Deep Submarine Groundwater Discharge Indicated by Chloride Anomalies in the Sediment Pore Water in the Gulf of Gdańsk, Southern Baltic Sea

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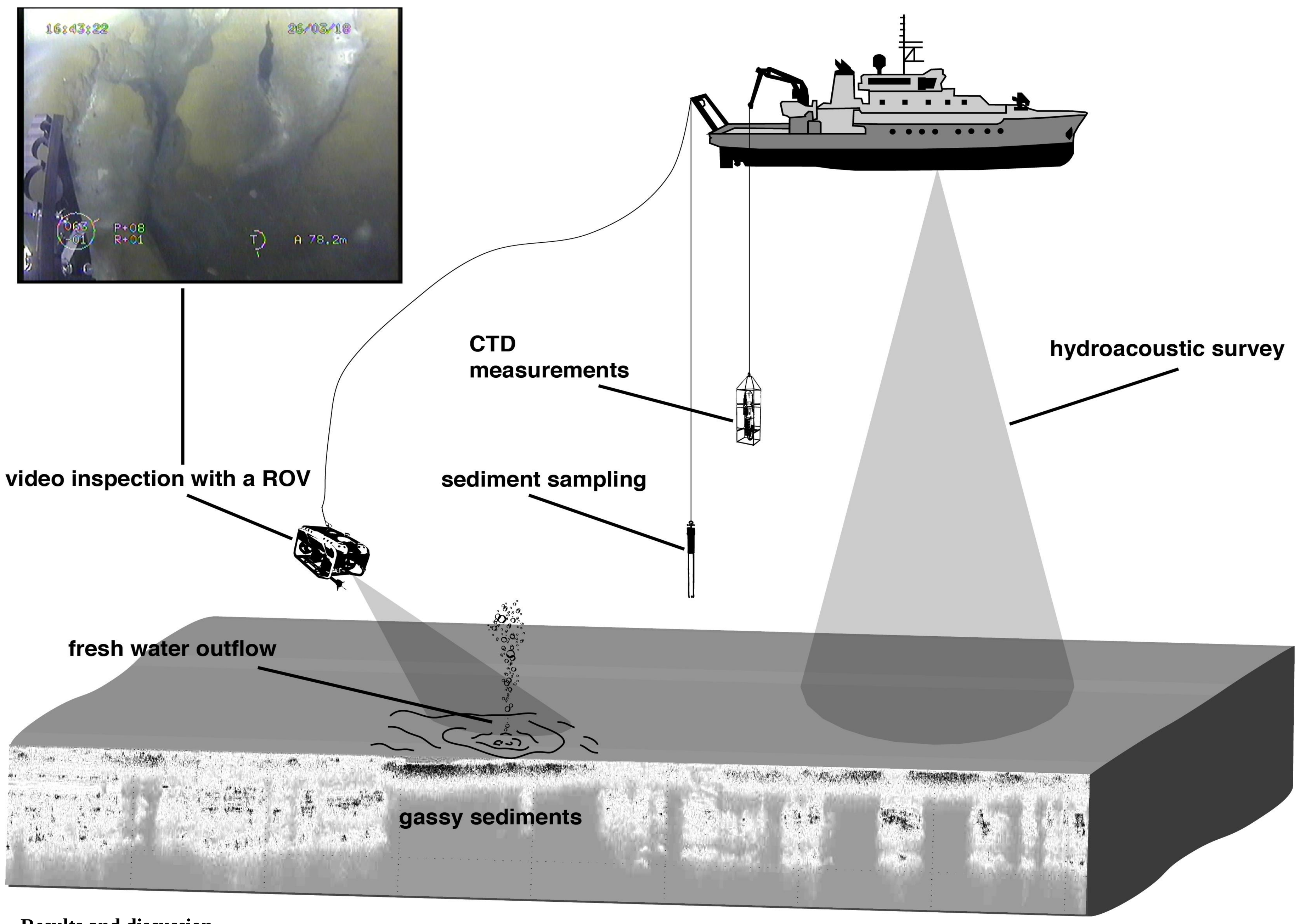
Abstract

Submarine groundwater discharge (SGD) is a significant source of water and of chemical substances, with inputs mainly to shallow coastal zones. Using chloride as the main tracer, in this study we investigated a deep SGD (Fig. 1), located at a water depth of 80 m, 30 km from the shoreline, within the methane ebullition zone (Fig. 2). The groundwater discharge rate of 0.5 ± 0.2 (L m−2 d−1) was estimated in a modeling approach. While the SGD was shown to be an insignificant source of water to the Gulf of Gdańsk, upward movement of the groundwater significantly influenced the pore water distribution and cycling of selected compounds (ions, nutrients, manganese, iron, sulfide and methane) and differed greatly from a biogeochemical zonation model. Based on these findings, we hypothesized that freshwater (SGD) flow and its oscillations are responsible for the formation and ebullition of methane bubbles.

Graphical Abstract



Results and discussion

SGD discharge rate

Chloride pore water profiles provides information about fluid transport in sediments (Schluter, et al., 2004), with diffusion indicated by a linear decrease in the Cl^- concentration and freshwater flow by a concave-shaped curve (Fig.3a, b) (Oehler, et al., 2017; Schluter, et al., 2004). Therefore, this approach was used to calculate the seasonal impact of the SGD on the study area. The discharge rate of 0.5 ± 0.2 (L m^{-2} d−1) clearly indicated an upward flow of freshwater that coincided with an upward migration of measured several chemicals. The pore water profiles of other major ions (Na, K, Mg and Ca) similarly followed the Cl^- profile and indicated the mixing of freshwater with seawater in the sediment (Szymczycha et al., 2012).

Biogeochemical cycles and methane release

Two main zones could be defined within the sediment column, at 4–17 cm and 17–69 cm. The first zone represented the intense redox reactions (IR) layer (shaded bars in Fig. 4) and the second an area of potential CH_4 loss and production. Within the IR layer, K and Ca were non-conservatively removed (Fig. 3) and the reduction of Mn and Fe led to the production of their reduced, more soluble forms (Mn^{2+} and Fe^{2+}), which caused an increase in the Mn and Fe concentrations up to a depth of 7 cm. Below, there was a rapid decrease in both metals, most likely due to precipitation with sulfide, as the H2S concentration decreased from 1.3 mmol L^{-1} to 0.9 mmol L^{-1}. The main sulfate reduction zone was detected 4 cm below the sediment surface, as a significant increase in H2S (Fig. 4a). These findings suggested a certain degree of overlap between sub-oxic processes and the zonation of Mn, Fe and S as well as in the cycling of these chemicals. Generally, redox reactions lead to pore water gradients across the redox boundaries of the reduced forms of metals (Burdige, 1993). In the case of S, this results in the production of sulfide that, together with the upward flow of freshwater, may lead to metals and sulfide re-oxidation as well as the formation of new oxides and probably also of sulfate (Fig. 4b). Sulfite has been observed in the shallow depths of other sites in the Gulf of Gdańsk but the layer extended several decimeters into the sediment (K. Lukawska-Matuszewska & Kielczewska, 2016) and there was no overlap with other redox reactions. The presence of methane in the IR layer was also noteworthy and can be explained by the rapid introduction of methane into the IR layer by vertical gas ebullition (Whiticar, 2002) and by the failure of the sulfate- methane transition zone (SMT), also located at the IR layer, to provide a complete barrier to methane escape following the anaerobic oxidation of methane (AOM). The SMT is typically located one to several meters below the sediment surface in continental margin sediments and plays a key role in the biogeochemistry of the sea bed (Jørgensen and Kasten, 2006). At the study site, the location of the SMT layer was very shallow while the influence of CH_4 ebullition and diffusion occurred in the bottom water, where the CH_4 concentration reached 0.02 mmol L^{-1}, which is 16 times higher than in the deep anoxic methane pool of the Baltic Sea (Jakobs et al., 2014).

In the second zone (17–69 cm), the pore water profiles of CH_4, Fe, Mn, DIC and DOC also did not follow the BZM but instead were scattered with depth, attributable to the complex interplay of various microbiological and physical processes (Whiticar, 2002) that caused a shift in the depth of the redox boundary between the different redox zones (Burdige, 1993), most probably due to the influence of the SGD. Mixing caused by the upward movement of freshwater and methane bubbles could also have been responsible for the inconsistent CH_4, Fe, Mn, DIC and DOC distributions. The provenance of the methane was not determined in our study, but it was most likely produced within the sediment due to methanogenesis, with its ebullition then SGD-driven. However, the SGD as a possible source of CH_4 as well as DIC, DOC, NH_4^+ and PO_4^{3-} cannot be excluded, as SGDs can transport chemical substances far away from the shoreline (Lin et al., 2010; Wilson, 2005). This scenario remains to be confirmed in further studies.

In SGD impacted sediments freshwater is a source of chemical substances to the pore water and water column, its movement cause advection-driven pore water circulation while the biogeochemical reactions taking place in the groundwater –seawater mixing area is influenced by SGD composition, intensity and residence time (Burnett, et al., 2006). SGD intensity and its both seasonal and annual oscillations depend on several factors like precipitation, sea level changes, type of sediment and its permeability (Burnett, et al., 2006; Szymczycha, et al., 2012). The obtained within the study pore water profiles (Fig. 3 and 4) are significantly different from sites without SGD impact in the Gulf of Gdańsk (Katarzyna Lukawska-Matuszewska, 2016; K. Lukawska-Matuszewska, et al., 2014). Therefore we propose that freshwater discharge can significantly change the biogeochemical processes in the highly permeable (Brodecka et al., 2013) and hydrated (high WC) deep see sediment of the Gulf of Gdańsk. The study located in other part of the Gulf of Gdańsk (the Bay of Puck) indicated that SGD is highly anoxic (Szymczycha, et al., 2012) and is a source of methane to the atmosphere (Donis, et al., 2017) therefore submarine groundwater discharge into our site can possible characterizes with similar features. Based on results obtained within this study and findings proposed in others studies (Beck & Brumsack, 2012; Boano, et al., 2010; Janssen, et al., 2005; Treude, Kruger, Boetius, & Jorgensen, 2005) we suggest that freshwater (SGD) flow and its oscillations can probably cause 1) change of hydrostatic pressure that can enable methane bubbles formation and ebullition 2) movement of several organic matter oxidants and cause overlapping of several redox reactions within one shallow and narrow layer 3) transport of bacteria that result in increased microbial activity on certain depths and increase of methane production. This hypothesis needs further studies however a clear relationship between SGD and methane release was detected.

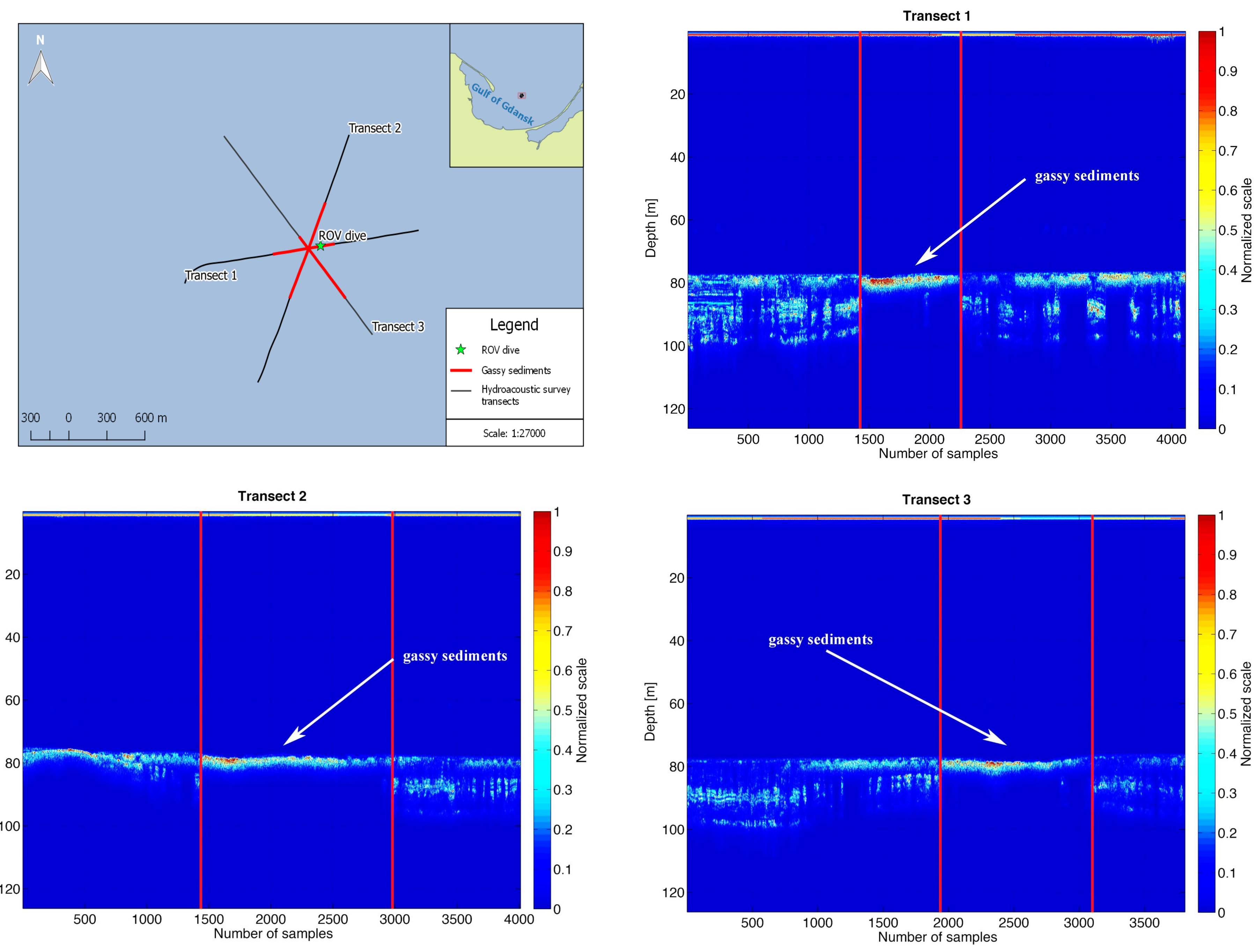


Figure 2. (a) The map of hydroacoustic survey done in the northeast part of the Gulf of Gdansk along three perpendicular transects, which lengths were about 2.5 km each, gassy sediments are marked red. (b) Echogram form Transect 1 with marked gassy sediments between 1440 and 2440 sample.(c) Echogram form Transect 2 with marked gassy sediments between 1450 and 2950 sample. (d) Echogram form Transect 3 with marked gassy sediments between 1950 and 3100 sample. (e) A visual inspection of the sea bottom with the ROV – gassy sediments in close proximity of Transect 1.

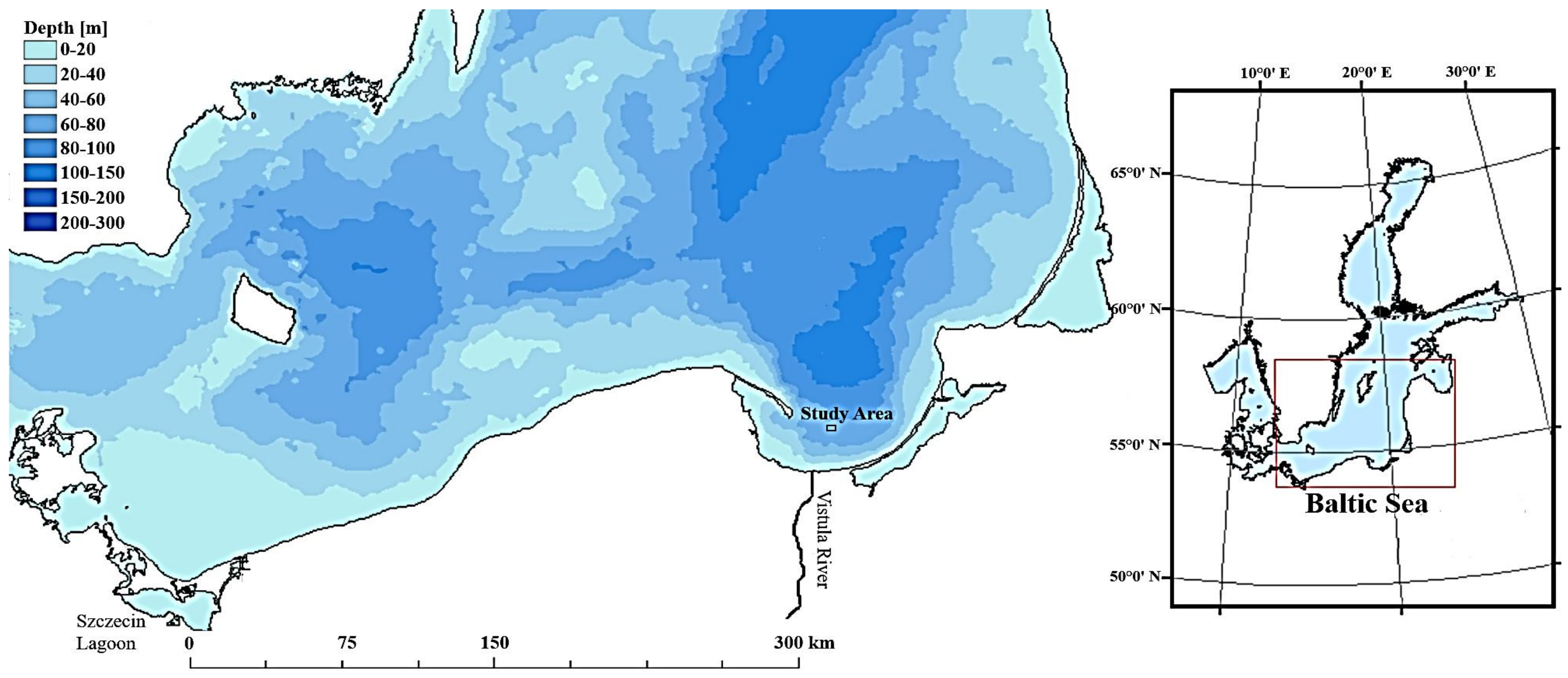


Figure 1. Map of the study area.

Methods

Calculation of groundwater discharge rates

Cl– pore water profiles do not depend on time and their distribution below this depth can thus be described by vertical, one-dimensional advection-diffusion model (Shlüter et al. 2004), as shown in Eq. (1):

$$v\frac{\partial(\Phi C)}{\partial x} - D\frac{\partial^2(\Phi C)}{\partial x^2} = 0 \qquad (1)$$

where C is the concentration of Cl^-, □ is the porosity, D is the molecular diffusion coefficient of Cl^- in the sediment and v is the velocity. The Cl^- diffusion coefficient for sediment (D) was based on an average bottom-water temperature of 5°C and corrected for the effect of tortuosity according to Boudreau (1997). Thus, D = 0.00001179 (m^2 s^{-1}). Porosity was determined according to Brodecka et al. (2013) and the linear function was calculated as shown in Eq. (2):

$$\Phi = -0.0028x + 0.8682 \qquad (2)$$

where Φ is porosity and x is depth.
For Cl^- interpolation the least squares method was used, and the best function was obtained:

$$C = a \cdot e^{b \cdot x} + c \cdot e^{d \cdot x} \qquad (3)$$

For each Cl^- profile a, b, c, d were calculated.
The SGD velocity was than calculated from:

$$v = \frac{D\frac{\partial^2(\Phi C)}{\partial x^2}}{\frac{\partial(\Phi C)}{\partial x}} \qquad (4)$$

Where:

$$\frac{\partial \Phi C}{\partial x} = a \cdot b \cdot e^{b \cdot x} + c \cdot d \cdot e^{d \cdot x} \qquad (5)$$

$$\frac{\partial^2 \Phi C}{\partial x^2} = a \cdot b^2 \cdot e^{b \cdot x} + c \cdot d^2 \cdot e^{d \cdot x} \qquad (6)$$

Taking into account average velocity ($\bar{v}$) and h equal to 40 cm:

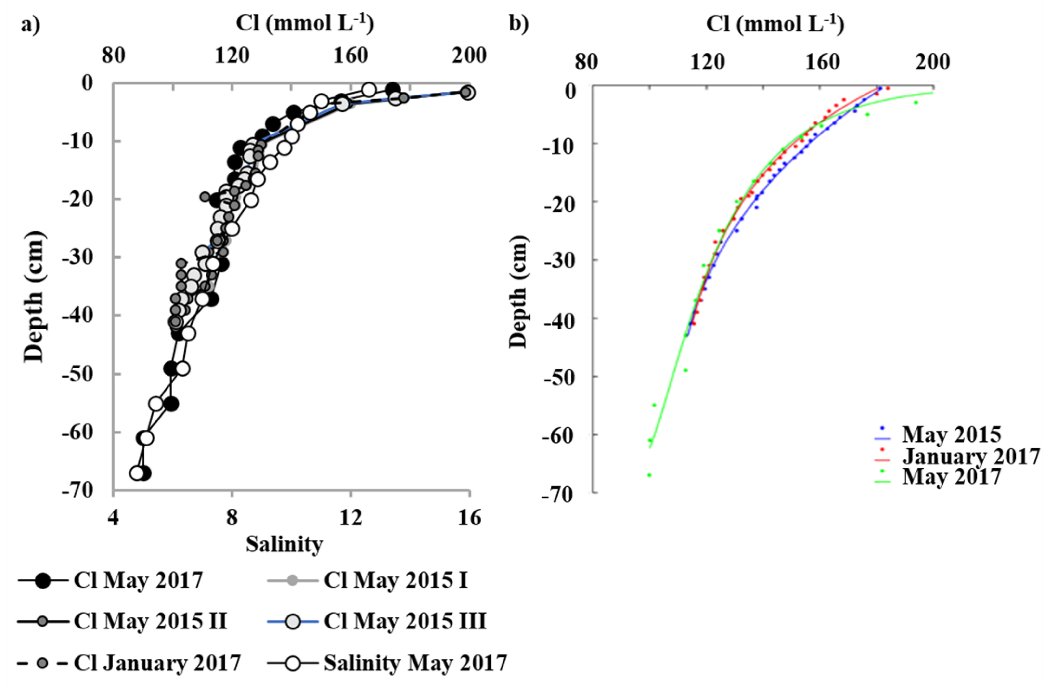


Figure 3. (a) Chloride (Cl^-) and salinity pore water profiles in the study area. (b) Measured (dots) and interpolated (lines) chloride concentrations in pore water (lines).

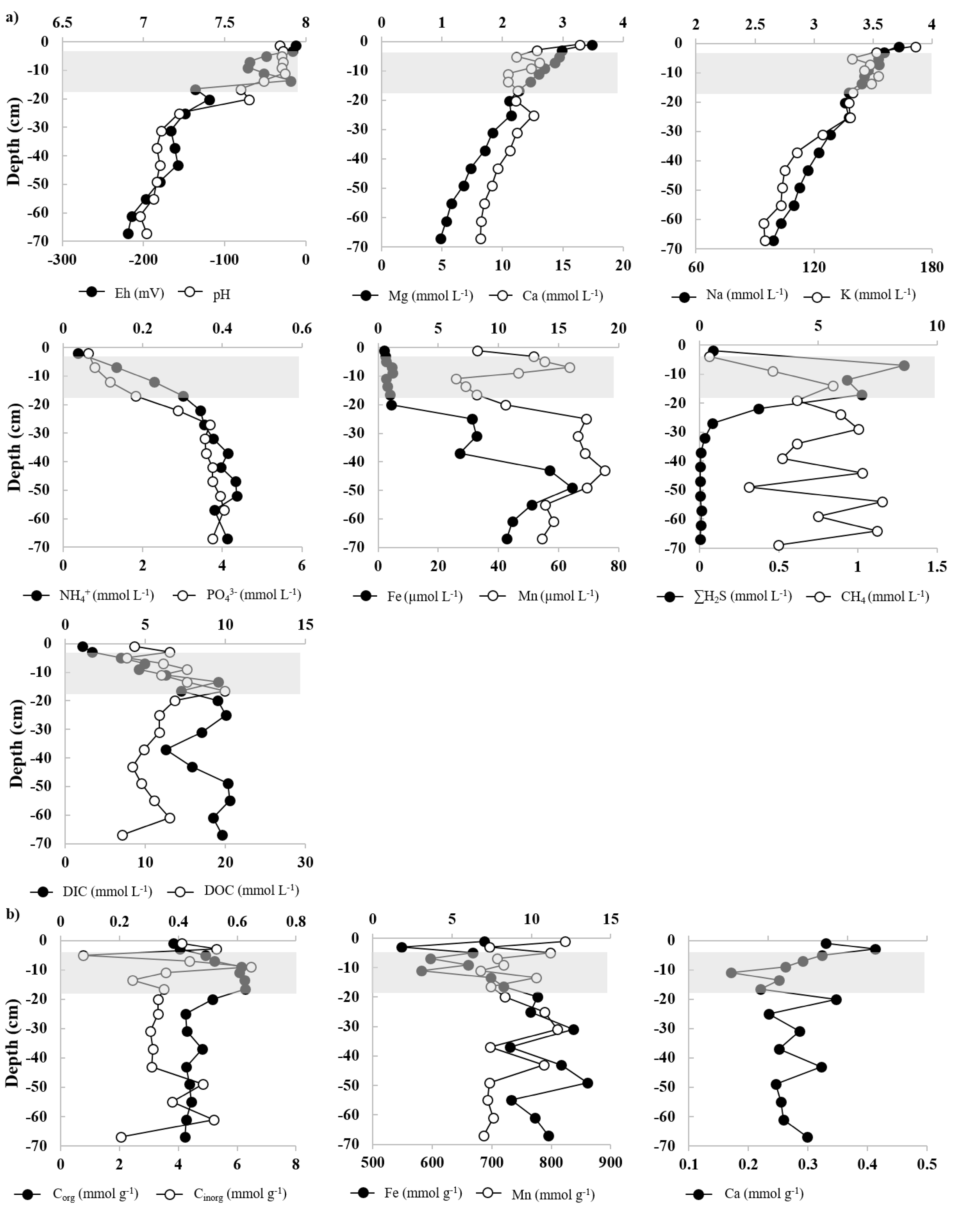


Figure 4. (a) Pore water profiles of Eh, pH, NH_4^+, PO_4^{3-}, Fe, Mn, DIC, DOC, H_2S and CH_4 in the study area. The white circles refer to upper axis while black to lower axis. The shaded area corresponds to the intense redox reaction layer (IR). (b) The sediment concentrations of organic carbon (Corg), inorganic carbon (Cinorg), iron, manganese and calcium in the study area. The white circles refer to upper axis while black to lower axis. The shaded area corresponds to the intense redox reaction layer (IR).

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