

# Carbon isotope and sulfate biogeochemistry of a rewetted brackish fen

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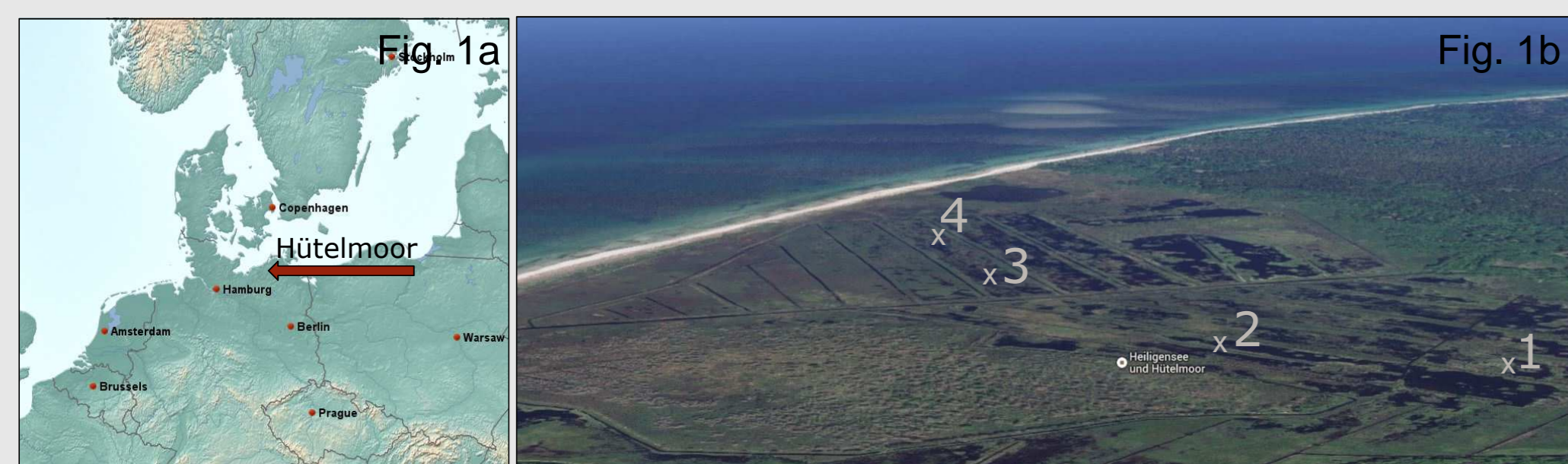
## Background

### Carbon metabolism of rewetted coastal peatlands

Rewetted freshwater peatlands are known to emit high amounts of CH<sub>4</sub>, a potent greenhouse gas with 25 times the global warming potential of CO<sub>2</sub>. In coastal peatlands intermittent sea water intrusion affects metabolic pathways, i. e. anaerobic carbon metabolism is progressively dominated by sulfate reduction with lower contribution of methanogenesis. Little is known about how rewetting affects CH<sub>4</sub> emissions in degraded coastal peatlands. Here, we present results of a comprehensive biogeochemical survey from a rewetted coastal fen that emits high levels of CH<sub>4</sub> **despite of locally high sulfate concentrations (up to 37 mM)**. Such studies are urgently needed in order to better understand the greenhouse gas emission potential of coastal peatlands and to provide a rewetting decision tool for policy-makers.

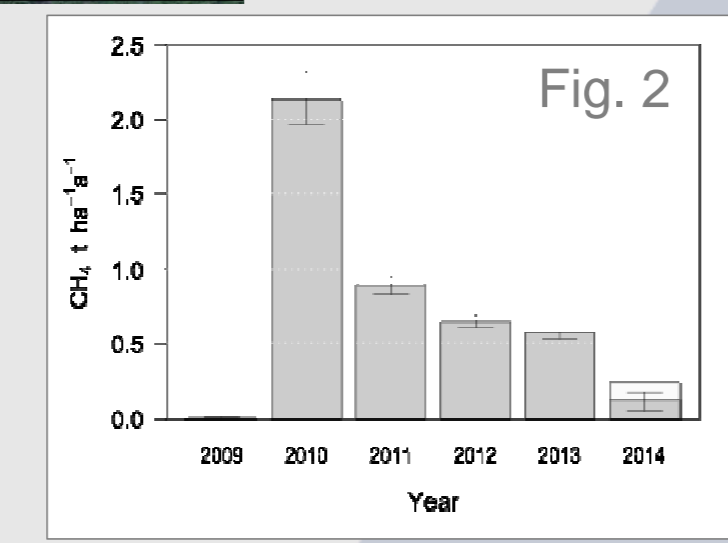
## Study site: The Hütelmoor

### At the interface between brackish and terrestrial freshwater



The „Hütelmoor“ is located in NE Germany. In the past, the fen was intermittently flooded by the adjacent Baltic Sea.

The Hütelmoor was rewetted in winter 2009/2010 which initiated year-round freshwater inundation. CH<sub>4</sub> emissions were negligible in the last year before rewetting (2009) but increased by a factor of 100 in 2010 up to 2.2 t ha<sup>-1</sup> a<sup>-1</sup>. Since then CH<sub>4</sub> emissions have decreased consistently but are still on a high level (0.25 t ha<sup>-1</sup> a<sup>-1</sup>). CH<sub>4</sub> fluxes were measured with the Eddy Covariance and the Closed Chamber approach. Sulfate concentrations in the pore water reached up to 37 mM.



## Objectives

- Assess the current Baltic Sea impact on pore water geochemistry using stoichiometry based on element:chloride ratios
- Identify lateral and depth-dependent geochemical pore water gradients using principal component analysis
- Identify CH<sub>4</sub> production and consumption zones as well as dominant methanogenesis pathways using stable isotopes and isotope mass balance calculations

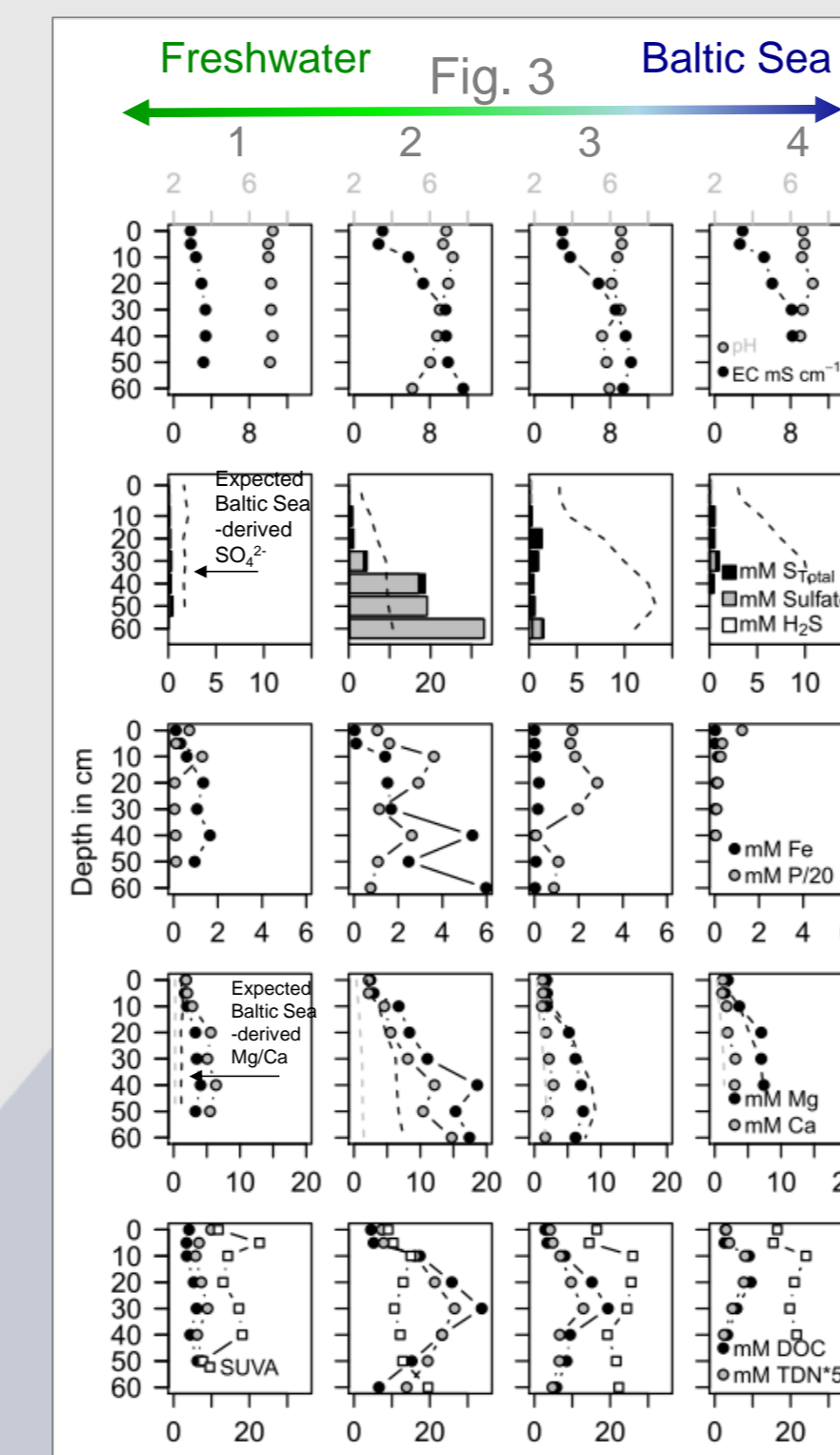
## Methods

Four pore water profiles and sediment samples were taken within a transect of 300-1500 m distance to the Baltic Sea in autumn 2014 (cf. Fig. 1b). Samples were filtered and preserved in the field.

Parameter	Measurement approach	Parameter	Measurement approach
In situ pH, DO, EC	WTW Multi-Parameter Instrument	DOC, DTN	Persulfate/ thermal catalytic oxidation
Total Alkalinity	Titration with 0.05 M HCl	δ <sup>13</sup> C-DIC	IRMS
SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , Br <sup>-</sup>	Ion chromatography	Ca, Mg, K, Mn, Na, S, P, Fe, Si, Ba, Li, Sr, Al	ICP-OES
DIC, δ <sup>13</sup> C-DIC	Gas-IRMS	H <sub>2</sub> S	Photometry
Dissolved CH <sub>4</sub>	Gas chromatography	Peat CNS	Elemental Analysis
δ <sup>13</sup> C-CH <sub>4</sub> , δD-CH <sub>4</sub>	GC-C-IRMS	Peat TOC, δ <sup>13</sup> C-TOC	MS

## Stoichiometry

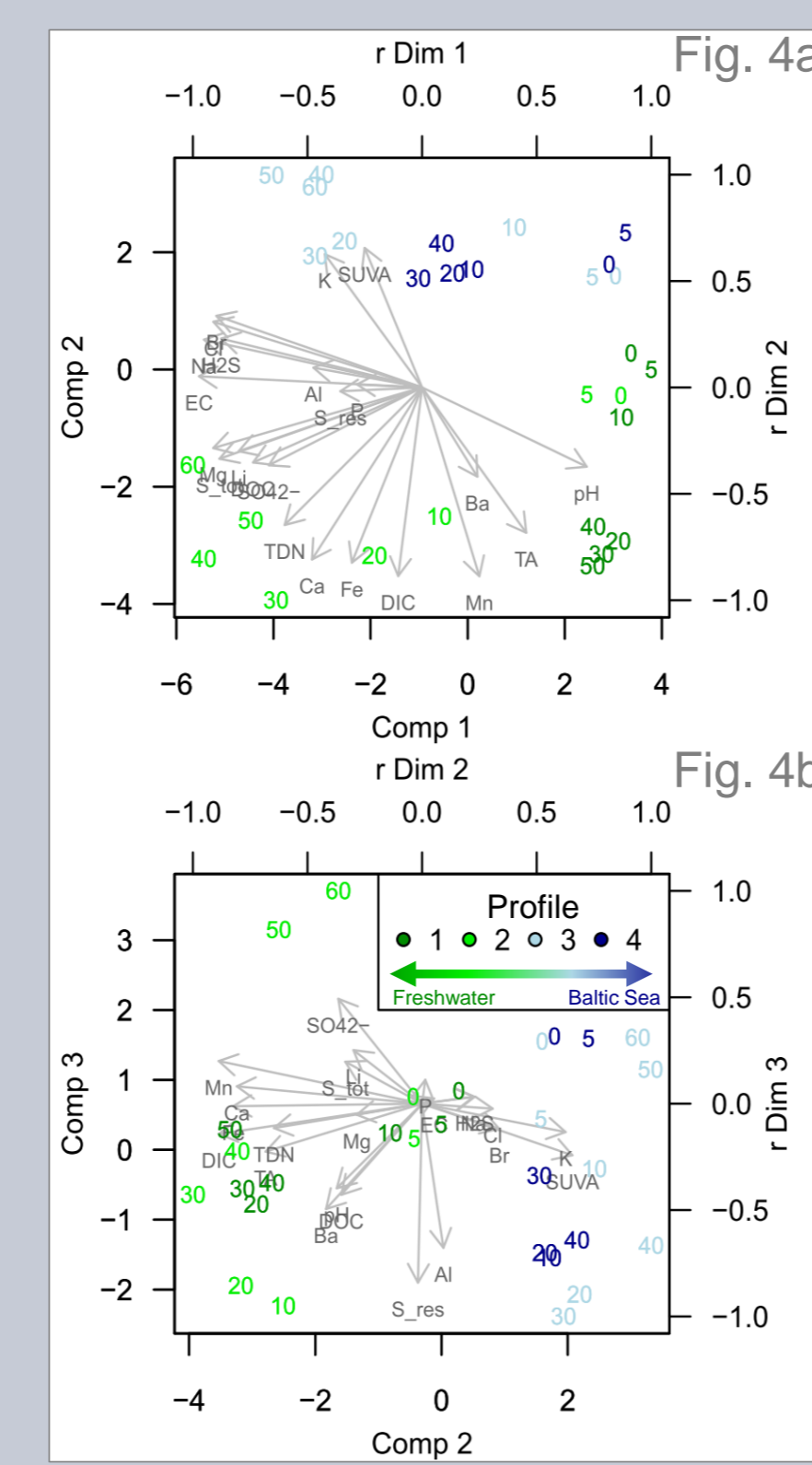
### Sulfate: excess and exhaustion



- Freshwater inundation decreased electrical conductivity (EC) and chloride concentration in the top profile
- In general:** SO<sub>4</sub><sup>2-</sup> concentrations < detection limit (0.01 mM) in top, increased with depth up to 1 mM
- Porewater SO<sub>4</sub><sup>2-</sup>:Cl<sup>-</sup> ratios << than Baltic Sea water indicate substantial net SO<sub>4</sub><sup>2-</sup> loss
- H<sub>2</sub>S concentrations negligible at the top, increased with depth (parallel to the SO<sub>4</sub><sup>2-</sup> concentrations) up to 0.3 mM
- SO<sub>4</sub><sup>2-</sup>-S+ H<sub>2</sub>S-S account only for a minor part of the total S fraction (S<sub>tot</sub>), the bulk of S (S<sub>res</sub>) is from a fraction we didn't specify (probably thiosulfate, sulfite and/or org S)
- In contrast:** significant excess of SO<sub>4</sub><sup>2-</sup> (up to 33 mM in 0 cm depth) at pore water profile 2 (1150 m apart from the Baltic Sea coast line)
- Similar magnitudes of SO<sub>4</sub><sup>2-</sup> concentrations reported from rewetted freshwater fens (e. g. Zak et al. 2009: 7.0 mM; Hahn-Schöfl et al. 2011: 8.9 mM), usually associated with the former oxidation of ferric sulfides and/or upwelling of SO<sub>4</sub><sup>2-</sup>-rich groundwater – this is consistent with high total Fe concentration and excess Mg and Ca at pore water profile 2

## Explorative data analysis

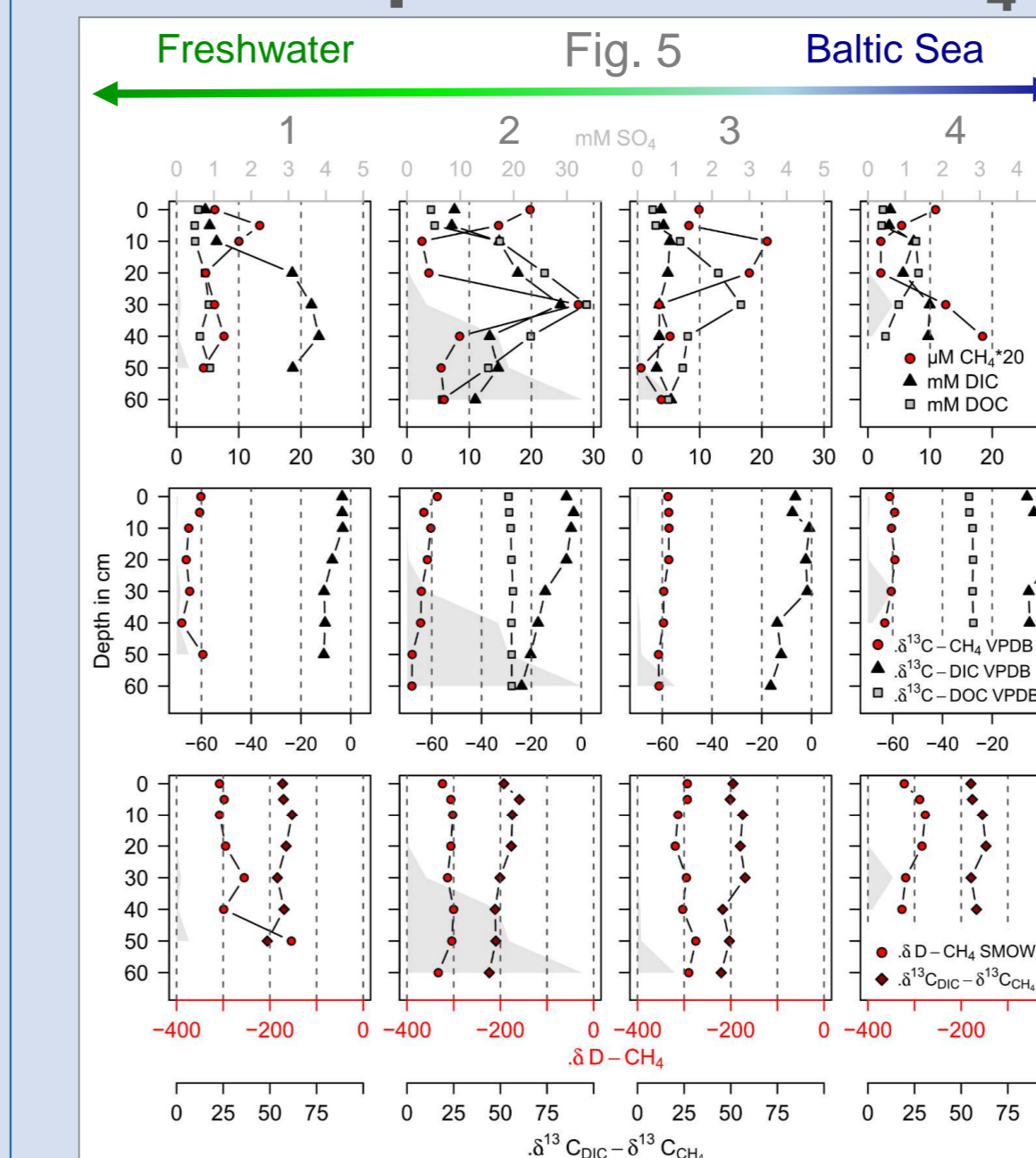
### Distinct geochemical gradients across sediment depth and across the freshwater-Baltic Sea transect



- Distinct depth gradient accounts for 44.0% of the total variation in the data set (component 1) and is strongly correlated with electrical conductivity (EC)
- Differentiation between profiles 1 and 2 and profiles 3 and 4 (component 2) reflects the lateral gradient within the freshwater-Baltic Sea transect and accounts for 26.7% of total variation
- EC at freshwater-dominated profiles is correlated with Mg, Li, S<sub>tot</sub>, SO<sub>4</sub><sup>2-</sup> and DOC whilst EC at brackish water-dominated profiles is highly correlated with Cl<sup>-</sup>, Br<sup>-</sup>, Na and H<sub>2</sub>S
- Geochemical gradient across the freshwater-Baltic-Sea transect is correlated with DIC, Fe, Ca, Mn, Mg, TA and TDN (prevailing at freshwater-dominated profiles) and K and SUVA (specific UV absorbance of DOC, prevailing at brackish-water dominated profiles)
- The distinct depth gradient at profile 2 (1150 m apart from the Baltic Sea coast line) accounts for 9.4% of the total variation in the data set and is associated with the shift of S species, i. e. increasing SO<sub>4</sub><sup>2-</sup> concentration with parallel drop in the residual S fraction (organic S, sulfite, thiosulfate) at depth

## Isotope mass balance calculations

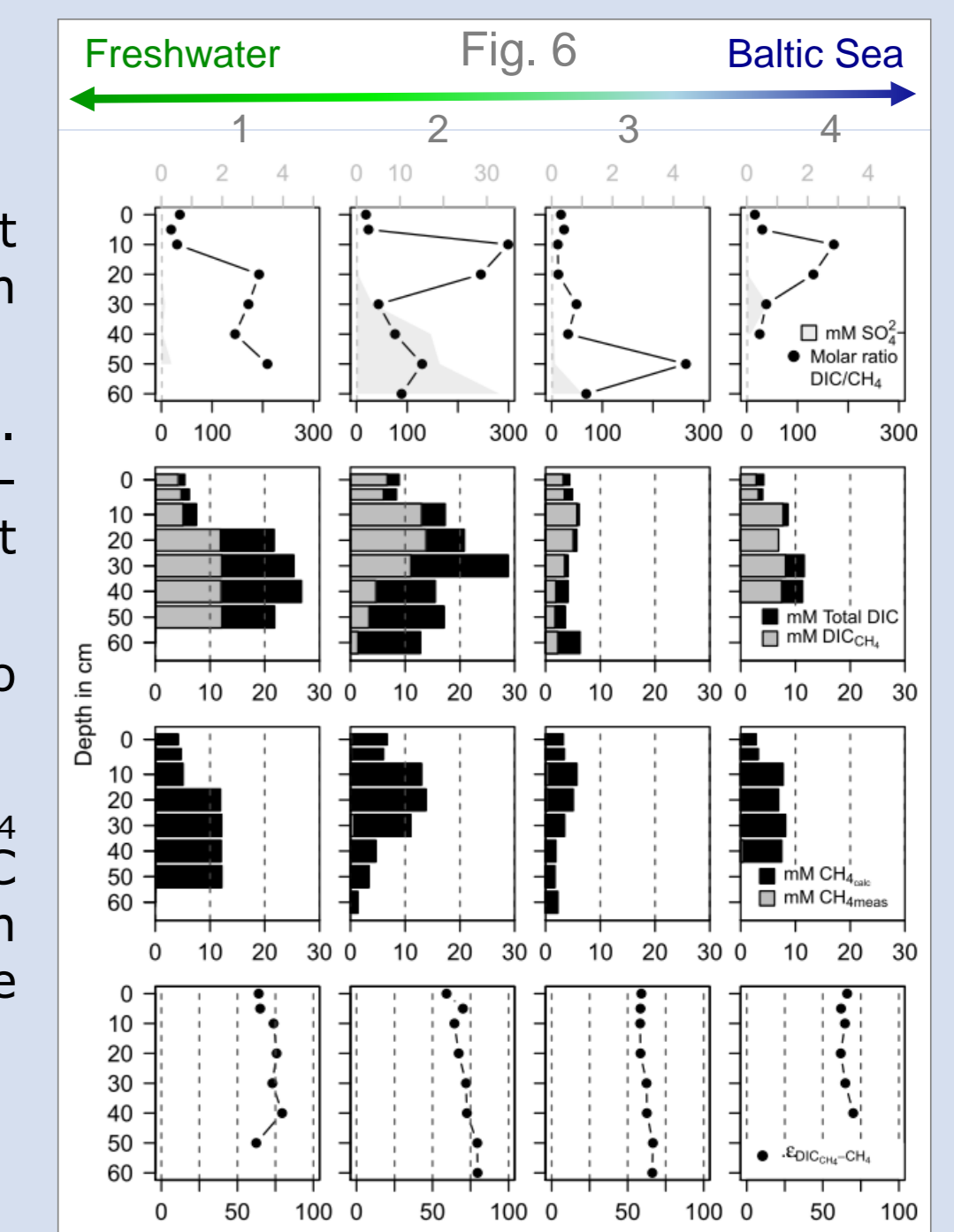
### From top to bottom: CH<sub>4</sub> production vs. SO<sub>4</sub><sup>2-</sup> reduction



- CH<sub>4</sub> concentration profiles were erratic and inconsistent across profiles
- δ<sup>13</sup>C-DIC shifted distinctively from -23.9‰ in the bottom up to +4.2‰ in the top profile
- Microbial CH<sub>4</sub> production is associated with a strong discrimination against <sup>13</sup>C - zones of isotopically heavy DIC in 0-30 cm depth might indicate high CH<sub>4</sub> production rates
- δ<sup>13</sup>C-DIC values below 30 cm approach the <sup>13</sup>C signature of DOC (av. δ<sup>13</sup>C -28.2±0.17‰) – here anaerobic respiration is dominated by non-fractionating processes such as SO<sub>4</sub><sup>2-</sup> reduction and high molecular weight OM fermentation
- CH<sub>4</sub> is depleted in <sup>13</sup>C with increasing depth - lower substrate availability and/or higher abundance of competitive substrates such as SO<sub>4</sub><sup>2-</sup>

### Consideration of non-methanogenic DIC production pathways

- DIC molar ratio >> CH<sub>4</sub> molar ratio – distinct contribution of other anaerobic respiration processes that contribute to the δ<sup>13</sup>C-DIC signature
- Isotope mass balance approach (Corbett et al. 2013) to separate the contribution of non-methanogenic DIC sources and provide more direct proxies for methanogenic pathways
- Non-methanogenic DIC contributes substantially to total DIC, contribution increases with depth
- Isotope separation factors ε<sub>c</sub> δ<sup>13</sup>C-DIC- δ<sup>13</sup>C-CH<sub>4</sub> corrected for non-methanogenic sources of DIC vary between 58.2 and 79.6‰ and increase with depth - increasing dominance of carbonate reduction methanogenesis



## Conclusions

- Freshwater inundation altered the former brackish conditions of the peatland, however, distinct vertical and lateral geochemical gradients still reflect the natural Baltic Sea impact
- SO<sub>4</sub><sup>2-</sup> reduction has exhausted the bulk of Baltic-Sea-derived SO<sub>4</sub><sup>2-</sup> pool, currently, SO<sub>4</sub><sup>2-</sup> reduction might take place only below 30 cm depth, locally very high amounts of SO<sub>4</sub><sup>2-</sup> do not originate from the Baltic Sea but are common for rewetted freshwater fens
- The bulk of CH<sub>4</sub> production occurs in the top 30 cm of the profile above the potential SO<sub>4</sub><sup>2-</sup> reduction zone, methanogenesis becomes less thermodynamically favourable in depth
- CH<sub>4</sub> production and SO<sub>4</sub><sup>2-</sup> reduction zones are spatially separated, hence the CH<sub>4</sub> emission potential of rewetted coastal peatlands depends on the mobility and replenishment of the SO<sub>4</sub><sup>2-</sup> pool - possibly also by non-marine SO<sub>4</sub><sup>2-</sup> sources



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