Air-Sea interaction of methane in shallow brackish inshore waters of the Baltic Sea

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Introduction:

The goal of this study was to establish the role of inshore areas of the Baltic Sea (less than 2 m deep) as a source of methane for the atmosphere and offshore waters for different seasons of the year and sites with varying vegetation and sediment type. The investigation included 5 sampling areas around Askö Laboratory during June-October 2019.

Main questions:

- **What are the contributions of different environmental properties for the sea-to-atmosphere flux of methane during the summer months in near-shore coastal brackish waters?**
- **What are the major sources of methane in the late spring, summer, and early fall? What roles do sediments, cyanobacterial blooms, and local ebullition play for the methane flux? Are there other major sources of methane?**

Methods:

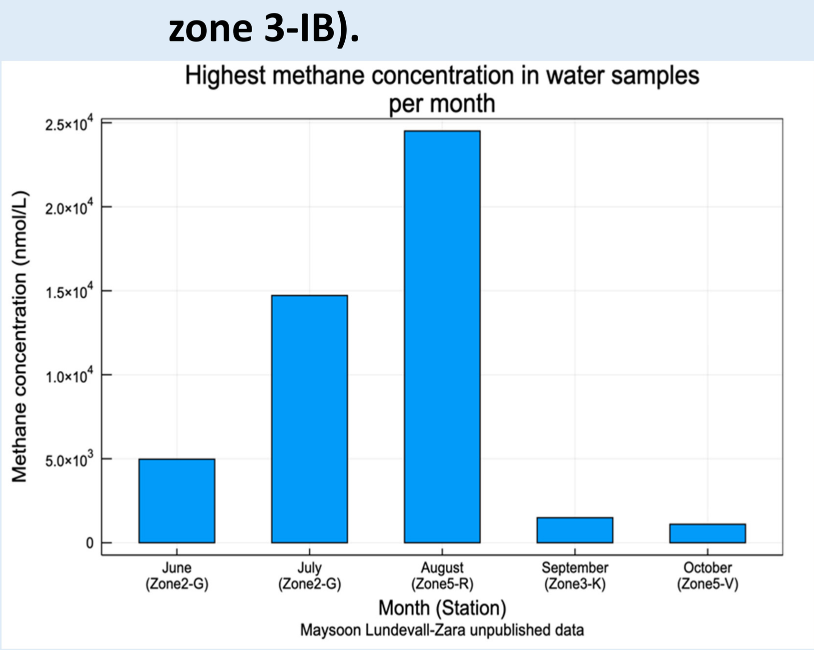
Floating air-flux chambers, with and without bubble barrier, were used to measure methane concentrations with daily measurements over 3-6 days each month. Five sampling areas were categorized into 23 stations. Water and air samples were taken at the same time and analyzed by gas chromatography on a Shimadzu GC-8A with FID detector. Wind data were obtained by SMHI's database (https://www.smhi.se/kustmatsystem/asko) in addition to temperature and salinity data taken with a handheld WTW salinometer.

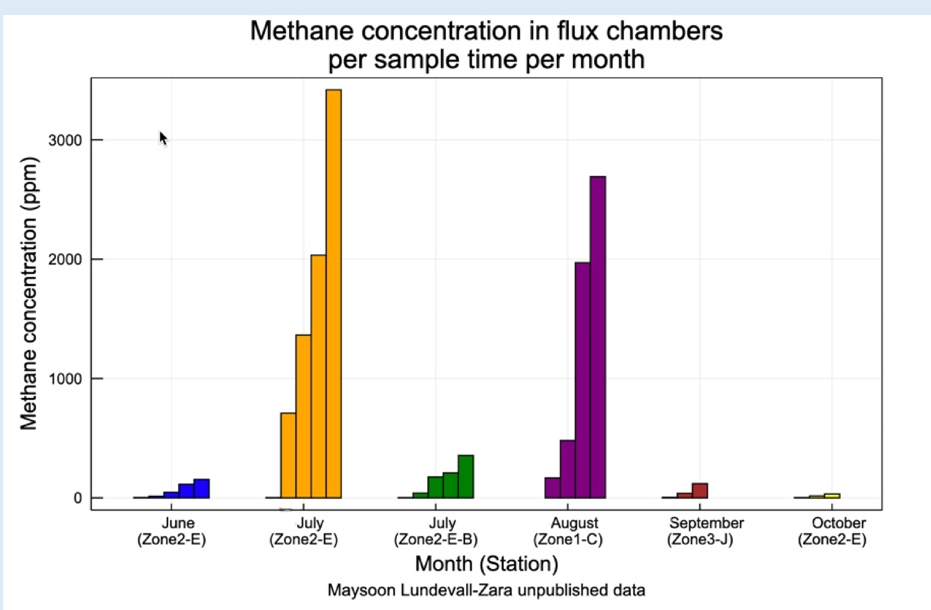
Investigated environments:

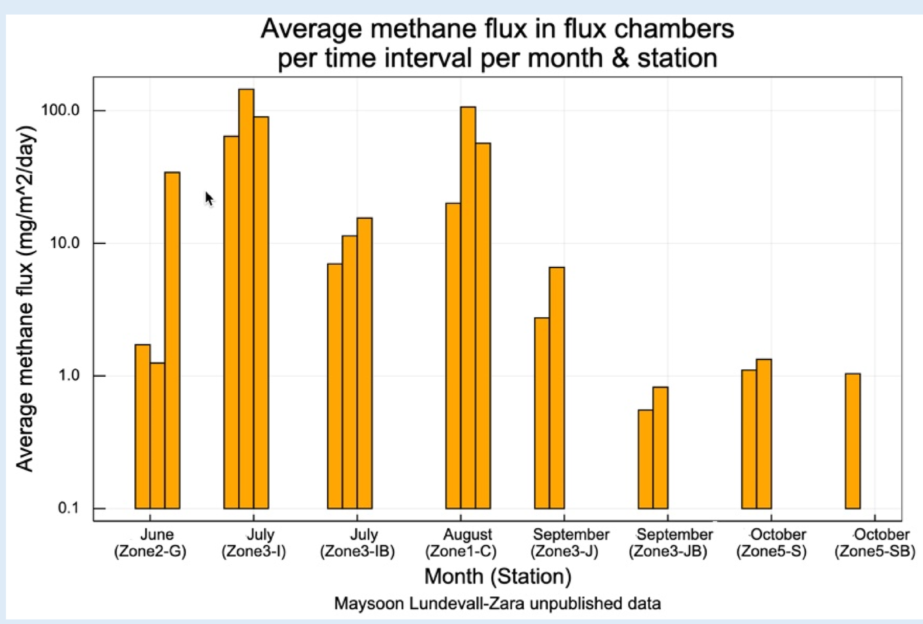
The shore environments consisted of a range of features including bare rocky cliffs, coniferous wood, deciduous trees, reed areas, and inshore water covered with water lilies. In July and August thick layers of algal mats accumulated inshore associated with a smell of H_2S and bubbles appearing on the surface. Water depths were between 0.5 m up to 2 m. Sediment and rock bottom types: vegetated/unvegetated bedrock, organic-rich and organic-poor clays and sands Indicator species and vegetation: dense or sparse vegetation of *Phragmites australis*, *Typha albida, Nymphaea alba,* and during July and August mats of *Archaeplastida* or *Cyanophyceae*

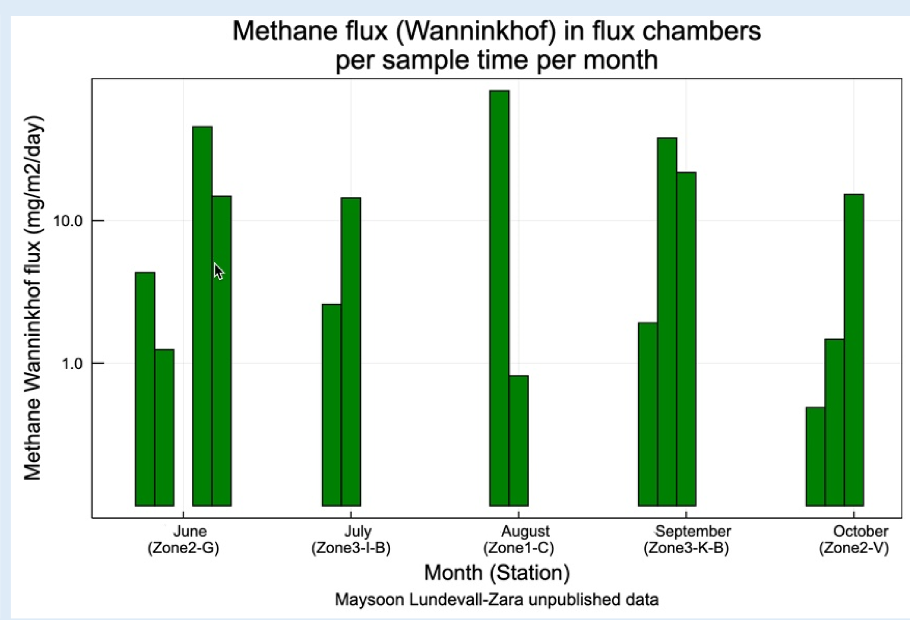
Results:

- **Water concentrations of methane increased through the spring to highest values in August and decreasing again in the fall.**
- **The concentration of methane in the air-flux chamber at the time of deployment was on average 2.55 ppm. The concentration of methane in the flux chambers increased on average after three days to more than 60 ppm. On the other hand, at specific locations with clearly visible bubbles methane concentrations were between 1000-5000 ppm at the end of the deployment periods.**
- **About half of the methane fluxes were between 0.3-29 mg/m²/day in June, July and August, while in September and October fluxes were between 0.2-2.7 mg/m²/day. A number of fluxes were significantly higher than that, up to 296 mg/m²/day. Fluxes in chambers with bubble barriers were always higher than those without barriers (see example zone 3-I and zone 3-IB).**









Equation used for calculation of fluxes from discrete daily air measurements: $F = \frac{conc_{t_{n+1}} - conc_{t_n}}{time_{t_{n+1}} - time_{t_n}}$

Equation used for the calculation of fluxes based on the water-side methane concentration and wind velocity, Wanninkhof Flux: $F = k(C_w - \alpha C_a)$

k=gas transfer velocity, C_w = Concentration in water sample, C_a = Concentration in air sample from flux-chamber, α =Ostwald solubility coefficient.

$k = 0.39u^2(\frac{Sc}{660})^{-0,5}$, u= Wind velocity

Sc= Schmidt number for the gas, $\alpha = \frac{\beta T}{273.15}$, β= Bunsen solubility coefficient, T= Temperature in Kelvin.

Discussion and conclusion:

- **Combination of high wind speeds and presence of rising methane bubbles occurred mostly in July and August, rarely in June and September, and almost never in October.**
- **High (> 1000 ppm) concentrations of methane were analyzed at stations with dense algae mats with and without strong smell of H_2S.**
- **Higher concentrations were measured in flux chambers without bubble barriers than in flux chambers with barriers indicating the contribution of methane bubbles to the methane flux.**
- **The inshore methane fluxes exceed those measured in offshore coastal areas by a factor of 2 to 200 with high variability in space and time (Gülzow et al., 2013). The shallow inshore areas of the Baltic Sea are therefore an important contributor to the total methane flux emitted from the Baltic Sea.**

Future work:

- **Stable isotope analysis of methane; analysis of nitrous oxide and carbon dioxide and their fluxes; microbiological studies of methanogenesis and methane oxidation**

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Reference:

Gülzow, W., Rehder, G., Schneider von Deimling, J., Seifert, T., Tóth, S. (2013) One year of continuous measurements constraining methane emissions from the Baltic Sea to the atmosphere using a ship of opportunity. Biogeosciences 10, 81-99.