

Waterside convection and microbial consumption control the fate of Nord Stream pipeline methane in the Baltic Sea until early winter

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Article

Keywords:

Posted Date: October 9th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10703963/v1>

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Additional Declarations: No competing interests reported.

Abstract

On 26 September 2022, explosions ruptured the Nord Stream 1 and 2 pipelines in the Baltic Sea, releasing an estimated 496 kt of methane. While the total release and its initial split between atmosphere and ocean have been quantified, the subsequent fate of the fossil methane dissolved in seawater remained unclear. Here we compare data from two surveys in October 2022 and January 2023, using methane concentrations and the distinct isotopic offset of the fossil methane from the natural background to trace its pathways during the seasonal transition from summer stratification to winter mixing. During that period, the fate of pipeline-released methane depended strongly on changes in water mass stratification: in shallow, well-mixed areas, most fossil methane had escaped to the atmosphere, while in deeper, stratified waters, cooling and downward convection mixed fossil methane from the surface back into deeper layers. The water mass below the seasonal thermocline remained unaffected by mixing and acted as a temporary buffer for fossil methane. Below the halocline, fossil methane trapped near the leak sites was intensely oxidized by microbes, evidenced by an extreme enrichment in ^{13}C of the residual methane pool.

Introduction

On 26 September 2022, three explosions damaged the Nord Stream 1 pipeline (Fig. 1) and one the Nord Stream 2 pipeline (not shown in Fig. 1), both located in the Bornholm Basin of the Baltic Sea within the Swedish and Danish economic zones. The pipelines, running offshore from Russia to Germany and pressurized with natural gas (> 96% methane) at the time, began leaking from four strings simultaneously. The explosions were detected by several Danish and Swedish seismic stations and by large bubble plumes formed at the sea surface which were observed by aircraft and satellites (Abrahamsson et al., 2024; Harris et al., 2025; Mohrmann et al., 2025). In-situ airborne measurements (Reum et al., 2025) and satellite observations (Jia et al., 2022; Dogniaux et al., 2024; MacLean et al., 2024; Wilson et al., 2024) were used to constrain rupture emission rates and to integrate estimates of methane dissolution and sea-surface outgassing to model the evolution of atmospheric emissions from the leaks (Harris et al., 2025). Further, ship-based investigations and autonomous glider measurements starting after the Nord Stream pipeline explosions were conducted to quantify the entrance of fossil methane into seawater and to capture the size and shape of the methane plume formed therein after the explosions (Abrahamsson et al., 2024; Mohrmann et al., 2025). Combined, these observations provided a quantitative framework for estimating the magnitude and partitioning of methane released to the atmosphere and the marine environment.

In total, 496 ± 14 kt of fossil methane are estimated to have been released into the natural environment, constituting the largest single-event methane emission recorded in recent times (Harris et al., 2025). It is further assumed that more than 90% of the fossil methane rapidly crossed the water column, which was between 70 and 80 m deep, as bubble current and hence vented directly to the atmosphere after bubble bursting (Dissanayake et al., 2023; Harris et al., 2025). Depending on the leak site, bubble bursting ceased at the sea surface after 3–7 days, i.e., between 1 and 4 October 2022 (Harris et al., 2025; Reum et al., 2025).

Contemporaneously during bubble ascent, methane dissolution occurred, leaving fossil methane in seawater once the bubble current stopped. Shown by an enhancement of concentration in dissolved methane several orders of magnitude above the natural background level, a total estimated amount of 9–15 kt of fossil methane was taken up by seawater after the gas pipeline leaks (Abrahamsson et al., 2024). This portion of fossil methane, trapped in plumes around the explosion sites, remained enclosed in seawater far beyond the emission phase (Abrahamsson et al., 2024; Mohrmann et al., 2024; Harris et al., 2025). Previous studies quantified the magnitude of the Nord Stream methane release and its initial partitioning between atmosphere and ocean. However, the subsequent fate of dissolved fossil methane in seawater remained unresolved. Here we focus on pathways of fossil methane in seawater in the period between autumn and winter when the onset of cooling triggers the seasonal transition from a stratified water column to a vertically mixed water column. We discuss how both the physical impact of surface water turbulence and vertical convection of water layers, and the microbial oxidation activity in isolated water layers affected the pathways of fossil methane and give an outlook on a potential final fate of this fossil methane in the marine methane pool of the western Baltic Sea.

Results and Discussion

1. Seasonal hydrographic transition

In the southwestern Baltic Sea, water masses are mainly controlled by in- and outflow from the North Sea and the inner Baltic Sea, as well as freshwater from surrounding catchments. This regional setting regulates the lateral and vertical exchange of water masses, including the retention of dissolved substances therein (Meier et al., 2006; Meier et al., 2011). The water masses are additionally seasonally modified, with persisting stratified conditions during the warm seasons while cooling and wind forcing favour convection and vertical mixing in cold seasons (Burchard et al., 2008). The hydrographic data from October 2022 reflect a typical late summer to early autumn situation, where a stable thermocline and halocline preserved four distinct water layers (Abrahamsson et al., 2024). Thus, a warm and fresh surface water (SW) layer overlay a slightly cooler and slightly more saline subsurface water (SSW). The onset of cooling started the mixing of SW and SSW, shifted the thermocline down to 45 m and, by January, had formed a winter mixed layer (MW) down to this depth. Then the thermocline separated the MW from the intermediate water (IW) underneath. Hence, the IW remained unaffected by vertical mixing from the time of the explosion event in autumn until January (Fig. 2; Fig. 3; Table 1). However, as winter progresses, ongoing cooling drives convective mixing that forces the thermocline further downwards. If this cooling is sufficiently intense, the deepening thermocline potentially homogenizes the entire IW with the MW at the end of the winter (Gülzow et al., 2014). In shallow regions, winter mixing extended down to the halocline until December (Mohrmann et al., 2024), while in deeper waters the IW was still localized between the thermocline on top and the halocline at the bottom in January. Underneath the halocline, Bottom Water (BW) remains separated from seasonally induced changes in hydrographic conditions during most years (Gülzow et al., 2013; Fig. 2; Fig. 3; Table 1).

Table 1
Water layers in autumn 2022 and early winter 2023

Layer	Depth (m)		Temperature (°C)		Salinity		Density (kg m ⁻³)	
	Oct	Jan	Oct	Jan	Oct	Jan	Oct	Jan
Surface Water (SW)	0–20 m		15.2 ± 0.2		7.5 ± 0.1		4.8 ± 0.1	
Subsurface Water (SSW)	20–43 m		10.8 ± 3.8		8.1 ± 1.7		5.8 ± 1.3	
Mixed Water (SW + SSW; MW)	0–43 m		6.4 ± 0.4		7.7 ± 0.4		6.1 ± 0.1	
Intermediate Water (IW)	43–60 m	43–65 m	9.7 ± 1.8	10.0 ± 1.6	10.6 ± 1.6	11.9 ± 1.9	8.0 ± 1.1	9.1 ± 1.4
Bottom Water (BW)	60–74 m	65–86 m	8.7 ± 1.7	11.0 ± 0.8	14.0 ± 1.0	15.8 ± 0.8	10.8 ± 0.6	11.9 ± 0.6

2. Methane pools in seawater

The widespread release of microbially produced methane from sediments results in an excess of methane in seawater relative to the atmospheric equilibrium concentration. In general, the SW is only slightly supersaturated, at around 10 nM and the resulting sea-air flux is therefore less pronounced. However, the pool of marine methane varies between regions and seasons (Bange, 2006; Schmale et al., 2010; Jakobs et al., 2013). The stable carbon isotopic signatures (in the following written as isotopic signature; $\delta^{13}\text{C-CH}_4$) of methane in seawater range between – 47‰VPDB and – 68‰VPDB and reflect its microbial source, as microbes preferentially utilize ¹²C during methanogenesis (Whiticar, 1999; Pataki et al., 2003; Gülzow et al., 2013; Jakobs et al., 2014). By comparison, the global atmospheric background isotopic signature varies between – 45 and – 47‰VPDB (Lan et al., 2023). During both campaigns, both concentrations and isotopic signatures at the background stations corresponded to those from former studies in this region (Gülzow et al., 2013; Gülzow et al., 2014; Jakobs et al., 2014, Henriksson et al., 2026; Fig. 1; Table 2; Table 3).

The detonation of the Nord Stream pipelines in late September 2022 added locally large amounts of fossil methane to the marine background methane pool. Immediately after these events, methane concentrations in seawater increased to an average of 3500 nM, with peaks of up to 20000 nM forming plumes around the explosion sites. Crucially, this pipeline-released methane, with an isotopic signature of -37‰ VPDB , featured a pronounced depletion in ^{12}C compared to the marine background (Abrahamsson et al., 2024; Damm et al., 2024), revealing its thermogenic, i.e. fossil origin (Whiticar, 1999). This clear isotopic offset enabled, to a certain extent, the tracing of pathways of fossil methane in the marine environment during the seasonal transition of the water column. The chronological tracking of the plume's isotopic evolution in January thus effectively constrains the processes that mitigated the fate of fossil methane in the natural methane pool months after the pipeline leaks.

2.1 Loss to the atmosphere vs. merging of fossil methane in the Winter Mixed Layer (MW)

The explosive release transported methane toward the surface in rapidly rising bubbles. When the power of the explosion slowed down, visible surface bubbling ceased as the bubble flux weakened and progressive dissolution reduced the size of bubbles that still remained in the surface water. The behaviour of such bubble plumes has been described in experimental and field studies, demonstrating that fragmentation near the surface enhances gas transfer into the surrounding surface water (Rehder et al., 2009). This process produced a counterintuitive vertical pattern within the water column shortly after the explosion: the fossil methane reached the highest concentration in surface waters (Abrahamsson et al., 2024; Table 2; Table 3). The distinct supersaturation related to the atmospheric background induced a continued sea-air flux of fossil methane even after bubble bursting ceased at the sea surface. Remarkable flux rates of $35 \pm 25 \text{ nmol m}^{-2} \text{ s}^{-1}$, approximately two orders of magnitude higher than the natural background, point to an ongoing sea-to-air gas exchange in early October 2022 (Abrahamsson et al., 2024). Enhanced gas transfer efficiency by surface turbulence and wave breaking (Wanninkhof, 2014) favours sea-air flux in shallow and coastal areas (Bange et al., 1994; Bange, 2006; Weber et al., 2019). Indeed, by January more than 90% of fossil methane detected in October had escaped to the atmosphere at the shallowest station. There, background values throughout the whole water column indicated that the sea-air flux had effectively ceased in shallow areas by this time (Fig. 3; Fig. 4; Fig. 5). Although the methane concentration strongly decreased to background levels, the isotopic signature reveals that the methane originated from the fossil methane source. Moreover, the isotopic signature of the residual fossil methane pool in shallow water showed a slight shift. While, a week after the explosion, methane with the fossil signature of -37‰ VPDB persisted throughout the whole water column (Damm et al., 2024), a relative ^{13}C enrichment up to 5‰ was observed in January (Fig. 3; Fig. 4). This shift might result from a kinetic isotopic fractionation (KIF) during the ongoing sea-air flux over the previous months. KIF occurs during gas transfer at the sea-air interface because $^{12}\text{C-CH}_4$ escapes preferentially over $^{13}\text{C-CH}_4$, owing to its lower molecular mass (Knox et al., 1992; Happell et al., 1995). Consequently, the residual fossil methane in shallow water became enriched in $^{13}\text{C-CH}_4$.

By comparison, in regions with deeper water, wind-driven turbulence and wave breaking decline (Wanninkhof, 1992). Consequently, the impact of sea-air flux slowed down while vertical mixing induced by water convection became relevant for the fate of fossil methane still stored in SW and SSW. The onset of cooling in autumn weakened the stratification between both water layers and eventually formed the MW (Fig. 2; Fig. 3; Table 1). Accordingly, a portion of fossil methane, originally accumulated in SW, subsequently moved downward by water convection. Eventually, the vertical mixing of SW and SSW redistributed and mixed fossil methane into the natural methane pool within the newly formed MW. The heterogeneous methane distribution in MW in January 2023 reflects the ongoing mixing of SW and SSW, as well as of the fossil and marine methane pools, at that time (Fig. 3; Table 2; Table 3). However, the progressive mixing of fossil methane into the marine methane pool is clearly shown by the shift of the isotopic signature of methane in MW towards a ^{13}C enrichment compared to the background values and towards a ^{12}C enrichment compared to the initially fossil methane (Fig. 4). Hence, apart from the coastal station, the initial isotopic signature of fossil methane is missing in MW, as fossil methane is taken up and mixed into the natural background pool, which, conversely, means that the isotopic signature of the marine background pool in this region becomes finally enriched in ^{13}C (Fig. 3; Fig. 4).

2.2 Storage and lateral transport of fossil methane within Intermediate Water (IW)

Compared to the SW, only a small proportion of bubble-mediated methane became dissolved within the IW immediately after the explosion. Therefore, only patchy spots of fossil methane were observed in October 2022 in this water mass (Abrahamsson et al., 2024). Those spots of fossil methane were still preserved during ongoing lateral spreading in regions with deeper water, while, by comparison, in shallow regions, convective deepening of the MW down to the halocline caused outgassing of fossil methane formerly stored in the IW, until December 2022 (Mohrmann et al., 2025). However, in regions where the seasonal thermocline at 45 m still existed in January 2023, the portion of methane originally trapped in the IW remained decoupled from surface-driven processes (Table 2; Table 3; Fig. 3; Fig. 5). Furthermore, a pattern opposite to that in October 2022 existed in January 2023, as then the IW was higher charged with methane than the overlying MW (Figs. 3 & 5). However, this relative change between both water masses over time is mainly driven by processes coupled to the formation of MW as described above. A simplified budget based on the excess methane relative to background values related to the volume of IW calculated for October 2022 and January 2023 reveals a decrease from 94.2 t CH₄ to 0.8–2.5 t CH₄ over three months. This corresponds to a reduction of more than 95% of the fossil methane initially stored in IW in this area. The loss is mainly driven by lateral transport within the water mass, away from the leak sites, while the vertical loss can be assumed to be small, as the thermocline above and halocline below restricted vertical exchange. This assumption is corroborated by the homogeneous isotopic signatures of the methane spots. As shown for MW, vertical mixing of water masses alters the isotopic composition therein. Instead, the observed pattern is consistent with lateral transport of fossil methane within the IW beyond the spatial extent of the sites influenced by the pipeline explosions (Mohrmann et al., 2025). Hence, the IW functions as buffer, while the fossil methane enclosed therein may serve as a tracer for future studies investigating evidence of the leaks during longer-term lateral spreading into the inner Baltic Sea or westward to the Kattegat.

2.3 Microbial Consumption of fossil methane in Bottom Water (BW)

The October 2022 cruise had to circumnavigate a safety radius around the leak sites, and the measured BW appeared unaffected by the fossil gas (Abrahamsson et al., 2024). Yet, the inclusion of deeper stations during the January survey successfully captured the regions close to the leak sites (Fig. 1). Here, an extraordinary ¹³C enrichment within the BW relative to background signatures (mean $\delta^{13}\text{C-CH}_4 \sim -51.1\text{‰ VPDB}$) demonstrated a strong, localized modification of the methane pool following the Nord Stream gas release. It shifted the $\delta^{13}\text{C-CH}_4$ values considerably from background values to a mean of -1.4‰ VPDB and a maximum of $+63.9\text{‰ VPDB}$ (Fig. 3; Fig. 4; Table 2). These extreme isotopic signatures observed in the BW of these stations in January were linked to comparatively low methane concentrations. Such a coupling of low methane concentrations and enrichment in ¹³C points to a highly accelerated microbial oxidation, driven by the preferential microbial uptake of ¹²C-CH₄ (Coleman et al., 1981). The isotopic shift we observed below the halocline strongly suggests that a substantial fraction of the fossil methane that entered and became trapped below the halocline immediately after the pipeline leaks formed a pool that was subsequently oxidized by the microbial community over the following months.

In the Baltic Sea, methane oxidation by microorganisms is frequently observed (Jakobs et al. 2014; Gustafsson et al. 2024; Ketzer et al., 2024; Henriksson et al. 2026) and methane oxidation rates are influenced by, e.g., stratification, redox zones, and seasons (Jakobs et al., 2014). Jakobs et al. (2014) reported elevated methane oxidation rates within the redox zone compared to lower values in the oxic and anoxic zone of the water column, and $\delta^{13}\text{C-CH}_4$ values ranging up to near-zero at Landsort Deep. Thus, while microbial fractionation under low methane concentrations in hypoxic deep waters is a known feature in the Baltic Sea (Gülzow et al., 2014; Henriksson et al., 2024), the extreme $\delta^{13}\text{C}$ enrichment in our data vastly exceeded these previously reported values. This microbial response was likely triggered by the high availability of fossil methane. This intense consumption is reflected by the Rayleigh distillation model (Fig. 4B), whose close agreement with the observed data supports that microbial oxidation acted as the primary control on methane loss and isotopic enrichment in the BW.

Table 2
Averages, ranges and standard deviations of the stable carbon isotopic signature of methane (‰VPDB) in different water layers at plume and background stations

		Background stations		Plume stations	
		October 2022	January 2023	October 2022	January 2023
SW	Mean	-52.4		-37.5	
	Range	-58.1 to -44.1		-44.3 to -35.1	
	SD	3.8		1.7	
SSW	Mean	-60.0		-49.2	
	Range	-67.1 to -45.9		-64.3 to -37.0	
	SD	6.1		10.4	
MW	Mean		-45.3		-47.4
	Range		-58.4 to -49.7		-58.8 to -33.5
	SD		2.2		5.3
IW	Mean	-61.1	-46.8	-53.0	-34.5
	Range	-68.9 to -58.9	-56.5 to -30.3	-65. to -36.3	-55.4 to -3.0
	SD	3.2	11.4	10.5	13.5
BW	Mean	-59.7	-51.1	-57.0	-1.4
	Range	-75.0 to -44.8	-60 to -40.5	-71.9 to -42.7	-44.0 to + 63.9
	SD	9.4	7.2	10.6	27.9

Table 3
Averages, ranges and standard deviations of the CH₄ concentrations (nM) in different water layers at plume and background stations

		Background stations		Plume stations	
		October 2022	January 2023	October 2022	January 2023
SW	Mean	9.8		2638.1	
	Range	7.3–20.8		19.8–17681.8	
	SD	3.9		4126	
SSW	Mean	27.0		2169.5	
	Range	13.0–50.6		13.0–17681.8	
	SD	10.2		4878.3	
MW	Mean		5.1		7.6
	Range		4.5–6.5		2.8–18.8
	SD		0.8		3.6
IW	Mean	56.3	25.1	1211.3	25.3
	Range	26.6–135.5	8.0–49.1	12.5–12716.8	5.4–73.5
	SD	32.9	16.5	2954.2	13.8
BW	Mean	106.5	26.5	142.2	11.8
	Range	6.9–252.5	18.5–39.2	36.5–318.8	1.1–43.1
	SD	73.5	7.8	78.4	11.6

Outlook and conclusions

The sudden rupture of the Nord Stream pipelines introduced a local plume of methane around the leak sites in the Baltic Sea, distinct from the surrounding marine methane background in both concentration and stable carbon isotopic signature. We used this distinct isotopic offset to trace the pathways of the fossil methane within the water column during the seasonal transition from autumn to winter.

In shallow regions, ongoing outgassing reduced the content of fossil methane in the water. By comparison, in deeper water masses, stratification inhibited the sea-air flux of fossil methane in early autumn. The onset of cooling later in the season shifted the thermocline further downward and, contemporaneously, drove a retransport of fossil methane from surface water back into deeper waters. Below the seasonal thermocline, the water remained unaffected by mixing, and the decline in methane concentration until January 2023 instead pointed to lateral transport away from the leak sites. Hence, this water mass functioned as a temporary buffer for fossil methane as long as a thermocline persisted in winter.

The portion of fossil methane enclosed in bottom water remained decoupled from seasonal convection by the halocline. There, intense microbial consumption induced an extraordinary ¹³C enrichment of methane relative to background signatures, indicating that a substantial fraction of the original pipeline methane was initially trapped below the halocline after the explosions.

The pronounced isotopic deviation of Nord Stream- leaked methane from the natural background will enable the tracing of fossil methane during its journey within the Baltic Sea.

Methods

Our sampling took place on the research vessel (RV) Skagerrak on 3–5 October 2022 and 9–12 January 2023. During both cruises, 20 stations northeast of the island Bornholm were sampled, using different station grids for each cruise (Fig. 1), and comprising stations influenced by the Nord Stream pipeline leak and background stations representing unaffected conditions typical of the central Baltic Sea. Profiles of salinity and temperature in the water column were recorded by a Sea-Bird SBE911, a conductivity–temperature–depth (CTD) system. Water samples for the analysis of concentrations of dissolved methane and $\delta^{13}\text{C-CH}_4$ values were taken from up to 10 discrete water depths across the entire water with Niskin bottles mounted on a rosette sampler. The deepest bottles were closed at about 1–2 m above the sea floor. The selection of water sampling depths was determined taking the thermocline and halocline depths into consideration. Sampling procedure was performed as follows: Seawater from the rosette was filled in 500 ml glass vials, sealed with rubber stoppers, and crimped with aluminium caps. Care was taken to avoid any bubbles. A head-space was created by injecting 20 ml hydrocarbon free synthetic air while at the same time water was pushed out via a second needle to balance the pressure. When equilibrated, a subsample was removed with a gas tight syringe and injected to the Small Sample Isotope Module (SSIM) coupled to a Picarro G2132-i cavity ring-down spectrometer. For calibration, we used standard gas mixtures with different concentrations (Fa. Linde), and standard gas mixtures with isotopic ratios of – 25‰ vs. VPDB, – 45‰ vs. VPDB and 69‰ vs. VPDB (Fa Airgas). Considering the complete sampling procedure, the overall total uncertainty was < 5% estimated on duplicates. The calculation of the dissolved methane concentration followed Wiesenburg and Guinasso (1979).

A Rayleigh distillation model. i.e., $\delta^{13}\text{C-CH}_4 = (1/\alpha - 1) * \ln f + (\delta^{13}\text{C-CH}_4)_0$ is used to calculate the $\delta^{13}\text{C}$ signature of methane which results when methane is being microbially consumed (α , the isotope fractionation factor 1.02 and 1.005); f is the fraction of methane remaining, $(1-f)$ is the methane consumed by oxidation and $(\delta^{13}\text{C-CH}_4)_0$ is the initial isotopic composition).

A Keeling type plot is used to calculate the mixing between two assumed end-members. The calculated mixing trend is compared with the measured values to illustrate potential mixing of methane of different isotopic signatures.

To quantify the temporal evolution of methane storage within the IW, a simplified methane inventory was calculated for October 2022 and January 2023 based on excess methane concentration relative to background conditions and the estimated volume of the IW layer.

$$\text{M}_{\text{IW}} = \left(C_{\text{IW}} - C_{\text{bg}} \right) * V_{\text{IW}}$$

With C_{IW} = mean concentration IW plume, C_{bg} = mean background concentration from background station, V_{IW} = Volume IW

V_{IW} = plume area x thickness

With plume area: 300 km² (Abrahamsson et al., 2024) and IW thickness in October 2022 (17 m) and January 2023 (22 m).

Declarations

Author Contribution

A.S and E.D. carried out the methane measurements, analyzed the methane data, wrote the initial draft and provided the figures. K.A. provided funding and ship time. A.S., E.D., K.A., C.B. and A.L. were involved in the scientific discussions, and in revising the manuscript.

Acknowledgement

This work was funded by the Innovationsgesellschaft Technische Universität Braunschweig, Germany and University of Gothenburg, Sweden. We would like to thank the crew on RV Skagerrak, University of Gothenburg, for their support.

Data Availability

The datasets of the October 2022 survey are available on PANGAEA (Damm et al., 2024; <https://doi.org/10.1594/PANGAEA.964690>). The data of the January 2023 survey will be available in the PANGAEA repository and will be given a DOI number after publication.

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Figures

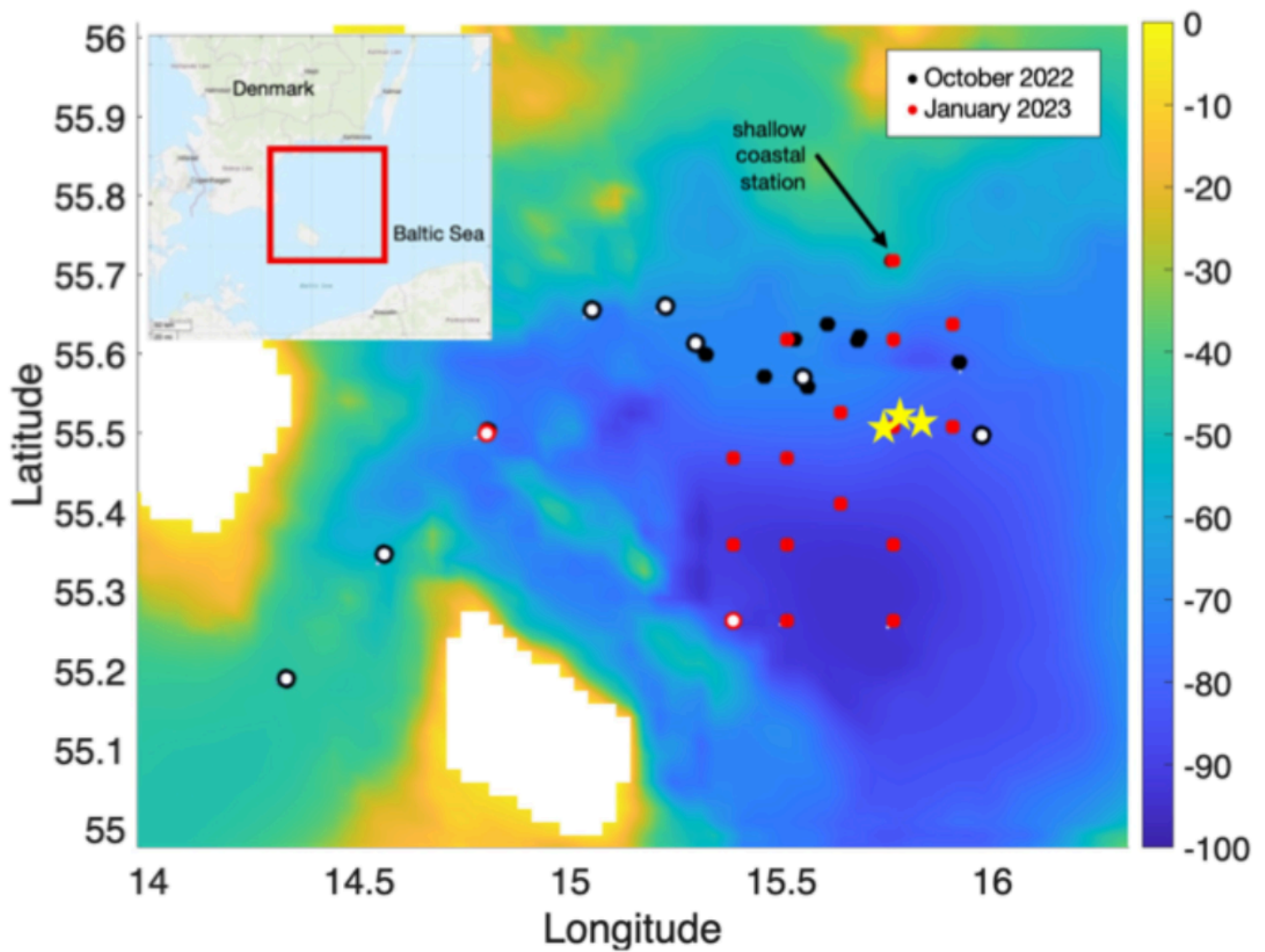


Figure 1

Station grids of two research cruises aboard the RV Skagerak in the southwest Baltic Sea. The first one (black filled dots) was carried out 7 days after the explosions of the North stream pipeline on 26 September 2022, outside of the restricted area during that time within the Swedish EEZ. During the second cruise in January 2023 (red filled dots), stations were directly positioned above former explosion sites (yellow stars) and within the Bornholm basin. Open black and red dots give the positions of stations uninfluenced by the explosion events, in the following called background stations. The color bar indicates the water depth in m.

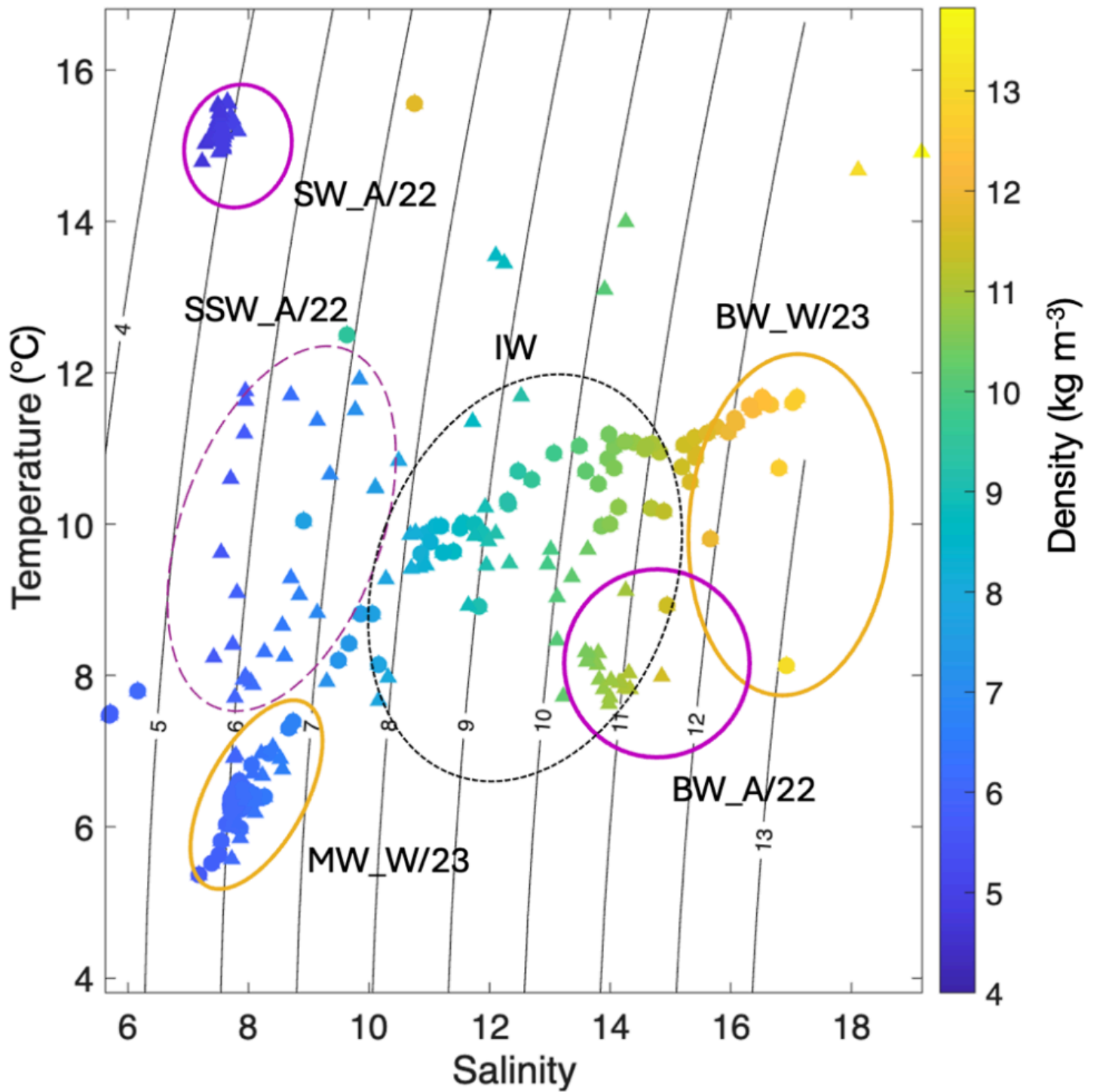


Figure 2

Temperature–salinity (T/S) diagram from October 2022/ autumn (A; triangles) and January 2023/ early winter (W; circles), respectively. The color-codes and the isopycnals give the calculated potential density. Water masses are classified in Surface Water and Subsurface Water in autumn (SW_A/22; SSW_A/22), Mixed Water Layer during early winter (MW_W/23), Intermediate Water in autumn and early winter (IW), and Bottom Water in autumn (BW_A/22) and early winter (BW_W/23) (see Table 1). Seasonal deviations in BW result from different sampling sites between both cruises (see Fig. 1).

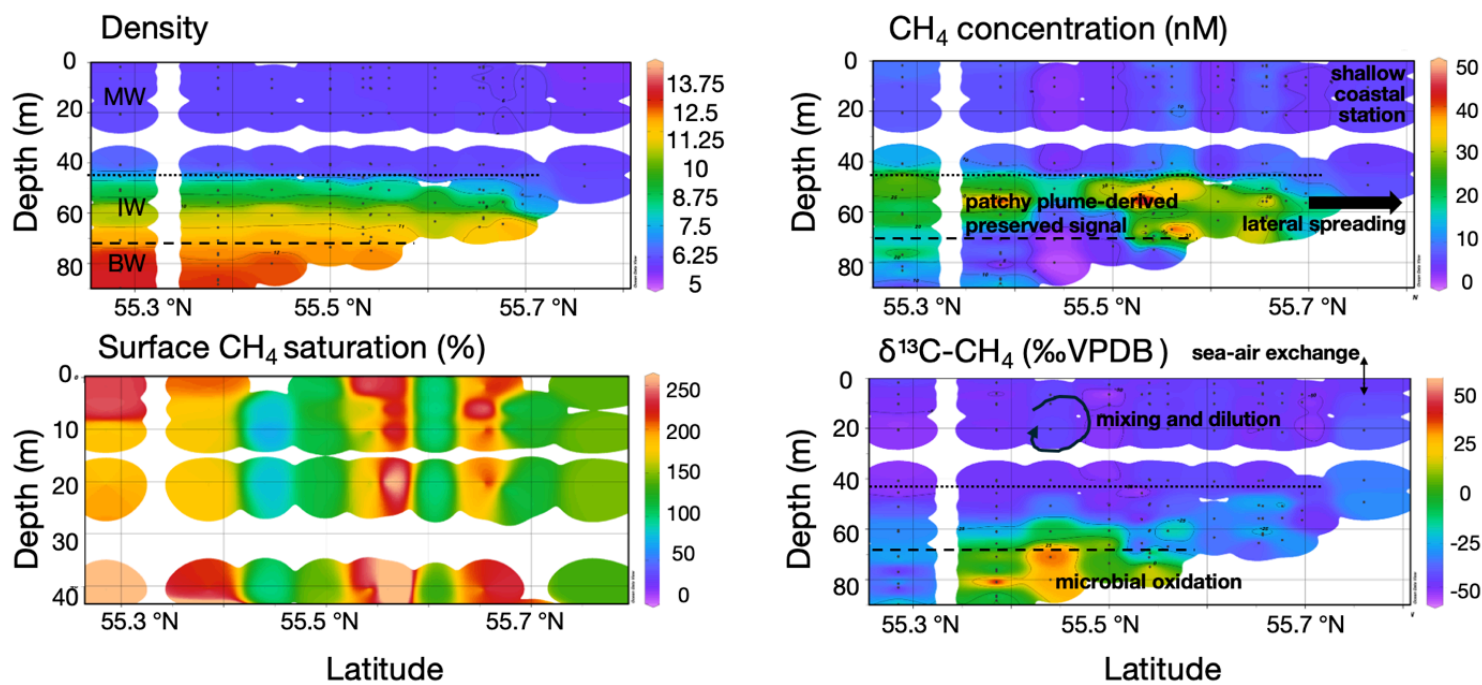


Figure 3

Potential density (A), CH_4 concentration (B), CH_4 saturation (C), and $(\delta^{13}\text{C}-\text{CH}_4)$ (D) in early winter 2023. White areas indicate data gaps.

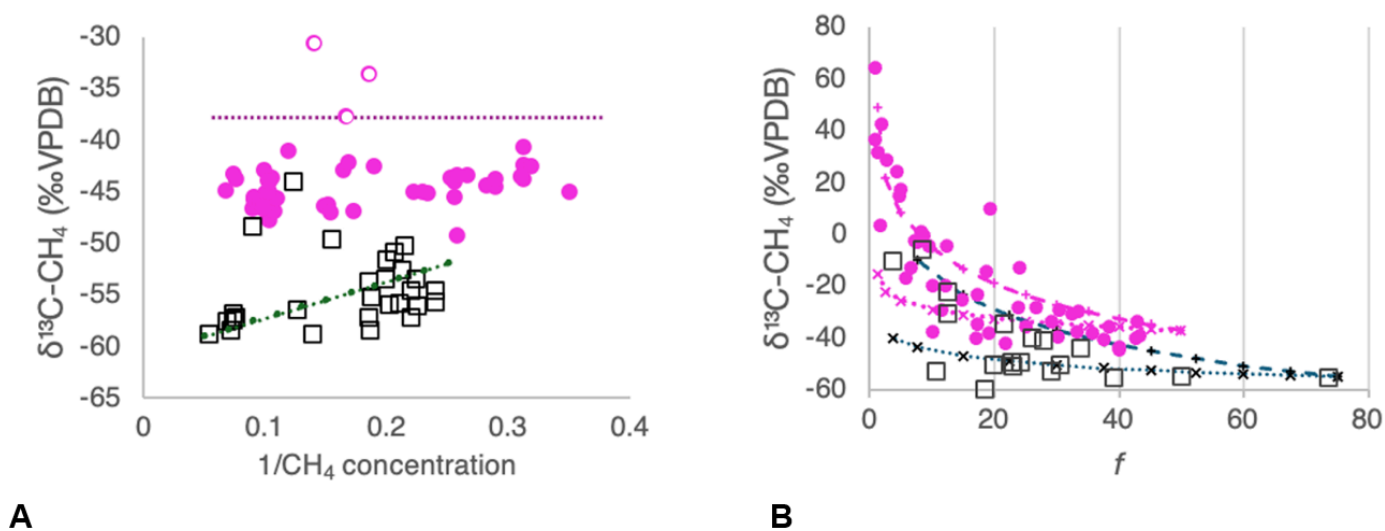


Figure 4

A: Keeling plot analysis showing $\delta^{13}\text{C}-\text{CH}_4$ vs. the reciprocal of the methane concentration in MW. Methane from the background stations (open squares) scatters around a mixing line calculated with -59 ‰VPDB and -52 ‰VPDB, respectively as endpoints. Methane from the plume stations scatter over the whole concentration range between the isotopic signature of background methane and initial fossil methane (purple dotted line). Methane (open circles) at the coastal station is not mixed with background methane but points to kinetic isotope fractionation (KIF) during ongoing sea-air flux (see text).

B: Measured methane fitted to Rayleigh distillation curves (RC) depicting microbial consumption, where $\delta^{13}\text{C}-\text{CH}_4 = (1/\alpha - 1) * \ln f + (\delta^{13}\text{C}-\text{CH}_4)_0$. For each regime, RC1 (dashed lines with $\cdot$) and RC2 (dotted lines with $+$) indicate fractionation factors of $\alpha_1 =$

1.020 and $\alpha_2 = 1.005$, respectively. f is the fraction of methane remaining, $(1 - f)$ is the methane consumed by oxidation. Methane from plume stations (pink dots) clusters around curves initialized with the pristine fossil signature (-37‰ VPDB), while methane from background stations (open squares) fits curves initialized with the regional marine background (-55‰ VPDB).

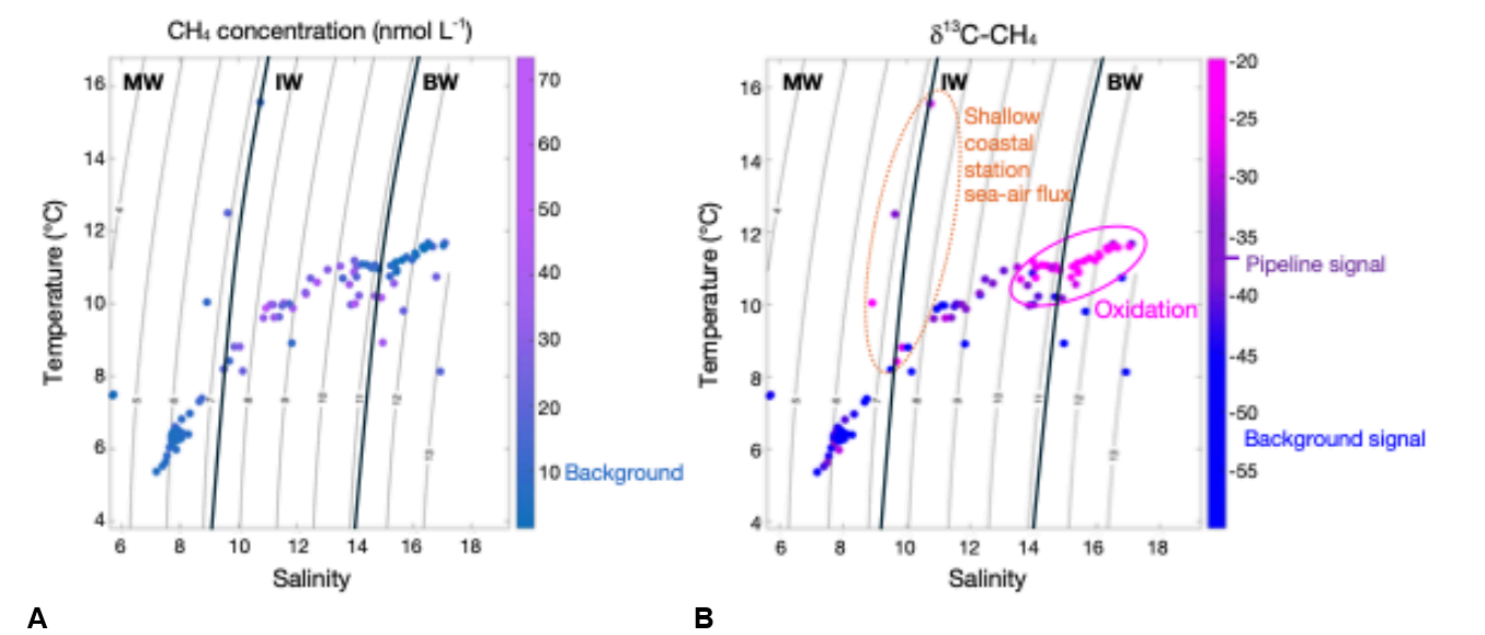


Figure 5

T/S diagram for January 2023 observations. Data points are color-coded by (A) dissolved methane concentration and (B) methane isotopic composition ($\delta^{13}\text{C-CH}_4$). (A) Purple colors in IW show highest concentrations, while blue colors in ML and BW show comparably low concentrations. (B) Pink colors indicate $\delta^{13}\text{C}$ values enriched in ^{13}C relative to the pipeline signal, suggesting methane oxidation in the BW. IW retains the original pipeline signature of approximately -37‰ , while the ML shows isotopic compositions close to the marine background indicating mixing and dilution. The color scale for $\delta^{13}\text{C-CH}_4$ is cut at -20 for better visualisation, the exact values outside this range are shown in Table 2 and Table 3.