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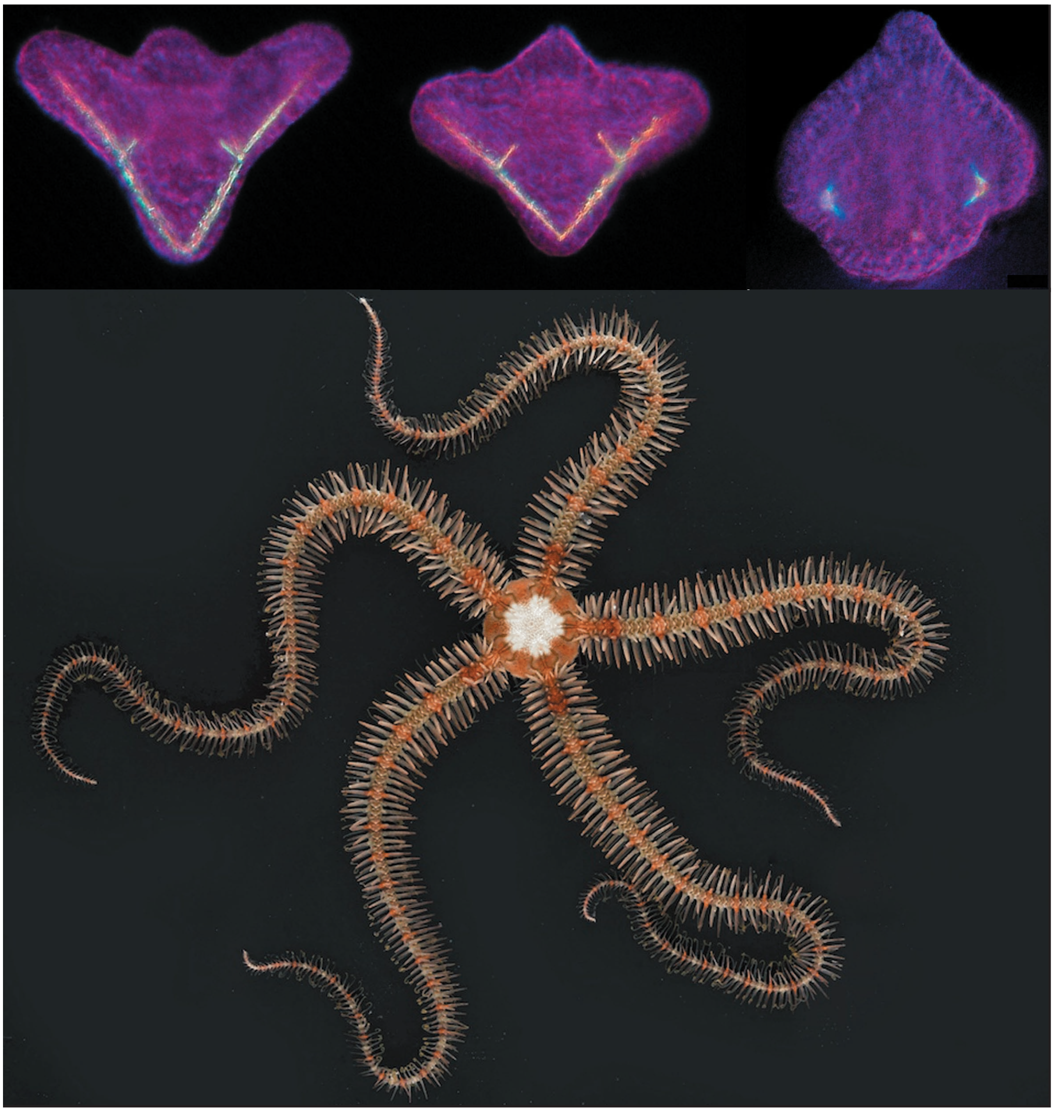

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On effects and monitoring of marine acidification in the seas surrounding Sweden

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Editor:	Clients:		Report No:
Pia Andersson, SMHI	The Swedish National Environmental Protection Agency		Oceanography No 92
Reviewers:	Review date:	Diary no:	Classification:
Co-authors	2008-04-15	2007/2444/1933	Public

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Distribution By conditions from the Swedish National Environmental Protection Agency.	
Classification (x) Public	
Keywords Marine acidification, Co_2, monitoring, pH, trends, biology, ecology, stations, parameters	
Other	

Marine Acidification

On effects and monitoring of marine acidification in the seas surrounding Sweden

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REVIEWERS	Co-authors
FRONT PAGE	Photo: One day old larvae of the brittlestar *Ophiothrix fragilis* reared at pH 8.1 (left), pH 7.9 (middle), pH 7.7 (right) and a fully grown brittlestar (bottom). Photographer: Sam Dupont.
LAYOUT	Pia Andersson
PRODUCTION	Swedish Meteorological and Hydrological Institute
YEAR	2008
CITY	Gothenburg, Sweden
PAGES	62
CONTACTS	Pia Andersson, Bertil Håkansson, Swedish Meteorological and Hydrological Institute, Sverker Evans, Swedish National Environmental Protection Agency,
URL	www.smhi.se

CONCLUSIONS

Surface waters in the world oceans have already experienced a pH reduction of about 0.1 units (OSPAR, 2006.) The trend indicates further decrease of pH and is most probably due to increased uptake of atmospheric CO_2 and less buffering capacity of ocean waters. The trend is similar in the waters surrounding Sweden.

RESEARCH NEEDS

Since there is an alarming absence of information regarding the effects of near-future levels of ocean acidification on Swedish marine taxa, there is a clear research need on:

- investigations of the effects of ocean acidification on the early life-history stages of key ecosystem-structuring species, and commercially important species of fish and shellfish
- ecosystem-level mesocosm studies of the impacts of ocean acidification on Swedish marine systems
- improved regional-scale modelling of acidification mechanisms in Swedish coastal waters
- testable ecosystem-scale food-web models to articulate with regional acidification models
- improved definition of chemical equilibrium constants between pH, A_T and CO_2 in low saline waters.

ACTIONS TO IMPROVE MONITORING

At present, pH and AT are monitored monthly at standard depths at 7 stations in Skagerrak, Kattegat and Baltic Proper within the national monitoring programme. Of these are 2 located in coastal waters (Halland and Småland; Type 5 and 9).

<u>We recommend</u> that Sweden work to improve the status of pH and A_T to be Core variables instead of Main variables in HELCOM COMBINE “High frequency Sampling” program taking into account the last 15 years negative trends in pH in waters surrounding Sweden as well as in the global oceans.

<u>We recommend</u> that besides the standard parameters monitored in the national monitoring program, pH, A_T and DIC should be monitored. For completeness, primary production should also be monitored.

Below are three monitoring recommendations, where the first is divided into a lowest level and a recommended level.

<u>1. Lowest level:</u> Within the national monitoring program, at least one station per open sea area and all costal stations measure acidification parameters on a monthly basis in the entire water column at standardized depths. The national and regional monitoring programmes should be upgraded in the Gulf of Bothnia so that pH and A_T is monitored at standard depths at least monthly at one station each in the Bothnian Bay and Bothnian Sea. Also 2 coastal stations in the Gulf of Bothnia should be established. In addition, one coastal station should be established within Type 14 in the Baltic Proper.

<u>1. Recommended level:</u> the national monitoring program should have at least one station per open sea area and if the area is characterized by strong gradients or other features, there should be more than one station. Some of the stations in the regional monitoring programmes should be upgraded with acidification parameters, for a better geographical coverage. The acidification parameters should be measured on a monthly basis in the entire water column at standardized depths.

<u>2. We recommend</u> that an investigative monitoring is established by extending the parameters that are needed to firmly improve the chemical stability constants between pH, A_T, DIC and pCO_2 in low saline waters. This can be done by just extending the sampling program at selected monitoring stations. Sampling should cover a period of 2 to 3 years.

<u>3. We recommend</u> that direct water measurement of pCO_2 for monitoring purposes should be assessed after the recommendation above is evaluated and that ongoing research projects on pCO_2 measurements using ferryboxes are finalised.

RECOGNISED PROBLEM AREAS

- There are only few long time series of acidification parameters. The time period of measurements is rather short.
- The geographical coverage of measurements is rather limited in the waters surrounding Sweden.
- The chemical stability constants between pH, A_T, DIC and pCO_2 are not optimized in low saline waters.
- pH budgets are difficult to calculate.
- Models need to be improved in order to display present and future small and large scale scenarios.
- Little is known of the biological, ecological and economical effects of the current and near future marine acidification. Further research is required.

ACKNOWLEDGMENTS

This report is a joint effort from SMHI and Gothenburg University.

To commence the work of this report, a CO_2 workshop was held at Nya Varvet in Gothenburg. Several experts in marine acidification were invited and the contribution during and after the workshop from was greatly appreciated.

Attending from the University of Gothenburg: Prof Jonathan Havenhand, Prof Leif Anderson and Prof Anders Omstedt. From SMHI, Dr Bengt Karlson and Christer Persson attended.

Prof Jonathan Havenhand, Dr Sam Dupont and Prof Mike Thorndyke, all from the Sven Lovén Centre for Marine Sciences, have contributed in the report with the chapter on biological effects from decreasing pH levels and general description of ocean trends. All experts have reviewed the final draft of this report.

The effort of Dr Elisabeth Sahlsten, Johan Håkansson, Lars S. Andersson, Ass. Prof Bertil Håkansson and Bengt Yhlen from SMHI is greatly appreciated. The support and effort from the Swedish Environmental Protection Agency is, as always, greatly appreciated.

CONTENTS

BACKGROUND AND AIM

The Swedish Environmental Protection Agency has commissioned and funded this report and the aim is to assess the need, how and where to monitor marine acidification in the seas surrounding Sweden.

The European Commission has suggested a framework and common goals to protect and preserve the marine environment. In the strategy proposal for the marine environment, common principles, that the member countries should apply when constructing their own strategies to reach good ecological status in their marine waters, were provided.

The member countries must evaluate the ecological state in their waters to assess the anthropogenic impact. In the strategy, there are proposals to monitor the marine acidification, since it can have serious impacts on the marine environment.

INTRODUCTION MARINE ACIDIFICATION

AIR CO2

Fossil fuel emissions of CO_2 have increased more than 1200% over the last 100 years, and an overwhelming literature now shows that rising atmospheric CO_2 levels are changing global climate (Raven et al., 2005). The IPCC future climate scenarios (SRES scenarios (IPCC, 2007)) predict that CO_2 concentrations will rise 150-250% (to ≤ 1000ppm) by the year 2100. These scenarios are modelled on CO_2 release data for the period 1990-1998. Recently the rate of CO_2 release has been shown to have more than doubled (to 2.9 $\%.yr^{-1}$) in the last 6 years (Canadell et al., 2007), raising the very real possibility that predictions of future CO_2 levels will be revised sharply upwards.

GENERAL DESCRIPTION OF GLOBAL OCEANS

The sea surface pH is generally above 7, which indicates a basic solution. Increasing levels of CO_2 in the atmosphere leads to a pressure, driving CO_2 across the air-sea interface. Atmospheric CO_2 levels then depend not only on CO_2 release rates but also on rates of CO_2 absorption by terrestrial and oceanic systems. This uptake can be substantial: oceans typically exchange ~ 100 $GtC.yr^{-1}$ with the atmosphere, but currently draw down ~ 2 $GtC.yr^{-1}$ more than they release (Feely et al., 2004). This rate of uptake declines as atmospheric CO_2 levels rise, due to progressive saturation of the seawater carbonate buffer system. Less carbon will be buried in the sediments by the sedimentation of organisms with calcium compounds.

Box 1: Ocean Acidification – a simplified primer

In seawater, CO_2 dissolves to form an equilibrium with water, carbonate ions and bicarbonate ions:

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \leftrightarrow 2H^+ + CO_3^{2-}$$

This equilibrium is dominated by bicarbonate, ($CO_2 \approx$ 1%, $CO_3^{2-} \approx$ 8% and $HCO_3^- \approx$ 91%, of total dissolved inorganic carbon, "DIC"). Continued uptake of CO_2 by the oceans drives this equilibrium to the centre, reducing pH. This shift in pH changes the equilibrium between bicarbonate and carbonate, driving that balance also toward the centre, thereby depleting the available carbonate pool.

This process increases the rate of dissolution of deposited $CaCO_3$. The rate of dissolution depends on the crystalline form of the $CaCO_3$: aragonite (found in corals and molluscs) is twice as soluble as calcite (found in echinoderms and crustaceans).

When CO_2 is absorbed by the oceans it reacts with water and carbonate ions to form bicarbonate (Box 1), reducing the saturation of carbonate in the system and causing the pH to fall. Surface waters in the world oceans have already experienced a pH reduction of about 0.1 pH units. (OSPAR, 2006.) The trend indicates further decrease of pH.

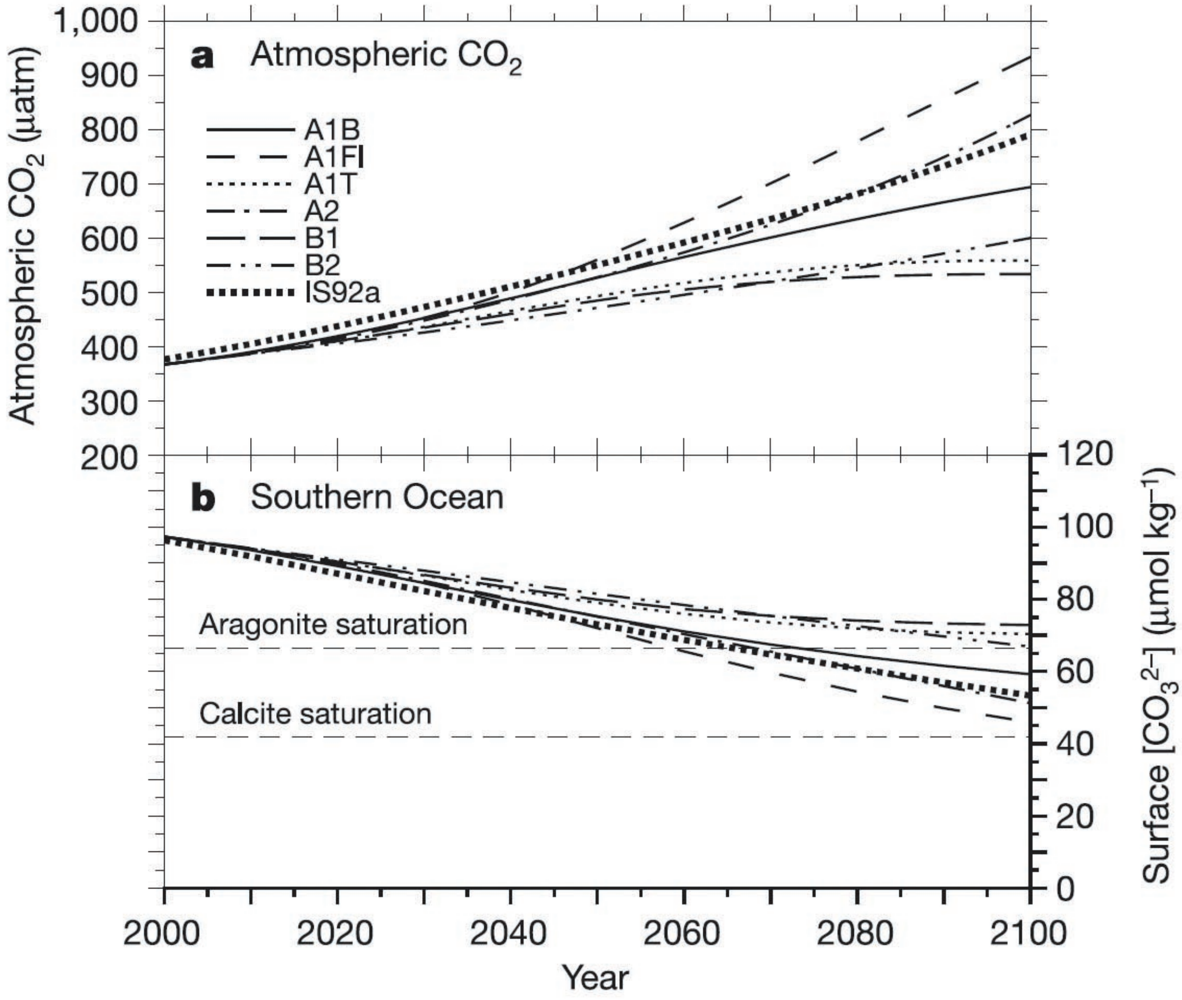

Figure 1. Predicted levels of CO_2 atm and future surface CO_3^{2-} concentrations in the Southern Ocean (Orr et al., 2005).

The changes are not trivial: in some regions the surface ocean could become undersaturated for aragonite by the middle of this century (Orr et al., 2005) (figure 1), and a drop of up to 0.5 pH units in the surface oceans by 2100 has been predicted "with a high level of confidence" (Raven et al., 2005).

This seemingly small shift is equivalent to a 3-fold increase in the concentration of hydrogen ions, and will have unprecedented impacts on oceanic biogeochemistry and biogenic calcification. The effect of the recently reported (Canadell et al., 2007) 2.9%.yr^{-1} increases in atmospheric CO_2 on these estimates is as yet unknown.

Ocean Acidification – the Global Context

Very few hard data are available from which to extrapolate likely outcomes and costs, but the long-term consequences of these changes for marine biota are predicted to be catastrophic (Orr et al., 2005; Riebesell, 2004; Ruttimann, 2006). While primary production by phytoplankton may (Riebesell et al., 2007), or may not (Riebesell, 2004; Riebesell, 1993), be stimulated, profound changes in phytoplankton community composition are highly likely because calcareous species will be less able to form a skeleton (Riebesell, 2004).

Similarly, other calcifying species such as corals, molluscs, echinoderms and crustaceans will be severely affected by declining aragonite and calcite saturation (Orr et al., 2005; Hoegh-Guldberg et al., 2007; Kleypas et al., 2006). Indeed recent work suggests that within the next 40-50 years tropical corals will be unable to calcify because aragonite saturation will fall below 3.0 - a value very close to current levels in the Southern Ocean (Hoegh-Guldberg et al., 2007).

Today, the surface ocean is saturated with respect to calcium carbonate (including its several mineral forms, i.e., high-magnesium calcite, aragonite, and calcite), meaning that under present surface conditions these minerals have no tendency to dissolve and that there is still enough calcium and carbonate ions available for marine organisms to build their shells or skeletons. Colder and deeper waters are naturally under saturated with respect to calcium carbonate, where the water is corrosive enough to dissolve these minerals. The transition between saturated surface waters and under saturated deep waters is called the saturation horizon. Because of the increase in CO_2 entering into the ocean from the atmosphere, the saturation horizons for calcium carbonate have shifted towards the surface by 50-200 meters compared with their positions before the industrial revolution (Doney, 2006). This means that the zone occupied by under saturated deep waters is growing larger and the zone occupied by the saturated surface waters is growing smaller. By 2050, this saturated surface zone will begin to completely disappear in some areas of the ocean. High-latitude surface waters, already naturally low in calcium and carbonate ion concentration, will be the first to have under saturated surface waters with respect to aragonite, with under saturations for the calcite phase of calcium carbonate expected to follow 50-100 years later (Orr et al., 2005).

The figure 2 by Feely (Feely et al., 2006) shows aragonite saturation levels from before the industrial revolution to 2100 and how these saturation levels affect the growth of both shallow and deep corals (models based on the work of Orr et al., 2005). Before the industrial revolution, we see large bands of the tropical ocean that are optimal for growth. By 2040, these same bands are only adequate, and by 2100 most areas are only marginal at best.

Critically, there is an extreme lack of information about the impacts of CO_2-mediated acidification on marine species in general. Even single-species studies of dominant ecosystem-structuring organisms are only now just beginning (Dupont et al., in press; Berge et al., 2006; Kurihara et al., 2007; Kurihara et al., 2004), and attempting to generalise these results to other species, or to use these as a basis for predictions of broader ecosystem-level consequences, is extremely problematic.

At a socio-economic level, depleted fisheries, increased coastal erosion (due to coral reef loss), lower ecosystem resilience, and reduction in provision of essential ecosystem services will push the likely costs of ocean acidification into many billions of dollars (Raven et al., 2005). In a recent review, a Royal Society expert working group concluded: “Research into the impacts of high concentrations of CO_2 in the oceans is in its infancy and needs to be developed rapidly.”(Raven et al., 2005).

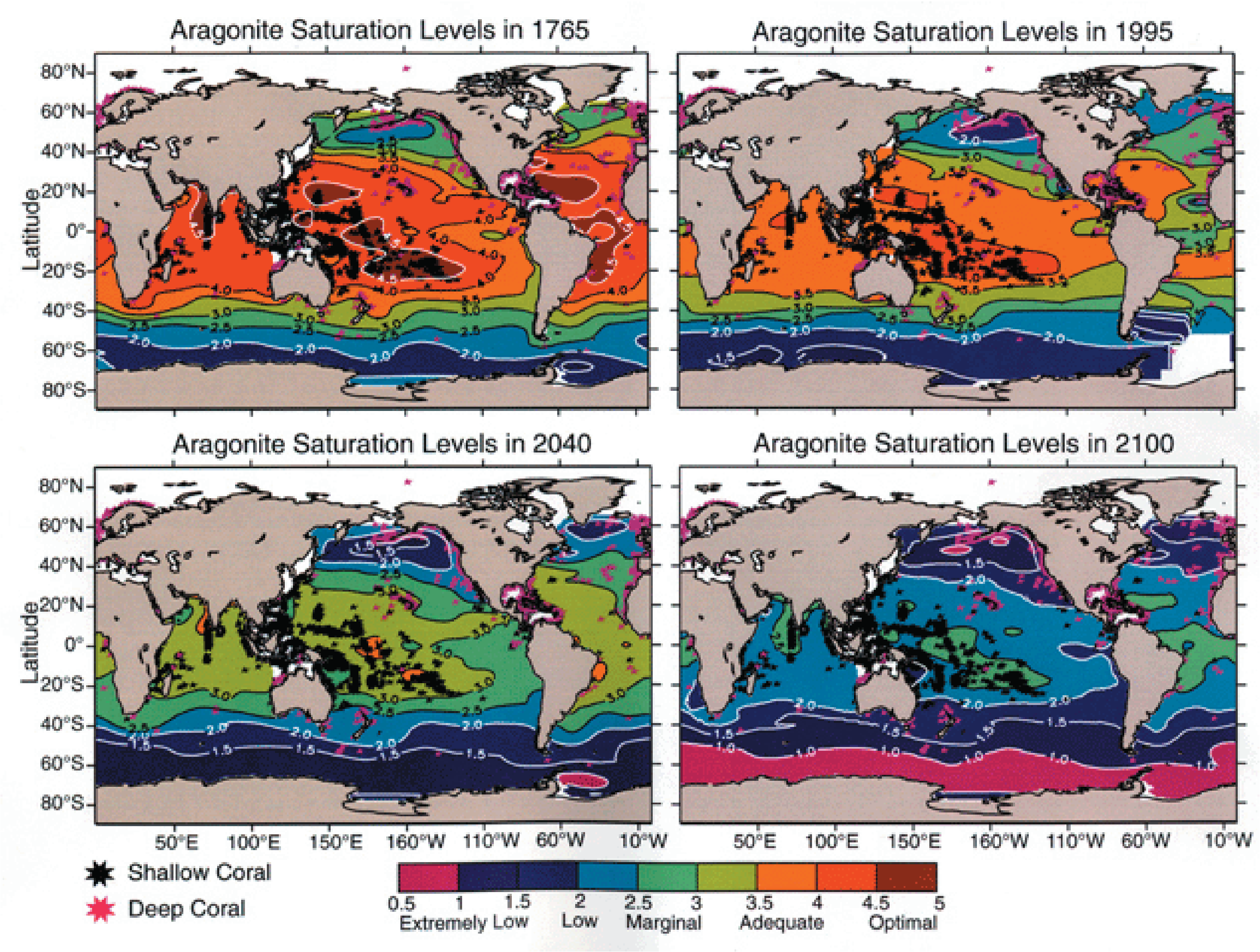

Figure 2. Estimated aragonite saturation states of the surface ocean for the years 1765, 1995, 2040, and 2100 (Feely et al., 2006), based on the modelling results of Orr et al. (2005) and a Business-As-Usual CO_2 emissions scenario. The distributions of deep-sea coral banks are from Guinotte et al. (2006).

PH TRENDS

There are only few long time series of pH. Carbonate chemistry measurements at the Hawaiian Ocean Time-series (HOT) starting around 1990, the Bermuda-Atlantic Time-series (BATS) starting around 1984, and the European Station for Times Series in the Ocean at the Canary Islands (ESTOC) starting around 1995, show a shift in carbonate equilibrium consistent with increases in atmospheric CO_2. Parts of the HOT and Bats series are displayed in figure 3 (Kleypas et al, 2006). The pH rate of decline in the BATS time series is about -0.0012 pH units yr^{-1}.

DECREASING PH-VALUES IN THE SEAS SURROUNDING SWEDEN

Existing data from Swedish measurements indicate that the situation in the seas surrounding Sweden is similar.

All measured data in the seas surrounding Sweden, available in the SMHI database Svenskt Havsarkiv (SHARK), from 1993 to the middle of 2007, have been analysed to see if any trends could be detected. The pH values from the database have been temperature adjusted to 25°C, to avoid any temperature effects in the evaluation.

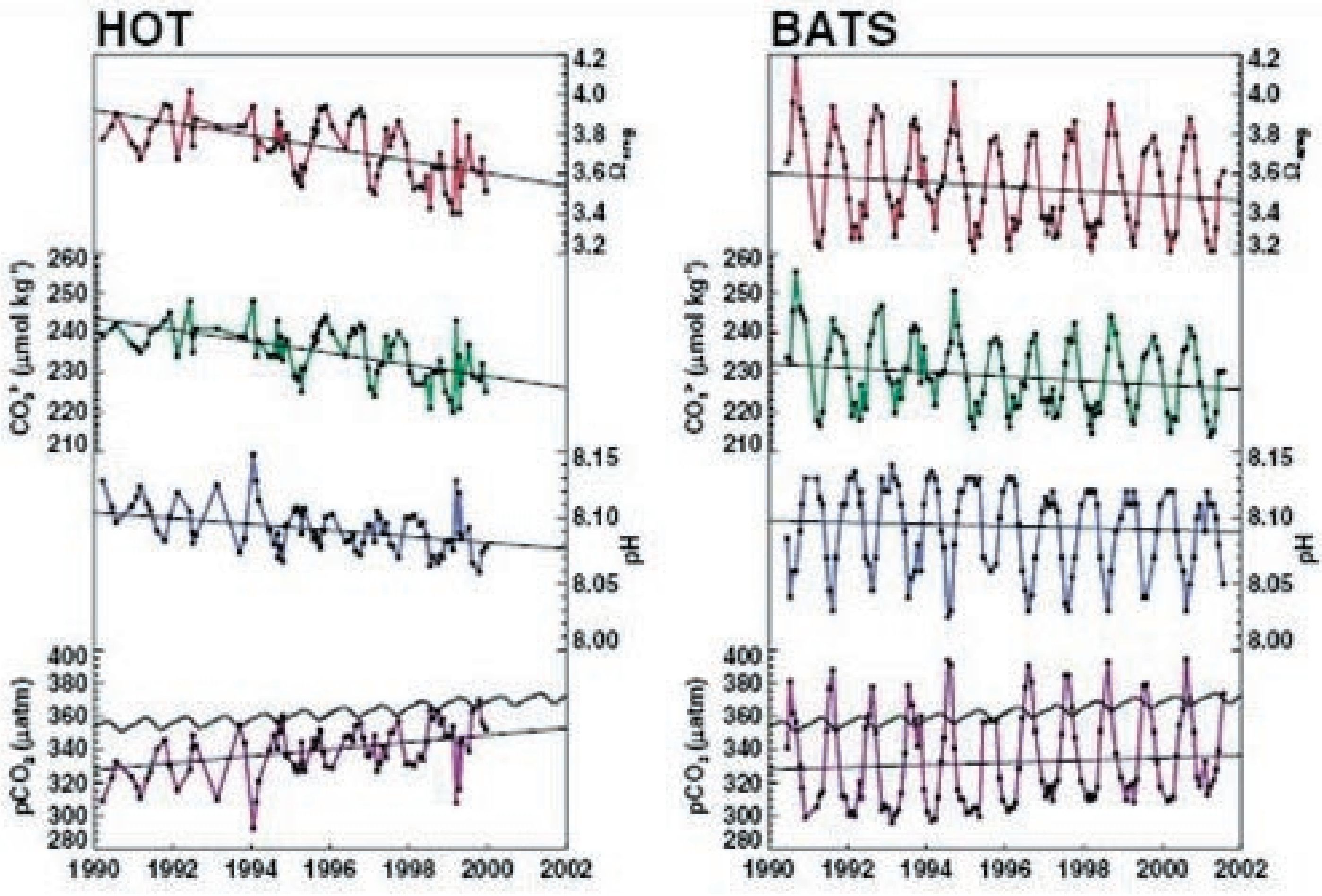

Figure 3. Monthly carbon-system parameters at two time-series stations in subtropical gyres: HOT (Hawaii Ocean Time series station) and BATS (Bermuda-Atlantic Time-series Station). The lowest plot in each graph includes both the surface water pCO_2 (line with dots), and the Mauna Loa atmospheric CO_2 record (line without dots).

Table 1: Overview of the rate of pH change per year, pH values, significance and forecast scenarios (based on calculated values) in different sea areas and depths. The last column indicates the total pH decline between 1993 and 2007.

Sea Area	Depth m	pH/yr	pH 2007	p	pH 2050	pH 2100	Change pH 1993-2007
Skagerack	0 – 50	-0.0028	8.15	0.136			
	> 75	-0.0026	8.09	0.156			
Kattegat	**0 – 25**	**-0.0044**	**8.15**	**< 0.0001**	**7.96**	**7.74**	**0.06**
	> 30	**-0.0079**	**8.00**	**< 0.0001**	**7.66**	**7.27**	**0.11**
S Baltic Proper	**0 – 20**	**-0.0041**	**8.19**	**0.0941**	**8.01**	**7.81**	
	30 – 60	**-0.0142**	**7.86**	**< 0.0001**	**7.25**	**6.54**	**0.2**
	> 70	**-0.0156**	**7.36**	**< 0.0001**	**6.69**	**5.91**	**0.2**
C & N Baltic Proper	**0 – 20**	**+0.0024**	**8.19**	**0.347**			
	30 – 60	**-0.0102**	**7.79**	**< 0.0001**	**7.35**	**6.84**	**0.14**
	> 70	**-0.0063**	**7.22**	**< 0.0001**	**6.95**	**6.63**	**0.09**
Bothnian Sea	0 – 30	-0.0316	7.69	< 0.0001	6.33	4.75	**0.44**
	> 40	-0.0192	7.62	0.0006	6.79	5.84	**0.27**
Bothnian Bay	0 - 30	-0.0143	7.61	0.0133	7.00	6.28	**0.20**
	> 40	-0.0130	7.60	0.0002	7.05	6.40	**0.18**

The analysis has been made for six areas, Skagerrak, Kattegat, southern Baltic Sea, northern and central Baltic Sea, Bothnian Sea and Bothnian Bay. In addition the water column has been divided into surface water and deep water.

The results are based mainly on monthly measurements on several stations in each area. From all measurements in every area and depth layer of the water column, monthly mean values have been calculated. In addition yearly mean values are reported, although not for Bothnian Sea and Bothnian Bay due to a lower number of data, compared to other areas. In the Skagerrak, there have been no pH-measurements during the period 2001-2007, which makes the volume of data smaller.

The statistical trend and the level of significance have been calculated by using simple linear regression. Only results which are significant on the 95% level are reported ($p<0.05$). The changes in the other water masses are not statistically significant.

All changes refer to the period 1993 to 2007. Generally the analysis indicates a decrease in pH in most of the areas.

In the surface waters of Kattegat there was a pH decrease with 0.06 units, and in the deep waters 0.11 units, during the period. The linear regression made on the monthly mean values show a significant decrease in pH in both surface and deep water of Kattegat (figure 4).

In the deep water of the Baltic proper where oxygen deficiency exists the pH values vary also due to the amount of hydrogen sulphide in the water. Due to this reason the water column in this area has been divided into three layers, surface water, intermediary water, and deep water. In the surface water there is a more or less pronounced yearly cycle which is connected to the primary production processes of the microalgae, while the conditions in the deep waters are more stable. In the intermediary and deep layer of the southern Baltic Proper the decreasing trend is 0.20 units (figure 5).

Several additional significant trends of decreasing pH have been found (see figures in appendix I), see table 1.

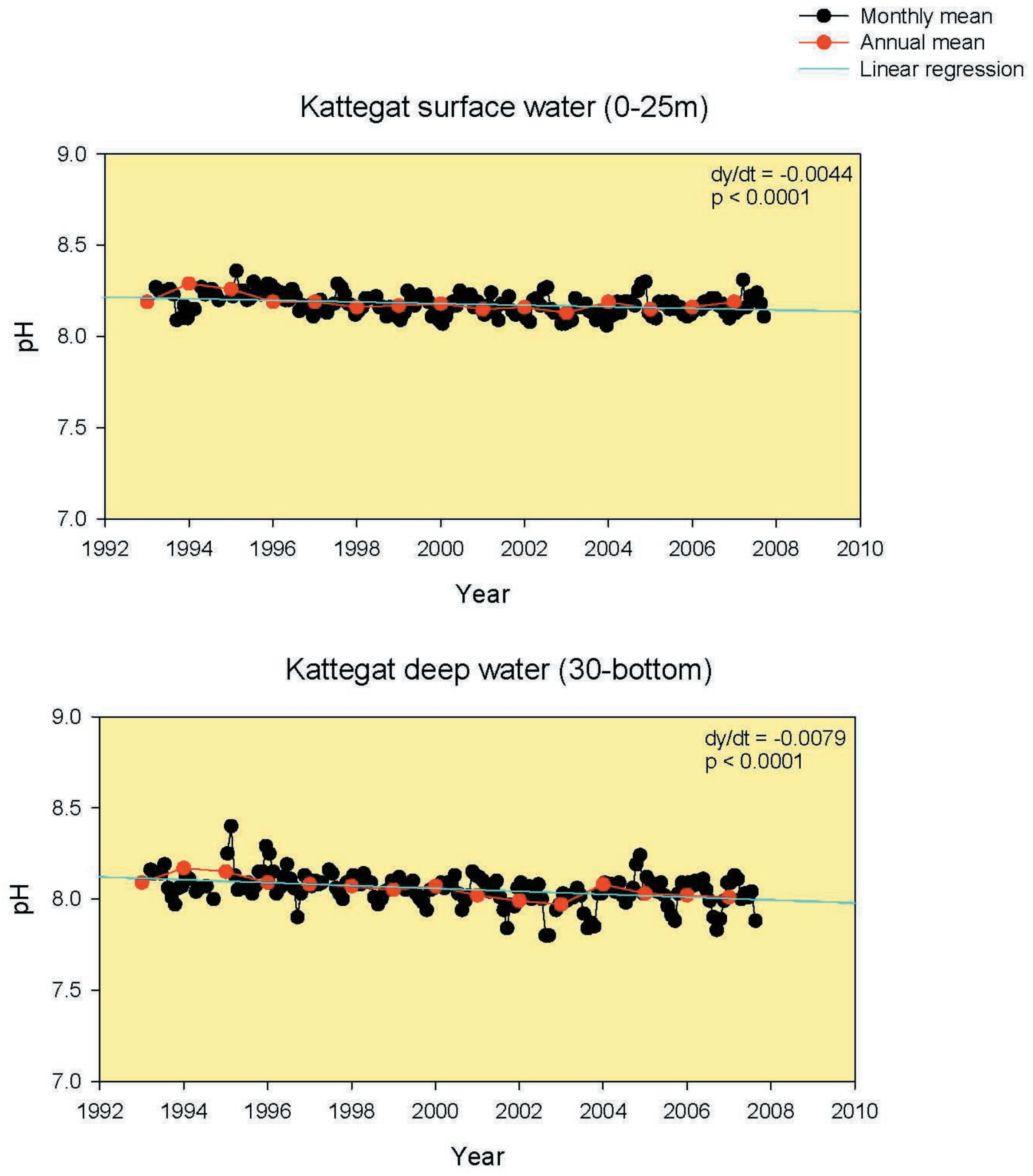

Figure 4. Time series of pH in the Kattegat. Significant trend calculated using linear regression.

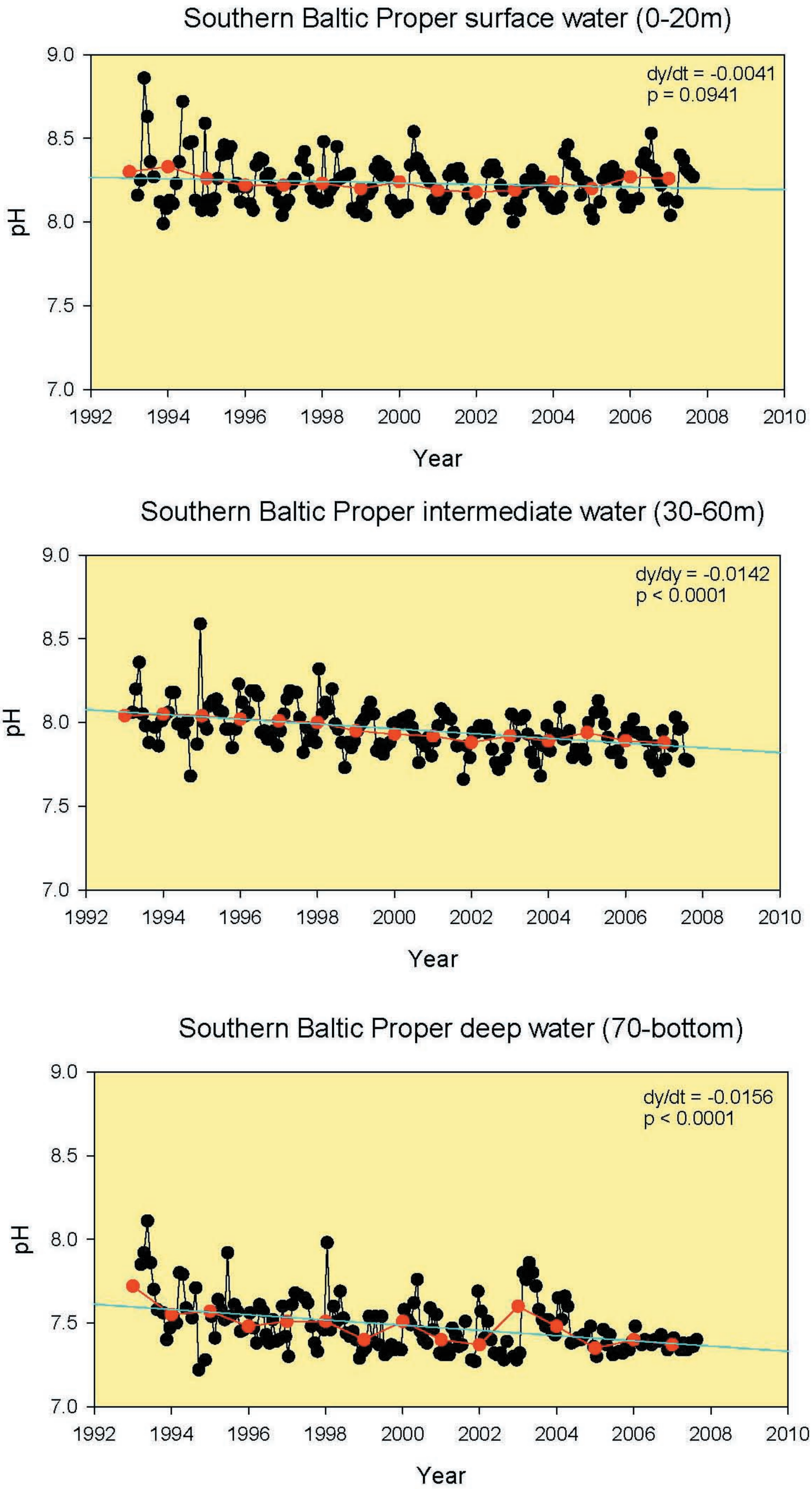

Figure 5: Time series of pH in the southern Baltic Proper. Trends calculated using linear regression.

The results show that the largest changes, except for the intermediary and deep waters of the southern Baltic proper presented above, can be detected in the surface (0.44 units) and deep waters (0.27 units) of the Bothnian Sea, and in the surface waters of Bothnian Bay (0.20 units). In the Bothnian Bay the decrease in the deep water was 0.18 units. The decrease in the intermediary layer of the central and northern Baltic proper is 0.14 units and in the deep water 0.09 units.

It is obvious that generally the pH in the surface water is more fluctuating than the conditions in the deeper water layers. This can be explained by the dynamics of pH connected to the photosynthetic fixation of carbon dioxide by the micro algae in the surface photic zone during the productive season. The fluctuations in the surface water may also be explained by the exchange between air and seawater.

The water column data from one station in Kattegat (Anholt E), one station in the southern Baltic proper (BY5) and one in the central Baltic proper (BY15) have been divided into several depth intervals and linear regressions have been calculated for all data points in each water layer (Appendix I). In these figures the pH values show larger decreases over time with increasing depth. One exception is the deep waters of station BY15 (200 m depth) where the pH decrease is weak, which may be explained by the effect from hydrogen sulphide in the bottom water.

ATMOSPHERIC DEPOSITION

There is a large exchange between the air and the sea surface. The level of some components in the air highly influences the corresponding levels in the sea surface. Since the late 1960s, the hypothesis for the ocean surface was that the deposition of CO_2 to the surface water is of minor importance compared to the effect of increasing CO_2 level in the air. There are several parameters in the air that are of interest for the acidification of marine waters.

The deposition parameters of interest are:

- SO_4^{2-}
- NO_3^-
- NH_4^+
- H^+ (strong acids)
- pH of the precipitation
- Basic cations

(A cation is a positively charged (i.e. attracted to the cathode) ion. The basic cations are those which would make strongly basic (alkaline) solutions in the hydroxide form, e.g. Na^+ gives NaOH.)

For budget calculations, the areas of the sea basins are necessary.

Area of the entire Baltic (including the Kattegat):	410 000 km2
Area of the Baltic Proper:	228 000 km2
Area of the Bothnian Sea and Bothnian Bay:	110 000 km2
Area of the entire drainage area:	410 000 km2
Volume of the entire Baltic (including the Kattegat):	22 500 km3

(Deposition over land is not included in the calculations below.)

MODEL CALCULATIONS FROM MATCH

MATCH is the acronym for Multi-scale Atmospheric Transport and Chemistry Model. MATCH models the basic processes of atmospheric transport and content and fallout of different air pollutants like nitrogen and sulphur compounds or radioactive fallout. (The model is Eulerian and can be configured with an arbitrary number of layers in the vertical and for different geographical areas with different resolution.) The model is driven by meteorological data taken from operational numerical weather prediction models such as HIRLAM or ECMWF, objective analyses, such as MESAN, or from combinations of these.

According to the MATCH model, the sulphur deposition from air is larger in the southern than the northern Baltic. The calculated amount of sulphur deposition over the entire Baltic has strongly decreased during the last 20 years. The deposition of nitrogen has also decreased, but to a lesser extent.

The amount of DOC in the seas is increasing even if the sulphur in the atmosphere has decreased. CO_2 is more soluble than sulphur and CO_2 in the atmosphere is steadily increasing.

The acid level in the air has reduced and the CO_2 level has increased – could this influence the surface water in the open sea so that despite the pH trend in the sea, there is no significant trend in the top surface waters, balancing the acidity? Or is the main cause of this the biological activity? One thing is clear and that is that further research in this area is required.

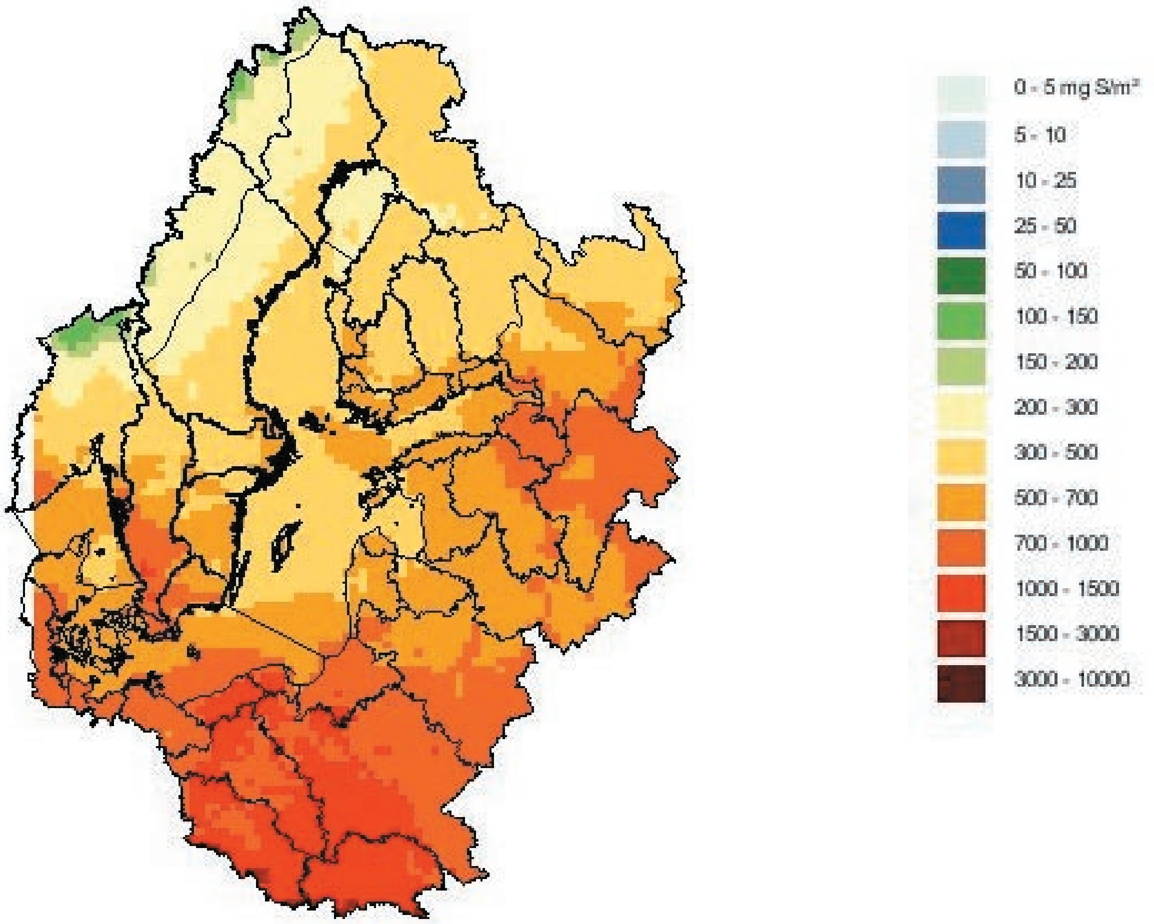

Figure 6: Fallout of the sulphur compound air pollutant 1998 according to the MATCH model.

Table 2: Deposition from air over the entire Baltic different years and prediction (1000 tonnes, mg/m²).

Ref.	Yr	SOx-S	NOx-N	NHx-N	Total-N
HELCOM Decis. 2005/26	*2010 Scen-2*				*202*
HELCOMDecis. 2005/26	*2010 CLE*				*216*
EMEP jan - 2004	*2010*	*198*	*122*	*112*	*234*
EMEP jan - 2007	2005	168 (410)	130 (317)	94 (229)	224 (546)
HELCOM Decis. 2005/26	2003				217
EMEP jan - 2003	2000	229	180	113	293
EMEP jan - 1998	1995	257	122	84	206
EMEP jan - 1998	1990	412	178	102	280
EMEP jan - 1998	1985	600	190	133	323

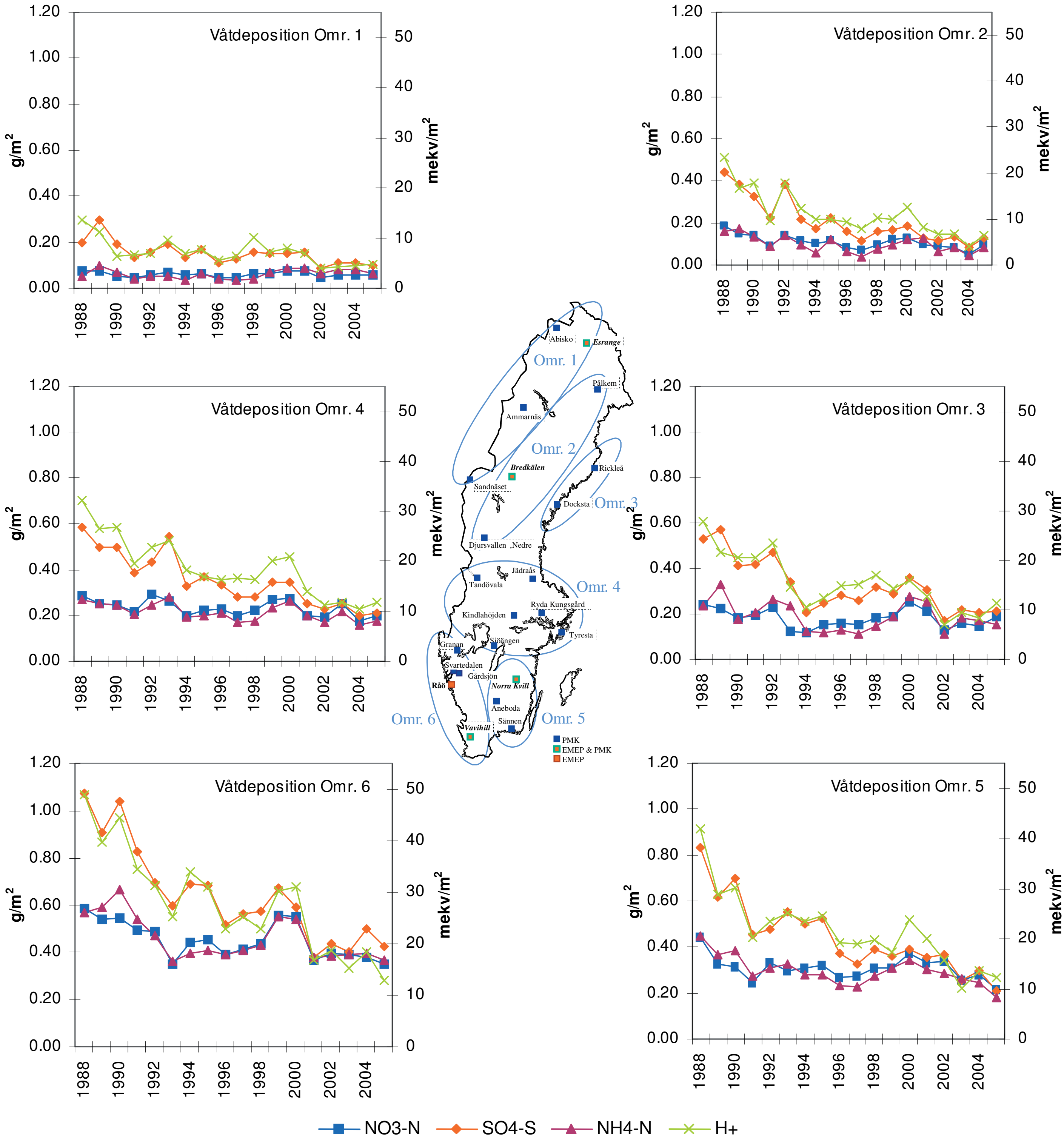

Figure 7. Measured (wet) deposition in the figure above. Estimated total deposition of H^+ to the entire Baltic during the year 2006 is about $6*10^{12}$ mekv.

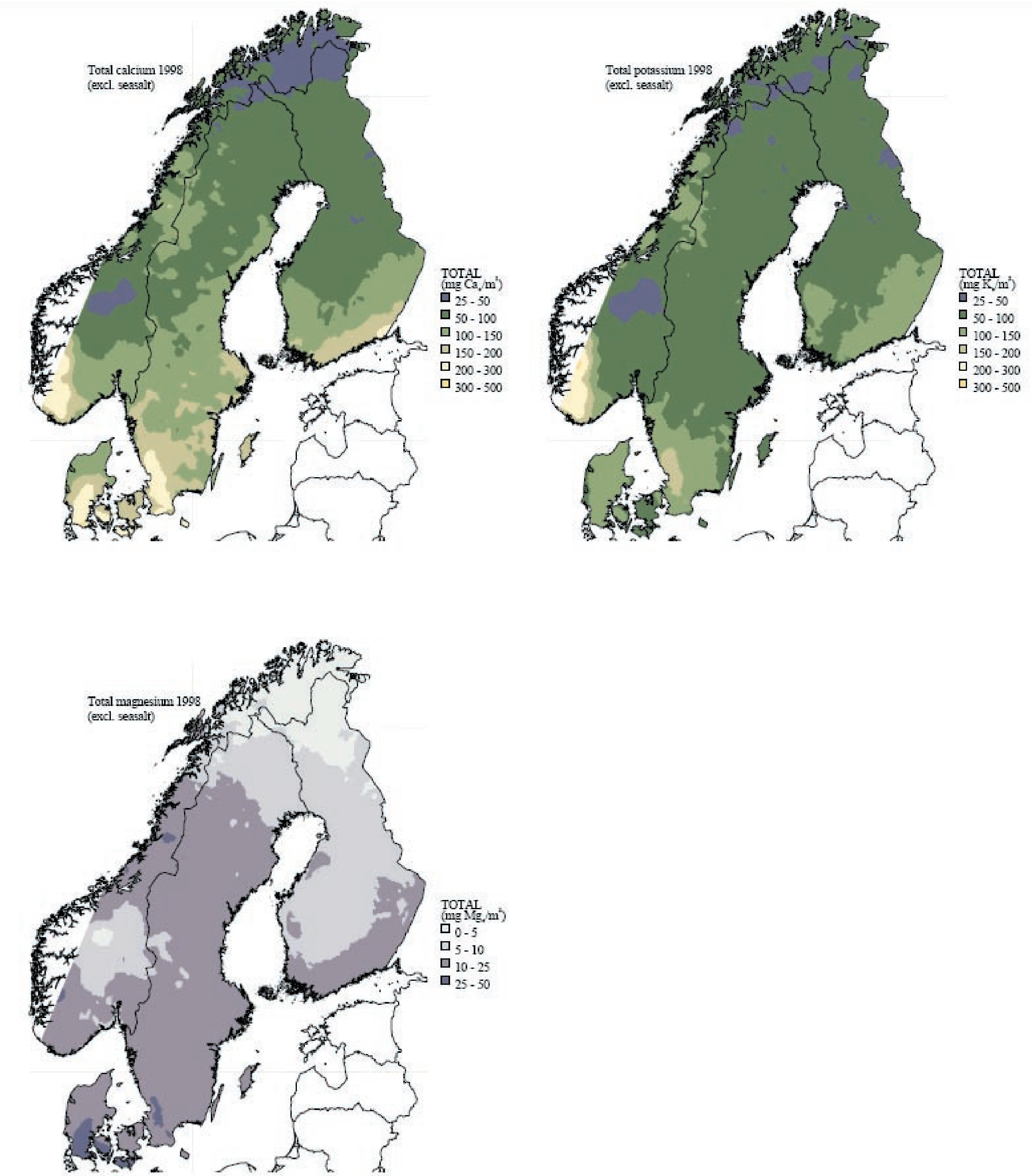

Figure 8. Deposition of basic cations (sea salt excluded).

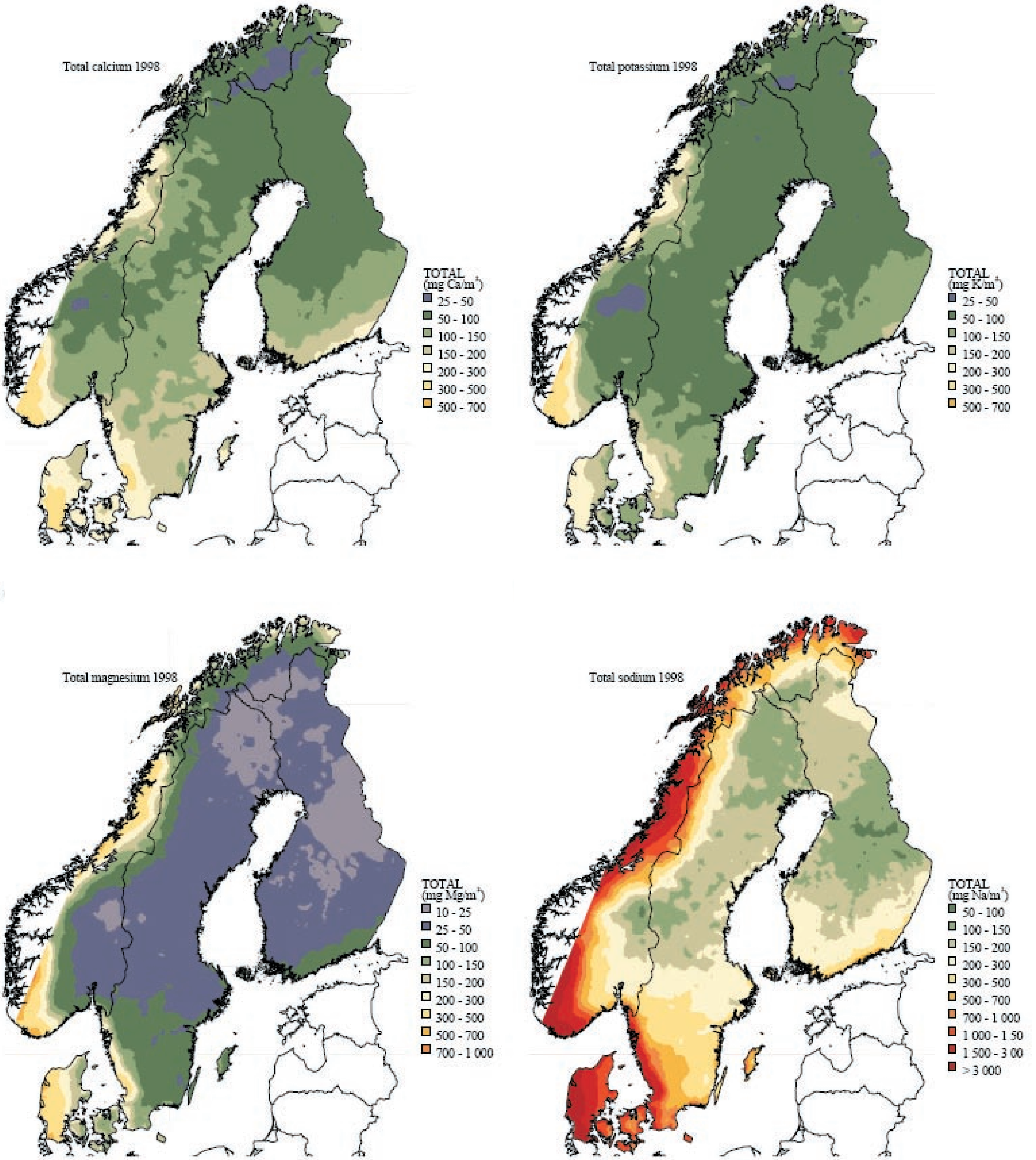

Figure 9. Deposition of basic cations (sea salt included).

THE CARBONATE SYSTEM

WHAT IS ACIDIFICATION?

Carbon dioxide (CO_2) is dissolved in water and makes carbonic acid (eq 1 and 2 below). In the water the carbonic acid makes hydrogen ions and hydro carbonate ions (eq 3). The hydrogen ions make the water more acidic, i.e. we will measure a decrease in pH. In acidic water the carbonate ions will react with the hydrogen ions to make hydro carbonate (eq 4 towards the left). This may result in a lack of carbonate ions for calcifying organisms. With continued decrease of pH, the seawater turns undersaturated for aragonite and calcite which would cause spontaneous dissolution of organisms with calcified structures.

THE CARBONATE BUFFER SYSTEM

Since atmospheric carbon dioxide is in equilibrium with carbon dioxide in the surface water of the sea, the concentration of carbon dioxide in the sea is proportional to the concentration in the air. The transfer rate between water and air is rather slow, so short-time fluxes in atmospheric carbon dioxide levels have no effect on the carbon dioxide content of the sea.

Solubility of carbon dioxide in water increases with decreasing temperature, so cold seas in the north are probably the first to be affected by acidification.

Gaseous carbon dioxide is relatively inert, but when dissolved in water, it reacts to form carbonic acid:

$$CO_2(g) \leftrightarrow CO_2(aq) \qquad (1)$$

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3 \qquad (2)$$

Carbonic acid is deprotonated in two steps:

$$H_2CO_3 \leftrightarrow H^+ + HCO^{3-} \qquad (3)$$

$$HCO^{3}- \leftrightarrow H^+ + CO_3^{2-} \qquad (4)$$

Alkalinity is a measure of the buffering capacity, the ability to neutralise an addition of acid without a change in pH. The buffering ions neutralise some of the added protons, making the change in pH much less than in an unbuffered system. In the ocean, silicate, borate and phosphate ions, among others, contribute to the total alkalinity (A_T), but carbonate and bicarbonate are the most important ingredients:

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] – [H^+] + [OH^-] + 2\,[PO_4^{2-}] + [SiO(OH)_3^-] \quad (5)$$

When acid is added, protons are absorbed by carbonate and bicarbonate ions (3, 4). These reactions are the main buffers in sea water. In hypoxic waters, hydrogen sulphide and phosphate are the main contributors to total alkalinity.

Since carbonate is consumed in the buffering process, the result of acidification is not only a lower pH, but also a reduction of carbonate ion concentration.

A greater buffering effect than the one described above could be expected from the carbonate-rich sediments in the oceans:

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \quad (6)$$

As pH and carbonate ion concentration decreases, calcium carbonate will dissolve and buffer acidification. The mixing of surface water and deep ocean water is however so slow that the surface water is likely to be acidified before any buffering effect by the sediments could be detected.

PH AND ALKALINITY IN THE BALTIC SEA

In the oceans, alkalinity is proportional only to salinity. From the northernmost part of the Bothnian Bay to the Danish Straits and the Sound, the Baltic Sea is highly affected by river runoff, and alkalinity varies not only with salinity but is also affected by geology. The northern part of the drainage area is dominated by silicate rock, which gives the river runoff a low pH and a low alkalinity. The south-eastern part is rich in limestone areas, and the carbonate content of the river water gives runoff from this area a high alkalinity. This gives the Gulf of Riga and the south-eastern part of the Baltic Proper a higher alkalinity than other parts of the Baltic Sea with similar salinity.

While pH in ocean surface water is relatively constant, pH in the Bothnian Bay shows great spatial and seasonal variation. In river mouths and estuaries, pH might sink as low as 5.0-5.5 at spring flood. This is believed to seriously affect the reproductive success of spawning fish. The acidification of river water originates from sulphur-rich soils, and is not connected to pollution (Hudd, R. 2000).

RESEARCH IN THE WATERS SURROUNDING SWEDEN

During the workshop, a few research groups were discussed:

- ”Vasa-gruppen” examine effects of acid increase during the spring in the northern Quark. The pH level can drop to 5 which results in migration of fish to areas further away from the coast, where the pH is higher (reference: Lauri Urho and Richard Hudd at the Finnish Game and Fisheries Institute).
- Mesocosm-experiments exist for example in Germany, but there are often large decreases of pH in those experiments.
- NIVA
- Tjärnö – experiments on cold water corals.
- At Sven Lovéns Centre for Marine Sciences: FORMAS project by Jonathan Havenhand, Mike Thorndyke and Sam Dupont. Researching effects on fertilization and early life stages of marine invertebrates due to decreased levels of pH.
- Berndt Schneider at the Baltic Sea Research Institute (in cooperation) - measurements of pCO_2 along the Alg@line route. Though the research is not on the ecological scale.
- Sopran-project, Germany.
- EPOKA, biological effects on marine acidification. Research and modelling.
- Uppsala University has pCO_2 measurements in air and water at Gotland. Contact: Anna Rutgersson on Earth Science, Uppsala University.

EFFECTS ON THE MARINE BIOLOGY

THE SWEDISH CONTEXT

There is very little work on the existing – or future – effects of acidification on Swedish marine ecosystems. A recent report (Tyrrell et al., 2007) suggests that the absence of calcifying phytoplankton (notably coccolithophores) in the Baltic Proper, is caused by the low saturation state of aragonite in these waters, and that this, in turn, is a result of naturally low carbonate concentrations and high pCO_2 levels (low pH) in winter. Tyrrell et al. (2007) conclude that the Baltic Proper is already undersaturated for aragonite and calcite in winter – a condition that would cause the spontaneous dissolution of calcified structures.

The only published experimental work of the effects of ocean acidification on Swedish coastal species shows reduced growth of blue mussels, Mytilus edulis, but only at levels of ocean acidification expected beyond the year 2400 (pH 7.4, Berge et al., 2006). Although studies of adult organisms (and using extreme levels of ocean acidification) are of value, the Royal Society working group (Raven et al., 2005) again identified "... an urgent requirement for experiments addressing the effects of smaller increases in CO_2 on the reproduction of marine animals".

The results of experiments answering this call are only just becoming available, and Sweden is among the world-leaders in this field. Results for Swedish species to date show: rapid 100% mortality of larvae of a common brittlestar, Ophiothrix fragilis, in response to a 0.2 pH unit fall (Dupont et al., in press) (figure 10); reduced survivorship of larvae of another common brittlestar species, Amphiura filiformis, and the seastar Asterias rubens, in response to a 0.2 pH unit fall (Dupont et al., unpublished); increased generation times in the copepod Acartia tonsa, and increased survivorship and growth rates in the tunicates Ciona intestinalis, and Ascidiella aspersa (Dupont et al., unpublished).

All of these data show negative impacts of near-future levels of ocean acidification on calcifying species, and are consistent with predictions of earlier reports (Raven et al., 2005; Orr et al., 2005; Feely et al., 2004; Ruttimann, 2006; Kleypas et al., 2006).

What can we predict about future impacts?

Notwithstanding the paucity of hard evidence, it is highly probable that a number of biological processes will be significantly affected by ocean acidification. These include basic metabolic functions such as photosynthesis (Riebesell et al., 2007), mode of metabolism (Pörtner et al., 2004), fertilisation success (Kurihara et al., 2007; Havenhand et al., submitted), larval developmental success (Dupont et al., in press; Kurihara et al., 2007; Kurihara et al., 2004; Dupont et al., unpublished; Havenhand et al., submitted), and biogenic calcification (Riebesell, 2004; Berge et al., 2006; Green et al., 2004; Renegar et al., 2005; Shirayama et al., 2005).

These latter processes are pivotal to the sustained health and functioning of marine ecosystems: for example, preliminary estimates for sea urchins suggest that the effects of acidification (by 0.4 pH units) on fertilization success, larval- and post-larval survivorship could reduce population viability by ≤ 50% (Havenhand et al., submitted). If general, these results have pervasive implications for the structure and viability of marine communities and the ecosystem services they provide. In contrast, the only available work on metabolic impacts of acidification suggests that many species will be affected only marginally (Pörtner et al., 2004), although reduced aerobic performance, and substantial depression of metabolic activity may occur, not least due to pH-induced reductions in oxygen-transport capacity in the blood of marine animals (Pörtner et al., 2004) (so-called Bohr-shift; figure 11).

Importantly, genetic variability – and hence capacity to adapt – in response to these changes is critical for understanding the longer-term resilience of marine communities to acidification (Raven et al., 2005). Here again, the Royal Society expert working group stated: "...we are generally unable to say whether organisms will be able to adapt... in the short term, or evolve in the long term" (Raven et al., 2005). This issue requires urgent attention.

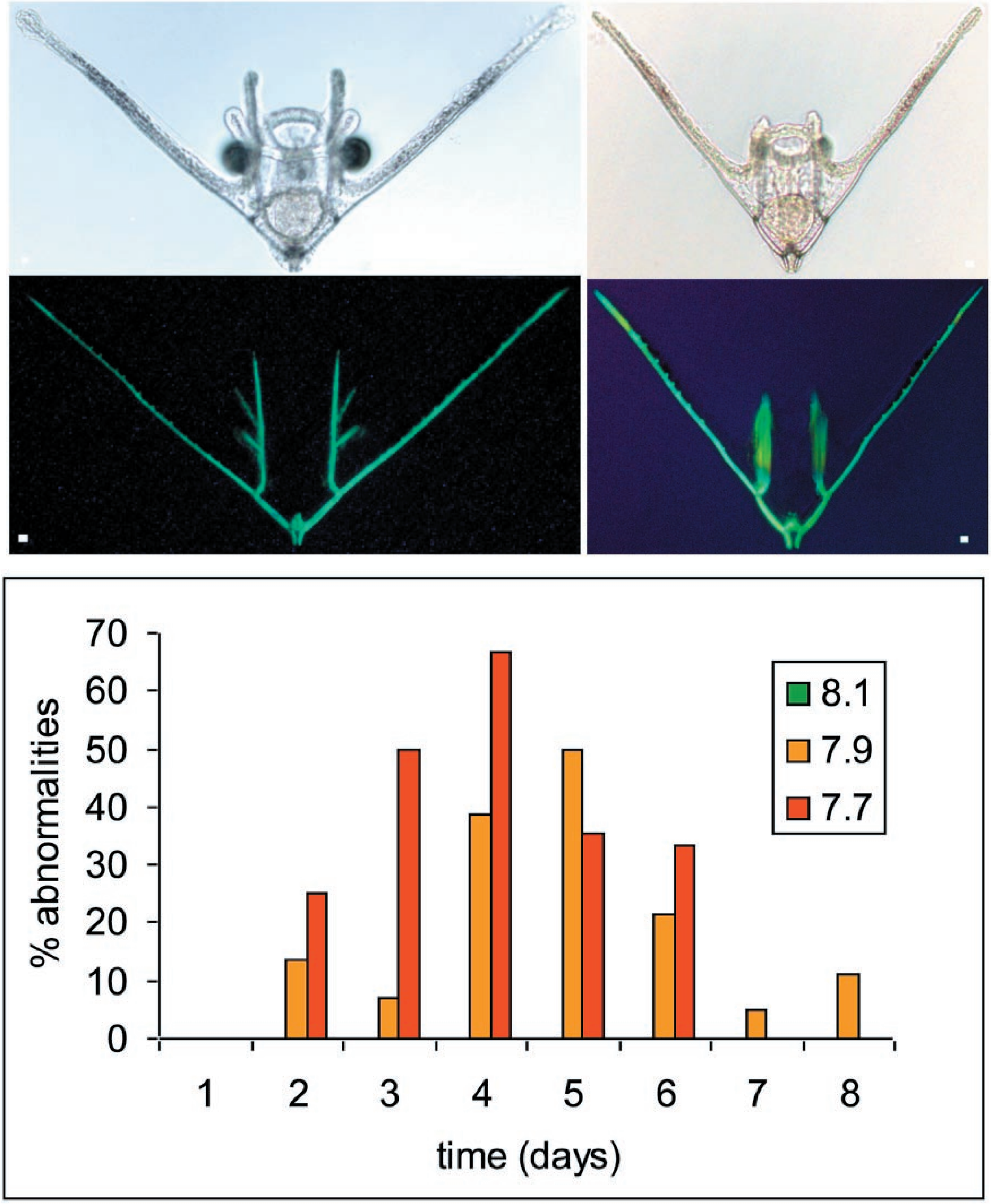

Figure 10. (upper) 8 d old larvae of the brittlestar Ophiothrix fragilis reared at pH 8.1 (left) and pH 7.7 (right). Arm-length, body-size and development at pH 7.7, are all significantly reduced. (lower) percent abnormality in larvae of Ophiothrix fragilis raised at pH 8.1, 7.9 and 7.7. Note absence of abnormalities in pH 8.1. All larvae at pH 7.9 and 7.7 died after 9days. The normal larval period for this species is 3 weeks (Dupont et al,, in press).

The most common species of the phytoplankton group coccolithophorids in the open oceans is Emiliania huxleyi. It is an important sink for carbon, through the sedimentation of the calcareous shells, called coccoliths, ($CaCO_3$) to the deep sea bottoms. The equations below show how E. huxleyi produce calcium carbonate (equation a), and how carbon is fixed through the photosynthesis (equation b). The coccolithophorids thus fix carbon in two ways, first by the calcification of the calcareous shells and second by the photosynthesis which is in common with all other plants.

a) $2HCO_3^- + Ca^{2+} + H^+ \leftrightarrow CaCO_3 + CO_2 + H_2O$

b) $CO_2 + H_2O \leftrightarrow CH_2O + O_2$

If the concentration of carbon dioxide increase in the seawater, and thus there will be decrease in pH, then the coccoliths of the coccolithophorids (in the form of calcite) will dissolve. Experimental studies have shown this effect by using scanning electron microscopy (Riebesell et al., 2000) , and Tyrrell et al. (2007) have suggested that the near-absence of Emiliania from the Baltic proper is entirely due to the low saturation state of carbonate (= high pCO_2) in these waters.

With specific reference to Swedish coastal waters, calcifying species such as the coccolithophorid Emiliania huxleyi, the blue mussel Mytilus edulis, the barnacle Balanus improvisus, the cold-water coral Lophelia pertusa, and a number of crustaceans and echinoderms (eg Amphiura filiformis),

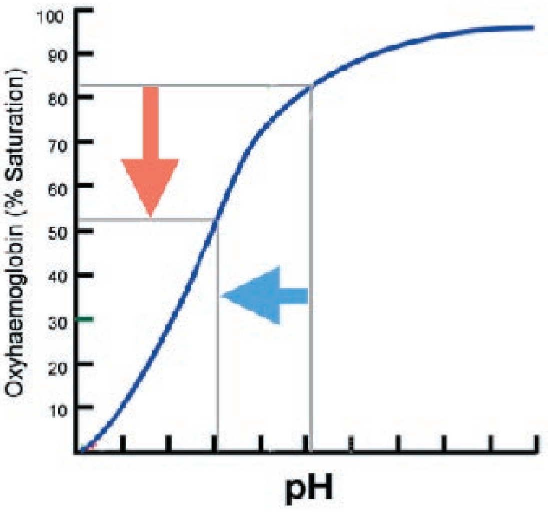

Figure 11. Effects of decreasing pH on oxygen-carrying capacity of a typical respiratory pigment in the blood of a marine organism (from Pörtner et al., 2004). Oxygen carrying capacity decreases disproportionately (red arrow) with small reductions in pH (blue arrow).

Table 3. Marine organisms with calcification of shells or skeletons.

Group	**Form of Calcium carbonate**
Foraminifera	calcite
Coccolithophorids	calcite
Echinoderms	calcite
Crustaceans	calcite
Molluscs	aragonite (pteropods), aragonite and calcite (other)
Corals	aragonite
Macroalgae	aragonite or calcite

play major roles as ecosystem engineers in the Baltic and/or Skagerrak. Given the experimental results obtained to date and the observed trends of declining pH in Swedish coastal waters (http://www.smhi.se/cmp/jsp/polopoly.jsp?d=10407&a=31432&l=sv), it is likely that significant ecosystem-wide effects will be observed within 50 – 100 years, and possibly sooner.

Some species are probably to gain or not to be affected to any appreciable extent from a decrease of pH. It may be favourable to some jellyfish and sea squirts and primary production, but this is also uncertain. Some macro algae probably gain from the decrease, since they are carbon limited.

Probable outcomes include the increasing prevalence of non-calcifying taxa, and increased likelihood that marine ecosystems will pass a "tipping-point" and change to a completely different quasi-stable structure. Unabated decreases in coastal ocean pH will "tip" the current ecological dominance of (eg) blue mussels in the Baltic proper, change the recruitment patterns of many key marine species (eg brittlestars, and some fish), and likely cause complete local extinction of the recently-discovered Lophelia pertusa biodiversity "hotspots" in the Skagerrak.

Given that the marine science community is only now awakening to the possible consequences of ocean acidification, it is likely that some level of impact has already occurred. Equally it is probable that this will continue (and possibly accelerate) in the coming decades. Nonetheless, predicting the precise nature and timescale of these effects with any reasonable degree of certainty is presently impossible.

There is an alarming absence of information regarding the effects of near-future levels of ocean acidification on Swedish marine taxa. [It is noteworthy that although scant, the data summarized here comprise most of the available published information in this field].

There is an urgent need for:

- investigations of the effects of ocean acidification on the early life-history stages (reproduction, fertilization, larval development, recruitment) of key ecosystem-structuring species, and commercially important species of fish and shellfish
- assessment of the extent of pre-existing genetic variation (ie capacity for adaptation) to ocean acidification in key ecosystem-structuring and commercially important species.
- ecosystem-level mesocosm studies of the impacts of ocean acidification on Swedish marine systems
- improved regional-scale modelling of acidification mechanisms in Swedish coastal waters
- testable ecosystem-scale food-web models to articulate with regional acidification models.

ONGOING MONITORING PROGRAMMES AND ACTIVITIES

Monitoring is essential to be able to provide the basis for environmental surveillance and macroecological analysis of the potential impacts of acidification for ecosystems and dependant services, such as fisheries. These observations would be used to assess the extent of the problem and for the validation of models and predictions. Specifically these should have broad geographic coverage to monitor response over a range of salinities and alkalinities. Continued monitoring is also required to assess the impact of any remediation measures that have been undertaken (ICES, 2007).

An aspect not included further in the report is the need for development of models. To assess the likely implications to the ecosystem and fisheries, a joined-up approach is required whereby models of higher trophic levels are coupled to physical and biogeochemical models. In relation to fisheries dynamics, there are two critical issues that experiments cannot incorporate: (i) population-scale processes, such as broadcast spawning, migration and spatial population structure or (ii) community and ecosystem structuring processes such as competition and predation (ICES, 2007).

MONITORING OF PH AND ALKALINITY

According to the HELCOM COMBINE Manual, pH and A_T are parameters included in the National Monitoring programmes of Finland, Germany, Lithuania and Sweden. The focus of monitoring these parameters in coastal and open-sea areas differ between the countries in the following way:

Finland:	pH and A_T measured at several near-coastal stations.
Germany:	pH and A_T measured at open-sea stations.
Lithuania:	pH at near-coastal stations.
Sweden:	pH and A_T measured at near-coastal and open-sea stations.

It is obvious that there has not been any joint HELCOM effort on monitoring the acidification of the Baltic Sea. This is a new area of monitoring for future years. Fortunately there is data available, which can be used for the long term analysis.

The monitoring programmes so far have been focused on the problems of eutrophication and anoxia, so analysis of acidification and buffering capacity have not been a main priority. pH and alkalinity have been included in monitoring programmes not so much for their own importance, but as a supplement to analysis of primary production. The DIC concentration required for analysis of primary production is usually calculated from pH and A_T.

MONITORING OF CARBON DIOXIDE PARTIAL PRESSURE (PCO2) IN THE SEA

Continuous measurements of pCO_2 are performed from cargo ship on route between Lübeck and Helsinki. This has been going on since 2003 in cooperation with the Finnish Algaline project (Schneider et al., 2007).

Hourly measurements of pCO_2 in air and water are recorded from a moored instrument east of Gotland since 1995 (ref. Uppsala University).

LEGITIMATE CLAIMS

WEAK LEGITIMATE CLAIMS ON MARINE ACIDIFICATION AS A THREAT TO MARINE ECOSYSTEMS

Marine acidification according to most textbooks on marine chemistry and oceanography is not an issue due to high buffer capacity of ocean water. Recently (Royal Society 2005) a comprehensive study discussed the matter in detail, indicating the opposite, that acidification takes place under the pressure of increasing atmospheric CO_2 burden. It was also a key issue discussed under the latest AAAS meeting in Boston (Bojs, 2008).

Also in brackish water systems acidification can take place. SMHIs own trend station data on pH and Alkalinity indicate a decrease in pH similar to what the global ocean data indicate. The factors causing this trend are still unclear. Nevertheless, the consequences for brackish water life can be devastating.

Since marine and brackish water acidification is a new and unexpected negative disturbance there is little information on how to deal with it from a management point of view. In the Water Framework Directive acidification is an issue but to be understood only for freshwater. Recently Swedish EPA decided on methods and classification rules to evaluate acidification in lakes and rivers. There is a possibility to extend and/or adapt the methods and classes to coastal and transitional waters but so far there is no monitoring data available from these waters. Alkalinity and pH data are only collected at a few open sea trend stations in Skagerrak, Kattegat and Baltic Proper by SMHI.

The upcoming Marine Strategy Framework Directive (MSFD) will be the instrument to achieve good environmental status by 2010 in all European Marine Regions. In the present form, decided by the Council and the Parliament in December 2007, the status shall also include marine acidification. In the Annex III, Indicative lists of characteristics, pressures and impacts, under physical and chemical features, pH, pCO_2 profiles or equivalent information used to measure marine acidification is prerequisite. Hence, when the final decision on the MSFD is taken a firm basis exist to deal with marine acidification from a legal point of view.

In HELCOM COMBINE monitoring programme nothing is said about acidification and the need for monitoring and assessment in brackish water bodies of the Baltic Sea area. The COMBINE programme does give advice on how to measure pH and Alkalinity, while in the assessment procedures acidification in itself has not been evaluated so far.

A possible Swedish action would be, either ask HELCOM MONAS to prepare a pilot study on the state of affairs and possible causes and consequences, or make a national report to be presented at HELCOM to increase awareness on the this issue.

We recommend that Sweden work for improving the status of pH and A_T to be Core variables instead of Main variables in HELCOM COMBINE “High frequency Sampling” programme taking into account the last 15 years negative trends in pH in waters surrounding Sweden as well as in the global oceans.

MONITORING PARAMETERS

The definition of acidification is a decrease in pH in the environment. Thus, the obvious method for monitoring the acidification process in the marine environment is to measure the parameter pH in the water.

At present, pH and A_T are monitored monthly at standard depths at 8 stations in Skagerrak, Kattegat and Baltic Proper within the national monitoring programme. Of these are 3 located in coastal waters (Halland, Småland & Sörmland; Type 5, 9 & 12).

Anthropogenic carbon dioxide emissions, however, have been found to change the chemical state of seawater towards increased acidification. Thus, to understand the process of marine acidification it is important to monitor the concentration of inorganic carbon (DIC) in the seawater. pH is a function of total alkalinity (A_T) minus DIC. If temperature and salinity is known, as well as two of the following parameters, the remaining two can be calculated: tot DIC, A_T, pH and pCO_2 (partial pressure, or fugacity of CO_2).The concentration of inorganic phosphate and silicate affects the calculation and should be included in the equations (if measured in the water sample).

The equation above uses the stability constants (K0, K1 and K2) of the inorganic carbon system. These constants are temperature and salinity dependant and are not optimized for the Baltic Sea brackish environment less than 10 psu.

It is important to optimise the methods. The choice of pH-scale should be documented.

DIFFERENT LEVELS OF AMBITION FOR MONITORING:

1. Monitor acidification: Measure pH
2. Monitor/examine acidification and buffer capacity of the water, i.e. how sensitive is the system for continued acidification: measure pH, A_T, and temperature and salinity. DIC (dissolved inorganic carbon, i.e. carbonate) can be calculated. NB! Weakness: the stability constants in the equations are adjusted for oceanic water.
3. Direct measurement of the carbonate ystem. As in 2, with added direct analysis of DIC in water sample (several analytical techniques available)
4. Refined calculation of buffer capacity: As above, with nutrient analysis added, mainly silicate and phosphate which affect the calculation of alkalinity to a certain extent.
5. The balance between carbon dioxide in air and water may be investigated to cal culate where sources and sinks may be found. For this reason the partial pres sure of carbon dioxide, pCO_2, in air and water is analysed and calculated. This varies considerably in space and time, however, especially in air (i.e. exhaust from combustion), which makes this approach most suitable for long time continuous monitoring efforts.
6. Include studies on the effects of the marine life, e.g. effects on calcification of specific organisms, and effects on the biodiversity of populations and communities.

RECOMMENDATION

We recommend that besides the standard parameters, pH, A_T and DIC are monitored. For completeness, primary production should also be monitored.

We recommend that an investigative monitoring is established by extending the parameters that is needed to firmly improve the chemical stability constants between pH, A_T, DIC and pCO_2 in low saline waters. This can be done by just extending the sampling program at selected monitoring stations. Sampling should cover a period of 2 to 3 years.

We recommend that direct water sampling of pCO_2 for monitoring purposes should be assessed after the recommendation above is evaluated and that ongoing research projects on pCO_2 measurements using ferryboxes are finalised.

METHODS - SAMPLING AND ANALYSIS

PH

pH is defined as the concentration (or to be more accurate, the activity) of hydrogen ions in a sample.

$$pH = -\log [H^+]$$

The definition of pH is operational, and a few different scales are used, with slight differences in definition. It is usually determined with an ion-selective glass electrode, calibrated with a set of reference buffers. This method requires careful handling of the electrodes, and regular calibration. Samples must be analysed within a few hours after sampling. Samples are thermostated while analysed, ideally as close to the in situ temperature as possible.

The NBS scale is based on buffers with low ionic strength, and is widely used for analysis of freshwater samples. It is not optimal for analysis of high salinity seawater, since the difference in ionic strength between sample and buffer causes changes in electrode potential.

A few other scales have been suggested for determination of pH in sea water, based on buffers with higher ionic strength. pH measured according to these scales includes not only the concentration of free hydrogen ions, but also hydrogen ions interacting with other species (such as SO_4^{2-} and F^-). These scales are preferable to the NBS scale for oceanic water, but not for low-saline water such as the Bothnian Bay.

When pH is determined, it is often corrected to in situ temperature, and sometimes to in situ pressure. When sets of pH data are compared, pH scale and corrections must be considered.
The HELCOM COMBINE Manual recommends that pH should be determined according to the NBS scale, using thermostated samples, and be corrected for in situ temperature but not for in situ pressure. The temperature correction should be made using the temperature coefficient by Gieskes (1969). No depth correction should be applied because the pressure coefficient is not precisely known. pH sensors (e.g., attached to a CTD) are also allowed.

One example of a pH sensor is the SeaBird pH sensor (SBE 18) which uses a pressure-balanced glass-electrode/Ag/AgCl-reference pH probe to provide in situ measurements at depths up to 1200 meters (www.seabird.com). Another pH sensor available for seawater is the YSI pH sensor (YSI 6561 pH sensor, www.ysi.com).

During the last years, the method of determining pH with spectrophotometric techniques has proven to be reliable and accurate. With a spectrophotometer and a suitable indicator dye, such as thymol blue, pH can be determined with high accuracy. The method is based on knowledge of stability constants and molar absorptivity constants of the indicator, rather than depending on calibration of the instrument. It has successfully been applied also in automated systems.

The spectrophotometric method requires more expensive and complex instruments, but appears to fulfil the demands of accuracy and reliability.

When samples are handled, it is important that they are kept out of contact with air, since exchange of carbon dioxide will change pH. Samples must be analysed within a few hours after sampling.

TOTAL ALKALINITY (A_T)

A_T is a measure of the total content of buffering ion species, of which the carbonate system is the most important (5).

A_T is expressed in mol/kg (the number of protons required to neutralise the proton acceptors in a 1 kg sample). It is sometimes expressed in mol/l.

It is usually determined with potentiometric titration, which is also recommended by the HELCOM COMBINE Manual. A sample of known weight is titrated with hydrochloric acid, while the change in pH is monitored continuously. The same type of instrumentation as for pH determination can be used, supplemented with a burette for acid dispension. Ideally, burette operation as well as data collection is controlled by appropriate computer software.

Alkalinity is sometimes used in physical oceanography for tracing and identification of water masses. Just as salinity, alkalinity is a conservative parameter which remains constant for a certain water mass. As opposed to pH, older data are usually very reliable. The samples are less sensitive to handle and store than the pH samples, since the exchange of carbon dioxide will affect pH but not alkalinity.

DISSOLVED INORGANIC CARBON (DIC)

When the sample is acidified, all carbonate and bicarbonate is converted to free carbon dioxide. The carbon dioxide is purged out with an inert gas, such as nitrogen or helium. The gas is bubbled through an ethanolamine solution, Carbon dioxide reacts with ethanolamine to form hydroxethylcarbamic acid, which then is coulometrically titrated.

The method demands high purity nitrogen or helium gas, and requires hazardous chemicals such as ethanolamine and dimethyl sulfoxide. It also requires high purity carbon dioxide gas for calibration.

PCO$_2$

The partial pressure of a gas is ideally defined as the product of the mole fraction of the gas and the total pressure of the gas phase. Since carbon dioxide does not behave like an ideal gas, the term fugacity should be used rather than partial pressure. Still, most data are presented as pCO_2 values, since the difference is rather small.

When pCO_2 in seawater and pCO_2 in air is measured at the same time, the difference shows the momentary flux of carbon dioxide between sea and atmosphere. The difference, $\Delta\ pCO_2$, is the driving force in the net flux of carbon dioxide.

The mole fraction of carbon dioxide is determined using a non-dispersive infrared analyser (NDIR). The principle can be applied to both discrete sampling (measuring collected samples in flasks) and continuous systems (measuring in an equilibrated flow of air/water). The latter version has successfully been applied to underway systems (Körtzinger et al. 1996).

The method requires calibration gases with a matrix similar to air (a mix of nitrogen, oxygen and argon) with known mole fractions of carbon dioxide.

pCO_2 can also be determined with gas chromatography, but such systems are usually too delicate for use at sea.

CALCULATIONS WITH TWO PARAMETERS MEASURED

For the system described by the equations 2-5 in chapter (The carbonate system and processes in the Baltic Sea and Skagerrak/Kattegat), it is possible to calculate the two remaining parameters when two others out of the four (pH, A_T, DIC and pCO_2) are known. Since the stability constants for equation 2-4 above are dependant of salinity and temperature, these two parameters need also to be analysed.

Since uncertainties in measurements and constants are magnified in these calculations, reliability may vary between. If DIC and pCO_2 are measured, A_T can be calculated with accuracy similar to that obtained in direct measurements. The parameters A_T and DIC are a poorer base for calculations; pH or pCO_2 should not be calculated from these two measured parameters.

SPATIAL AND TEMPORAL ANALYSIS OF SAMPLING STATIONS

The spatial analysis of pH in the Baltic, Kattegat and in Skagerrak indicates that stations at sea, partitioned more than 50 to 100 km are independent of each other, whereas temporal resolution longer than 1 month are more or less independent. (See figures in appendix II.) Similar analysis for costal stations is not performed due to insufficient data.

Stations for trend analysis (Andersson et al., 2004) indicate that pH and total Alkalinity are robust parameters, which easily fulfils the goal to show a 10% trend in ten years time at 80% significance level.

Hence, a national monitoring program on profiling marine acidification can be based on monthly water sampling at standard depths of pH. Stations should be distributed spatially with ca 2 sampling stations in each sub-basin, except in Bothnian Bay, where salinity gradients are low as well as salinity itself.

Techniques to measure in situ pCO_2 are available. Presently this sampling technique based on automatic system onboard ferries is under development in the Baltic Sea. There are different opinions how precise this technique is. We therefore propose to wait with this kind of semi-automatic monitoring until ongoing research projects have been finalised and reports published.

Ferrybased measurements resolve higher spatial and temporal scales in the variability of pCO_2. However, it remains to be proven if this is a possibility and in fact needed for monitoring purposes, having in mind high quality data and ISO-standards as a basis for national monitoring programmes.

MONITORING PROGRAM PROPOSAL

Monitoring is essential to be able to provide the basis for environmental surveillance and analysis of the potential impacts of acidification for ecosystems and dependant services. These observations are used to assess the extent of the problem and can be used for the validation of models and predictions.

STATIONS WHERE PH AND AT IS MONITORED

At present, the two main acidification parameters pH and A_T are monitored monthly at standard depths at 7 stations in Skagerrak, Kattegat and Baltic Proper within the national monitoring programme (see table 4). Of these are 2 located in coastal waters (Halland and Kalmar; Type 5 and 9 (NFS 2006:1)).

Table 4. Stations that currently monitor pH and A_T in the Skagerrak, the Kattegat and the Baltic Proper within the national monitoring programme.

Station	**SMHI monthly measurements**	**Comment**	**SMHI winter survey, once per year**	**UMF 3 times per year**	**Comment**	**UMF monthly measurements**	**Comment**	**SMF twice per month**	**Comment**
Open sea	Anholt, Kattegat	2 times per month	US5B, Bothnian Sea	C3	Only pH (not A_T), non standardised depths	B3, Bothnian Sea	Only pH (not A_T), non standardised depths	BY31, Baltic Proper	Only pH is monitored
Open sea	Å17, Skagerrak	Still measured since SMHI decided not to terminate a longer time series	F16	C14	Only pH (not A_T), non standardised depths				
Open sea	BY5, Baltic Proper		F9, Bothnian Bay	A5	Only pH (not A_T), non standardised depths				
Open sea	BY15, Baltic Proper			A13	Only pH (not A_T), non standardised depths				
Open sea	BY31, Baltic Proper	SMF monitor this station during the summer. Only pH is measured during summer.			*At UMF, pH is measured in the hose sampling (0-10 m) at all stations, in favour for the primary production measurements*				
Costal	N14, Kattegatt	Type 5				B7, Bothnian Sea	Only pH (not A_T), non standardised depths	B1, Baltic Proper	Only pH is monitored Type 12.
Costal	Ref M1-V2, Baltic Proper	Type 9							

RECOMMENDATIONS FOR MONITORING PROGRAMS

Below are three monitoring recommendations, where the first is divided into a lowest level and a recommended level.

Monitoring program – lowest level

Within the national monitoring program, at least one station per open sea area and all costal stations (Släggö, N14, B1, Ref M1-V1 and B7) measure acidification parameters on a monthly basis in the entire water column at standardized depths. The national and regional monitoring programmes should be upgraded in the Gulf of Bothnia so that pH and A_T is monitored at standard depths at least monthly at one station each in the Bothnian Bay and Bothnian Sea. Also 2 coastal stations in the Gulf of Bothnia located far from river mouths should be established in order to assess coastal trends in waters with less influence of river water. In addition, one coastal station should be established within Type 14 (i.e. Östergötland) in the Baltic Proper in an area not influenced by river waters. (SLU monitor some acidification parameters near the mouth of larger runoff rivers (http://info1.ma.slu.se/db.html).)

Monitoring program – recommended level

The national monitoring program should have at least one station per open sea area and if the area is characterized by strong gradients or other features, there should be more than one station. Some of the stations in the regional monitoring programmes should be upgraded with acidification parameters, for a better geographical coverage. The acidification parameters should be measured on a monthly basis in the entire water column at standardized depths. See table 5 and figure 12 for suggestion of additional stations (to be added to the current stations).

Investigative monitoring

We recommend that an investigative monitoring is established by extending the parameters that is needed to firmly improve the chemical equilibrium constants between pH, A_T and pCO_2 in low saline waters (including temperature, salinity, silicate and phosphate). This can be done by just extending the sampling program at selected monitoring stations. Sampling should cover a period of 2 to 3 years.

pCO_2 monitoring

We recommend that direct water sampling of pCO_2 for monitoring purposes should be assessed after the recommendation above is evaluated and that ongoing research projects on pCO_2 measurements using ferryboxes are finalised.

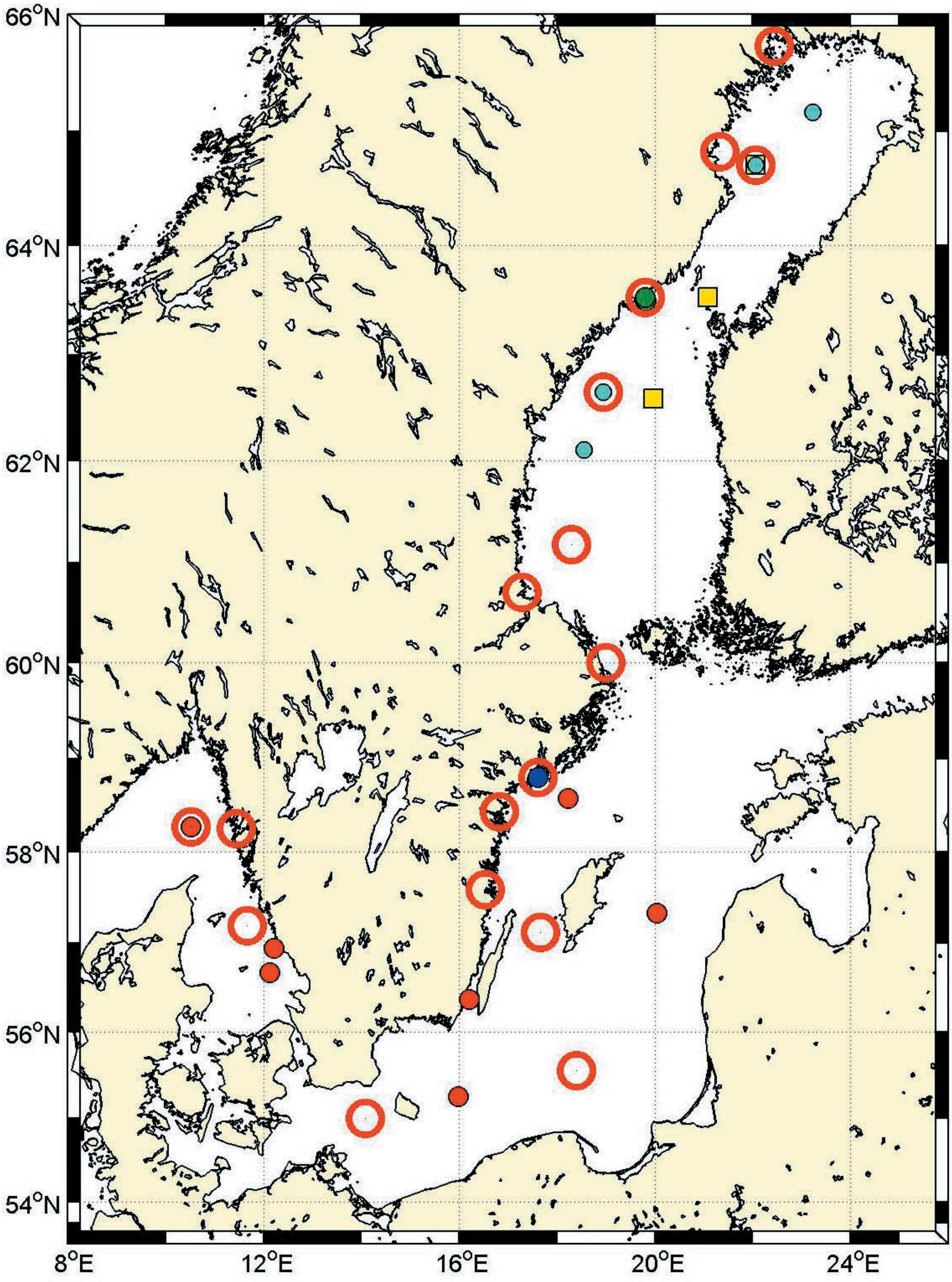

Figure 12. Overview of stations that currently measure pH and suggestion of additional stations. Red dot: Monthly measurements, SMHI. Yellow square: Winter survey, once a year, SMHI. Green dot: Monthly measurements, UMF. Cyan dot: Measurements 3 times per year, UMF Blue dot: Measurements 24 times per year, SMF. Red circles: Suggestion of additional stations.

Table 5. Overview of additional stations in different sea areas.

Open sea /Costal	Sea area	Additional number of stations	Station suggestion	Motivation
Open sea	Bothnian Bay	1	F9	Only one additional station in the central part, due to rather homogenous water mass.
Open sea	Bothnian Sea	2	C3 and SR3	Two stations due to slightly increased salinity gradients (east-west direction).
Open sea	Baltic Proper	3	BY38, BY2 and BCSIII-10	No current monitoring in these sea areas. (BCSIII-10 extra interesting due to the proximity to alkaline waters from runoff.)
Open sea	Kattegat	1	Fladen	Large variability and strong salinity gradients in the area.
Open sea	Skagerrak	1	Å17	Reference to a station with higher salinity.
Costal	Bothnian Bay	2		Situated in the middle and southern archipelago. For improved geographical coverage and to follow up acidification in costal areas (motivation for all costal stations).
Costal	Bothnian Sea	3	B7, new station, K627	At B7 and two additional, suggestion near Norrtälje and Gävle.
Costal	Baltic Proper	2 (-3)	No03, V6-VMS, (B1)	
Costal	Kattegat			
Costal	Skagerrak	1	Släggö	

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APPENDIX

APPENDIX I

TIME SERIES OF PH

Remaining figures of pH time series in the seas surrounding Sweden. Several significant trends of decreasing pH have been found. Figures of the statistical trend and the level of significance have been calculated by using simple linear regression. Only results which are significant on the 95% level are reported ($p<0.05$). All changes refer to the period 1993 to 2007.

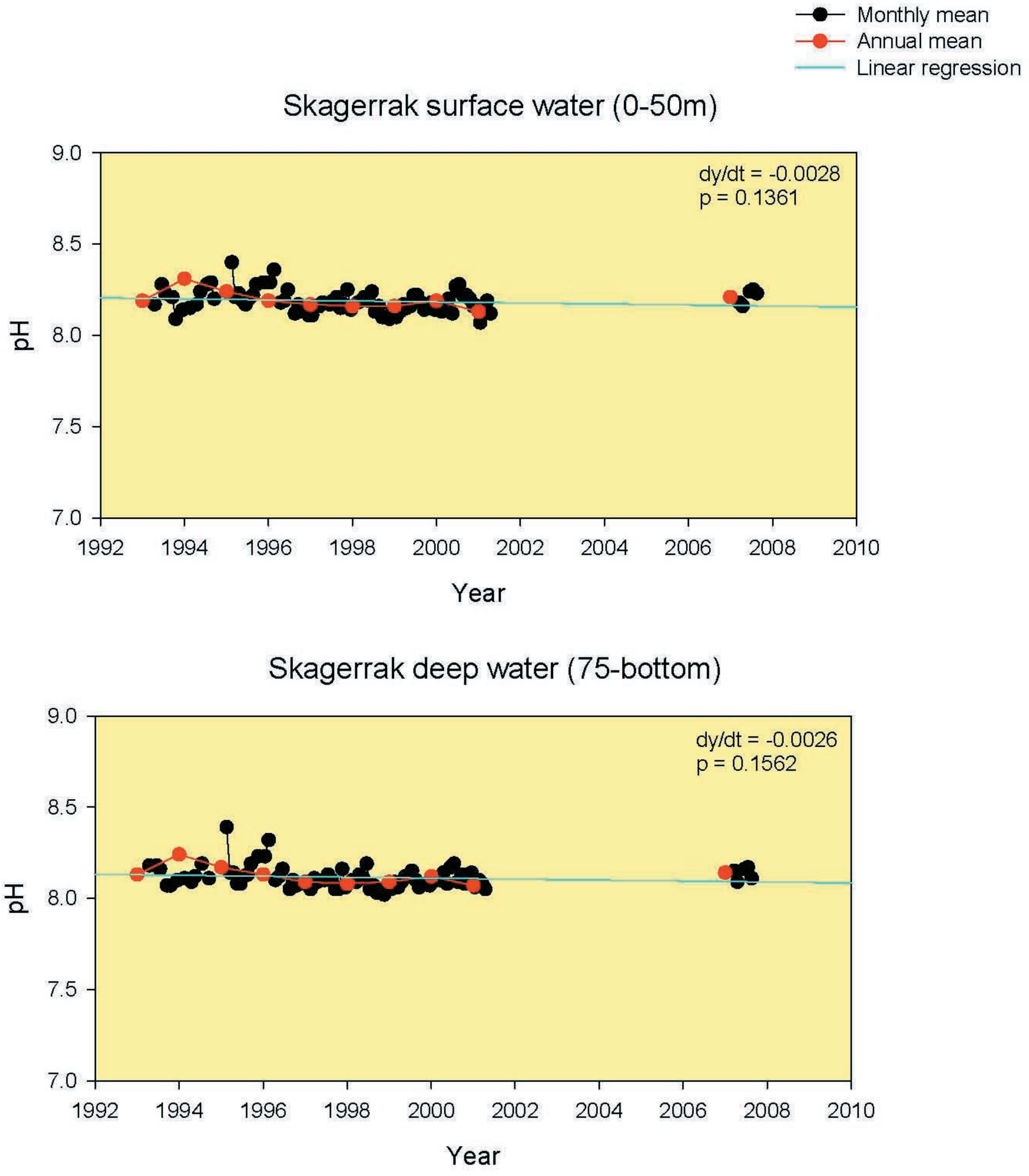


Figure 13. Time series of pH in the Skagerrak. Trends calculated using linear regression.

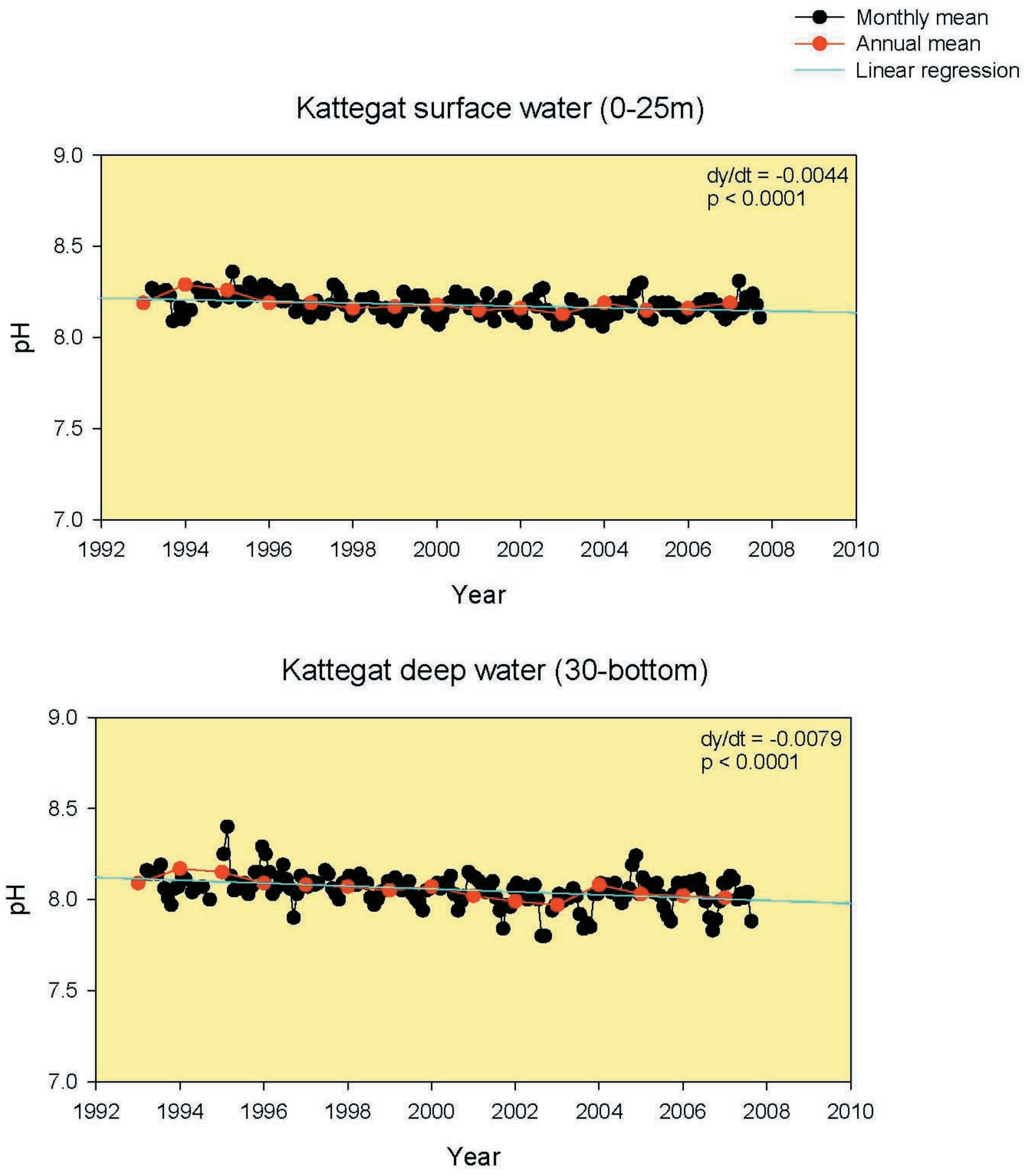


Figure 14. Time series of pH in the Kattegat. Trends calculated using linear regression.

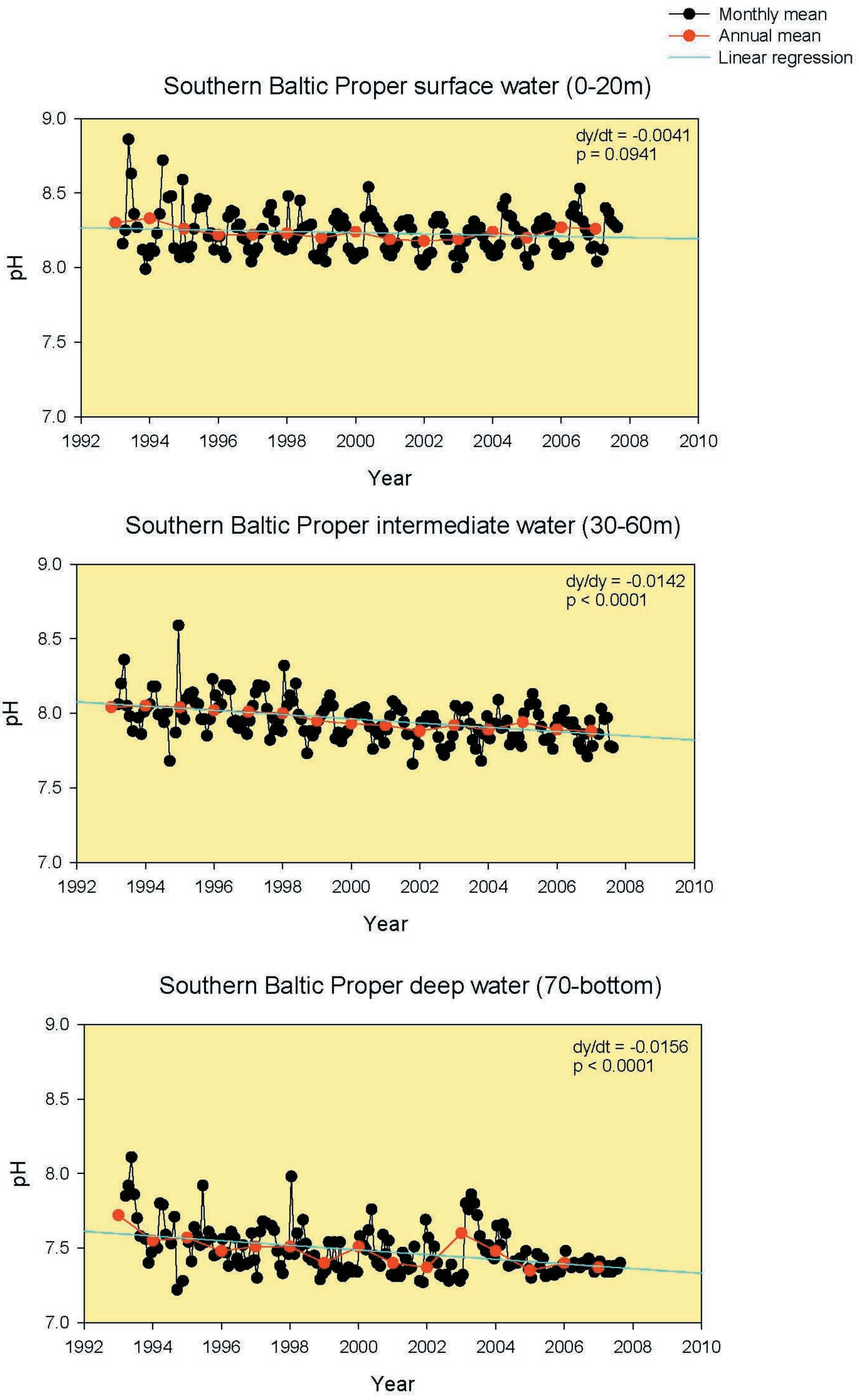


Figure 15. Time series of pH in the southern Baltic Proper. Trends calculated using linear regression.

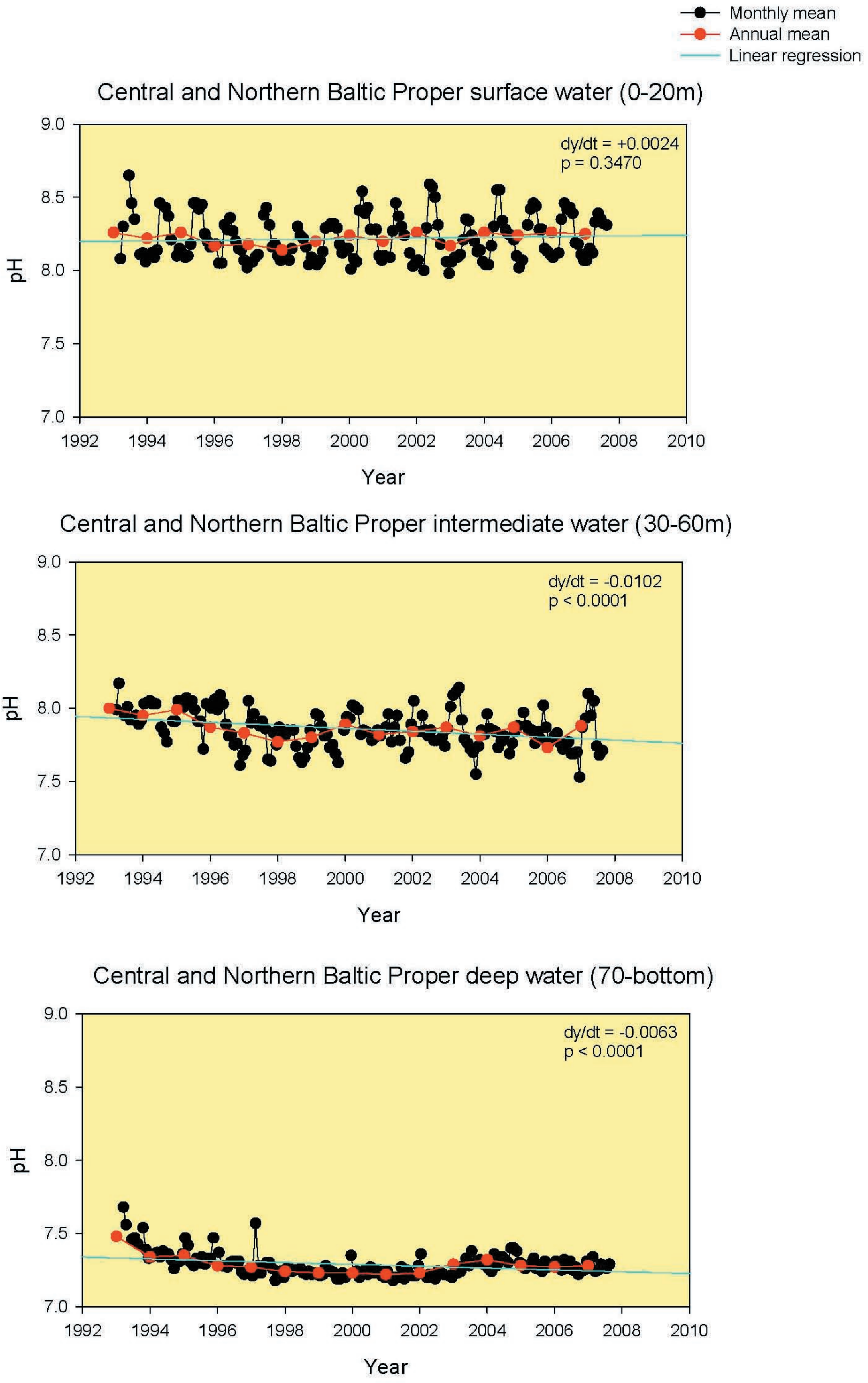


Figure 16. Time series of pH in the central and northern Baltic Proper. Trends calculated using linear regression.

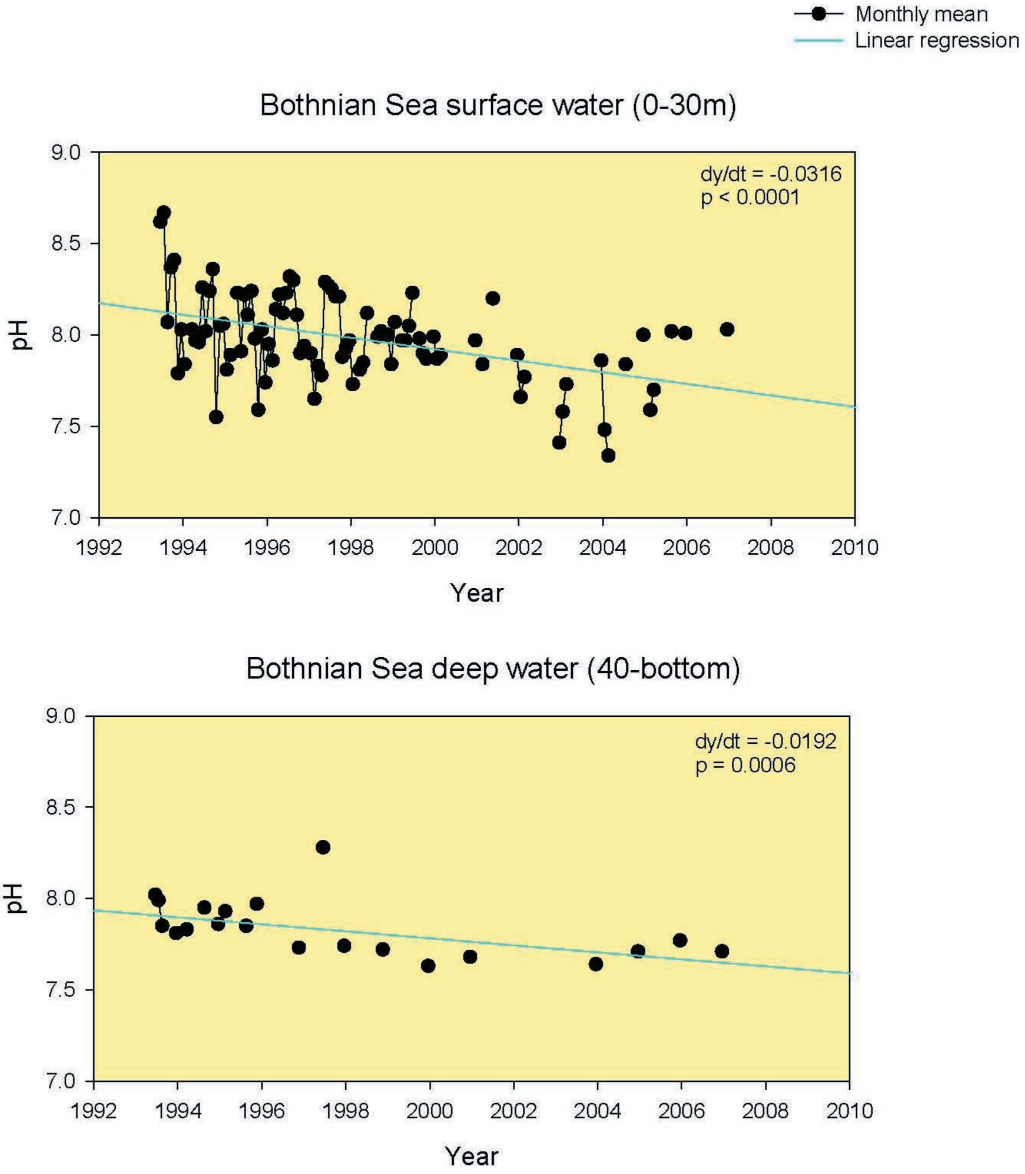
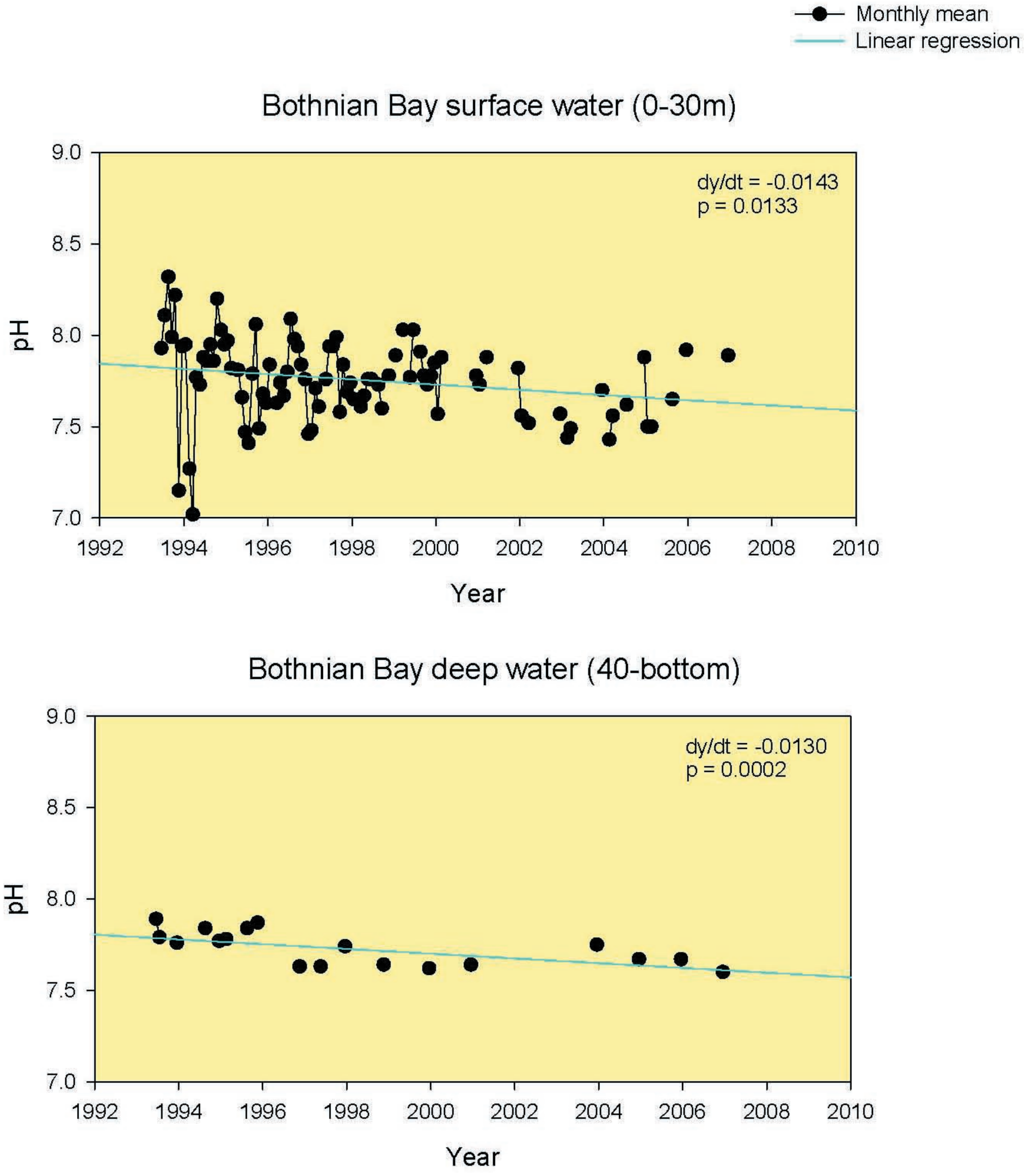


Figure 17. Time series of pH in the Bothnian Sea. Trends calculated using linear regression.


Bothnian Bay surface water (0-30m)

Bothnian Bay deep water (40-bottom)

Figure 18. Time series of pH in the Bothnian Bay. Trends calculated using linear regression.

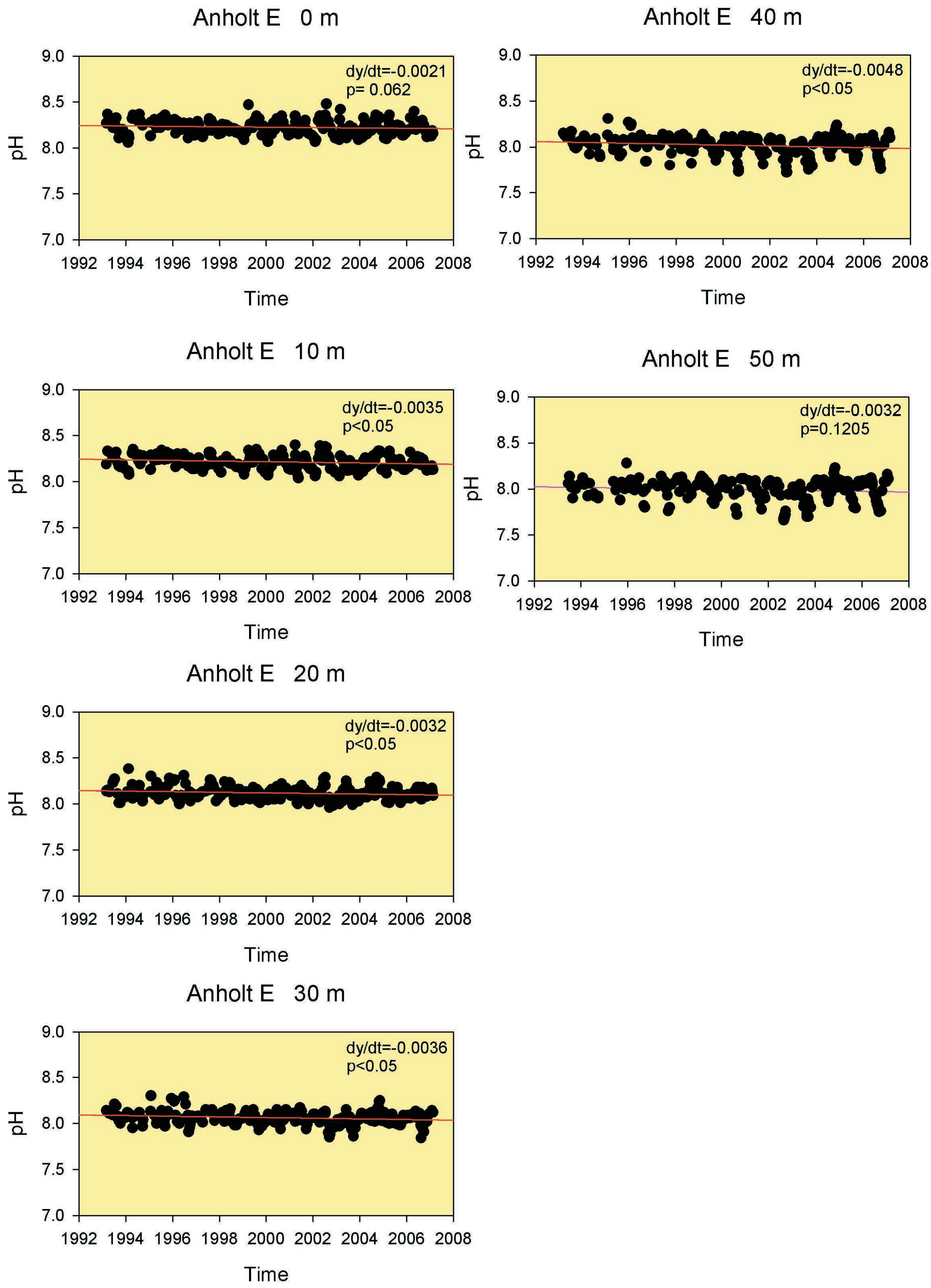


Figure 19. Time series of pH at Anholt E, increased depth scale. Trends calculated using linear regression.

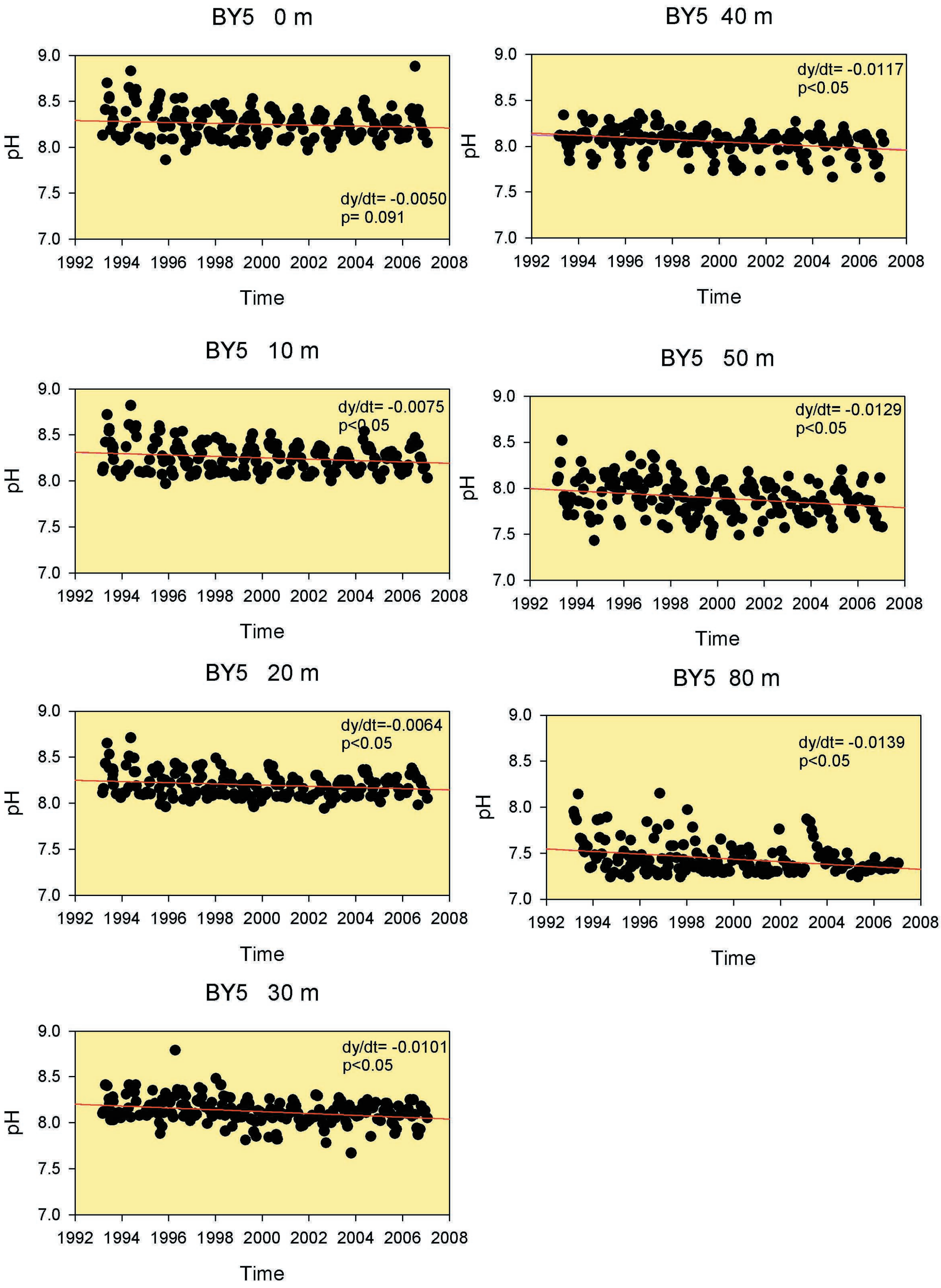


Figure 20. Time series of pH at BY5, increased depth scale. Trends calculated using linear regression.

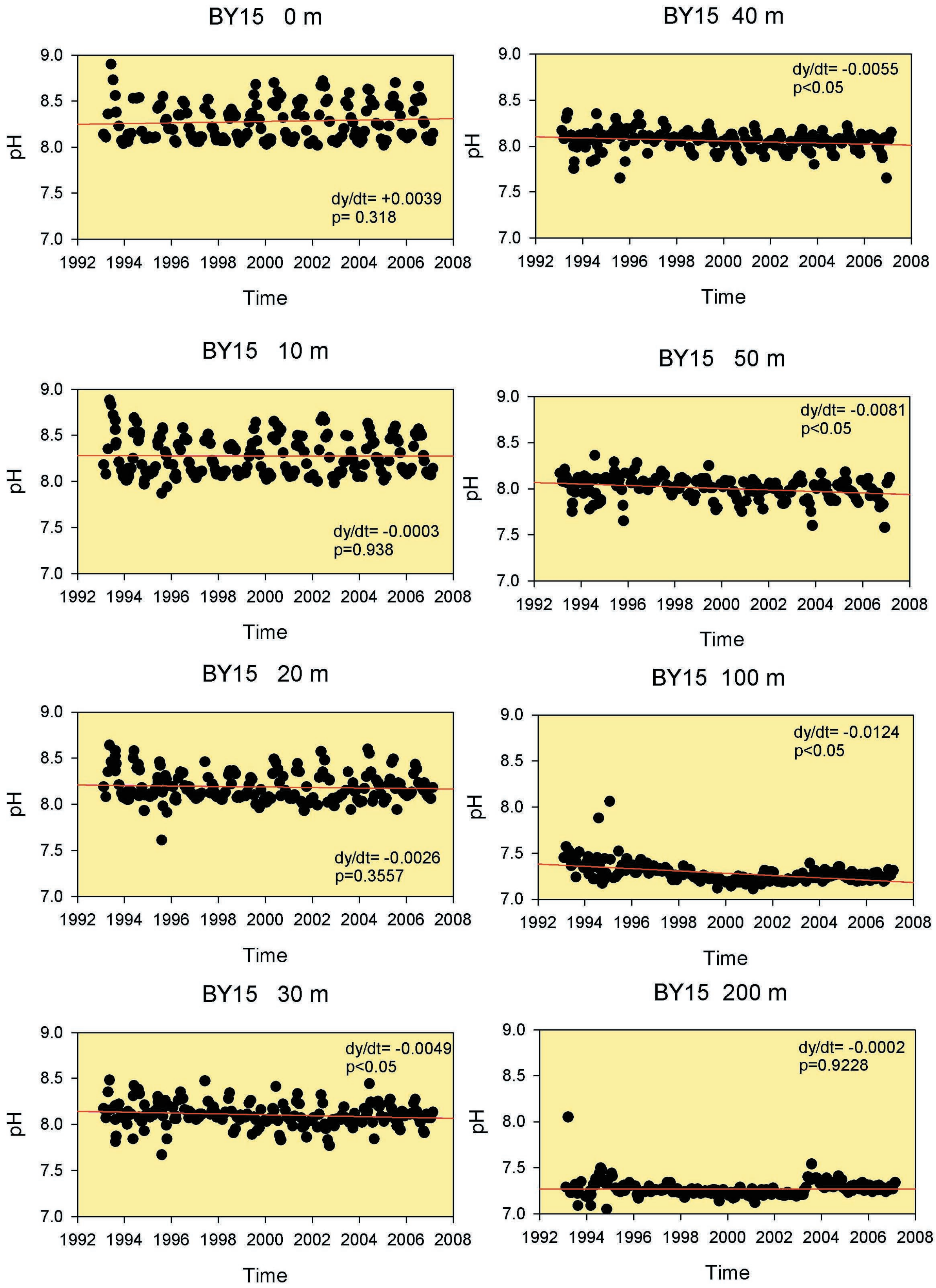


Figure 21. Time series of pH at BY15, increased depth scale. Trends calculated using linear regression.

APPENDIX II

FIGURES OF SPATIAL AND TEMPORAL ANALYSIS FROM SAMPLING STATIONS

Spatial analysis

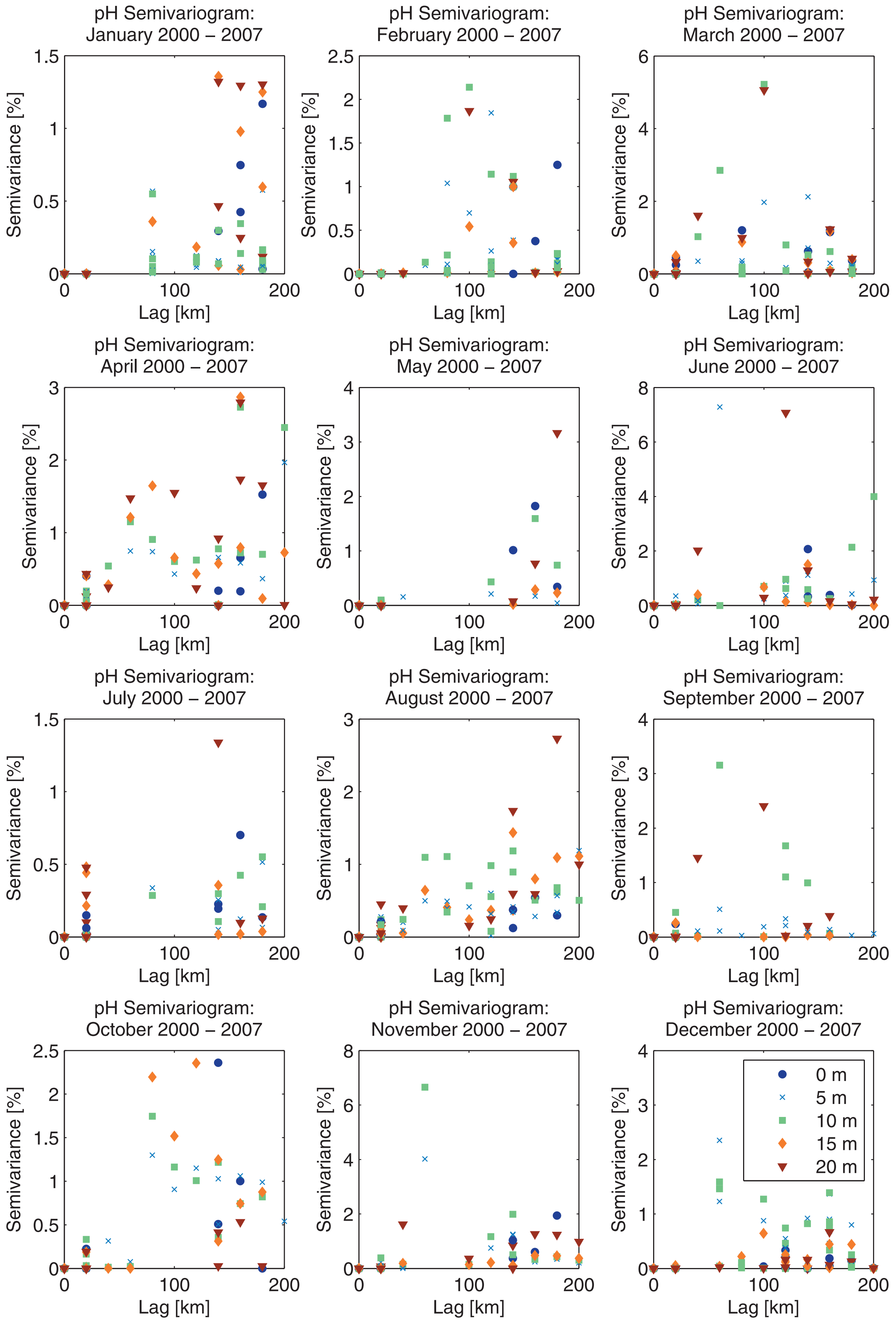
All SHARK pH data has been included in the analysis. The data is normalized and separated into different depths and months. The distance is on the x-axis and the semivariance on the y-axis. If the semi variance is zero, the stations are identical, if the semivariance is high, the difference is high. The calculations represent open sea stations since there is not sufficient data to analyze costal stations.

Interpretation of plot:
Find a plateau where the maximum values have levelled out. The distance between stations is half the distance to where the maximum values have started to level out. The plots are very noisy, but an estimation representing all months is that stations at sea, partitioned more than 50 km are independent of each other. To ensure independent stations, the distance is recommended to 50-100 km.

Temporal analysis

Only Anholt has been used. Both Swedish and Danish measurements have been used which has resulted in up to several measurements per day. The plot is separated over depth.

Interpretation of plot:
The curve increases until it levels out (a lot of noise makes the interpretation more difficult). For the top layers the levelling out starts after 40-50 days. The remaining layers level out after 50 days or more. Use the surface level since it has the most variability. If the levelling out starts after 40-50 days, 20-25 days (half) will represent the frequency. Attempts to similar analyses were made at Örefjärden, but the results were not obvious. Anholt is expected to have as large or larger variability compared to remaining open sea stations in the Baltic, the Kattegat and the Skagerrak hence this station can be used to represent the open sea stations in the temporal analysis. Similar calculations for costal stations were not made due to insufficient data.



pH Semivariogram: January 2000 – 2007

pH Semivariogram: February 2000 – 2007

pH Semivariogram: March 2000 – 2007

pH Semivariogram: April 2000 – 2007

pH Semivariogram: May 2000 – 2007

pH Semivariogram: June 2000 – 2007

pH Semivariogram: July 2000 – 2007

pH Semivariogram: August 2000 – 2007

pH Semivariogram: September 2000 – 2007

pH Semivariogram: October 2000 – 2007

pH Semivariogram: November 2000 – 2007

pH Semivariogram: December 2000 – 2007

Figure 22. Spatial analysis. Semivariogram at different depths and months. All SHARK pH data included.

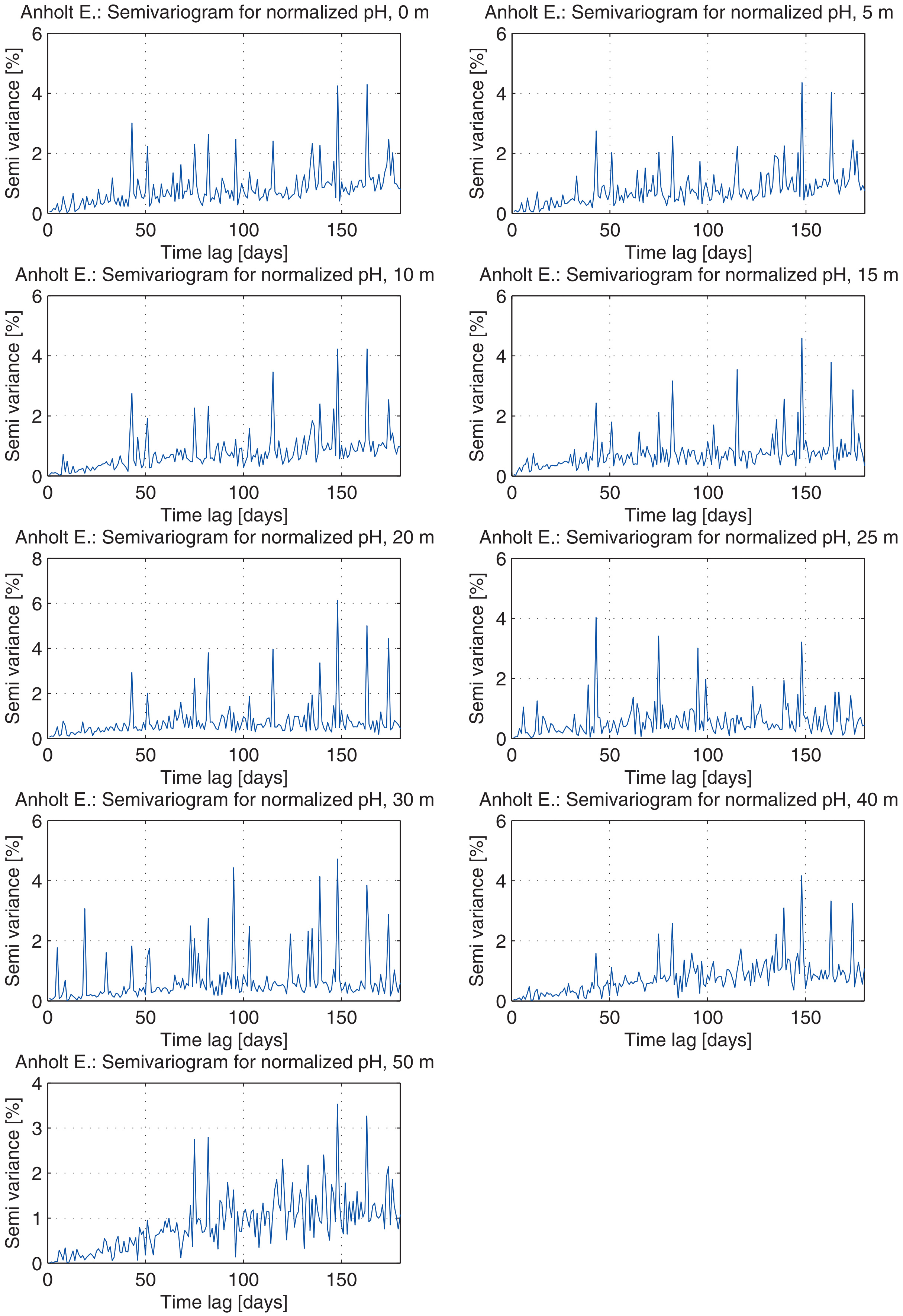


Figure 23. Temporal analysis. Semivariogram at different depths of normalized pH values at Anholt 1990 to 2008.

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Slutrapport för perioden
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Recipientkontroll vid Breviksnäs fiskodling 1987.

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ISSN 0283-7714