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## Research papers

## Methane flux from sediment into near-bottom water and its variability along the Hel Peninsula–Southern Baltic Sea



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## ABSTRACT

Methane in the sediments of the Bay of Puck occurs in the form of free gas bubbles and is released from the sediments into near-bottom water in the form of a flux. The sediments of the Bay of Puck also contain methanogens whose biological activity results in the production of methane. Research carried out in the coastal areas of the bay along the Hel Peninsula proved the existence of a methane flux ranging from  $0.81 \text{ mmol m}^{-2} \text{ d}^{-1}$  to  $33.41 \text{ mmol m}^{-2} \text{ d}^{-1}$  in 2011, while in 2010 ranged from  $0.91 \text{ mmol m}^{-2} \text{ d}^{-1}$  to  $49.15 \text{ mmol m}^{-2} \text{ d}^{-1}$ . Seasonal and annual fluctuations were also observed. Other factors contributing to the change in methane flux are water temperature and other environmental factors. An increase in temperature causes an increase in the flux. Fluctuations of the flux within individual sampling sites were also observed. A test performed with specific methanogenic inhibitor—sodium dodecyl sulfate (SDS) unexpectedly revealed higher methane concentrations (10–13%) in samples to which SDS was added. We speculate that these higher methane concentration result from the lysis of methane-forming bacteria cells when exposed to SDS.

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## 1. Introduction

Since the beginning of the twentieth century a significant and rapid upward trend in the concentration of methane in the atmosphere has been observed (Masse et al., 2003). The increase in global atmospheric methane content has also been confirmed by the IPCC (2007). Seas and oceans are involved in the biogeochemical cycle of gas circulation, including methane, and it is believed that biological decomposition of organic matter under anaerobic conditions accounts for the largest share of global methane emissions. Methane in the marine environment can come from microbial decomposition of the organic fraction, but also from thermogenic changes resulting in the production of fossil deposits of this gas (Judd, 2004; Reeburgh, 2007). Primary production intensified by the inflow of anthropogenic pollution the transformation of organic matter. Pollution triggers a chain of reactions which include, quite significantly, the biochemical production of greenhouse gases, and the gradual increase of waters threatened with eutrophication contributes to the increase of areas rich in greenhouse-gas-producing substrates (Bange et al., 1994; Bange, 2006; Edlund, 2007; Wegener, 2008). In view of the progressive growth of both eutrophication, resulting in the production of substrates for methanogenesis, and the gradual increase of greenhouse gas emissions, including methane, it is important to know the locations where methane occurs. It is also crucial to determine methane fluxes at the sediment level in marine ecosystems.

In the Polish part of the Baltic, the presence of methane was detected in the sediments of Gdansk Bay (Brodecka and Boląlek, 2011) and research in Puck Bay carried out by Reindl and Boląlek (2012a, 2012b) proved the presence of methane bubbles in the sediments and its flux into the near-bottom water, as well as the presence of methane forming bacteria DNA in the sediment. Additionally, methane released into the atmosphere was observed during annual monitoring studies along Baltic ferry routes (Gülzow et al., 2013). The presence of methane in the Baltic is characterized by temporal and spatial variations reaching their maximum in estuaries and fjords. Europe's coastal zones are a source of methane emissions into the atmosphere and contribute to the global share of emissions from natural sources. The presence of methane in the coastal zones of the Baltic is strictly linked to the degree of eutrophication and it may grow in the future due to progressing anthropopressure (Bange et al., 1994; Bange, 2006). Therefore, it is crucial to know the location of methane in those Baltic estuaries which are particularly vulnerable to eutrophication—such as the coastal zone of Puck Bay. This study involved estimating the volume of the flux passing between sediments and near-bottom water in Puck Bay along the Hel Peninsula.

## 2. Materials and methods

## 2.1. The area of research

Methane flux at the sediment–water interface was determined at twelve sampling points located along the Hel Peninsula in Puck

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Bay from April to October 2011 (Table 1). Changes in methane flux at an individual sampling station were recorded at two sites, the first of which was located in the inner part of the bay and the second in the outer part (this is a sub-region of Gdansk Bay which is separated by the Hel Peninsula from the deep areas of the Gdansk Basin). Research on flux change at individual stations was conducted in July, August and September 2011 with six sampling points at each station (Fig. 1). The inner part of the bay, which bears the characteristics of a coastal lagoon, exchanges water with the outer bay through a strait which is about 3.5–4.5 m deep. Varying depth of Puck Bay (the eastern, outer part of the bay much deeper than the western, inner part) determine the environmental conditions and processes taking place in this ecosystem. While the outer waters of the bay have higher salinity and are significantly more dynamic, the inner part of Puck Bay is an ecosystem which receives constant fresh water influx from rivers (Nowacki, 1993). Changes in the concentration of biogenic components in the waters of the bay undergo seasonal fluctuations which are among other things, by biogenic processes. Inorganic nitrogen and phosphorus compounds contribute to an increase of the phytoplankton mass and, in coastal zones, the cyclical changes in concentration of these biogenic compounds are determined by the level of influx from the land (Bolalek et al., 1993). Eutrophication of the Baltic begins around gulf areas with primary production higher than in the open sea (Renk, 1993). The concentration of biogenic substances can also be influenced by periodic mixing of the inner

gulf's water, which determines the vertical distribution of phytoplankton (Pliński, 1993). The oxygen content in the waters of Puck Bay is determined by a number of factors, among which the most important are biological processes and the influx of sea and fresh water. The level of oxygen saturation is the result of interconnected biological, physicochemical and dynamic factors which determine the direction of oxygen exchange between the atmosphere and water. Local water pollution causes oxygen depletion which, in turn, results in anoxic conditions (Bolalek et al., 1993). Biological factors are some of the most important causes affecting the formation of anoxic conditions. The biochemical breakdown of organic compounds in a marine environment causes oxygen depletion; as a consequence, reductive reactions occur including processes involving methane-producing microorganisms (Edlund, 2007). Previous studies of the coastal sediments of Puck Bay along the Hel Peninsula confirmed the presence of nucleotide sequences bearing similarities to the known methanogenic Archaea (Reindl and Bolalek, 2012b).

## 2.2. Sampling and sample preparation

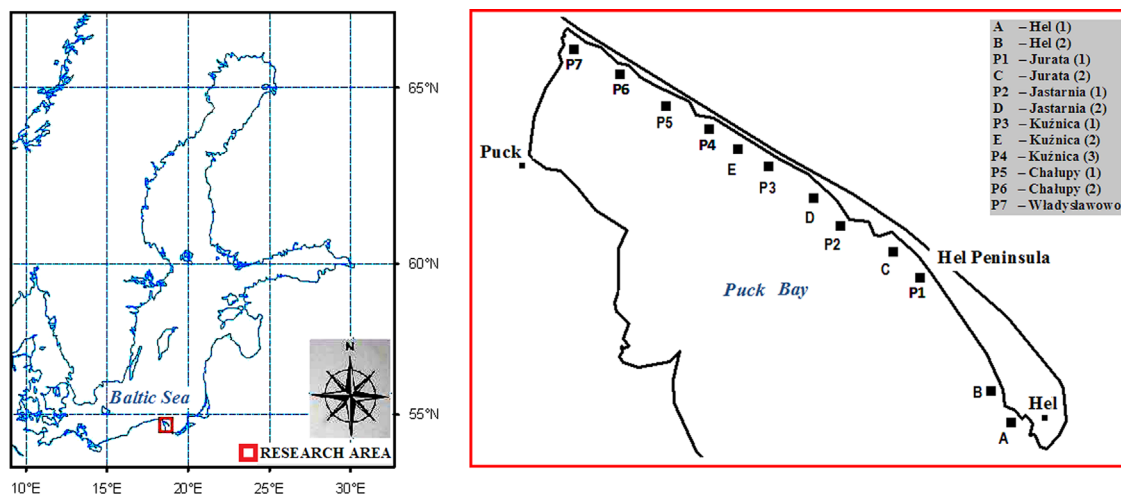
Following around 24 h of exposure to methane flux from sediments, near-bottom water samples were collected using benthic chambers according to a method which has been described in detail in previous research papers (Liikanen et al., 2009; Reindl and Bolalek, 2012a). Degassing was carried out by changing the gas saturation in the analyzed water using NaCl, in accordance with a previously described method (Schmaljohann, 1996; Piker et al., 1998; Sommer et al., 2006; Reindl and Bolalek, 2012a).

Methane flux measurements were conducted at twelve sampling stations located along the Hel Peninsula, as well as at station P1 (located in the outer part of the bay) and at station P4 (in the inner part of the bay), using six chambers located at each sampling station. Flux estimation was then conducted at selected measurement points at six sampling stations in July, August and September 2011.

Experimental measurements of methane flux with the use of a specific methanogenic inhibitor – sodium dodecyl sulfate (SDS) – were carried out at the stations in the inner part of the bay in July, and in the outer part of the bay in August. The research consisted of simultaneous sampling of a methane flux in two benthic chambers placed next to each other, one of which had a 10% SDS solution placed under it.

**Table 1**  
Sampling stations in coastal area of Puck Bay GPS localization.

Stations descriptions		GPS localization	
		(N)	(E)
A	Hel (1)	54°36'23.1"	018°48'02.4"
B	Hel (2)	54°37'27.1"	018°46'53.0"
P1	Jurata (1)	54°40'40.4"	018°42'57.0"
C	Jurata (2)	54°41'06.4"	018°42'23.2"
P2	Jastarnia (1)	54°41'44.1"	018°40'14.0"
D	Jastarnia (2)	54°41'56.5"	018°39'50.7"
P3	Kuźnica (1)	54°44'10.0"	018°34'30.6"
E	Kuźnica (2)	54°44'21.2"	018°33'51.0"
P4	Kuźnica (3)	54°44'48.2"	018°32'38.3"
P5	Chałupy (1)	54°45'27.9"	018°30'35.4"
P6	Chałupy (2)	54°46'46.4"	018°27'05.4"
P7	Władysławowo	54°47'18.5"	018°25'27.5"



**Fig. 1.** Sampling stations along the Hel Peninsula–Puck Bay, Southern Baltic Sea.

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