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Methane ebullition as the dominant pathway for carbon sea-air exchange in coastal, shallow water habitats of the Baltic Sea

Thea Bisander et al.

Correspondence to: Thea Bisander (thea.bisander@sh.se)

S1. Extended methods: Habitat classification using HELCOM HUB

The HELCOM HUB structure is hierarchical, with the first level “A” representing the Baltic Sea, and the second level, also designated as “A”, is for the photic benthic zone. In level three the habitats are classified based on their bottom substrate. If 90 % of the habitat was covered by a single substrate type, it was assigned that specific classification. Otherwise, it was classified as ‘mixed substrate’. To determine substrate type, a visual assessment was conducted, and for areas deemed to have more than 90 % coverage of a specific soft substrate, surface sediment samples were collected and analysed using a sediment sieve. Based on this classification, the seven sampling locations were grouped into four substrate categories: (1) Coarse sediment, in which >30 % of the sediment had a grain size between 2 and 63 mm (AA.I), (2) muddy sediment, if >20 % was less than 63 μm (AA.H), (3) sand, if none of these two criteria were met and grain sizes between 0.063 and 2 mm dominated (AA.J), and (4) mixed substrate (AA.M).

At level four in HELCOM HUB the percentage of vegetation cover is described. All sampling locations in this study were categorized as having either >10 % coverage of macroscopic epibenthic biotic structures, or sparse epibenthic macrocommunities, between 0 – 10 % coverage. Locations with sparse coverage were not further subdivided at this level. Level five describes the type of vegetation community, with classifications determined visually as emergent vegetation, submerged rooted plants, or perennial algae, depending on the dominant group. At level six, the taxa are to be identified, with species contributing over 50 % of the biomass volume within the dominant vegetation community determining the classification. However, in this study, only locations with submerged vegetation where the dominant taxa could be visually determined were classified to this level.

Ultimately, the seven sampling locations were divided into five distinct habitats based on substrate and vegetation cover: Coarse sediment with perennial algae cover (AA.I1I), sand with sparse epibenthic macrocommunity (AA.J2T), sand with submerged rooted plants (AA.J1C), mixed substrate with submerged rooted plants (AA.M1C) and muddy sediment with emerged plants Phragmites australis (AA.H1A1).

S2. Extended methods: Extrapolation into yearly fluxes

Daily diffusive fluxes were converted to annual fluxes by averaging the daily fluxes from each sampling period to determine monthly fluxes for the month(s) that the sampling period represented. The representativeness of the sampling dates to the month in question was examined by comparison of the locally measured air temperatures and wind speeds with nearby long-term weather observations from the Swedish Meteorological and Hydrological Institute (SMHI) for the years 2020 through 2022 at Skarpö, Gustavsberg and Trosa. Fluxes from unsampled months were linearly extrapolated from adjacent sampled months, except August, which had similar SMHI wind and temperature data as July and was assumed to have the same flux. The monthly average ebullition flux was extrapolated in a similar way as the diffusive fluxes and was assumed to be zero the months where it was not measured. Monthly diffusive and ebullition fluxes were summed to calculate the annual flux at each location.

The months, or parts of the month, where ice cover prevented sampling, were assumed to have zero flux. The mixed substrate habitat D was ice-covered in January and February, and reed habitat F and submerged plant-covered habitat C were ice-covered in January, February, and half of March. Mixed substrate habitat E and the macroalgae habitat A were ice-covered during the first half of January and the sand habitat B was ice-covered for the entire January and for half of February. During these periods, these sampling locations could not be sampled and in the yearly calculations they have been counted as zero fluxes. The channel in reed bed G was never fully ice-covered due to flowing water.

This simple extrapolation method was chosen over a more complex approach using drivers such as temperature or wind speed due to the generally low and heterogeneous relationship between the fluxes and temperature and/or wind (Table S1).

S3. Extended methods: Detection of ebullition

Ebullition events were detected as concentration spikes in the flux measurements. These spikes were similar to those seen recorded by the GGA when the analyser was run in the lab, in a closed loop (inlet and outlet tubes were connected to each other) and three injections of 50 ml 10 ppm CH_4 standard gas was introduced to the system (Fig. S2a).

Diffusive flux curves measured with the GGA in the field and acceptable for flux calculations had linear gradients, lacking peaks and drastic (at least three times the standard deviation of the change from the diffusive flux for a 20 second measurement interval) gradient changes (Fig. S2b). Flux measurements where disturbances by the chamber deployment, gas leakage in the tubing, or other interference could not be ruled out were omitted from further analysis. An example of a discarded experiment is shown in Fig. S2f where spikes appear in both CO_2 and CH_4 concentrations and the surrounding diffusive flux curves are noisy.

The measurement was interpreted to display ebullition when the previous diffusive flux gradient was steady, CO_2 was relatively unaffected at the time of the CH_4 peak and no other interference, as mentioned above, could be inferred (Fig. S2c-e). Ebullition events could either reveal themselves as peaks of CH_4 (Fig. S2c-d) or a step-up in CH_4 concentration (Fig. S2e), and either of these events were further analysed to obtain the ebullition flux.

Table S1. R-square values for linear least-squared relationships between diffusive CH_4 or CO_2 or ebullitive CH_4 (marked in cursive) and the environmental parameters wind speed (U_{10}), water temperature, water depth and distance to shore. For relationships between U_{10} and CO_2, absolute CO_2 values have been used. Bold R-squares indicate statistically significant ($p < 0.05$) relationships. Negative relationships are marked with (-). The relationships with ebullitive flux are only plotted for the locations where sufficient ebullition events to do regression analysis occurred ($n > 3$), and on the fluxes calculated for single ebullition events.

Habitats	**Locations**	U_{10}		**Water temp**		**Water depth**		**Distance to shore**		**Salinity**	
		CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
All		**0.02**	**0.03**	**0.13**	**0.03 (-)**	0.00	0.00	0.01	**0.04 (-)**	0.00	**0.18 (-)**
		0.06		*0.01*		***0.15***		*0.10*		*0.05*	
Coarse sed. - Macroalgae	A	**0.60**	0.09	**0.13**	**0.33 (-)**	0.01	0.00	0.03	0.06	0.01	0.00
Sand – sparse veg.	B	**0.34**	**0.33**	**0.08**	**0.45 (-)**	0.04	0.04	0.00	0.02	0.00	0.04
		0.16 (-)		*0.49 (-)*		*0.11*		*0.06 (-)*		*0.09*	
Sand – subm. plants	C	**0.37**	**0.23**	**0.16**	0.02	0.00	0.03	0.01	0.06	**0.13 (-)**	**0.15**
		0.63		*0.57*		*0.00*		*0.40 (-)*		*0.10*	
Mixed sub. – subm. plants	D	0.02	0.00	**0.22**	0.01	**0.04**	0.03	0.08	0.00	0.06	0.00
		0.16 (-)		***0.49***		*0.31*		*0.37 (-)*		*0.16*	
	E	**0.26**	0.06	0.01	**0.17 (-)**	0.02	0.08	0.01	0.03	**0.16 (-)**	0.07
		0.12		*0.34*		*0.29*		*0.19*		*0.22 (-)*	
Muddy sed. - Reeds	F	0.03	0.02	**0.37**	0.04	0.00	0.03	0.04	0.04	0.05	**0.21 (-)**
	G	0.01	**0.14**	**0.13**	0.01	0.05	**0.13**	0.00	0.01	0.02	0.05

Figure S1: Pictures of the floating chamber (a) and of the sampling locations (b-i).

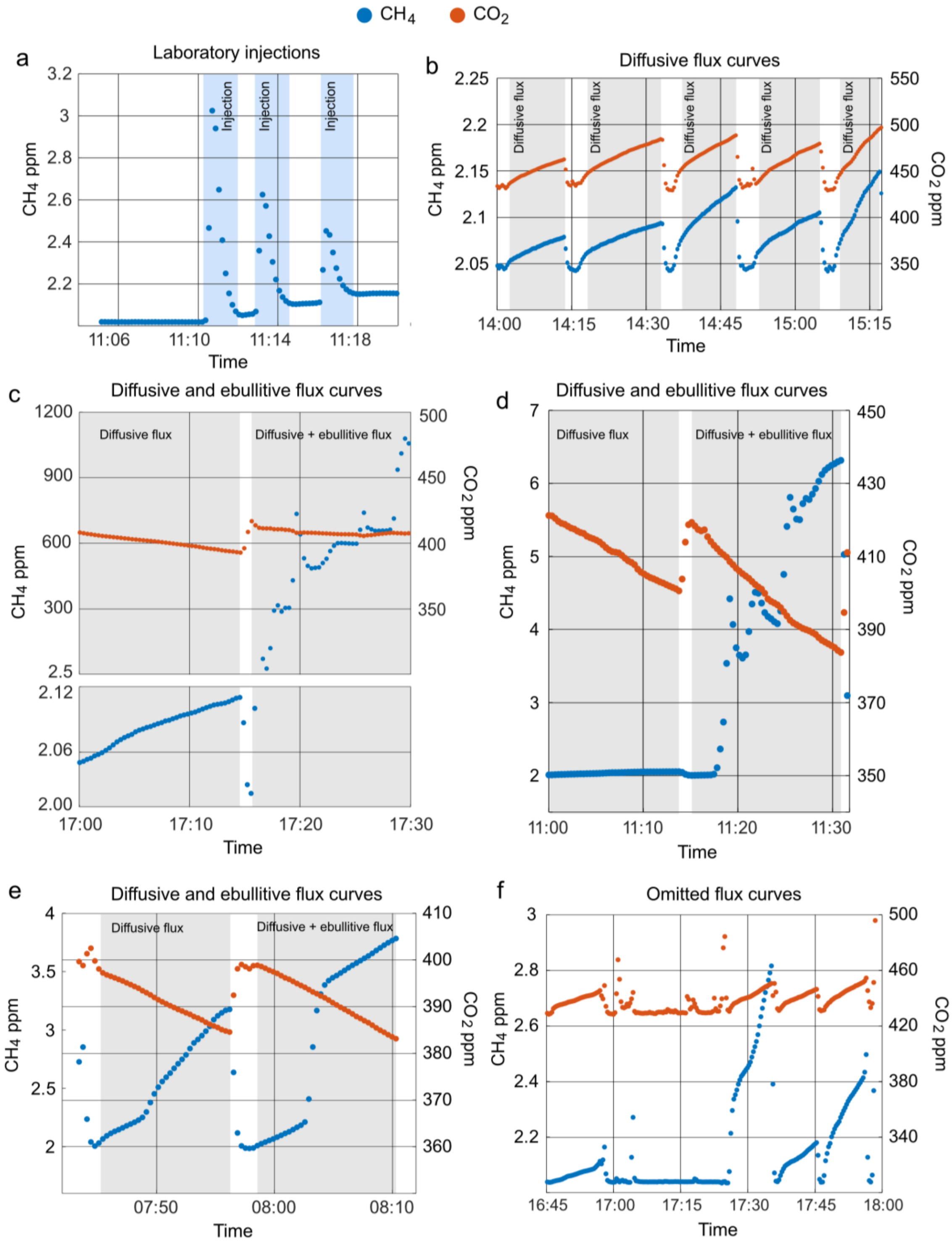

Figure S2. Raw data from the GGA showing a) a laboratory experiment where standard gas was injected in a close loop, b) diffusive flux curves in the field, c-e) diffusive and ebullitive flux curves in the field, and f) flux curves that were omitted since instrument errors or other interferences could not be ruled out.

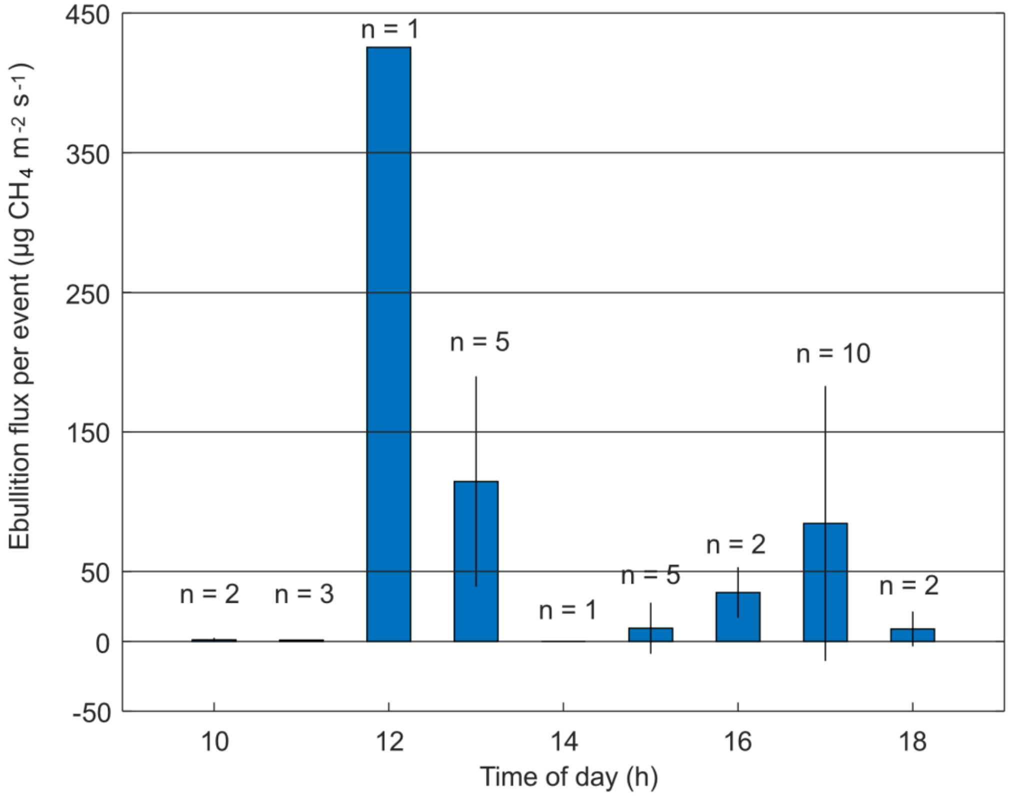

Figure S3. CH_4 released per ebullition event as a function of time of day. The data is from all periods and all locations.