



ERANET BONUS Verbundprojekt

BONUS-73: Baltic Gas Methanemissionen in der Ostsee Vorhaben TP 1

03F0488A

Schlussbericht über den Beitrag des AWI zum BONUS Projekt BalticGas

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Das BONUS-Projekt Baltic Gas startete Anfang des Jahres 2009 mit einem Kick-off Meeting am MPI in Bremen. Die wissenschaftlichen Arbeiten wurden sofort begonnen, obwohl vom Projektträger die Finanzierung der wissenschaftlichen Arbeiten nur für einen Zeitraum von ~2.5 Jahren unterstützt werden konnte. Hierfür haben wir zusätzliche AWI-Eigenmittel (u. a. Dr. Kerstin Jerosch, Dipl.-Ing. T. Gentz) eingebracht.

Unsere Beiträge zum Baltic Gas Projekt untergliedern sich in folgende Aktivitäten:

WP 2: Data mining and GIS-mapping (Lead: GEUS)	Task 2.2: GIS-Mapping (AWI)
WP 5: Modelling and data integration (Lead: DESUU)	Task 5.2 GIS Modelling (AWI)

Weiterhin haben wir zum Work Package 4 beigetragen.

WP 4: Biogeochemistry (Lead MPI) Task 4.2.3: Water column methane and ferry box surface methane measurements - Application of Membrane inlet mass spectrometry and underwater mass spectrometry (AWI)

Unsere Arbeitsschwerpunkte waren:

- Datenrecherche zur Verteilung gasreicher Sedimente in der Ostsee
- Datenrecherche zum Vorkommen von Pockmarks und anderer Indizes die für die Bildung und Freisetzung von Methan und anderen klimarelevanten Gasen von Bedeutung sind
- Integration dieser Daten in ein Geoinformationssystem
- Weiterentwicklung der Geo-Daten-Infrastruktur
- Weiterentwicklung von Verfahren zur in situ Messung und Beprobung von gasreichen (Methan) Sedimenten und Wasserproben
- Aufbau eines Web-Map-Servers (WMS) zur Bereitstellung interaktiver Karten

- Die räumliche Modellierung mittels GIS und Geostatistik zur Erstellung von Vorhersage Karten zum Vorkommen von „freiem Gas“ in Sedimenten der Ostsee

Der vorliegende Abschlussbericht untergliedert sich in die Work Packages und die „AWI-Deliverables“, die im Abschlussbericht des Baltic GAS Projektes enthalten und fristgerecht eingereicht wurden, sowie weitere inhaltliche Ergänzungen.

WP 2: Data mining and GIS-mapping (Lead GEUS)

Task 2.2: GIS-Mapping (AWI)

AWI - Deliverable 2.2.1: Mapping of mined data

GIS-mapping of mined data has so far been focusing on collecting basic map themes from the Baltic Sea like bathymetry, economic zones, bottom water chemistry as well as the spatial distribution of pockmarks. In addition we integrated data into the Geo-Information-System ArcGIS (ESRI) about sedimentology, seafloor properties like slope angles or bottom water currents, as well as -from a process oriented and descriptive perspective- data sets directly related to the presence or the formation of methane in surface sediments (Fig. 1).

The later includes free gas areas observed by seismic surveys, known pockmark sites as well as gas flares released from the accumulation rates of particulate organic matter were compiled and integrated into the GIS (Fig. 2). The entire set of different parameters, geodata compiled within Task 2.1 as well as maps were georeferenced to a common map projection (Equal Area Projections like the Albers projection), suitable for calculations of mass budgets.

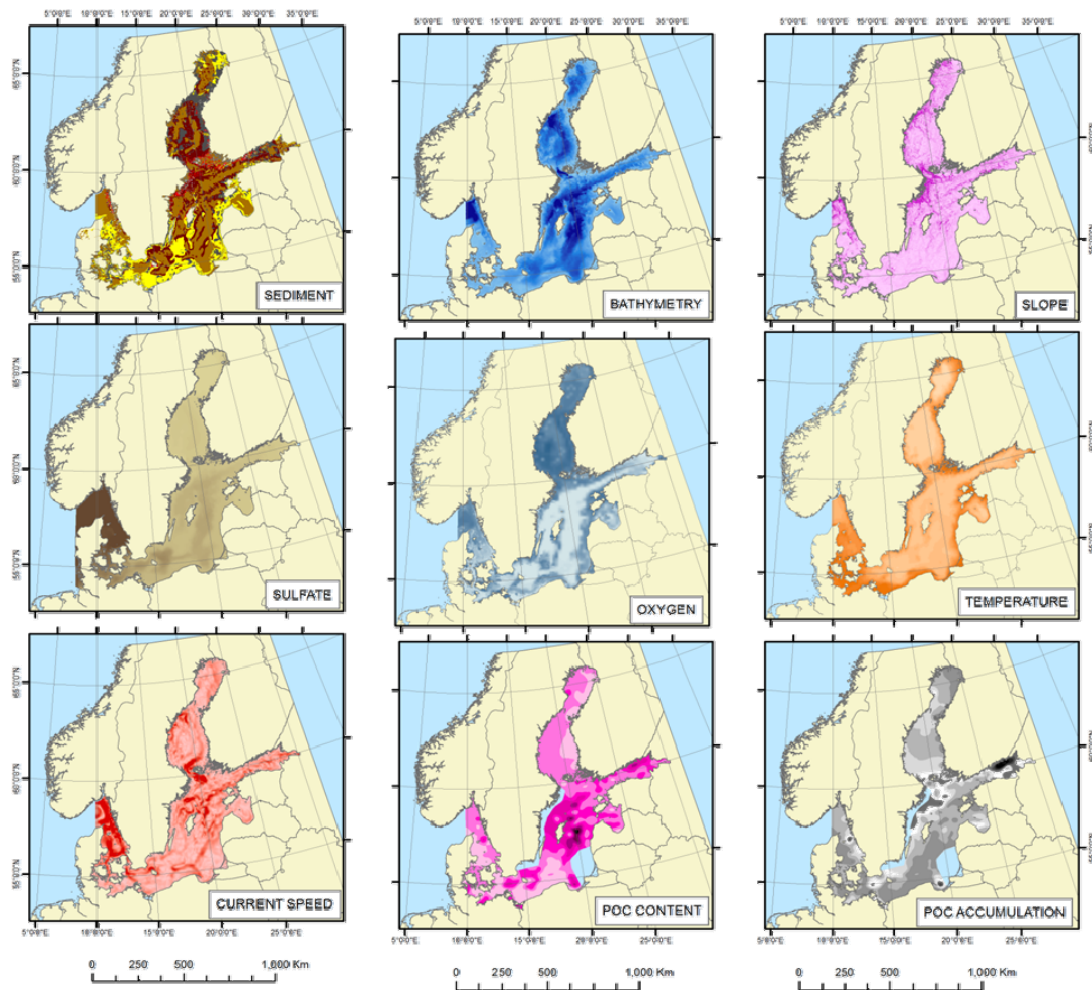
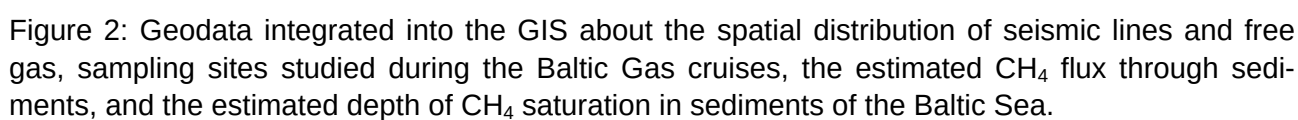


Figure 1: Examples for mined geodata integrated into the GIS.



For mapping of methane fluxes as well as the distribution of free gas in surface sediments the data derived within Task 2.1, data measured by the Baltic Gas partners during research cruises, information derived from seismic lines as well as geochemical data derived from literature recherche were considered.

For aquatic environments like the Baltic Sea, the transition from the degradation of organic matter by microbial mediated processes driven by agents like oxygen, nitrate or sulfate to the formation of methane by fermentation is indicated by the sulfate-methane-transition-zone (SMTZ). Within the SMTZ the pore water concentration of sulfate is entirely consumed by degradation of organic matter and re-oxidation of methane (Fig. 3).

Production of methane is starting below the SMTZ. In the close vicinity to the SMTZ concentration gradients of sulfate and methane are steep and well defined. From the perspective of biogeochemical analysis and sampling techniques, the depth of the SMTZ can be well defined by pore water studies, whereas measurement of methane fluxes from sediments into the water column or atmosphere are much more demanding. Therefore, the sediment depth of the SMTZ provides a robust – in terms analytical accuracy and data availability- proxy for identification of regions at the seafloor of the Baltic Sea where high or low methane production as well as fluxes of CH_4 into the water column are expected. For example, low SMTZ depths, suggesting high CH_4 concentrations and fluxes into the SMTZ, are mainly observed within mud sediment located in basins and valleys. In these regions the median value of the SMTZ is about 0.2 m. For muddy sediments located in plains, a much wider range (0.2 to 2.2 m) and a median depths of the SMTZ of about 0.6 m were derived (Fig. 4).

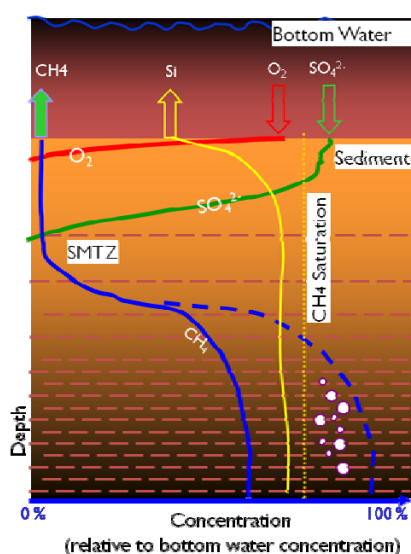


Figure 3: Pore water profiles in sediments related to the Sulfate-Methane-Transition-Zone.

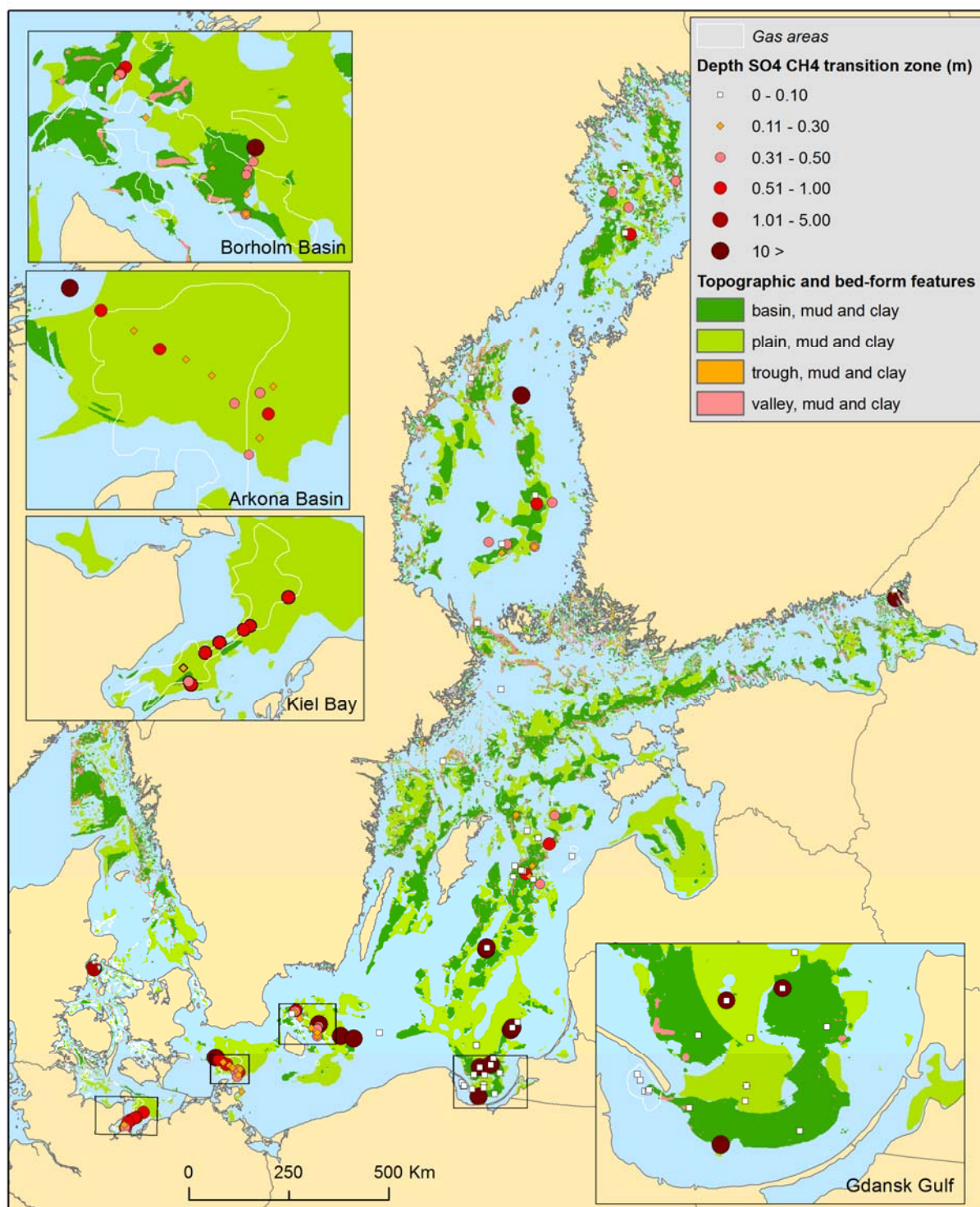


Figure 4: Spatial distribution of the sediment depth of the Sulfate-Methane-Transition-Zone (SMTZ) in surface sediments of the Baltic Sea. The spatial relationships between the depths of the SMTZ and sedimentology, mass accumulation of particulate organic matter, bottom water chemistry as well as morphological bed forms were considered.

AWI - Deliverable 2.2.3: Mapping of hot-spots of present and future CH₄-emission

Worldwide hot spots for methane formation and fluxes are observed. For examples, this includes (1) pockmarks (morphological depression at the seafloor) where high methane concentrations were often detected, (2) gas flares, where methane gas bubbles are released from the seabed, (3) shallow gas regions, where gas bubbles are detected in close vicinity to the sediment-water interface as well as (4) chemo-autotrophic communities nourished by upward fluxes of e.g. methane. Such hot spots are related to geological as well as environmental conditions, favorable for formation of biogenic methane or the transport of thermogenic methane, produced within deeper strata and transported along conduits to the sediment surface.

In close cooperation with the partners of the BalticGas project, we compiled data about the spatial distribution of such hot spots for methane fluxes and integrated these information into the Geo-Information-System. An example for the spatial distribution of pockmarks as well as free gas regions is shown by figure 5. Especially in the western part of the Baltic Sea Pockmarks and free gas areas were observed. In the eastern part of the Baltic Sea pockmarks were detected in Gdansk Bay or the Gulf of Finland. For some of these sites, there seems to be indications for thermogenic sources for methane. The GIS maps considering hot spots of methane fluxes are intended to be applied by the BalticGas partners as well as for the modeling of methane distribution and fluxes.

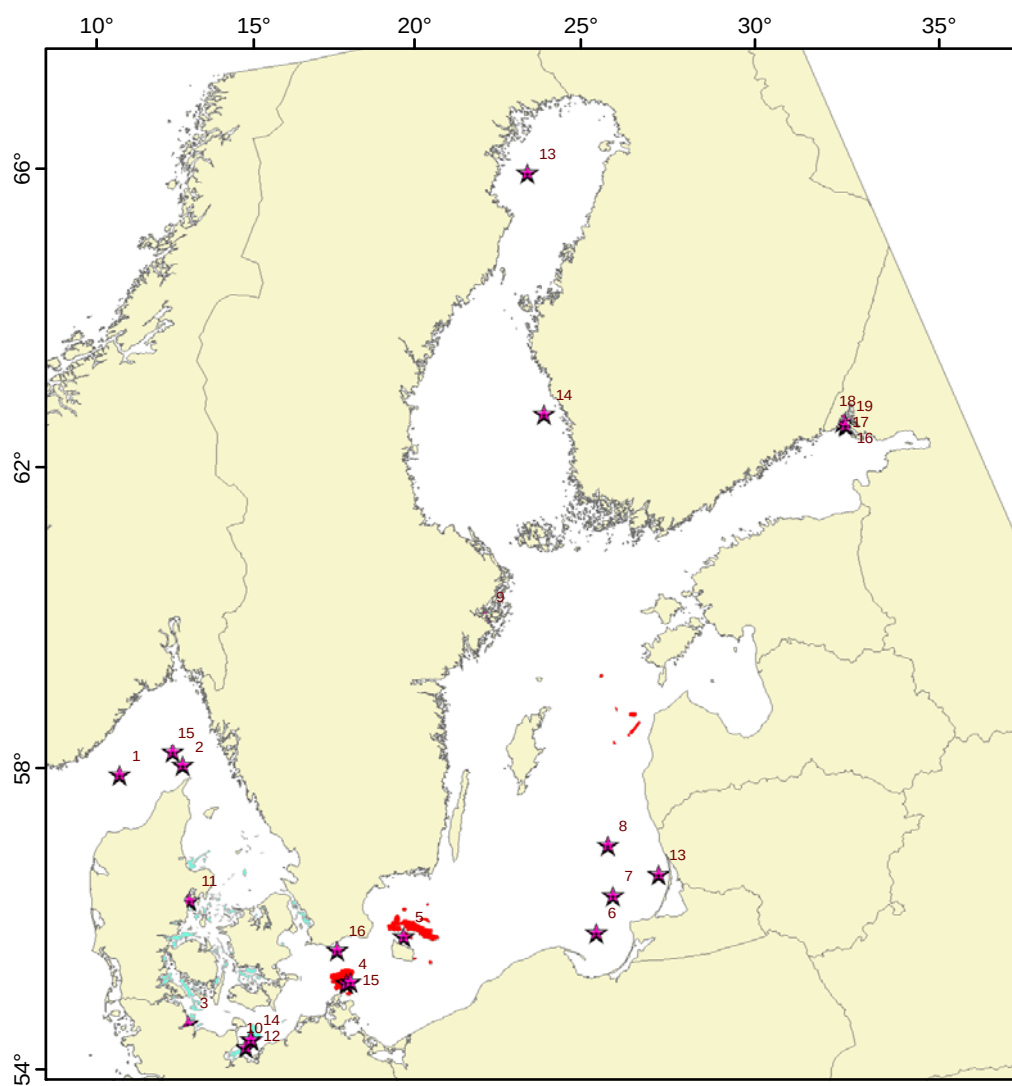


Figure 5: GIS map about the occurrence of pockmarks as well as areas where free gas is observed. These regions are considered as potential sites for methane fluxes.

WP 5: Modelling and data integration (Lead: DESUU)

Task 5.2 GIS Modelling (AWI): Regionalization and budgeting of methane cycle

In sediments of the Baltic Sea high concentrations of methane (CH_4) were observed by biogeochemical as well as geophysical investigations. Biogeochemical investigations are based on sediment and pore water sampling at selected sites and subsequent chemical and microbiological analysis. This provides very detailed information about the production and fate of biogenic methane, generated by microbial mediated processes, as well as the potential release of this greenhouse gas into the water column. Geophysical methods like shallow seismic surveys provides information about the spatial distribution of free gas (methane gas bubbles) in sediments.

Data derived by biogeochemical or geophysical studies provide very detailed information for selected sites as well as along of survey lines. Nevertheless, the spatial coverage of these studies is – due to the time consuming and costly techniques- rather sparse. For considerations of large scale spatial patterns and budgets, a combination of elaborated, site specific measurements with geodata about forcing factors which are available with sufficient spatial coverage, are required. This might support computations of budgets as well as identification of regions where high/low methane concentrations are expected.

For spatial modelling (Fig. 6, 7) forcing factors like the accumulation rate of particulate organic matter (POC), the POC-content, bottom water concentrations of e.g. sulfate and oxygen, bathymetry, slope, morphological units, bottom water temperature and current speed as well as indicators for methane formation like pockmarks were considered.

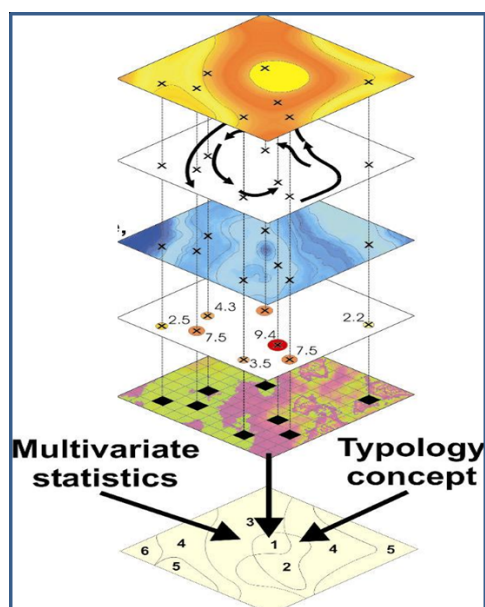


Figure 6: For spatial modeling, different information layers about sediment type, POC-content, mass accumulation rate etc. are combined within the GIS and multivariate statistical techniques are applied.

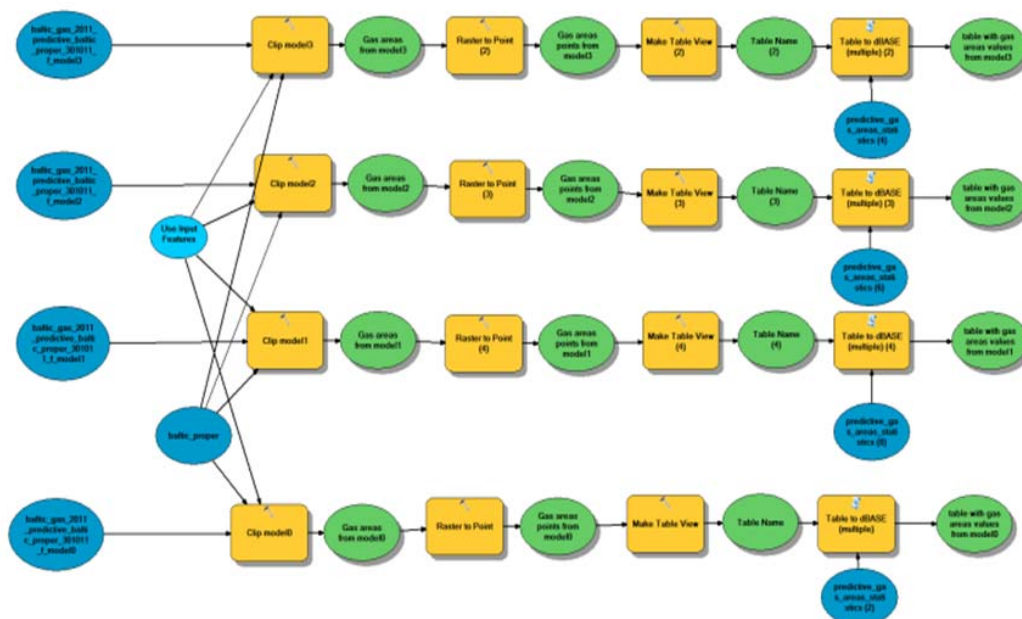


Figure 7: Example for a work flow (implemented in the ModelBuilder of the ArcGIS) applied for spatial modelling.

All data sets were projected and combined applying the Lambert azimuthal equal-area projection and similar grid size. By statistical analysis we compared former mentioned parameters for regions where free gas was observed with regions in the surrounding, where free gas was not observed (Fig. 8).

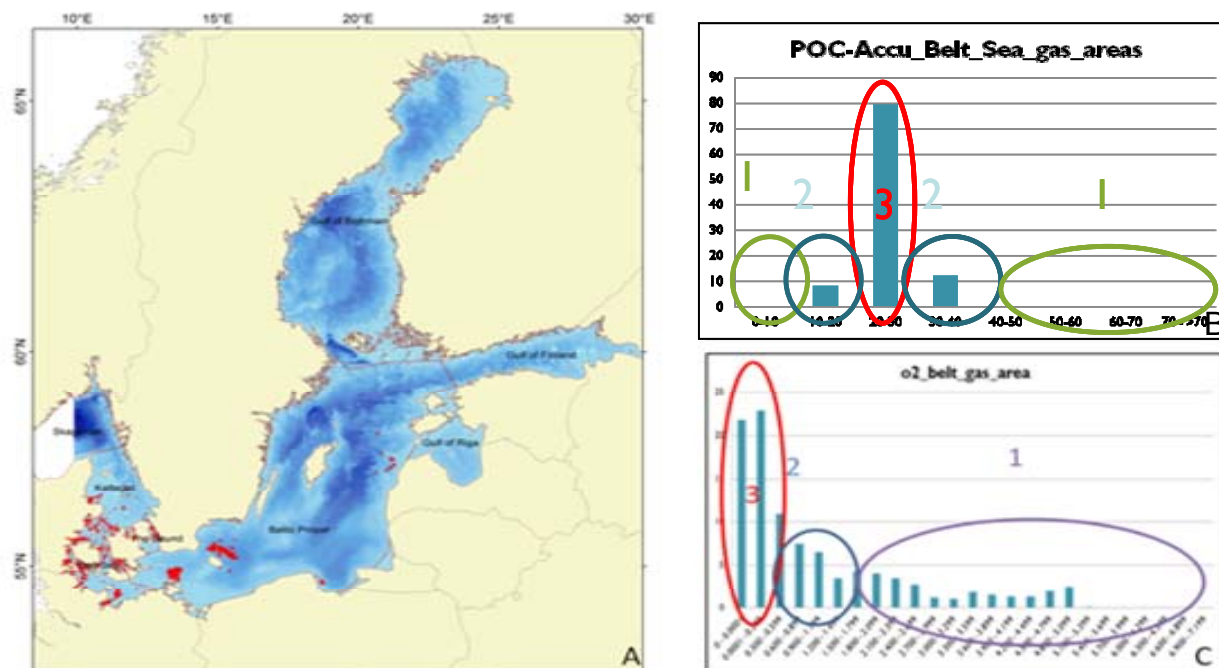


Figure 8: (A) Map of areas where free gas in surface sediments were observed (red polygons). For spatial analysis data about the accumulation rate of particulate organic matter (B) or oxygen distribution concentrations in bottom water (C) were considered. Based on the statistical analysis of forcing factors related to the formation of free gas in surface sediments weighting coefficients were derived.

The spatial modeling was applied for the sub-regions of the Baltic Sea. For each region, a set of factors was derived which are likely to contribute to the formation of free gas. These factors were iteratively improved and applied to compute predictive maps about the spatial distribution and the total area of free gas in sediments of the Baltic Sea (Fig. 9).

The match between known and predicted free gas areas was considerably improved during the course of the project. This is mainly due to the increased amount of geodata which were compiled and combined within GIS and new publications about e.g. mass accumulation rates. We consider the GIS-mapping of hot-spots as well as the computation of predictive maps as a step towards a hypothesis based approach. Such an approach could be used for identification of new survey areas as well as retrospective analysis. By this means regions where highest benefit, in terms of falsification as well as improvement, might be achieved.

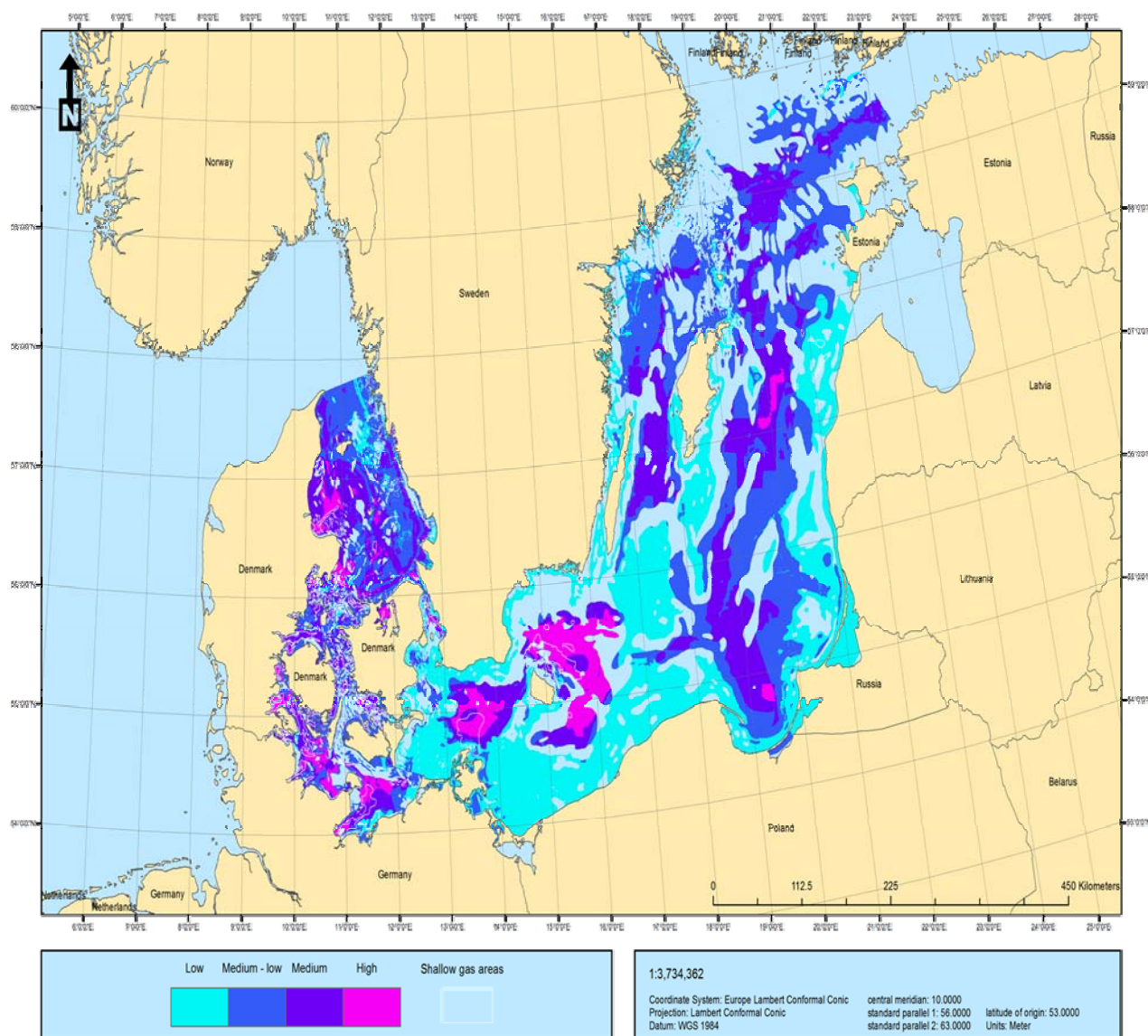


Figure 9: Prediction map about the occurrence of free methane gas in surface sediments of the Baltic Sea. Regions where a high probability for the occurrence of free gas are predicted are indicate by purple colored polygons.

Internet Map Server (IMS)

The geodata compiled within the Baltic Gas project - as well as former projects like METROL (EU) or MarGIS (Geotechnologien) - were integrated into an Internet Map Server (<http://gissrv5.awi.de/margis/NorthSea-BalticSea/>).

The IMS allows an interactive access to these geodata (Fig. 10).

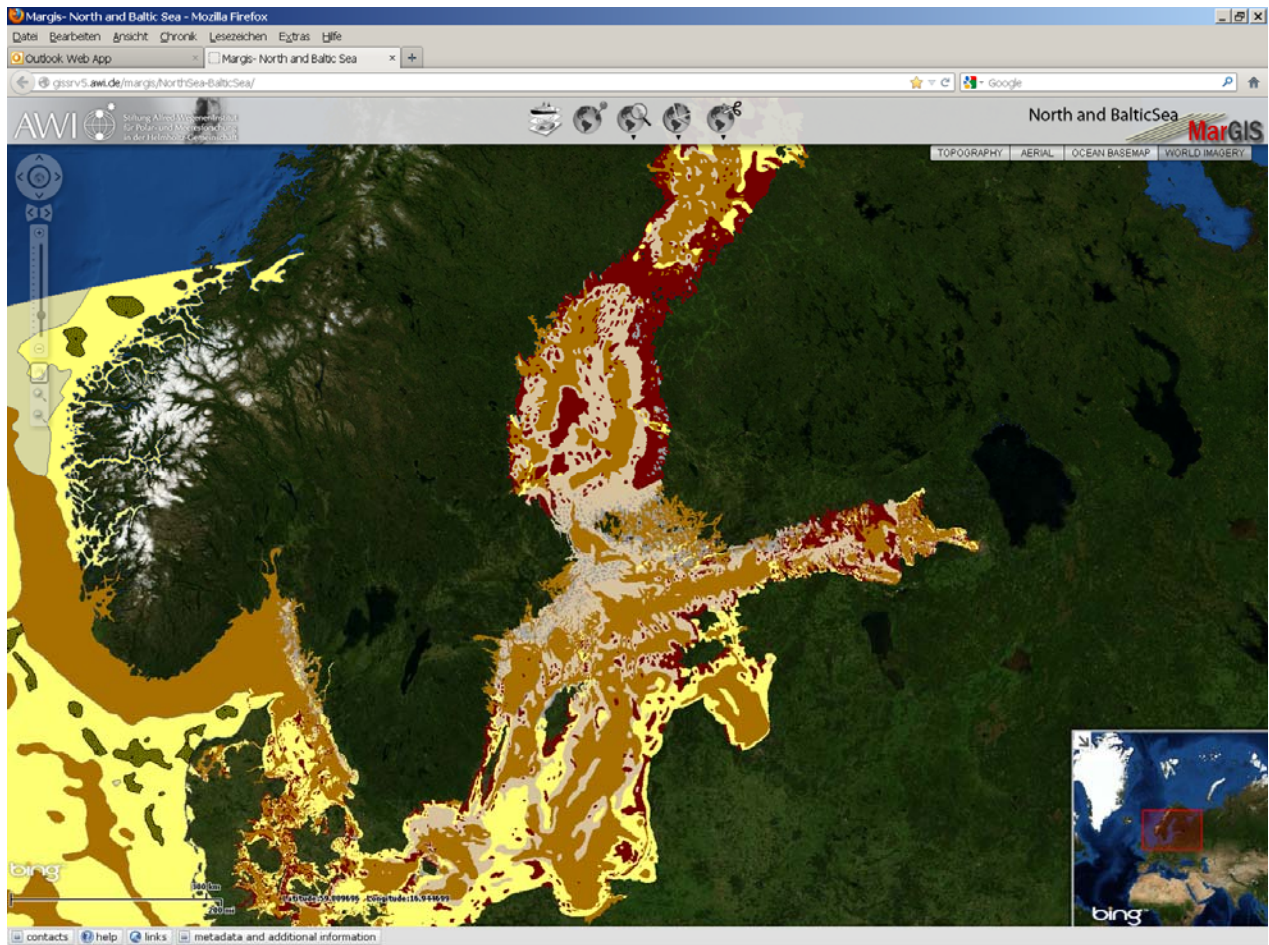


Figure 10: Screenshot of the internet map server (<http://gissrv5.awi.de/margis/NorthSea-BalticSea/>) which provides interactive access to the geodata compiled within Baltic Gas.

WP4: Biogeochemistry (MPI)

AWI Contribution Application of Membrane inlet mass spectrometry and underwater mass spectrometry (AWI)

Related to the work package 4 we contributed by (a) application of novel Underwater Mass Spectrometry (UWMS) as well as (b) in situ pore water sampling.

The Underwater Mass Spectrometer (Fig. 11) allows the in situ analysis of gases like CH_4 , CO_2 , N_2 or higher hydrocarbons (C_2^+) in water depths of up to 200m (Schlüter and Gentz, 2008). For this purpose a Membrane Inlet System (MIS) is applied. Within the MIS a tubular Polydimethylsiloxane (PDMS) membrane is installed. The membrane allows gas permeation from aqueous phase (at ambient hydrostatic pressure) through the PDMS membrane (0.69 mm ID) into the high-vacuum section of the mass spectrometer unit.

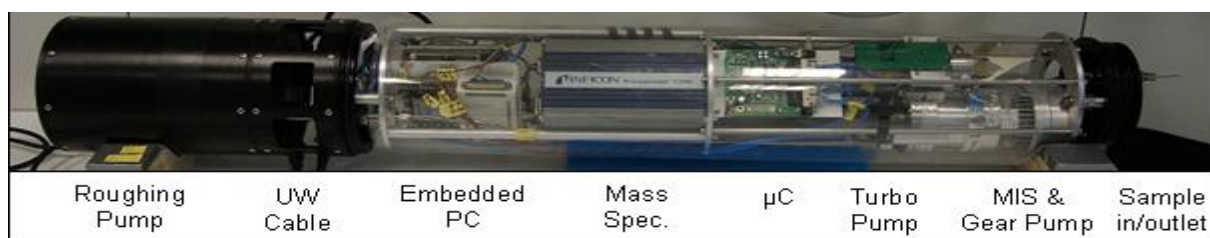


Figure 11: Underwater Mass Spectrometer for insitu analysis of gases in water depths of up to 200 m.

To improve the detection limit of the UWMS we developed a underwater cryo-trap system (Fig. 12)

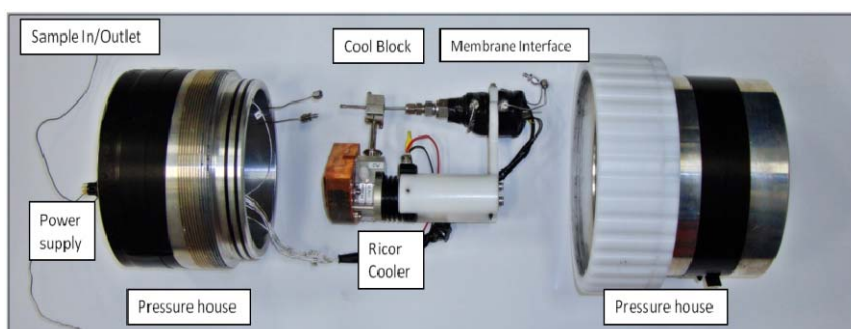


Figure 12: Underwater cryo-trap system (Gentz & Schlüter, 2012)

We applied the UWMS for measurements of benthic fluxes of CH_4 across the sediment water interface in Gdansk Bay or Askö, for example. Figure 13 provides an example for the increase of gas concentrations within a benthic chamber systems deployed at the sea-floor for about 5 hours.

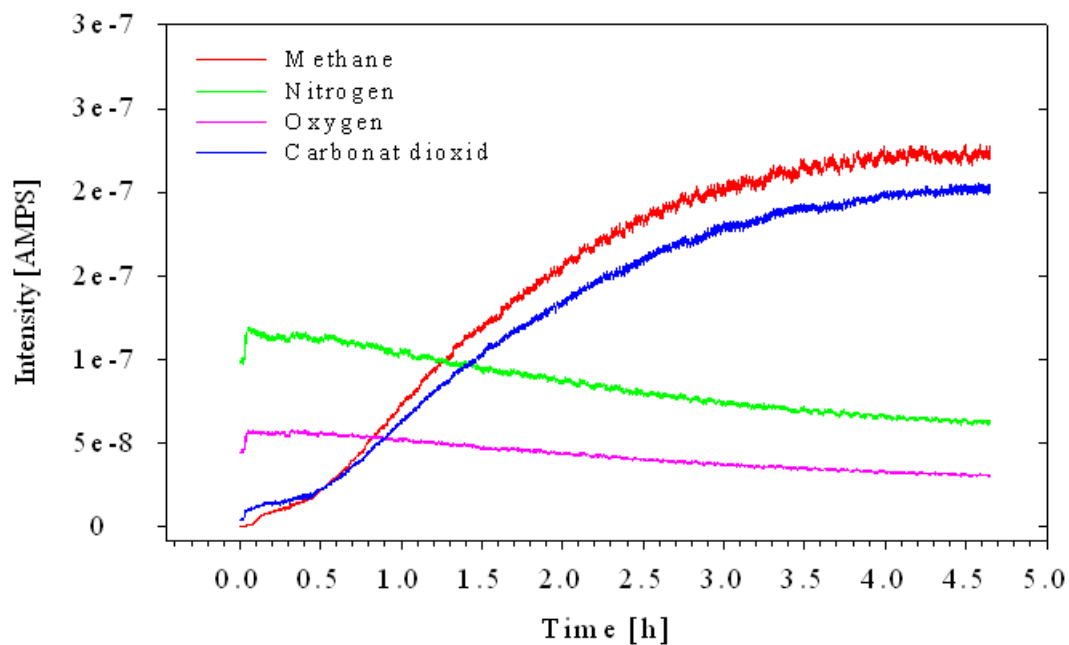


Figure 13: Increase of gases within a benthic chamber system measured by UWMS.

For in situ sampling of pore waters a deployment and sampling system was developed (Fig. 14). The system consists of pore water lances, equipped with Rhizon samplers, and an in situ peristaltic pump to retrieve and store the pore water samples.



Figure 14: in situ pore water sampling during a FS Merian cruise (Baltic Gas).

Compared to ex situ pore water sampling, biased by degassing of the sediment, in situ sampling allows an improved detection of the sulfate-methane-transition-zone as well as CH_4 etc. pore water profiles for gassy sediments.(Fig. 15).

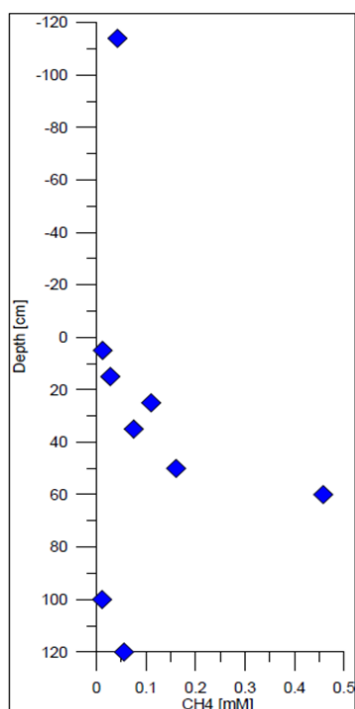


Figure 15: Example for a pore water profile derived from the in situ pore water sampler.

Literature

Gentz, T. and Schlüter, M. (2012) Underwater cryotrap-membrane inlet system (CT-MIS) for improved in situ analysis of gases *Limnology and Oceanography: Methods*, 10 , pp. 317-328. doi:10.4319/lom.2012.10.317.

Schlüter, M. and Gentz, T. (2008) Application of Membrane Inlet Mass Spectrometry for online and in situ analysis of methane in aquatic environments, *Journal of the American Society for Mass Spectrometry*, 19 (10), pp. 1395-1402. doi:10.1016/j.jasms.2008.07.021