

Pia Andersson

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Drivers of Marine Acidification in the Seas Surrounding Sweden





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Drivers of Marine Acidification in the Seas Surrounding Sweden

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Drivers of Marine Acidification in the seas surrounding Sweden

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SUMMATION

It is of common consensus in the ocean acidification community that the increase of atmospheric CO₂ is the main driving force of the downwards pH trends in the world's oceans. In the stations surrounding Sweden, that is most probably the main underlying factor as well, however the rate of change differs from the oceanic rates and there are different rates of change at different depths and different seasons.

To investigate further, four monitoring stations with long time series of pH data in the Kattegat and the Baltic Proper have been analysed both for trends and what the main drivers of the change of pH values for those stations could be.

Besides a linear trend analysis, a non parametric trend analysis has been applied to the pH data sets. It appears that the carbonate system generally works in the surface layer where the biologic processes are most active, reducing or prohibiting the decline of pH in most of the evaluated stations. It also seems like the downward trends of pH in most of the remaining water masses are influenced and accelerated by oxygen deficiency and eutrophicated water masses.

A multivariate analysis was then performed to see what or what combination of parameters influence the change of the pH values the most. The results from the analysis were either significant or not significant, indicating either more trustworthy or not as trustworthy results. A result showing high correlation for a parameter or a set of parameters that influence pH, in combination with being significant, was then an indication of a trustworthy result.

Several parameters were included in this analysis, however some key parameters that perhaps influence the changes of the pH values the most may have been missed due to the lack of available data or knowledge or included in the analysis, but in a wrong way. What this study was able to do, was to use the available parameters at hand and make assumptions on how to prepare the data to be able to combine it with the pH data. The results can give an indication as to how much the parameters influence the pH values out of the included parameters, in the manner they were included.

Of all the parameters included in the analysis, O₂, O₂ saturation, PO₄ and DIN were the main parameters influencing the pH values.

When looking at what single parameter influence pH the most or the least of the included parameters, a table was put together to display what parameters were ranked to be most important and then second most important and so on to the least important parameter.

For all stations, all seasons and all depths, there was a slight tendency for the parameters chl-a, atmospheric CO₂, North Atlantic Oscillation Index, precipitation pH, river pH and river alkalinity to be ranked the least important. DIN seemed to be more important at the surface layers than at the bottom layers. Salinity and alkalinity seemed to be more important in the bottom layers than in the surface layers. At all depths, O₂, O₂ saturation, PO₄ and SiO₄ seemed to be of higher importance.

Another interesting feature was that O₂ seemed to be of importance throughout all depths except for the 10-20 meters depth, probably due to high variability at that depth. SiO₄ seemed to be more important at the Kattegat station than at the other stations.

Chl-a did not seem to be important. Since biological activity should have a large impact on pH, chl-a as included in the analysis, was not a good choice as a representative of the biological activity. O₂ and O₂ saturation were very much influencing the pH patterns. Perhaps in the top layers, they were better representatives for the biological activity in this analysis.

It is also interesting to see the lack of importance of the atmospheric CO₂. However, when performing trend analysis, not many pH trends were present at the surface (probably due to the biological and of course chemical/physical processes), opening up for O₂, O₂ saturation and nutrients to be the dominant parameters.

In the report, the monitoring need of acidification parameters from a modelling point of view was addressed. The model validation would be very much improved if the concentrations of organic matter could be validated. Today only measurements of total nitrogen and phosphorus and dissolved inorganic nutrients are available. Including standard observations of particulate organic matter (PON, POP and POC) as well as dissolved organic matter (DON, DOP and DOC) would much improve the possibility to further develop the biogeochemical models.

Another recommendation is to do a separate investigation based on the results from the coupled oceanographic and biogeochemical model RCO-SCOBI to recommend possible new stations that are important and not yet covered by the present sampling strategy.

To calculate and model the saturation state over depth of calcite and aragonite, of high importance for calcifying organisms, the ions CO_3^{2-} and Ca^{2+} need to be determined. Either CO_3^{2-} directly could be measured, or pCO_2 and C_T (total carbon) could be measured, calculating the desired ion. Furthermore, the ion Ca^{2+} could be directly measured, or if not the highest accuracy is needed, estimations could be made from Ca/salinity relationships.

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I AIM

The aim of this report is to enhance the trend analysis previously performed on the pH parameter for a few chosen stations in the seas surrounding Sweden.

It is also to assess what parameters affect the changes of the pH values out of a selection of parameters at hand and which ones affect the changes of the pH values the most.

Another aim is to address the monitoring need of acidification parameters from a modelling point of view.

2 INTRODUCTION - CAUSES AND DRIVERS OF MARINE ACIDIFICATION

Surface waters in the world oceans have experienced a pH reduction of about 0.1 pH units (OSPAR, 2006). The trend indicates further decrease of pH (Andersson et al., 2008).

It is of common consensus in the ocean acidification community that the downward pH trends are most probably due to increased uptake of atmospheric CO₂ and less buffering capacity of the ocean waters. Continuing decrease at this fast rate can have devastating effects on marine key calcifying organisms such as corals, molluscs, echinoderms and crustaceans. This in turn can lead to indirect effects on the marine food chain which eventually may lead to structural changes of ecosystems.

The decreasing trends of the pH values are indicators of marine acidification. The oceanic drop in the surface layers is as mentioned about 0.1 units over about 15 years. In the Swedish waters, the rates range from no trends to much faster rates than the general oceanic trends.

It is stated in many articles and generally accepted that the increase of atmospheric CO₂ is the cause of the general 0.1 unit increase in the surface waters of the marine environment. There is no real doubt that this is the case also in the Baltic and the Kattegat and the Skagerrak. However, since the trends do not follow the general patterns found in oceanic waters, there should be other parameters or processes that affect the change of the pH values to a large extent.

In this report, a multiparameter analysis on the dataset was performed in the attempt to find what affects the changes of the pH values in the seas surrounding Sweden the most.

In Andersson et al., 2008 only linear regression was used when analysing for trends. In this report, a non-parametric method (Mann-Kendall) is also applied, to assess the trends further. In the previous report, recommendations were made to expand the national monitoring program to encompass all major sea areas, monthly measurements at standard depths and procedures and methods. In this report, there is an aim to address the monitoring need of acidification parameters from a modelling point of view.

3 STATION SELECTION

In Andersson et al. (2008), Swedish pelagic stations with long time series of pH data available within the national oceanographic data centre database was listed. Four of the stations with consistent time series since 1993 were selected in this study: Anholt E (station 1) in the Kattegat; BY15 (station 2) in the central Baltic Proper, east of Gotland; BY31 (station 3) in the north-western Baltic Proper, north of Gotland; BY5 (station 4), east of Bornholm.

SMHI has been the main analyzing laboratory. Only at BY31, the Stockholm Marine Research centre has been the analyzing laboratory during all but the winter months, during which time SMHI was the analyzing laboratory. Unfortunately, the time series for pH and Alkalinity at BY31 ends in the end of the year 2000, whereas data until 2008 has been used for the other stations.

At the stations, samples are taken at standard depths. In the previous report (Andersson et al., 2008) a number of standard depths were combined to aggregate data into depth sections for the surface layers, above and below the perennial halocline. This time, the depth sections were chosen to be slightly finer with five aggregated depth ranges 0-4m, 5-9m, 10-20m, 21-60m and 80-150m. At Anholt E (station 1), the depth of the station is only 50 meters, so only the first four depth intervals have been used.

At Anholt E, the halocline is normally located at depths between 10-20 meters hence depth four should be regarded as being under the halocline. At Anholt E, the depth of the surface mixed layer mainly coincides with the halocline. During winter, the halocline is regularly deepened by stronger wind events. At BY15 and BY31, the halocline is at about 60-70m and the summer thermocline reaches about 20-30m. At BY5 the halocline is shallower than at BY15 and BY31, whereas the summer thermocline reaches about the same depths. At depth 5 of the Baltic stations, oxygen deficiency or depletion commonly exists.

There are seasonal differences in the pH, therefore the winter and summer seasons have been included separately as well as including all months as a third assessment. The winter months are in the Baltic represented by December, January and February, whereas in the Kattegat they are represented by November, December and January. The summer months are in the Baltic represented by June, July and August, whereas in the Kattegat they are represented by May, June and July.

4 AVAILABLE PARAMETERS

The time period chosen is 1993-2008 mainly due to the uncertain quality of Swedish pH and alkalinity data prior to 1993. Measurements of pH, alkalinity, oxygen saturation and chl-a were used for calculating trends. pH, alkalinity, temperature, salinity, DIN, PO₄, oxygen, oxygen saturation and chl-a were included in the multiparameter analysis along with atmospheric CO₂ as well as pH and alkalinity at the closest runoff station. NAOI and measurements of precipitation pH from EMEP have also been used.

An example from Anholt E of some of the included parameters is displayed in figure 1.

4.1 PH, ALKALINITY AND NUTRIENT DATA

All measured data from the four selected stations is available in the Svenskt Havs ARKiv (SHARK) database, at the oceanographic data centre at SMHI. Data was collected during monthly expeditions to the Baltic Sea and the Kattegat and the Skagerrak with the R/V Argos. The measurements taken by SMHI follow the HELCOM Combine Manual. The analyzing laboratory has been ISO certified throughout the length of the time series.

The pH values have been temperature corrected to 25 °C to avoid any temperature effects in the evaluation. In the multiparameter evaluation, the parameter temperature is not included. The pH values are not salinity adjusted since no clear correlation has been found in the used dataset. It corresponds to the procedure in Andersson et al. (2008). In all parts of the report, alkalinity is represented as total alkalinity.

In the trend analysis, every value was used. In the multiparameter analysis, a mean value for each depth for each season was used in combination with monthly values for the rest of the included data.

4.2 BIOLOGIC ACTIVITY AT SURFACE LAYERS

In this report, the biological and chemical aspect is barely touched upon. However, they are of great importance when trying to find out what affects the pH. To simplify for the analysis performed in this study, chl-a and oxygen saturation are used as indicators of biologic activity.

CO₂ is the main source material for the photosynthesis. In the water it exists as dissolved CO₂, as carbonic acid and as the ions HCO₃⁻ and CO₃²⁻. The uptake of CO₂ by the algae leads to increasing pH (Feistel et al., 2008). The anthropogenic increase of CO₂ may increase primary production (Riebesell et al., 1993; Chen and Durbin, 1994; Hein and Sand-Jensen, 1997; Wolf-Gladrow et al., 1999; Qiu and Gao, 2002). So, the increase of dissolved CO₂ in the surface layers, could result in higher productivity, probably seen as an increase of oxygen saturation and/or chl-a. This is why these two parameters have been included in the trend analysis along with pH and alkalinity. An increase in dissolved CO₂, which decreases the pH value, can induce an increase in productivity, which in turn increases the pH value. This may be the reason why pH trends were absent in surface waters at many stations when looking at the trends in Andersson et al., 2008.

If there is a pronounced difference in the distribution of trends over depth and season, with trends absent above the mixed layer, this could also be interpreted as that the carbon system is generally functioning above the mixed layer.

4.3 RUNOFF

Acidification in Swedish lakes has been a known fact for decades. To attempt to come to terms with the problem, large scale programs to raise the pH has been in operation for several years, commissioned by the Swedish Environmental Protection Agency. It has improved the environment in for example several lakes and rivers. However, these types of programs are not applicable at sea, due to the large scale difference of the water masses. To see if the pH and alkalinity from the runoff in any way affect the stations at sea, the closest large runoff stations were included in the multiparameter analysis.

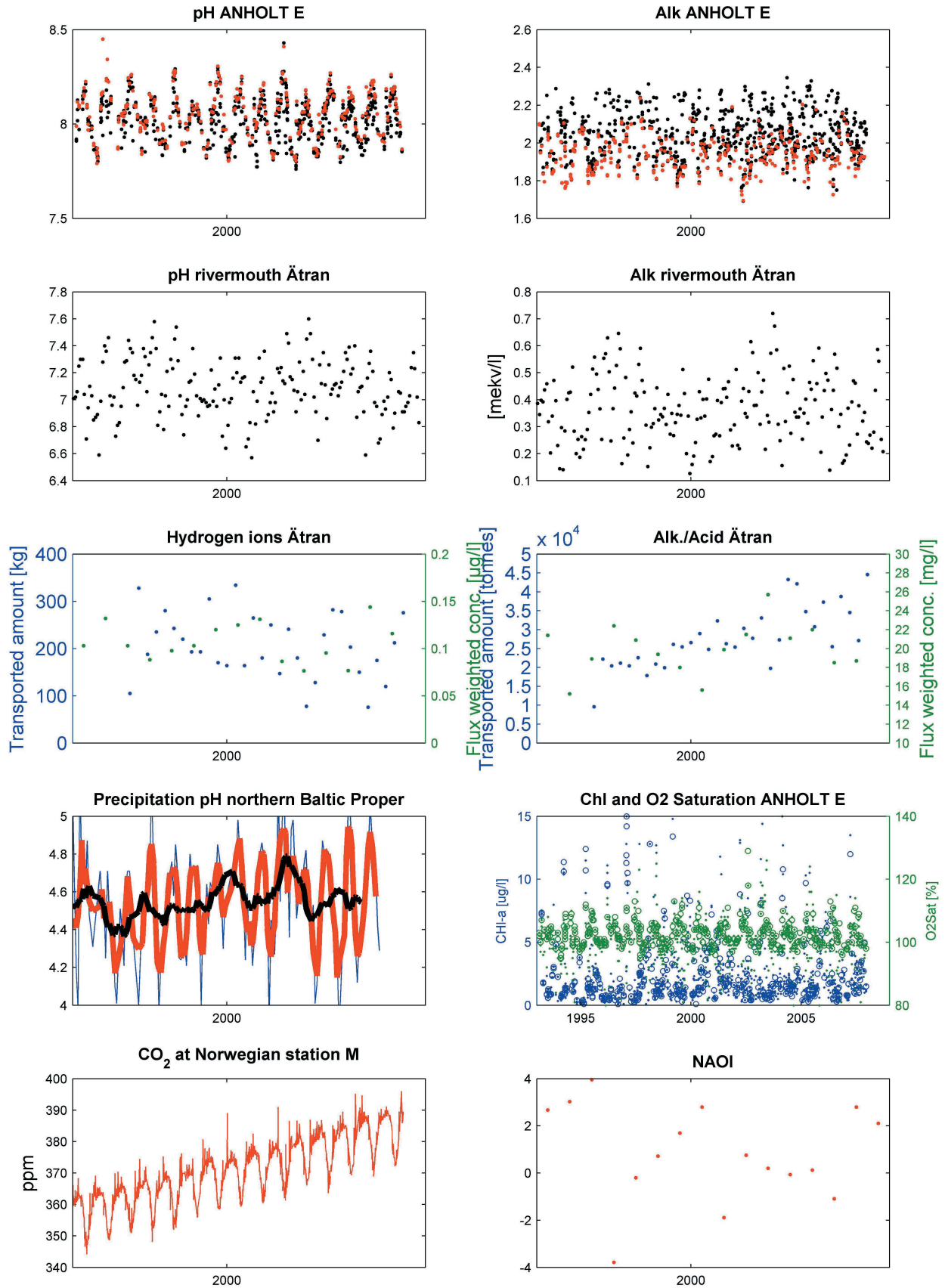


Figure I: An example of time series for some of the included parameters in the multiparameter analysis for the station at Anholt E.

The closest large runoff station to Anholt E was Ätran, the closest to BY15 was Gothemsån, BY31 was coupled to Norrström and BY5 to Mörrumsån. Most of the sea stations are far away from the runoff stations, Anholt E being the closest one.

To assess the general tendency of the runoff pH and Alkalinity, a trend analysis was performed between 1993 to 2008. Monthly values of pH and Alkalinity were used. Other parameters like total amount of H ions or flow weighted values could have been used as well however these parameters were mainly feeding back the general runoff signal, i.e. the amount of water transported from land to the sea.

Data is retrieved from the Department of Aquatic Sciences and Assessment (SLU) and can be downloaded from their website at <http://www.ma.slu.se/> as well as the description of measuring methods applied.

4.4 AIR CO₂

Atmospheric CO₂ was contributed by NOAA/GMD retrieved from an air sampling observation stationary platform at Ocean Station “M” outside the coast of Norway, longitude 2, latitude 66 at an altitude of 5m. CO₂ was sampled by flasks at a weekly rate with the WMO CO₂ mole fraction scale, unit ppm, covering period 1981-2007. The general atmospheric trend is obvious in the figure below, as is the yearly cycle with lower CO₂ levels during the summer.

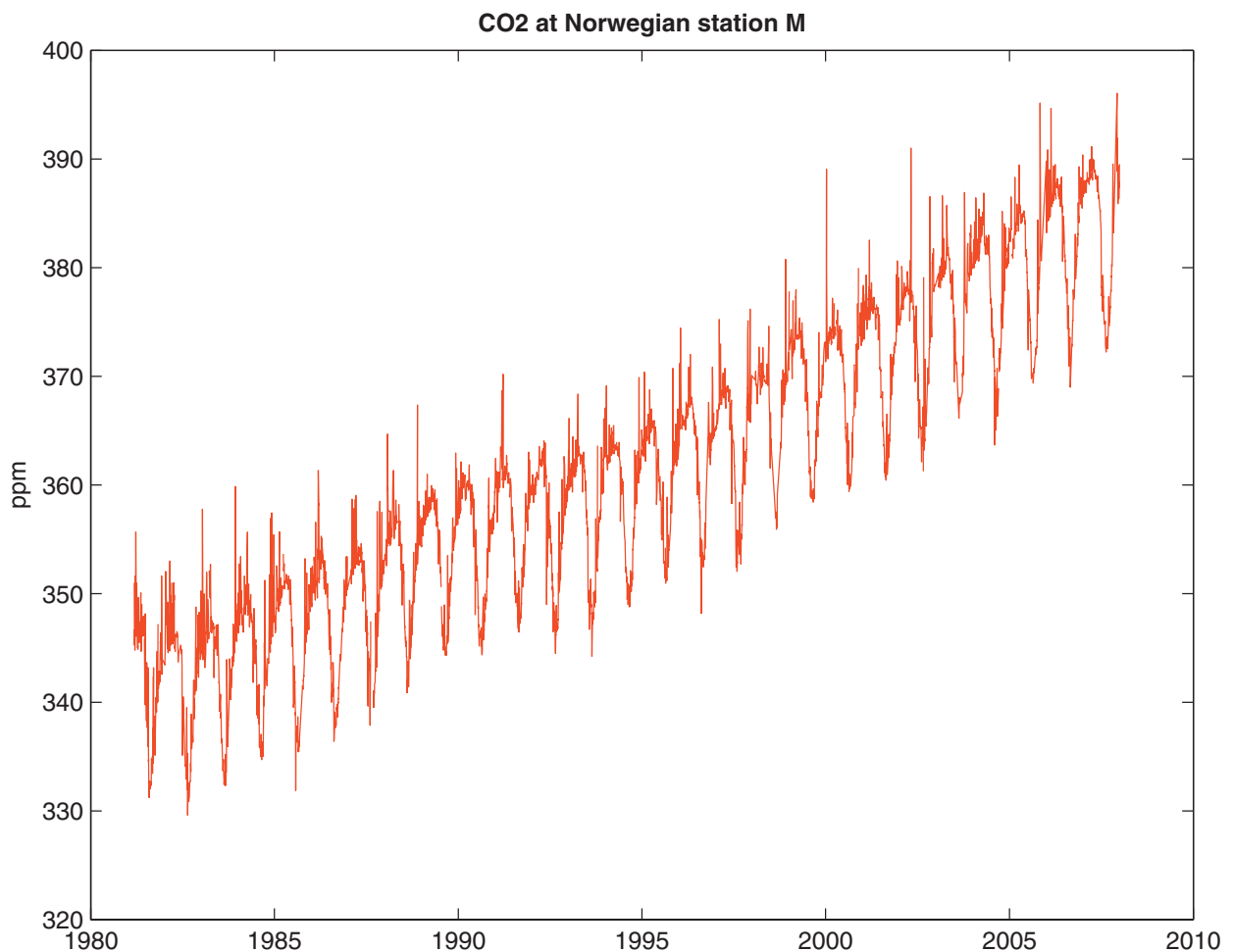


Figure 2: Time series of atmospheric CO₂ from an air sampling observation stationary platform at Ocean Station “M” outside the coast of Norway.

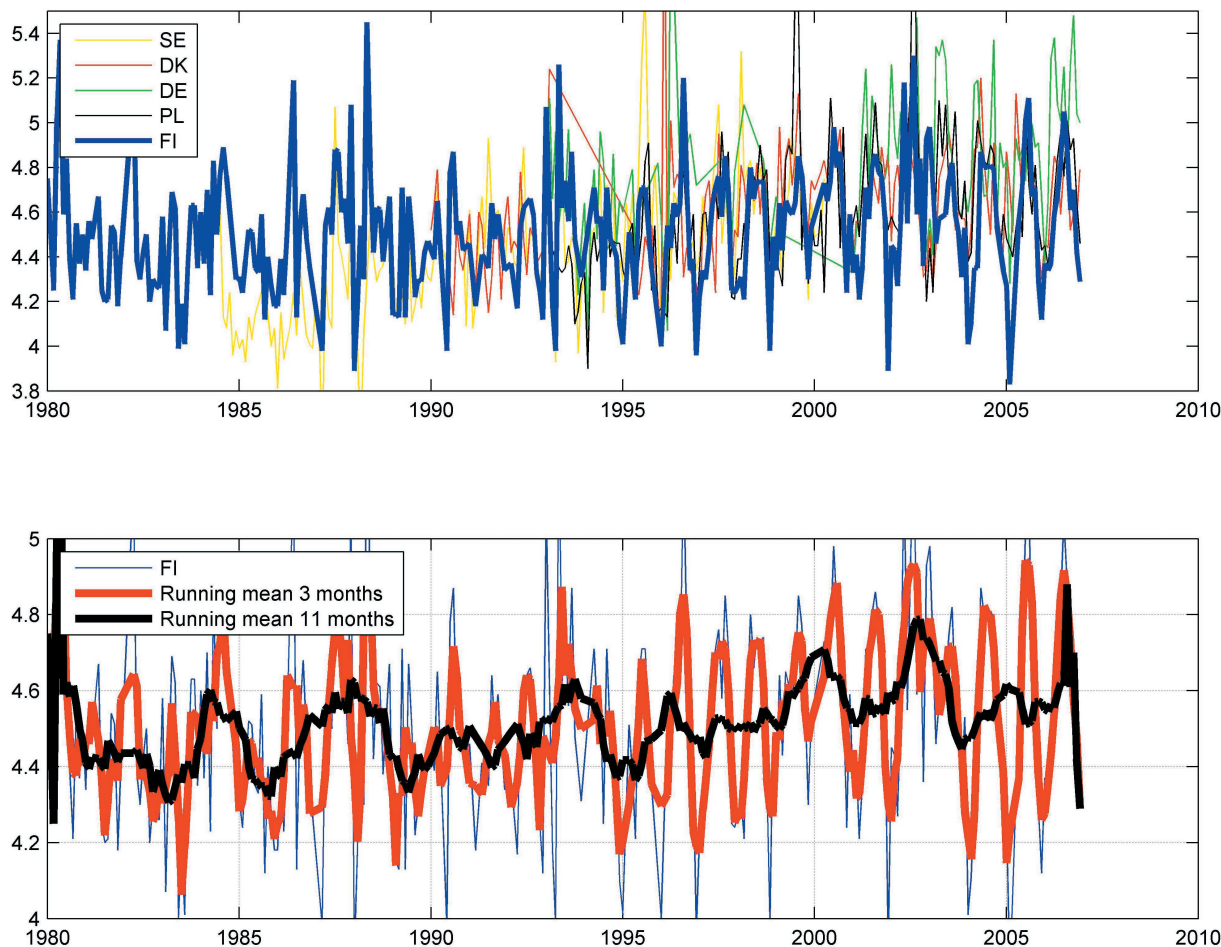


Figure 3: Measured data of the precipitation pH as time series. Data was retrieved from EMEP.

4.5 PERCIPITATION PH FROM EMEP

Measured data of the precipitation was retrieved from EMEP – measurement data on line at <http://tarantula.nilu.no/projects/c3c/emepdata.html>. In Andersson et al. (2008) modelled data from MATCH was assessed to compare possible other sources of acidifying parameters from the air (like sulphur compounds), but there was no clear increasing trend of other parameters when comparing to the air CO₂ trend. Hence none of those parameters from MATCH or EMEP are included in the multiparameter analysis. However precipitation pH is included.

A number of stations could have been chosen, but only the Finnish station has been used due to the fact that the Finnish station corresponded well to all other possibly closer stations and the dataset was complete throughout the time period requested. Data from the EMEP stations are displayed in figure 3.

4.6 NAOI

Monthly values of the North Atlantic Oscillation Index (NAOI) have been included. The North Atlantic Oscillation (NAO) is based on the difference of normalized sea level pressure (SLP) between Lisbon, Portugal and Stykkisholmur/Reykjavik, Iceland. A Positive index indicates stronger westerly winds bringing warmer and wetter winters to Scandinavia. Data can be retrieved at <http://www.cpc.ncep.noaa.gov/products/precip/CWlink/pna/> or at http://gcmd.nasa.gov/records/GCMD_NAO_HURRELL.html.

5 RESULTS OF IMPROVED TREND ANALYSIS

The calculation of trends in Andersson et al., 2008 used linear regression through the statistical tool MatLab. A slight different approach regarding depths and the use of seasonal values motivated the recalculation of trends using linear regression in this report as well. The other analysis used was a non-parametric method, Mann-Kendall, giving slightly more profound trend results. The two methods used to calculate trends are described in appendix 2.2 and 2.3.

5.1 GENERAL TRENDS – PRECIPITATION pH, NAOI, CO₂ AND RUNOFF

In table 1, a compilation of the trends are presented, giving in the first section the change over one year and then over 15 years, to put in relation with the pH time series. If there is a number in a cell, the trend is significant and the number represents the rate of change. If the cell has a beige colour in the background, the trend is very close to being significant (indicated by the value of P). The limiting value of P to indicate a trend or not is in this study set to be 0.05. Read more of the trend methods in appendix 2.

For precipitation pH, not only data from the Finnish station FI0009R is analysed, but also data from Anholt E and data from the Polish station PL0004R. Focusing on the non-parametric trend

Table 1. A compilation over the linear and non linear trends over precipitation pH, NAOI, atmospheric CO₂, and pH and alkalinity at the river runoff stations. In the first section, the change over one year is displayed and then the next set of numbers display the change over 15 years, to put in relation with the pH time series. If there is a number in a cell, the trend is significant and the number represents the rate of change. If the cell has a beige colour in the background, the trend is very close to being significant.

Years	Station	Parameter	B: pH change per year				Change over 15 years (BY31: 93-00)							
			L	NL	L	NL	L	NL	L	NL	L	NL	L	NL
95-06	ANHOLT E	Prec pH			0,02933	0,02000	0,01292	0,01500			0,43995	0,30000	0,19380	0,22500
93-06	PL0004R	Prec pH	0,01809	0,01348	0,03555	0,03646	0,02868	0,02750	0,27135	0,20220	0,53325	0,54690	0,43020	0,41250
93-06	FI0009R	Prec pH			0,02277	0,01875		0,01182			0,34155	0,28125		0,17730
93-08	Azores-Iceland	NAOI												
93-07	Norwegian station M	CO2	1,91835	1,92042	1,86096	1,91115	1,88409	1,91544	28,77525	28,80630	27,91440	28,66725	28,26135	28,73160
93-08	Åtran	pH												
93-08	Åtran	Alk												
93-08	Gothemsån	pH	0,00833	0,00750			0,00506	0,00571	0,12495	0,11250			0,07590	0,08565
93-08	Gothemsån	Alk												
93-08	Norrström	pH			-0,05404	-0,05000	-0,02964	-0,02183			-0,81060	-0,75000	-0,44460	-0,32745
93-08	Norrström	Alk	-0,01803	-0,01701	-0,01068	-0,00860	-0,01176	-0,01000	-0,27045	-0,25515	-0,16020	-0,12900	-0,17640	-0,15000
93-08	Mörrumsån	pH	0,01014		0,01032	0,01000	0,01057	0,01111	0,15210		0,15480	0,15000	0,15855	0,16665
93-08	Mörrumsån	Alk			0,00274	0,00331	0,00165	0,00185			0,04110	0,04965	0,02475	0,02775

analysis Mann-Kendall, there are positive trends on all stations during summer and during all months included. During the winter season, only the Polish dataset has a positive trend. Hence, in this case, it seems like the precipitation does not contribute with further lowering pH in the surface water over the investigated years. Keep in mind however, that in the study, the changes are investigated, not the specific values per se.

Using linear regression and Mann-Kendall, there were no visible trends in the normalised NAOI monthly values with the selection of seasons or using all months.

As can easily be seen in figure 1, CO₂ has a robust upward trend during both seasons and all months included. However, when looking at figure 4 in appendix 1, one may wonder if the months chosen to represent summer and winter is a few months off since the top and bottom values of the yearly values have been missed. This could have had an effect on the results when running the multiparameter analysis. Probably that different choice of months should also have been used for the NAOI, which also could have resulted in different trend results.

For the four included runoff stations, both pH and alkalinity have been analysed for trends. Ätran was coupled to the Anholt E sea station. Ätran showed no trends in pH or alkalinity.

Conducting the same procedure for the sea stations, even if the distance to the river mouths were relatively far and there should be no possible link between the two stations, BY15 was coupled to a runoff station. The pH indicated a slight upward trend during winter and using all months. There was no trend in alkalinity. Norrström was coupled to the BY31 station, indicating downward trends for both pH and alkalinity during summer and when using all months combined. Only alkalinity showed a downward trend during winter. Mörrumsån was coupled to the BY5 sea station. During summer and when using all months, there were upward trends for both pH and alkalinity.

As a summary: all present trends for the parameters in this subchapter were upwards, except at Norrström, where the trends were downwards. Some selected trend figures are displayed in appendix 1.

Table 2. A compilation over the linear and non linear trends for the parameter chl-a at the four selected sea stations. In the first section, the change over one year is displayed and then the next set of numbers display the change over 15 years, to put in relation with the pH time series. If there is a number in a cell, the trend is significant and the number represents the rate of change. If the cell has a beige colour in the background, the trend is very close to being significant.

		B: pH change per year				Change over 15 years (BY31: 93-00)							
		L	NL	L	NL	L	NL	L	NL	L	NL	L	NL
		Winter	Winter	Summer	Summer	All Year	All Year	Winter	Winter	Summer	Summer	All Year	All Year
0-4	ANHOLT E			0,0451						0,67650			
5-9	ANHOLT E												
10-20	ANHOLT E												
30-60	ANHOLT E	0,14579	0,09167	-0,21053	-0,16835	-0,09688		2,18685	1,37505	-3,15795	-2,52525	-1,45320	
0-4	BY15 GOTLANDSDJ	0,04271	0,03083				0,03429	0,64065	0,46245				0,51435
5-9	BY15 GOTLANDSDJ	0,04275	0,03333				0,02857	0,64125	0,49995				0,42855
10-20	BY15 GOTLANDSDJ	0,0386	0,03333				0,03	0,57900	0,49995				0,45000
30-60	BY15 GOTLANDSDJ												
0-4	BY31 LANDSORTSDJ						-0,02289						-0,34335
5-9	BY31 LANDSORTSDJ												
10-20	BY31 LANDSORTSDJ			-0,03462	-0,03194		-0,01667			-0,51930	-0,47910		-0,25005
30-60	BY31 LANDSORTSDJ			-0,0276	-0,02268	-0,02013	-0,01874			-0,41400	-0,34020	-0,30195	-0,28110
0-4	BY5 BORNHOLMSDJ	0,07734	0,06583	-0,0475				1,16010	0,98745	-0,71250			
5-9	BY5 BORNHOLMSDJ	0,07591	0,05	-0,04859				1,13865	0,75000	-0,72885			
10-20	BY5 BORNHOLMSDJ	0,07041	0,05524					1,05615	0,82860				
30-60	BY5 BORNHOLMSDJ					-0,15234						-2,28510	

Table 3.A compilation over the linear and non linear trends for the parameter oxygen saturation at the four selected sea stations. In the first section, the change over one year is displayed and then the next set of numbers display the change over 15 years, to put in relation with the pH time series. If there is a number in a cell, the trend is significant and the number represents the rate of change. If the cell has a beige colour in the background, the trend is very close to being significant.

		B: pH change per year				Change over 15 years (BY31: 93-00)							
		L	NL	L	NL	L	NL	L	NL	L	NL	L	NL
		Winter	Winter	Summer	Summer	All Year	All Year	Winter	Winter	Summer	Summer	All Year	All Year
0-4	ANHOLT E												
5-9	ANHOLT E												
10-20	ANHOLT E												
30-60	ANHOLT E												
0-4	BY15 GOTLANDSDJ												
5-9	BY15 GOTLANDSDJ												
10-20	BY15 GOTLANDSDJ												
30-60	BY15 GOTLANDSDJ	-0,78379		-0,49761	-0,4881	-0,49265	-0,22222	-11,75685		-7,46415	-7,32150	-7,38975	-3,33330
80-150	BY15 GOTLANDSDJ	-1,61904	-1,44861	-1,80008	-1,85397	-1,7907	-1,84167	-24,28560	-21,72915	-27,00120	-27,80955	-26,86050	-27,62505
0-4	BY31 LANDSORTSDJ	-0,13554	-0,14286					-2,03310	-2,14290				
5-9	BY31 LANDSORTSDJ												
10-20	BY31 LANDSORTSDJ	-0,10591	-0,125					-1,58865	-1,87500				
30-60	BY31 LANDSORTSDJ				-0,47619	-0,29585	-0,41071				-7,14285	-4,43775	-6,16065
80-150	BY31 LANDSORTSDJ	-2,11758	-2,01477	-1,76782	-1,71429	-1,95828	-1,78819	-31,76370	-30,22155	-26,51730	-25,71435	-29,37420	-26,82285
0-4	BY5 BORNHOLMSDJ												
5-9	BY5 BORNHOLMSDJ												
10-20	BY5 BORNHOLMSDJ					0,1273	0,05556					1,90950	0,83340
30-60	BY5 BORNHOLMSDJ												
80-150	BY5 BORNHOLMSDJ			-1,30236		-1,1397	-0,30952			-19,53540		-17,09550	-4,64280

5.2 GENERAL TRENDS – SEA STATIONS CHL-A AND OXYGEN SATURATION

In this study, Chl-a and oxygen saturation is a simple approach to represent biological activity. The tables 2 and 3 give an overview of the trends for chl-a and oxygen saturation. Focusing on the Mann-Kendall method results, there are upward trends during winter, downwards during summer and a mixture when combining all the months for chl-a.

At Anholt E, there is no trend of chl-a in the surface waters (table 2). Below the halocline there is an upward trend during winter and a (close to being significant) downward trend during summer. The slopes of change are strongest at Anhot E compared to the other stations. The chl-a parameter is not measured throughout the fourth depth layer 30-60m, only in the upper part. The fifth depth is not included for chl-a.

At BY15 there are upward trends in the top 20 meters during winter and when including all the months of the year, This could be due to an increase of productivity in the top layer during winter or perhaps a shift of community to species with higher chl-a.

At BY31 however, there are no trends during the winter, but a downward trend just above the seasonal thermocline and above the halocline. The trends are similar when using all months of the year, but the slopes are weaker and there is a close to being significant downward trend in the top layer as well. This can perhaps be caused by lesser productivity or a shift of community species.

At BY5 there is a similar feature as found in BY15 during winter. The top 20 meters have upward trends.

For oxygen saturation (table 3), there are mainly downward trends at deeper depths, probably more reflecting the oxygen consumption processes rather than changes in oxygen production at shallower depths.

There is no trend at Anholt E.

At BY15 there are downward trends below the halocline during winter and below the seasonal thermocline during summer. Looking at all months, there are downward trends below 30 meters.

BY31 is the only station with trends above 30 meters of depth, all having small slopes. All trends are downwards. At winter, there is a trend at

the surface and a close to being significant trend at 10-20m depth. The fifth depth, being oxygen depleted, has a downward trend. During summer and when using all months, there are downward trends below 30 meters.

At BY5 there is a downward trend at depth 5 and a close to being significant trend at the 10-20m depth layer.

5.3 GENERAL TRENDS – SEA STATIONS PH AND ALKALINITY (A_T)

Looking at the main parameter of interest in this study, pH indicates only downward trends (table 4). Using the Mann-Kendall method, there are slightly fewer significant trends compared to the linear method and the slopes are generally slightly less steep. There are markedly more trends during summer than during winter.

At Anholt E, there is a close to being significant trend above the halocline, at 10-20m depth when including all months.

At BY15 at winter, there is a trend at the 30-60m depth, but not below. However during summer, when the seasonal thermocline is present, there are trends present from as high up as 10 meters and down. Including all months, there are trends below 30 meters. It is slightly strange that there is no trend present during winter at the deepest layer at BY15, however there is a linear trend present.

During winter at BY31, there are no trends present, but during summer and when using all months, there are trends at the deepest depth and a close to being significant trend at 10-20m during summer.

At BY5, there are no trends at the deepest depth, probably due to the proximity to the Sound and the Belt Seas and occasional presence of inflowing deep oxygenated water. However during summer, there are trends present between 10-60m (approximately between the seasonal thermocline and the halocline). Using all months, there is a trend in the 30-60m depth layer.

The values of the slopes indicate the pH change over one year and over 15 years. Comparing the 15 year change of the non-parametric method Mann-Kendall, the values of the changes are quite similar to the general change in the surface waters of the world oceans (0.1). But at BY15 from 30 meters and down, the rate of change is approximately doubled, as well as at the deepest depth at BY31 and the rate is about 3-4 fold the world oceans rate at BY31 at depth 10-20m.

All present trends of alkalinity (read total alkalinity, A_T) are upwards. Summing up table 5, there are no trends at Anholt E; there are trends at every depth besides the top surface layer during summer at BY15; there are trends at the deepest depth at BY31 and below 30 meters when using all months; there are mainly trends at all depths at BY5 besides at below 80 meters during winter and at the 10-20m depth when using all months.

The proximity to rivers with higher alkalinity could matter when it comes to alkalinity trends at the sea stations. In the south-eastern parts of the Baltic Proper, the river runoff has high alkalinity, compared to the rivers along the Swedish coast. BY31 and Anholt E are far away from the south-eastern Baltic Proper, BY15 and BY5 are not.

Table 4.A compilation over the linear and non linear trends for the parameter pH at the four selected sea stations. In the first section, the change over one year is displayed and then the next set of numbers display the change over 15 years, to put in relation with the pH time series. If there is a number in a cell, the trend is significant and the number represents the rate of change. If the cell has a beige colour in the background, the trend is very close to being significant.

		B: pH change per year						Change over 15 years (BY31: 93-00)					
		L	NL	L	NL	L	NL	L	NL	L	NL	L	NL
		Winter	Winter	Summer	Summer	All Year	All Year	Winter	Winter	Summer	Summer	All Year	All Year
0-4	ANHOLT E												
5-9	ANHOLT E												
10-20	ANHOLT E						-0.00201						-0,03015
30-60	ANHOLT E			-0.00437		-0.00311				-0,06555		-0,04665	
0-4	BY15 GOTLANDSDJ												
5-9	BY15 GOTLANDSDJ												
10-20	BY15 GOTLANDSDJ			-0.00863	-0.00854					-0,12945	-0,12810		
30-60	BY15 GOTLANDSDJ	-0.00831	-0.00411	-0.01180	-0.01193	-0.00875	-0.00860	-0,12465	-0,06165	-0,17700	-0,17895	-0,13125	-0,12900
80-150	BY15 GOTLANDSDJ	-0.01045		-0.01173	-0.01153	-0.01006	-0.00790	-0,15675		-0,17595	-0,17295	-0,15090	-0,11850
0-4	BY31 LANDSORTSDJ			-0.05827		-0.03667				-0,46616		-0,29336	
5-9	BY31 LANDSORTSDJ			-0.05307		-0.03097				-0,42456		-0,24776	
10-20	BY31 LANDSORTSDJ			-0.04914	-0.04617	-0.02535				-0,39312	-0,36936	-0,20280	
30-60	BY31 LANDSORTSDJ												
80-150	BY31 LANDSORTSDJ	-0.02674		-0.02630	-0.02382	-0.02347	-0.02241	-0,21392		-0,21040	-0,19056	-0,18776	-0,17928
0-4	BY5 BORNHOLMSDJ												
5-9	BY5 BORNHOLMSDJ			-0.00799						-0,11985			
10-20	BY5 BORNHOLMSDJ			-0.00474	-0.00487					-0,07110	-0,07305		
30-60	BY5 BORNHOLMSDJ			-0.00718	-0.00814	-0.00553	-0.00672			-0,10770	-0,12210	-0,08295	-0,10080
80-150	BY5 BORNHOLMSDJ												

Table 5.A compilation over the linear and non linear trends for the parameter alkalinity at the four selected sea stations. In the first section, the change over one year is displayed and then the next set of numbers display the change over 15 years, to put in relation with the pH time series. If there is a number in a cell, the trend is significant and the number represents the rate of change. If the cell has a beige colour in the background, the trend is very close to being significant.

		B: pH change per year						Change over 15 years (BY31: 93-00)					
		L	NL	L	NL	L	NL	L	NL	L	NL	L	NL
		Winter	Winter	Summer	Summer	All Year	All Year	Winter	Winter	Summer	Summer	All Year	All Year
0-4	ANHOLT E												
5-9	ANHOLT E	0,00526						0,05415					
10-20	ANHOLT E												
30-60	ANHOLT E												
0-4	BY15 GOTLANDSDJ	0,00361	0,00378			0,00264	0,00305	0,05415	0,05670			0,03960	0,04575
5-9	BY15 GOTLANDSDJ	0,00358	0,0035	0,00343	0,00489	0,00321	0,0036	0,05370	0,05250	0,05145	0,07335	0,04815	0,05400
10-20	BY15 GOTLANDSDJ	0,0033	0,00253	0,00323	0,00383	0,00325	0,00325	0,04950	0,03795	0,04845	0,05745	0,04875	0,04875
30-60	BY15 GOTLANDSDJ	0,00418	0,00318	0,00613	0,00561	0,00511	0,0047	0,06270	0,04770	0,09195	0,08415	0,07665	0,07050
80-150	BY15 GOTLANDSDJ	0,00801	0,00781	0,00854	0,0085	0,0083	0,00801	0,12015	0,11715	0,12810	0,12750	0,12450	0,12015
0-4	BY31 LANDSORTSDJ												
5-9	BY31 LANDSORTSDJ												
10-20	BY31 LANDSORTSDJ	0,00536						0,08040					
30-60	BY31 LANDSORTSDJ	0,00453		0,00657		0,00569	0,00642	0,06795		0,09855		0,08535	0,09630
80-150	BY31 LANDSORTSDJ	0,01197	0,01066	0,01581	0,01384	0,01333	0,0122	0,17955	0,15990	0,23715	0,20760	0,19995	0,18300
0-4	BY5 BORNHOLMSDJ	0,00407	0,00413	0,0046	0,00509	0,00455	0,00407	0,06105	0,06195	0,06900	0,07635	0,06825	0,06105
5-9	BY5 BORNHOLMSDJ	0,00373	0,00356	0,00517	0,00511	0,00507	0,0045	0,05595	0,05340	0,07755	0,07665	0,07605	0,06750
10-20	BY5 BORNHOLMSDJ	0,00373	0,00367	0,00554	0,00567	0,00511		0,05595	0,05505	0,08310	0,08505	0,07665	
30-60	BY5 BORNHOLMSDJ		0,00262	0,00525	0,00494	0,00513	0,00476		0,03930	0,07875	0,07410	0,07695	0,07140
80-150	BY5 BORNHOLMSDJ	0,00376		0,00598	0,00604	0,00388	0,00372	0,05640		0,08970	0,09060	0,05820	0,05580

6 RESULTS OF MULTIPARAMETER ANALYSIS – WHAT AFFECTS THE MOST?

PRIMER stands for Plymouth Routines In Multivariate Ecological Research. The steps are described in appendix 2.4 and further motivated and described in the manual written by Clarke, K.R., and Gorley, R.N., 2006.

The approach of the multiparameter (multivariate) analysis was to examine the extent to which the physico-chemical (environmental) data is related to, or in other words explains, the observed pattern of the variable of interest (in this study: pH).

Two types of results are presented: to which extent a selection of environmental variables explain the pH patterns and what the corresponding significance of those results are; and the general description of what single parameter affect pH the most and the least over depth, station wise, season wise and all together.

6.1 CORRELATION OR RHO

In the analysis, the pH dataset and the environmental dataset is converted into similarity matrixes. The ranks of the two matrixes are then compared to each other with a Spearman rank correlation coefficient, seeking a combination of environmental variables which attains a good match of the high similarities in the matrixes (read more of the methods in appendix 2.4).

Combinations of the environmental variables are considered at steadily increasing complexity, starting with one variable, then the combination of two variables and then three and so on. As a result, a description of best variable combinations is produced, starting with using just one variable, giving the results in “best performance order” for each included environmental variable, then the results for the combination of two variables and so on.

Each variable (or combination of variables) is connected to a rho value which corresponds to how well the component accounts for the variability in the full matrix, or in other words, how well the rank correlation is between the two similarity matrixes (pH and environmental datasets).

As a summation, the top 10 results are displayed with highest rho value highest up, giving the best combination of variables in descending order. In the result table (table 6), the two top results for the datasets are displayed under the column with the title “Selections”. The selection could range from only one variable included (indicating that the best result was retrieved from only one variable) up to six variables. The results retrieved in this study, indicate that a combination of variables is more commonly producing better rho values, i.e. gives better result.

Rho lies in the range -1 to +1, with the extremes of -1 and +1 corresponding to the cases where the two sets of ranks are in complete opposition or in complete agreement. Values around zero correspond to the absence of any match between the two patterns.

How high rho should be to be referred to as a good result is not defined, but in the results table 6, values above 0.5 (describing 50% of variance) is marked as bold, indicating better results.

6.2 SIGNIFICANCE TEST

Permutation tests were performed to test the null hypothesis describing the significance of the correlation results (the relationship between the pH and the environmental data). Rho was re-computed a number of times and if the observed value of rho exceeded that found in 95% of the simulations, which by definition correspond to unrelated ordinations, then the null hypothesis can be rejected at the 5% level (read more of how to calculate p and the null hypothesis in appendix 2.2).

Low values of p mean there is a ‘statistically significant’ effect - in this case relationship between that selected set of environmental variables and the pH pattern. So you are looking for something around the $p < 5\%$ mark for a ‘good’ result.

The permutation test have not been performed as recommended (99 times) due to the lack of computer efficiency shortage. Instead only 10 permutations were made, making the results more indicative of the significance rather than

Table 6. An overview of the best variable combinations along with the correlation value. Only correlation values above 0.5 has been displayed. Each variable (or combination of variables) is connected to a correlation value which corresponds to how well the rank correlation is between the two datasets of pH and environmental data. In the result table, mainly the two top results for the datasets are displayed under the column with the title "Selections". Similar results are also presented when including only one variable or parameter. Those results are on display under the columns "Corr" and "one var."

Station 1												
	Winter				Summer				All Year			
	Corr	Selections	Corr	one var	Corr	Selections	Corr	one var	Corr	Selections	Corr	one var
Depth 1												
0-4m												
Depth 2									0,536	O2, PO4, DIN		
5-9m									0,531	O2, PO4, DIN, SiO4		
Depth 3					0,564	O2, PO4, DIN	0,522	PO4	0,576	PO4, DIN	0,548	PO4
10-20m									0,548	PO4, DIN		
Depth 4												
25-60m												

Station 2												
	Winter				Summer				All Year			
	Corr	Selections	Corr	one var	Corr	Selections	Corr	one var	Corr	Selections	Corr	one var
Depth 1									0,685	O2Sat, PO4, DIN	0,536	DIN
0-4m									0,666	O2Sat, PO4, DIN, PercipPH	0,529	PO4
Depth 2									0,717	O2Sat, PO4, DIN	0,568	PO4
5-9m									0,7	O2Sat, PO4	0,551	DIN
Depth 3									0,631	O2Sat, PO4, DIN	0,596	DIN
10-20m									0,617	O2Sat, PO4, DIN, PercipPH	0,526	PO4
Depth 4	0,594	O2Sat	0,594	O2Sat					0,545	O2Sat	0,545	O2Sat
25-60m	0,544	Salt, O2, O2Sat, PercipPH							0,516	O2Sat, PO4		
Depth 5	0,646	O2Sat	0,646	O2Sat	0,677	O2Sat, Alk			0,564	Salt, O2Sat, PO4, Alk	0,534	O2Sat
80-150m	0,64	O2Sat, Alk	0,517	Alk	0,658	O2Sat, Alk, SiO4			0,559	O2Sat, PO4, Alk		

Station 3												
	Winter				Summer				All Year			
	Corr	Selections	Corr	one var	Corr	Selections	Corr	one var	Corr	Selections	Corr	one var
Depth 1									0,672	O2Sat, PO4	0,516	O2Sat
0-4m									0,644	O2Sat, PO4, DIN		
Depth 2									0,688	O2Sat, PO4	0,545	PO4
5-9m									0,678	O2Sat, PO4, DIN, CO2Atm		
Depth 3												
10-20m												
Depth 4					0,783	O2Sat	0,783	O2Sat	0,758	O2Sat	0,758	O2Sat
25-60m					0,754	O2, O2Sat	0,709	O2	0,707	O2, O2Sat	0,617	O2
Depth 5	0,656	DIN, Alk, SiO4, RiverAlk			0,787	Salt, O2, DIN, Alk, PercipPH	0,713	Alk	0,519	Salt, O2, O2Sat, PO4, DIN, PercipPH		
80-150m	0,654	PO4, DIN, Alk, SiO4, RiverAlk			0,785	Salt, O2Sat, DIN, Alk, PercipPH	0,625	Salt	0,518	Salt, O2, O2Sat, PO4, DIN, SiO4		

Station 4												
	Winter				Summer				All Year			
	Corr	Selections	Corr	one var	Corr	Selections	Corr	one var	Corr	Selections	Corr	one var
Depth 1									0,64	O2Sat, PO4, DIN		
0-4m									0,63	O2Sat, PO4, DIN, PercipPH		
Depth 2									0,664	O2Sat, PO4, DIN		
5-9m									0,645	O2Sat, PO4, DIN, PercipPH		
Depth 3									0,609	O2Sat, PO4, DIN	0,589	DIN
10-20m									0,602	PO4, DIN		
Depth 4					0,515	O2Sat, SiO4, PercipPH, RiverAlk			0,566	O2Sat	0,566	O2Sat
25-60m					0,507	O2Sat, SiO4, NAOI, PercipPH, RiverAlk			0,522	O2, O2Sat		
Depth 5												
80-150m												

significant or not on the 5% level. With 10 permutations, which is only enough to give a significance at the best about the 10% level (to be precise, 9.1%). If a value of rho is pretty large, say above 0.6-0.7, it means a very high correlation and is almost certainly significant. To comply somewhat with the recommendations of 99 permutations, 10 tests were made performing both 10 and 99 permutations on different data sets that with 10 permutations resulted in a significance level of $p=9.1\%$. All the 10 results using 99 permutations gave the significance level of $<1\%$, raising the probability that the results giving 9.1% are in fact valid significant results.

6.3 CORRELATION RESULTS

In the results table 8 in appendix 1.2, values above 0.5 is marked as bold, indicating better results. If the numbers are black the permutation tests have indicated that the results are significant. If they are red, the permutation tests have indicated that the results are not significant. Out of the 57 analyses, only 10 are indicated as not significant results where only one has one rho value higher than 0.5 (station 3, depth 1, during summer).

The two first values of the best fit when combining parameters is displayed, indicating what parameters from the list to the left are combined to produce the rho correlation value. The two first parameters from the one variable result list are also presented for each depth, season and station.

The higher rho values are generally found in the all year columns and also at the deeper depths during winter and summer. The exceptions are at Anholt E (station 1) and at BY5 (station 4) where there rho values do not tend to grow larger with depth. Looking at the oxygen saturation trends, similarities can be found between the absence of trends at the deeper depths and lack of rho correlation here.

In table 4, only significant rho values above 0.5 are displayed, with corresponding parameter combinations. At Anholt E (station 1) the parameters O_2 , PO_4 and DIN frequently appear, indicating that these parameters are the most important of all included parameters.

At BY15 (station 2) using all months, the parameters O_2 saturation, PO_4 and DIN frequently

appear throughout the depths with Salinity and Alk appearing at depth 5. Also during winter and summer at deeper depths, O_2 saturation and Alk are common with appearances of Salinity and SiO_4 .

At BY31 (station 3) using all months, the parameters O_2 saturation, PO_4 and DIN frequently appear throughout the depths with O_2 and Salinity appearing at depth 4-5 and a rare appearance of CO_2 Atm at depth 2. During winter at depth 5 Nutrients and Alk appear as well as the unlikely presence of RiverAlk. During summer O_2 , O_2 saturation, Salinity and Alk appear as well as the unlikely presence of PercipPH.

At BY5 (station 5) using all months, the parameters O_2 saturation, PO_4 and DIN frequently appear throughout the depths 1-3 with PercipPH appearing at depth 1-2. At depth 4, O_2 saturation and O_2 appear. During summer at depth 4 O_2 saturation, SiO_4 PercipPH and RiverAlk appear as well as the uncommon NAOI.

Generally, O_2 , O_2 saturation, PO_4 and DIN have the most frequent appearance when singling out only significant results with higher correlation.

6.4 RESULTS OVERVIEW WHEN USING ONE VARIABLE RESULTS

There are five depths, four stations and three seasons (winter, summer and using all the months) analysed. An attempt to give an overview of what parameters effect the pH the most, the results from describing the pH dataset using only one variable is used and presented in table 7. For one dataset, the most important parameter comes in first place, the next important parameter comes in second place and so on until all included parameters have been listed. To give an overview, a combination of datasets must be made to prevent giving 60 result cases.

In appendix 1.3 there are a number of tables displaying the combination of one variable results. There should be differences over depth which is why the results from different depths are not combined, but presented separately. Chl-a is not measured at depth 4-5.

The structure of the first table in appendix 1.3, is each parameter listed as columns and the place

on which each parameter appears in the analysis is listed as rows. In the first table, all stations and all seasons are combined. Hence each column (parameter) should have a total of 12 (4 stations times 3 seasons). If a parameter has high or many values on the top rows (representing a frequent appearance high up on the importance / placement scale), say between rows 1-4, the parameter has an important effect on the pH. In contrast, if high or many values are found in the bottom rows, it is not an important parameter to pH.

In the next set of tables in appendix 1.3, all seasons are combined, but presented station by station. Each column (parameter) should then have the total of 3. In the next set of tables, all stations are combined, presenting season by season. Each column (parameter) should then have the total of 4.

All one variable results are included, not only the analyses with significance and high correlation, but also the analyses without significance and with low correlation. It is the general tendency this overview is based upon.

Looking, still in appendix 1.3, at the tables displaying all stations and all seasons combined, the spread of the numbers are rather evenly distributed in the top three depths compared to the bottom two depths, where the numbers cluster more to the top left and bottom right. At all depths there is a slight tendency for the parameters 8-13 (chl-a, CO₂ Atm, NAOI, PercPH, RivPH and RivAlk) to have none or a low score high up on the place list. That means that these parameters are not that important. Keep in mind all the assumptions made in the analyses and the uncertainties of including the parameters in a right manner, influencing the outcome of the results.

Three other features can be noted: DIN seems to be more important at the top layers than at the bottom layers; Salinity and Alk seem to be more important at the bottom layers than at the top layers; At all depths, O₂, O₂ saturation, PO₄ and SiO₄ seem to be of higher importance.

The features mentioned above can be recognised when dividing up the results both on stations and on seasons however the numbers tend to cluster slightly better when dividing up the results over seasons rather than over stations (combining results from all seasons). The parameters placed

mainly on the top four rows are parameters best describing the pH patterns.

An overview of the general tendencies described above, have been assembled in table 7 in this chapter. The top four place results from the tables in appendix 1.3 are condensed. For each separate parameter, for each division of station or season just described and visible in appendix 1.3, if there is an overwhelming presence of numbers in the top four rows (place 1-4), then this is displayed in table 7 as an "X". If there is no "X" in a cell in table 7, that means that there are no or very few numbers in the top four place results from the tables in appendix 1.3.

As a reminder: the most important parameter comes in first place, the next important parameter comes in second place and so on. That means that in table 7, if there is an "X" in a cell, that parameter is of importance when it comes to effecting pH the most.

An interesting feature visible in table 7 is the absence of marks (X's) at depth 3 for O₂, probably due to that there is a lot of variability at 10-20 meters.

SiO₄ seems to be more important at station 1 than the other stations.

Chl-a does not seem to be important. Since biological activity should have a large impact on pH, chl-a as included in the analysis, was not a good representative for the biological activity. O₂ and O₂ saturation are very much included as parameters influencing the pH patterns. Perhaps in the top layers, they are better representatives for the biological activity in this analysis.

It is also interesting to see the complete lack of marks in the CO₂Atm column, a column the author thought would be filled at the surface depths. However, when performing trend analysis, not many pH trends were present at the surface (probably due to the biological and of course chemical/physical processes), opening up for O₂, O₂ saturation and nutrients to be the dominant parameters.

In the open surface waters of the ocean, the nutrient level difference to the Baltic surface layers is large hence biological activity should also differ. Perhaps the sites for the few existing pH trend series from the Hawaiian Ocean Time-series (HOT)

Table 7. An overview of what parameters effect pH the most, from the results describing the pH dataset using only one variable. The top four place results from the tables in appendix 1.3 have been used. For each separate parameter, for each division of station or season (visible in appendix 1.3), if there is an overwhelming presence of numbers in the top four rows (place 1-4), then this is displayed as an "X". If there is no "X" in a cell, that means that there are no or very few numbers in the top four place results from the tables in appendix 1.3. That means that if there is an "X" in a cell, that parameter is of importance when it comes to effecting pH the most.

	Station	Season	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
Depth 1	All stations	All seasons		X	X	X	X		X						
Depth 1	1	All seasons		X		X	X		X						
Depth 1	2	All seasons		X	X	X			X						
Depth 1	3	All seasons			X				X						
Depth 1	4	All seasons				X	X								
Depth 1	All stations	Winter		X			X							X	
Depth 1	All stations	Summer		X		X									
Depth 1	All stations	Yearly data		X	X	X	X								
Depth 2	All stations	All seasons		X	X	X	X		X						
Depth 2	1	All seasons		X		X	X		X						
Depth 2	2	All seasons		X			X								
Depth 2	3	All seasons			X		X								
Depth 2	4	All seasons				X									
Depth 2	All stations	Winter		X		X	X		X						
Depth 2	All stations	Summer		X						X					
Depth 2	All stations	Yearly data			X	X	X								
Depth 3	All stations	All seasons			X	X	X								
Depth 3	1	All seasons				X	X		X						
Depth 3	2	All seasons				X	X								
Depth 3	3	All seasons			X	X	X								
Depth 3	4	All seasons			X	X									
Depth 3	All stations	Winter				X	X		X						
Depth 3	All stations	Summer			X	X							X		
Depth 3	All stations	Yearly data			X	X	X								
Depth 4	All stations	All seasons	X	X	X	X									
Depth 4	1	All seasons			X		X		X			X			
Depth 4	2	All seasons		X	X	X									
Depth 4	3	All seasons	X	X	X	X									
Depth 4	4	All seasons		X	X	X			X						
Depth 4	All stations	Winter	X	X	X										
Depth 4	All stations	Summer		X	X										
Depth 4	All stations	Yearly data		X	X	X			X						
Depth 5	All stations	All seasons	X	X	X			X	X						
Depth 5	1	All seasons													
Depth 5	2	All seasons	X	X	X	X		X							
Depth 5	3	All seasons	X	X	X	X		X							
Depth 5	4	All seasons	X	X	X				X						
Depth 5	All stations	Winter	X	X	X	X		X							
Depth 5	All stations	Summer	X	X	X			X	X						
Depth 5	All stations	Yearly data	X	X	X			X	X						

and the Bermuda-Atlantic Time-series (BATS) are not experiencing large blooms, resulting in less interference from the biology so that the downward pH trends are even seen at surface layers, not only

at slightly larger depths as seen in the Baltic. This being said without looking further at data from HOT or BATS.

7 MONITORING REQUIREMENTS – FROM A MODELLING POINT OF VIEW

Since pre-industrial time, the release of CO₂ to the atmosphere due to the burning of fossil fuel has increased causing a decrease in both the pH and the saturation level of calcium carbonate (CaCO₃). As a result, negative effects on marine organisms, especially those forming CaCO₃-skeletons, seem increasingly common.

In the Baltic Sea and the Kattegat seasonal sediment-related biogeochemical processes have an impact on the pH level causing a substantial seasonal variability, influenced e.g. by eutrophication, and on top of this seasonal pattern a multi-decadal decrease in the pH has been observed at many sampling locations around the Swedish coast over the last two decades. Also changes of total alkalinity (A_T) in the river runoff to the Baltic Sea have occurred during the last century. A_T affects the buffering capacity in the acid–base (pH) balance, affects CO₂ atmosphere uptake, and controls the formation of calcium carbonate shells.

To understand possible effects from future anthropogenic and climate induced changes on the acidification in the Baltic Sea we need models that can provide simulations and experiments under different future scenarios. Model experiments and controlled hind casts that are validated against observations may show model sensitivities and lacks in knowledge that need to be further understood. In this way the data provided from observations play a necessary role increasing our understanding of processes and supporting the development of even better models. Results from high-resolution coupled 3D biogeochemical-physical models may further provide information about regional and temporal variability that are not resolved within e.g. the national monitoring programs and may serve as a basis for the planning of measuring campaigns.

In order to study ocean acidification the present high-resolution coupled 3D biogeochemical-physical RCO-SCOB model system need to include both the organic and inorganic carbon cycle. A good description of the biological processes and the cycling of organic matter are essential for the description of the carbon system.

The validation of the model results from hind casts are e.g. validated in the central of major sub

basins against available standard observations of inorganic nutrients, nitrate (and nitrite), ammonium and phosphate, and observations of oxygen (and hydrogen sulphide as negative oxygen). The horizontal variability is as far as possible validated against maps of interpolated and extrapolated values from measurements. The phytoplankton is validated by the chlorophyll concentrations. Methods to validate modelled phytoplankton groups to phytoplankton species and zooplankton data are under development.

The validation would be very much improved if the concentrations of organic matter could be validated. Today only measurements of total nitrogen and phosphorus and dissolved inorganic nutrients are available. Including standard observations of particulate organic matter (PON, POP and POC) as well as dissolved organic matter (DON, DOP and DOC) would much improve the possibility to further develop the biogeochemical models.

For oceanic conditions all the parameters of the inorganic carbon system (total dissolved inorganic carbon (DIC), total alkalinity (A_T), partial pressure of CO₂ (pCO₂) and pH) can be estimated from any two of these. In low salinity waters however, uncertainty in the determined relevant chemical stability constants and lack of knowledge of the ionic composition of the water results in errors in computations of the non-determined parameters. Thus the most accurate result is achieved by determining these parameters by direct measurements.

Another important factor of the biogeochemical model is the variability of sediment concentrations of nutrients which we have very little knowledge on. It is of great interest for the model validation to find standard methods that might resolve at least the seasonal and interannual variability of the surface sediment concentrations of carbon, nitrogen and phosphorus. In this case the spatial distribution of monitoring stations needs to incorporate not only the sediments of the central basins since these stations are not representative on the basin scale.

A recommendation would be to start with monthly sampling of data at the standard monitoring stations (except in sediments as mentioned above).

Another recommendation is to do a separate investigation based on RCO-SCOBI model results to recommend possible new stations that are important and not covered by the present sampling strategy.

This discussion above and recommendations have not taken into account the needs of data assimilation in operational models where there is a greater need of higher temporal and spatial resolution. Measurements made from Ferryboxes and other high resolution measurement tools can give better information regarding that kind of variability.

Another interesting aspect is to calculate and model the saturation state over depth of calcite and aragonite, of major importance for many calcifying organisms. In Tyrell et al., 2008, they found that the Baltic Sea becomes undersaturated (or nearly so) in winter, with respect to both the aragonite and calcite mineral forms of CaCO_3 .

It is of ecological importance to have knowledge about the saturation depths of both aragonite and calcite in the different sea areas in the Baltic. For calculating the saturation state, the ions CO_3^{2-} and Ca^{2+} need to be determined. Either CO_3^{2-} could be measured, or calculated using measurements from the partial pressure of CO_2 (pCO_2) and total carbon (C_T) (with the use of marine equilibrium constants). Further more either Ca^{2+} could be measured, or estimated from Ca/salinity relationships described in Tyrell et al., 2008.

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APPENDIX I: RESULT TABLES AND FIGURES

APPENDIX I.1: SELECTION OF TREND FIGURES

Some selected figures of the parameters presented in this study are presented as time series. Each parameter is divided into winter, summer and using all months of the year. When the amount of data points is sufficient, both a linear regression and non-linear (non-parametric) analysis have been supplied on the data sets to analyse for possible trends. The black dots in the figures represent each observation. The black line is the yearly mean of the season and the dashed black lines represent the standard deviation of the mean values. The red line displays the maximum observations and the blue the minimum observations.

In the case there are sufficient data to analyse for trends. There is a green line representing the best fit of a linear regression of the first order. The dashed green lines represent the 95% confidence interval for the linear trend. The inserted text box in most figures gives some indication as to if there is a significant trend present. In the first part of the text box, with the letters LR, the inclination of the linear regression line is presented followed by the letter x. If LR is positive, the direction of the line is positive and vice versa. The two following numbers in the text box belong to the non-linear seasonal Mann-Kendall analysis. NL B is the slope of a possible trend. The NL P value is the significance of the trend. If the NL P value is less than 0.05, the trend is significant. The choice of a critical p-value to determine whether the result is judged "statistically significant" is left to the researcher. It is common to declare a result significant if the p-value is less than 0.05.

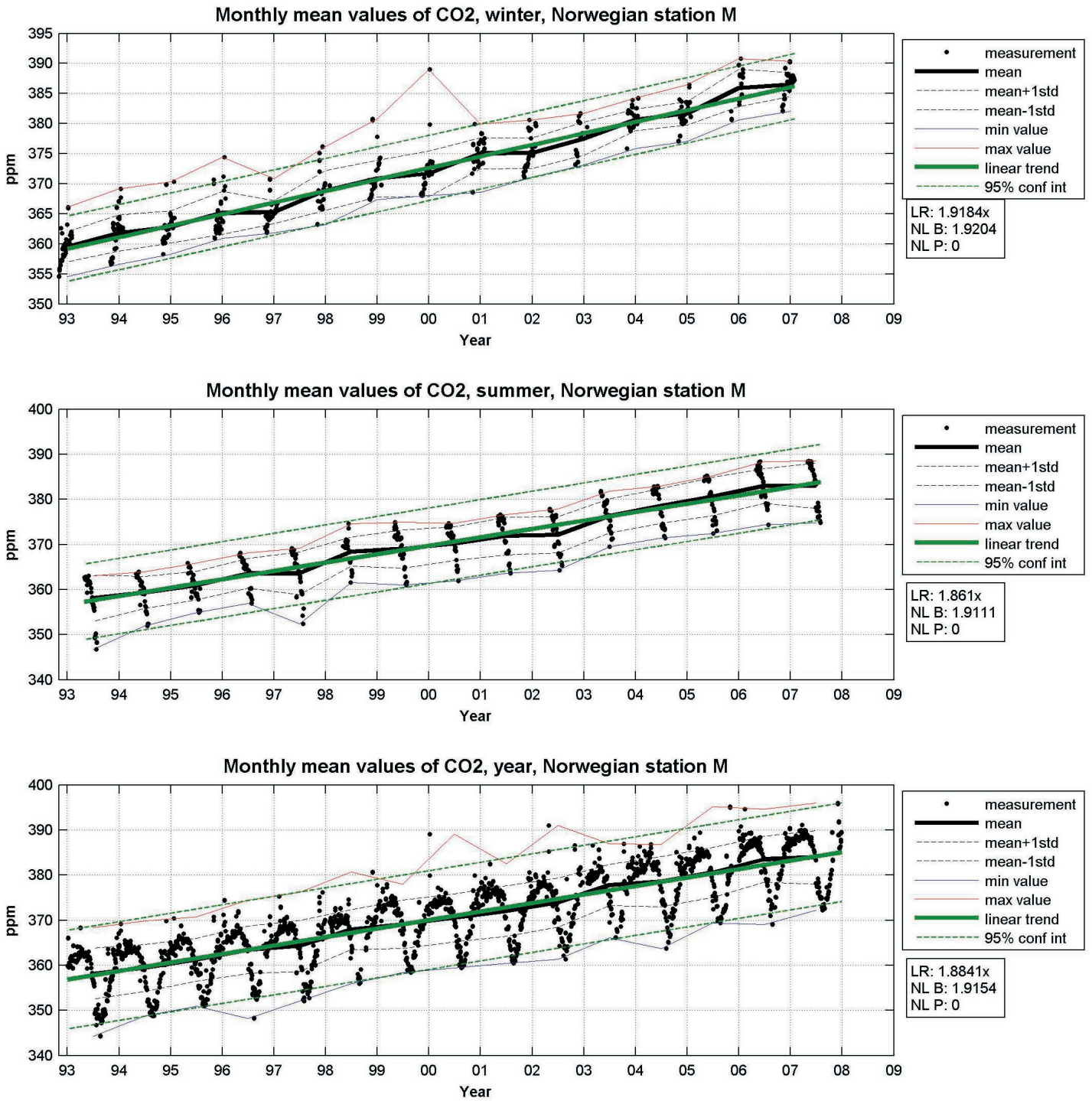


Figure 4. Time series of atmospheric CO₂ from the Norwegian sea statin M. Trends calculated using linear regression and the non parametric analysis Mann-Kendall.

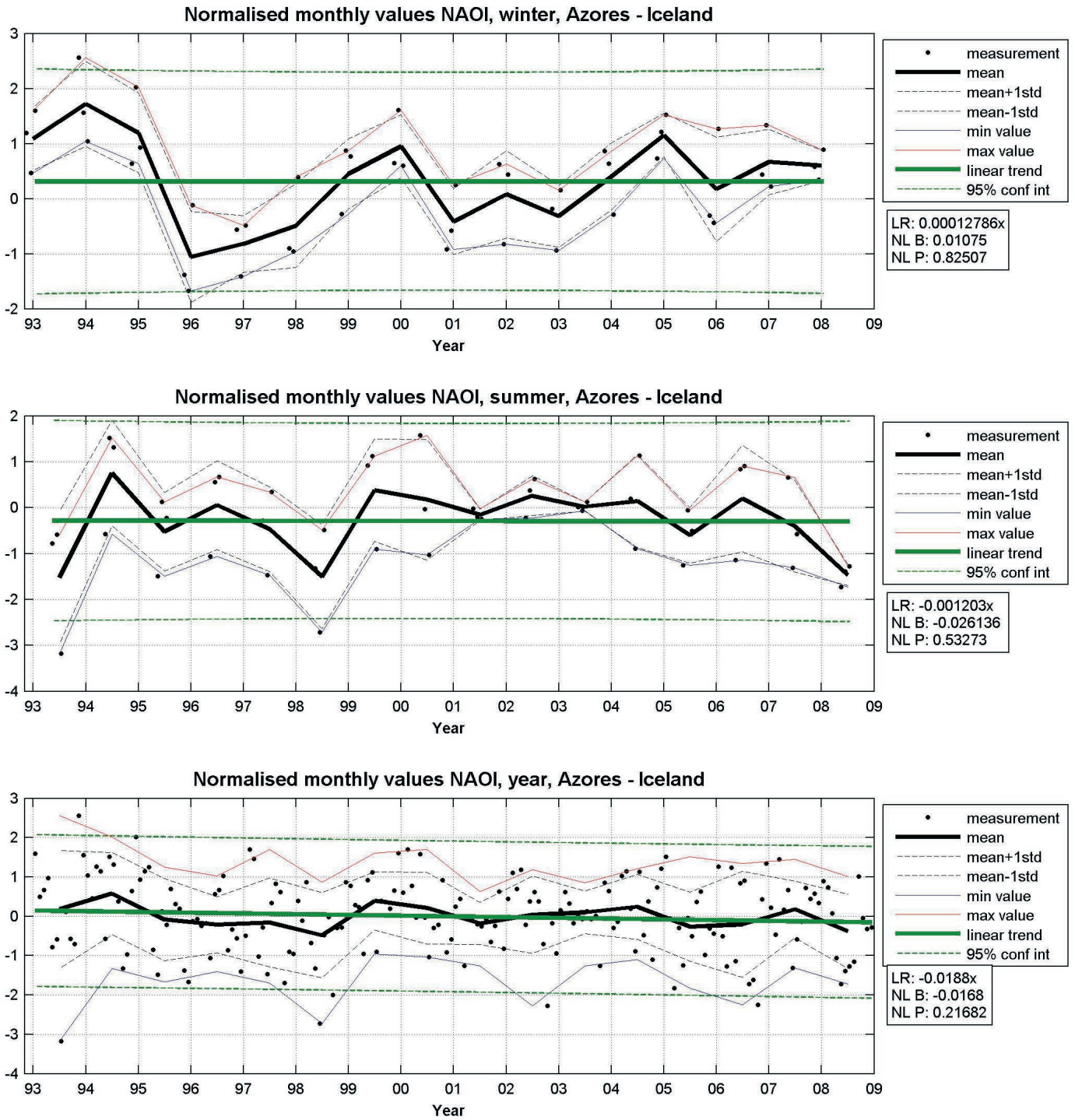


Figure 5. Time series of normalised monthly values of the NAOI. Trends calculated using linear regression and the non parametric analysis Mann-Kendall.

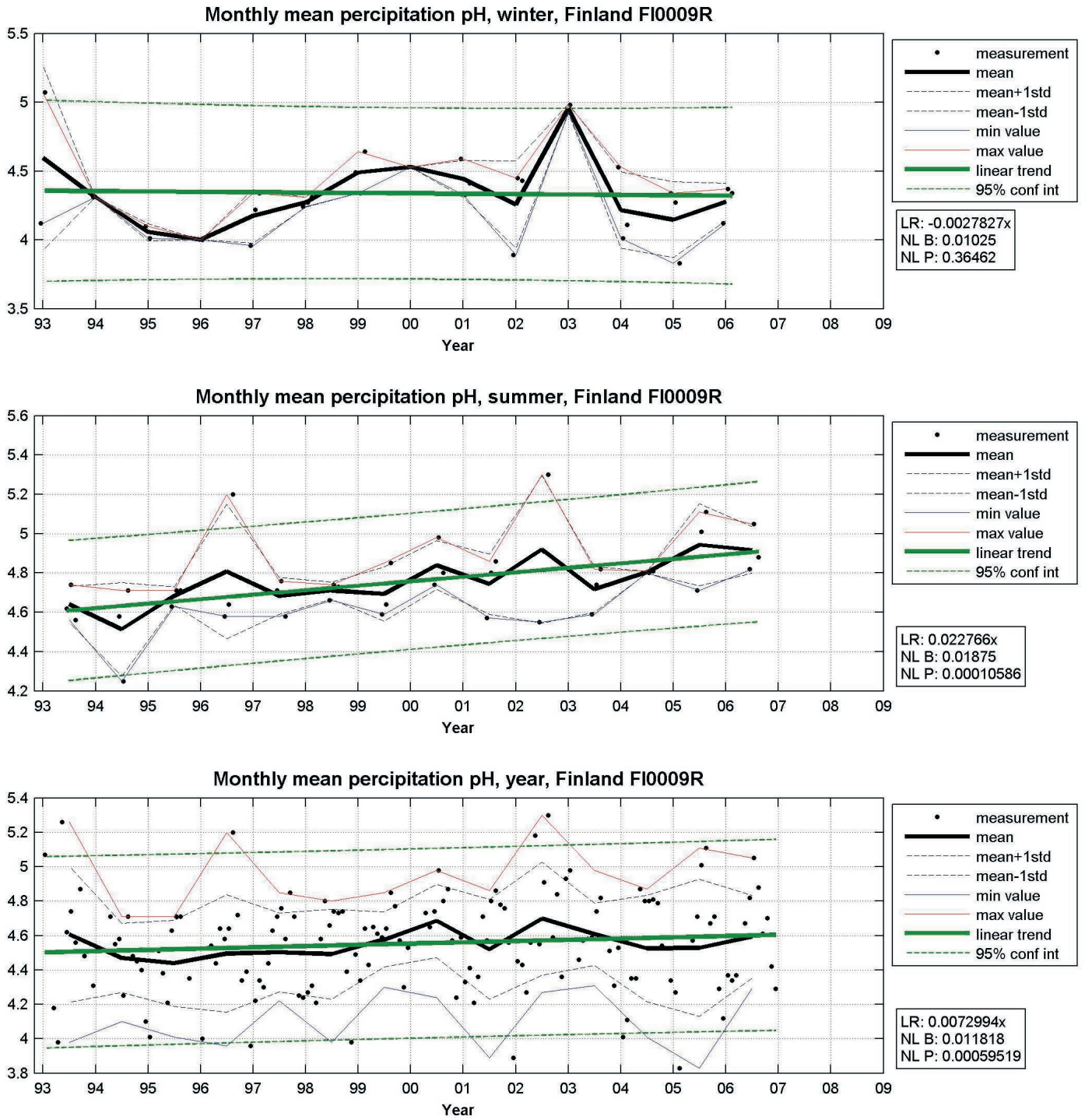


Figure 6. Time series of the monthly mean precipitation pH values from station FI0009R in Finland. Trends calculated using linear regression and the non parametric analysis Mann-Kendall.

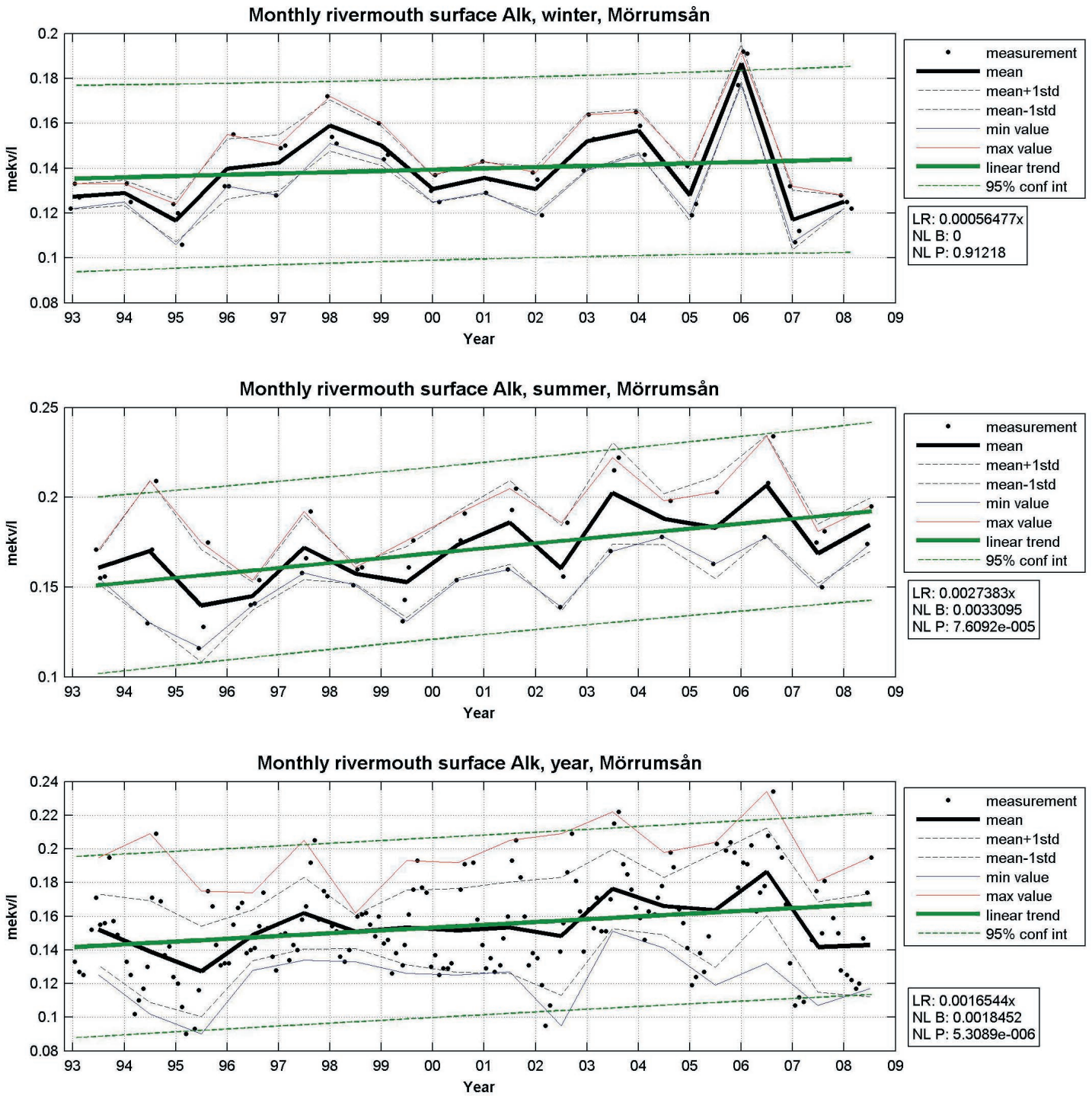


Figure 7. Time series of the monthly rivermouth surface alkalinity at Mörrumsån. Trends calculated using linear regression and the non parametric analysis Mann-Kendall.

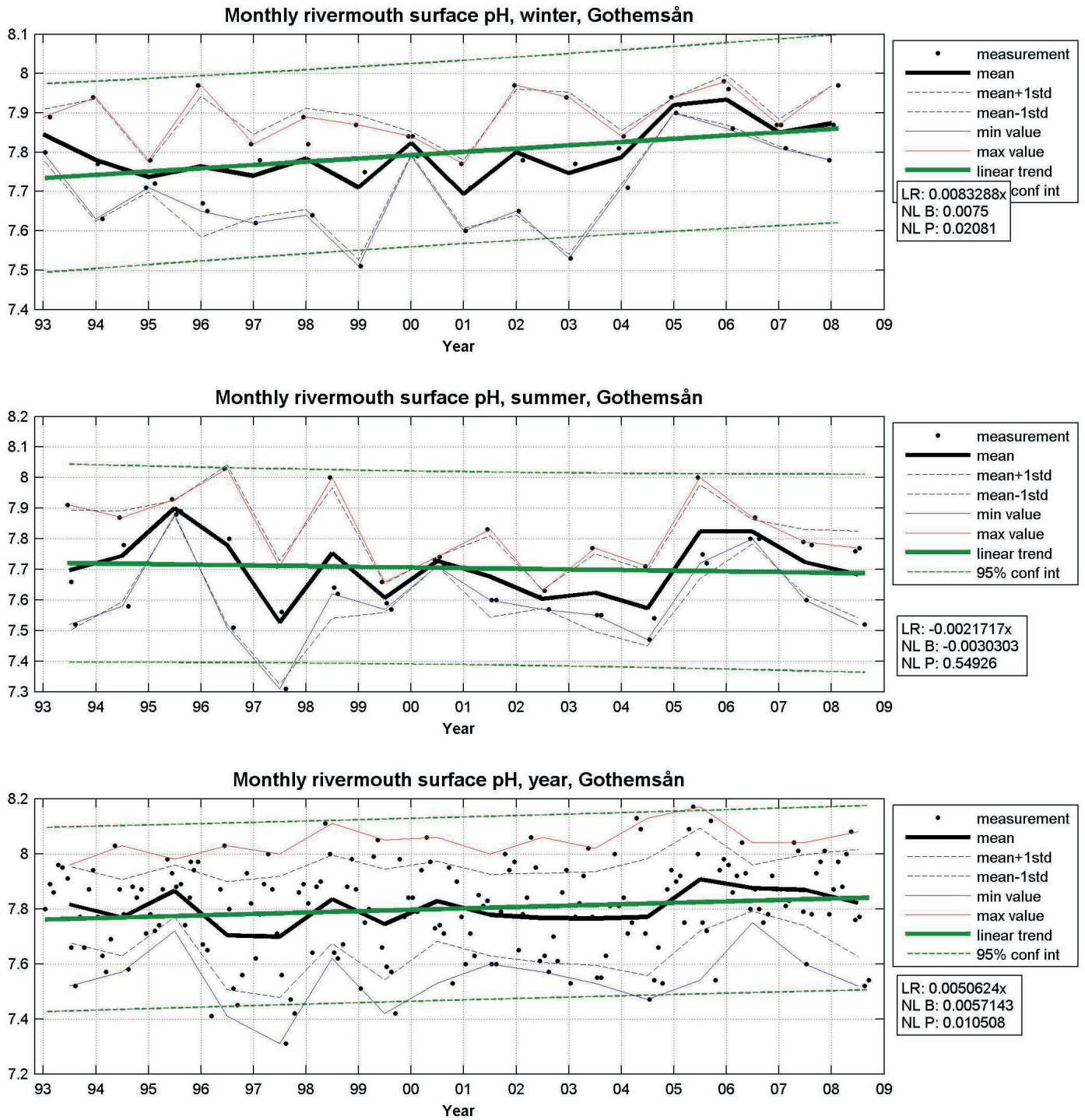


Figure 8. Time series of the monthly rivermouth surface pH at Mörrumsån. Trends calculated using linear regression and the non parametric analysis Mann-Kendall.

APPENDIX I.2: CORRELATION TABLE FROM MULTIPARAMETER ANALYSIS

Table 8. An overview of the best variable combinations along with the correlation value. Each variable (or combination of variables) is connected to a correlation value which corresponds to how well the rank correlation is between the two datasets of pH and environmental data. The two first values of the best fit when combining parameters is displayed, indicating what parameters from the list to the left are combined to produce the rho correlation value. The two first parameters from the one variable result list are also presented for each depth, season and station. Values above 0.5 is marked as bold, indicating better results. Black numbers means that the permutation tests have indicated that the results are significant. If they are red, the permutation tests have indicated that the results are not significant.

Station 1

	Param nr	Winter				Summer				All Year			
		Corr	Selections	Corr	one variable	Corr	Selections	Corr	one variable	Corr	Selections	Corr	one variable
Depth 1	1 Salt	0,285	7,10	0,262	7	0,331	2,5,8,9	0,204	2	0,499	2-5	0,411	5
0-4m	2 O2	0,284	5,7,10	0,201	5	0,33	2,5,8,9,13	0,171	5	0,489	2-5,7	0,402	4
	3 O2Sat												
Depth 2	4 PO4	0,347	4,5,7,10	0,328	7	0,412	2,8,9,13	0,251	2	0,536	2,4,5	0,472	4
5-9m	5 DIN	0,345	2,4,5,7,10	0,309	4	0,385	2,8,13	0,224	8	0,531	2,4,5,7	0,429	5
	6 Alk												
Depth 3	7 SiO4	0,355	4-6,12	0,336	5	0,564	2,4,5	0,522	4	0,576	4,5	0,548	4
10-20m	8 Chla	0,346	4-7,12	0,246	4	0,56	2,4,5,7	0,371	5	0,548	4	0,461	5
	9 CO2atm												
Depth 4	10 NAOI	0,206	5,6,10,12	0,107	12	0,139	3,5,10	0,121	5	0,326	3,5,7,10,11	0,263	7
25-60m	11 PercipPH	0,203	1,5,6,10,12	0,079	10	0,139	3,5,9,10	0,08	10	0,32	2,3,5,7,10,11	0,245	3
	12 RiverPH												
	13 RiverAlk												

Station 2

	Param nr	Winter				Summer				All Year			
		Corr	Selections	Corr	one variable	Corr	Selections	Corr	one variable	Corr	Selections	Corr	one variable
Depth 1	1 Salt	0,25	2	0,25	2	0,278	2-4,8,10	0,186	10	0,685	3-5	0,536	5
0-4m	2 O2	0,233	2,7	0,102	7	0,274	3,4,8,10	0,126	4	0,666	3-5,11	0,529	4
	3 O2Sat												
Depth 2	4 PO4	0,251	2,4,11	0,249	2	0,29	2,3,8,10	0,168	10	0,717	3-5	0,568	4
5-9m	5 DIN	0,249	2	0,144	7	0,283	3,8,10	0,112	8	0,7	3,4	0,551	5
	6 Alk												
Depth 3	7 SiO4	0,266	2,8,11	0,232	2	0,263	1,4,8,10	0,235	1	0,631	3-5	0,596	5
10-20m	8 Chla	0,263	2,8,10,11	0,173	8	0,261	1,4,7,8,10	0,128	4	0,617	3-5,11	0,526	4
	9 CO2atm												
Depth 4	10 NAOI	0,594	3	0,594	3	0,436	3	0,436	3	0,545	3	0,545	3
25-60m	11 PercipPH	0,544	1-3,11	0,453	2	0,421	3,4	0,225	2	0,516	3,4	0,323	2
	12 RiverPH												
Depth 5	13 RiverAlk	0,646	3	0,646	3	0,677	3,6	0,641	3	0,564	1,3,4,6	0,534	3
80-150m		0,64	3,6	0,517	6	0,658	3,6,7	0,545	6	0,559	3,4,6	0,454	6

Station 3

	Param nr	Winter				Summer				All Year			
		Corr	Selections	Corr	one variable	Corr	Selections	Corr	one variable	Corr	Selections	Corr	one variable
Depth 1	1 Salt	0,433	5,10,13	0,265	10	0,514	1,7,9	0,361	7	0,672	3,4	0,516	3
0-4m	2 O2	0,391	2,10,13	0,241	13	0,497	6,7,9	0,313	1	0,644	3-5	0,495	4
	3 O2Sat												
Depth 2	4 PO4	0,481	5,10,13	0,362	13	0,419	1,7,9	0,353	1	0,688	3,4	0,545	4
5-9m	5 DIN	0,445	5,10,12,13	0,205	10	0,399	1,4,7,9	0,317	7	0,678	3-5,9	0,486	3
	6 Alk												
Depth 3	7 SiO4	0,381	5,12,13	0,344	13	0,413	5,7,11-13	0,302	11	0,487	3,4	0,368	4
10-20m	8 Chla	0,362	4,12,13	0,146	5	0,408	4,7,11-13	0,255	12	0,47	3-5	0,311	3
	9 CO2atm												
Depth 4	10 NAOI	0,487	3,5,13	0,413	3	0,783	3	0,783	3	0,758	3	0,758	3
25-60m	11 PercipPH	0,479	2,3,5,13	0,255	1	0,754	2,3	0,709	2	0,707	2,3	0,617	2
	12 RiverPH												
Depth 5	13 RiverAlk	0,656	5-7,13	0,416	1	0,787	1,2,5,6,11	0,713	6	0,519	1-5,11	0,478	1
80-150m		0,654	4-7,13	0,413	4	0,785	1,3,5,6,11	0,625	1	0,518	1-5,7	0,475	2

Station 4

	Param nr	Winter				Summer				All Year			
		Corr	Selections	Corr	one variable	Corr	Selections	Corr	one variable	Corr	Selections	Corr	one variable
Depth 1	1 Salt	0,397	1,7,8,12	0,265	7	0,217	2,3,9	0,134	9	0,64	3-5	0,48	5
0-4m	2 O2	0,393	1,4,8,12	0,165	1	0,213	2,3,9,10,12	0,095	2	0,63	3-5,11	0,419	3
	3 O2Sat												
Depth 2	4 PO4	0,356	5-7,12	0,313	7	0,228	2-4,9,12	0,142	2	0,664	3-5	0,492	5
5-9m	5 DIN	0,356	5,7,12	0,207	12	0,226	2,3,9,12	0,139	9	0,645	3-5,11	0,445	4
	6 Alk												
Depth 3	7 SiO4	0,418	2,4-6,12	0,29	7	0,25	1,3,4,6,10,11	0,181	11	0,609	3-5	0,589	5
10-20m	8 Chla	0,416	4-6,12	0,236	12	0,249	1,3,4,10,11	0,063	3	0,602	4,5	0,382	4
	9 CO2atm												
Depth 4	10 NAOI	0,472	2,3,7	0,391	3	0,515	3,7,11,13	0,404	3	0,566	3	0,566	3
25-60m	11 PercipPH	0,469	1-4,7,12	0,338	2	0,507	3,7,10,11,13	0,316	13	0,522	2,3	0,454	2
	12 RiverPH												
Depth 5	13 RiverAlk	0,445	7	0,445	7	0,485	35	0,485	7	0,487	7	0,487	7
80-150m		0,442	2,7	0,413	2	0,468	1,2,7,10,13	0,392	2	0,43	2,7	0,358	2

APPENDIX I.3: COMBINATION OF ONE VARIABLE RESULTS TABLES FROM MULTIPARAMETER ANALYSIS

Table 9. Overview of what parameter effects the pH the most, the results from describing the pH dataset using only one variable is used. The structure of the table is each parameter listed as columns and the place on which each parameter appear in the multiparameter analysis is listed as rows. In this table, all stations and all seasons are combined. Hence each column (parameter) should have a total of 12 (4 stations times 3 seasons). If a parameter has high or many values on the top rows (representing a frequent appearance high up on the importance / placement scale), say between rows 1-4, the parameter has an important effect on the pH. In contrast, if high or many values are found in the bottom rows, it is not an important parameter to pH.

All stations, all seasons

Depth 1

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1			2	1		3		3		1	2		
2		2	1	1	4	2		1					1
3			1	3	2	2	1		1			2	
4			3		1	1		2		1		2	1
5			2					5	1	2	1	1	
6			1	1		2			1	1		2	3
7	3		2	1	2		1		1		1	1	
8				2			2	2	1	1	1	2	1
9	1				1		3	1		2	1		3
10	2							1	1	3	1	1	3
11	1			1		2	2	2		1		2	
12	1			1	2		2		2		1		1
13	2			1			1			1	4	1	2

All stations, all seasons

Depth 2

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1		1	3		3	1		2			1		1
2				1	2	2		2	2	1	1		1
3			1	2	2	5		1					1
4			3	2		1	1	1	1			1	2
5	1		2		2				1	2	1	2	1
6	1	1	1	1	1		1		2	1		3	1
7	1	1	1	1	2			1	1	2	1	1	1
8	1		1				1	4	1		1	1	2
9	1				2		2		1	3			1
10				3			1	1	1	2	1		2
11				1		1	2				3	1	3
12	5						1		2		1	2	1
13	1			1			3			1	2	1	3

All stations, all seasons

Depth 3

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1	1		1		3	3		1				2	
2				2	4	3			1				2
3				3	1	2		3	2	1			
4	1		1		1	2	3	1	1			2	
5	2		3	1	1		1	1		1	1		1
6			3		1			1	2		2	1	2
7	1		1	1	1		3	1		1	1		2
8	1						2	1	1		2	1	1
9			1	1				1		4	1	1	2
10	1		1	1		1		1			2	2	1
11	2			1					2	2	1		3
12	1			1		1	2			2	2	2	1
13	2		1	1			1		3		1	1	2

All stations, all seasons

Depth 4

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1				9		1		1					1
2	1		7	1							2		1
3	2		2		3	1	1	2					1
4	1		1		4	1	1	1		1	2		
5	2				4	1	2	2					1
6	2			1		2	1	2			1	2	1
7					1		1	1		2	2	1	4
8				1		1	1	1		4	1	2	1
9						2	1	2		1		2	3
10	1		2				4	2			1	3	1
11						3				3		2	4
12	3									5		1	2
13													

All stations, all seasons

Depth 5

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1	2			3			1	3					
2	1		4		1		3						
3	3		1	3	1		1						
4	1		1	2	3			2					
5	1			1	4	1	1	1					
6	1					1	1	1		3		1	1
7						3	1	2		1	1	1	
8						1	1				2	2	3
9						1				3	1	2	2
10											1	3	1
11						1					2	4	2
12						1				2	2	1	
13													

Table 10. Overview of what parameter effects the pH the most, the results from describing the pH dataset using only one variable is used. The structure of the table is each parameter listed as columns and the place on which each parameter appear in the analysis is listed as rows. In this table, all seasons are combined, but presented station by station. Hence each column should have a total of 3 (3 seasons). If a parameter has high or many values on the top rows, say between rows 1-4, the parameter has an important effect on the pH. In contrast, if high or many values are found in the bottom rows, it is not an important parameter to pH.

Station 1, all seasons
Depth 1

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1			1			1		1					
2					1	2							
3			1		1				1				
4			1					1					1
5										1	1		1
6				1									2
7	1			1					1				
8							1					1	1
9							1			1			1
10	1									1	1		
11							1	1				1	
12				1	1				1				
13	1										1	1	

Station 1, all seasons
Depth 2

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1			1		1			1					
2					1	1			1				
3						1		1					1
4			2									1	
5										1	1		1
6	1				1				1				
7				1						1		1	
8							1	1					1
9						1				1			1
10				2									1
11							1				1	1	
12	2								1				
13							1				1	1	

Station 1, all seasons
Depth 3

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1					2	1							
2					1	2							
3								3					
4	1		1				1						
5	1						1			1			
6			1										2
7	1		1	1									
8							1			1	1		
9										1	1		1
10				1								1	1
11									1		1		1
12				1								1	1
13									2			1	

Station 1, all seasons
Depth 4

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1						1		1					1
2				1							2		
3			1			1	1						
4	1									1	1		
5					2		1						
6				1		1							1
7					1							1	1
8				1								1	1
9								2					1
10			2				1						
11										1		1	1
12	2									1			
13													

Station 1, all seasons
Depth 5

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													
11													
12													
13													

Table 11. Overview of what parameter effects the pH the most, the results from describing the pH dataset using only one variable is used. The structure of the table is each parameter listed as columns and the place on which each parameter appear in the analysis is listed as rows. In this table, all seasons are combined, but presented station by station. Hence each column should have a total of 3 (3 seasons). If a parameter has high or many values on the top rows, say between rows 1-4, the parameter has an important effect on the pH. In contrast, if high or many values are found in the bottom rows, it is not an important parameter to pH.

Station 2, all seasons
Depth 1

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1		1			1					1			
2				2				1					
3								1					
4		1		2							1	1	
5		1							2				
6					1			1				1	
7	2				1								
8							1	1				1	
9							1	1			1		
10										1			2
11			1							1			1
12	1						1				1		
13										1			2

Station 2, all seasons
Depth 2

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1			1		1						1		
2						1		1	1				
3			1	1		1							
4				1					1			1	
5	1				1				1				
6			1									2	
7	1				1						1		
8								2					1
9							2						1
10										2			1
11				1		1							1
12	1						1				1		
13										1			2

Station 2, all seasons
Depth 3

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1		1	1			1							
2					2	1							
3						1			2				
4							1	1				1	
5				1							1		1
6			1								1	1	
7					1		1	1					
8							1	1		1			
9						1				2			
10	1					1							1
11				1									2
12	1										1	1	
13			1										2

Station 2, all seasons
Depth 4

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1				3									
2			3										
3		1			2								
4					1		1				1		
5	1					1	1						
6								1			1	1	
7								1		2			
8						1		1			1		
9												1	2
10							1				1	1	
11						1				1			1
12	1												2
13													

Station 2, all seasons
Depth 5

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1				3									
2							3						
3		2			1								
4					1			2					
5	1				1		1						
6										3			
7						1					1	1	
8											2		1
9						1						1	1
10											1		2
11						1						2	
12													
13													

Table 12. Overview of what parameter effects the pH the most, the results from describing the pH dataset using only one variable is used. The structure of the table is each parameter listed as columns and the place on which each parameter appear in the analysis is listed as rows. In this table, all seasons are combined, but presented station by station. Hence each column should have a total of 3 (3 seasons). If a parameter has high or many values on the top rows, say between rows 1-4, the parameter has an important effect on the pH. In contrast, if high or many values are found in the bottom rows, it is not an important parameter to pH.

Station 3, all seasons
Depth 1

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1				1				1			1		
2	1				1								1
3				1		1	1						
4			1					1		1			
5									2			1	
6						1				1			1
7			2									1	
8				1					1	1			
9	1				1								1
10	1											1	1
11						1	1	1					
12					1								1
13							1				2		

Station 3, all seasons
Depth 2

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1	1				1								1
2				1				1			1		
3						3							
4				1			1	1					
5			1		1					1			
6									1	1		1	
7			1		1				1				
8			1						1			1	
9	1									1			1
10				1			1	1					
11											1		2
12	1											1	
13							1				1		1

Station 3, all seasons
Depth 3

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1					1							1	1
2				1		1							1
3				2		1							
4					1	1			1				
5			1		1			1					
6			1					1			1		
7							1			1			1
8	1								1			1	
9												1	1
10			1					1			1		
11									1	1			1
12							2			1			
13	2										1		

Station 3, all seasons
Depth 4

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1				3									
2	1		2										
3	1				1								1
4			1		1	1							
5					1			2					
6	1				1			1					
7							1				1		1
8							1				1		1
9						1				1			1
10							1				1	1	
11										1		1	1
12										1		1	1
13													

Station 3, all seasons
Depth 5

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1	2						1						
2	1		1		1								
3	1			1			1						
4			1	1	1								
5				1	1		1						
6													1
7						1		2					
8						1						1	1
9										2		1	1
10												1	1
11											1	1	1
12										1		2	
13													

Table 13. Overview of what parameter effects the pH the most, the results from describing the pH dataset using only one variable is used. The structure of the table is each parameter listed as columns and the place on which each parameter appear in the analysis is listed as rows. In this table, all seasons are combined, but presented station by station. Hence each column should have a total of 3 (3 seasons). If a parameter has high or many values on the top rows, say between rows 1-4, the parameter has an important effect on the pH. In contrast, if high or many values are found in the bottom rows, it is not an important parameter to pH.

Station 4, all seasons
Depth 1

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1						1		1		1			
2	1	1	1										
3				1								2	
4				1	1						1		
5		1							1		1		
6		1									1		1
7				1			1					1	
8			1				1	1		1			
9							1		1	1			1
10								1	1	1			
11	1				1						1		
12							1		1				1
13	1		1							1			

Station 4, all seasons
Depth 2

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1			1			1		1					
2					1					1			1
3				1	2								
4			1			1							1
5		1										2	
6			1				1						1
7								1		1			1
8	1							1		1	1		
9						1			1	1			
10								1		1			
11							1			1			1
12	1							1				1	
13	1		1				1						

Station 4, all seasons
Depth 3

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1						1		1				1	
2				1	1								1
3				1	1					1			
4						1	1					1	
5	1	2											
6					1			2					
7							1				1		1
8												1	2
9			1					1		1			
10										1	1		1
11	2							1					
12						1				1	1		
13				1			1		1				

Station 4, all seasons
Depth 4

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1				3									
2			2										1
3			1					2					
4					2		1						
5	1				1								1
6	1						1						
7											1		2
8										2		1	
9						1	1					1	
10	1						1					1	
11						2							1
12										3			
13													

Station 4, all seasons
Depth 5

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1								3					
2			3										
3	1			2									
4	1			1	1								
5					2	1							
6	1						1					1	
7						1	1			1			
8							1					1	1
9										1			1
10										1	1		1
11										1			1
12						1				1			1
13													

Table 14. Overview of what parameter effects the pH the most, the results from describing the pH dataset using only one variable is used. The structure of the table is each parameter listed as columns and the place on which each parameter appear in the analysis is listed as rows. In this table, all stations are combined, presented season by season. Hence each column should have a total of 4 (4 stations). If a parameter has high or many values on the top rows, say between rows 1-4, the parameter has an important effect on the pH. In contrast, if high or many values are found in the bottom rows, it is not an important parameter to pH.

All stations, winter
Depth 1

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1		1						2			1		
2	1		1			1							1
3			1		1								1
4			2			1							1
5									3		1		
6			1			1						1	1
7					2				1			1	
8							1			1	1		
9					1		1			1	1		
10		2								2			
11				1			1	1				1	
12		1		1									1
13				1			1					1	1

All stations, winter
Depth 2

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1			1					2					1
2					1			1			1		1
3					1	3							
4			1	1		1		1					
5			2		1						1		
6							1		2			1	
7					1					2	1		
8		1										1	2
9							1		1	1			1
10				1				1		1	1		
11				1			1						1
12		3											1
13				1			1					1	1

All stations, winter
Depth 3

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1			1			1		1					1
2					1	1			1				1
3				1	1	1		1					
4					1	1	1	1					
5		1	2								1		
6									1		1	1	1
7			1		1		1					1	1
8							1		1		1		1
9										3		1	
10								1				1	1
11		1		1					1	1			
12		1					1			1	1		
13		1		1								1	1

All stations, winter
Depth 4

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1				3									1
2		1	2								1		
3		1				1		1					1
4		1	1		2								
5		1			1		2						
6				1			1	2					
7					1		1			1			1
8											3	1	
9						2		1				1	
10			1									2	1
11						1				1			2
12										2			1
13													1

All stations, winter
Depth 5

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1		1		1				1					
2			1		1		1						
3		1		1			1						
4			1		1			1					
5				1	1	1							
6		1				1				1			
7							1	1					
8											1		2
9									1	1		1	
10											2		1
11													3
12										1	1		
13													

Table 15. Overview of what parameter effects the pH the most, the results from describing the pH dataset using only one variable is used. The structure of the table is each parameter listed as columns and the place on which each parameter appear in the analysis is listed as rows. In this table, all stations are combined, presented season by season. Hence each column should have a total of 4 (4 stations). If a parameter has high or many values on the top rows, say between rows 1-4, the parameter has an important effect on the pH. In contrast, if high or many values are found in the bottom rows, it is not an important parameter to pH.

All stations, summer
Depth 1

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1		1						1		1			
2	1		1		1	1							
3				1			1		1			1	
4			1		1					1			1
5								2	1	1			
6					1						1	2	
7	1	1	1			1							
8			2									2	
9						1	1						2
10							1			1	1	1	
11					2		1						1
12				2		1		1					
13	2								1	1			

All stations, summer
Depth 2

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1	1	2								1			
2								1	2	1			
3			1		1	1							1
4				1			1					2	
5	1			1						1		1	
6			1	1					1			1	
7				1				1	1		1		
8		1						2		1			
9						2						1	1
10			2									1	1
11					1	1				2			
12	1					1		1			1		
13	1						1		1				1

All stations, summer
Depth 3

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1	1			1								2	
2				1	1								1
3				1				1	1	1			
4	1				1	2							
5	1			1		1							1
6		1		1						1			
7			1			1	1			1			
8	1									2			1
9	1		1								1		1
10		1			1							1	1
11							1	1				2	
12					1					1		1	1
13		1						2		1			

All stations, summer
Depth 4

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1			2	3		1						1	
2			2								1		1
3		1			2		1						
4					1			1		1	1		
5					2	1		1					
6	1											2	1
7										1	2		1
8				1				1					1
9						1	1						2
10	1	1				2							
11					1							2	
12	2									2			
13													

All stations, summer
Depth 5

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1				1			1	1					
2	1	1					1						
3	1	1			1								
4				2				1					
5	1				2								
6										1		1	
7						1		1			1		
8						1	1						1
9										1		1	
10											1	1	1
11					1					1			1
12										1			1
13													

Table 16. Overview of what parameter effects the pH the most, the results from describing the pH dataset using only one variable is used. The structure of the table is each parameter listed as columns and the place on which each parameter appear in the analysis is listed as rows. In this table, all stations are combined, presented season by season. Hence each column should have a total of 4 (4 stations). If a parameter has high or many values on the top rows, say between rows 1-4, the parameter has an important effect on the pH. In contrast, if high or many values are found in the bottom rows, it is not an important parameter to pH.

All stations, Yearly data
Depth 1

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1			1		3								
2			1	3									
3		1	1	1	1								
4								2				2	
5		2									1	1	
6			1						1	1			1
7	2	1											1
8							1	2	1				
9	1						1			1			1
10									1	1			2
11	1						1			1		1	
12							1		1		1		1
13											3		1

All stations, Yearly data
Depth 2

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1				3	1								
2			1	2									
3			2		1			1					
4		2						1				1	
5									1	1		1	1
6	1	1										1	1
7	1	1	1										1
8							1	2	1				
9	1						1			2			
10							1		1	1			1
11											1	1	2
12	1										1		1
13							1				2		1

All stations, Yearly data
Depth 3

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1				2	2								
2			1	2	1								
3			1		1			1	1				
4		1	1					1	1			2	
5		1	1						1				
6		2							1				1
7	1						1			1			1
8							1	1				1	1
9							1			1		1	1
10	1		1								2		
11	1										1		1
12							1			1		1	1
13	1						1		1				1

All stations, Yearly data
Depth 4

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1				3				1					
2			3	1									
3	1	1			1			1					
4				2			1				1		
5	1			1				1					1
6	1										1		
7					2			1				1	2
8						1	1				1		1
9										1		1	1
10							2				1	1	1
11						1				2			1
12	1									1		1	1
13													

All stations, Yearly data
Depth 5

Place	Parameter												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Salt	O2	O2Sat	PO4	DIN	Alk	SiO4	Chla	CO2atm	NAOI	PercPH	RivPH	RivAlk
1	1			1				1					
2			2				1						
3	1			2									
4	1				2								
5					1		1	1					
6							1	1		1			
7						1						1	
8										1		2	
9						1				1			1
10												1	2
11											1	1	1
12						1					1		
13													

APPENDIX 2: METHODS

APPENDIX 2.1: TEMPERATURE CORRECTION OF PH AND CALCULATION OF DIN

For the temperature correction, a formula from the HELCOM Combine manual was used:

$pH_{t1} = pH_{t2} + 0.0118 (t2 - t1)$
 $t1$ = temperature in situ
 $t2$ = temperature in the calibration bath (at R/V Argos, which is 25°C)

I.e. in our case when correcting all pH values to 25 °C, the formula was:

$pH_{25} = pH_{t1} - 0.0118 (25 - t1)$

Description of DIN: the sum of NO_2 , NO_3 and NH_4 is used.

APPENDIX 2.2: TREND ANALYSIS: LINEAR REGRESSION

When performing linear regression you find the coefficients of a polynomial $p(x)$ of degree n that fits the data, $p(x(i))$ to $y(i)$, in a least squares sense. The result p is a row vector of length $n+1$ containing the polynomial coefficients in descending powers. The equation to find the coefficients of a polynomial is:

$$p(x) = p_1x^n + p_2x^{n-1} + \dots + p_nx + p_{n+1}$$

In a polynomial of the first degree ($n = 1$), p_1 gives the slope of the linear regression (MATLAB function: polyfit). To plot the linear regression line and to create the 95% confidence intervals of the line, the MATLAB function polyconf, that evaluates the polynomial at each value of x , was used. The function polyconf uses input created by polyfit and assumes that the errors in the data input to polyfit are independent normal with constant variance.

A hypothesis test is performed to test a null hypothesis, H_0 (a statement that there is no trend),

to a counter hypothesis, H_1 (a counter statement that there is a trend). H_0 is true until a test rejects it. The test gives a value of how wrong you are to claim that there is a trend when there in actuality is no trend. This value is the P value and it is the likelihood that the null hypothesis is wrongfully rejected. The lower the P value the more likely it is that rejection of the null hypothesis is the correct measure. The limiting value of P to indicate a trend or not, is determined regarding the cause of the study. Here, the limiting value of P is set to be 0.05.

APPENDIX 2.3: NON-PARAMETRIC TREND ANALYSIS: MANN-KENDALL

To analyse data for trends, it is necessary that sample handling and measurement procedures have been consistent throughout the study period. Time series can exhibit stepwise changes, indicative of a change of state, or (largely) monotonic changes. Hirsch presented a comparison of classical linear regression methods compared against non-parametric methods (the Mann-Kendall test and Sen's method for slope determination) for randomly generated data (Monte-Carlo method) with seasonal signals and linear trends overlain.

Where the input data were normally distributed, the increased statistical strength of linear regression made it more likely to correctly identify the presence of a trend. The relative advantages of the non-parametric methods became greater as the data distribution became less Gaussian. The non-parametric methods were also better able to deal with values below the detection limit and also 'missing' values. For further discussion the reader is referred to Hirsch et al, 1994.

One method that fits the latest description of non-parametric method and performs calculations of a monotonous change is the Mann-Kendall test. When there are seasonal variations, the detection of possible trends becomes difficult and the strength of the test decreases. To disregard the effects of seasonal changes, the Seasonal Kendall method, closely linked to the Mann-Kendall method, was used. The Seasonal Kendall method

disregards the effect of seasonal changes by comparing values within one season or within one month and then combining the results.

When applying Seasonal Kendall, a mean value of the measurements each year and month has been used to produce a test quantity and variance for each month. The real test quantity is the quota between the sum of the test quantities for the months of interest and the square root of the sum of the variances for the months of interest. The received value is entered into the cumulative normal distribution equation in order to produce a P value.

The P value is a measure of the probability that the null hypothesis is wrongfully rejected (how likely it is that it is a mistake to reject the null hypothesis and instead say that there is a trend). The less the P value the higher probability that there is a trend (Spent). In the event of a trend, the magnitude of the trend is calculated by the Kendall slope estimator. The trend is expressed in the form of a slope, but that does not imply that the trend is linear.

All possible pairs of values within each month (month is $i=1:12$), where $k > j$, the quota

$$b_{ijk} = \frac{(x_k - x_j)}{k - j}$$

is calculated which is equivalent to the direction coefficient (slopes) between time j and k . All slopes for all the months are sorted in order of magnitude. The Kendall slope estimate B is the median of these b_{ijk} values.

To receive an error estimate, a confidence interval of the B value is calculated. The level of confidence is set to 95%, which implies that estimated error of the slope estimation is within 5%. If the signs of the upper and lower bound values differ, the zero level lies within the upper and lower bounds, which indicates that there is no trend present.

APPENDIX 2.4: PRIMER-STEP BY STEP IN A MULTIPARAMETER ANALYSIS

PRIMER stands for Plymouth Routines In Multivariate Ecological Research (www.primer-e.com). The steps described below are further motivated and described in the manual written by Clarke, K.R., and R.N. Gorley 2006.

The approach of the multiparameter (multivariate) analysis was to examine the extent to which the physico-chemical (environmental) data is related to (explains) the observed pattern of the variable of interest (in this study: pH).

First there is an analysis of the pH data, then of the environmental data and then there is an analysis to see how well the information from the environmental data matches the structure of the pH.

All parameters included in the analysis have very different values to be compared to each other and in some cases the range of value change over the years is very small and in others very large. To compare parameters with each other both sets of data (pH and environmental data) are firstly subjected to a fourth root transformation. If the parameters were more similar in values and change of values over the years, a simple root transformation could have sufficed. This was the first assumption made in the analysis. Other choices, like choosing a log transformation, could have been made that would have altered the outcome of the results. However the values appeared to have become sufficiently in the same order of magnitude so that a fourth root was the best choice. This is a process to weight the contribution of different parameters to each other.

The pH data was then analysed to create a resemblance matrix (a similarity matrix), using Euclidian distances. In short, the values of the now triangular matrix gives the similarity or distance (or value difference compared to all other value differences in the matrix) between two data values. It can help to think of a triangular road map giving the city to city distances for many cities. Read more about similarities, dissimilarities and different methods to calculate distances in the Principal Components Analysis section of the manual. The choice of using Euclidian distance was the second assumption made in the analysis however that is recommended for environmental parameters.

The third assumption was to follow the recommendations of the manual to normalise the environmental dataset, to bring the parameter values to the same mean level.

Then the environmental dataset is analysed using the BEST function, creating a similarity matrix using Euclidian distances (assumption four however recommended) and the Spearman coefficient (assumption five, choice based on the simplest approach) to correlate the ranks of the two similarity matrixes.

Measuring agreement in pattern by comparing similarity matrixes:

In the BEST analysis, the similarity matrixes ranks are then compared to each other with the Spearman rank correlation coefficient, seeking a combination of environmental variables which attains a good match of the high similarities in the matrixes. Combinations of the environmental variables are considered at steadily increasing complexity, starting with one variable, then the combination of two and so on.

Each variable (or combination of variables) is connected to a rho value which corresponds to how well the component accounts for the variability in the full matrix, or in other words, how well the rank correlation is between the two similarity matrixes. As a result, a description of best variable combinations is produced, starting with using just one variable, giving the results in “best performance order” for each included environmental variable, then the results for the combination of two variables and so on.

As a summation, the top 10 results are displayed with highest rho value on top giving the best combination of variables in descending order. In the result table (table 6 on page 22), the two top results for the datasets are displayed under the title “Selections”.

The selection could range all one variable included (indicating that the best result was retrieved from only one variable) to six variables (the maximum amount of parameters was an active choice made). The results indicate that a combination of variables is more commonly producing better rho values, i.e. gives better result.

Further comments on rho or the correlation is that the sample statistic here is Spearman’s rho between the pair wise elements of the two matrixes. That makes it more like a correlation r , not a

coefficient of determination r -squared. However, don’t be lulled into thinking a matrix correlation of this sort is exactly the same sort of thing as a direct correlation between two variables, say from a scatter plot.

There is an internal dependence structure among the elements of any resemblance (similarity, dissimilarity, distance) matrix so when you are calculating correlations between two such matrixes do not expect the values to be the same as if you were calculating a direct correlation between two (internally) independent sets of readings.

Rho lies in the range -1 to +1, with the extremes of -1 and +1 corresponding to the cases where the two sets of ranks are in complete opposition or in complete agreement. Values around zero correspond to the absence of any match between the two patterns.

How high rho should be to be referred to as a good result is not defined, but in the results table 6, values above 0.5 (describing 50% of variance) is marked as bold, indicating better results.

If key environmental variables are omitted, the match between the two datasets will deteriorate. By the same token, the match will also worsen if environmental data which are irrelevant to the community data are included. As a rule of thumb, would be to reduce all subsets of variables that have mutual correlations averaging more than about 0.95 to a single representative. This suggests that some parameters are so highly inter-correlated that it would serve no useful purpose to leave them all in the BEST analysis.

By the use of a Draftsman plot, all possible pair wise scatter plots were created, making it possible to find the highly inter-correlated parameters. Oxygen was highly correlated to temperature. However, the decision to exclude temperature was that pH had been temperature adjusted from start, hence should be excluded from the analysis. DIN and DIP were correlated, but both were still included.

The inclusion of too many insignificant parameters and / or the lack of experience to include some of the parameters calculated differently and / or the total absence of key parameters are definitely the reasons why some of the results are poor.

A question which naturally can arise is the extent to which conclusions from the BEST analysis can

be supported by significance tests. A permutation test was performed (for each set of data) to test the null hypothesis that there is no relationship between the pH and the environmental data, i.e. that the rho value should be effectively zero. Rho was recomputed a number of times (recommended lower limit of permutations is 99) and if the observed value of rho exceeded that found in 95% of the simulations, which by definition correspond to unrelated ordinations, then the null hypothesis can be rejected at the 5% level (read more of how to calculate p and the null hypothesis in appendix 2.2).

Low values of p (or p%, as given here) mean there is a 'statistically significant' effect - in this case relationship between that selected set of environmental variables and the pH pattern. So you are looking for something around the $p < 5\%$ mark for a 'good' result.

The permutation test have not been performed as recommended (99 times) due to the lack of computer efficiency shortage. 99 permutations demanded more powerful computers than available for the author, taking hours to compute one dataset. Instead only 10 permutations were made, making the results more indicative of the significance rather than significant or not on the 5% level. With 10 permutations, which is only enough to give a significance at the best about the 10% level (to be precise, 9.1%) because 11

correlations in all - the 10 permutations under the null hypothesis and the 1 real one - have been looked at. Of these the real one is the largest, hence it has a significance level - the chance of getting a value of this or larger purely by chance when there is no link between pH and environmental variables - of less than 1 in 11, i.e. 9.1%. If a value of rho is pretty large, say above 0.6-0.7, it means a very high correlation and is almost certainly significant.

More permutations should be made the suggestion is at least 99. Then if the observed real correlation is still the most extreme of the calculated 100 (1 real one and 99 permutations) then it is now an event of probably 1 in 100 by chance if the null hypothesis is true (and there is no link between pH and environment variables). So, now there would be a significance level of $< 1\%$ (or < 0.01 if preferred).

With more permutations the significance level is determined even more precisely, and may well be better still. To comply somewhat with the recommendations of 99 permutations, 10 tests were made performing both 10 and 99 permutations on different data sets that with 10 permutations resulted in a significance level of $p = 9.1\%$. All the 10 results using 99 permutations gave the significance level of $< 1\%$, raising the probability that the results giving 9.1% are in fact valid significant results.

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