the novel concept of the 'Knowledge-Base' (KB) in which the conceptual and quantitative understanding of complex biogeochemical systems is systematically assimilated. The KB Reactive Transport Model (RTM) is accessible via a web-based server.

The first stage of modelling has provided a better understanding of the most sensitive parameters in the AOM process and their relationship with thermodynamic constraints. This preliminary information shows how the rate of sulphate reduction carried out by the sulphate reducing bacteria within the AOM consortia varies under typical ambient hydrogen partial pressures.

WP4

The microbial populations responsible for methane oxidation in the methane-sulphate transition zone are identified through 16S rDNA-based techniques and isotopic biomarker analyses. The current state of the WP tasks can be characterised as follows:

Sulphate reducing bacteria:

The general gene library of sulphate reducing bacteria associated with methane seeps is published in the public data base GeneBank, and as a paper in the international journal Geomicrobiology. It has thus been made fully available for further development within METROL.

Anaerobic methanotrophs:

The general gene library for anaerobic methanotrophs (phylogenetic groups ANME-1, ANME-2, newly discovered ANME-3) is finalised. It will be submitted for publication soon, and then made available to all METROL partners. The group ANME-3 was recently

detected by a new method (Card-FISH) in the methane-sulphate transition zone in North Sea sediments. This information will be published soon.

Isotopic signature of microbial biomarkers:

A first biomarker library for sulphate reducing bacteria has been developed and tested with North Sea sediments. Isotopically depleted biomarkers of sulphate reducing bacteria were detected in the SMTZ. The quantification of bacterial biomass is completed for samples from 2002 North Sea cruises. In two cores from the pock mark site "Tommeliten", clear peaks in lipid abundance and stable isotope depletion were recognised indicating the presence of a microbial filter for methane. Biomarker analysis is partially completed also for the 2003 cruises to the Kattegat and Skagerrak. A representative neutral polar chromatogram clearly shows the archaeal biomarker archaeol and a pair of C₁₅/C₁₅ non-isoprenoidal ether lipids inferred to derive from SRB. This provides first evidence that the organisms mediating methane oxidation in continental margin sediments are the same as those at cold seeps. Abundance estimations of these compounds confirm the association of archaeal and bacterial diethers within zones with AOM activity.

WP5

Experimental studies:

Sediment samples from the SMTZ are used to study chemical key parameters, which regulate anaerobic methane oxidation. These experiments are conducted under carefully controlled laboratory conditions. Optimised methods and equipment for these enrichment cultures have been established previously. Experiments with Tommeliten sediments were performed for 280 days, because of low methane oxidation rates, which are most likely due to the very low biomass and extremely slow growth of anaerobic methane oxidisers. Only in one sediment sulphide production developed over time indicating a relatively higher AOM in this sediment horizon compared to the other stations.

Microbial energy yield calculations:

A thorough analysis of the energetics of the pertinent reactions occurring in and around the sulphate-methane transition zone (SMTZ) has been performed, including sulphate reduction, methane oxidation, methanogenesis, acetogenesis and acetrophy. In the near future, thermodynamic constraints will be transferred to the numerical reactive transport model.

Socio-economic relevance and policy implications:

The results will have significance for our understanding of the regulation of methane fluxes in ocean margin sediments in relation to climate change.

Conclusions:

Seismic-acoustic mapping, in situ video observations, and diverse sediment sampling have shown extensive occurrences of shallow gas and gas seeps in the ocean margin sediments studied. In combination with geochemical analyses the new data demonstrate how the subsurface depth of the methane oxidation zone and of the free gas occurrence depends on the thickness of an organic-rich Holocene sediment deposit. By the use of the PANGAEA database these accumulating results will be used for areal GIS mapping and transport-reaction modeling of methane fluxes.

Keywords: Ocean margin sediments, methane, sulphate-methane transition zone, methane barrier, anaerobic oxidation of methane (AOM).