An evaluation of long-term physical and hydrochemical measurements at the Sylt Roads Marine Observatory (1973-2019), Wadden Sea, North Sea

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1. Abstract

The Sylt Roads pelagic time series covers physical and hydrochemical parameters at five neighboring stations in the Sylt-Rømø Bight, Wadden Sea, North Sea. Since the beginning of the time series in 1973, sea surface temperature (SST), salinity, ammonium, nitrite, nitrate and soluble reactive phosphorus (SRP) were measured twice a week. Other parameters were introduced later (dissolved silicate (Si) – since 1974, pH - since 1979, dissolved organic nitrogen (DON) - since 1996, dissolved organic phosphorus (DOP) - since 2001, chlorophyll *a* - since 1979, suspended particulate matter (SPM) - since 1975) and in case of dissolved oxygen were already discontinued (1979-1983). In the years 1977, 1978 and 1983 no sampling took place. Since the start of the continuous sampling in 1984, the sea surface temperature in the bight has risen by +1.11 ^{o}C, with the highest increases during the autumn months, while the pH and salinity decreased by 0.23 and 0.33 units, respectively. Summer and autumn salinities are generally significantly elevated compared to spring and winter conditions. Dissolved nutrients (ammonium, nitrite, nitrate and SRP) displayed periods of intense eutrophication (1973 – 1998) and de-eutrophication since 1999. Silicate showed significantly higher winter levels since 1999. Interestingly, phytoplankton parameters did not mirror these large changes in nutrient concentrations, as a seasonal comparison of the two eutrophication periods showed no significant differences with regard to chlorophyll *a*. This phenomenon might be triggered by an important switch in nutrient limitation during the time series: With regard to nutrients, the phytoplankton was probably primarily limited by silicate until 1998, while since 1999 SRP limitation became increasingly important.

Repository-Reference: Rick et al. (2017b-e, 2020a-o): ~~and Rick et al. submitted:~~ doi:10.1594/PANGAEA.150032, 873549, 873545, 873547, 918018, 918032, 918027, 918023, 918033, 918028, 918024, 918034, 918029, 918025, 918035, 918030, 918026, 918036, 918031

2. Introduction

The Sylt-Rømø Bight (SRB) is a Marine Protected Area (MPA) in the Wadden Sea UNESCO World Heritage area since 2009. It is a large tidal lagoon (ca. 400 km^2) in the northern part of the Wadden Sea (SE North Sea). In the previous century two causeways connecting the islands of Rømø and Sylt with the mainland were built. Since then a narrow inlet between Sylt and Rømø is the only connection with the open German Bight through which almost 50% of the bights' water is exchanged each tidal cycle. Local riverine discharge is estimated to be 0.1 % of the total water input. Tides are semidiurnal with a range of about 2m. At mean low tide 33% of the bight is exposed, 10% of the remainder comprising deep channels with a maximum depth of 40m and 57% is a shallow subtidal area with depths less than 5m (Gätje & Reise, 1998, Figure 1).

In 1973 the Sylt Roads **L**ong **T**erm **E**cological **R**esearch time series (Sylt Roads LTER) was initiated in this hydrographically and ecologically interesting area. This consists of a "twice a week" sampling of oceanographic, hydrochemical and biological (phyto-, zooplankton, fish) parameters. Meanwhile, most of these Sylt Roads data (> 1000 data sets) has been published online in the open access data bank PANGAEA (www.pangaea.de). In this work we summarize for the first time the information on physical and hydrochemical parameters of this time series and provide a brief overview of the development over the last 45 years.

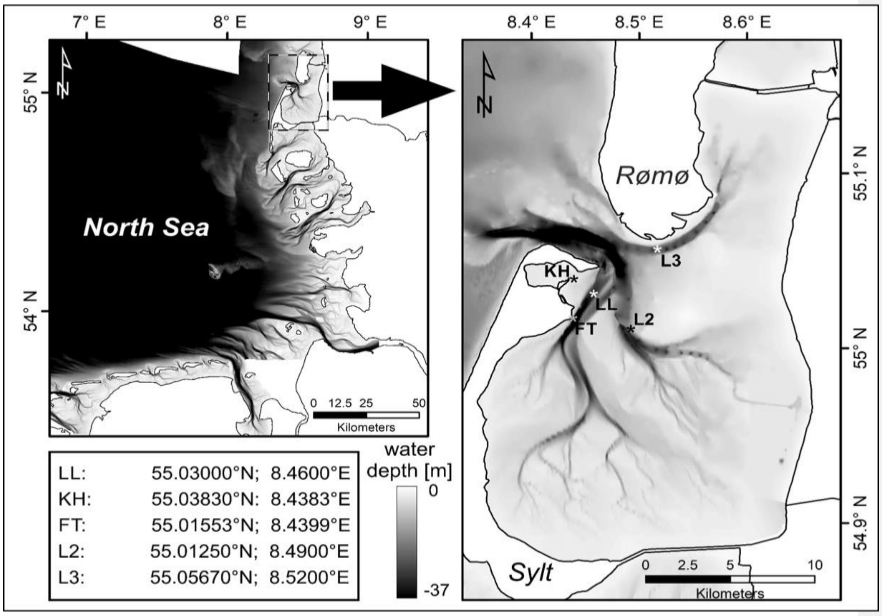


Figure 1: Map of the German Bight with the sampling area (Sylt-Rømø Bight) enlarged with main sampling stations of the SYLT ROADS LTER time series and their geographical position. LL: Lister Ley or List Reede, KH: entrance Königshafen, FT: List Ferry Terminal, L2 and L3: List 2 and 3 stations sampled in early part (until 1991) of the time series only.

3. Data coverage and parameters measured

Coverage:

North: 55.01250 - 55.05670; East: 8.43830 - 8.52000

Location names and positions:

LL: List_Reede (Lister_Ley), Sylt Rømø Bight, Wadden Sea, North Sea: North: 55.03000; East: 8.46000

L2: List_2, Sylt-Rømø Bight, German Bight Wadden Sea, North Sea: North: 55.01250; East: 8.49000

L3: List_3, Sylt-Rømø Bight, German Bight Wadden Sea, North Sea: North: 55.05670; East: 8.52000

KH: List_Entrance_Königshafen, Sylt-Rømø Bight, German Bight Wadden Sea, North Sea: North 55.03830; East: 8.43830

FT: List_Ferry_Terminal, Sylt-Rømø Bight, German Bight Wadden Sea, North Sea:

North: 55.01553; East: 8.43990

Date/Time Start: 1973-06-28T00:00:00

Date/Time End: 2019-12-31T00:00:00

Parameter	Short Name	Unit	Comment
DATE/TIME	Date/Time		Geocode
DEPTH, water	Depth water	M	Geocode
Salinity	Sal		
Temperature, water	Temp	°C	
pH	pH		
Dissolved Oxygen	O_2	µmol/l	
Chlorophyll *a*	Chl *a*	µg/l	Filtered through GFC, stored frozen (-20°C), Extraction by Acetone
Phosphate	$[PO_4]^{3-}$	µmol/l	Filtered 0.4 µm Nucleopore, stored frozen (-20°C)
Silicate	$Si(OH)_4$	µmol/l	Filtered 0.4 µm Nucleopore, stored frozen (-20°C)
Ammonium	$[NH_4]+$	µmol/l	Filtered 0.4 µm Nucleopore, stored frozen (-20°C)
Nitrite	$[NO_2]^-$	µmol/l	Filtered 0.4 µm Nucleopore, stored frozen (-20°C)
Nitrate	$[NO_3]^-$	µmol/l	Filtered 0.4 µm Nucleopore, stored frozen (-20°C)
Nitrogen, organic, dissolved	DON	µmol/l	Filtered precombusted GFC, stored frozen (-20°C)
Phosphorus, organic, dissolved	DOP	µmol/l	Filtered precombusted GFC, stored frozen (-20°C)
Suspended matter	SPM	mg/l	Filtered 0.4 µm Nucleopore, stored frozen, dried (60°C)

4. Instrumentation and methods

Sea surface temperature (SST), salinity, ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), soluble reactive phosphorus (SRP) and reactive silicate (Si) measurements were started in 1973 and interrupted temporarily in the years 1977, 1978 and 1983. Temperatures of the sea surface (SST) were gathered using reversing thermometers (Thomas & Dorey, 1967). For the period 1973 – 1982 the inductive salinometer method was used for salinity measurements (Brown & Hamon, 1961). Since 1983, we measured the salinity using a Guildeline AutoSal 8400B salinometer (Kawano, 2010). pH-measurements were initiated in 1979. Until 1984, diverse pH meters were applied and since 1985 a WTW pH 3000 Meter is in use. Dissolved oxygen was measured only during the period from 1979-1983 using the Winkler method (e.g. Culberson et al., 1991). Table 1 gives an overview on the methods applied within the time series for several chemical analyses on nutrient components and chlorophyll *a*. For both DON and DOP filtration we used precombusted CFC filters and filtrates were frozen at -20°C, while for chlorophyll *a* analysis untreated GFC filters were employed instead. For gravimetric suspended matter (SPM) analyses we used precombusted CFC filters from 1975 to 1998, since 1999 0.4 – 0.45 µm NUCLEOPORE filters were employed.

parameter	time period	analysis
soluble reactive phosphate (SRP)	1973-1983	Koroleff (1976a)
reactive Si (Si)	1974-1982	Koroleff (1976b)
ammonium (NH_4^+)	1973-1982	Grasshoff & Johannsen (1972)
nitrite (NO_2^-)	1973-1982	Bendschneider & Robinson (1952)
nitrate (NO_3^-)	1973-1982	Grasshoff & Wenck (1983)
SRP, Si, NH_4^+, NO_2^-, NO_3^-	1984-ongoing	Grasshoff et al. (1983)
dissolved organic nitrogen (DON)	1996-ongoing	Grasshoff et al. (1983)
dissolved organic phosphorus (DOP)	2001-ongoing	Grasshoff et al. (1983)
chlorophyll a (Chl *a*)	1979-ongoing	Jeffrey & Humphrey (1975)

Table 1: Compilation of methods applied in the Sylt Roads time series

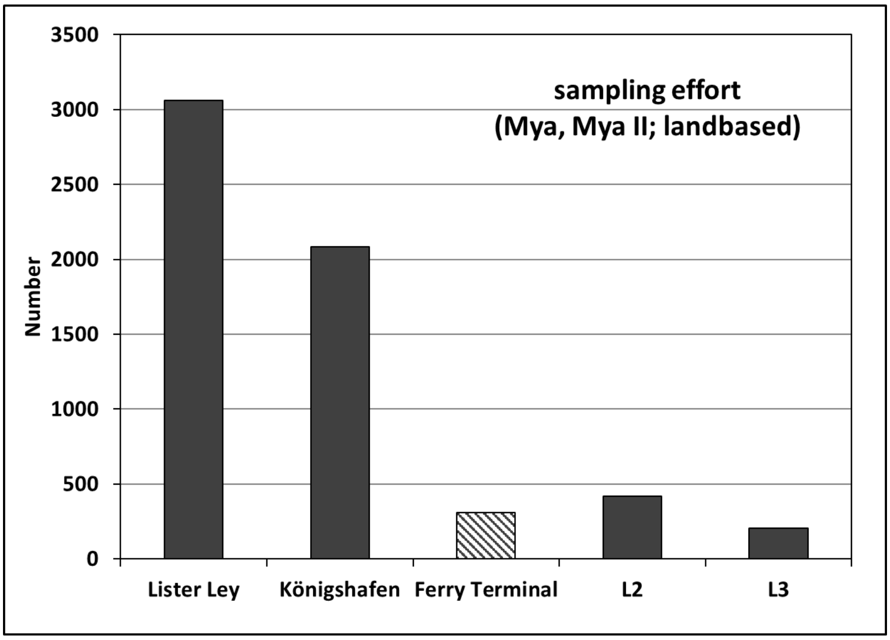
Since the start of the Sylt Roads time series, six analysts have been engaged in the hydrochemical analyses (Table 2).

analyst	time period	years, months
1	1973 – 09/1977	4y 9 m
2	10/1978 – 01/1992	13y 4m
3	09/1992 – 08/1994	1y 11m
4	10/1994 – 02/1999	4y 5m
5	05/1999 – 12/2000	1y 7m
6	since 05/2001	>18y

Table 2: Analysts within the Sylt Roads hydrochemistry time series

Sampling was mostly conducted from small research vessels (RV Mya till 2012, since 2013 RV Mya II), or sometimes, in severe weather conditions it was land-based at the List Ferry Terminal. Figure 1 provides an overview on the geographical position of the main sampling locations in the Sylt-Rømø Bight (SRB).

Statistical analyses were performed using the Analyse**-it tool for Microsoft Excel 6.15**, build 8265.19231. For the Correlation and Principal Component Analyses seasonal averages (three month means; winter: Dec-Feb) were calculated for each parameter. Prior to PCA these data were standardized so that each variable had a variance of 1.



~~Figure 2a: Overall sampling efforts (ship- and land-based [Ferry Terminal] campaigns) at the five sampling stations (1973-2019)~~

5. Datasets and Discussion

5.1 General description of the basic data

Ship based sampling was carried out with the research vessels Mya (till 2013) and Mya II (2014-ongoing). The Lister Ley station (LL) and the Königshafen station (KH) were visited most frequently, while stations List 2 and 3 (L2, L3) were sampled only during the early periods (1973-1976; 1987-1991) of the time series. Since 1999 the List Ferry Terminal station (FT) was used as a backup when ship-based sampling was not possible due to adverse weather conditions. Until December 20th 2019, 43.712 data (SST, salinity, pH, nutrients, chlorophyll, SPM) were collected during 5133 RV Mya and Mya II samplings and 150 land-based efforts at the List Ferry Terminal. ~~Ship- and land-based sampling efforts are displayed in Figure 2a. The Lister Ley station (LL) and the Königshafen station (KH) were visited most frequently, while stations List 2 and 3 (L2, L3) were sampled only during the early periods (1973-1976; 1987-1991) of the time series. Since 1999 the List Ferry Terminal station (FT) was used as a backup when ship-based sampling was not possible due to adverse weather conditions. Overall, more than 63.000 data were collected during more than 5.700 RV Mya and Mya II cruises and about 300 land-based sampling efforts at the List Ferry Terminal.~~ Figure 2~~b~~ provides an overview of the seasonal sampling efforts summarized for all stations. Generally, the number of samples per season varied during the first part of the time series, since 1999 seasonal sampling was more homogenous. The inserted box plots compare the earlier with the more recent parts of the time series. For winter and summer sampling significant differences in sampling effort are obvious (Figure 2b, Table A1 l).

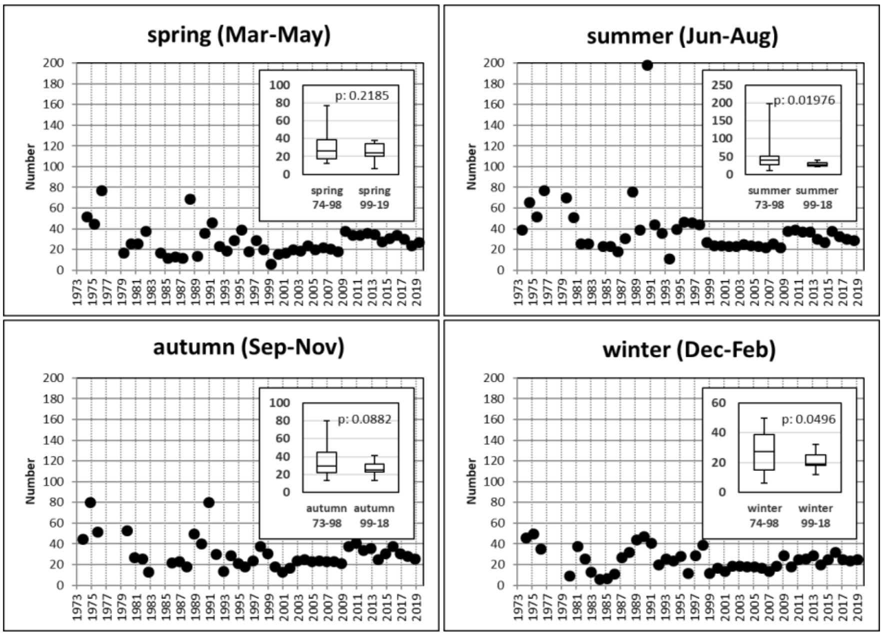


Figure 2b: Seasonal sampling efforts summarized for all Sylt Roads stations in the SRB (1973-2019). The inserts compare seasonal efforts from early days (1973/74 – 1998) with the more recent part (1999-2019) of the time series.

Most of the measured parameters are shown as original data in Figures 3a-j. Due to the physical proximity of stations and the extremely well-mixed waters in the SRB, data from all sampling stations (Figure 1) were included in the graphs. Most of the parameters, even salinity (Figure 3a), show seasonal signals.

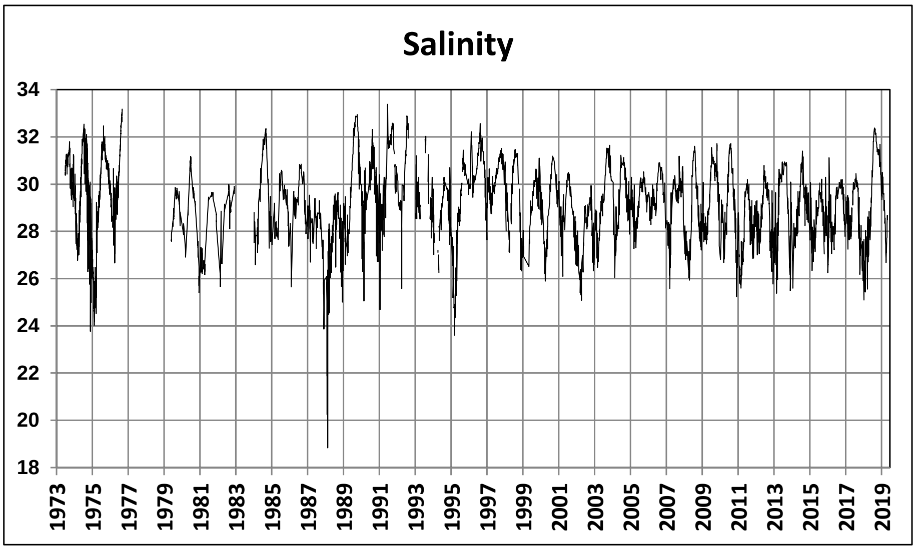


Figure 3a: Salinity time series at Sylt Roads. Data of the five sampling stations (Figure 1) are included in all subgraphs of Figure 3.

For salinity this is mainly triggered by the enhanced freshwater runoff in late winter and spring. Seasonal patterns are most evident for the SST (Figure 3b) and the associated oxygen content of the waters (data not shown) as well as for the major inorganic nutrients as NH_4^+, NO_2^-, NO_3^-, SRP and reactive silicate (Figures 3c-g). Not too much should be read into the nutrient data from early years since some (e.g. NH_4^+, SRP) show quite high variability or exceptionally low values (Si, NO_3^-) especially in the initial period (1973-75). From 1992 to 1994 all NH_4^+ numbers were also exceptionally low, which coincided with a specific analyst (Table 2) and are obviously erroneous. All questionable values were eliminated from the graph (Figure 3c).

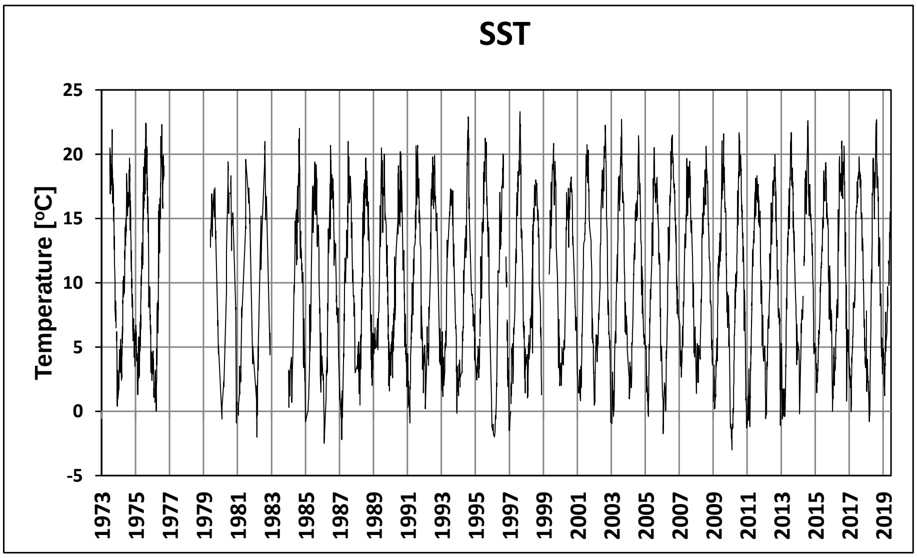


Figure 3b: Time series of the sea surface temperature (SST) at Sylt Roads

Dissolved inorganic nutrients display an opposite behavior compared to the SST with high values in winter/early spring and minimal numbers during summer. As expected Chlorophyll *a*, pH (Figure 3h, i) as well as dissolved organic nutrients (data not shown) are inversely related to levels of inorganic nutrients due to the nutrient uptake by the phytoplankton.

High SPM is mostly found in winter due to the large amounts of sediment mixed into the water column by wind forcing (Figure 3j, Bayerl et al., 1998). In summer SPM decreases to minimum values. A deviation from this pattern was seen in the period from 1993-1997, which is likely due to inaccurate sample treatment: following the filtration process, the sea salt retained by the filter material is normally leached out using distilled water. When the salt is not completely removed in this process the measured SPM load will be biased. This was probably the case for the 1993-1998

SPM measurements and the respective data should not be used and consequently have been omitted from the graph.

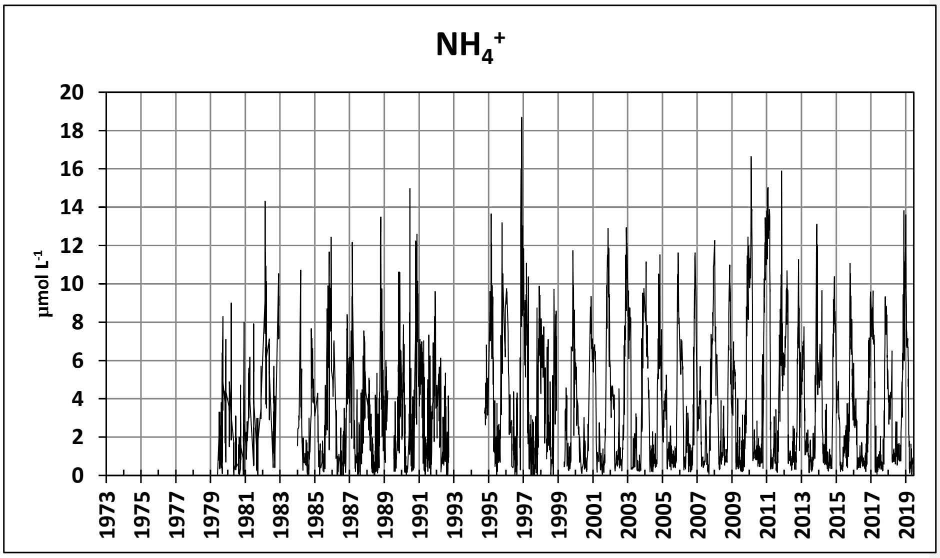


Figure 3c: Development of ammonium concentrations at Sylt Roads (1979-2019). Data from 1973 - 1978 and 1993 - 1994 were biased and are not shown in the graph.

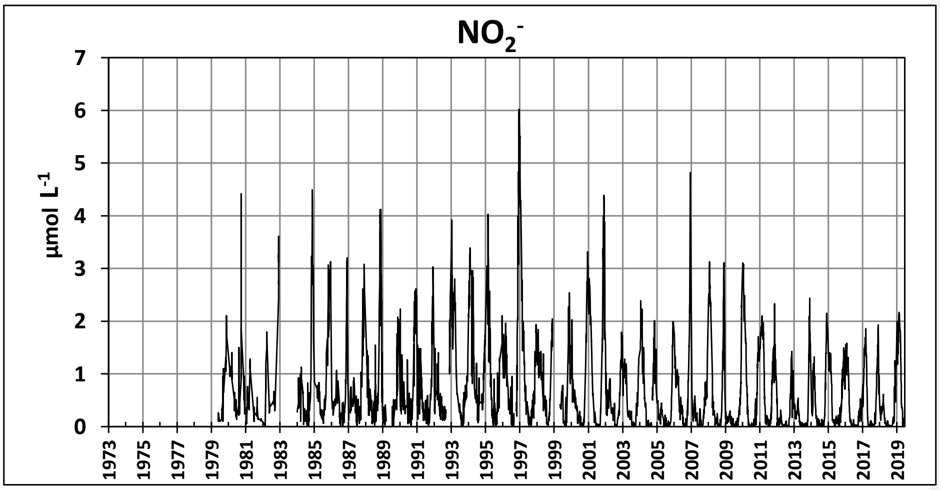


Figure 3d: Development of nitrite concentrations at Sylt Roads.

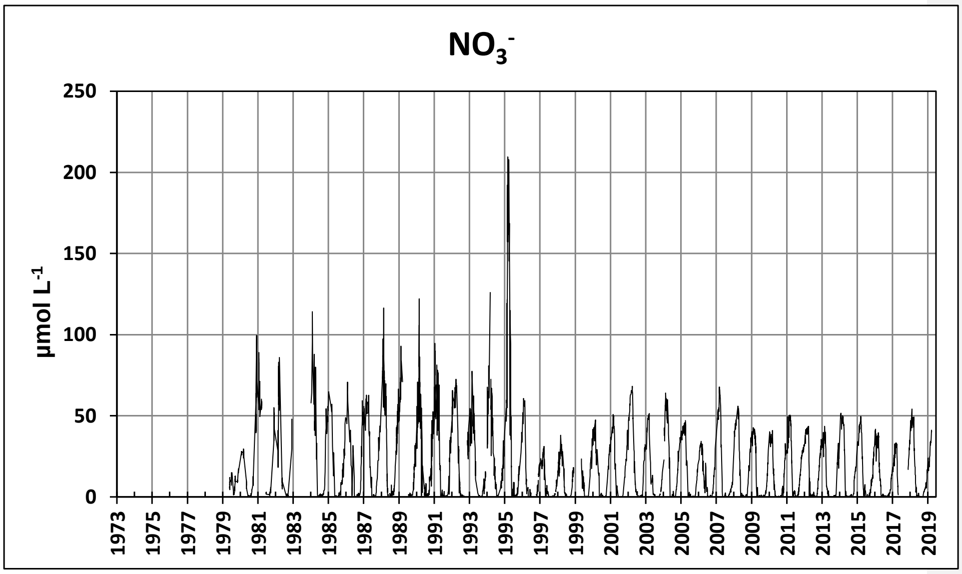


Figure 3e: Development of nitrate concentrations at Sylt Roads.

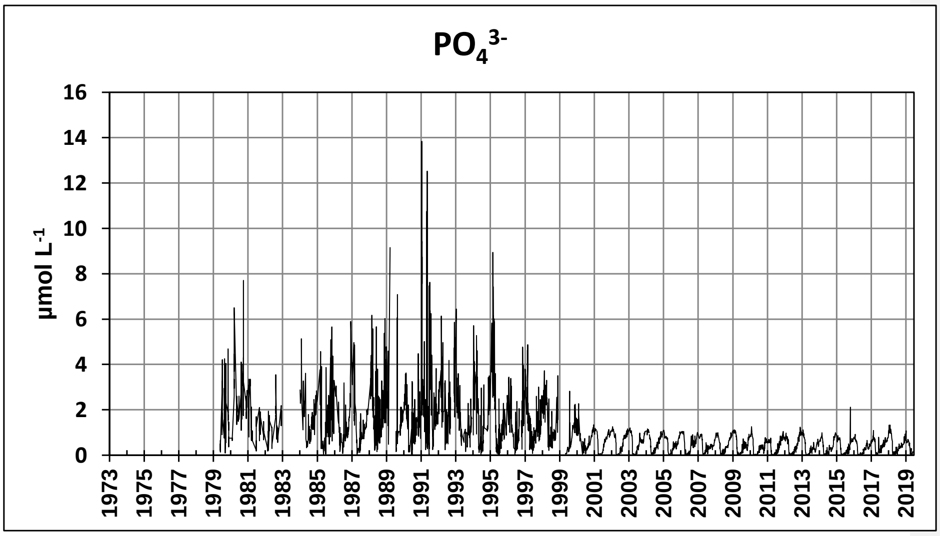


Figure 3f: Development of soluble reactive phosphate (SRP)

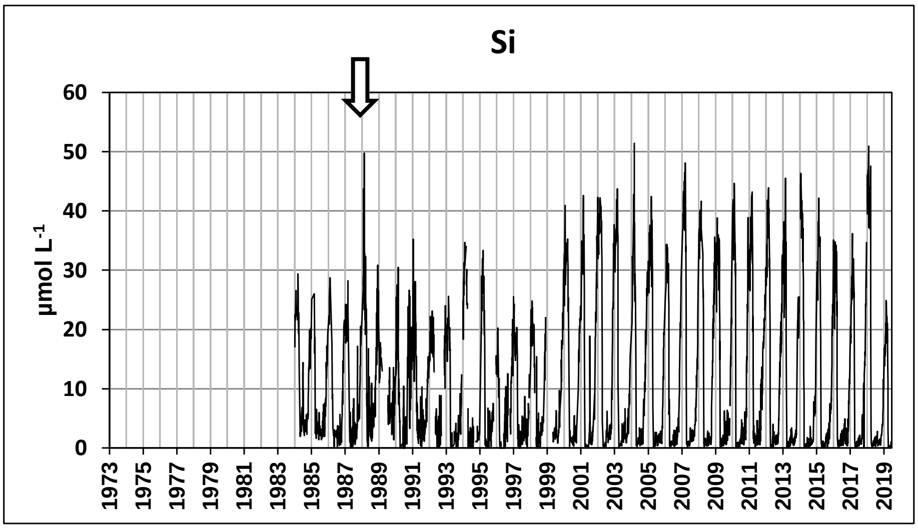


Figure 3g: Development of reactive silicate (Si) concentrations at Sylt Roads. The "1988 Si anomaly" is marked with an arrow

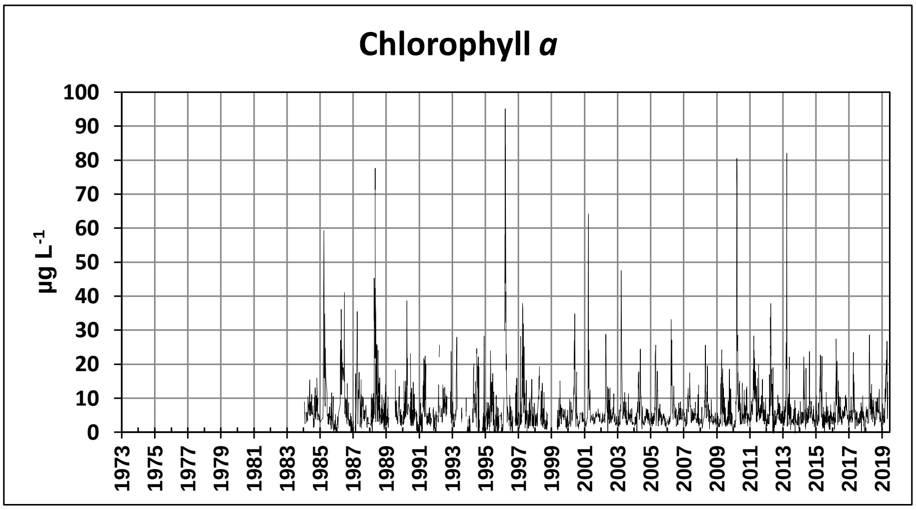


Figure 3h: Development of Chlorophyll *a* concentration at Sylt Roads.

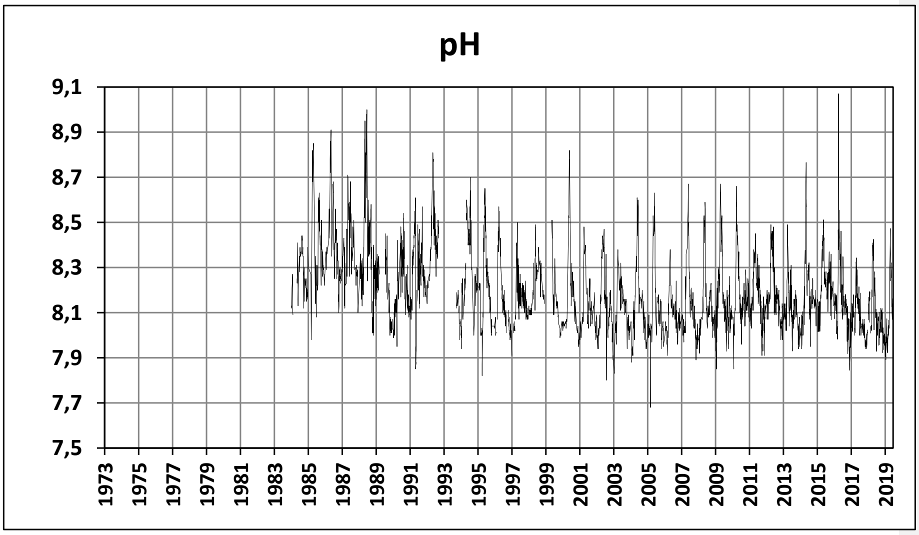


Figure 3i: pH development at Sylt Roads. Data before 1984 and from 1992 were biased and are not included in the graph.

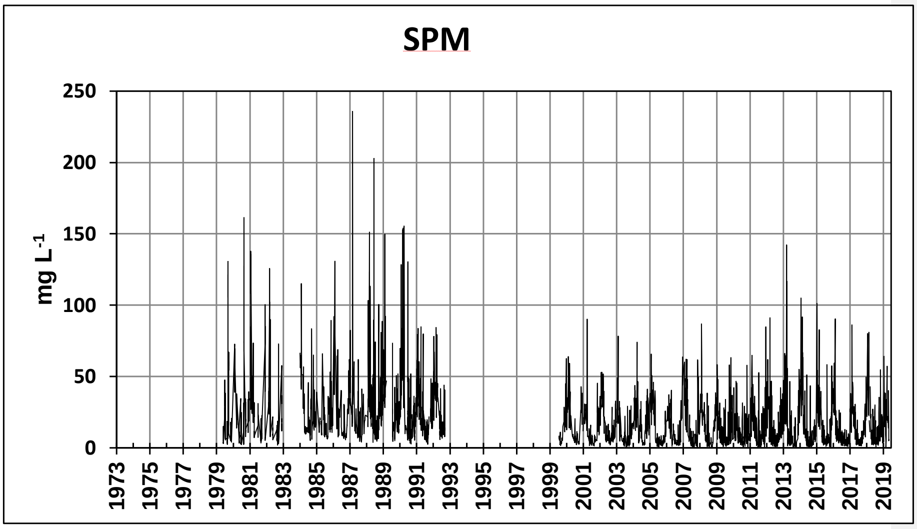


Figure 3j: Development of suspended particulate matter concentrations (SPM) at Sylt Roads. No data are shown for the period of biased handling (1993-98)

The nutrient plots (e.g. Figure 3e, f) indicate a change in the eutrophication status of the bight. Until 1998, nitrate as well as SRP concentrations were high, since 1999 they have been decreasing. This is in line with several observations from the southern North Sea area and mainly due to strong reductions of phosphorus and nitrogen loads in the rivers Rhine, Ems, Weser and Elbe (e.g. Carstensen et al., 2006; van Beusekom et al., 2005, 2018, 2019).

Much a higher variability in nutrient values was evident for the high eutrophication period (1973-1998) compared with more recent times (1999 – 2019) of reduced nutrient loads. This high variability might be partly related to the fact that till 1998 only unfiltered nutrient samples were analyzed, from 1999 on the samples were finally filtered (van Beusekom et al., 2009). The early eutrophication period was additionally characterized by intense marine or inshore construction and dredging activities. Sediments originating from the Sylt-Rømø Bight were intensively used for dike building (e.g. the polders Margarethenkoog and Rickelsbüller Koog), the Hoyer lock was constructed, the Ruttebüll Lake dredged out and the river Vidå renatured. All these activities certainly have influenced e.g. the loads of SRP and contributed potentially to the high variability in nutrient concentrations. An intense blue mussel fishery in the early period of the time series with its associated dredging impact as well as the shutdown of the List sewage plant in 2005 might have played an important role in nutrient variability, too.

To evaluate more generalized relationships between all the parameters we calculated seasonal averages (3 months each, winter as December – February) for the years and performed (1) a correlation analysis as well as (2) a principal component analysis (PCA) on these data since the start of the continuous sampling in 1984. For the PCA the data were standardized so that each variable had a variance of 1.

The correlation table (Tab. 3a) shows the Pearson's r values for all parameter in the correlation analysis. Salinity is highly correlated with SST and negatively correlated to nutrients illustrating the dominance of nutrient poor open North Sea waters during warmer seasons. All dissolved nutrients as well as SPM are negatively correlated to salinity and SST displaying the importance of the elevated freshwater inflow as well as the higher storm frequency during cold seasons. The primarily river-born components nitrate and silicate show the most negative correlation to both salinity and SST. Generally, all nutrients are highly correlated to each other. A strong connection between pH and chlorophyll is obvious, underlining the importance of the biogenic decalcification process in aquatic photosynthesis.

Pearson's r	**salinity**	**SST**	**pH**	**NH4**	**NO2**	**NO3**	**PO4**	**Si**	**Chl**	**SPM**
salinity	-									
SST	**0,64**	-								
pH	-0,08	0,14	-							
NH4	-0,28	**-0,62**	**-0,47**	-						
NO2	-0,32	**-0,61**	-0,22	0,76	-					
NO3	**-0,63**	**-0,81**	0,02	0,36	**0,43**	-				
PO4	-0,10	-0,29	0,16	0,23	0,23	**0,59**	-			
Si	**-0,60**	-0,83	-0,33	**0,65**	**0,56**	**0,72**	0,23	-		
Chl	-0,19	**-0,05**	**0,62**	**-0,43**	-0,22	0,02	-0,18	-0,25	-	
SPM	**-0,45**	**-0,70**	0,09	0,31	0,38	**0,87**	**0,61**	**0,62**	0,01	-

Table 3a: Pearson's r values from a correlation analysis of Sylt Roads LTER physical and hydrochemical parameters based on seasonal averages (1984 – 2019). Values > 0,4 and < -0,4 are in bold numbers.

The PCA variance table (Tab.3b) shows the amount of variance in the original data described by each principal component. The first three principal components explain more that 80% of the variance in the data. All results are consistent with those of the correlation analysis. PC1 is mostly determined by SST, Si, NO3, SPM, NH4 and NO2, PC2 by pH and chlorophyll, while PO4 dominates PC3 (Table A2)

Component	Variance	Proportion	Cumulative proportion
1	4,797	0,480	0,480
2	2,109	0,211	0,691
3	1,190	0,119	0,810
4	0,7237	0,072	0,882
5	0,4103	0,041	0,923
6	0,2651	0,027	0,949
7	0,2223	0,022	0,972
8	0,1347	0,013	0,985
9	0,09610	0,010	0,995
10	0,05286	0,005	1,000

Table 3b: Variance and (cumulative) proportion of principal components; physical and hydrochemical parameters Sylt Roads LTER time series, seasonal averages (1984-2019)

A Correlation Monoplot of the first two principal components representing 69 % of the variability in the data set is shown in Figure 4. Most parameters are represented very well with the exception of PO4 (short arrow), which is the most dominant feature in the third component (see Table A2). The small angle between the salinity and SST vectors shows their close correlation. NO3, SPM and (PO4) display a complete negative correlation with salinity. All nutrients are strongly negatively correlated with SST, with highest numbers for Si and NO3. The close similarity of the chlorophyll and pH vectors again shows the strong influence of the photosynthesis on the pH. Both parameters do not have any correlation to either salinity and SST or SPM, PO4 and NO3, while they are slightly negatively correlated to Si, NO2 and NH4.

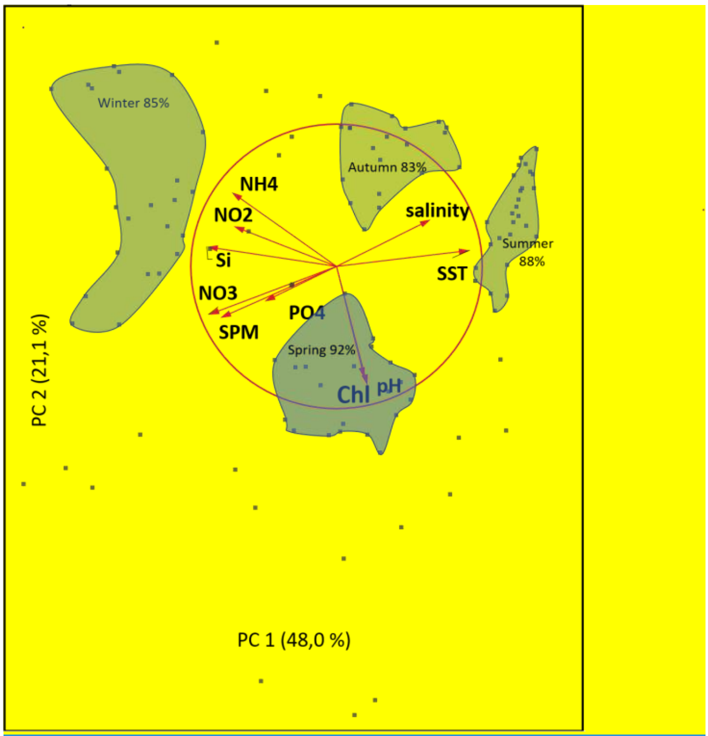


Figure 4: PC Analysis Correlation Monoplot of the first two principal components. Sylt Roads LTER time series on physical and hydrochemical parameters, seasonal averages. Areas covering > 83% of the data points are displayed for each season.

Additionally, point areas representing data for the seasons are shown. The provided percentages describe the amount of the seasonal data within the respective area. Summer seasons are characterized by high temperature and SST combined with low nutrient and SPM values. The opposite is the case for winter seasons. Spring seasons show chlorophyll and pH as major factors, highlighting the importance of the phytoplankton spring bloom in the SRB. Autumn is characterized by medium salinity and SST levels. Additionally, the intermediate nitrogen components NH4 and NO2 are most important in autumn which points to an increased relevance of remineralization processes during this season.

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5.2 Nutrients, chlorophyll *a*, nutrient ratios and SPM

Since most of the parameters show seasonal signals, it was considered appropriate to focus on changes for the four main seasons in the course of the time series.

Figure 5a4a gives an example for the nutrient SRP. For each year in the time series

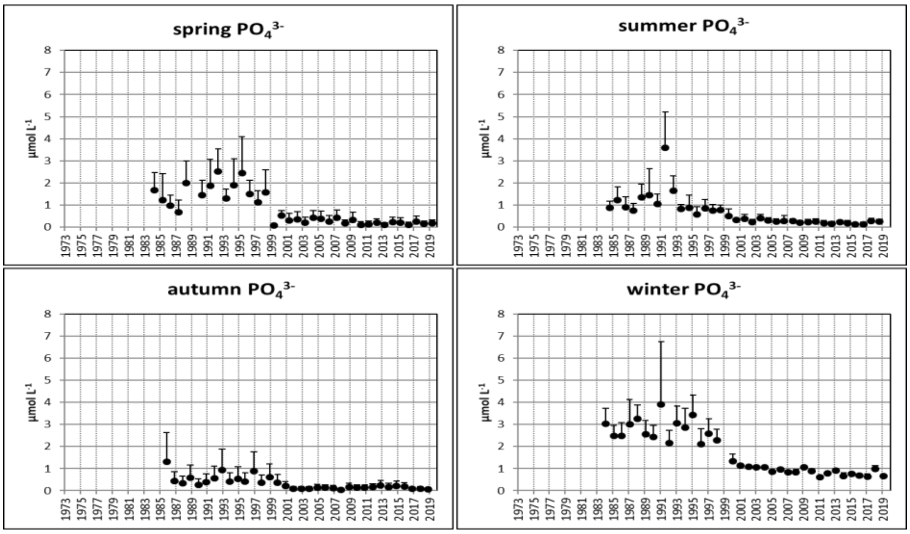

Figure 5a4a: Development of SRP over the course of continuous measurements (1984-2019) within the Sylt Roads LTER time series. Seasonal averages (Dec, Jan, Feb – winter; Mar, Apr, May – spring; Jun, Jul, Aug – summer; Sep, Oct, Nov – autumn) are displayed with standard error of means (SEM) as error bars.

seasonal averages are presented together with their respective standard errors. As already seen to some extent in Figure 3f, a first period (1984-1998) of relatively high values shifts towards a second one (1999-2019) with a lot lower SRP concentrations. A comparison of both periods using a t-test (two-sided, different variances assumed) results in highly significantly lower (p: 0.0003 – 1.1×10^{-10}) and much less variable SRP values for all seasons in the period of low eutrophication (1999-2019; Figure 5b4b, Table A1 a).

Dissolved inorganic nitrogen (DIN, i.e. sum of nitrate, nitrite and ammonium) shows a similar pattern although the respective t-tests yielded significant differences for spring (p: 0.017) and winter (p: 0.001) seasons only (Figure 65, Table A1 b).

Silicate (Si), a nutrient important for diatoms, shows a completely different pattern (Figure 76, Table A1 c). The more recent (1999-2019) low eutrophication winters and

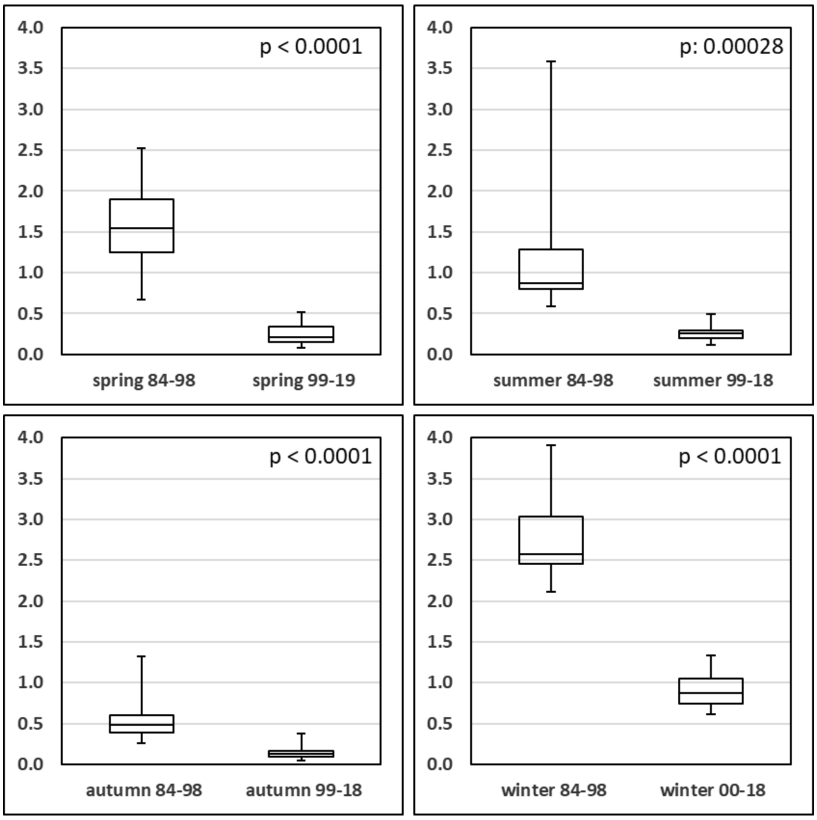

Figure 5b4b: Seasonal comparison of SPR concentrations [$\mu mol*l^{-1}$] for high/low eutrophication periods. Boxplots give median values, with quartiles 1 and 3 attached as boxes and min and max values shown as endpoints of the error bars. All data including possible outliers are shown in the graph. The p-values of the respective t-tests are given in the upper right.

autumns (N and P) showed significantly (p: 1.16 x 10^{-6} and 0.026) elevated Si values compared with the respective data of high eutrophication (1973-1998). For the spring comparison Si values remained in the same range. In summer (p = 0.001), the low eutrophication set showed a significantly lower value. Generally, the variability of Si was a lot higher in the period from 1973-1998 compared to 1999-2019 (Figure 76; Table A1 c). Interestingly, the silicate anomaly from 1988 (Raabe & Wiltshire, 2009) shows its imprint (highlighted in Figure 3g) in the Sylt Roads data, too.

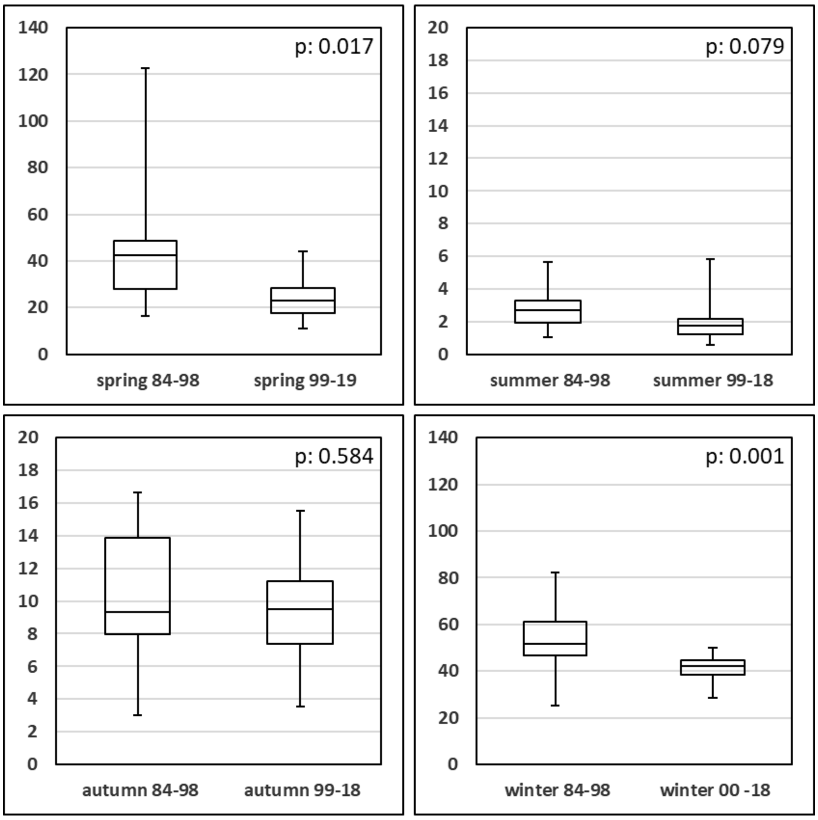

Figure 65: Seasonal comparison (boxplots and t-test p-values) of dissolved inorganic nitrogen (DIN) concentrations [µmol*l^{-1}] for high/low eutrophication periods. Detailed information is available in Figure 4b.

Despite these large changes in nutrient concentrations, phytoplankton parameters such as chlorophyll *a* (Figure 3h, 87 and Table A1 i) or phytoplankton carbon (Rick et al., 2017a) did not shift accordingly, as probably expected (e.g. Cadee & Hegeman, 2002).

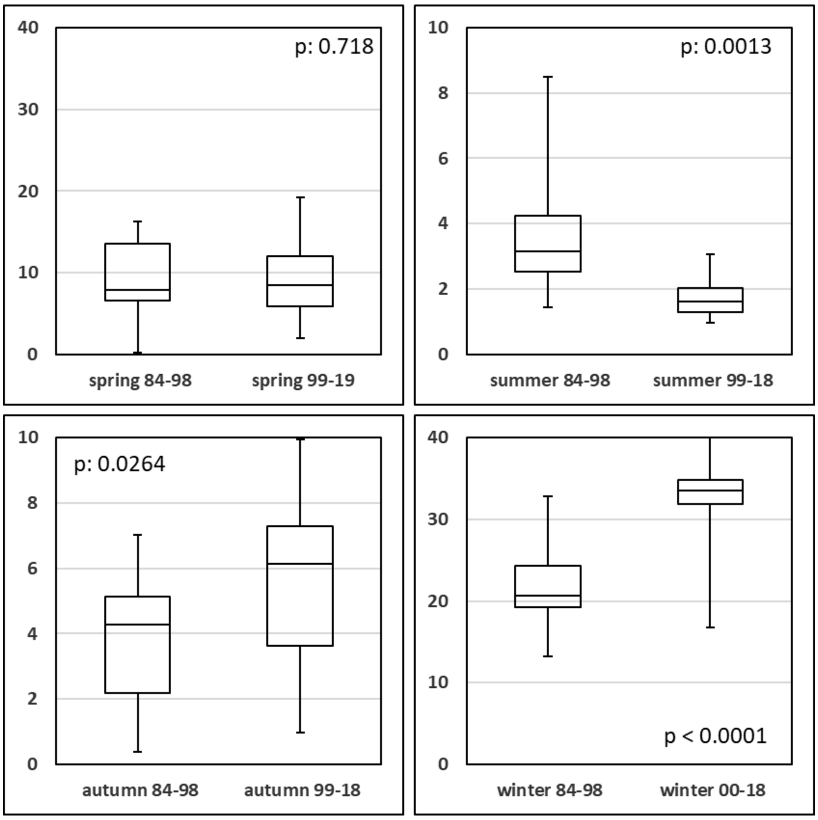

Figure 76: Seasonal comparison of reactive silicate concentrations [µmol*l^{-1}] for high/low eutrophication periods.

Planktonic algae are not solely influenced by the total concentrations of single nutrients – but rather it is the nutrient ratios have an essential impact (Dugdale, 1967). For most algae the DIN/SRP ratio (Figure 98, Table A1 j) is of major importance (Redfield, 1934, 1958), diatoms are additionally affected by the DIN/Si (Figure 9, Table A1 k) ratio (Brzezinski, 1985). In Figures 98 and 109 the optimal nutrient ratios, based on molar concentrations, are highlighted as grey bars.

Generally, the DIN/SRP ratio in most cases is highly significantly elevated in the low eutrophication period when compared with the high eutrophication period (Figure 98).

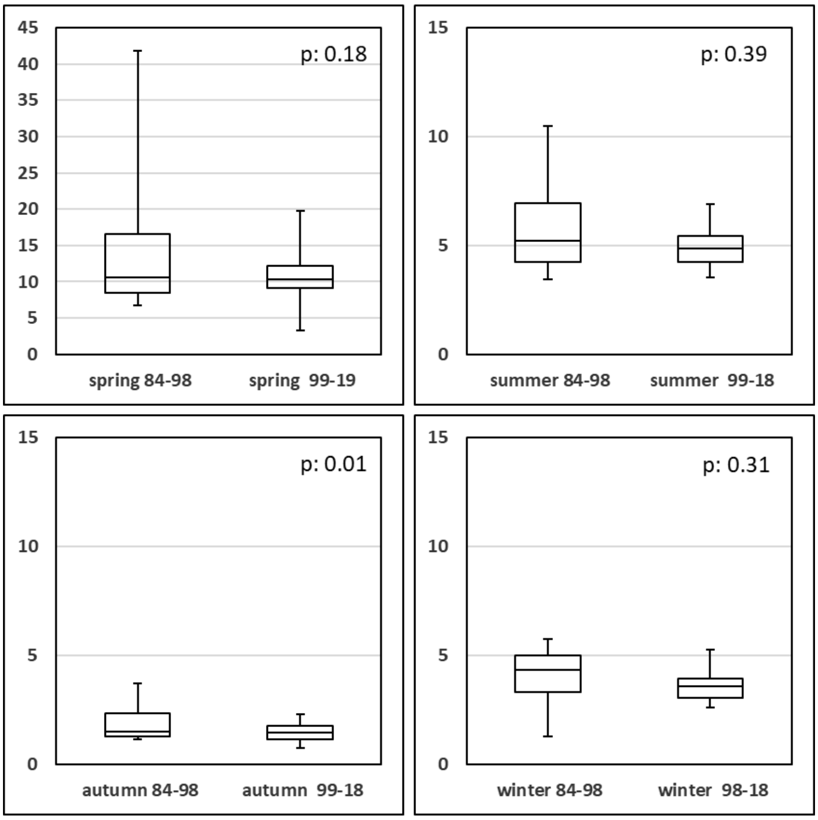

Figure 87: Seasonal comparison of Chlorophyll *a* concentration [µg*l^{-1}] for high/low eutrophication periods.

For winter and spring this change moved the ratio towards an increasing phosphorous limitation, while for summer and autumn it diminished the N-limitation during the high eutrophication period.

The spring and winter DIN/Si ratios (Figure 10~~9~~, Table A1 k) moved from higher (1973-1998) to more balanced values (1999-2019). For winter ($p = 0.018$) this change is significant. For the summer and autumn comparisons DIN/Si remained close to a ratio of 1.

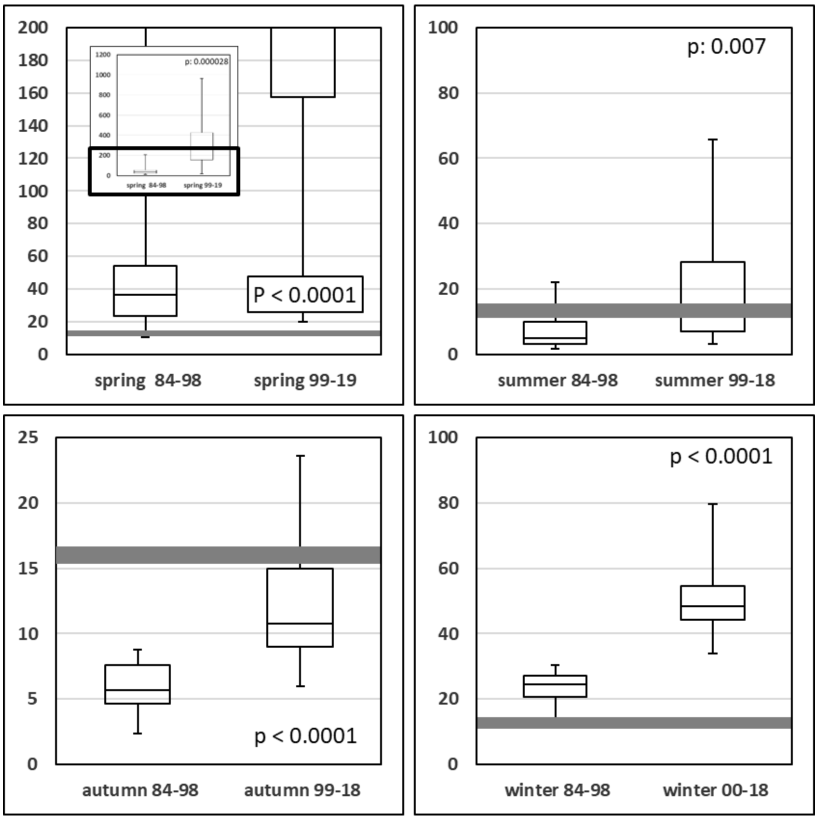

Figure 9~~8~~: Seasonal comparison of DIN/SRP molar ratios for high/low eutrophication periods. The optimum value around 16 is highlighted as a grey bar. The black boxed part of the spring plot is shown enlarged.

Diatoms are the most prominent phytoplankton group in the bight during all seasons (Rick & Wiltshire, 2016; Rick et al., 2017a, 2018). In addition to diatoms, solely the prymnesiophyte *Phaeocystis globosa* (Scherffel, 1899) may add substantially to the photosynthetic biomass in late spring and early summer (Rick et al., 2017a). During the period of high phosphorus and nitrogen loads (1973-1998), silicate was probably not available in sufficient amounts with the result that the diatoms were, at least for the spring bloom, limited by silicate. Since the decline of SRP and DIN in the second half of the time series (1999-2019) silicate limitation was replaced by a limitation by

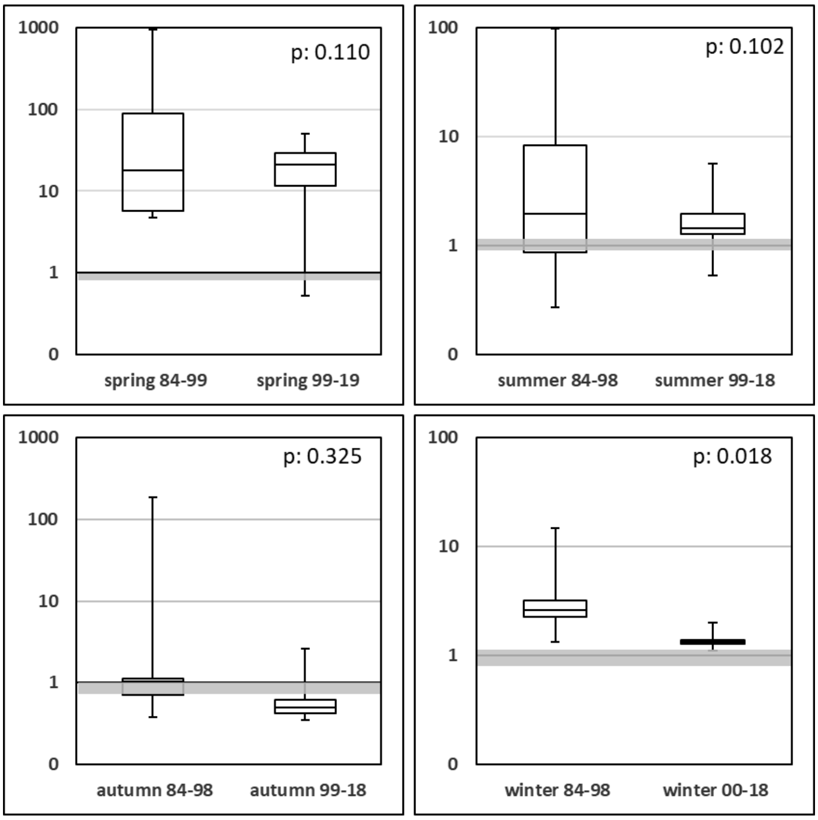

Figure 109: Seasonal comparison of DIN/Si molar ratios for high/low eutrophication periods. The optimum value around 1 is highlighted as light grey bars. Note the log scaled y-axes.

phosphorus. This explains the almost unchanged Chlorophyll *a* pattern despite the strong nutrient changes (Figure 7, Table A1 i). These results are in accordance with the findings of Loebl et al. (2009), who studied patterns of phytoplankton limitation along the southern North Sea coast for the period 1990 to 2005. The authors concluded that aside from underwater light, silicate limitation of the phytoplankton was most common followed by the restraining effects of low phosphorus concentrations.

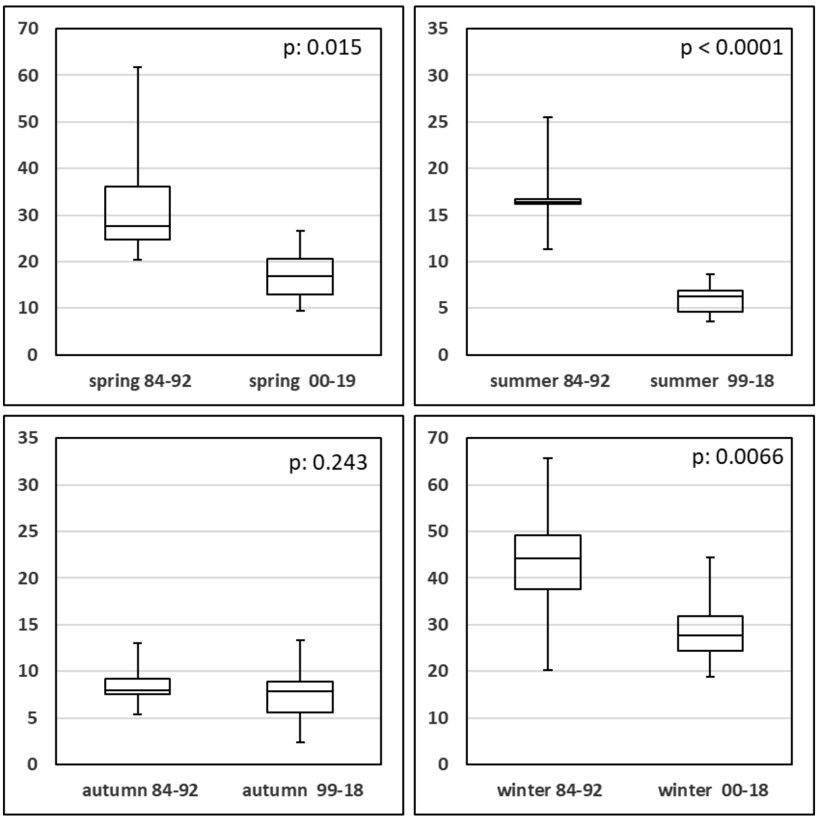

Figure 11: Seasonal comparison of SPM values [mg*l^{-1}] for high/low eutrophication periods.

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~~Figure 10: Seasonal comparison of SPM values [mg*l^{-1}] for high/low eutrophication periods.~~

A comparison of seasonal SPM data for both eutrophication periods is given in Figure 11~~0~~ and Table A1 h. Despite the omission of the biased values (1993-1997) a t-test comparison for all seasons resulted in significantly lower values for the low eutrophication period (1999-2019). This cannot be explained either by lowered plankton biomass (Rick et al., 2017a) or by less sediment input into the water during these years. We assume a change in the SPM methodology might be the cause. Since 1999, Nucleopore filters were used instead of GF/C-filters. Therefore, comparisons of recent and earlier SPM data should be avoided.

5.3 Development of sea surface temperature, salinity and pH

SST rose since the start of continuous measurements in 1984 until 2019 by 1.11 ºC, which is close to the temperature development at Helgoland Roads (Wiltshire & Manly, 2004). Summers warmed by 1.24 ºC, spring seasons by 1.14 ºC, autumn seasons actually by 2.04 ºC but winters even cooled slightly by -0.16 ºC (Figure 12~~1~~a).

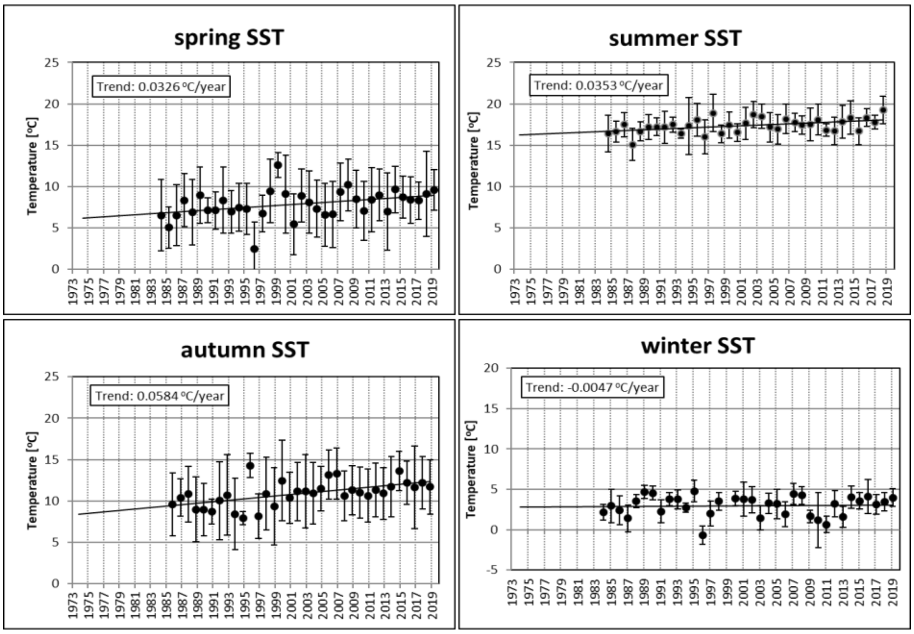

Figure 12~~1~~a: Development of SST over the course of the Sylt Roads LTER time series. Seasonal averages with standard error of means (SEM) as error bars. Data on linear seasonal trends (1984-2019) are shown in boxes

Figure 12~~1~~b and Table A1 d show a t-test comparison of identical seasons for the two periods defined in the previous chapter. For all seasons the period 1999-2019 shows higher average SST values compared with the earlier years of the time series. This finding is significant for summer (p: 0.043) and autumn data (p: 0.0004).

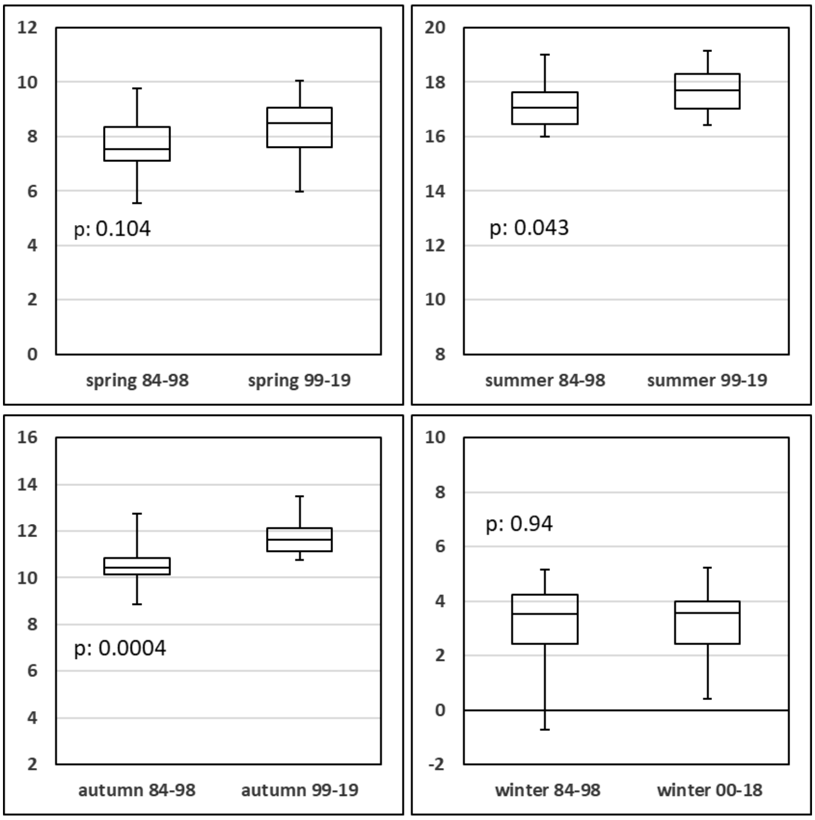

Figure 12~~1~~b: Seasonal comparison of SST values [ºC] for the early and recent part of the time series.

Figure 13~~2~~ and Table A1 f give an "all" season comparison of salinity values for the entire time series: Generally, the salinities in winter and spring are highly significantly lower compared to summer and autumn. Additionally, the summers show slightly significantly higher salinities compared to autumn data.

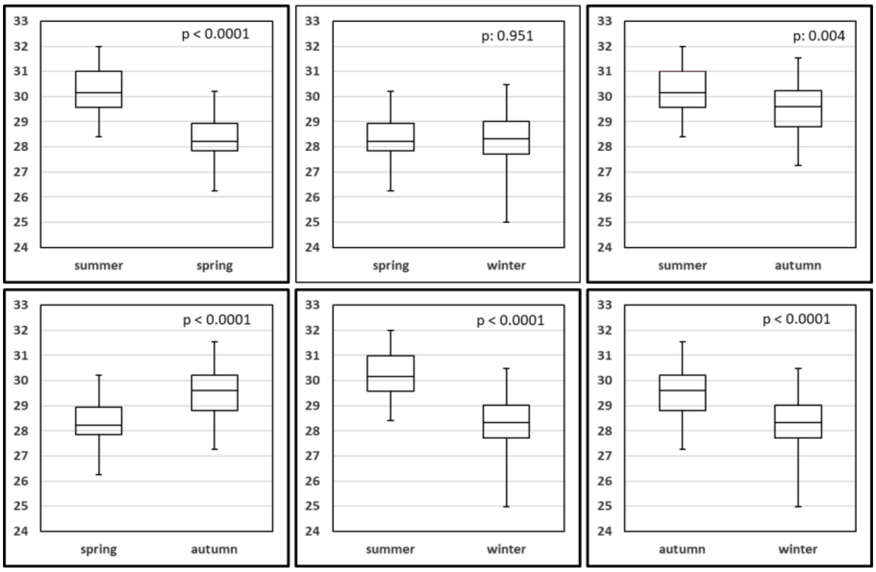

Figure 13~~2~~: All-season comparison of salinity values for the entire time series.

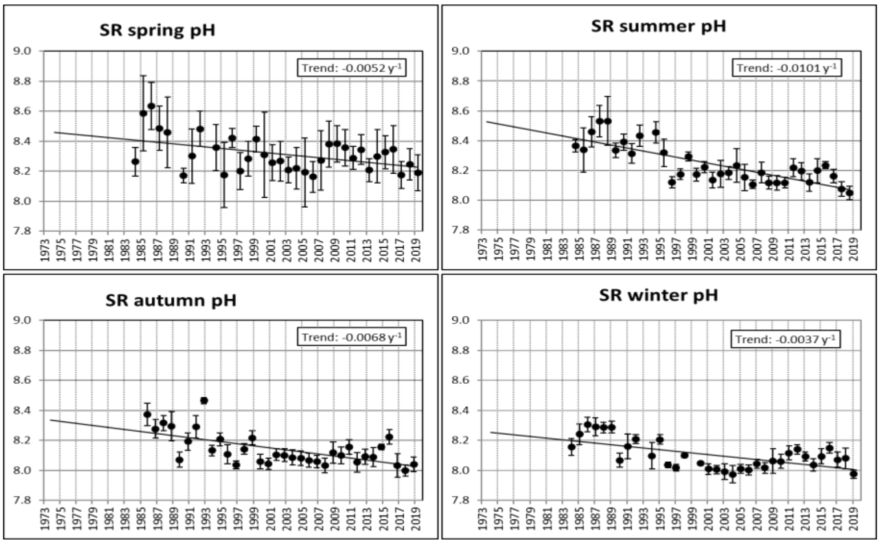

Figure 14~~3~~a: pH development over the course of the Sylt Roads LTER time series. Seasonal averages with standard error of means (SEM) as error bars. Data on linear seasonal trends are shown in the boxes.

This overall picture is explained by the more prominent freshwater impact in winter and spring to the area (Pätsch & Lenhart, 2004; van Beusekom et al., 2017). Comparisons of seasonal salinities for the high and low eutrophication periods yielded in no significant differences at all (Table A1 e).

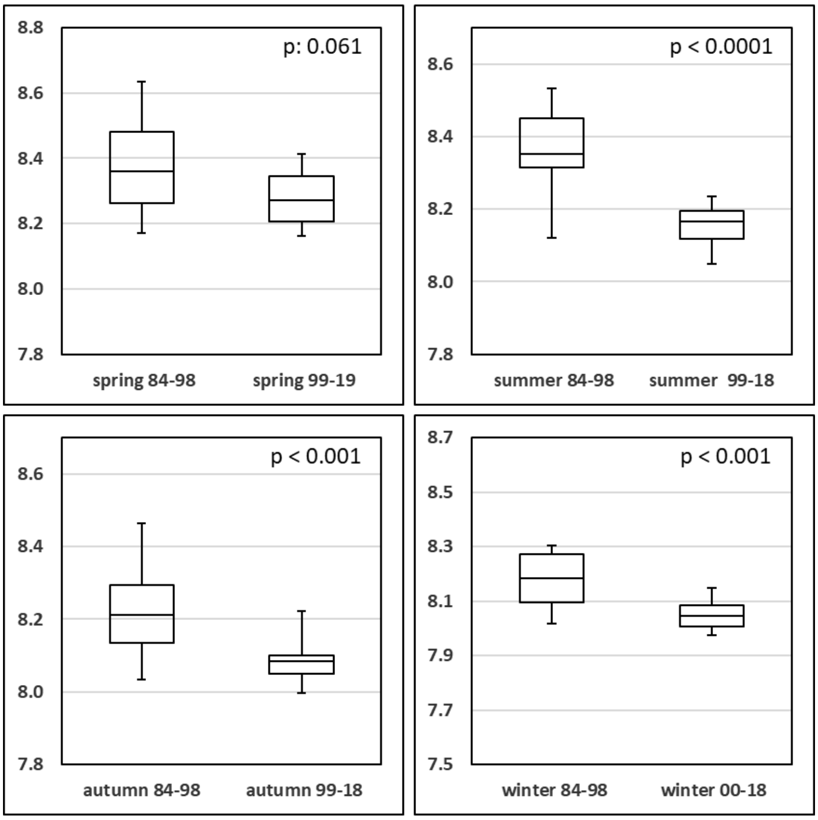

Figure 143b: Seasonal comparison of pH values for high/low eutrophication periods.

On average, the pH decreased since the start of continuous measurements in 1984 till 2019 by 0.23 units. This was evident for all seasons (Figures 143a) with summer, autumn and spring showing most pronounced declines (-0.36, -0.24, -0.18). A t-test comparing pH values from 1984-1998 with values from 1999-2019 yielded significant differences for winter, summer and autumn seasons ($p<0.001$, Figure 14~~3~~b, Table A1 g). Progressively declining pH levels in coastal regions have been documented elsewhere e.g. from the US East Coast (Waldbusser et al., 2011, Wallace et al., 2014).

6. Related Datasets

Over the years several data sets closely related to this physical-hydrochemical time series were compiled at the Sylt Marine Observatory:

1. The **Sylt Roads zooplankton time series** was initiated by Peter Martens. Quantification of abundant zooplankton (> 50 species/groups) occurred weekly from 1979 to 2011. For this time period all data (32 years) are stored in the open access repository PANGAEA (e.g. Martens, 2007, 2012). Due to the retirement of the lead scientist the series is on hold since 2012. Zooplankton samples are still taken weekly and stored for further analysis.
2. The **Sylt Roads quantitative microplankton time series** was started in June 1992 by Wolfgang Hickel. Mostly on a twice a week basis microplankton abundance and related biomass parameters, such as plankton biovolume and carbon were recorded. All data until 2013 are compiled in the PANGAEA repository (Rick et al., 2017a)
3. In 1987, the **Sylt Roads semiquantitative microplankton time series** was initiated by Gerhard Drebes, Malte Elbrächter and Hannelore Halliger. Weekly in depth microscopic and regular electron microscopic analyses of

living plankton and fixed, respectively, samples resulted in high quality data sets (> 700 taxa) compiled in PANGAEA until 2020 (Rick et al., 2018; Castillo-Ramírez et al., 2021)

4. In 1994, the **planktonic primary productivity and respiration time series** was started by Ragnhild Asmus. Monthly measurements based on the oxygen method (Gaarder and Gran, 1927) using oxygen sensitive electrodes (WTW OxyCal) were performed in the List Königshafen area till 2020.~~are ongoing in the List Königshafen area.~~ All data including 2014 are archived in PANGAEA (Asmus & Hussel, 2010; Asmus, R., 2016a)
5. The **Sylt Roads gelatinous zooplankton time series** was initiated by Ragnhild Asmus. The data are available on a weekly basis since May 2009 (Asmus, R. et al., 2017 a, b)
6. The **Sylt Roads bivalve larvae time series** was established in 1995 by Matthias Strasser (Strasser & Günther, 2001). Twice a week sampling is ongoing and the data are currently available via PANGAEA until 2014 (e.g. Asmus, R., 2010, Asmus & Asmus, 2016)
7. The **Sylt Roads Meroplankton time series** was established in 1996 by Ragnhild Asmus. Sampling (twice a week) is ongoing and the data are available in Pangaea till 2021 (Strasser et al., 2022)
~~7. The **Sylt Roads Meroplankton time series** was established in 1996 by Ragnhild Asmus. Sampling (twice a week) is ongoing and the data were submitted to Pangaea in March 2022 (e.g. Kadel et al., submitted)~~
8. The **Sylt Roads fish survey** was established in 2007 by Harald Asmus in order to analyze the Wadden Sea fish fauna with special focus on migration changes, species composition and feeding habits. Seven stations are sampled monthly inside the Bight while two additional reference

stations, one outside the Bight and one close to the Danish border, are sampled four times a year. The data are stored in the PANGAEA repository from 2007 until 2020 (Asmus, H. et al., 2020)

6. Data Access

Data retrieval is ensured via PANGAEA (Rick et al. (2017b-e, 2020a-o & Rick et al., submitted; doi:10.1594/PANGAEA.150032, 873549, 873545, 873547, 918018, 918032, 918027, 918023, 918033, 918028, 918024, 918034, 918029, 918025, 918035, 918030, 918026, 918036, 918031).

7. Appendix

a. SRP	min	Q1	median	Q3	max	average	SEM	SD	variance	n	p	remarks
Spring 84-98	0.670	1.249	1.541	1.895	2.529	1.583	0.413	0.511	0.261	14	2.18 E-07	HSD
99-19	0.077	0.145	0.205	0.338	0.513	0.250	0.101	0.121	0.015	21		
Summer 84-98	0.582	0.795	0.873	1.286	3.585	1.185	0.456	0.708	0.501	15	0.0003	HSD
99-19	0.120	0.194	0.252	0.293	0.497	0.243	0.068	0.089	0.008	20		
Autumn 84-98	0.264	0.388	0.484	0.601	1.317	0.513	0.210	0.280	0.079	14	1.0 E-6	HSD
99-19	0.046	0.091	0.131	0.170	0.372	0.133	0.053	0.072	0.005	20		
Winter 84-98	2.111	2.457	2.578	3.036	3.913	2.755	0.412	0.487	0.237	15	1.1 E-10	HSD
00-19	0.618	0.741	0.873	1.056	1.336	0.866	0.157	0.189	0.036	20		

b. DIN	min	Q1	median	Q3	max	average	SEM	SD	variance	n	p	remarks
Spring 84-98	16.616	27.897	42.565	48.694	122.825	44.042	15.528	24.888	619.434	14	0.017	SD
99-19	11.094	17.817	22.847	28.455	44.126	25.246	7.261	8.855	78.413	21		
Summer 84-98	1.049	1.943	2.676	3.314	5.641	2.834	0.935	1.218	1.484	15	0.079	MSD
99-19	0.566	1.204	1.756	2.146	58.325	1.787	0.842	1.194	1.425	20		
Autumn 84-98	3.010	7.945	9.339	13.889	16.655	10.202	3.561	4.193	17.584	14	0.584	NSD
99-18	3.513	7.391	9.518	11.234	15.508	9.081	2.642	3.310	10.954	20		
Winter 84-98	25.271	46.666	51.586	61.329	82.092	51.623	11.646	15.309	234.367	15	0.010	SD
00-18	28.448	38.568	42.246	44.744	50.021	41.256	4.463	5.712	32.623	20		

c. Si	min	Q1	median	Q3	max	average	SEM	SD	variance	n	p	remarks
Spring 84-98	0.163	6.603	7.933	13.567	16.226	8.501	3.896	4.691	22.002	14	0.718	NSD
99-19	1.962	5.908	8.451	12.011	19.196	9.943	3.959	4.937	24.375	21		
Summer 84-98	1.434	2.536	3.156	4.236	8.480	3.449	1.273	1.709	2.919	15	0.001	HSD
99-19	0.962	1.282	1.616	2.015	3.060	1.677	0.489	0.606	0.368	20		
Autumn 84-98	0.369	2.191	4.268	5.150	7.035	3.874	1.558	1.849	3.420	14	0.026	SD
99-19	0.965	3.626	6.134	7.276	9.940	5.588	2.113	2.447	5.988	20		
Winter 84-98	13.185	19.282	20.635	24.317	32.853	21.880	3.843	4.802	23.060	15	1.16 E-06	HSD
99-19	16.742	31.893	33.473	34.832	40.717	32.980	3.717	5.552	30.828	20		

d. SST	min	Q1	median	Q3	max	average	SEM	SD	variance	n	p	remarks
Spring 84-98	5.55	7.12	7.53	8.35	9.78	7.73	0.77	0.99	0.99	15	0.104	NSD

99-19	5.99	7.60	8.48	9.06	10.05	8.17	0.87	1.08	1.16	20		
Summer 84-98	16.00	16.47	17.06	17.64	19.01	17.23	0.69	0.82	0.68	15	0.043	SD
99-19	16.44	17.03	17.71	18.29	19.15	17.79	0.61	0.72	0.52	20		
Autumn 84-98	8.846	10.156	10.425	10.831	12.755	10.614	0.618	0.865	0.748	15	0.00036	HSD
99-19	10.745	11.140	11.610	12.116	13.473	11.781	0.605	0.765	0.585	20		
Winter 84-98	-0.736	2.416	3.527	4.220	5.141	3.094	1.253	1.557	2.423	15	0.994	NSD
99-18	0.422	2.438	3.548	3.973	5.211	3.139	0.987	1.213	1.472	20		
e. Sal (1)	min	Q1	median	Q3	max	average	SEM	SD	variance	n	p	remarks
Spring 84-98	26.244	28.053	28.903	29.248	30.222	28.535	0.832	1.011	1.021	15	0.136	NSD
99-19	26.399	27.824	28.210	28.377	29.476	28.106	0.466	0.640	0.410	21		
Summer 84-98	28.408	29.794	30.926	31.670	31.996	30.528	0.987	1.121	1.258	15	0.140	NSD
99-19	28.727	29.591	30.052	30.699	31.274	30.127	0.519	0.639	0.408	20		
Autumn 84-98	27.261	29.110	29.645	30.838	31.532	29.804	1.052	1.258	1.582	13	0.443	NSD
99-18	27.959	28.758	29.449	30.019	31.475	29.407	0.804	0.945	0.893	20		
Winter 84-98	24.989	27.677	28.450	29.605	30.469	28.532	1.006	1.316	1.731	15	0.433	NSD
99-18	26.584	27.763	28.284	28.585	29.860	28.213	0.661	0.817	0.668	21		
f. Sal (2)	min	Q1	median	Q3	max	average	SEM	SD	variance	n	p	remarks
Autumn	26.244	27.838	28.226	28.943	30.222	28.284	0.640	0.848	0.719	33	1.48 E-06	HSD
Spring	27.261	28.810	29.606	30.226	31.532	29.567	0.900	1.091	1.191	36		
Summer	28.408	29.584	30.160	30.993	31.996	30.312	0.770	0.915	0.837	35	0,004	HSD
Autumn	27.261	28.810	29.606	30.226	31.532	29.567	0.900	1.091	1.191	33		
Summer	28.408	29.584	30.160	30.993	31.996	30.312	0.770	0.915	0.837	35	3.41 E-14	HSD
Spring	26.244	27.838	28.226	28.943	30.222	28.284	0.640	0.848	0.719	36		
Summer	28.408	29.584	30.160	30.993	31.996	30.312	0.770	0.915	0.837	35	3.61 E-12	HSD
Winter	24.989	27.713	28.330	29.024	30.469	28.298	0.801	1.065	1.135	36		
Autumn	27.261	28.810	29.606	30.226	31.532	29.567	0.900	1.091	1.191	33	9.1 E-06	HSD
Winter	24.989	27.713	28.330	29.024	30.469	28.298	0.801	1.065	1.135	36		
Winter	24.989	27.713	28.330	29.024	30.469	24.989	28.330	29.024	30.469	36	0.95100	NSD
Spring	26.244	27.838	28.226	28.943	30.222	26.244	28.226	28.943	30.222	36		

g. pH	min	Q1	median	Q3	max	average	SEM	SD	variance	n	p	remarks
Spring 84-98	8.170	8.263	8.359	8.482	8.635	8.380	0.130	0.148	0.022	13	0.060	MSD
99-19	8.162	8.208	8.273	8.345	8.413	8.272	0.063	0.073	0.005	21		
Summer 84-98	8.120	8.314	8.351	8.449	8.532	8.361	0.091	0.115	0.013	14	0.00002	HSD
99-19	8.049	8.118	8.166	8.195	8.234	8.158	0.043	0.051	0.003	20		
Autumn 84-98	8.035	8.134	8.211	8.294	8.465	8.211	0.097	0.117	0.014	14	0.0009	HSD
99-19	7.998	8.051	8.083	8.101	8.221	8.085	0.038	0.050	0.003	20		
Winter 84-98	8.016	8.097	8.182	8.273	8.305	8.176	0.085	0.097	0.009	14	0.0004	HSD
00-19	7.974	8.007	8.044	8.083	8.149	8.048	0.043	0.050	0.003	20		
h. SPM	min	Q1	median	Q3	max	average	SEM	SD	variance	n	p	remarks
Spring 84-92	20.448	24.721	27.551	36.204	61.743	33.677	10.077	12.809	164.071	8	0.015	SD
00-19	9.486	13.019	16.943	20.631	26.581	16.936	4.054	4.770	22.753	20		
Summer 84-92	11.343	16.153	16.437	16.682	25.519	16.901	2.381	3.661	13.406	9	2.0 E-5	HSD
00-19	3.624	4.614	6.295	6.894	8.628	6.117	1.226	1.454	2.115	20		
Autumn 84-92	5.407	7.540	7.908	9.225	12.996	8.126	1.988	2.435	5.927	8	0.243	NSD
99-18	2.347	5.613	7.847	8.877	13.275	7.422	2.198	2.773	7.690	20		
Winter 84-92	20.339	37.672	44.247	49.250	65.783	40.977	8.916	11.777	138.687	9	0.007	SD
99-19	18.897	24.425	27.762	31.819	44.512	28.515	5.342	6.613	43.738	20		
i. Chl a	min	Q1	median	Q3	max	average	SEM	SD	variance	n	p	remarks
Spring 84-98	6.683	8.525	10.625	16.578	41.797	14.911	6.199	8.847	78.268	14	0.175	NSD
99-19	3.300	9.085	10.314	12.194	19.795	11.060	2.287	3.205	10.274	21		
Summer 84-98	3.461	4.229	5.233	6.946	10.493	6.042	1.859	2.200	4.839	15	0.390	NSD
99-19	3.523	4.226	4.867	5.426	6.913	5.286	1.250	2.248	5.055	21		
Autumn 84-98	1.163	1.302	1.513	2.340	3.740	1.810	0.629	0.759	0.577	14	0.099	NSD
99-18	0.755	1.165	1.465	1.774	2.321	1.488	0.366	0.435	0.189	20		
Winter 84-98	1.276	3.313	4.320	5.003	5.753	3.911	1.175	1.379	1.903	15	0.314	NSD
99-19	2.622	3.035	3.582	3.937	5.261	3.625	0.502	0.627	0.394	20		
j. DIN/SRP	min	Q1	median	Q3	max	average	SEM	SD	variance	n	p	remarks

Spring 84-98	10.231	23.279	36.167	54.111	206.208	51.74	29.90	47.21	2229.11	14	2.8 E-5	HSD
99-19	19.640	157.680	264.042	424.961	964.970	343.38	188.76	238.16	56720.93	21		
Summer 84-98	1.670	3.059	5.059	9.899	22.039	7.984	4.872	6.009	36.114	15	0.007	SD
99-19	3.235	6.901	12.770	28.299	65.835	20.174	14.832	17.846	318.492	20		
Fall 84-98	2.393	4.614	5.661	7.593	8.806	5.558	1.719	1.992	3.970	14	2.4 E-6	HSD
99-18	5.985	9.018	10.794	14.957	23.639	12.167	3.227	3.981	15.845	20		
Winter 84-98	11.838	20.789	24.408	27.149	30.496	22.953	4.496	5.545	30.749	15	1.0 E-10	HSD
99-19	33.947	44.347	48.459	54.687	79.728	51.408	7.747	10.510	110.455	20		

k. DIN/Si	min	Q1	median	Q3	max	average	SEM	SD	variance	n	p	remarks
Spring 84-98	4.656	5.699	17.727	89.838	935.061	158.576	197.078	264.416	69915.647	14	0.110	NSD
99-19	0.517	11.661	20.777	28.856	50.656	22.338	9.369	11.782	138.826	21		
Summer 84-98	0.269	0.856	1.949	8.357	97.664	15.361	18.789	26.587	706.861	15	0.102	NSD
99-19	0.525	1.263	1.449	1.958	5.616	1.930	0.915	1.274	1.622	20		
Autumn 84-98	0.382	0.704	1.039	1.139	185.168	15.208	24.424	47.420	15.208	14	0.325	NSD
99-18	0.345	0.422	0.503	0.623	2.599	0.744	0.411	0.630	0.744	20		
Winter 84-98	1.324	2.254	2.624	3.213	14.752	3.754	2.047	3.303	10.912	15	0.018	SD
99-19	1.112	1.276	1.339	1.374	1.993	1.355	0.103	0.175	0.031	20		

l. n	min	Q1	median	Q3	max	average	SEM	SD	variance	n	p	remarks
Spring 74-98	12	17.25	26	38.75	77	29.762	14.165	17.635	310.994	22	0.219	NSD
99-19	6	20	24	34	38	26.4	6.925	8.08	65.293	21		
Summer 73-98	11	26.5	40	51.5	198	48.682	21.928	36.463	1.329.584	23	0.0197	SD
99-19	22	24	26	33	39	28.75	5.17	5.893	34.726	21		
Autumn 73-98	13	22	29	45	80	34.45	15.084	18.743	351.283	21	0.088	NSD
99-18	13	23	25	31.75	41	27.421	6.14	7.379	54.448	20		
Winter 73-98	6	14.75	27.5	38.75	50	26.857	11.273	13.525	182.926	22	0.05	SD
99-19	12	18	19	25	32	21.65	4.694	5.333	28.440	21		

Table A1: Descriptive statistics related to boxplot figures (4b, 5-10, 11b, 13b) with p-values of associated t-tests (two sided, unequal variances assumed) comparing seasonal data for two time periods within the Sylt Roads LTER characterized by different eutrophication potential (High: 1978-1998; Low: 1999-2019). In case of salinity (part e. of Table) seasons are compared to each other for the complete series (1973-2019). Q1 = 1st quartile; Q3 = 3rd quartile; SEM: standard error of means; SD: standard deviation

	principal components									
parameters	1	2	3	4	5	6	7	8	9	10
salinity	**0,30**	0,23	**0,42**	-0,25	**0,69**	-0,22	0,19	-0,20	-0,05	0,14
SST	**0,42**	0,08	0,21	0,01	-0,30	-0,09	-0,24	0,16	**0,57**	**0,52**
pH	0,10	**-0,57**	0,07	**-0,40**	-0,32	**-0,47**	**0,37**	-0,03	-0,16	0,07
NH4	**-0,33**	**0,36**	-0,07	**-0,37**	-0,07	0,26	**0,50**	**0,43**	0,00	**0,34**
NO2	**-0,32**	0,20	-0,10	**-0,66**	-0,04	-0,20	**-0,57**	-0,18	0,09	-0,07
NO3	**-0,40**	-0,23	0,13	0,22	0,09	0,04	-0,22	-0,23	**-0,34**	**0,71**
PO4	-0,23	-0,17	**0,71**	-0,12	-0,20	**0,46**	0,07	-0,23	0,20	-0,23
Si	**-0,41**	0,10	-0,16	0,24	0,04	**-0,33**	**0,36**	**-0,43**	**0,56**	0,01
Chl	0,09	**-0,54**	**-0,38**	-0,24	**0,42**	**0,43**	-0,01	-0,02	**0,36**	0,10
SPM	**-0,36**	-0,25	0,27	0,15	**0,31**	**-0,32**	-0,16	**0,66**	0,19	-0,15

Table A2: PCA coefficients of PCs for the tested physical and hydrochemical parameters, Sylt-Roads time series, seasonal averages (1984-2019). Coefficients > 0,3 or < -0,3 in bold.

8. Author contribution

JR prepared the manuscript with the contribution of the following co-authors (MS, TR, JB, RA, HA, FM, AK, KW). RS compiled the data in Pangaea. TR performed the hydrochemical measurements since 2000.

9. Competing interest

The authors declare that they have no conflict of interests.

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