Pathways of dissolved carbon dioxide and methane in the Kattegat

Report as part of *BIO450 - Chemical Dynamics in the Sea*

Author: Julia Mari Murata
Supervisor: Alex Cabral Dos Santos

Department of Marine Science, University of Gothenburg

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Abstract

Carbon dioxide (CO_2) and methane (CH_4) are major contributors to anthropogenic climate change. Coastal waters and particularly, estuaries emit substantial amounts of CO_2 and CH_4 to the atmosphere. A plethora of studies has investigated coastal carbon dynamics and drivers of greenhouse gases. However, coastal ecosystems are naturally heterogeneous and are affected differently by human activity. Therefore, site-specific investigations are of particular importance. This study provides the first survey of drivers of dissolved greenhouse gases considering groundwater discharge in the Kattegat. Using automated measurements of CO_2, CH_4 and ^{222}Rn, a natural tracer, groundwater could be excluded as major source of these greenhouse gases. The study revealed rivers as a source of both CO_2 and CH_4 but at different locations. The findings highlight the complexity of trace gas pathways and the interaction between physical and biological parameters in the Kattgat.

Introduction

Rising levels of carbon dioxide (CO_2) and methane (CH_4) are major drivers of anthropogenic global warming (Stocker et al., 2013). The oceans absorb about a quarter of the carbon emitted by human activity through inorganic and biological processes (Heinze et al., 2014). Especially, the land-sea interface is characterised by complex carbon dynamics showing a high variability in time and space. Depending on the latitude and distance to the land, coastal waters may act as net sink or as source of CO_2 (Bauer et al., 2013). Mainly carried by rivers, organic carbon undergoes various biochemical processing and is transported through upwelling and lateral transport between the shelf and the open ocean (Bauer et al., 2013). Despite showing high rates of primary productivity, coastal regions are considered to be important suppliers of CO_2 and CH_4 to the atmosphere (Bange, 2006), (Weber et al., 2019). *In situ*, CO_2 is produced through respiration (Bauer et al., 2013). The largest proportion of CH_4 in aquatic environments results from anaerobic methanogenesis in sediments (Borges and Abril, 2010). Other sources are zooplankton and the aerobic decomposition of suspended particles in surface layers (Holmes et al., 2000).

In addition to rivers, groundwater plays a major role in transporting nutrients and organic matter and thus, affects biochemical dynamics in coastal areas (Santos et al., 2021). It is furthermore linked to the dispersion of greenhouse gases (i.e., CO_2, N_2O and CH_4) to surface waters (Sadat-Noori et al., 2018) Fluxes of trace gases and groundwater in coastal areas have been widely examined by applying ^{222}Rn as tracer (Sadat-Noori et al., 2018), (Santos et al., 2012), (Wada et al., 2013), (Wang et al., 2022). As a member of the ^{238}U-decay chain, the radioactive noble gas decays from ^{226}Ra. Due to the ubiquity of uranium in the soil, ^{222}Rn steadily emanates through cracks and pores into groundwater (Skeppström and Olofsson, 2007). The resulting concentration difference of ^{222}Rn between groundwater and surface waters and the short half-life of 3.82 days make the isotope very suitable as tracer (Kluge et al., 2007).

European coastal waters, particularly estuaries, are considered to be significant emitters of CO_2 and CH_4 (Bange, 2006), (Bauer et al., 2013), but data on high latitude locations such as fjärds (Borges and Abril, 2010). Pathways of greenhouse gases taking into account the contribution of groundwater have not yet been investigated in the area. This study aimed to describe the spatial physico-chemical characteristics of surface waters in the Kattegat and to identify sources of CH_4 and CO_2 by using ^{222}Rn as tracer. The main research questions were: (1) How do the hydrographic and biochemical surface properties vary spatially with regard to different water-mass sources? (2) What role does groundwater discharge play as a source of dissolved greenhouse gases in surface waters?

Methods

Study site

The Kattegat is a shallow sea between Sweden and Denmark, bordering the Baltic Sea in the south and the Skagerak Sea in the north (Nordberg et al., 1999). Main tributaries along the Swedish coast are the rivers Göta Älv, Viskan, Ätran, Nissan, Lagan, and Rönne Å(Carstensen et al., 2003).

Brackish Baltic water masses and more saline water from the North Sea condition the regional hydrography (Nordberg et al., 1999), and favour a generally strong stratification (Boesch et al., 2006). Salinities range between 8-12PSU at the surface to 30-35PSU in bottom waters and have minimum values along the Swedish west coast and in the south (Nordberg et al., 1999). Temperature fluctuations of the Baltic currents are more pronounced than those from the North Sea (Matthews et al., 1999).

Primary production by phytoplankton in the Kattegat has increased during the past decades attributed to elevated nitrogen levels and a high N:P ratio (Skogen et al., 2014). Peaks values of chlorophyll-α (hereinafter, Chl-α) especially occur at freshwater inflows (Spokes et al., 2006).

Sample collection

Sampling occurred on board of the R/V Skagerak between April 25 and April 29, 2022. On 25 April, the ship departed Nya Varvet harbour (57.686337, 11.893295) in Gothenburg and arrived at Höganäs (56.197794, 12.550154) in the evening (Fig. 1).

The next day, on 26 April, samples were taken in Skälder Bay near Ängelholm and southern Laholm Bay near Halmstad. After the ship had anchored in Halmstad overnight, samples were collected further north in Laholm Bay and along the coast until Falkenberg on 27 April. On 28 April, samples were taken on the way back to Nya Varvet.

The ship was equipped with a -4H-FerryBox (JENA Engeneering GmbH, Germany), an automatic flow-through system with various sensors measuring hydrographic and biochemical parameters (-4H-JENA engineering GmbH, n.d.). Water is pumped through a subsurface-inlet and circulates with a speed of $1\,\mathrm{m\,s^{-1}}$ in the system. Bubbles and particles are removed by a debubbling unit (FerryBox Task Team, n.d.).

To measure ^{222}Rn, CO_2 and CH_4, a RAD AQUA Gas Exchanger (Durridge Company Inc., USA), a RAD7 Real-time ^{222}Rn Detector (Durridge Company Inc., USA), and a LI-7810 $CH_4/CO_2/H_2O$ Trace Gas Analyzer (LI-COR Biosciences UK Ltd., UK) were installed. From here on, the apparutus are referred to as gas exchanger, RAD7 and LI-COR, respectively.

The vessel's clean water system continuously supplied the gas exchanger with water, which equilibrates the ^{222}Rn concentrations of air and water (DURRIDGE Company Inc., 2020). The three devices were connected by a closed air loop, first pumping the air in the LI-COR and then the RAD7. The measurement of trace gases in the LI-COR relies on Optical Feedback - Cavity-Enhanced Absorption Spectroscopy (LI-COR Biosciences, 2021). The RAD7 estimates the ^{222}Rn gas activity through counts of particles of the ^{222}Rn alpha-decay (DURRIDGE Company Inc., 2022). Methane and carbon dioxide were measured in minute intervals and ^{222}Rn was detected every half hour. For further analysis, the data set was trimmed to the points in time when all measurements were available.

Data analysis

The data analysis was carried out in R Studio (v. 4.0.4) and Python (v. 3.10.4). Outliers were removed from the dataset depending on each variable's interquartile range (IQR) and the relative distance to the 0.25 quartile (Q1) and the 0.75 quartile (Q3). The criterion to define an outlier was: $value > 1.5 \times IQR + Q3$ or $value < Q1 - 1.5 \times IQR$. To examine statistical relations between variables, Pearson's rank correlation assuming a confidence interval of 0.95 was applied. Data and scripts are available on: https://github.com/codymoly/GU-student-projects.

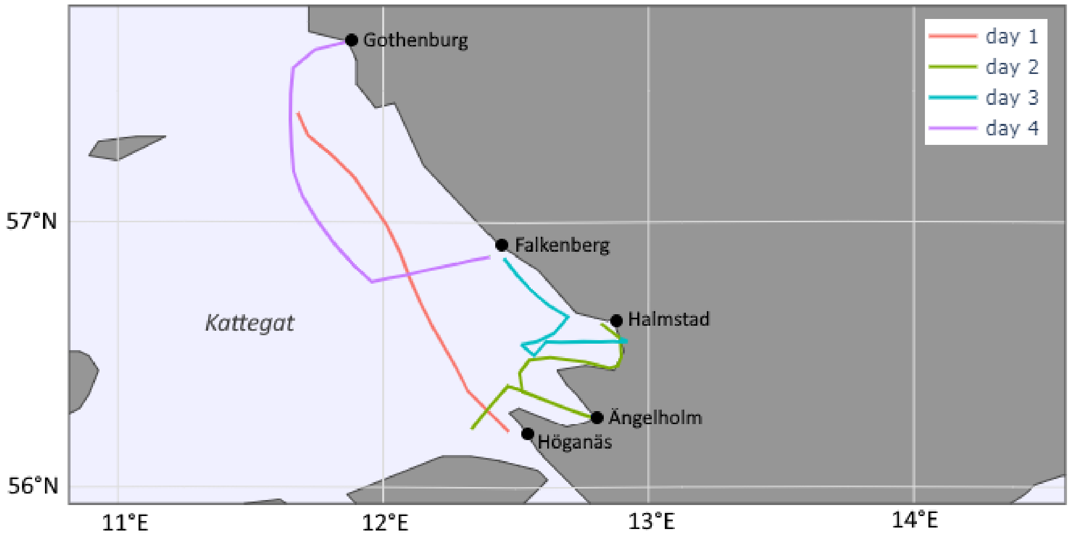

Figure 1: Ship route derived from the FerryBox data. The different colours indicate the sampling days (i.e., 25 to 28 April). Gaps result from decommissioning the FerryBox.

Results & discussion

Spatial variation of hydrographic and biochemical surface parameters

Based on observations from the ship, the weather was mixed with alternating sunny and cloudy periods and no rainfall. The average wind speed was between 3 and 11 $m\,s^{-1}$. Air temperatures varied between 5 and 10°C.

Some hydrographical parameters showed spatially dependent fluctuations with regard to the relative distance to the coast and river outlets (Fig. 2). The surface-water temperature ranged between 8 and 10°C. It was highest offshore in the northern Kattegat and along the shoreline with local maxima in Skälder Bay, Laholm Bay and Falkenberg (Fig. 2a). Salinity varied between 9 and 18PSU with the highest values offshore and an interim decrease along the north-south axis (Fig. 2b). Minima occurred near Höganäs and between Laholm Bay and Falkenberg. Chl-α concentrations varied between 0.3 and 0.8 $\mu g\,L^{-1}$ (Fig. 2c). Peaks were found in the outlet of Göta Älv and near the coast in Skälder Bay, Laholm Bay and Falkenberg. CO_2 levels fluctuated between 375 and 467 ppm and increased from south to north (Fig. 2d). Lowest values were found in Skälder Bay, Laholm Bay and Falkenberg. CH_4 values ranged between 2204 and 2905 ppb (Fig. 2e). Peaks occurred near the river outlets and offshore near Gothenburg. ^{222}Rn varied between 2.8 and 8.3 $Bq\,m^{-3}$, and showed several peaks near the tributaries but also offshore (Fig. 2f).

The results largely reflect previous physical characterisations of the study area as shown by Matthews et al. (1999) and Nordberg et al. (1999). Higher temperatures and lower salinities in the bays and along the coastline may be linked to river discharge. Generally, salinities of the southern Kattegat are relatively low as a result from low-saline Baltic currents (Matthews et al., 1999). Partly following the physical conditions, Chl-α concentrations are higher along the coast and peak near the river outlets which confirms earlier examinations (Spokes et al., 2006), (Bauer et al., 2013). It should be noted, that the surface distribution reflects not only spatial but also temporal variability as samples were taken on multiple days. The FerryBox data indicated some interdiurnal variability of the hydrography (e.g., visually, temperatures increased over the days and the surface pressure decreased) (Appendix, Fig. 5), which may have been driven by a changing weather during the cruise. As the meteorological conditions were recorded rather qualitatively for the sampling days, assessing the influence of those fluctuations on spatial patterns may be uncertain.

Pathways of dissolved greenhouse gases and biological interactions

The results indicate that CO_2 and CH_4 likely originate from different sources and that biological interactions may affect the traceability of greenhouse gases. Looking at the sampling area as a whole, ^{222}Rn correlated neither significantly with CO_2 nor

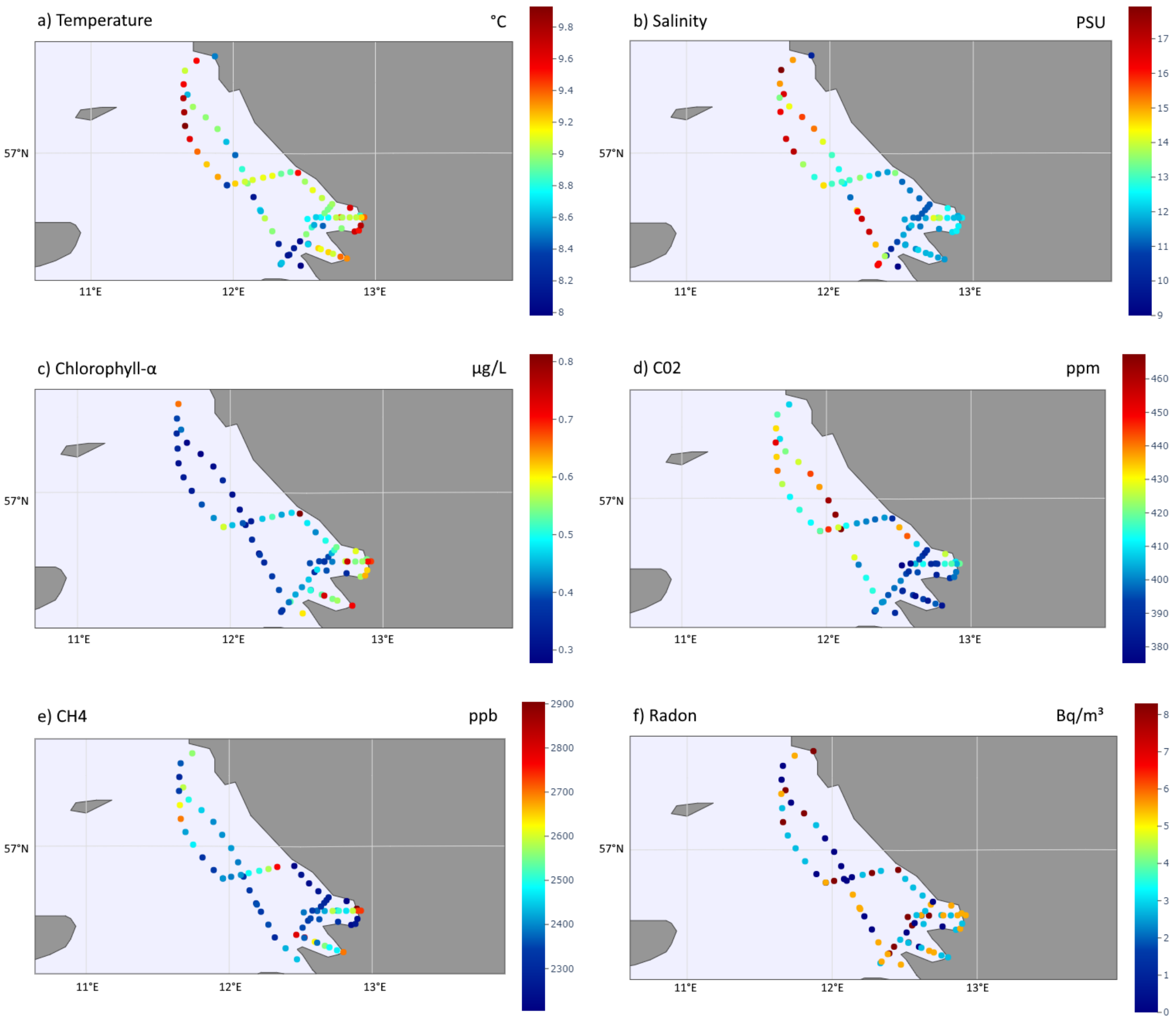

Figure 2: Surface distribution of selected parameters measured by the FerryBox, LI-COR and RAD7. Outliers were removed from the data.

with CH_4 ($\rho = 0.035$, $p = 0.82$, $\rho = 0.16$, $p = 0.3$, respectively) (Fig. 3a & b). CO_2 and CH_4 also showed no significant association ($\rho = 0.0034$, $p = 0.98$) (Fig. 3c). In accordance with Sadat-Noori et al. (2018), this indicates that groundwater is likely not the major source of the two greenhouse gases and moreover that both trace gases do not come from the same source. CO_2 and salinity showed a positive correlation ($\rho = -0.5$, $p = 3.8 \times 10^{-5}$) and CH_4 was not significantly correlated to salinity ($\rho = 0.19$, $p = 0.14$), which makes river input as driver unlikely (Fig. 3d & e) (Sadat-Noori et al., 2018).

However, Chl-α showed an inverse correlation with CO_2 ($\rho = -0.46$, $p = 1.3 \times 10^{-4}$) (Fig. 3f), which could be led back to biological effects. In the Kattegat, spring blooms of phytoplankton occur between March and May (Carstensen et al., 2003). Although Chl-α does not represent an estimate of primary productivity, an increase of Chl-α may be accompanied by a decrease of CO_2 during growth periods resulting from elevated CO_2-intake by phytoplankton (Song et al., 2016). CO_2 could also result from heterotrophic respiration in the surface layer (Rivkin and Legendre, 2001). Consequently, the biological interference may distort the statistical association between CO_2 and other parameters.

Taking into account a higher temporal variability over the days, both trace gases still did not significantly correlate with ^{222}Rn confirming that sources other than groundwater likely predominate (Fig. 4a & b). With regard to the first day on which samples were taken further away from the shoreline, CO_2 showed a significant negative correlation with salinity (Fig. 4d). In view of the numerous river estuaries along the Kattegat coast, river

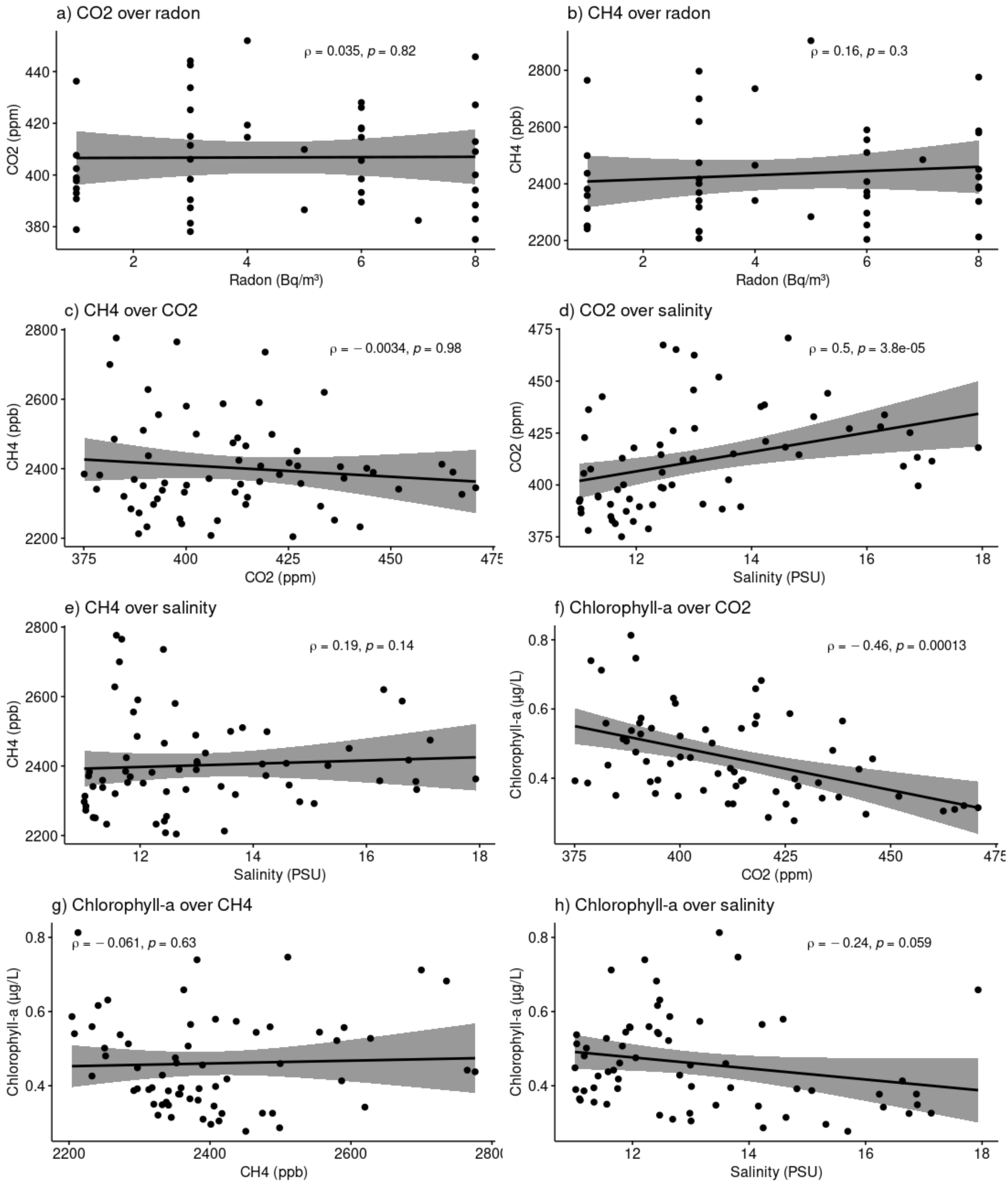

Figure 3: Correlations of selected parameters measured by the FerryBox, LI-COR and RAD7. Outliers were removed. Correlation coefficients (ρ) and p-values base on Spearman's rank correlation with a confidence interval of 0.95.

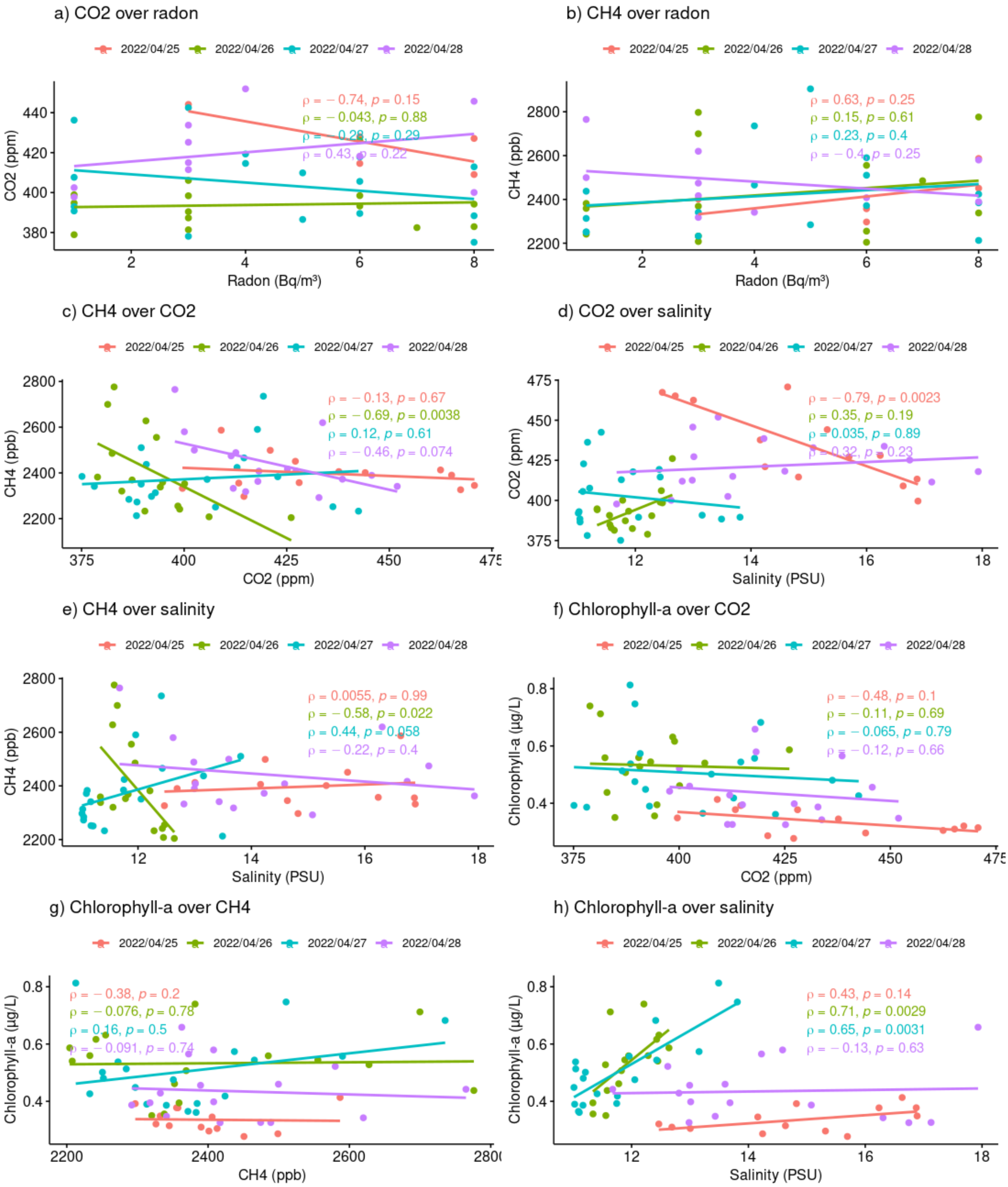

Figure 4: Correlations of selected parameters measured by the FerryBox, LI-COR and RAD7 grouped by sampling days. Outliers are removed. Correlation coefficients (ρ) and p-values base on Spearman's rank correlation with a confidence interval of 0.95.

discharge could be an explanation for surface CO_2 levels. The samples of the second day, mainly collected in Skälder Bay and Laholm Bay, showed an inverse correlation between CH_4 and CO_2 as well as salinity (Fig. 4c & e). Two conclusions can be drawn from this: in the bays, CH_4 and CO_2 are carried through different pathways and river discharge is likely the main source of CH_4. On the second and third day, which covered the whole coastline of the sampling route, Chl-α correlated with salinity (Fig. 4h). In the Kattegat, phytoplankton blooms are associated to higher salinities as a result of upwelling water masses rich in nutrients (Spokes et al., 2006). Hence, this may indicate the alteration of the surface hydrography through vertical transport processes.

Carbon dynamics in some coastal regions are primarily affected by oceanic circulation (Weber et al., 2019). The hydrography of the Kattgegat is highly dynamic due to the contrasting influences of the Skagerak and the Baltic Sea. The upper layer is a composition of waters of both origins whereby Baltic currents are the main driver of the seasonal variability (Matthews et al., 1999), (Nordberg et al., 1999). Inferring rivers as source of CO_2 from its association with salinity may be uncertain since the Baltic inflow and upwelling events affect salinity, especially in the southern Kattegat (Nordberg et al., 1999). The inverse correlation of CH_4 and CO_2 supports the argumentation that CO_2 may be driven by other sources in the southern part. In the case of CH_4, the contribution of river discharge emerges as more unambiguous. Nonetheless, surface waters of the north-western Baltic Sea show periodically high concentrations of CH_4, resulting from ebullition and groundwater discharge (Schmale et al., 2010). Ascending bubbles can carry large amounts of methane to the upper layer despite a potentially highly stratified water column (Schmale et al., 2010). Consequently, the southern Baltic currents could also contribute CH_4 to surface water with a spatially varying extent. Schmale et al. (2010) have further attributed the CH_4 occurrence in surface waters to seep sites in the Kattegat.

Conclusion

Coastal oceans play a major role in the global carbon cycle and are bidirectionally associated with the impacts of climate change (Heinze et al., 2014), (Stocker et al., 2013). This was the first study examining the drivers of trace gas fluxes in surface waters considering groundwater as source in the Kattegat. The distribution of CO_2 and CH_4 can be explained by riverine input but each at different sites within the sampling area. In Skälder Bay and Laholm Bay, river discharge is likely the major driver of CH_4 in surface waters. Along the transect between Göta Älv estuary and Höganäs, CO_2 could be linked to river input. Groundwater could not be identified as significant source of both greenhouse gases. Ambiguity of the results may arise from the high spatio-temporal heterogeneity of the hydrography in the Kattegat accompanied by a lack of comparable studies for the area. The impact of seep sites and the exchange of adjacent water masses on the greenhouse gas budget in the Kattegat were not subject of this study but need consideration in future assessments. In summary, the findings emphasise the complexity of greenhouse gas pathways in coastal waters and the linkage to physical and biological factors.

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Appendix

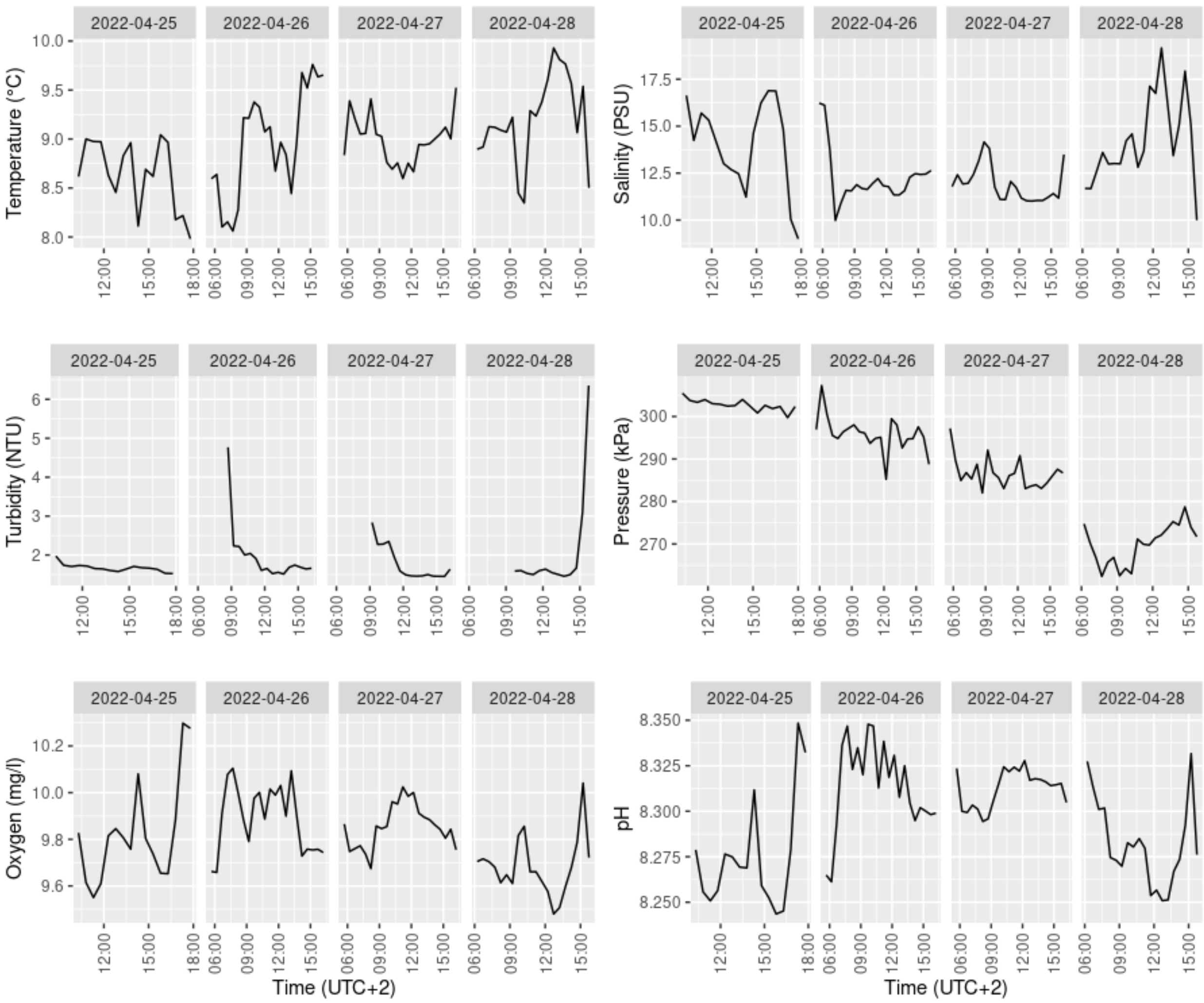

Figure 5: Time-series of the raw FerryBox data grouped by sampling day.