WP 3.3 Deliverable: Detection and monitoring of methane ebullition

Authors:

Schneider v. Deimling, J.; Gülzow, W.; Ulyanova, M.; Klusek, Z.; Rehder, G.

Goal

Methane gas bubble emissions from the seafloor into the water column have scarcely been investigated in the Baltic Sea, even though large areas show significant amounts of very shallow gas hosted in the organic rich Holocene mud (Laier and Jensen, 2007; Endler et al., 2007, 2010). The extent of bubble-mediated methane transport originated at the seafloor and its potential contribution to the atmosphere remains unclear. Thus, direct evidence of free methane gas bubble ebullition into the water column as well as (indirect) indications of such gas seepages were pursued in WP 3.3 using hydroacoustic and geochemical methods.

Measurements and Monitoring

Methods

Hydroacoustics

Modern multibeam and traditional singlebeam hydroacoustic systems were used to map free gas bubbles in the water column (flares) and to identify gas seepage features including shallow gas hosted in the sediments, pockmarks, faults, and subsurface geological structures.

Beyond the conventional single beam approach (formerly used for free gas detection in the water column) next generation multibeam systems were operated for efficient remote sensing of bubbles by water column imaging (WCI).

The main goal of the multibeam studies was to identify gas seep localities in the Baltic Sea. We concentrated on the detection of gas bubble-mediated echoes in the water column (flares) in a similar way, as was performed earlier (Schneider von Deimling et al., 2007; Nikolowska et al., 2008) and moreover developed a new method (Schneider von Deimling and Papenberg, 2011a) for automated bubble detection. Special attention was given to suspicious bathymetric features such as pockmarks and elevated backscatter anomalies, which are often linked to methane seepage (Judd and Hovland, 2007).

Methane Measurements

For continuous measurement of methane concentration at the sea surface a new method was developed and presented in Gülzow et al. (2011a) using ships of opportunity. The system was installed on the cargo ship Finnmaid (Ferry Company Finnlines) in November 2009 as a complement to an existing system (Schneider et al., 1992). The ferry line commutes on a two to three day interval between Travemünde (Germany), Rostock (Germany), Gdynia (Poland) and Helsinki (Finland) and continuously measures parameters such as carbon dioxide, oxygen, temperature, salinity, chlorophyll a, fluorescence, and now methane in the surface water of the Baltic Sea (Fig. 1; Gülzow et al., 2011b). Since the installation of the system, more than 300 lines could be collected.

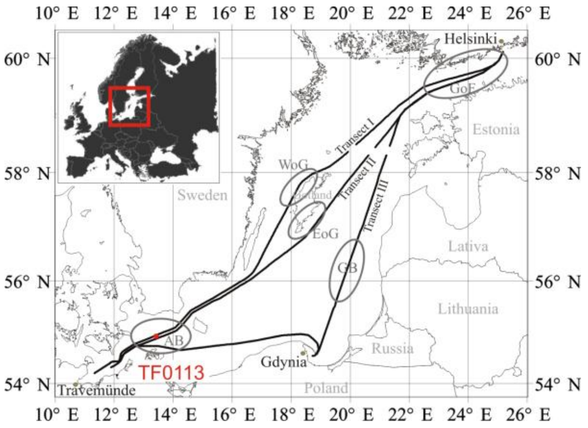


Figure 1: The ferry line crosses the Baltic Sea via three transects and connects Travemünde (Germany) with Helsinki (Finland) and Gdynia (Poland) in an interval of 2 to 3 days. Transect I passes the Arkona Basin (AB), Western of Gotland (WoG) and the Gulf of Finland (GoF). Transect II records the same route but Eastern of Gotland (EoG). Transect III passes Gdynia and the Gotland Basin (GB). Station TF0113 is part of a regular monitoring program of the Institute for Baltic Research Warnemünde.

Additional discrete water sampling and methane concentration measurements have been conducted during the Bonus program BALTIC GAS objecting the water column of the Baltic Sea (Fig. 2). At more than 230 CTD/Rosette stations, water samples were collected for vertical profiling of methane in the water column from 2008 to 2011. The water samples were generally analyzed for methane using a modification of the vacuum degassing method described by Lammers and Suess (1994).

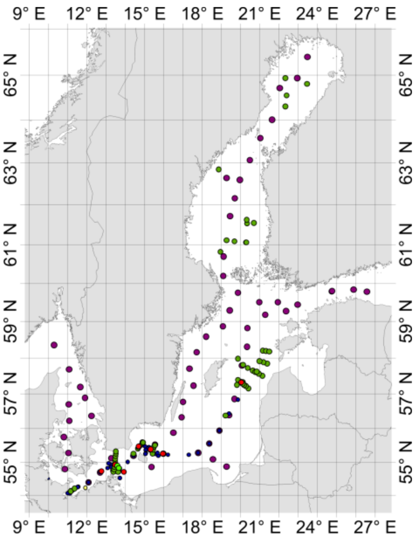


Figure 2: The map shows sampling stations taken on a variety of cruises accomplished in 2008 to 2010. Purple dots: July 2008 (Merian 08, Schmale et al., 2010); Yellow dots: January 2009 (Penk 0903); Blue dots: December 2009 (Poseidon 392); Green dots: August 2010 (Merian 16/1); Red dots: monitoring starting in 2009.

Baseline assessment

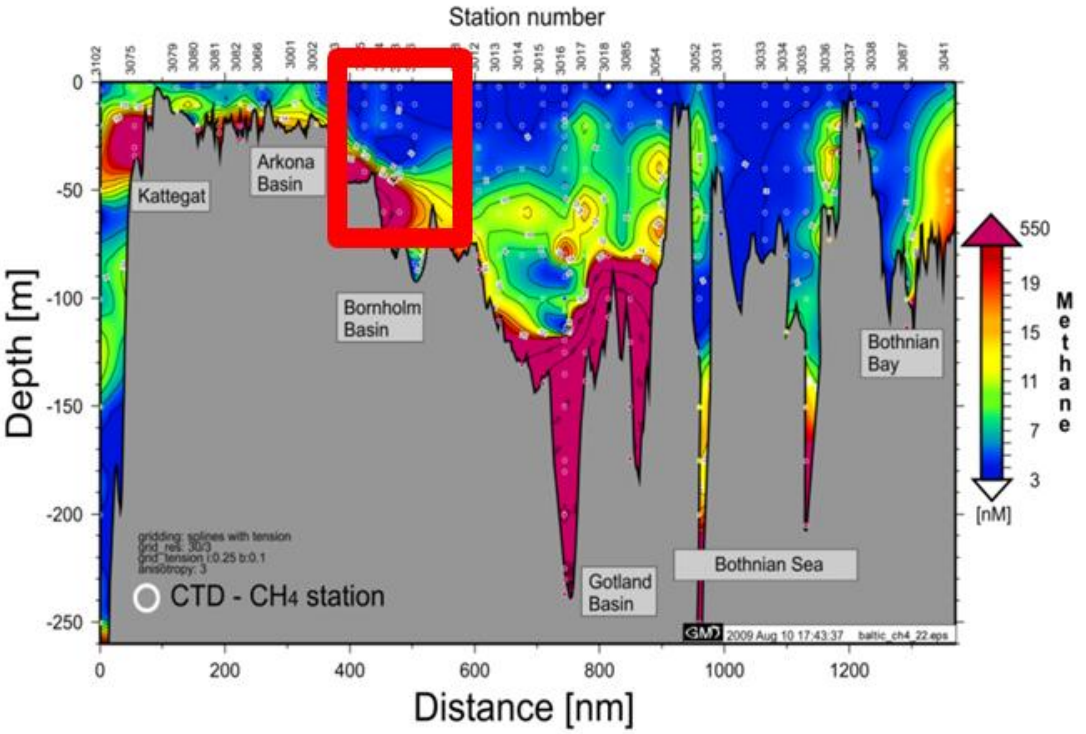


Figure 3: Methane distribution in the Baltic Sea after Schmale et al. (2010). The red rectangle clearly highlights the distinct transition between high methane concentrations in the salty deep water and low methane concentration in the shallower/fresher water.

At the beginning of the project the baseline methane concentrations of the Baltic Sea were assessed by Schmale et al. (2010). A strong correlation between the vertical density stratification, the distribution of oxygen, hydrogen sulfide, and methane has been identified (Fig. 3). A widespread release of methane from the seafloor is indicated by increasing methane concentration with water depth. The deep basins in the central Baltic Sea show the strongest methane enrichments in stagnant anoxic water bodies (max. 1086 nM and 504 nM, respectively), with a pronounced decrease towards the pelagic redoxcline and slightly elevated surface water concentrations (saturation values of 206% and 120%, respectively). Elevated bulk surface methane concentration point to the fact, that the Baltic Sea can be considered as a net source of methane to the atmosphere. However, geochemical pattern of bubble-mediated transport to the atmosphere (Schneider et al., 2011b) could not be identified in this primary study.

Results

Direct evidence of gas bubbles

Much work has been conducted in the westerly basins of the Baltic Sea (Mecklenburg Bay, Bornholm and Akona basins). Those areas host gassy sediments close to the seabed in the Holocene mud (Laier and Jensen, 2007; Fiedler and Wever; 1997; Endler 2007). Some natural flares could be observed during surveys and station work (Tóth et al., 2010). Moreover, gas ebullitions were triggered at various stations by coring. At such an artificially triggered seep site the WCI multibeam system sensibility was tested several times in regard to detection and identification of acoustic scatterers in the water column. Individual gas bubbles rising from the 24 m deep seafloor clearly emerged in the acoustic images and rise velocities could be determined. A sophisticated processing scheme was developed to identify those rising gas bubbles in the hydroacoustic data (Schneider von Deimling and Papenberg, 2011a). The application of this processing scheme to our field data gives impressive results with respect to unambiguous bubble detection and remote bubble rise velocimetry. The method can identify and exclude the main driver for misinterpretations, i.e. fish-mediated echoes. Even though image-based cross-correlation techniques are well known in the field of fluid mechanics for high resolution and non-invasive current flow field analysis, this technique was never applied in the proposed sense for an acoustic bubble detector.

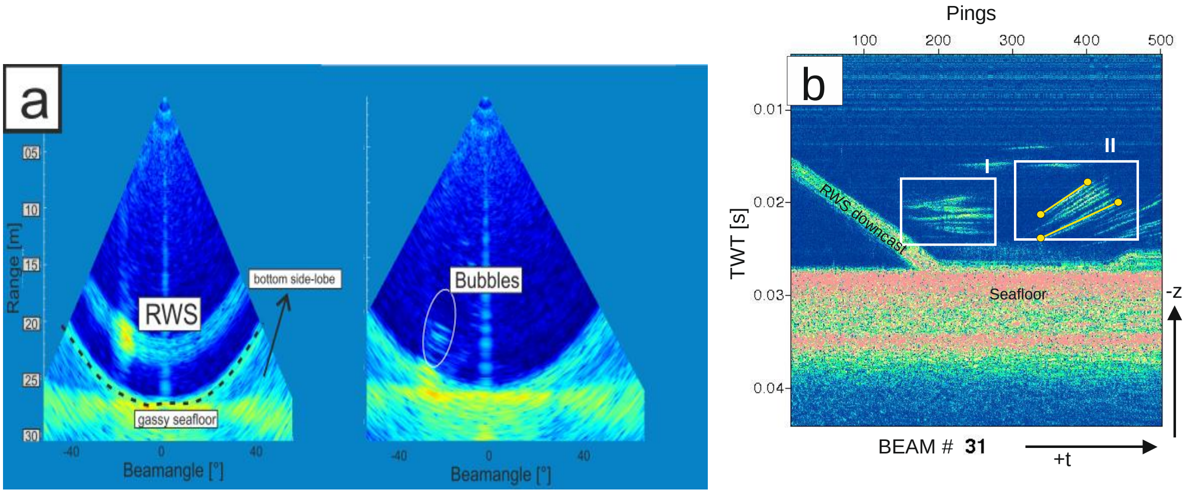


Figure 4: adapted from Schneider von Deimling and Papenberg (2011a): (a) Successive echo-image frames recorded during water column imaging with SB3050 showing CTD-Rosette downcast, contact with gassy sediments, and induced bubble escape into the water column. (b) "Beam-Slice" presentation with the x axis representing the ping times in seconds where the y-axis is two-way-travel time [s]. Horizontal features represent non-buoyant microbubbles(I) where to the right some ascending bubbles occur (II).

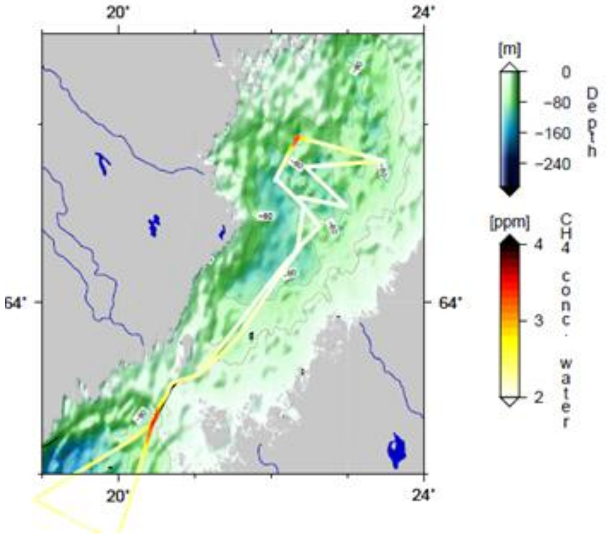


Figure 5: Methane concentration of the surface water measured during MSM16 with the equilibrator system. Only data gathered at ship speed larger than 4 knots are presented.

In the northwesterly part of the Bothnian Sea an elevated surface methane concentration was measured (Fig. 5) above relatively deep water (~80m). Subsequent flare imaging revealed the only persistent flare site during our studies and single gas bubbles could be tracked via the primary 18kHz signal of Parasound. Bubbles were released from the 84 m deep seafloor and rise velocities between 6 and 15cm/s were derived from the echo image while the vessel was resting (Fig. 6). Their size was estimated from the rise – radius relation of gas bubbles after Clift et al. (1978) to range between 0.3-0.5mm, which is considerably small.

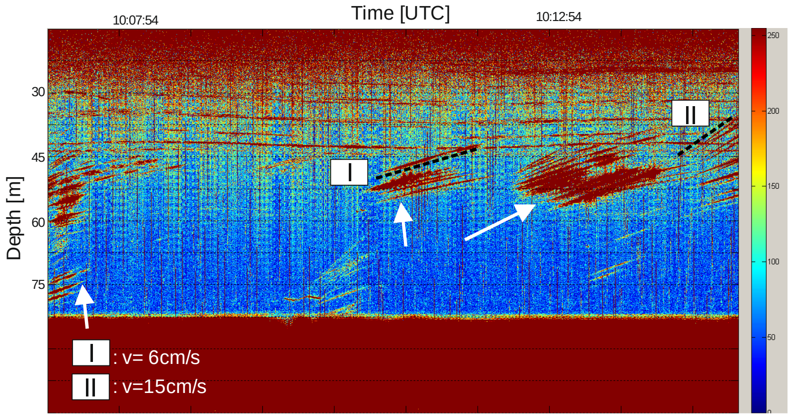


Figure 6: Rising gas bubbles acoustically detected using the ATLAS PARASOUND (PHF, 18kHz) subbottom profiler; Bothnian Sea; 64°56.0‘ N, 22°20.7‘E; (Rehder et al., 2010).

To constrain a first flux estimate the succession rate was depicted from the echograms by measurement of vertical distance between each echo bubble trace to be [0.3 – 2.6]m distant apart. Assuming a quick ebulltion rate of 10 seconds of 0.4mm radius 100% methane gas bubbles results in an insitu (12°C, 80m water depth) flux of 38g CH_4 per year. Compared to other seep localities (Judd, 2004) this represents a minor gas seep flux.

Potential CH_4 seepage sites

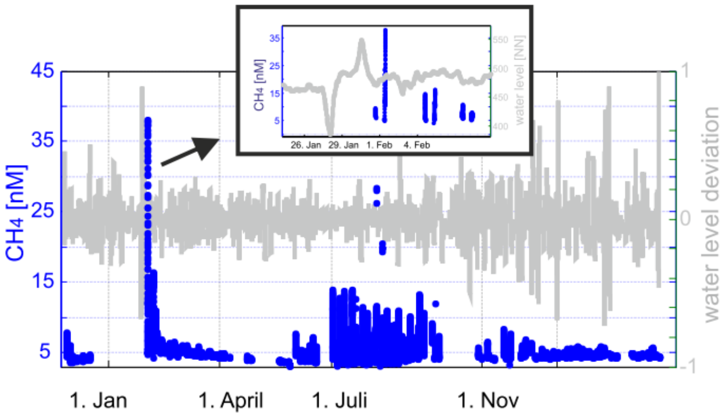


Figure 7: Results from a three month survey in the Arkona Basin in 2010 showing sea surface methane concentration s(blue dots) and sea level data (grey line) measured at station Sassnitz (Germany).

In February 2nd, 4th and 5th 2010, an extraordinary methane concentrations (collected during the Ferrybox program) could be measured in the surface water of the Arkona Basin rising up to 38 nM, 15 nM and 16.5 nM respectively (Fig. 7, Gülzow et al., 2011b). This exceptional event of high methane concentrations in the surface water was accompanied by a longer period of strong wind and a shift of the sea water level of almost 1.5m within a day. As a first hypothesis a strong pressure release might have caused degassing/expansion of the shallow gas methane deposits, that occur close to the seafloor in this area (Thiessen et al., 2006). Alternatively, this extraordinary peak was produced by mixing processes bringing deeper and methane-rich water to the sea surface.

Pockmarks

Results from the BALTIC GAS research cruises exposed areas of shallow gas in the Mecklenburg Bay very close to the seafloor (<2mbsf). Corresponding bathymetric measurements revealed an elongated 250 m large depression of approximately 20 cm depth (Fig. 8). Small pockmarks plot within and in the vicinity of this 250 m depression. Simultaneous profiling using the EA 600 38 kHz showed a good correlation between the depression and shallow gas pockets. A subsequent drift survey over the pockmark showed only one flare (Tóth et al., 2010). No further gas ebullition activities were found in the water column.

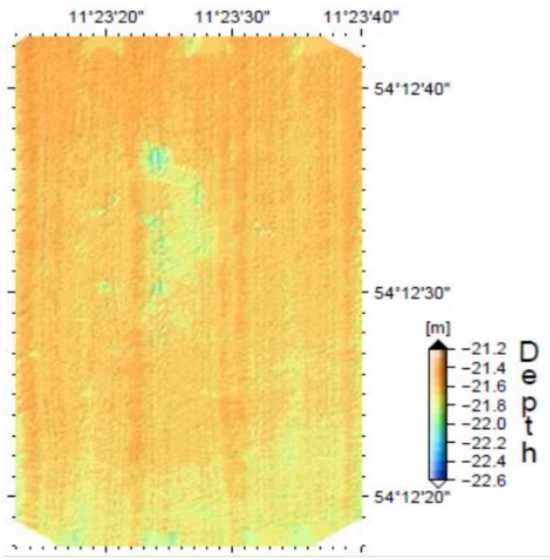


Figure 8: Gridded bathymetry from EM1002 showing pockmark structure.

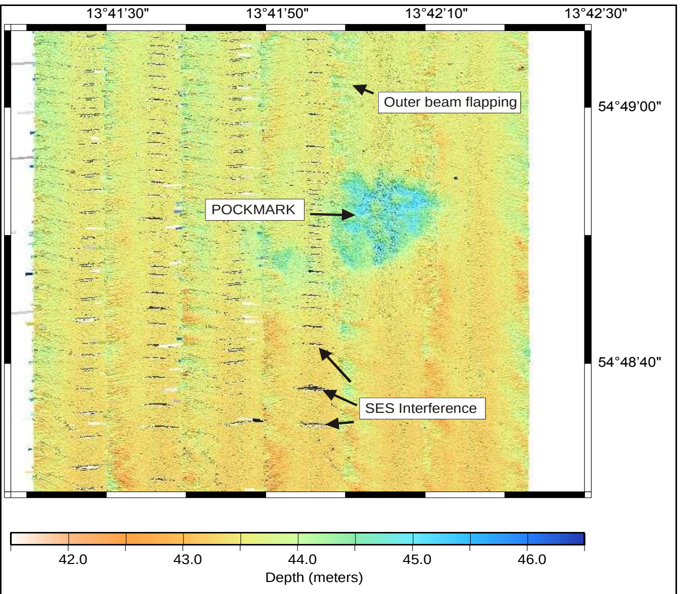


Figure 9: Raw data bathymetry plot showing a pockmark.

An approximately 2 meters deep pockmark of similar extension was identified in the Arkona Basin. Potential correlation of these pockmarks to methane discharge as previously found in the Baltic Sea (Schlüter et al., 2004) represents a future task.

Previous single-beam surveys in the Stolpe Foredelta area indicated pockmark-like features to occur. Thus, combined subbottom and multibeam surveys were conducted to gather their spatial extent. It could be shown, that the depressions formerly found in singlebeam data actually derive from crossing several channels striking SW-NE (Fig. 10, up to 5 m deep and 150m wide). The origin of those features remains unknown. The respective subbottom profiles indicate a succession of the channels into deeper strata. Moreover the bathymetry resolves distinct criss-crossing pattern in the channel area, which are interpreted as features caused by fishery trawling activities.

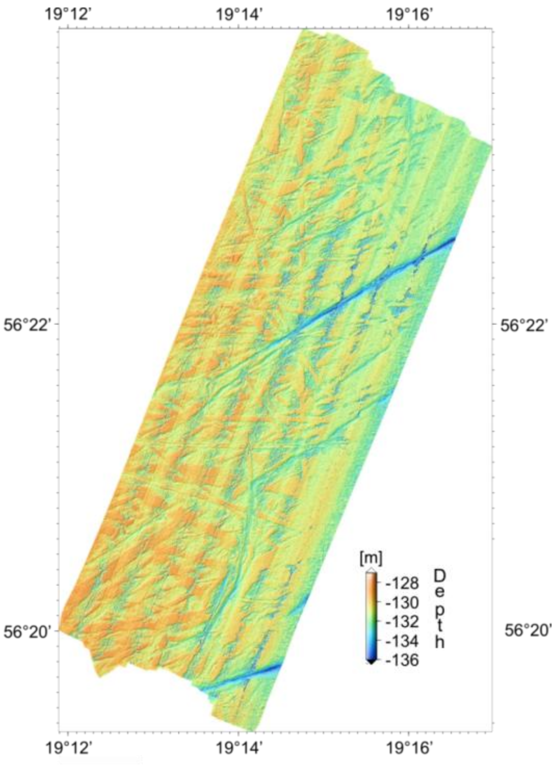
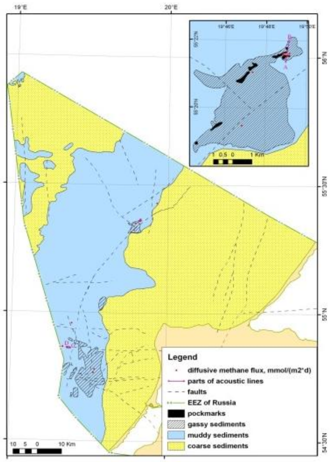


Figure 10: Gridded and color coded bathymetric chart recorded with EM1002 in the Stolpe Foredelta area.

Detailed acoustical profiling during several cruises made it possible to specify the location of the pockmarks and shallow gas on the northeastern slope of the Gdansk Deep (Pimenov et al., 2010). Seven pockmarks of various morphology, typically elongated from the southwest to the northeast, were revealed (Fig. 11, 12).



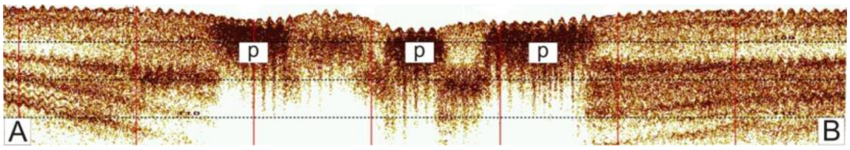
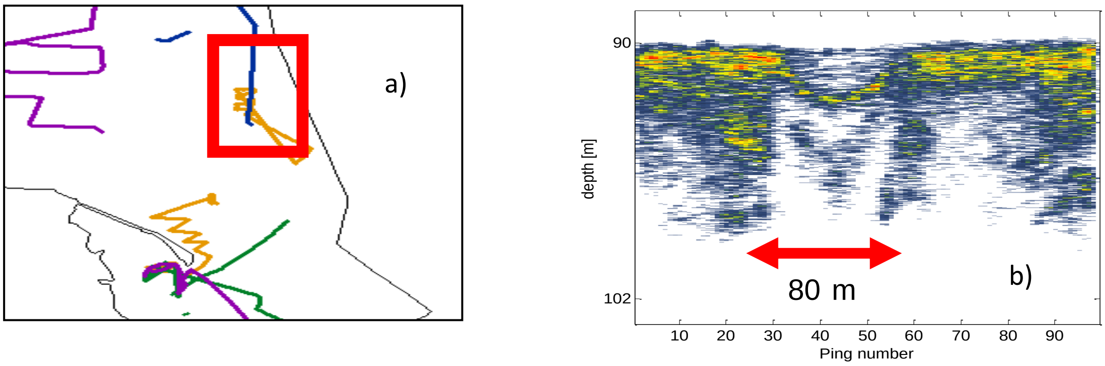


Figure 12: A part of echogram with group of pockmarks cross-section.

Figure 11: Spatial distribution of gassy sediments in Russian sector of the south-eastern Baltic.

Even more patches of higher gas content in sediments in the Gulf of Gdansk have been classified as pockmarks. The employed chirp echosounder together with classical echosounders provided good quality results in detection of gassy structures such as pockmarks and various types of sediment structure inhomogeneity - probably consequence of the free gas presence.

Many sea bottom structures classified as pockmarks were detected on the Gdansk Deep (eastern part of the Polish Economic Zone) and all of them occur in the Holocene unit. One example of these structures is shown in Fig. 13. Small gas pockets of only a few meters horizontal extension were also observed with the 12 kHz echosounder to the north from the Hel Peninsula and with the 38 kHz echosounder on the Slupsk Furrow area. Similar categorization was obtained with a chirp echosounder 40-60 kHz. Cross-sections values of identified pockmarks were determined along line transects and their histograms and statistical distributions were calculated for different sediment provinces.



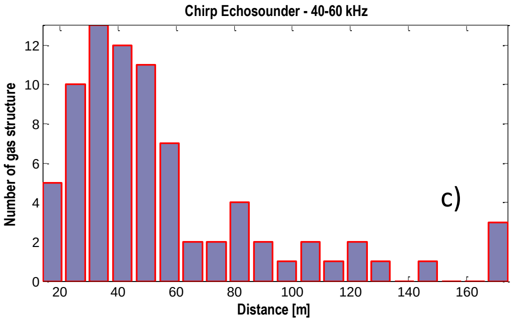


Fig.13 (a) The pockmark area inside of the red square (b) Example of an acoustic image of the pockmark's cross-section (the depth in the sediment is given approximately) obtained using the chirp echosounder, in the Gdansk Deep area.
(c) The pockmark cross-section statistics in the area.

Subbottom gas mapping by multibeam

Prior to this project it was predicted that deep water multibeam systems might be ideally suited for mapping shallow gas in Baltic Sea Holocene mud. This approach was very successful and Schneider et al. (2010) showed the 2D distribution of shallow gas. EM120 and Parasound were operated in parallel and shallow gas zones clearly emerge in both datasets showing free gas between 1.5 and 4.5 mbsf (Fig. 14). Obviously, the 12 kHz signal penetrates the soft sediment at least 4.5 m over the entire swath width. At other localities penetration and respective bottom mis-detection was even 10 mbsf. Obviously the EM120 bathymetry rather mimics the depth of the shallow gas front than presenting the seafloor. The data demonstrate that low frequency multibeam is a feasible tool for area wide subsurface shallow gas mapping in soft sediments.

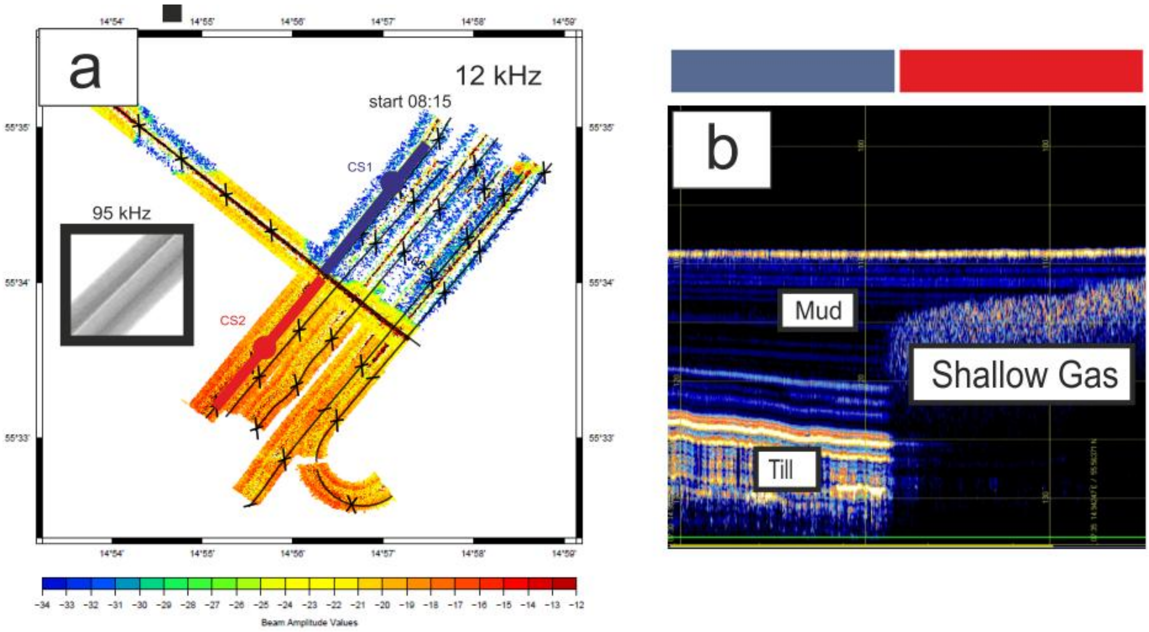


Figure 14: The blue and red line indicate the sediment settings, i.e. Holocene 'mud with' and 'mud without' free gas (a) Backscatter amplitude chart of EM120. The zone between bluish and yellowish colors indicates the transition between 'mud without' and 'mud with' free gas. The inlet presents amplitude backscatter data gathered with a 95 kHz system not showing any transition (b) PARASOUND subbottom data recorded during NE to SW profile within (a) starting at 08:15 UTC. The transition zone plots exactly at the same time as seen in the multibeam data (a) (Schneider et al., 2010).

Conclusion

Innovative Methods for continuous methane gas measurements (Gülzow et al., 2011a) and remote seep bubble detection (Schneider von Deimling and Papenberg, 2011a) have been successfully developed during BALTIC GAS. Various acoustic single- and multibeam systems were operated and the respective data demonstrate high sensitivity in terms of remote imaging of free gas; even single gas bubbles could be sensed within large sample volumes. Nevertheless, only two offshore gas ebullition sites in 'deeper' water (>70m) were identified (Gulf of Gdansk, Bothnian Bay). Further indications of seepage emerge from high resolution multibeam data in the form of pockmarks. However, those structures may also form from fluid flow, e.g. groundwater. The origin of the newly discovered pockmarks remains unclear.

First results from the continuous surface methane measurements point to the fact, that gas seepage in the Baltic Sea is rather an erratic phenomena triggered by water level changes. For the future, a permanent gas seepage monitoring study could be used to constrain potential transient methane gas bubble discharge events.

A baseline study in the very beginning of BALTIC GAS (Schmale et al., 2010) as well as ongoing methane measurements shed light into the distribution of methane in the water column of the Baltic Sea. Even though areas of high methane concentrations exist, no clear indication for gas bubble mediated methane transport from the deeper seafloor into the water column and atmosphere are visible from these data.

Close to the coast several gas ebullition sites were identified accompanied by pockmark structures. At deeper water only rare direct evidence for free gas ebullition was found. Thus natural gas emissions off the coasts of the Baltic Sea are considered having a minor importance in regard to the overall methane fluxes from the seafloor into the water column and atmosphere. One reason for the low gas seepage activity could be the geological setting of the Holocene mud. Even though this layer holds large amounts of organic matter and was often found to host free methane gas, no caprock nor trap structures exist. Thus no focused gas flow can establish to sustain permanent seepage.

References

Clift, R., J. R. Grace, and M. E. Weber (1978), *Bubbles, Drops, Particles*, Academic Press, New York.

Endler, R., J. Harff, S. Kotov, and G. Nickel (2007), Acoustic stratigraphy of the Stolpe Channel Fore Delta in the Baltic Proper, Poster, Rostock.

Endler, R., J. Wunderlich, and J. Schneider von Deimling (2010), Acoustic imaging of shallow gas in Baltic Sea sediments, International Conference HYDRO, Warnemünde.

Fiedler, H. M., and T. F. Wever (1997), Kartierung gashaltiger Sedimente in der Mecklenburger Bucht, FWG Report, Kiel, Germany.

Gülzow, W., G. Rehder, B. Schneider, J. Schneider v. Deimling, and B. Sadkowiak (2011a), A new method for continuous measurement of methane and carbon dioxide in surface waters of the Baltic Sea using off-axis integrated cavity output spectroscopy (ICOS), *Limnology Oceanography Methods*.

Gülzow W., Schneider von Deimling, J., Rehder G., Schneider B. (2011b), Seasonal and spatial distribution of methane in the surface water of the Baltic Sea, *BSSC*, St. Petersburg.

Judd, A. G. (2004), Natural seabed gas seeps as sources of atmospheric methane, *Environmental Geology, 46*, 988–996.

Judd, A. G., and M. Hovland (2007), *Seabed Fluid Flow*, Cambridge University Press, New York.

Laier, T., and J. Jensen (2007), Shallow gas depth-contour map of the Skagerrak-western Baltic Sea region, *GeoMarine Letters, 27*(2), 127-141.

Lammers, S., and E. Suess (1994), An improved head-space analysis method for methane in seawater, *Mar. Chem.*, *47*, 115-125.

Nikolovska, A., H. Sahling, and G. Bohrmann (2008), Hydroacoustic methodology for detection, localization, and quantification of gas bubbles rising from the seafloor at gas seeps from the eastern Black Sea, *Geochem. Geophys. Geosyst.*, *9*(Q10010), 1-13, doi:10.1029/2008GC002118.

Pimenov, N., M. Ulyanova, T. Kanapatsky, E. Veslopolova, P. Sigalevich, and V. Sivkov, (2010) Microbially mediated methane and sulfur cycling in pockmark sediments of the Gdansk Basin, Baltic Sea, *Geo-Marine Letters*, *30*(3), 439-448, doi:10.1007/s00367-010-0200-4.

Rehder, G. J., Fossing, H., Lapham, L., Endler, R., Spiess, V., Bruchert, V., Nguyen, T., Gülzow, W., Schneider von Deimling, J., Conley, D. J., and Jorgensen, B. (2010), Methane fluxes and their controlling processes in the Baltic Sea, *AGU*, San Francisco.

Schlüter, M., E. J. Sauter, C. E. Andersen, H. Dahlgaard, and P. R. Dando (2004), Spatial distribution and budget for submarine groundwater discharge in Eckernförde Bay (Western Baltic Sea), *Limnol. Oceanogr.*, *49*, 157-167.

Schmale, O., Schneider v. Deimling, J., Gülzow, W., Nausch, G., Waniek, J. and Rehder, G. J. (2010), The distribution of methane in the water column of the Baltic Sea, *GRL*.

Schneider, B., K. Kremling, and J. C. Duinker (1992), CO2 partial pressure in Northeast Atlantic and adjacent shelf waters: Processes and seasonal variability, *Journal of Marine Systems*, *3*(6), 453-463, doi:10.1016/0924-7963(92)90016-2.

Schneider von Deimling, J., J. Brockhoff, and J. Greinert (2007), Flare imaging with multibeam sonar systems: Data processing for seep bubble detection, *doi:10.1029/2007GC001577 Geochem., Geophys., Geosyst. (G3, g-cubed.org)*, *8*(6), 1-7.

Schneider v. Deimling, J., Weinrebe, W., Bürk, D., Thot, Z., Endler, R., Fossing, H., Spiess, V., and Rehder, G. (Ed.) (2010), Subbottom mapping of shallow gas in the Baltic Sea using medium to low frequency multibeam sounders, *AGU*, San Francisco.

Schneider von Deimling, J., and C. Papenberg (2011a), Technical Note: Detection of gas bubble leakage via correlation of water column multibeam images, *Ocean Sci. Discuss.*, *8*(4), 1757-1775, doi:10.5194/osd-8-1757-2011. [online] Available from: http://www.ocean-sci-discuss.net/8/1757/2011/

Schneider von Deimling, J., G. Rehder, J. Greinert, D. McGinnis, A. Boetius, and P. Linke (2011b), Quantification of seep-related methane gas emissions at Tommeliten, North Sea., *Continental Shelf Research*, *31*, 867-878, doi:10.1016/j.csr.2011.02.012.

Thiessen, O., M. Schmidt, F. Theilen, M. Schmitt, and G. Klein (2006), Methane formation and distribution of acoustic turbidity in organic-rich surface sediments in the Arkona Basin, Baltic Sea, *Continental Shelf Research*, *26*(19), 2469-2483, doi:10.1016/j.csr.2006.07.020.

Tóth, Z., Schneider von Deimling, J., and Spieß, V. (2010), Distribution of shallow gas accumulations in the sediments of the Mecklenburg Bay, Baltic Sea; based on multi-frequency seismo-acoustic mapping., Int. Conf. Poster, 26-27th of March 2010, *Mátrafüred*, Hungary (www.isza.hu).