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Detecting sinks and sources of CO_2 and CH_4 by ferrybox-based measurements in the Baltic Sea: Three case studies

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ABSTRACT

A fully automated measurement system for recording of the surface water CO_2 partial pressure, pCO_2, was deployed on VOS (voluntary observation ship) “Finnpartner/Finnmaid” in 2003. Since 2009, an amendment of the system also allows for the continuous detection of the surface water partial pressure of methane, pCH_4. The ship commutes regularly at 2–3 day intervals between the Gulf of Finland (Helsinki) and the Mecklenburg Bight (Lübeck) in the southwest of the Baltic Sea.

The pCO_2 data in the central Gotland Sea showed a pronounced seasonality that was mainly controlled by the biological production and decomposition of organic matter in combination with stratification/mixing of the water column. CO_2 consumption in spring/summer caused pCO_2 that were by up to 300 μatm below the atmospheric level. In contrast, the pCO_2 exceeded the atmospheric values during autumn/winter when deep mixing transports CO_2-enriched water to the surface. To identify the central Baltic Sea as a sink or source for atmospheric CO_2, an air–sea CO_2 gas exchange balance was established for three selected years (2005, 2008 and 2009). During each year the surface water acted as a net sink for atmospheric CO_2 with uptake rates ranging between 0.60 and 0.89 mol m^{-2} yr^{-1}. The rates correspond approximately to the enhanced carbon burial in sediments during the last century and suggest a link between eutrophication and CO_2 uptake.

The data of the surface methane concentration are used to focus on situations were extraordinarily high methane concentrations were observed. Temporary methane peaks were observed south of the Island of Gotland, which could clearly be attributed to frequent upwelling events.

Between spring 2012 and 2013, Finnmaid went at a few occasions to St. Petersburg in the east of the Gulf of Finland. Methane concentration of up to 130 nmol L^{-1} where found close to the River Neva mouth but decreased rapidly to the west. The plume of methane-enriched waters was observed farthest to the west during the winter period. This was attributed to air–sea gas exchange that was most effective during summer but inhibited during winter because of the ice coverage.

1. Introduction

The analysis of trace gases such as CO_2 and methane in ocean surface waters has received a boost during the last decades in order to identify the ocean as a sink or source for these greenhouse gases (e.g.Bange, 2006; Bange et al., 1994; Takahashi et al., 2002). It was shown that the oceans are a major sink for anthropogenic CO_2 emissions (e.g., Sabine and Tanhua, 2010), however, the uptake rate is still associated with a considerable uncertainty. The marine methane cycle has been extensively investigated because its role in the carbon cycle and the mechanisms of methane oxidation, strongly limiting the emission of methane to the atmosphere in most marine areas (Reeburgh, 2007).

Coastal and marginal seas may play a pivotal role because of their potential for enhanced carbon sequestration as a consequence of increased near-shore primary production (eutrophication), and because of the major contribution of these systems to the marine source strength of methane (Bange, 2006), which is also believed to be affected by naturally or anthropogenically induced changes in organic matter production, redox conditions, or seafloor temperature (Best et al., 2006). Investigations of the marine CO_2 system are performed to assess ocean acidification and to analyze biogeochemical processes that are linked with the uptake or release of CO_2. For methane, processes enhancing the flux to the atmosphere, as well as the response of methanogenesis to enhanced organic matter production and reduced oxygen availability need to be understood (Best et al., 2006). To achieve these goals, data with a temporal and spatial resolution that account for the time and spatial scales of the involved processes are necessary. This poses a challenge especially in the Baltic Sea where small-scale changes of the

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hydrographic conditions and a pronounced seasonality of the biogeochemical state of the surface water affect both the concentrations of CO_2 and CH_4.

Although useful data and findings were obtained during several measurement campaigns with research vessels (Abril and Iversen, 2002; Bange et al., 1994; Löffler et al., 2012; Schmale et al., 2010; Schneider et al., 2000, 2003; Thomas and Schneider, 1999) these provided only a limited spatial coverage and a coarse seasonal resolution due to limitations in the availability of the costly ship time. Therefore, a fully automated pCO_2 measurement system was deployed on a cargo ship ("Finnpartner" and later on "Finnmaid") in 2003 and is in operation since then in cooperation with the Finnish Algaline project. This "voluntary observing ship" (VOS) commutes regularly between Helsinki and Lübeck and thus crosses the entire Baltic Proper and parts of the Gulf of Finland (Fig. 1). At a few occasions "Finnmaid" visited also St. Petersburg in the east of the Gulf of Finland. The pCO_2 data were used to calculate seasonal changes of the total CO_2 concentrations (C_T), which are mainly controlled by the uptake and release of CO_2 due to biological production and mineralization of organic matter. Based on mass balance calculations that included the CO_2 gas exchange with the atmosphere, the C_T decrease during spring and summer yielded the net community production in different areas of the Baltic Proper (Schneider et al., 2006). Relating the net community production to the elemental composition of particulate organic matter facilitated the quantification of nitrogen fixation rates (Schneider et al., 2009). In 2005 an oxygen optode was added to the measurement device in order to obtain O_2 data as complement to the CO_2 data (Schneider et al., 2007).

A further amendment of the measurement system was realized in November 2009 when a sensor for the determination of the methane partial pressure was installed (Gülzow et al., 2011). The system also records the pCO_2 independently from the existing system, which allows an improved quality assessment due to the "shared variable". The data of the first full year after installation of the new sensor (2010) were used to reveal mechanisms of enhanced methane transport such as sporadic gas venting or coastal upwelling, but in particular to reveal the general controls on the seasonal trends in methane surface concentration patterns and sea-air fluxes (Gülzow et al., 2013).

Here we

a) present an air–sea CO_2 gas exchange balance for the central Baltic Proper and assess the sink/source function in relation to anthropogenic CO_2 emissions and to the oceanic cycling of CO_2,
b) discuss controls and variability of coastal upwelling induced enhanced methane fluxes to the atmosphere, and
c) display the strong variability of the surface methane pattern caused by the plume of the Neva river.

The choice of these case studies follows the intention to demonstrate the potential of continuous trace gas measurements both for process understanding and parameterization as well as for the refinement of air–sea flux estimates relying on dense spatiotemporal data coverage.

2. Methods

2.1. Cruise details

After three years of operation of the fully automated pCO_2 measurement system on "Finnpartner" the line between Helsinki and Lübeck was taken over by "Finnmaid" in 2006. This caused a break in the measurements of almost two years because of the laborious reinstallation work. Until 2008 the ship commuted at two to three day intervals between Helsinki and Lübeck taking without any regularity either the route through the eastern or western Gotland Sea. From 2009 to 2012 Finnmaid frequently travelled via Gdynia and at a few occasions in 2012/2013 visited out of schedule also St. Petersburg in the east of the Gulf of Finland (Fig. 1). A few gaps in the measurement series occurred due to incidental malfunctions of the measurement system and to few stays of the ship in a shipyard. For our CO_2 gas exchange balance that focuses on the central and northern Gotland Sea (3.2), we used the data from 2005, 2008 and 2009 for which the most even temporal data distribution was obtained. The number of transects passing this area amounted to 74, 76 and 118 per year, respectively, and correspond to a mean temporal resolution of the data of 3–5 days. The nearshore region of the Island of Gotland is covered by Finnmaid at high frequency, as both main routes of the ship pass close to the island, either along its southern or northern coast. The area south of the island of Gotland was thus chosen

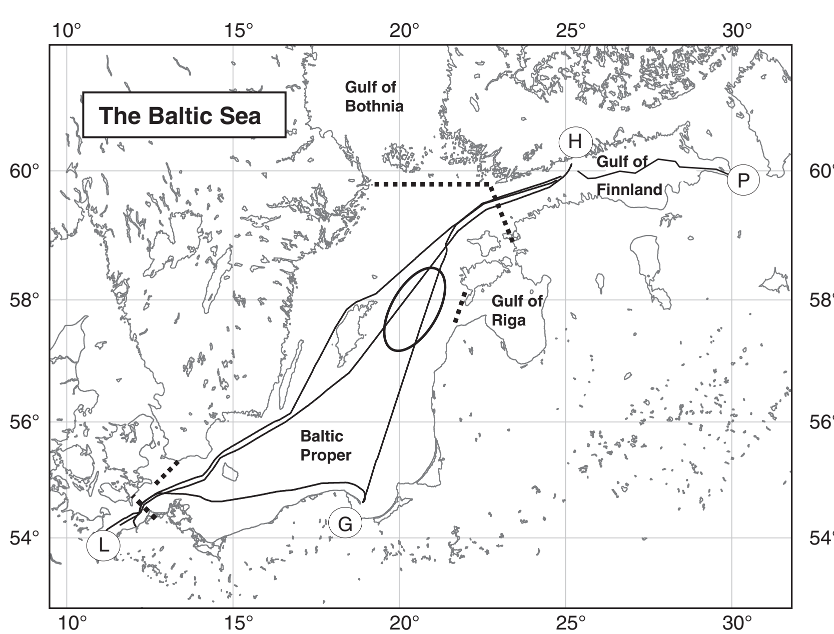

Fig. 1. Ship tracks of VOS Finnpartner and Finnmaid between Helsinki (H), Lübeck (L), Gdansk (G) and St. Petersburg (P). The data from the encircled region were used for the CO_2 air–sea gas exchange balance (3.2), the methane-related case studies on upwelling (3.3) and on the Neva River plume (3.4) were performed at the southern tip of the island of Gotland and in the eastern Gulf of Finland, respectively. The dashed lines indicate the boundaries of the Baltic proper.