Alkalinity sources in the Dutch Wadden Sea

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Abstract

Total alkalinity (TA) is an important chemical property playing a decisive role in the oceanic buffering capacity of CO_2. TA is mainly generated by weathering on land, and by various anaerobic metabolic processes in water and sediments. The Wadden Sea, located in the southern North Sea is hypothesized to be a source of TA for the North Sea, but quantifications are scarce. This study shows observations of TA, dissolved inorganic carbon (DIC), and nutrients in the Dutch Wadden Sea in May 2019. Along several transects, surface samples were taken to investigate spatial distribution patterns and to compare them with data from the late 1980s. A tidal cycle was sampled to further shed light on TA generation and potential TA sources. We identified the Dutch Wadden Sea as a source of TA and estimated an export of 6.6 Mmol TA per tide to the North Sea. TA was generated in the sediments with deep pore water flow during low tide enriching the surface water. A combination of anaerobic processes and $CaCO_3$ dissolution were potential TA sources in the sediments. We deduce that seasonality and the associated nitrate availability in particular influence TA generation by denitrification, which is low in spring and summer.

1 Introduction

As the regulator of the ocean carbon dioxide (CO_2) sink, total alkalinity (TA) is of increasing scientific interest and is investigated worldwide in the so called "Anthropocene" (Abril and Frankignoulle, 2001;Bozec et al., 2005;Chen and Wang, 1999;Dickson, 1981;Middelburg et al., 2020;Norbisrath et al., 2022;Renforth and Henderson, 2017;Thomas et al., 2004;2009;Sabine et al., 2004). The "Anthropocene" describes the current era of our planet, when environmental changes, driven by humans, have become identifiable in geological records (Zalasiewicz et al., 2010;Crutzen, 2002). One of the most threatening changes for our climate is the anthropogenic driven increase in atmospheric greenhouse gases (GHG), such as CO_2. To counteract the increasing atmospheric CO_2 concentrations and the ongoing climate warming, a combination of several pathways is needed. Beside a strict reduction of CO_2 emissions, also net-negative emissions are required, which capture the atmospheric CO_2 and store it either based on land or in the ocean (e.g., Keith et al., 2006;Matthews and Caldeira, 2008;Zhang

30   et al., 2022). The climate and the increasing atmospheric CO_2 content is also naturally regulated by the open ocean, and around

31   a quarter of the global anthropogenic CO_2 emissions are already removed by it (Friedlingstein et al., 2022). The carbon storage

32   capacity of the North Sea is an important atmospheric CO_2 sink as it exports the absorbed CO_2 in the deep layers of the Atlantic

33   Ocean where it is stored on longer time scales (Borges et al., 2005;Bozec et al., 2005;Burt et al., 2016;Brenner et al., 2016;Hu

34   and Cai, 2011;Schwichtenberg et al., 2020;Thomas et al., 2004;2009). Two important aspects of the oceanic climate regulation

35   are the oceanic circulation and TA. TA, primarily consisting of bicarbonate and carbonate, is generated by chemical rock

36   weathering (Suchet and Probst, 1993;Meybeck, 1987;Berner et al., 1983), and in various stoichiometries by calcium carbonate

37   ($CaCO_3$) dissolution and anaerobic metabolic processes, such as denitrification, which is the reduction process of nitrate to

38   dinitrogen gas in the nitrogen cycle (Hu and Cai, 2011;Wolf-Gladrow et al., 2007;Chen and Wang, 1999;Brewer and Goldman,

39   1976). Since TA, CO_2 uptake and its export to the deep ocean are mainly disentangled in the open ocean, TA and the oceanic

40   circulation interact closely in highly active and shallow ocean areas such coastal zones and continental and marginal shelves.

41   In these shallow areas, TA is susceptible to changes due to various metabolic processes and the influence of adjacent zones

42   like rivers, estuaries, marshes, and tidal flats (e.g., Norbisrath et al., 2022;2023;Wang et al., 2016;Voynova et al., 2019). A

43   previous study by Norbisrath et al. (2022) showed that an enhanced riverine, metabolic alkalinity would lead to increasing

44   CO_2 absorption in the coastal zones of the North Sea, highlighting the need to further investigate TA regulation in adjacent

45   zones of coastal oceans.

46   Coastal zones, which are the direct interface between most, if not all, compartments of the Earth system (i.e., atmospheric,

47   terrestrial, aquatic, and oceanic) and human societies, appear particularly vulnerable to environmental and climate change

48   (Glavovic et al., 2015). This holds true for the Wadden Sea, the shallow, coastal sea along an approximately 500 km coastline

49   of the Netherlands, Germany, and Denmark, in the southern North Sea, which is declared as an UNESCO world natural heritage

50   site since 2009. Most of the Wadden Sea is located between the protecting barrier Islands and the Mainland, which makes it

51   the world's largest uninterrupted stretch of tidal flats with multiple tidal inlets (Fig. 1). Due to the topography, the Wadden

52   Sea is a highly dynamic ecosystem with influences from the mainland and the North Sea (Hoppema, 1993;Postma, 1954;van

53   Raaphorst and van der Veer, 1990). Driving forces of the biogeochemical dynamics in the Wadden Sea are nutrient imports

54   by rivers and high suspended particulate matter (SPM) and organic matter (OM) imports from the North Sea (van Beusekom

55   et al., 2019;van Beusekom et al., 2012;Postma, 1954). Physical sources of variability in the Wadden Sea are oceanic driven

56   wind, waves, and tidal currents, as well as the counterclockwise circulation of the North Sea (Elias et al., 2012). Large tidal

57   amplitude and currents in conjunction with shallow water depths allow for vertical water column mixing and an exchange

58   between the pelagic and benthic realms including deep pore water exchange (Røy et al., 2008). The strong tidal currents also

59   impact the biogeochemistry of the North Sea (Postma, 1954), as they cause an exchange of water between the North Sea and

60   the Wadden Sea and play an important role in the import of particulate matter from the North Sea (Burchard et al., 2008).

61   Previous studies identified the Wadden Sea as a TA source for the North Sea with a loading between 39 Gmol yr^{-1}

62   (Schwichtenberg et al., 2020) and 73 Gmol yr^{-1} (Thomas et al., 2009). Both studies suggested the entire Wadden Sea as one of

63   the most important TA sources of the carbon storage capacity for the North Sea. Burt et al. (2016) highlighted the importance

64 of coastal TA production for regulating the buffer system in the North Sea, and suggested denitrification as the major TA

65 source. Due to the strong connection between the North Sea and the Wadden Sea, a better understanding of TA generation in

66 the latter is required. Here, we focus on the Dutch Wadden Sea that has been well-studied during the past decades (Hoppema,

67 1990, 1991, 1993;De Jonge et al., 1993;Elias et al., 2012;Ridderinkhof et al., 1990;Postma, 1954;van Beusekom et al.,

68 2019;Schwichtenberg et al., 2017). In particular Hoppema (1990);(1993) observed the spatial and temporal variability of TA

69 in May in the late 1980s, which we compare with our observed transect data to detect potential differences over the last 30

70 years. In addition, we further discussed potential TA sources in the Dutch Wadden Sea.

2 Methods

2.1 Study site and sampling

73 This study is based on samples collected on a research cruise (LP20190515) in the Dutch Wadden Sea (Frisian Islands) on RV

74 *Ludwig Prandtl* in May 2019 (Fig. 1). We collected water samples in the Wadden Sea starting at Harlingen, through the Vlie

75 Inlet along the islands Vlieland and Terschelling, through the Ameland Inlet to Ameland Island, from there on via the Frisian

76 Inlet to Lauwersoog, and around Schiermonnikoog Island via the Ems-Dollard Inlet to Emden. In addition, we sampled a half

77 tidal cycle during ebb tide (from high tide to low tide) on 21 May 2019. To set the range of ebb tide data in relation, we also

78 sampled a half tidal cycle during flood tide (from low tide to high tide) on 23 May 2019 for comparison. Both half tidal cycles

79 were sampled as an anchor station in the waterway at the western side of Ameland in the Ameland Inlet on each day.

80 Nearly half-hourly, we collected discrete surface (1.2 m depth) water samples with a bypass from the onboard flow-through

81 FerryBox system, which also provided essential physical parameters such as salinity with an accuracy of 0.02 (PSU) and

82 temperature with an accuracy of 0.1 °C (Petersen et al., 2011). The FerryBox was cleaned and the system checked prior to the

83 cruise, and salinity is occasionally checked using discrete samples, which is considered sufficient for gradients in near-shore

84 investigations (pers. comm. Y. Voynova). We complemented our salinity and temperature data with data from three

85 Rijkswaterstaat stations (Dantziggat, Terschelling 10, and Vliestroom; Table B3), which were close to our stations.

86 For TA and DIC measurements we sampled water with overflow into 300 mL BOD (biological oxygen demand) bottles and

87 preserved them with 300 µL saturated mercury chloride solution (HgCl$_2$) to stop biological activity. Each BOD bottle was

88 filled without air bubbles and closed by using a ground-glass stopper coated in Apiezon® type M grease and a plastic cap. The

89 samples were stored in a cool dark environment until measurements in the lab.

90 Water for nutrient samples was filtered through pre-combusted (4 h, 450 °C) GF/F filters and the filtrate was stored frozen in

91 three 15 mL Falcon tubes for triplicate measurements in the lab.

92 To determine the total carbon (C), organic carbon (C$_{org}$) and nitrogen (N) concentrations in SPM and associated C$_{org}$:N ratios,

93 we used pre-combusted (4 h, 450 °C) GF/F filters, which were dried after sampling at 50 °C to remove all humidity and were

94 stored frozen afterwards until measurement.
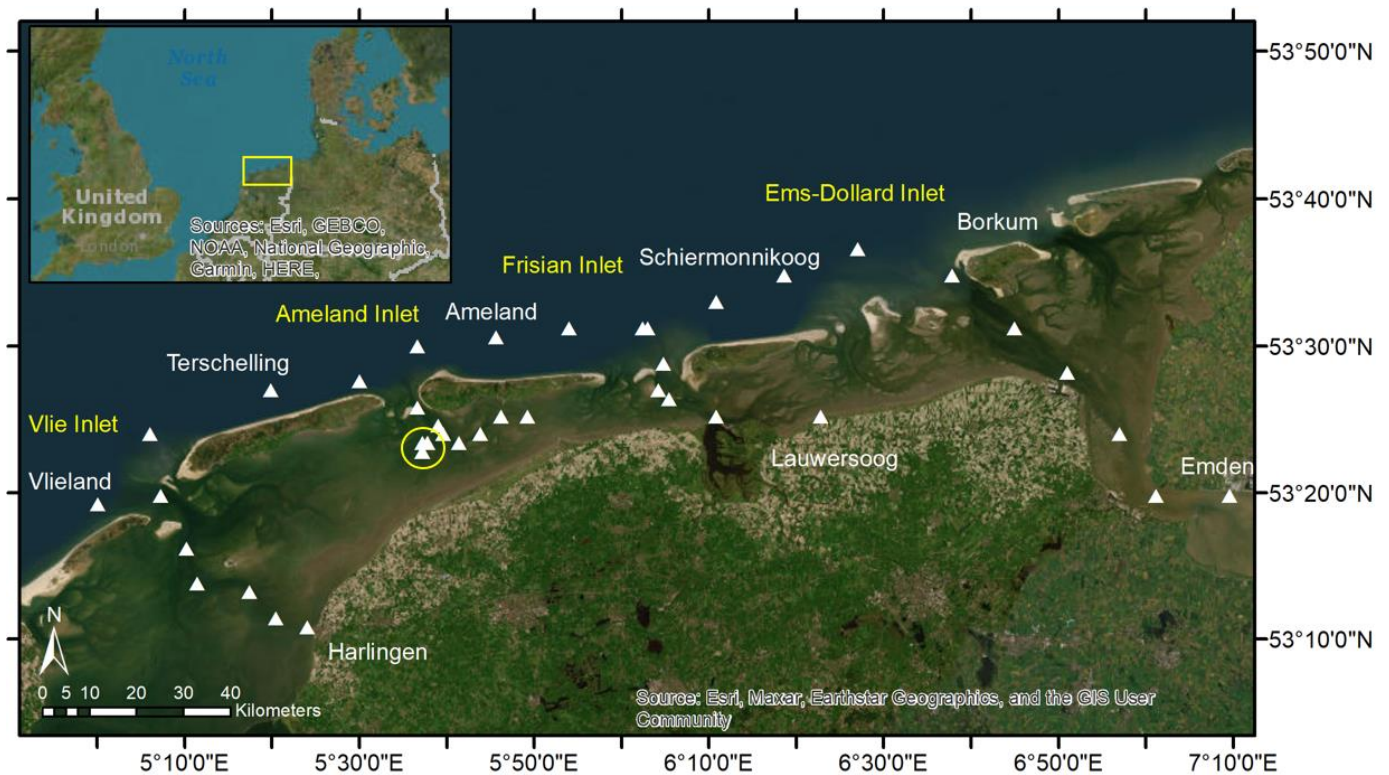
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96 **Figure 1** Sampling site in the Dutch Wadden Sea. The sampling stations around the Frisian Islands in May 2019 are visualized

97 with white triangles. The yellow circle highlights the anchor stations for the tidal cycle sampling in the Ameland Inlet on two

98 days. During the sampling day from low tide to high tide, we had two samples that we took slightly more western due to

99 drifting. The island and city names are shown in white, the inlets in yellow. The tidal flats and sedimentary structures are well

100 visible between the barrier islands and the mainland.

101 **2.2 Carbon species analyses**

102 The parallel analyses of TA and DIC were carried out in March 2020 by using the VINDTA 3C (Versatile INstrument for the

103 Determination of Total dissolved inorganic carbon and Alkalinity, MARIANDA - marine analytics and data), which measures

104 TA by potentiometric titration and DIC by coulometric titration both with a measurement precision < 2 µmol kg^{-1} (Shadwick

105 et al., 2011). Certified reference material (CRM batch # 187) provided by Andrew G. Dickson (Scripps Institution of

106 Oceanography) was measured before and after the samples and used to ensure a consistent calibration of both measurements.

107 The calcite and aragonite saturation states (Ω), the pH, and the seawater partial pressure of CO_2 (pCO$_2$)were computed with

108 the CO$_2$SYS program (Lewis and Wallace, 1998), using the measured parameters TA and DIC, and salinity, temperature,

109 silicate and phosphate as input variables, together with the dissociation constants from Mehrbach et al. (1973), as refit by

110 Dickson and Millero (1987). Reported calculation uncertainties are $\pm$ 0.0062 for pH (Millero et al., 1993), $\pm$ 4.9 % for the

111 aragonite saturation state and $\pm$ 3.5 % for pCO$_2$ (Orr et al., 2018).

4

2.3 Nutrient analyses

The nutrients were measured with a continuous flow automated nutrient analyzer (AA3, SEAL Analytical) and a standard colorimetric technique (Hansen and Koroleff, 2007) for nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), and silicate (Si), and a fluorometric method (Kérouel and Aminot, 1997) for ammonium (NH_4^+) (Grasshoff et al., 2009). The nutrient samples were measured against Eurofins reference materials VKI SW4.1B (for NOx, NO_2 and NH_4) and VKI SW4.2B (for Si and PO_4) in July 2019. The maximum standard deviations were 0.322 µmol L^{-1} for NO_3^-, 0.014 µmol L^{-1} for NO_2^-, 0.081 µmol L^{-1} for NH_4^+, 0.014 µmol L^{-1} for PO_4^{3-} and 0.165 µmol L^{-1} for Si.

For the C_{org} determination, filters were acidified with 1N HCl and dried overnight to remove all inorganic carbon content. Filters were measured with a CHN-elemental analyzer (Eurovector EA 3000, HEKAtech GmbH) in the Institute of Geology, University Hamburg, and calibrated against a certified acetanilide standard (IVA Analysentechnik, Germany). The standard deviations were 0.05 % for carbon and 0.005 % for nitrogen.

2.4 Data analyses

The data analyses were performed by using RStudio Version 1.3.1073 © 2009-2020 RStudio, PBC. The linear regression Model II was performed by using the "lmodel2" R package, and the plots were created with the "ggplot2" R package.

3 Results

3.1 Spatial parameter distribution

To investigate the spatial distribution of TA in the Dutch Wadden Sea and compare its general status with earlier studies (in particular Hoppema, 1990), we observed TA and related parameters in surface water along a transect from the coastal mainland towards the North Sea.

The temperatures varied between 12 and 16 °C with higher temperatures towards the coastal mainland (Fig. 2a). We identified two main sub regions based on the salinity values. First the Ems-Dollard Inlet, which showed salinities lower than 28 and with the minimum value of 20.25 at the most upstream station. And second, around Ameland Island and the remaining of our investigated region in the Dutch Wadden Sea with salinities showing only smaller variations varying from 28 to 33 (Fig. 2b). Spatial transect TA concentrations ranged from 2332 µmol TA kg^{-1} to 2517 µmol TA kg^{-1}. We observed lower concentrations on the North Sea side of the Frisian Islands with somewhat higher concentrations around Ameland (Fig. 2c). In contrast to the North Sea side, the values were higher (> 2380 µmol TA kg^{-1}) in the Wadden Sea. In the Ems-Dollard Inlet, the concentrations were even higher, with values up to 2517 µmol TA kg^{-1} at the most upstream station.

Silicate (Si) showed higher concentrations in the Wadden Sea and lower ones towards the North Sea (Fig. A1a). Highest concentrations were observed at the coastal mainland and in the Ems-Dollard Inlet. Silicate concentrations ranged between 0.3 and 56.3 µmol Si L^{-1}. Both, the calcite and aragonite saturation states (Ω) were supersaturated in the entire study region.

142   Saturation state values ranged from 2.3 to 4.6 for calcite (Fig. A1b), and from 1.4 to 2.8 for aragonite (Table B3). Highest

143   values were observed at the North Sea side of the barrier islands, and lowest values near Harlingen and in the Ems-Dollard

144   Inlet. Like the calcite and aragonite saturation states, the pH values were higher in the North Sea, and lower in the Wadden

145   Sea and near the coastal mainland (Fig. A1c). The pH values ranged from 7.86 to 8.19, and lowest values were observed near

146   Harlingen and in the Ems-Dollard Inlet. The nitrate (NO_3^-) concentrations were in a low range (< 3 µmol NO_3^- L^{-1}) throughout

147   the study region. Higher concentrations (< 6 µmol NO_3^- L^{-1}) were observed only at a few stations close to land, and maximum

148   concentrations (< 38 µmol NO_3^- L^{-1}) were observed in the Ems-Dollard Inlet (Fig. A1d). DIC concentrations ranged from 2097

149   µmol DIC kg^{-1} to 2430 µmol DIC kg^{-1} (Fig. A1e). DIC values showed a similar pattern as TA values, with higher concentrations

150   near the coastal mainland and in the Ems-Dollard Inlet, and decreasing concentrations toward the North Sea, where DIC

151   reached minimum values.
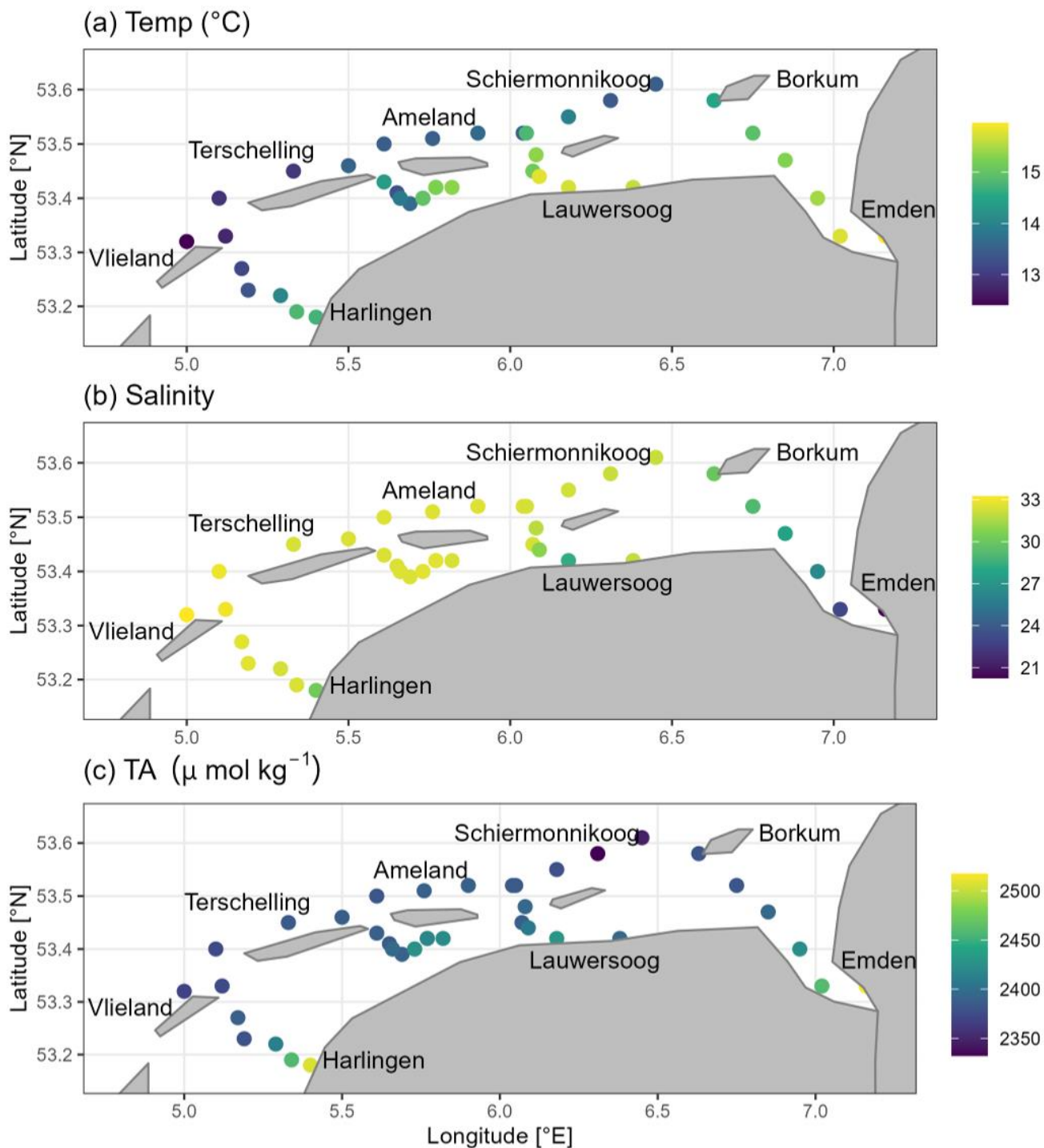
Figure 2 Spatial distribution of a) temperature (°C), b) salinity (PSU), and c) total alkalinity (TA; µmol kg⁻¹) from surface water samples in May 2019.

155 Compared to the other transects of this study region, the strong influence of the inner Ems Estuary is visible at the most
156 upstream station in the Ems-Dollard Inlet, showing lowest salinity, lowest pH and calcite saturation state values, and highest
157 values of TA, DIC, nitrate, silicate and phosphate. The outer side of the Vlie Inlet reflects the North Sea conditions with lower
158 temperatures and higher salinities. The North Sea impact is also visible in the mixing plot between TA and salinity (Fig.
159 3).Statistical significant linear mixing behavior was observed in the transect through the Ems-Dollard Inlet ($R^2 = 0.81$) and
160 through the Vlie Inlet ($R^2 = 0.77$), where TA concentrations decreased with increasing salinities from the mainland towards
161 the North Sea (Fig. 3). Whereas in the Ems-Dollard Inlet mixing is dominated by riverine water with high TA concentrations,
162 the mixing in the Vlie Inlet showed a more prominent mixing of Wadden Sea and North Sea water. The TA concentrations in
163 the Vlie Inlet and around Ameland, both at the North Sea side (Ameland NS) and the Wadden Sea side (Ameland WS) were
164 higher than the TA concentration computed for the salinity end-member in the Ems-Dollard Inlet, suggesting the Dutch
165 Wadden Sea as a source of TA (Fig. 3). Both the Ameland NS and WS data clearly indicated a non-conservative behavior with
166 a range of TA concentrations at near constant salinities.

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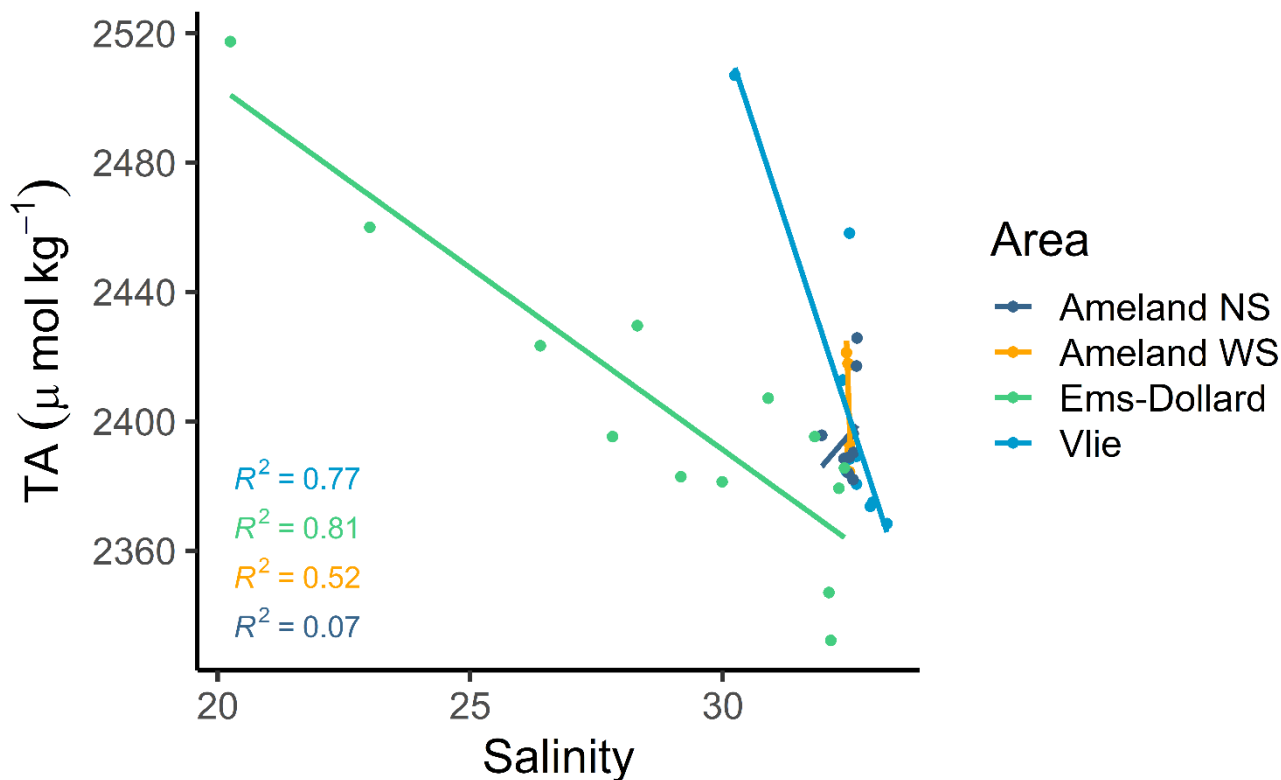
168 **Figure 3** Mixing plot of total alkalinity (TA) and salinity (PSU) in the North Sea side of Ameland and the Frisian Inlet
169 (Ameland NS), in the Wadden Sea site of Ameland (Ameland WS), around Schiermonnikoog and in the Ems-Dollard Inlet
170 (Ems-Dollard), and in the Vlie Inlet (Vlie).

171 **3.2 Tidal cycle**

172 We observed a half tidal cycle at an anchor station in the Ameland Inlet during ebb tide, to 1) identify potential TA sources
173 and 2) to quantify potential TA export to the North Sea. We identified patterns in several biogeochemical parameters in water
174 leaving the tidal flats (Fig. 4, Table B1). Temperature increased from 13.25 to 14.7 °C (Fig. 4a). Salinity was constant around
175 32.5 (Fig. 4b), which is in the range of coastal southern North Sea water excluding admixture of local fresh water sources.
176 During ebb tide, TA ranged from 2387 μmol TA kg^{-1} during high tide to 2438 μmol TA kg^{-1} during low tide (Fig. 4c). We
177 observed an increase of 51.6 μmol TA kg^{-1} (ΔTA) during ebb tide (6.8 h), resulting in a TA increase of 7.6 μmol TA kg^{-1} h^{-1}
178 at the sampling location.
179 DIC concentrations behaved similar to TA with minimum values at high tide (2172 μmol DIC kg^{-1}), and maximum values
180 (2273 μmol DIC kg^{-1}) at low tide, resulting in an increase of 101.3 μmol DIC kg^{-1} (ΔDIC) or 14.9 μmol DIC kg^{-1} h^{-1} (Fig. 4d).
181 DIC increased almost twice as much as TA.
182 Nitrate increased during ebb tide by 0.92 μmol NO_3^- L^{-1} (ΔNO_3^-) from a minimum of 1.26 μmol NO_3^- L^{-1} to a maximum of
183 2.17 μmol NO_3^- L^{-1} (Fig. 4e), resulting in a nitrate increase of 0.13 μmol NO_3^- L^{-1} h^{-1}.
184 Silicate showed a similar pattern with low values (1.8 μmol Si L^{-1}) at high tide increasing during ebb tide to a maximum of
185 11.2 μmol Si L^{-1}, resulting in a silicate increase (ΔSi) of 9.4 μmol Si L^{-1} or 1.4 μmol Si L^{-1} h^{-1} during ebb tide (Fig. 4f).
186 Ammonium increased from 3.47 μmol NH_4^+ L^{-1} to 6.22 μmol NH_4^+ L^{-1} during ebb tide (Fig. 4g), resulting in an ammonium
187 increase (ΔNH_4^+) of 2.74 μmol NH_4^+ L^{-1}, or 0.4 μmol NH_4^+ L^{-1} h^{-1}.
188 The calcite and aragonite saturation states had maximum values (Ω_{Ca} = 3.8, Ω_{Ar} = 2.4) at high tide and decreased to their
189 minimum (Ω_{Ca} = 3.1, Ω_{Ar} = 2.0) during ebb tide (Fig. 4h). The influence of the North Sea is indicated by the observed maximum
190 at high tide, which decreased during the ebb.
191 The seawater pCO$_2$ had minimum values at high tide (385.1 μatm) and increased up to 576.6 μatm during low tide (Fig. 4i).
192 Like Ω, the maximum pH was 8.07 at high tide and decreased to a minimum (7.93) during ebb tide (Fig. 4j).
193 C_{org}:N ratios of SPM increased during ebb tide (Fig. 4k). A minimum C_{org}:N ratio of 5.6 was observed around high tide and
194 increased to a maximum of 13.0 during ebb tide. Simultaneously, the SPM concentration increased during ebb tide, from 12.8
195 mg SPM L^{-1} to a maximum of 82.4 mg SPM L^{-1} at the second last station (Table B1).
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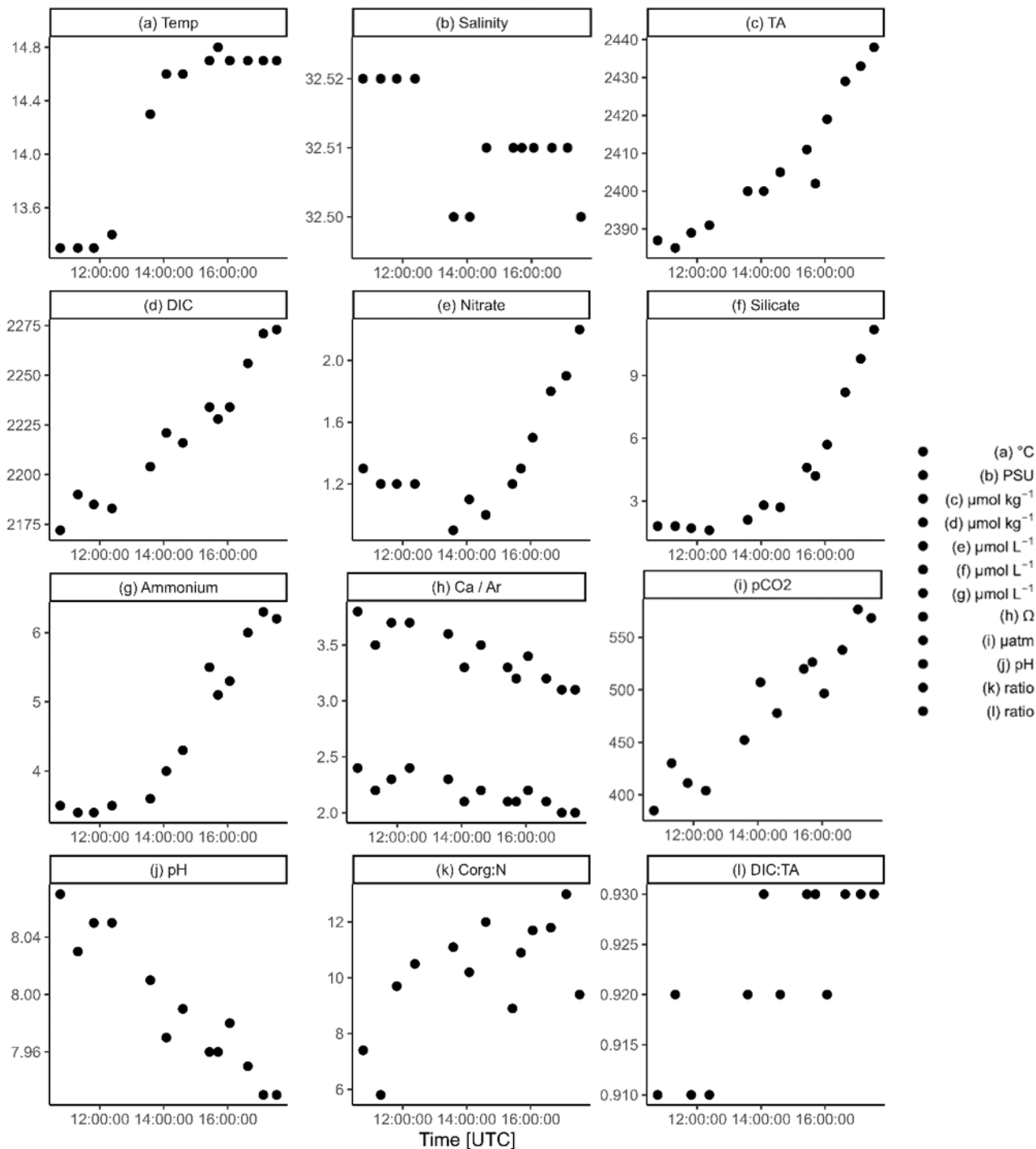
Figure 4 A half tidal cycle from high tide to low tide. Temporal distribution of a) temperature, b) salinity, c) total alkalinity

(TA), d) dissolved inorganic carbon (DIC), e) nitrate, f) silicate, g) ammonium, h) calcite (upper points) and aragonite (lower

10

200 points) saturation states (Ω), i) pCO_2 (µatm), j) pH, k) C_{org}:N ratio of SPM, and l) DIC:TA ratio. Note the different y-axes
201 and the +1 hour time difference between the local time and the UTC time.

3.3 TA generation

203 Tidal forcing leads to a bi-diurnal exchange between Wadden Sea and North Sea water. The tidal forcing also induces a strong
204 benthic-pelagic coupling (Huettel et al., 2003;Røy et al., 2008). Many studies support that the outflowing water exports
205 material from the sediment including remineralization products from organic matter (e.g., Billerbeck et al., 2006;Røy et al.,
206 2008). Here, we focus on the hypothesis that the sediments are a significant source of TA.

207 For a first rough estimate of a maximum TA export during ebb tide, we used the mean observed TA increase (ΔTA / 2) of 25.8
208 µmol TA kg^{-1} during ebb tide (in the Ameland Inlet, part of the Borndiep tidal basin), a tidal prism of 478 *10^6 m^3 of the
209 Borndiep tidal basin, and a share of intertidal flats of 53 % (Louters and Gerritsen, 1994). Assuming that only the intertidal
210 sediments exchange TA, we estimated a TA export of 6.6 Mmol TA per tide to the North Sea. Assuming two ebb tides and a
211 lunar cycle of 24.8 hours this would result in a daily export of 12.7 Mmol TA.

212 The significant correlation of TA and silicate ($R^2 = 0.93$), and the insignificant relation between TA and salinity ($R^2 = 0.32$),
213 as well as silicate and salinity ($R^2 = 0.21$), suggest that TA originates from the tidal flats in this part of the Dutch Wadden Sea
214 and is not from admixture carried by river runoff. The significant correlation between TA and silicate both during ebb tide
215 point to the same source (Fig. 5b).

216

217 To further elucidate potential TA sources in the Dutch Wadden Sea, we correlated TA with DIC, silicate, nitrate, and
218 ammonium in the half tidal cycle from high tide to low tide, respectively (Fig. 5).

219 The correlation between TA and DIC is a measure between anaerobic and aerobic processes. Our data show a strong positive
220 correlation between DIC and TA ($R^2 = 0.93$) with TA concentrations being higher than DIC concentrations (Fig. 5a). We
221 observed a release excess of DIC compared to TA as indicated by the slope of 1.89 and by an increase in DIC (ΔDIC = 101.3
222 µmol kg^{-1}) almost twice as high as TA (ΔTA = 51.6 µmol kg^{-1}) (Fig. 5a). This excess DIC may be caused by strong CO_2
223 production due to high aerobic OM degradation, which can be supported by seawater being supersaturated in pCO_2 with respect
224 to the atmosphere (Fig. 4i). The TA increase can be fueled by various processes which we will discuss below. We detected a
225 linear positive correlation of increasing TA and silicate ($R^2 = 0.93$) during ebb tide, supporting pore water outflow (Fig. 5b)
226 as pore water is the major Si source during summer (van Bennekom et al., 1974). A stronger influence of the pore water with
227 ongoing ebb tide is indicated by increasing values. The positive correlation between nitrate and TA ($R^2 = 0.67$) (Fig. 5c) was
228 less strong than the correlations between TA and DIC, and TA and Si, which could be traced back to an effect of the first four
229 sampling points that were probably at the tipping point from high tide to low tide. In the remaining samples, the increasing
230 nitrate and TA concentrations suggest a stronger TA generation than nitrate production, balancing TA that may be consumed
231 by nitrification (i.e., nitrate production).
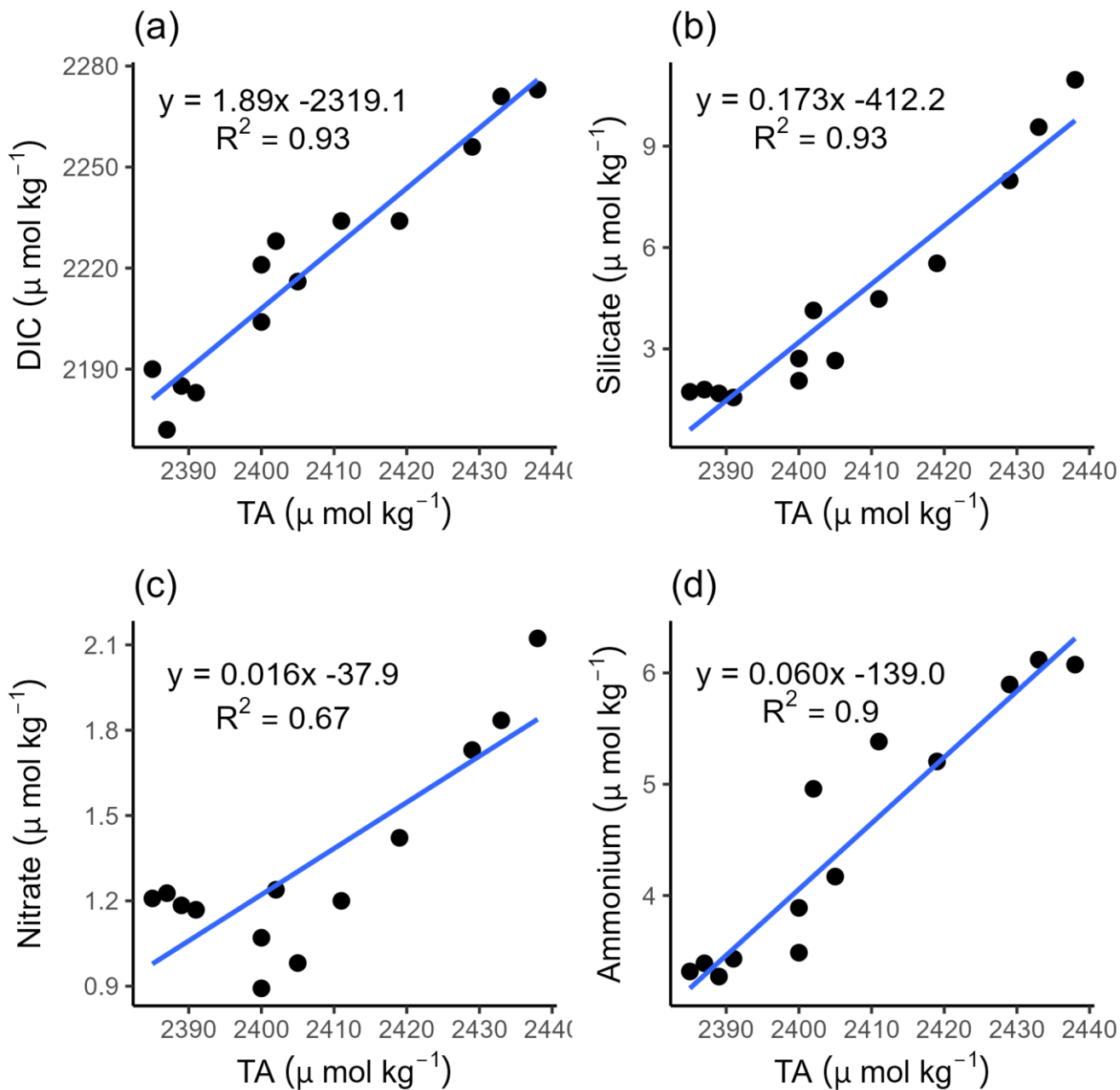
Figure 5 Correlations of TA with a) dissolved inorganic carbon (DIC), b) silicate, c) nitrate, and d) ammonium during ebb tide in the Ameland Inlet.

4 Discussion

4.1 Spatial TA variability

Hoppema (1990) reported TA distributions in the westernmost part of the Dutch Wadden Sea around the barrier islands Texel, Vlieland, and Terschelling. He focused on the tidal basins drained by the tidal inlets Marsdiep and Vlie located more to the west than our sampling stations (not visible on the map). Hoppema (1990) did not observe a continuous increase of salinity in the Wadden Sea from the fresh water source towards the North Sea and associated this to the influence of tidal differences and an arbitrary sampling scheme. The presence (dominance) of North Sea water in the Dutch Wadden Sea and on the tidal flats is supported by our transect data, which show relatively high salinities at coastal North Sea level. Brackish salinities were only detected in the Ems-Dollard Inlet, which receives fresh water from the river Ems, and close to Harlingen and Lauwersoog, which have direct fresh water inflows by smaller rivers and streams. The absence of clear salinity gradients in the more eastern part of the Dutch Wadden Sea investigated in our study suggest that most of the IJsselmeer discharge was exchanged with the North Sea through the Marsdiep (e.g., Duran-Matute et al., 2014).

The spatial TA data by Hoppema (1990), show lower TA concentrations at stations with more fresh water influence and higher TA concentrations in the tidal inlets. The data of this study also show high TA concentrations in the tidal inlets, suggesting TA generation in sediments, which is possibly fueled by high imports of nutrients and OM (van Beusekom and De Jonge, 2002). The even higher TA concentrations at stations with lower salinities close to the mainland observed in this study also show the influence from the catchment area on the coast, and possibly TA generation in the shallow sediments near the coast. In May 1986, Hoppema (1990) found TA concentrations ranging between 2319 and 2444 µmol TA kg^{-1} at salinities between 18.62 and 29.17. Our lowest observed TA concentration was 2332 µmol TA kg^{-1} at a salinity of 32.14, and our highest TA concentration was 2517 µmol TA kg^{-1} at a salinity of 20.25 close to the coastal mainland. A comparison of both studies shows that the general TA levels are in a similar range, but that the spatial gradients are opposite.

A conservative mixing between TA and salinity is only visible in the Ems-Dollard Inlet and the Vlie Inlet (Fig. 3). While the conservative mixing in the Ems-Dollard Inlet is more dominated by the fresh water discharge from the Ems River, the conservative mixing in the Vlie Inlet is more dominated by North Sea water passing through this deep inlet and allowing more North Sea water to be transported towards the coast. After the Marsdiep Inlet, the Vlie Inlet has the highest average tidal prism and is the second largest inlet in the Dutch Wadden Sea (Elias et al., 2012). Similar to our findings, Hoppema (1990) noted a linear mixing of TA and salinity in the Vlie Inlet, and suspected a lower fresh water contribution there as well, which is in accordance with model data (Duran-Matute et al., 2014).

In the Ems-Dollard Inlet, conservative mixing was observed, indicating minor contributions from other sources. In a previous study, Norbisrath et al. (2023) observed very high TA concentrations and TA generation in the upper tidal river of the highly turbid Ems Estuary, which may explain the high levels of TA in the Ems-Dollard Inlet (at low salinities) observed in this study.

13

267 Hoppema (1990) also observed a range of TA concentrations in the Dutch Wadden Sea and related these to different sinks and
268 sources. TA sinks can be calcium carbonate ($CaCO_3$) precipitation, or extraction of seawater carbonate by mollusks (e.g., Chen
269 and Wang, 1999;Hoppema, 1990). Variable fresh water inflows can either serve as a sink or a source (e.g., Chen and Wang,
270 1999;Hoppema, 1990). Other TA sources can be $CaCO_3$ dissolution, anaerobic metabolic processes in the sediment, or erosion
271 of TA enhancing sediments (e.g., Hoppema, 1990;Chen and Wang, 1999).

272 Except for the Ems-Dollard Inlet and close to Harlingen, we observed mainly marine salinities (> 30) but higher TA values in
273 the Dutch Wadden Sea than in the North Sea. We therefore exclude possible TA sinks and focus only on TA sources. According
274 to Hoppema (1990), the main causes for TA variations in the Dutch Wadden Sea were fresh water inflows and sources in the
275 sediment. In our study, fresh water inflows with high TA concentrations were only observed in the Ems-Dollard Inlet, but not
276 around the islands and the tidal flats. For a further TA source identification in the Dutch Wadden Sea, we investigated the TA
277 variability during ebb tide in a tidal channel close to Ameland.

278 **4.2 Determination of TA generation**

279 Burt et al. (2016) and Schwichtenberg et al. (2020) indicated TA generation in the Wadden Sea as an important source for the
280 North Sea's carbon storage capacity. Here, we want to further identify TA generation and potential TA sources.

281 In a study from the late 1980s, Hoppema (1993) observed a tidal cycle in the Marsdiep in May and September. Focusing on
282 TA, DIC, and oxygen, he also observed increasing TA values during ebb tide and assumed the tidal flats and discharging rivers
283 and canals as TA sources. Comparing our present TA data and the historical TA data, there is not a large difference in the
284 range of values observed during a tidal cycle. However, a further in-depth interpretation and comparison of both TA data sets
285 is limited by the low number of data, leading us to focus on TA generation during our cruise.

286 We made a very rough first estimate of the daily TA export. By using a 3D ecosystem model, Schwichtenberg et al. (2020)
287 estimated an annual export of 10 to 14 Gmol TA yr^{-1} for the entire Dutch Wadden Sea. Given that the Borndiep tidal basin
288 covers about 14% of the Dutch Wadden Sea and assuming no seasonal dynamics, our estimate of 12.7 Mmol d^{-1} compares
289 well with the annual averaged model estimate of 4.6 Mmol TA d^{-1}, but the overestimation suggests that seasonal dynamics
290 may be involved. Since our TA export based only on a half tidal observation, the inclusion of it into the model used by
291 Schwichtenberg et al. (2020) would be unreliable (pers. comm. J. Pätsch, 2022). To test whether the observed TA generation
292 matches their suggested TA export, observational data of at least each season are required to run the model and gain a
293 representative result (pers. comm. J. Pätsch, 2022).

294 **4.3 TA source attribution**

295 **4.3.1 Local sediment outwash**

296 In order to gain further insight into potential sources of TA, we compared our TA and nutrient data. The main focus was on
297 dissolved silicate (Si) as van Bennekom et al. (1974) showed that this nutrient is depleted in the Wadden Sea during the spring

298   diatom blooms and further showed that pore water is the main source of dissolved Si during summer. It is important to note
299   that winter concentrations in the Rhine (main contributor to the IJsselmeer) have not changed much since the 1970s and
300   showing maximum concentrations of about 125 µmol Si L^{-1} in winter and clear seasonal dynamics due to uptake by diatoms
301   (unpublished results based on data provided by Pätsch (2024); available through https://wiki.cen.uni-
302   hamburg.de/ifm/ECOHAM/DATA_RIVER). We identified a silicate increase of 1.4 µmol Si L^{-1} h^{-1} during ebb tide. Due to
303   the absence of large estuaries nearby and salinity consistently being above 32 at our tidal sampling station near the island of
304   Ameland, we exclude fresh water runoff as a major silicate source and indicate TA sources within the Wadden Sea.

305   Submarine groundwater discharge (SGD) was identified as a source for nutrient fluxes in tidal flat ecosystems in previous
306   studies (e.g., Billerbeck et al., 2006;Røy et al., 2008;Santos et al., 2021;Waska and Kim, 2011;Wu et al., 2013). Since we
307   observed relatively constant marine salinities, we suspect that deep pore water flow (e.g., Røy et al., 2008) enriched with
308   nutrients act as a source for our observed increasing TA and nutrients parameters. TA generation in tidal flats was also observed
309   by Faber et al. (2014), who focused on a large macro tidal embayment in southern Australia. They also found increasing TA
310   values during ebb tide, associated the TA increase with a higher fraction of pore water, and determined the tidal cycle as the
311   controlling force for pore water exchange. Their findings and the observed silicate outwash support our assumption that TA is
312   generated in the sediments of the tidal flats and is washed out during ebb tide. In addition, we exclude lateral advected signals
313   from more western regions as the Vlie Inlet, since the TA concentrations in the surface transect samples in the Vlie Inlet
314   (except of the two samples close to the coastal mainland near Harlingen) were in the same range as the other observed TA
315   concentrations and were smaller than the increasing TA concentrations during ebb tide. Both increases in TA and silicate are
316   tidal signals, and we identify TA generation in the sediments of the tidal flats here as the major local TA source.

317   **4.3.2 TA generating processes**

318   The deduced TA generation of 7.6 µmol TA kg^{-1} h^{-1} and the silicate increase of 1.4 µmol Si L^{-1} h^{-1} indicated an excess of TA
319   compared to silicate (also Fig. 5b). Considering a supposed TA:Si ratio of 2:1 (Marx et al. 2017), the observed 1.4 µmol Si L^{-1}
320   h^{-1} would then account for a TA generation of 2.8 µmol TA kg^{-1} h^{-1}. High silicate concentrations in tidal flat pore water
321   (Rutgers van der Loeff, 1974) and in situ production of silicate from dissolving diatom frustules are the most probable sources
322   of the silicate (e.g., van Bennekom et al., 1974). Since we observed more TA generated than silicate being washed out, other
323   biogeochemical processes must be responsible for the TA generation in the sediments of the tidal flats in the Dutch Wadden
324   Sea.

325

326   We exclude $CaCO_3$ dissolution as TA source in the water column, since the Ω values were supersaturated with $\Omega > 1$ (Fig. 4h,
327   Table B1). The continuous calcite supersaturation nicely indicated the inflow and dominance of North Sea water during the
328   flood, with Ω values similar to previously observed North Sea values ($\Omega \sim 3.5$ to 4) (Charalampopoulou et al., 2011;Carter et
329   al., 2014). In pore water, carbonate undersaturation and associated $CaCO_3$ dissolution can only be driven metabolically, due

330 to CO_2 production by OM remineralization, or due to the reoxidation of compounds reduced previously by anaerobic processes

331 (Brenner et al., 2016;Jahnke et al., 1994).

332

333 Other potential sources of TA generation in the sediments can be further narrowed down by a more detailed interpretation of

334 changes in DIC (ΔDIC) and TA (ΔTA) during ebb tide, and their combination with various nutrient ratios. The correlation of

335 DIC and TA reveals an increase in DIC (ΔDIC) almost twice as high as in TA (ΔTA) (Fig. 5a), as indicated by the slope of

336 1.89. The high ΔDIC points to high aerobic OM degradation and remineralization, resulting in high CO_2 production, which is

337 also indicated by seawater being supersaturated in pCO_2. High aerobic OM degradation was also previously observed in the

338 heterotrophic Wadden Sea (e.g., De Beer et al., 2005;van Beusekom et al., 1999), assuming an OM degradation and

339 remineralization occurring in the water and sediment in about equal parts (van Beusekom et al., 1999). High OM degradation

340 is indicated by the increasing C_{org}:N ratios of SPM during ebb tide (Fig. 4k, Table B1). Because we observed constant coastal

341 North Sea salinities, we rule out fresh water runoff and terrestrial signals as source for the increasing C_{org}:N ratios of SPM.

342 We assume that fresh OM is rapidly degraded in the water column, and the older OM settles on and in the sediment where the

343 degradation continues and where it is resuspended at the low prevailing water levels during ebb. Therefore, we assume that

344 the increase of SPM concentrations and their C_{org}:N ratios is an indicator for older and more refractory OM. The increase in

345 TA concentrations point to anaerobic processes, $CaCO_3$ dissolution, or a combination thereof as TA sources occurring in the

346 sediments.

347

348 For an upper bound estimate of sedimentary $CaCO_3$ dissolution as source of TA, we considered a ΔDIC: ΔTA ratio of 1:2.

349 Considering this ratio and the observed ΔTA of 51.6 µmol TA kg^{-1}, $CaCO_3$ dissolution would lead to a ΔDIC of 25.8 µmol

350 DIC kg^{-1}. The remaining 75.5 µmol DIC kg^{-1} (101.3 – 25.8 µmol DIC kg^{-1}) of the observed ΔDIC in this study could then be

351 produced by OM degradation and remineralization, and would, using the theoretical expected Redfield ratio of C:N (6.6) for

352 fresh OM (Hickel, 1984), correspond to an estimated dissolved inorganic nitrogen (DIN) production of 11.4 µmol DIN kg^{-1}.

353 However, this estimated DIN production (11.4 µmol DIN kg^{-1}) of OM degradation and remineralization exceeds the observed

354 increase of ΔDIN (3.97 µmol DIN L^{-1}; Table B1, sum of NO_3^-, NO_2^- and NH_4^+) during ebb tide. Based on this estimation and

355 the assumption that all DIN produced is released and thus lost, TA is probably produced by $CaCO_3$ dissolution and anaerobic

356 metabolic processes other than denitrification in the sediment. In addition to that, and with an N-focused perspective, the DIN

357 loss also hints to the occurrence of other processes that consume nitrogen species but have no net effect on TA, such as

358 anammox and coupled nitrification-denitrification (Hu and Cai, 2011;Middelburg et al., 2020). The suggested DIN loss can

359 be supported by considering the marine DIN:Si ratio, which is supposed to be about 1:1 (Brzezinski, 1985). We observed

360 DIN:Si ratios decreasing from 2.7 to 0.8 during ebb tide, showing that both parameter concentrations increased, whereby DIN

361 concentrations increased less than silicate concentrations. The silicate excess with respect to DIN at the end of ebb tide supports

362 the DIN loss.

Denitrification, the anaerobic irreversible reduction of NO_3^- to N_2 that generates 0.9 mole TA by using 1 mole NO_3^- as electron acceptor (Chen and Wang, 1999) is a net TA source. Denitrification depends on the supply of nitrate, which seasonally varies (van der Zee and Chou, 2005 and references therein). Generally, nitrate is depleted in summer due to high photosynthetic activity and occurs in higher concentrations in winter (Kieskamp et al., 1991;Jensen et al., 1996;van der Zee and Chou, 2005). This seasonality leads to denitrification rates also being lower in summer and higher in winter (Kieskamp et al., 1991;Jensen et al., 1996). In previous studies, Faber et al. (2014) identified denitrification as a minor source of TA due to low denitrification rates, and also Kieskamp et al. (1991) observed low denitrification rates in the Wadden Sea, with low nitrate concentrations (< 2.5 µmol L^{-1}) in the water column. We observed nitrate concentrations (< 2.17 µmol L^{-1}) lower than the concentration sufficient for denitrification assumed by Kieskamp et al. (1991). Therefore, we do not exclude denitrification, but suspect it as a minor source of TA in the Dutch Wadden Sea at least in spring and summer due to the seasonal lack of nitrate. Thomas et al. (2009) detected TA seasonality in the southern bight of the North Sea, which is also influenced by the TA generation in the Wadden Sea. In addition, the estimated DIN production compared to the observed DIN not only hints to other N consuming processes that have no effect on TA, but also suggests that allochthonous nitrate would be needed to fuel the TA increase by denitrification.

The simultaneous increase of ammonium and TA (Fig. 4c, 4d, 5d) is important to notice, because under oxic conditions the occurrence of ammonium is coupled with nitrification, a process that consumes ammonium and also TA (Chen and Wang, 1999). However, under anoxic conditions, such as in deeper sediment layers, ammonium cannot be reoxidized, accumulates, and is washed out during ebb tide. Since we observed low nitrate concentrations and rule out terrestrial nitrate inputs here, the increase in ammonium and TA implies the occurrence of other anaerobic processes of the redox system, such as sulfate and iron reduction, to generate TA in the deeper, anoxic sediment layers in the Dutch Wadden Sea.

Sulfate reduction followed by iron reduction and the formation and burial of pyrite are net sources of TA, since TA consumption by reoxidation is excluded when buried in sediments (Berner et al., 1970;Faber et al., 2014). Whether and to what extent these processes contribute to TA generation in the deeper sediments of the Dutch Wadden Sea cannot be further identified without the necessary data. However, sulfate reduction was also mentioned as source of TA by Thomas et al. (2009), and the temporary slight appearance of noticeable sulfuric odor could be another indirect indicator for the occurrence of sulfate reduction. In previous studies of tidal flats in the German Wadden Sea, Beck et al. (2008a);(2008b) observed increasing TA concentrations with depth and identified sulfate reduction as the most important process for anaerobic OM remineralization in pore water cores.

A strict comparison of the more northern (north of the Elbe Estuary) and the more western (Texel – Elbe Estuary) parts of the Wadden Sea is difficult because the areas vary in terms of OM import and eutrophication effects (van Beusekom et al., 2019), sediment composition, and extent between the barrier islands and the mainland, all of which influence the occurrence and interaction of biogeochemical processes (Schwichtenberg et al., 2020). The area characteristics of the northern and western

397 Wadden Sea differ especially in terms of OM turnover being lower in the norther Wadden Sea. However, a previous study by

398 Brasse et al. (1999) identified high TA and DIC concentrations in the sediment of the North Frisian Wadden Sea and identified

399 $CaCO_3$ dissolution and sulfate reduction as major TA sources, which is consistent with our findings.
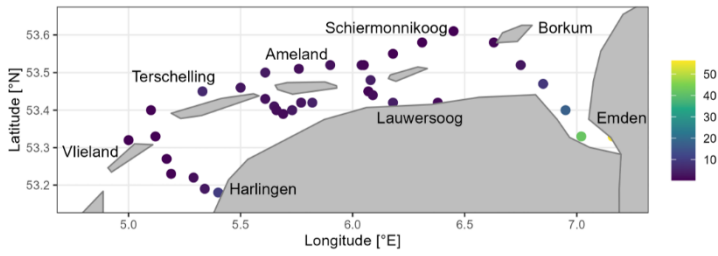
5 Conclusion

401 The Dutch Wadden Sea is a unique and highly dynamic ecosystem. We observed higher TA values in the Dutch Wadden Sea

402 than in the North Sea and identified the Dutch Wadden Sea as a TA source for the North Sea's carbonate system. Compared

403 to previous studies (Hoppema, 1990, 1993), the TA values we observed were in a similar range, with high TA values in the

404 tidal basins. Beside the need for seasonal observations, future work should also focus on regional and seasonal impacts of fresh

405 water inflows of TA on the TA status in the Dutch Wadden Sea.

406 By observing salinity and using dissolved silicate as a tracer, we excluded fresh water and river runoff as significant TA sources

407 on the tidal flats, and instead, deduced local outwash from the sediments as sources of TA. Considering various stoichiometries,

408 we suggest that $CaCO_3$ dissolution generates TA in the more upper oxic sediment layers, and anaerobic, metabolic processes

409 such as denitrification, sulfate and iron reduction are potential TA sources in the deeper anoxic sediment layers. However, in

410 spring and early summer, denitrification seems to play a minor role in generating TA in the sediments of the Dutch Wadden

411 Sea due to seasonality and associated limited nitrate availability.

412 **6 Appendices**

413 **Appendix A**

(A1a) Silicate (μ mol L^{-1})

(A1b) Calcite saturation state (Ω)

(A1c) pH

(A1d) Nitrate (μ mol L^{-1})

(A1e) DIC (μ mol kg^{-1})

414
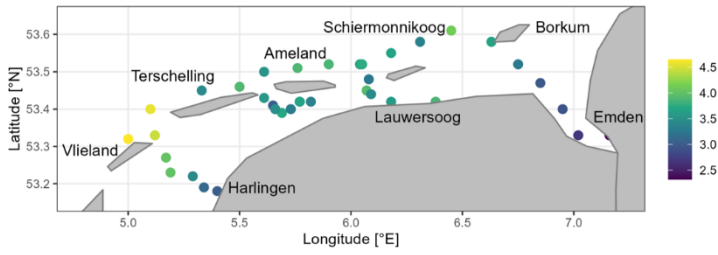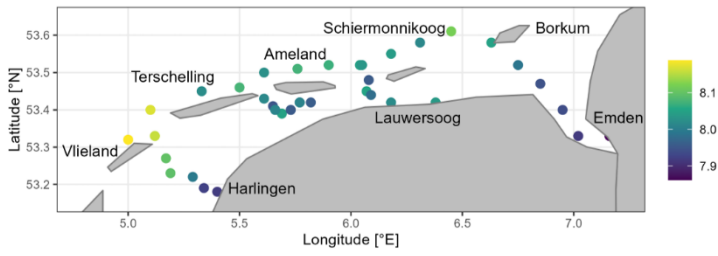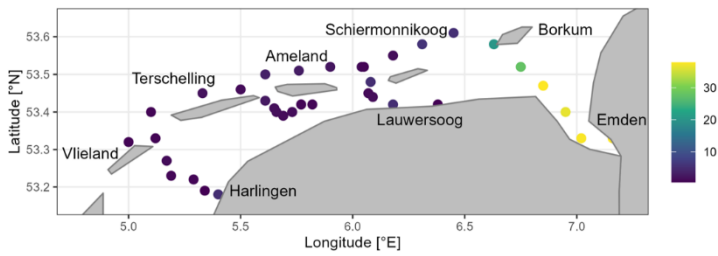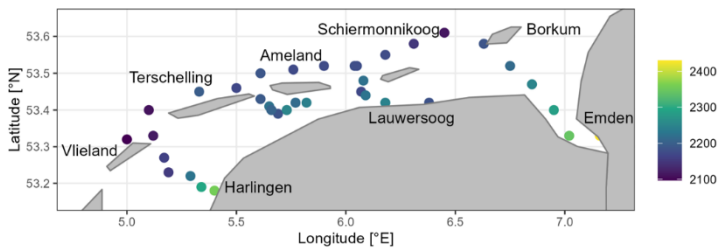
415   **Figure A1** Spatial distribution of A1a) silicate (Si; μmol L^{-1}), A1b) calcite saturation state (Ω), A1c) pH, A1d) nitrate (NO$_3^-$;

416   μmol L^{-1}), and A1e) dissolved inorganic carbon (DIC; μmol kg^{-1}) from surface water samples in May 2019.

417

Appendix B

Table B1 Half tidal cycle sample parameter during ebb tide. Sample no. 545 is the first sample at high tide and sample no. 557 is the last sample at low tide on 21 May 2019 (53.38°N & 5.62°E). Shown are values of temperature (Temp), salinity (Sal), total alkalinity (TA), dissolved inorganic carbon (DIC), silicate (Si), nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), phosphate (PO_4^{3-}), dissolved inorganic nitrogen (DIN), the amount of carbon (C) and organic carbon (C_{org}) of SPM, the amount of nitrogen (N) of SPM, the calcite (Ca) and aragonite (Ar) saturation states, the pH, and the seawater partial pressure of CO_2 (pCO_2) per sample.

Sample No.	Time [UTC]	Temp [°C]	Sal [PSU]	TA / DIC [μmol kg^{-1}]	Si [μmol L^{-1}]	NO_3^- [μmol L^{-1}]	NO_2^- [μmol L^{-1}]	NH_4^+ [μmol L^{-1}]	PO_4^{3-} [μmol L^{-1}]
545	10:46	13.26	32.52	2387 / 2172	1.84	1.26	0.19	3.47	0.12
546	11:19	13.25	32.52	2385 / 2190	1.77	1.24	0.19	3.40	0.11
547	11:49	13.28	32.52	2389 / 2185	1.72	1.21	0.19	3.35	0.11
548	12:23	13.38	32.52	2391 / 2183	1.6	1.19	0.19	3.52	0.12
549	13:35	14.32	32.50	2400 / 2204	2.11	0.91	0.25	3.57	0.32
550	14:05	14.61	32.50	2400 / 2221	2.78	1.09	0.29	3.98	0.42
551	14:36	14.64	32.51	2405 / 2216	2.72	1.01	0.29	4.27	0.47
552	15:26	14.73	32.51	2411 / 2234	4.59	1.23	0.34	5.51	0.57
553	15:42	14.77	32.51	2402 / 2228	4.24	1.26	0.33	5.08	0.54
554	16:04	14.72	32.51	2419 / 2234	5.66	1.46	0.36	5.33	0.54
555	16:38	14.66	32.51	2428 / 2256	8.18	1.77	0.43	6.04	0.58
556	17:07	14.68	32.51	2433 / 2271	9.79	1.87	0.47	6.27	0.62
557	17:32	14.70	32.50	2438 / 2273	11.22	2.17	0.50	6.22	0.63

Sample No.	Time [UTC]	DIN [μmol L^{-1}]	C / C_{org} (SPM) [μmol L^{-1}]	N (SPM) [μmol L^{-1}]	C_{org}:N (SPM)	SPM [mg L^{-1}]	Ca / Ar [Ω]	pH	pCO_2 [μatm]
545	10:46	4.93	86.8 / 65.1	8.8	7.4	12.8	3.8 / 2.4	8.07	385.1
546	11:19	4.83	72.7 / 42.4	7.4	5.8	8.7	3.5 / 2.3	8.03	430.2
547	11:49	4.76	112.4 / 93.4	9.6	9.7	15.4	3.7 / 2.3	8.05	411.4
548	12:23	4.91	108.5 / 104.6	9.9	10.5	16.8	3.7 / 2.4	8.05	404.1
549	13:35	4.73	111.1 / 97.8	8.8	11.1	13.9	3.6 / 2.3	8.01	452.3
550	14:05	5.37	233.0 / 180.3	17.7	10.2	32.2	3.3 / 2.1	7.97	507.2
551	14:36	5.56	193.2 / 174.3	14.5	12.0	29.6	3.5 / 2.2	7.99	477.9
552	15:26	7.08	248.6 / 163.5	18.4	8.9	34.3	3.3 / 2.1	7.96	520.0
553	15:42	6.67	257.6 / 199.3	18.3	10.9	41.6	3.2 / 2.1	7.95	526.4
554	16:04	7.15	324.4 / 271.1	23.2	11.7	55.0	3.4 / 2.2	7.98	496.6
555	16:38	8.24	440.4 / 345.2	29.2	11.8	75.7	3.2 / 2.1	7.95	538.0
556	17:07	8.61	430.5 / 363.3	27.9	13.0	82.4	3.1/ 2.0	7.93.	576.6

22

| 557 | 17:32 | 8.90 | 308.9 / 199.1 | 21.2 | | 9.4 | 48.8 | 3.1 / 2.0 | 7.93 | 568.4 |

Table B2 Half tidal cycle sample parameter during high tide. Sample no. 564 is the first sample at low tide and sample no. 578 is the last sample at high tide on 23 May 2019 (53.39°N & 5.63°E, 5.62°E*). Shown are values of temperature (Temp), salinity (Sal), total alkalinity (TA), dissolved inorganic carbon (DIC), silicate (Si), nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), phosphate (PO_4^{3-}), dissolved inorganic nitrogen (DIN), the amount of carbon (C) and organic carbon (C_{org}) of SPM, the amount of nitrogen (N) of SPM, the calcite (Ca) and aragonite (Ar) saturation states, the pH, and the seawater partial pressure of CO_2 (pCO_2) per sample.

Sample No.	Time [UTC]	Temp [°C]	Sal [PSU]	TA / DIC [μmol kg^{-1}]	Si [μmol L^{-1}]	NO_3^- [μmol L^{-1}]	NO_2^- [μmol L^{-1}]	NH_4^+ [μmol L^{-1}]	PO_4^{3-} [μmol L^{-1}]
564	05:09	14.04	32.66	2431 / 2246	8.53	1.25	0.47	3.31	0.38
565	05:32	14.02	32.68	2441 / 2287	9.14	1.26	0.45	3.08	0.37
566	06:01	13.95	32.69	2436 / 2284	8.88	1.33	0.38	2.46	0.34
567	06:33	14.16	32.69	2443 / 2284	8.68	0.95	0.37	2.37	0.33
568	07:02	14.21	32.69	2432 / 2280	6.94	0.75	0.34	2.63	0.32
569	07:31	14.15	32.55	2401 / 2223	2.12	0.98	0.27	4.12	0.33
570	08:04	14.20	32.55	2403 / 2218	2.10	1.04	0.27	3.88	0.30
571	08:35	14.27	32.55	2409 / 2228	2.15	0.92	0.25	4.18	0.32
572	09:04	14.37	32.53	2400 / 2209	1.88	1.00	0.22	3.86	0.26
573	09:34	14.16	32.52	2398 / 2200	1.70	1.03	0.21	3.51	0.21
574*	10:02	14.17	32.52	2391 / 2197	1.72	1.07	0.21	3.40	0.18
575*	10:34	14.11	32.51	2389 / 2195	1.78	1.18	0.20	3.45	0.16
576	11:04	14.21	32.50	2390 / 2187	1.76	1.12	0.19	3.29	0.14
577	11:34	14.50	32.51	2399 / 2193	1.66	1.10	0.20	3.32	0.16
578	12:03	13.96	32.51	2390 / 2187	1.75	1.41	0.19	3.72	0.11

Sample No.	Time [UTC]	DIN [μmol L^{-1}]	C / C_{org} (SPM) [μmol L^{-1}]	N (SPM) [μmol L^{-1}]	C_{org}:N (SPM)	SPM [mg L^{-1}]	Ca / Ar [Ω]	pH	pCO_2 [μatm]
564	05:09	5.03	353.7 / 253.2	27.5	9.2	52.3	3.0 / 2.2	7.99	490.3
565	05:32	4.78	333.5 / 220.1	26.1	8.4	49.7	3.0 / 1.9	7.92	592.9
566	06:01	4.17	330.3 / 232.9	25.5	9.1	51.7	2.9 / 1.9	7.91	600.3
567	06:33	3.68	274.7 / 195.7	21.8	9.0	36.9	3.0 / 1.9	7.92	582.6
568	07:02	3.72	317.8 / 220.2	24.5	9.0	46.1	2.9 / 1.9	7.91	601.8
569	07:31	5.37	88.6 / 59.1	7.0	8.5	14.7	3.3 / 2.1	7.98	500.7
570	08:04	5.20	96.8 / 73.6	8.8	8.4	18.1	3.4 / 2.2	7.99	482.6
571	08:35	5.35	114.2 / 109.6	9.9	11.0	14.8	3.3 / 2.1	7.98	497.6

572	09:04	5.08	107.5 / 73.9	9.9	7.5	16.4	3.5 / 2.2	8.00	466.6
573	09:34	4.75	82.1 / 72.7	7.2	10.0	11.8	3.6 / 2.3	8.02	445.3
574*	10:02	4.68	85.2 / 62.9	7.2	8.7	9.9	3.5 / 2.3	8.01	450.5
575*	10:34	4.83	83.5 / 65.9	7.2	9.2	11.1	3.5 / 2.3	8.01	449.6
576	11:04	4.60	82.7 / 52.1	8.2	6.3	8.5	3.7 / 2.3	8.03	429.9
577	11:34	4.62	65.8 / 50.8	6.5	7.8	7.2	3.7 / 2.4	8.03	430.8
578	12:03	5.32	71.6 / 54.6	7.7	7.1	7.7	3.7 / 2.3	8.04	425.3

Table B3 Transect parameter of cruise LP20190515 on RV *Ludwig Prandt* in the Dutch Wadden Sea in May 2019. Shown are values of latitude (Lat), longitude (Lon), temperature (Temp), salinity (Sal), total alkalinity (TA), dissolved inorganic carbon (DIC), silicate (Si), nitrate (NO_3^-), the calcite (Ca) and aragonite (Ar) saturation states, and pH per sample. Our salinity and temperature data were complemented by data of three Rijkswaterstaat stations, which were close to our stations. There, Dantziggat* (53°24'4.093", 5°43'37.132") showed temperatures of 11.4 and 14.9 °C and salinities of 31.9 and 31.2 on 10 and 27 May 2019, respectively, Terschelling 10** (53°27'37.318", 5°5'58.129") showed temperatures of 11.4 and 12.9 °C and salinities of 32.8 and 33.4 on 15 and 28 May 2019, respectively, and Vliestroom*** (53°18'48.054", 5°9'35.655") showed a temperature of 11.8 °C and a salinity of 31.1 on 14 May 2019.

Sample No.	Time [UTC]	Day May	Lat. [°N]	Lon. [°E]	Temp [°C]	Sal [PSU]	TA / DIC [µmol kg^{-1}]	Si / NO$_3^-$ [µmol L^{-1}]	Ca / Ar [Ω]	pH
535	07:56	20	53.18	5.4	14.72	30.24	2507 / 2357	10.00 / 5.10	3.0 / 1.9	7.92
536	08:26	20	53.19	5.34	14.81	32.51	2458 / 2296	3.45 / 0.46	3.1 / 2.0	7.92
537	08:53	20	53.22	5.29	14.05	32.38	2413 / 2227	1.92 / 0.85	3.4 / 2.2	8.00
538	09:28	20	53.23	5.19	13.36	32.65	2381 / 2153	0.52 / 1.02	4.0 / 2.6	8.10
539	09:53	20	53.27	5.17	13.17	32.65	2389 / 2161	0.45 / 1.37	4.0 / 2.6	8.10
540***	10:36	20	53.33	5.12	12.77	32.97	2375 / 2118	0.32 / 0.84	4.4 / 2.8	8.16
541	11:03	20	53.32	5.0	12.41	33.25	2368 / 2097	0.34 / 0.77	4.6 / 3.0	8.19
542**	11:49	20	53.4	5.1	12.93	32.92	2374 / 2109	0.44 / 0.81	4.6 / 2.9	8.17
543	12:49	20	53.45	5.33	12.95	32.45	2385 / 2196	6.25 / 1.85	3.4 / 2.2	8.02
544	13:31	20	53.46	5.5	13.55	32.51	2388 / 2169	3.02 / 1.30	3.9 / 2.5	8.08
558	11:33	22	53.41	5.65	13.31	32.51	2384 / 2224	2.57 / 1.56	3.0 / 1.9	7.95
559	12:04	22	53.4	5.66	13.45	32.51	2393 / 2195	1.58 / 1.41	3.6 / 2.3	8.03
560	12:40	22	53.39	5.69	13.67	32.52	2391 / 2183	1.52 / 1.33	3.7 / 2.4	8.05
561	13:09	22	53.4	5.73	14.23	32.48	2418 / 2242	2.04 / 1.04	3.3 / 2.1	7.97
562	13:32	22	53.42	5.77	14.71	32.51	2417 / 2237	3.23 / 1.04	3.3 / 2.1	7.97

563*	13:56	22	53.42	5.82	15.33	32.45	2421 / 2242	4.68 / 0.86	3.3 / 2.1	7.96
579	09:05	24	53.42	5.77	15.26	32.65	2417 / 2215	2.71 / 0.86	3.7 / 2.4	8.01
580	09:31	24	53.4	5.73	14.99	32.66	2426 / 2249	3.52 / 1.46	3.3 / 2.1	7.95
581	10:01	24	53.4	5.66	13.87	32.58	2396 / 2205	1.69 / 1.60	3.5 / 2.2	8.01
582	10:25	24	53.43	5.61	14.36	32.51	2389 / 2193	2.23 / 2.52	3.6 / 2.3	8.02
583	10:59	24	53.5	5.61	13.48	32.58	2382 / 2187	3.69 / 3.41	3.5 / 2.2	8.03
584	11:31	24	53.51	5.76	13.50	32.59	2390 / 2172	1.93 / 2.96	3.9 / 2.5	8.07
585	12:00	24	53.52	5.9	13.65	32.59	2390 / 2173	2.34 / 2.23	3.9 / 2.5	8.07
586	12:30	24	53.52	6.04	13.50	32.48	2384 / 2179	2.00 / 1.53	3.7 / 2.3	8.05
587	13:02	24	53.45	6.07	15.13	32.40	2389 / 2169	0.70 / 1.19	3.9 / 2.5	8.05
588	13:31	24	53.42	6.38	15.63	31.96	2396 / 2182	1.33 / 0.62	3.9 / 2.5	8.04
589	07:20	25	53.42	6.18	15.73	28.31	2430 / 2245	4.16 / 5.13	3.6 / 2.3	8.02
590	07:52	25	53.44	6.09	15.80	30.90	2407 / 2225	1.58 / 1.39	3.4 / 2.2	7.98
591	08:21	25	53.48	6.08	15.34	31.82	2395 / 2222	4.16 / 5.09	3.3 / 2.1	7.96
592	08:51	25	53.52	6.05	14.80	32.41	2386 / 2178	0.71 / 0.67	3.8 / 2.4	8.04
593	09:22	25	53.55	6.18	13.96	32.30	2379 / 2175	0.36 / 1.52	3.7 / 2.3	8.04
594	09:53	25	53.58	6.31	13.43	32.14	2332 / 2148	0.34 / 5.75	3.3 / 2.1	8.01
595	10:24	25	53.61	6.45	13.47	32.10	2347 / 2113	0.26 / 5.19	4.1 / 2.6	8.12
596	11:05	25	53.58	6.63	14.50	29.99	2381 / 2184	0.78 / 20.25	3.7 / 2.3	8.05
597	11:33	25	53.52	6.75	14.94	29.17	2383 / 2214	3.04 / 27.84	3.3 / 2.1	7.99
598	12:00	25	53.47	6.85	15.28	27.82	2395 / 2249	8.90 / 37.93	3.0 / 1.9	7.94
599	12:30	25	53.4	6.95	15.46	26.39	2423 / 2284	17.63 / 36.54	2.9 / 1.8	7.94
600	12:59	25	53.33	7.02	15.76	23.01	2460 / 2343	41.93 / 37.68	2.7 / 1.7	7.92
601	13:29	25	53.33	7.16	15.96	20.25	2517 / 2430	56.32 / 37.94	2.3 / 1.4	7.86

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Data availability

445 The data of this study are presented in the appendices of this article.

Author Contributions

MN wrote the manuscript, did the carbon sampling and sample measurement, analyzed and evaluated the data, and led the study. JvB led the research cruise. JvB and HT contributed with editorial and scientific recommendations. MN prepared the manuscript with contribution from all co-authors.

Competing interests

The contact author has declared that none of the authors has any competing interests.

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