Geochemical and acoustic evidence for the occurrence of methane in sediments of the Polish sector of the southern Baltic Sea*

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Abstract

This paper presents the results of geochemical and acoustic investigations of sediments in the Polish sector of the southern Baltic Sea. Its objective was to

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indicate areas of gas bubble formation and the occurrence of methane. Over 3000 nautical miles of transects were recorded using a variety of hydroacoustic instruments, and five coring points were selected for further analyses of pore waters (CH_4, SO_4^{2-}, H_2S, NH_4^+, total alkalinity) and sediments (grain size distribution, C_{org}, N_{tot}, LOI and WC). Gas turned out to be present at shallow depths in different forms such as recent and buried pockmarks, and gas-saturated sediments (including gas pockets and seepages). It was found that methane was widespread in the sediments of the study area, both in the surface sediments, e.g. in the vicinity of the Hel Peninsula or in the central Gulf of Gdańsk, and in deeper sediment layers, e.g. in the Gdańsk Deep and the Słupsk Furrow. Chemical analysis showed that as a result of the rapid decomposition of organic matter, sulphates were depleted in the top 20 cm layer of sediments and that methane was produced at relatively shallow depths (in some areas even at depths of 20–30 cm bsf) compared to other regions of the Baltic, reaching concentrations of > 6 mmol l^{-1} in the 30–40 cm layer below the sediment surface. The sulphate-methane transition zone (SMTZ) was 4–37 cm thick and was situated in the uppermost 50 cm of the sediments.

1. Introduction

The occurrence of methane in the marine sediments of shallow seas is closely associated with organic matter decomposition and is governed by various biological and geochemical processes (Claypool & Kaplan 1974, Davis 1992, Reeburgh 1996). The organic-rich sediments of coastal regions play an important role in the global methane cycle, which is important in the context of the greenhouse effect and global warming.

The southern Baltic Sea receives a large input of organic matter, mainly due to the constant supply from the Polish Rivers Vistula and Oder/Odra (Łysiak-Pastuszak et al. 2004), as well as intensive primary production in the water column during the warm months (Witek et al. 1997), as demonstrated by frequent algal blooms. Seasonal changes of water temperature and salinity, variable weather conditions, freshwater runoff and limited exchange with ocean waters (Brink & Robinson 2005) give rise to a distinct stratification in the deeper parts of the southern Baltic, which, together with the large supply of organic matter, result in seasonally occurring hypoxic or even anoxic conditions in the near-bottom waters (Łysiak-Pastuszak & Drgas 2004, Hansson et al. 2011). In view of this, an investigation into the extent to which methane occurs in the marine sediments of this region is called for.

Methane can be produced by non-biological thermogenic processes deep in the sea bed or by microbial organic matter decomposition in the muddy sediments of coastal productive environments (Barnes & Goldberg 1976, Claypool & Kvenvolden 1983). During the mineralization process in organic-rich sediments, electron acceptors (O_2, NO_3^-, Fe^{3+}, Mn^{4+}, SO_4^{2-}) are successively depleted. Once sulphates are no longer available, methane

starts to form as a result of organic matter degradation. Distribution of methane within the sediments is controlled by its oxidation processes, gas bubble formation and transport to the near-bottom water (Martens et al. 1998). Anaerobic oxidation of methane (AOM) ($CH_4 + SO_4^{2-} \Rightarrow HCO_3^- + HS^- + H_2O$), mediated by anaerobic methanotrophic archea (ANME) and sulphate-reducing bacteria (SRB) (Zehnder & Brock 1980, Hoehler et al. 1994), plays an important role in controlling methane emission from the sea bottom (Reeburgh 1976, Boetius et al. 2000). The sediment layer where AOM occurs and both sulphate and methane are present is called the sulphate-methane transition zone (SMTZ). This zone acts as a barrier preventing methane diffusion to the overlying water and then to the atmosphere. It has been estimated that in some areas some 90% of the diffusing methane is consumed within the SMTZ by AOM and never reaches the atmosphere (Kiene 1991, Treude 2003). The layer below SMTZ is where methane formation occurs through CO_2 reduction (dominant in marine environments) or acetate fermentation (Martens & Berner 1974, Whiticar et al. 1986).

Methane in marine sediments can either be dissolved in pore waters or – in the case when the in situ saturation is exceeded – exist as a free gas (Fleischer et al. 2001). The saturation level is controlled by pressure, temperature and salinity (Yamamoto et al. 1976). Gas bubbles in marine sediments, due to their significant influence on the acousto-mechanical properties of the sediments (Anderson & Hampton 1980, Wilkens & Richardson 1998), are fairly easy to detect, and their presence can be investigated by seismo-acoustic methods (Schüler 1952, Anderson & Hampton 1980, Abegg & Anderson 1997). The high impedance contrast between water and the gas bubbles trapped in the sediments to a large extent affects acoustic wave propagation. That is to say, changes in the elastic parameters of the sediments in which gas bubbles reside greatly increase the scattering and diminish the speed of sound compared with gas-free sediments, which in turn leads to changes in the reflection coefficient. Moreover, sound is excessively attenuated in gas-containing media, which may cause these sediments to become acoustically opaque.

Changes in the acoustic parameters of sediments caused by the presence of gases are manifested in echograms in the form of characteristic patterns, such as acoustic blanking, masking or acoustic turbidity This enables gas-charged sediments to be distinguished. Acoustic sounding allows the presence of gas bubbles to be detected in the water column of the areas where gas outflows from the sediments occur and, moreover, to record their rising velocities and changes in size.

The presence of gas in the surficial layer of marine sediments was first discovered in the Kiel Bight, where there are thick mud layers (Schüler 1952, Hinz et al. 1971). With respect to the occurrence of methane and gas bubble formation, bottom sediments were intensively investigated in Eckernförde Bay by Bussmann & Suess (1998), Martens et al. (1998, 1999), Wever et al. (1998), Wever et al. (2006) and Whiticar (1982, 2002). Gas-containing sediments were also found in the Arkona Basin by Thiessen et al. (2006) and Mogollón et al. (2012), in the Bornholm Basin by Laier & Jensen (2007) and Jørgensen et al. (2011), and in the north-eastern part of the Gdańsk Basin by Geodekyan & Trotsiuk (1990) and Pimenov et al. (2010). The distribution of methane in the water column of the Baltic Sea was investigated by Schmale et al. (2010). The Polish sector of the southern Baltic Sea was not geochemically examined for methane in the sediments before 2009. However, long before 2009, Jankowska (1993) had suggested that gaseous structures existed in the sediments of the Gulf of Gdańsk. Klusek et al. (1995) found free gas bubbles in the sandy sediments below the coastal waters of the Gulf. Subsequently, Brodecka & Bolałek (2011) and Reindl & Bolałek (2012) confirmed that the marine sediments in the Hel Peninsula area contained methane. Tęgowski et al. (2003) found gas-containing sediments in the inner Gulf of Gdańsk, and Rudowski et al. (2010) reported gas seepage in Puck Bay (Gulf of Gdańsk). These latter authors investigated acoustic anomalies and sediment deformations related to the presence of gas in the deeper (< 40 m) part of Puck Bay and suggested that methane was the main component of the gas. Additionally, Orłowski (2009) and Majewski & Klusek (2011) reported methane in the sediments of the outer Puck Bay, off the tip of the Hel Peninsula. Research into submarine groundwater discharges carried out as part of the AMBER project (Assessment and Modelling Baltic Ecosystem Response) by Vogler et al. (2010) also revealed that methane was being emitted from the sediments of that area. However, to date there have been no reports of joint geochemical and acoustic investigations into the occurrence of methane in different subareas of the Gdańsk Basin.

It was planned to carry out a thorough acoustic and geochemical examination of sediments in selected areas of the Polish sector of the southern Baltic Sea. Specifically, the aim of this study was to investigate the spatial distribution of gas bubble formation and methane occurrence in sediments of the Gdańsk Basin and the Słupsk Furrow. High-resolution acoustic surveys were designed to image the shallow bottom subsurface Quaternary layers using different acoustic sources and to choose optimum coring positions. In the geochemical part of the study we focused principally

on measuring methane concentrations and determining the depth of the SMTZ for further studies on the AOM.

2. Study area

The investigations were carried out in the Gdańsk Basin (Gulf of Gdańsk, Gdańsk Deep) and the Słupsk Furrow (Figure 1). Most of the acoustic transects and core sampling points (4 out of 5 stations) were located within the Gdańsk Basin, an area strongly influenced by anthropogenic activity. The hydrological conditions as well as the chemical properties of the seawater in the region are affected by the Vistula river discharge
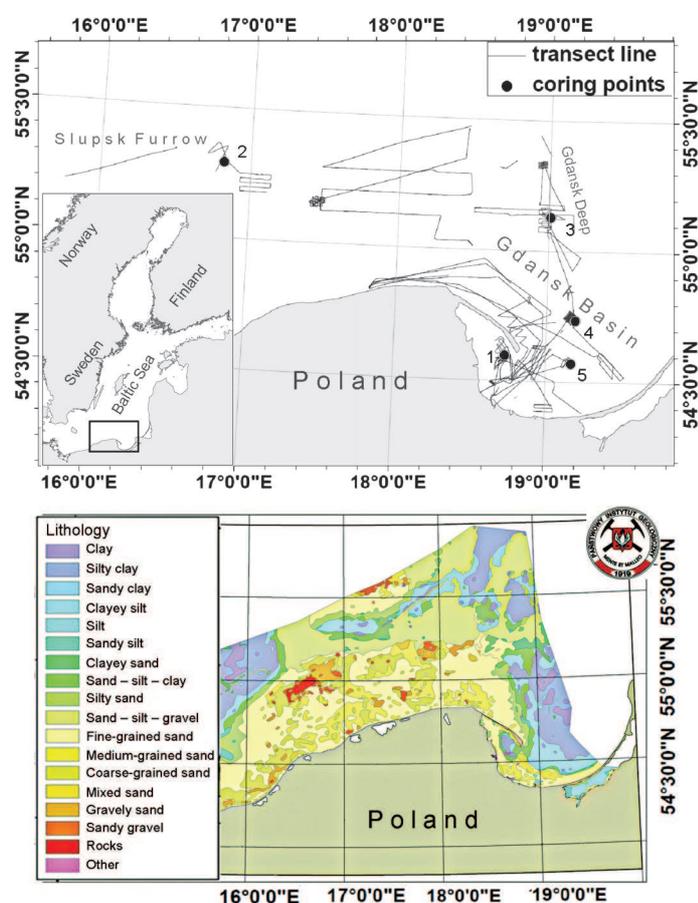

Figure 1. Map of the study area with acoustic and seismo-acoustic transects and coring points (black dots) (upper) and sedimentary units (lower) (map taken from Geochemistry of Baltic Sea Surface Sediments, Polish Geological Institute – National Research Institute, Warsaw 2011, S. Uścinowicz (ed.))

(Majewski 1994). Almost one third of the total fresh water load into the Baltic Proper comes from that river (HELCOM 1998). The seasonal thermocline occurs at a depth of ca 40 m in the warm months, and the permanent pycnocline lies at about 70 m (Cyberska 1990). Such stratification influences the near-bottom water and very often leads to anoxic/hypoxic conditions (Andrulewicz & Witek 2002). The primary production rate for the Gulf of Gdańsk is 190 g C m^{-2} y^{-1} (Witek et al. 1999).

Sediments of different grain-size fraction are found in the Gdańsk Basin and Słupsk Furrow. Generally, fine and coarse-grained sands are present in the southern and south-western coastal parts of the Gdańsk Basin, while silty and clayey sediments cover central parts of the basin (Mojski et al. 1995). The bottom sediments of the Słupsk Furrow are poorly sorted and usually contain fine-grained fractions with a gravel admixture. As far as the layers 1 m below the sea bottom surface are concerned, it is mainly Holocene marine clays, silts and sands that can be found in the central part of the Gulf of Gdańsk and the Gdańsk Basin, and there are Pleistocene glaciomarine silts and clays or subaqueous tills in the Słupsk Furrow (Kramarska 1995). The thickness of the Quaternary deposits in the Gdańsk Basin and Słupsk Furrow is generally > 20 m. However, in some areas of the south-eastern part of the Słupsk Furrow it does not exceed 10 m (Uścinowicz 1995). The rate of mud sedimentation is between 1.65 and 2.04 mm y^{-1} in the deepest part of the Gdańsk Basin (Gdańsk Deep), nearly 1.5 mm y^{-1} in the central part of the Gulf of Gdańsk and 0.62 mm y^{-1} in the Słupsk Furrow (Szczepańska & Uścinowicz 1994, Mojski et al. (eds.) 1995).

3. Material and methods

3.1. Acoustics

Active hydroacoustic methods were used to cover the largest possible bottom area and to determine potential sites of occurrence of gas-charged sediments. The simultaneous use of many different types of echosounders previously not applied in such investigations, such as the side-scan sonar and geo-seismic boomer, allowed for a more accurate bottom diagnosis of the presence of gas bubbles in the sediments and in the water column, which is often not possible when using only one research instrument. Investigations were conducted during nine research cruises of r/v 'Oceania' (from February 2009 to September 2011). Over 3000 nautical miles of transects were recorded using a variety of hydroacoustic instruments selected to recognize different manifestations of gas, such as gas pockets in the

sediments, pockmarks or gas outflows. The measurement setups used during the cruises included broadband sources working in the 40–80 kHz frequency range and classical narrow band echosounders (CW) operating at frequencies 40/80 kHz, 38 and 200 kHz: a Kongsberg EA400 echosounder (in cooperation with the Atlantic Branch of the Institute of Oceanology RAN, Kaliningrad, Russia), a Simrad EK60 scientific echosounder system (70, 120 and 200 kHz), an Odom MK III echosounder working at 12 kHz, and the low-frequency SIG Energos 300 Boomer used to study deeper layers of sediments (in cooperation with the Maritime Institute in Gdańsk).

The total area of gas-charged sediments was estimated after the borders between sediments with and without gas bubbles had been demarcated using acoustic methods (e.g. acoustic blanking and shadowing). Owing to limitations arising from the inability to cover the entire area with a very dense grid of transects, the boundaries of the gas-saturated sediments were approximated using acoustic data from the nearest specified area. GIS software was applied to estimate the approximate surface area of gas-saturated sediments.

3.2. Core collection

Cores were collected at 5 sampling stations in March 2011 and September 2011 by means of a Niemistö type corer (inner diameter: 7.6 cm) or a Rumohr Lot corer (inner diameter: 7.8 cm) (Table 1). At each station three cores were collected to determine: (1) methane concentration, (2) pore water chemistry (SO_4^{2-}, H_2S, NH_4^+, Alk_{tot}) and (3) sediment properties

Table 1. Description of the core sampling stations

Station ID	Description of the site	Station depth [m]	Type of a corer	No. of cores retrieved	Core lengths [cm]	Bottom sediments
St1	S of Hel Peninsula (outer Puck Bay)	49	Niemistö corer	3	47, 46, 49	sandy silt /silt
St2	Słupsk Furrow	72	Niemistö corer	3	37, 34, 40	sandy silt
St3	Gdańsk Deep	93	Niemistö corer	3	48, 56, 60	silt
St4	NE of Hel Peninsula (Gdańsk Basin)	95	Rumohr Lot	3	83, 100, 92	sandy silt
St5	E of Hel Peninsula (central Gulf of Gdańsk)	82	Rumohr Lot	3	85, 103, 120	sandy silt /silt

(grain size, water content WC, loss on ignition LOI, organic carbon C_{org}, total nitrogen N_{tot}). Temperature, salinity and dissolved oxygen (DO) were measured in near-bottom water, taken from above the cores, by a WTW meter (model 3400i).

3.3. Methane concentration

Sediment samples for methane concentration were collected using 3 ml syringes with the luer tip removed, through round 1.1 cm holes in predrilled Plexiglas core tubes, at 5 cm intervals, immediately after core retrieval in order to avoid methane loss due to decompression. A 2 ml aliquot of sediment was then quickly transferred into a 20 ml vial containing 6 ml of 2.5% sodium hydroxide, closed with a butyl rubber stopper and capped with an aluminium crimp seal (Jørgensen et al. 2001). The vials were shaken vigorously to equilibrate the methane concentration between the aqueous and gaseous phases and then stored at ambient temperature for further analysis. The methane concentration was determined using standard headspace techniques on a gas chromatograph (Perkin Elmer) equipped with a flame ionization detector FID and a DB-624 column (60 m, 0.25 mm, 1.4 μm). High purity helium was used as carrier gas. Standards of 1, 50, 100, 5000, 10 000 and 20 000 ppm in capped serum vials were prepared prior to each series of analyses. The detection limit was 1 ppm. The methane results were corrected for sediment porosity and expressed in mmol l^{-1} of pore water.

3.4. Sediment properties

Cores for the measurements of sediment properties were cut into 2.5 cm (stations 1, 2, 3) or 5 cm (stations 4, 5) sections, placed in zip-lock polyethylene bags and frozen.

The laser diffraction analysis of grain size was carried out using a Mastersizer 2000 analyser on the uppermost 5 cm and deeper layers of sediments selected for each station. Sediment type was classified according to the Shepard scheme (1954).

Water content (WC, %) was determined after drying the sediment samples at 60°C to constant weight. Loss on ignition (LOI, %) was measured by combustion at 450°C for 8 hours in a muffle furnace.

Porosity was calculated according to the equation (Engvall 1978):

$$\varphi = W((100 - W)d_v^{-1} + W)^{-1},$$

where W [%] – sediment water content, d_v – sediment volume density, calculated from Carman & Jonsson (1991): $d_v = 260(100 + 1.6(W + IG))^{-1}$, where IG – loss on ignition as the percentage of the wet weight of a sample.

Total organic carbon (C_{org}) and nitrogen (N_{tot}) were measured using a CHNS autoanalyser (Perkin Elmer 2400) according to the methods of Parsons et al. (1985). Calcium carbonate was removed from dried and homogenized samples by adding 1 M HCl (Hedges & Stern 1984).

3.5. Pore waters

Pore water samples were obtained from sediments with Rhizon CSS samplers connected to 20 ml syringes (Seeberg-Elverfeldt 2005, Dickens et al. 2007). The Rhizons were inserted into capped core tubes through 4 mm holes at 2.5 cm (stations 1–3) or 5 cm (stations 4 and 5) intervals and left for 1–2 hours until approximately 15 ml of pore water had been collected.

Ammonium and hydrogen sulphide were analysed according to the standard methods used in marine chemistry (Grasshoff et al. 1983, 1999). The expression 'hydrogen sulphide' used in this paper refers to the sum of sulphides and hydrogen sulphide. Sulphates were determined spectrophotometrically following the methods of Hermanowicz et al. (1999) and Bolałek (2010). Total alkalinity (Alk_{tot}) was measured by titration to $pH = 3.5$ as described in Grasshoff (1983) and calculated using the equation by Schulz (2006).

4. Results

4.1. General parameters (T, S and DO of near-bottom waters)

Bottom-water temperatures were typical of the seasons when the samples were taken: early spring (stations 1, 2, 3) and early autumn (stations 4 and 5) (Table 2). The lowest value was reported in March at St2 (4.1°C) and the highest in late September at St5 (8.7°C). The bottom-water salinity at all five stations ranged from 10.1 to 12.4 PSU. Dissolved oxygen was measured only at three stations (St1, St2 and St3). The lowest value was recorded at St3 (2.52 mg l^{-1}) and constituted 19.3% of the oxygen saturation limit at the given temperature and salinity conditions (Table 2).

4.2. Acoustics

Over 20 potential areas of occurrence of gaseous sediment structures were found during the acoustic surveys. The total area of gas charged sediments was approximately 578 km^2, 563 km^2 of which comprised regions specified as larger areas of gas-saturated sediments or gas pockets. 24.6 km^2 were pockmark areas, 16.5 km^2 of which were marked as buried inactive pockmark regions. The one area where active gas outflows were observed during this two-year research was estimated to cover 0.6 km^2.

Table 2. Temperature, salinity, dissolved oxygen and oxygen saturation in near-bottom waters at the sampling stations

Station ID	T [°C]	S [PSU]	DO [mg l^{-1}]	O$_2$ saturation [%]
St1	4.3	10.1	2.97	22.5
St2	4.1	12.4	4.10	31.2
St3	4.9	11.3	2.52	19.3
St4	7.4	11.0	–	–
St5	8.7	10.8	–	–

Most of the gaseous structures were observed in the Gulf of Gdańsk (Figure 2a), where very extensive shallow gas zones were identified (even just a few cm below the sediment surface) as well as pockmark structures (ranging in diameter from several tens to 200 metres) and active gas outflow zones (coring point No. 5). Numerous structures resembling inactive methane craters buried as much as several metres beneath the sea bottom were detected in the Gdańsk Deep (Figure 2a), while shallow gas pockets were found in the western part of the region. In the Słupsk Furrow and Słupsk Bank regions (Figure 2b) we found gas zones in the surface sediment layers (mainly in the eastern part of the region) and deeper (even below 10 metres of sediment).
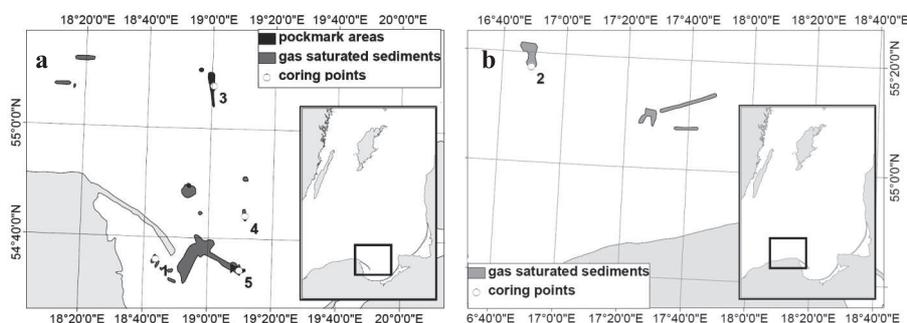
Figure 2. Areas with gas-saturated sediments and pockmarks in the Polish sector of the southern Baltic Sea: a) western part of the Gdańsk Basin and Gdańsk Deep, b) Słupsk Furrow and Słupsk Bank

4.3. Methane in near-bottom water and surface sediments

Dissolved methane was present in near-bottom waters at St1, St3 and St5 in concentrations of 0.006, 0.003 and 0.110 mmol l^{-1} respectively. High concentrations in pore waters of sediment layers < 20 cm were detected at

stations St1, St4 and St5. The values ranged from 0.455 mmol l^{-1} at St4 (22 cm bsf) up to 6.402 mmol l^{-1} at St5 (35 cm bsf). Stations St2 and St3 differed in their methane profiles: the concentrations observed in the upper sediments (0–37.5 cm) of the Słupsk Furrow (St2) were close to the detection limit, ranging from 0.000 to 0.012 mmol l^{-1}, and concentrations in the northern part of the Gdańsk Deep (St3) were only slightly higher than at St2 (0.000–0.130 mmol l^{-1}). Owing to the gaseous nature of the sediments at St5 (central Gulf of Gdańsk, outflows of gas from the sediments), an immediate loss of gas was observed from the cores as a result of decompression, so the methane concentrations reported for that station are lower than they in fact were immediately after core retrieval.

4.4. Sediment parameters: grain size distribution, WC, LOI, C_{org} and N_{tot}

Grain size analysis showed that the sediments at the stations were mainly sandy-silty or silty and that the contribution of the fine fraction < 0.063 mm increased slightly with sediment depth (Figure 3). The highest fine fraction content was reported for St3 (Gdańsk Deep). Water content (WC) ranged between 61.9 and 95.3% in the surface sediment layers (0–5 cm or 0–2.5 cm) and from 25.7 to 73.8% in the bottom layers of the cores (32.5–75 cm) (Figure 3). The highest average WC for the whole sediment profile (81%) was found at St5 (0–75 cm), where methane outflows were reported, and the lowest (40%) at St2 (0–35 cm), located in the Słupsk Furrow. Organic matter content expressed as LOI varied between 15.0 and 19.1% in the surface sediments (0–2.5 cm or 0–5 cm) at four sampling stations (St1, St3, St4, St5). At St4 and St5 LOI was relatively high even in the 70–75 cm layer below the sediment surface: 13.1% and 13.2% respectively. The exceptional station, as in the case of WC, was St2 where LOI in the uppermost layer was 5.1% and decreased down the profile to 0.8% in 32.5–35 cm of sediment below the bottom (Figure 3).

In the sediments from St1, St3, St4 and St5, C_{org} in the 0–10 cm layers ranged from 4.55 to 7.08 wt. %. However, in sediment layers < 10 cm, the range of values was wider: 2.23–6.94 wt. % (Figure 4). Station St2 differed from the other sampling sites in the organic carbon content. The highest amount at St2 (2.33 wt. %) was reported for the 5.0–7.5 cm layer, whereas the lowest (0.15 wt. %) was measured in the 32.5–37.0 cm layer. The total nitrogen content in the sediments ranged from 0.00 wt. % (< 17.5 cm at St2) to 1.00 wt. % (35–40 cm at St5) (av. $= 0.49$ wt. %).
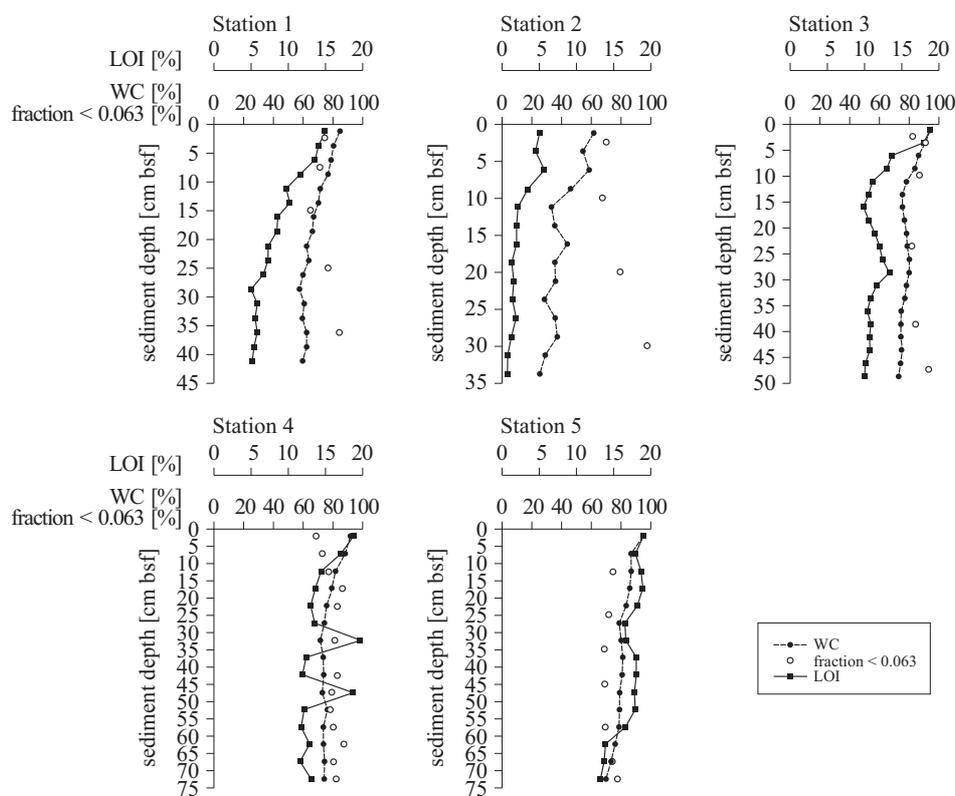
Figure 3. Water content, loss on ignition and the percentage of the < 0.063 mm fraction in the sediment profiles from the five coring stations

4.5. Pore water parameters

Concentrations of sulphates in sediments typically decreased with depth and their profiles were reversed in comparison with the methane concentrations at St1, St4 and St5. In methane-bearing sediment layers, sulphate concentrations were < 2 mmol l^{-1} and decreased sharply down the profiles to 0.21, 0.84 and 0.00 mmol l^{-1} respectively at St1, St4 and St5. The highest sulphate levels in the pore waters of the surface sediments (0–5 cm bsf) were measured at St1 (24.59 mmol l^{-1}) and the lowest at St5 (3.08 mmol l^{-1}). At the coring points off the Hel Peninsula (St1, St4, St5), the pore water profiles of hydrogen sulphide and ammonium were generally higher than at the points in the Słupsk Furrow (St2) and the northern part of the Gdańsk Deep (St3). The highest concentration of H_2S was found at St4 (97 cm, 1101.9 μmol l^{-1}) and that of NH_4^+ at St5 (48 cm, 6263.3 μmol l^{-1}) (Figure 7, see p. 968).
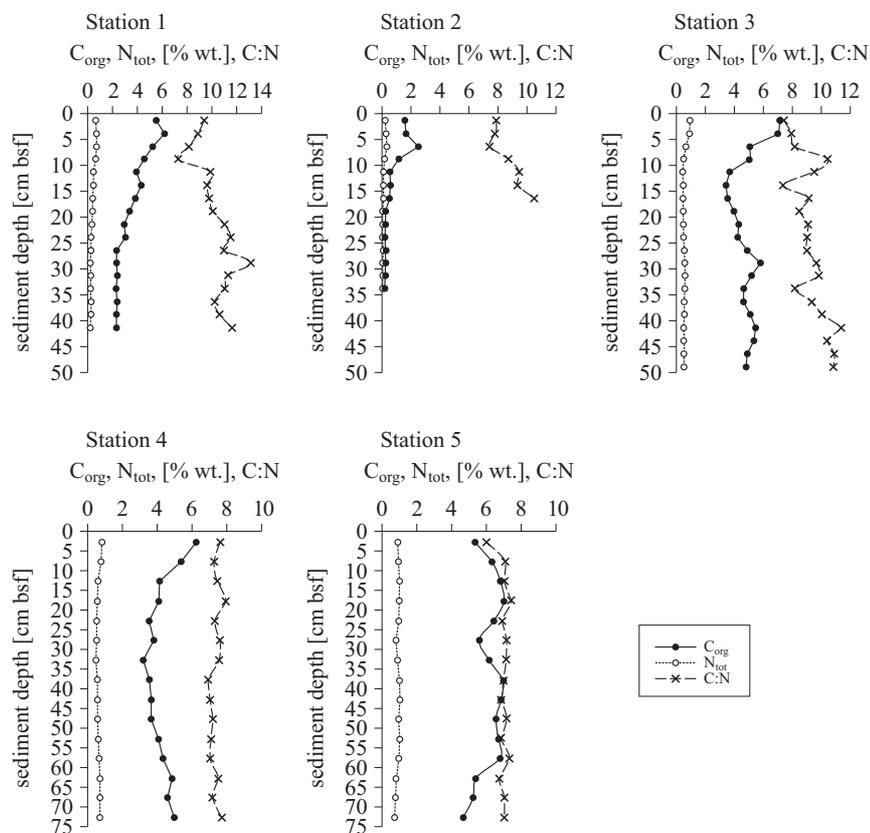
Figure 4. Organic carbon, total nitrogen and C:N ratio in the sediment profiles from the five coring stations

The ranges of sulphate concentrations at St2 and St3 were 24–42 mmol l^{-1} and 8–40 mmol l^{-1}, respectively. Hydrogen sulphide was not present in pore waters of St2, while at St3 concentrations > 100 μmol l^{-1} were recorded only in the layers between 27.5 and 35.0 cm below the sediment surface. Concentrations of ammonium at those stations were generally one order of magnitude lower than those off the Hel Peninsula (St1, St4, St5).

The total alkalinity in the pore waters at St1, St4 and St5 was generally much higher compared to that at St2 and St3, reaching the highest concentrations at St5 (58 cm bsf, 33.41 mmol l^{-1}) and the lowest at St2 (1 cm bsf, 2.16 mmol l^{-1}).

5. Discussion

Sediments in the southern Baltic Sea vary from sandy sediments dominating on banks within the shoals (Słupsk Bank, Stilo Bank and

Southern Middle Bank) and in the southern part of the Gulf of Gdańsk, while fine-grained sediments are typical of basin regions (central and northern part of the Gdańsk Basin, Słupsk Furrow) (Majewski (ed.) 1990, Mojski et al. (eds.) 1995). Water (WC) and organic matter (OM) content varied positively with the amount of fine fraction (< 0.063 mm) in surface sediments. The WC and LOI values obtained in the present study for the Gdańsk Basin were similar to those reported previously by Łukawska-Matuszewska & Bolałek (2008) and Bolałek & Frankowski (2003). The sampling stations chosen for our studies were located mainly within the basin areas of silty or sandy-silty surface sediments with high water ($> 84\%$) and organic matter (LOI $> 14\%$) contents (St1, St3, St4, St5) and could be related to the accumulation/transportation type of bottom (Graca et al. 2006).

5.1. Acoustic properties of the sediments

The presence of gas at shallow depths in the Polish region of the southern Baltic Sea (Polish Exclusive Economic Zone – PEEZ) manifests itself in various forms, such as recent and buried pockmarks, and gas-saturated sediments (including gas pockets and gas seepage) (Figure 5).

The best outcome in the acoustical imaging of the presence of gas in the study area was achieved with single-beam echosounders using frequencies of 12 or 38 kHz. This was especially visible along transects where acoustically transparent soft sediments change to gas-containing sediments, which are characterized by strong volume scattering and high attenuation. Such a situation occurred in a number of cases in the Gulf of Gdańsk, particularly in the outer Puck Bay. Along transects between the Hel Peninsula and the mainland, when going towards Gdynia, we noticed abrupt changes in the character of the echoes. However, on approaching the Hel Peninsula it was sometimes impossible to identify the northern boundary of the area of shallow gas-containing sediments, since the bottom off the peninsula consists of sound absorbing sands.

Using the broadband echosounder in this area, it was possible to acoustically observe the presence of gas bubbles in the sediments even several centimetres below the bottom surface (calculated on the assumption that the speed of sound in sediments is $c = 1430$ m s^{-1}) (Figure 5a). The occurrence of methane was confirmed by core sampling at St1 and subsequent chemical analysis. The methane concentration was 0.213 mmol l^{-1} already 9 cm below the bottom surface and increased down the core to over 6 mmol l^{-1} at 39 cm bsf (Figure 7, see p. 968). The chemical properties of the pore waters at that point (St1) changed rapidly within the top 10 cm of the sediment, as confirmed by the concentration profiles of hydrogen sulphide

(an increase from 0 to nearly 500 μmol l^{-1}) and ammonium (from 35 to nearly 500 μmol l^{-1}), as well as by the alkalinity (a four-fold increase).

Sounding in the areas where the bottom is regularly covered by acoustically hard material was performed in the fault zones (the Słupsk Furrow region) with the boomer and 38 kHz echosounder. Acoustic blanking was observed both in the first tens of centimetres of the sediments as well as deeper than ten metres. Owing to the very hard bottom in this area (St2), where WC at 30 cm bsf was $< 30\%$, it was not possible to collect cores longer than ca 40 cm. In consequence, we could not carry out full methane profiles (e.g. up to 100 cm bsf) at this station. Concentrations in the top 40 cm of the sediment varied from 0.003 to 0.012 mmol l^{-1} and were probably caused by migration from the lower layers as there were no signs of methane production in the top 40 cm layer (hydrogen sulphide was not detected and sulphates were present in concentrations > 20 mmol l^{-1}).

Soundings performed with low-frequency conventional (12/38 kHz) and chirp (40–80) echosounders allowed several areas with pockmarks to be identified. In the Gdańsk Basin it was possible to categorize both pockmarks on the surface of the bottom and older buried pockmarks (mainly in the Gdańsk Deep). In the central part of the Gdańsk Basin and the Gdańsk Deep, structures were found with vertical sections resembling buried furrows or riverbeds of sizes ranging from tens to 900 metres (Figure 5b). Detailed analysis of acoustic signals enabled the zones to be separated with significant attenuation of the acoustic wave below the 'furrow' level. This was subsequently identified as a gas chimney and enabled the structures to be classified as inactive pockmarks covered with a layer of sediment (coring station St3). The structures found at the bottom during the present studies were similar to those investigated by Pimenov et al. (2010) in the adjacent Russian sector of the Gdańsk Deep. The methane concentration in the sediments (0–55 cm) of that area (St3) was very low < 0.130 mmol l^{-1} compared to the rest of the stations and the accompanying sulphate concentration was relatively high (the average for the 0–50 cm core was 18.96 mmol l^{-1}), suggesting that methane was not produced within the 0–50 cm sediment layer but deeper, as indicated by the acoustics.

Moving along the transects to the north-east of the Hel Peninsula, horizontal fronts between sediments without gas bubbles were readily observed on the acoustic profiles (Figure 5c). The occurrence of such structures in that region can be associated with organic-rich sediments (organic matter content LOI 18.8% in the top 5-cm layer) and a high sedimentation rate of 1.5 to over 2 mm per year (Mojski et al. (eds.) 1995). The methane concentrations determined in the core collected within that
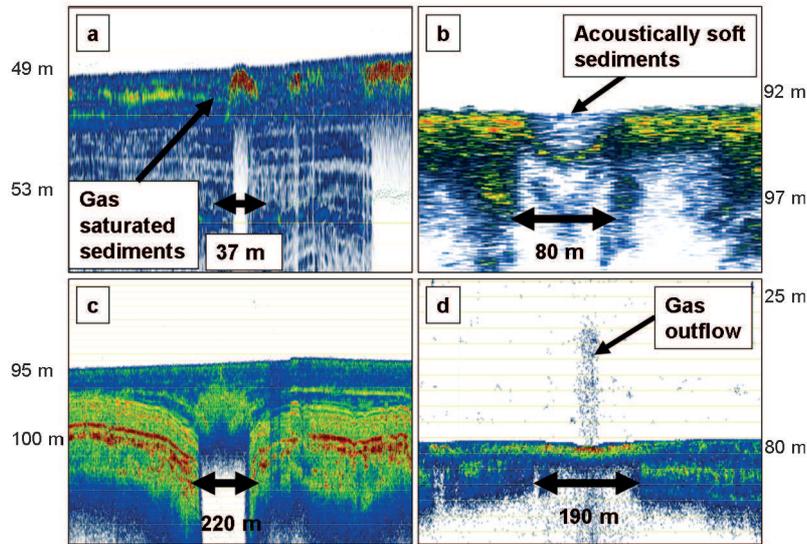
Figure 5. Different forms of shallow gas occurrence: gas pocket structures (a), buried pockmark (b), elongated pockmark or channel (c), active pockmark with a gas outflow (d). These forms were imaged with a 12 kHz ODOM III echosounder (a, c and d) and with a broadband chirp echosounder 40–80 kHz (b)

area (St4) gradually increased down the profile from 0.003 (2 cm bsf) to 5.062 mmol l^{-1} (82 cm bsf) (Figure 7, see p. 968).

An active, elongated, gas-seeping pockmark about 170–300 m wide and 2700 m long, centred at $\lambda = 54.5710°$N; $\varphi = 19.1650°$E (Figure 5d), was documented in the central Gulf of Gdańsk. Single gas bubbles could be seen seeping up from the sea bottom at 80 m up to 30 m under the sea surface. The cores collected at this point (St5) differed from the other cores, as the uppermost sediment layer (ca 25 cm) was mixed with the near-bottom water and looked as if it was boiling owing to the escaping gas bubbles – the effect of decompression. We are fully aware that despite the immediate collection of subsamples from the cores (up to 20 minutes), the measured concentrations of methane were lower than in situ concentrations and varied between 0.258 and 6.402 mmol l^{-1}. Additionally, the values measured in the 15–105 cm layers represented neither linear nor concave concentration profiles (they differed from those at the other stations), which suggested the migration of gas bubbles with methane within the sediment from deeper layers. Similar but transient outflows of methane off the Hel Peninsula were reported by Orłowski (2009).

The active, elongated pockmark in the Gulf of Gdańsk is unique in the Baltic Sea environment in the sense that there is continuous, low-intensity

seepage of gas. This was verified by observations in different seasons during two years. Single bubble behaviour at the gas seepage site was observed with a calibrated SIMRAD EK-60 echosounder working at three frequencies (70, 120 and 210 kHz). As the transducers were of the split-beam type, trajectories of individual ascending bubbles together with instantaneous values of target strength (TS) were obtained with Biosonic Echoview software. Data post-processing performed in the MATLAB environment enabled the bubble rising speed and bubble size to be calculated. The latter was converted using the classical approximate relationship between the bubble radius and backscattering cross sections ($\sigma_{bs} = 10^{(TS/10)}$). At frequencies much larger than the bubble resonance frequency we applied $\sigma_{bs} = a^2$, where 'a' is the radius of a gas bubble (Clay & Medwin 1977).

Examples of rising bubble trajectories and radius changes with depth of a single bubble, calculated on the basis of the instantaneous backscattering cross section, are given in Figure 6. Here, we assumed that a bubble was ascending as a rigid sphere. The observed rising velocities of single bubbles were in the range of 0.20–0.26 m s^{-1}.
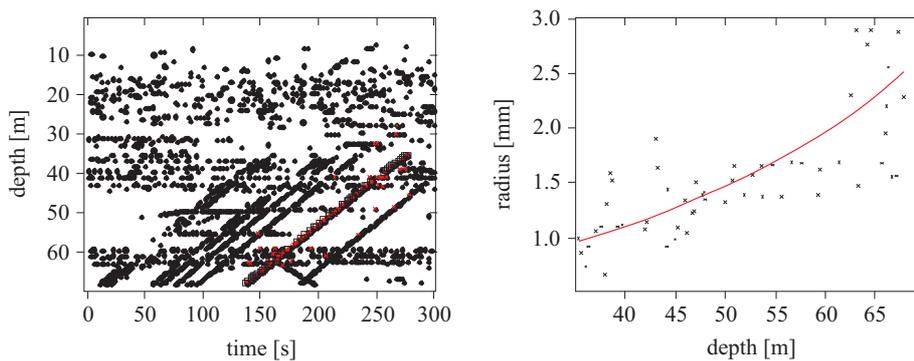

Figure 6. Images of traces of rising bubbles (red dots on the left) in the pockmark area as in Figure 5d, and radius changes with depth of a single bubble calculated on the basis of the measured instantaneous backscattering cross section (right)

5.2. Chemical evidence for the occurrence of methane

The occurrence of methane in the sediments of coastal estuarine sea regions is usually associated with the constant input of organic matter to the bottom and high sedimentation rates. The four sampling stations situated in the Gdańsk Basin (St1, St3, St4, St5) could be characterized as sites with relatively large amounts of organic matter in the surface sediments (LOI between 15.0 and 19.1%), while the one station (St2) in the Słupsk

Furrow was an area relatively poor in organic matter (LOI = 5.1%). The C_{org} content in sediments at the four first-mentioned stations were almost three times higher than at St2 (Figure 4). Obviously, there were no signs of methane formation (no hydrogen sulphide and several dozen mmol l^{-1} of sulphates) in the top sediment layers (0–37.5 cm) of St2, despite acoustic evidence pointing to the existence of gas in the deeper sediment layers. Oxic conditions, a low organic matter input and a low sedimentation rate (0.62 mm y^{-1} Mojski et al. (eds.) 1995, Szczepańska & Uścinowicz 1994) did not favour methane formation in the bottom sediments at St2. Alkalinity, the increase of which may be associated with mineralization processes (Whiticar 2002), was low throughout the profile: < 4.5 mmol l^{-1} (Figure 7). The same applied to the level of ammonium in pore waters: this was 10–40
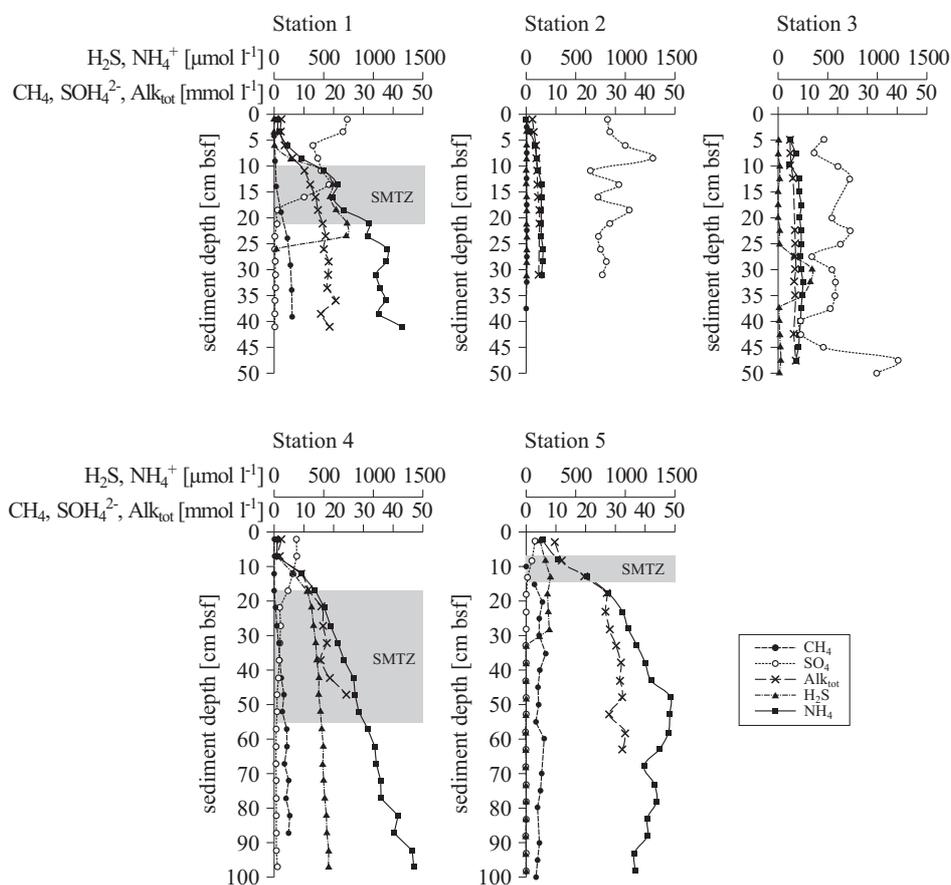

Figure 7. Concentrations of methane, sulphates, hydrogen sulphide, ammonium and total alkalinity in the sediment profiles at the five coring stations; the sulphate-methane transition zone SMTZ is marked in grey

times lower than at the stations where methane occurred (Figure 7). This suggests that the methane trapped under the hard thick layer of sediments (WC $< 26\%$ and $> 97\%$ of < 0.063 mm grain fraction) in the Słupsk Furrow does not originate from ongoing microbial degradation. Further analysis of δ^{13}C is needed at that site to determine the origin of methane there.

Signs of methane production were detectable at only three (St1, St4, St5) of the four stations with a high C_{org} content and LOI. At St3 (Gdańsk Deep), C_{org} was higher than at St1, St4 or St5 (Figure 4), the H_2S concentration in some layers was > 300 μmol l^{-1} and the sedimentation rate was ~ 2 mm y^{-1} (Szczepańska & Uścinowicz 1994, Mojski et al. (eds.) 1995). It was acoustically classified as an inactive pockmark and, surprisingly, the highest concentration of methane in the top 0–55 cm layer was only 0.130 mmol l^{-1}. Previous research by Brodecka & Bolałek (2011) also showed that, despite the geochemical conditions (an accumulation basin with a high sedimentation rate, a high organic matter content and anoxic conditions in the bottom sediments) being apparently favourable to methane formation, this process does not take place or is somehow limited in the surface sediments of some areas within the Gdańsk Deep. This is probably the result of a slower rate of mineralization. Further investigations into the decomposition and quality of the organic matter could explain why methane does not occur in the surface sediments of that area. High concentrations of sulphates (> 10 mmol l^{-1} in pore waters of 0–50 cm layer), which for some unknown reason are not depleted in the top layers of the sediments, act as preferable electron acceptors in mineralization processes. Methane is produced in the sediments of that station, as shown by acoustic methods, but only in the deeper layers (greater than 50 cm), where CO_2 reduction and/or acetate fermentation become the main pathway of organic matter degradation. At St3, ammonium concentrations did not exceed 250 μmol l^{-1}, and the maximum alkalinity was only 5–6.5 mmol l^{-1} (Figure 7), which additionally implied that mineralization was not as intensive and advanced as at the other stations in the Gulf of Gdańsk where methane occurred. At both St2 and St3 exceptionally high (40–42 mmol l^{-1}) concentrations of sulphates were recorded ~ 9 cm and ~ 48 cm below the bottom respectively. This could have been due to sulphide oxidation in sediments; further analyses will be needed to explain this, however.

The stations off the Hel Peninsula (St1 and St4) had typical methane and sulphate distribution profiles. Methane was produced below the sediment depths where sulphates were depleted. Intensive organic matter decomposition was followed by elevated levels of ammonium (nearly 3000 μmol l^{-1} at 97 cm bsf of St4) and alkalinity. A rapid sevenfold increase in Alk_{tot} in the layers 5–30 cm bsf at both St1 and St4 could also be associated with

AOM processes. The respective thickness of the SMTZ at St1 and St4 was about 10 and 37 cm. However, the methane and sulphate concentrations profiles at these two stations were different. In the 6–13.5 cm layers of sediments in the outer Puck Bay (St1), processes were probably taking place that modified the typical concave-up curvature of the sulphate profile above the SMTZ ($\sim$ 10–21 cm). At the station located NE of the Hel Peninsula (St4), the sulphate-methane transition range was over three times wider than at St1; moreover, the SMTZ lay at greater depths ($\sim$ 18–55 cm), although it was still relatively shallow compared to other regions of the Baltic: 80–160 cm bsf in the Kattegat and Skagerrak (Iversen & Jørgensen 1985), $\sim$ 150 cm bsf in the Aarhus Bay (Thomsen et al. 2001), 30–40 cm in the Gotland Deep (Piker et al. 1998) and 30–40 cm bsf (Martens 1999) or $\sim$ 150 cm bsf (Whiticar 2002) in Eckernförde Bay. As the SMTZ is so shallow in some regions of the Polish part of the southern Baltic, any serious disturbance to the sediments (e.g. dredging) deeper than 10–20 cm in those regions could interfere with the processes connected with AOM and, for example, cause a higher emission of methane from the sediments. To some extent, moreover, it could influence the carbon and sulphur cycles because DIC, sulphates and hydrogen sulphide are involved in anaerobic methane oxidation and/or methane production – processes which in some parts of the study area take place in the topmost 20 cm of the sediments.

The stations also differed in the nature of the C_{org} distribution in the sediment profiles (Figure 4): there was a rapid decrease in C_{org} down the profile at St1 in comparison to St4. That drop in organic carbon content could indicate a slower inflow of organic matter to the sediments of the outer Puck Bay in the past than nowadays.

The area of methane outflow from the sediments, represented by St5, was also exceptional as regards its chemical conditions. The C_{org} content changed only slightly with sediment depth (0–75 cm), even though the surface layer values were still lower than at St3 (Gdańsk Deep). Ammonium concentrations in pore waters were the highest of all the stations and even exceeded 6000 μmol l^{-1} in the 48–58 cm layers. Sulphates were depleted at a very shallow depth – between 13 and 18 cm bsf (Figure 7) – and organic matter was buried before it could be decomposed by anaerobic organisms. The alkalinity was above 30 mmol l^{-1} already at 33 cm bsf, suggesting intensive mineralization and/or bicarbonate addition as a result of the anaerobic oxidation of methane or methane formation. The average methane concentration for the whole profile at St5 was the highest, which was the effect of intensive methane production. The SMTZ thickness at this station was the smallest – only about 4 cm and situated close to the sediment-water interface, at $\sim$ 8–12 cm.

During the present investigations, low levels of methane (< 0.5 mmol l^{-1}) were generally observed when sulphate concentrations were > 2 mmol l^{-1}, which compared to Eckernförde Bay ($[CH_4] < 0.4$ mM when $[SO_4] > 0.5$ mM; Whiticar 2002) is a wider range of methane-sulphate coexistence. This was noticeable especially at St4.

The C:N ratios calculated for the five sampling stations were almost within the values expected for the Baltic Sea (7.4–9.6 – Szczepańska et al. 2012), the Gulf of Gdańsk (13.1 – Maksymowska 1998) and the Pomeranian Bay (7.6–14.3 – Burska et al. 1999) and ranged between 6.01 and 14.22 (Figure 4) with an average of 8.62. At the exceptional St5, organic matter was the freshest, as C:N values were the lowest (6.01–7.15). However, as Müller (1977) and Sampei & Matsumoto (2001) pointed out, low C:N rates could also be the effect of inorganic nitrogen (ammonium), which was present at very high concentrations in the pore waters at St5.

6. Summary

Joint acoustic and geochemical investigations aimed at finding and mapping the distribution of gas-charged sediments were performed in the Polish sector of the southern Baltic for the first time. Acoustic images acquired in different frequency ranges revealed distinct features, e.g. acoustic blanking, acoustic turbidity, bubble seeping and fresh or buried pockmarks, which are known to be associated with the presence of gas at shallow depths

It was found that methane is widespread in the sediments of the study area. The gas is common both in surface sediments, e.g. in the vicinity of the Hel Peninsula or in the central Gulf of Gdańsk, and in deeper sediment layers, e.g. in the Gdańsk Deep and Słupsk Furrow. The results of the study fully support earlier reports (Orłowski 2009, Rudowski et al. 2010) on the ebullition of gas from the bottom in the Gdańsk Basin. Only in the one case presented in this paper (Figure 5d) was gas seepage persistent, however. Chemical analyses revealed that as a result of intensive organic matter decomposition, sulphates are depleted in the topmost 20 cm layer of sediments and methane is produced at relatively shallow depths (in some areas even at 20–30 cm bsf) as compared to other regions of the Baltic. The SMTZ is 4–37 cm thick and is located in the uppermost 50 cm of the sediments.

The results obtained in the present study provide a foundation for further studies on the carbon cycle in the Baltic Sea. However, additional wide-ranging regional investigations to estimate methane fluxes from both seepages and undisturbed sediments into the water and its further release into the atmosphere are required.

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