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Linking process rates with modelling data and ecosystem characteristics

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Front cover: View on Bornö institute for ocean and climate studies. Bornö Station is a marine research station on the island of Stora Bornö in Gullmar Fjord, Bohuslän, on the Swedish West Coast. The complex was built in 1902 by Gustaf Ekman and Otto Pettersson and has been called the cradle of Swedish marine research (<http://www.bornoinstitute.o.se>).

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Summary

This report is related to the BONUS project “Nutrient Cocktails in COAstal zones of the Baltic Sea” alias COCOA. The aim of BONUS COCOA is to investigate physical, biogeochemical and biological processes in a combined and coordinated fashion to improve the understanding of the interaction of these processes on the removal of nutrients along the land-sea interface. The report is especially related to BONUS COCOA WP 6 in which the main objective is extrapolation of results from the BONUS COCOA learning sites to coastal sites around the Baltic Sea in general. Specific objectives of this deliverable (D6.4) were to connect observed process rates with modelling data and ecosystem characteristics.

In the report we made statistical analyses of observations from BONUS COCOA study sites together with results from the Swedish Coastal zone Model (SCM). Eight structural variables (water depth, temperature, salinity, bottom water concentrations of oxygen, ammonium, nitrate and phosphate, as well as nitrogen content in sediment) were found common to both the experimentally determined and the model data sets. The observed process rate evaluated in this report was denitrification. In addition regressions were tested between observed denitrification rates and several structural variables (latitude, longitude, depth, light, temperature, salinity, grain class, porosity, loss of ignition, sediment organic carbon, total nitrogen content in the sediment, sediment carbon/nitrogen-ratio, sediment chlorophyll-a as well as bottom water concentrations of oxygen, ammonium, nitrate, and dissolved inorganic phosphorus and silicate) for pooled data from all learning sites.

The statistical results showed that experimentally determined multivariate data set from the shallow, illuminated stations was mainly found to be similar to the multivariate data set produced by the SCM model. Generally, no strong correlations of simple relations between observed denitrification and available structural variables were found for data collected from all the learning sites. We found some non-significant correlation between denitrification rates and bottom water dissolved inorganic phosphorous and dissolved silica but the reason behind the correlations is not clear.

We also developed and evaluated a theory to relate process rates to monitoring data and nutrient retention. The theoretical analysis included nutrient retention due to denitrification as well as burial of phosphorus and nitrogen. The theory of nutrient retention showed good correlations with model results. It was found that area-specific nitrogen and phosphorus retention capacity in a sub-basin depend much on mean water depth, water residence time, basin area and the mean nutrient concentrations in the active sediment layer and in the water column.

Keywords: Coastal zone, Eutrophication, Biogeochemistry, Nutrient retention.

Contents

1. Introduction	6
2. Methods	8
2.1 The model data	8
2.2 The statistical approach	10
2.3 Theoretical modeling of nutrient retention	13
3. Results and discussion.....	17
3.1 Statistical analysis.....	17
Description of data	17
Data analysis	20
3.2 Theory.....	33
Importance of physical characteristics on nutrient retention.....	33
Biogeochemical impact on nutrient retention	34
Regional differences in nutrient retention	34
Theory related to monitoring.....	38
3.3 Other evaluations not shown	40
3.4 The benthic primary production	40
4. Conclusions	42
5. Acknowledgement.....	43
6. References	44
7. Appendix	45
Some model characteristics	45

1. Introduction

The work in this report, Deliverable (D) 6.4 is related to work package (WP) 6 in the BONUS project “Nutrient Cocktails in COAstal zones of the Baltic Sea” alias COCOA. The aim within the BONUS COCOA is to investigate physical, biogeochemical and biological processes in a combined and coordinated fashion to improve the understanding of the interaction of these processes on the removal of nutrients along the land-sea interface. The results from the project will be used to estimate nutrient retention capacity in the coastal zone of the entire Baltic Sea coast. Retention studies from the project have been published e.g. by Almroth et al. (2016) who performed a modelling study of nutrient retention in the Stockholm archipelago and by Asmala et al. (2017) who compiled removal rates from coastal systems around the Baltic Sea and analyzed their spatial variation and regulating environmental factors.

In BONUS COCOA WP 6, the main objective is extrapolation of results from the learning sites to coastal sites around the Baltic Sea in general. Specific objectives of D6.4 are to connect observed process rates with modelling data and ecosystem characteristics. The aim is to combine information from observed process rates from WP2 to WP4 and from modelling efforts in WP5 to investigate if there are any statistical relations that link process rates with general characteristics obtained from analyses of monitoring data. Most measurements made available for this study have been performed in shallow areas including the illuminated bottoms. A few observed process rates (denitrification) were also available from some deeper non-illuminated locations, the Öre and Vistula estuaries as well as in the Tvärminne archipelago. No monitoring data from the study sites were available for the analysis at the time for the field observations. We therefore focused on the examination of relations between modeled state variables and modeled rates. The model data that have been used for the statistical analysis are extracted results from the Swedish Coastal zone Model (SCM) that cover the entire Swedish Coastal area with 653 sub-basins as described in the BONUS COCOA project D5.1 published as an oceanographic report at SMHI (Eilola et al. 2015). Almroth-Rosell et al. (2016) used the SCM model to discuss modelling of nutrient retention in the Stockholm archipelago.

Eight structural variables were found common to both the experimentally determined and the model data sets. The observed process rate evaluated in this report was denitrification. The statistical approach utilizes Principal Components Analysis (PCA) to investigate resemblance in characteristics and denitrification between observed data from the learning sites and modelled sub-basins. In addition regressions were tested between observed denitrification rates and several structural variables.

As a complement to the statistical efforts a theoretical analysis was evaluated against the results from the SCM model. The aim was to further investigate and describe the potential links between process rates and nutrient retention to ecosystem characteristics and monitoring data. The analysis included nutrient retention due to denitrification as well as burial of phosphorus (P) and nitrogen (N). Retention of nutrients supplied to a sub-basin can be temporal or permanent as discussed in more detail by Almroth-Rosell et al. (2016). Permanent retention removes the supplied nutrients permanently from the coupled benthic-pelagic biogeochemical cycling under the time scales considered. The temporal retention, i.e. changes in the storage of nutrients that are still active in the biogeochemical cycling during a studied period, can be negative or positive depending on changes in the pelagic and benthic inventory of nutrients. Burial is the only retention process that permanently removes P. For N, in addition to burial, benthic and pelagic denitrification is also defined as permanent retention. Nitrogen fixation adds N and can thereby influence the net N-removal. In the present study,

we focus on the permanent retention efficiency of nutrient supplies defined as the internal loss divided by the total supplies of N and P from land, air and surrounding seas to each water body. In addition, we also calculate the area-specific permanent retention efficiency.

2. Methods

2.1 The model data

SMHI has developed a model system called the Swedish Coastal zone Model (SCM) for water quality calculations in the coastal waters around Sweden. The SCM calculates the state of the water bodies along the entire Swedish coast which is divided according to the Swedish water districts into 5 different parts, and one water district is further divided in 4 parts, resulting in 8 evaluated areas (Fig. 1). The names and the number of sub-basin in each area are; the Bothnian Bay 113 sub-basins, the Bothnian Sea 85 sub-basins, the northern Baltic Sea 167 sub-basins, the Östergötland coast 47 sub-basins, the Småland coast 55 sub-basins, the Gotland coast 21 sub-basins, the Skåne-Blekinge coast 52 sub-basins, and finally, the West coast has 113 sub-basins. The hydro-dynamical part of the SCM model calculates with high temporal resolution (10 minutes time step for hydrodynamics) changes in the physical characteristics, including e.g. diurnal variations, freshwater and nutrient supplies, water exchanges and transports of substances between the sub-basins. The biogeochemical model coupled to SCM calculates the changes (1 hour time step for the biogeochemistry) caused by biogeochemical sources and sinks in the sub-basins. The model is described in more detail in D5.1 (Eilola et al. 2015) and in the paper by Almroth-Rosell et al. (2016).



Figure 1. The eight different water districts of the SCM model domain.

In the present study, we used SCM data from the 5-year period 2010-2014 for the statistical analysis of model results in comparison with observed process rates. The model output is vertically integrated instantaneous values for each basin that are given at 7 days intervals, plus additional output at the beginning and end of each month. All modeled process rates are summarized during 24 hours. They are thus not representative for day or night time separately. Note also that even when observed data are from a specific depth range, the model

data are still vertically integrated over the entire depth of the water body. This affects the direct comparison with observations since modelled rates from the sediments are averages for the entire area of a sub-basin while the observations are made at specific points within sub-basins. For the evaluation of the theoretical results we used average SCM data for the period 1995-2014. Also these values were vertically integrated.

The different processes that affect retention have been calculated separately, as they are included in the biogeochemical model SCOBI (Almroth-Rosell et al. 2016). In the present report, we calculate permanent retention efficiency, R , from the SCM model as the internal loss divided by the total supplies of nitrogen and phosphorus from land, air and surrounding seas to each water body. In addition, we also calculate the area-specific permanent retention efficiency defined as R/A where A is the area of the sub-basin. The fraction that is retained is presented in % of the supplies. For N , the permanent internal loss is calculated as the sum of burial and net N_2 production (denitrification - N_2 -fixation).

The average rate of water renewal can be estimated from the average age of water (AvA) (Engquist et al. 2006). The water residence time is in the present report calculated as the twenty year mean of the vertical mean AvA in each sub-basin. The concept AvA that has been implemented to the SCM model is described in detail by Engquist et al. (2006). According to their description:

“This variable is reset to zero for water parcels outside the studied domain. The resulting variable (which represents the specific AvA time of the compartments of the actual subdivision of the domain) is increased one time-step unit for each time step the associated water parcel resides in the domain. In addition to aging, the water parcel is also being subjected to passive tracer advection and diffusion. In time, a quasi-steady state between aging (by remaining in the domain) and rejuvenation (by replacing aged water with new water of zero age) will occur.”

2.2 The statistical approach

The main aim of the present statistical approach was to investigate whether characteristics of observational data gathered at the study sites of BONUS COCOA are represented within the ensemble of modelled sub-basins. At the time when this report is produced there is neither monitoring data nor model results available for the times when observations of process rates are performed within the BONUS COCOA project. This is due to the lack of present forcing conditions for the models since none of the models are run in near-real-time operational mode. On the other hand, a very extensive number of numerical experimental sub-basins were made available for the analysis from the SCM model, but these data do not include areas which were covered by the experimental data made available for the report. The potential to study relations between “modelled monitoring data” and process rates in the large amount of model results is, however, large. We will therefore investigate if the observed environmental characteristics at the study sites fall within the range of the SCM model results. If so, the statistical analysis will support the potential generality of the conclusions we can get from the theoretical study.

The data set available from experimental efforts was compared with output from the SCM model in uni- and multivariate analyses. From a larger data set made available from the SCM model eight structural variables were common to both the experimentally determined and the model data sets: water depth, temperature, salinity, bottom water concentrations of oxygen, ammonium, nitrate and phosphate, as well as N content in sediment. The process rate evaluated in this report was denitrification, which was experimentally determined by ^{15}N -amendments. To investigate potential simple relations regression analyses (linear and quadratic) were performed with the experimental data set between observed denitrification rates and simultaneous observations of different structural variables (latitude, longitude, depth, light, temperature, salinity, grain class, porosity, loss of ignition (LOI), sediment organic carbon, total nitrogen content in the sediment, sediment carbon/nitrogen ratio (C/N-ratio), sediment chlorophyll *a* (Chl-*a*) as well as bottom water concentrations of oxygen (O_2), ammonium (NH_4), nitrate (NO_3), and dissolved inorganic phosphorus (DIP) and silicate (DSi) for pooled data from all learning sites.

PCAs were performed in Simca (v. 14.0, Umetrics AB, Sweden) to compare observed data with model data in terms of structural variables and denitrification. Where appropriate, variables were log transformed. The variables were mean centered and scaled to unit-variance. The models were diagnosed by R^2 and Q^2 , measuring model fit (R^2) and percent of the variation of the data that can be predicted by the model as calculated by cross validation (Q^2) (Eriksson et al., 2006). Initial analyses included all eight structural variables common to both data sets. Subsequent analyses were run on a subset of structural variables.

Although there were missing data in the experimentally determined variables, five study sites were considered to include sufficient information to run the analyses; Curonian Lagoon, Roskilde Fjord, Puck Bay, Tvärminne and Vistula Estuary (Table 1). Stations included from the Curonian Lagoon were sampled during all seasons in 2014 and 2015. From Roskilde Fjord three stations sampled in autumn 2015 were included. Data from two Puck Bay stations were collected during three seasons (2015-2016). At the Tvärminne study site, two illuminated stations were sampled in spring, summer and autumn and two deeper, non-illuminated stations were sampled monthly from spring to autumn in 2015 and 2016. Vistula stations were sampled during three seasons in 2014-2016 (Table 1).

The shallower, illuminated stations and the deeper, non-illuminated stations were analyzed separately as initial analysis indicated different characteristics for observed data. The illuminated stations were evaluated together with model sub-basins with a maximum depth of

10 m, which included 129 sub-basins in total. The 24 and 33 m Tvärminne and Vistula Estuary stations were modelled with 121 sub-basins with a maximum depth of 23 to 34 m. PCA was run on all sub-basins within the depth range along the Swedish coast as well as on each of the five Swedish Water Districts (as defined by the County Administrative Boards) for a more detailed analysis.

Table 1. Name of the stations and their depth, light condition and time period for the field work for the observation data used in the PCA and for the correlation tests. The data set was not complete from all study sites and the missing variables are indicated in the table. Data from stations not used in the PCA, but used in the correlation tests are shown in the end of the table (Vistula Estuary and Öre Estuary Corr.tests).

Study site	Station	Depth (m)	Illuminated	Year	Seasons	Missing variables
Curonian Lagoon	Litoral	1	Yes	2014-2015	All	Sal(partly), Denitr
	Vidmares	2	Yes	2014-2015	All	“
	Nida	4	Yes	2014-2015	All	“
Roskilde Fjord	Station 60	5	Yes	2015	Autumn	Temp, Sal, Ntot
	Zostera	2	Yes	2015	Autumn	“
	Sand	2	Yes	2015	Autumn	“
Puck Bay	Sand	2	Yes	2015, 2016	Spring/summer/autumn	
	Sand	5	Yes	2015, 2016	Spring/summer/autumn	
Tvärminne	Mud	2	Yes	2015, 2016	Spring/summer/autumn	Sal,Denitr, Ntot(partly)
	Sand	3	Yes	2015, 2016	Spring/summer/autumn	“
	Storfjärden	24	No	2015, 2016	Monthly, spring-autumn	Ntot
	i30	33	No	2015, 2016	Monthly, spring-autumn	“
Vistula Estuary	VE02	20	No	2015, 2016	Winter/spring	Ntot, NH4(partly), Denitr
	VE05	22	No	2014, 2015, 2016	Summer/winter/spring	Ntot, Denitr(partly)
	VE10	22	No	2015	Winter	Ntot, Denitr
	VE18	24	No	2014, 2016	Summer/spring	Ntot, NH4(partly), Denitr(partly)
	VE49a	26	No	2014, 2016	Summer /spring	Ntot
	VE13	28	No	2014, 2015, 2016	Summer/winter/spring	Ntot, Denitr(partly)
	VE09	29	No	2014, 2015, 2016	Summer/winter/spring	Ntot
	VE06	34	No	2015, 2016	Winter/spring	Ntot, Denitr(partly)
Vistula Estuary Corr.tests	VE04	13	No	2016	Spring	
	VE03	16	No	2014	Summer	
	VE15	43	No	2014, 2016	Summer /spring	
	VE46	48	No	2014	Summer	
	VE07	51	No	2016	Spring	
	VE38	68	No	2014, 2016	Summer/spring	
	VE43	94	No	2014	Summer	
	TF0233	104	No	2014	Summer	
Öre Estuary Corr.tests	N3	17	No	2015	Spring	
	N5	17	No	2015	Summer	
	N34	17	No	2015	Summer	
	N6	18	No	2015	Spring	
	N7	19	No	2015	Summer/Spring	
	N8	19	No	2015	Spring	
	N10	21	No	2015	Summer/Spring	
	N11	24	No	2015	Summer	
	N14	37	No	2015	Summer/Spring	
	NB8	35	No	2015	Summer/Spring	

2.3 Theoretical modeling of nutrient retention

In order to further understand the links between process rates and nutrient retention to ecosystem characteristics we formulate a theoretical concept to support the analysis. The aim is to describe the most important relations between nutrient retention efficiency in a coastal area and the environmental conditions that potentially can be related e.g. by statistical methods to processes both observed in-situ and described by model results.

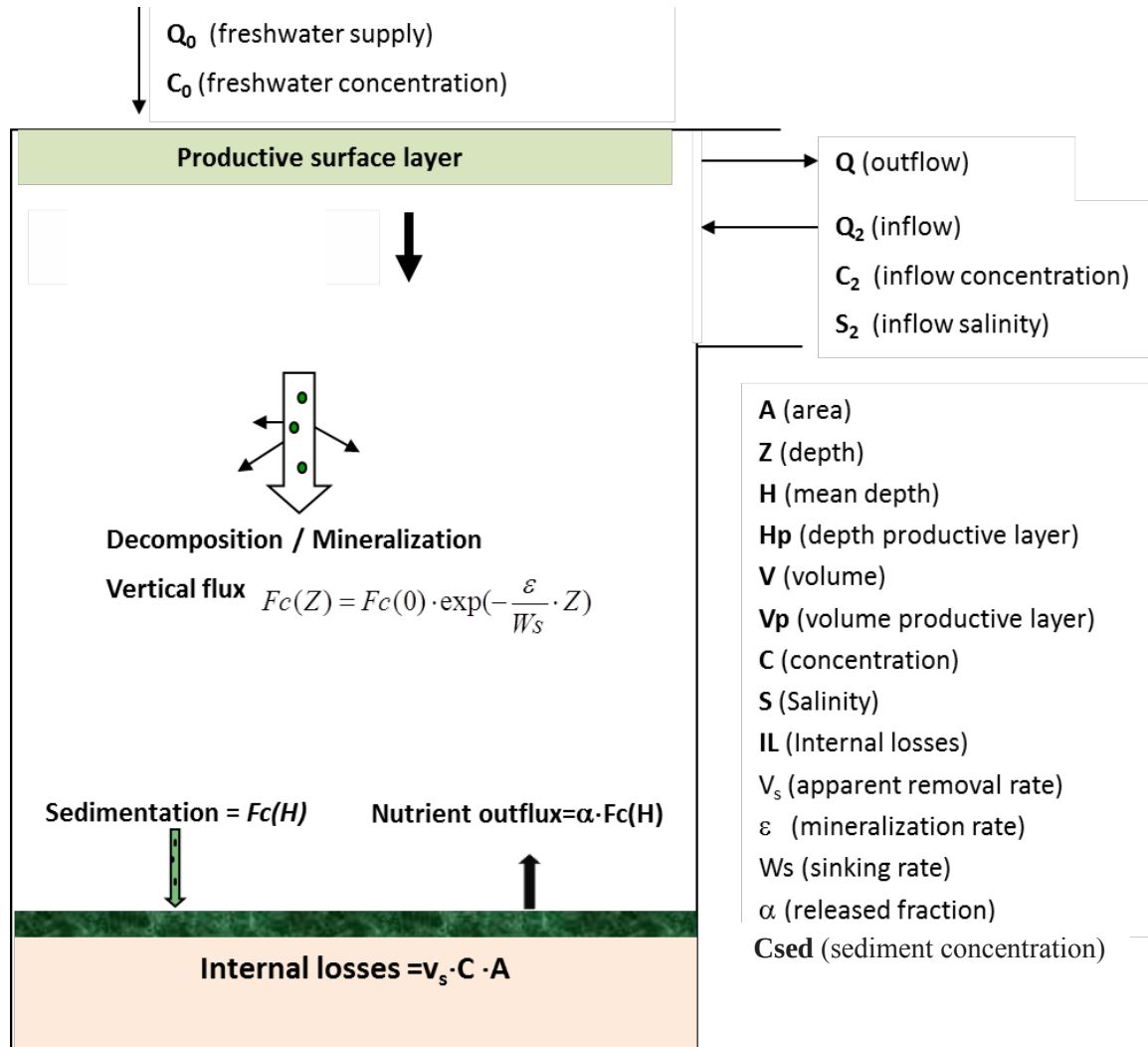


Figure 2. Schematic figure of the well-mixed basin and important biogeochemical processes. The freshwater nutrient concentrations are assumed to include also supplies from atmosphere and point sources in the freshwater nutrient supply. Internal losses are assumed mainly to take place at the sea floor.

For this we assume a well-mixed basin with a flat bottom with area (A) that is supplied with a bioactive tracer, with the freshwater from land and with inflowing water from the adjacent sea (Fig. 2). The bioactive tracer may be exported to the adjacent sea and also be removed due to internal losses (Wulff and Stigebrandt, 1989). Especially, we investigate the functioning of permanent internal losses (IL) and retention efficiency (R) in a case study where the bioactive tracer is a nutrient (nitrogen or phosphorus) also used for primary production of organic

matter in a productive layer at the surface of the sea. Production may also take place at the sea-floor if the productive layer extends down to the bottom of the sub-basin.

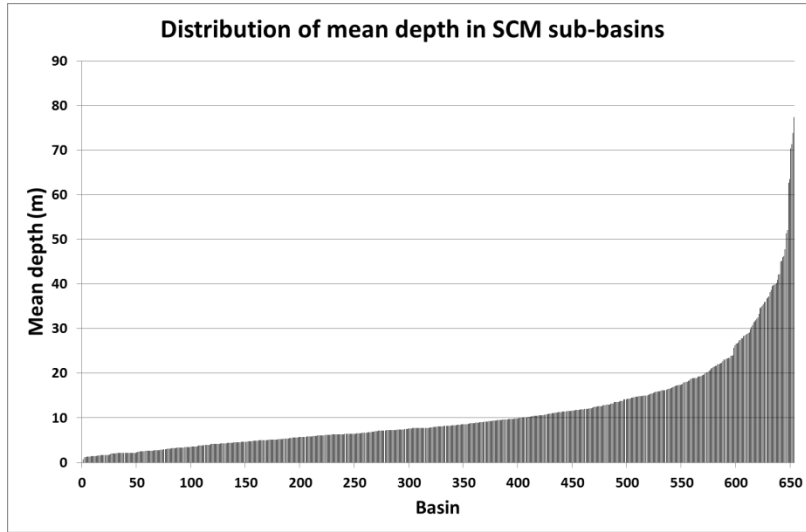


Figure 3. The distribution of mean depth (m) in the 653 sub-basins of the SCM model.

In quite many sub-basins of the SCM light may potentially reach the bottoms (Fig. 3). One should note that the production taking place at the seafloor on illuminated sediments is not explicitly described in the SCM model which the theory is evaluated against. This production is, however, at least partly compensated for by the pelagic production and sedimentation taking place in the shallow areas of the model. See further discussion in section 3.4.

The retention efficiency describes how large fraction of the supplied nutrients is removed within a sub-basin. Since we focus on shallow coastal areas we assume that the internal loss of the bioactive tracer mainly is due to permanent loss of nutrients in the sediment caused e.g. by burial and/or denitrification.

The basis for the analysis is the mass conservation equation where changes in the pools depend on nutrient supplies, exports and the internal losses. For simplicity we investigate the steady state conditions where changes in the nutrient pools are assumed small. In accordance with Wulff and Stigebrandt (1989) we first use the concept of apparent removal rate V_s . I.e., a fraction of the bioactive tracer mass in the water is removed with an apparent removal rate V_s caused by the internal losses ($IL = V_s \cdot C \cdot A$) where C is the mean nutrient concentration.

We use mass conservation (Eq.1) and assume a steady state to calculate the concentration C (Eq.2) and a definition of retention efficiency (Eq.3), defined as the ratio between internal loss and inflowing amount of the tracer (Almroth-Rosell et al. 2016), to derive (not shown) equation (Eq.4) that describes R as a function of mean depth (m), water residence time (days) and apparent removal rate (m day^{-1}).

$$V \cdot \frac{dC}{dt} = Q_0 \cdot C_0 + Q_2 \cdot C_2 - Q \cdot C - IL \quad (1)$$

Where V is the volume of water in the basin, dC/dt the change in concentration of the nutrient with time, Q_0 is the freshwater supply from land and C_0 is the concentration of the of the

nutrient in the inflowing freshwater (including here also the supplies from atmosphere and point sources), Q_2 is the inflowing water from an adjacent basin, C_2 the concentration of the nutrient in the inflowing water, Q is the outflowing water and C the mean concentration of the nutrient in the basin, thus, also in the outflowing water.

$$C = \frac{Q_0 \cdot C_0 + Q_2 \cdot C_2}{Q + V_s \cdot A} \quad (2)$$

$$R \equiv \frac{IL}{Q_0 \cdot C_0 + Q_2 \cdot C_2} \quad (3)$$

$$R = \frac{1}{1 + \frac{H}{V_s \cdot \tau}} \quad (4)$$

H is the mean depth and τ is the water residence time defined by:

$$\tau = \frac{V}{Q} \quad (5)$$

Because the retention is dependent on the extension of the sub-basin area (Almroth-Rosell et al. 2016) we also calculate the area-specific permanent retention efficiency, where the internal loss is divided by the area of the sub basin. The area-specific retention efficiency is therefore calculated as R/A where A is the area of the actual sub basin. This corresponds to the internal loss per area unit which gives a better comparison between the different sites regardless of their spatial extension.

Since internal losses are assumed to take place mainly at the sea floor in these shallow areas the apparent removal rate is related to the benthic loss rate Blr (day^{-1}) in the sediment $IL = V_s \cdot C \cdot A = Blr \cdot C_{sed} \cdot A$. Thus, V_s is then given as a function of the mean concentrations in the sediment C_{sed} (mmol m^{-2}) and in the water column C (mmol m^{-3}) which relate to measurable quantities in monitoring programs (Eq.6).

$$V_s = Blr \cdot \frac{C_{sed}}{C} \quad (6)$$

Here the benthic loss rate is related to the deposition of bioactive tracer to the sediment $F_c(H)$ and the benthic release rate (Brr) through Eq.7.

$$Blr = \frac{F_c(H)}{C_{sed} \cdot A} - Brr \quad (7)$$

Equation 7 is dependent on many local factors such as the supplies to the sub-basin, the productivity and mineralization in the basin which depend on the temperature, salinity oxygen and potentially other factors as well. The fact that the systems are dynamic and changing in time also will have some impact on Eq.7. The theoretical results are evaluated with model results from SCM (Table 2). See further description of model characteristics in Appendix.

Table 2. The parameters extracted from SCM model results and used for the evaluation of theory. The total number of sub-basins is 653.

Parameter		Unit
H	Mean depth	m
V	Basin volume	m ³
A	Basin area	m ²
N	total pelagic N content	ton
P	total pelagic P content	ton
Tau	IAVA residence time	days
NBT	total sediment N content	ton
PBT	total sediment P content	ton
R	retention efficiency	(%)

3. Results and discussion

3.1 Statistical analysis

Description of data

Measurements made available for this study have been performed both in shallow areas with illuminated bottoms (Curonian Lagoon, Roskilde Fjord, Puck Bay, Tvärminne) and in deeper non-illuminated locations (Tvärminne, Öre and Vistula estuaries). The data from illuminated bottoms have been analyzed and described in detail in the BONUS COCOA D3.1 and D3.3. Below we only briefly repeat the description of the data from study sites that is summarized e.g. in Table 1 of D3.3. The majority of learning sites were sandy while only two 5-m stations, in Curonian lagoon and Roskilde fjord, were muddy.

Bottom water oxygen concentrations were in general close to saturation and closely related to salinity, temperature and content of Chl-a in the sediment. For inorganic nutrients, lowest bottom-water concentrations were found in Tvärminne, while highest concentrations were observed in Curonian lagoon, Puck Bay and Roskilde Fjord.

A multivariate principal component analysis did not distinctly separate the learning sites. However, there seemed to be a progressive gradient so that stations were grouped in order of increasing organic content of the sediment. Gradients also appeared within the learning sites in order of increasing organic content of the sediment. In Curonian Lagoon, extraordinary high concentrations of nitrate and silicate were found in the bottom water.

Below we add descriptions of data from deeper stations as well as data extracted from the SCM model.

At the Tvärminne deep stations the LOI at the sandy station i30 (porosity 0.4) was lower, on average 0.9% (std 0.1), compared to that at the muddy station Storfjärden (porosity 0.94) where the LOI on average was 15 % (std 1.8). Thus, the variation of porosity was larger compared to the shallow stations in Tvärminne, which had a porosity of about 0.5 and 0.8. Both the deep stations were oxygenated with higher oxygen concentrations during spring compared to autumn. Denitrification rates were measured during summer and autumn and were low compared to the shallow stations in Roskilde Fjord and Puck Bay (discussed below). The ammonium, nitrate and phosphorus concentrations were higher ($[\text{NH}_4^+] < 2.6 \mu\text{M}$, $[\text{NO}_3^-] < 3.5 \mu\text{M}$, and $[\text{DIP}] < 1.19 \mu\text{M}$) at the deeper stations compared to the shallower ($[\text{NH}_4^+] < 1.0 \mu\text{M}$, $[\text{NO}_3^-] < 0.76 \mu\text{M}$, $[\text{DIP}] < 0.29 \mu\text{M}$) stations in Tvärminne (D3.1).

At the Vistula Estuary, 16 stations from land towards sea were visited. The depth ranged from 13 to 104 m (Table 1). Most of the stations were sandy with a low porosity (0.33-0.77), but the four deepest stations (VE46, VE38, VE43 and TF0233) were muddy with higher porosity (0.70-0.97). LOI were measured during spring and highest value was found at the deeper stations (17.49 % at station VE38). The oxygen concentrations were about 25% lower during summer compared to spring. The lowest concentrations of oxygen were found in summer at the two deepest stations ($[\text{O}_2] < 75 \mu\text{M}$). Denitrification rates were about twice as high during summer compared to spring. Highest concentrations of ammonium were observed during summer, $[\text{NH}_4^+] < 8.7 \mu\text{M}$, with lowest concentrations in the two deepest stations ($[\text{NH}_4^+] < 0.19 \mu\text{M}$), while the spring values were less than $2.1 \mu\text{M}$. For nitrate the concentrations were lower during summer ($[\text{NO}_3^-] < 3.2 \mu\text{M}$) at all stations except the two deepest ones where $[\text{NO}_3^-] < 7.8 \mu\text{M}$. During spring the bottom water concentrations of nitrate varied between 2.5-7.8 μM . The average concentrations of phosphorus was in the range of

0.61-2.13 during spring and 0.46-1.49 during summer with the average values of 0.91 (std 0.46) and 0.98 (std 0.3), respectively.

At the Öre Estuary, 10 stations were visited. The depth ranged from 17m to 37m. Porosity varied from 0.4 to 0.9 and LOI varied between 0.3 % and 9.2 % with no clear depth dependence. Apart from porosity and LOI only grain size was available from Öre Estuary. Denitrification (only August) values varied in the range 0.10 and 0.17 mmol m⁻² d⁻¹.

Two large datasets with several variables were extracted from the SCM model for the statistical analysis even though only a few parameters were found comparable to the observational data set. There were 129 sub-basins with a maximum water depth of 10 m from which ~47000 data points were extracted. Around 44000 data points were extracted from the 121 sub-basins with a maximum water depth of 22-34 m. For the curious reader the statistical properties of all the model data from shallow basins are shown in Table 3 and table 4.

For comparison of processes related to the permanent removal of nutrients we also show similar statistics based on the data of denitrification rates made available from the study sites (Table 5). Burial rates for comparison were not available for the present report. The mean denitrification value of the SCM model (0.58 mmol m⁻² day⁻¹) and the median (0.17 mmol m⁻² day⁻¹) from shallow basins (Table 4) is in the range of the mean SANBALTS model results (0.07 - 0.84 mmol m⁻² day⁻¹) and earlier measurements (0.01 - 1.86 mmol m⁻² day⁻¹) summarized by Savchuk and Wulff (2009) in their Table 6, as well as in the range of the mean BALTSEM model results (0.09 - 0.77 mmol m⁻² day⁻¹) presented by Savchuk et al. (2012). The results were also in the range of measurements from other studies in the Bothnian Bay, Bothnian Sea, Gulf of Finland, and Baltic Proper where the range varied between 0 - 1.2 mmol m⁻² day⁻¹ (Deutsch et al., 2010, and references therein).

The median and mean of denitrification measurements within BONUS COCOA are higher than those of the SCM model. It seems from the evaluation that the observed denitrification rates in the shallow parts of the Roskilde Fjord and Puck Bay area (Table 5) are quite high when compared both to the SCM model results and also when compared with the other data sources. These high values also affect the mean value of all data in Table 5 which becomes significantly higher than the median value. The maximum extreme value of denitrification rate in the SCM model output used here was 74 mmol m⁻² day⁻¹ while the 99% percentile was 6.5 mmol m⁻² day⁻¹, which is within the rates observed in the shallow areas. The driving factors of the modelled extreme value is not known at present but will be investigated in future research.

Table 3. List of structural variables output from SCM model results (2010-2014) extracted for the statistical analysis in shallow basins. The mean, median and standard deviation (std) values for all sub-basins are shown. Besides the basin mean depth, for the statistical analysis temperature, salinity, oxygen, ammonium, nitrate, phosphate and NBT were used.

	Unit	mean	median	std
Secchi depth	m	5.1	5.1	1.6
IAVA residence time	days	11	4.3	25
Temperature	°C	8.2	6.7	7.3
Salinity	g kg ⁻¹	6.6	4.5	6.9
TN pelagic mean total concentration	µmol L ⁻¹	27	22	16
NO ₃ nitrate mean concentration	µmol L ⁻¹	5.8	3.1	10.6
NH ₄ ammonium mean concentration	µmol L ⁻¹	0.39	0.07	1.18
NBT sediment concentration	mmol m ⁻²	332	190	488
TP pelagic mean total concentration	µmol L ⁻¹	0.64	0.58	0.83
PO ₄ phosphate mean concentration	µmol L ⁻¹	0.24	0.15	0.75
PBT sediment concentration	mmol m ⁻²	86	45	120
Bottom water O ₂	µmol L ⁻¹	363	374	59

Table 4. List of output with nitrogen (N) and phosphorus (P) rates from SCM model results (2010-2014) extracted for the statistical analysis in shallow basins. The mean, median and standard deviation values for all sub-basins are shown. For the statistical analysis only sediment denitrification rate was used.

	Unit	mean	median	Std
N permanent burial	mmol m ⁻² day ⁻¹	0.048	0.012	0.477
N sediment denitrification	mmol m ⁻² day ⁻¹	0.58	0.17	1.94
N sediment remineralization	mmol m ⁻² day ⁻¹	1.07	0.33	2.96
N outflux from sediment to water	mmol m ⁻² day ⁻¹	0.48	0.17	1.08
N NO ₃ from water to sediment denitrification	mmol m ⁻² day ⁻¹	0.0025	0.0000	0.1295
N pelagic denitrification	mmol m ⁻³ day ⁻¹	0.0001	0.0000	0.0063
N ₂ fixation	mmol m ⁻³ day ⁻¹	0.020	0.000	0.151
N sedimentation particulate orgN	mmol m ⁻² day ⁻¹	1.08	0.52	2.28
N pelagic assimilation	mmol m ⁻³ day ⁻¹	0.36	0.12	0.85
N pelagic zooplankton excretion	mmol m ⁻³ day ⁻¹	0.0094	0.0012	0.0461
N pelagic decomposition of N-detritus	mmol m ⁻³ day ⁻¹	0.0050	0.0011	0.0180
P permanent burial	mmol m ⁻² day ⁻¹	0.0098	0.0037	0.0196
P sediment remineralization	mmol m ⁻² day ⁻¹	0.060	0.018	0.306
P outflux from sediment to water	mmol m ⁻² day ⁻¹	0.060	0.018	0.306
P sedimentation particulate orgP	mmol m ⁻² day ⁻¹	0.067	0.033	0.143
P pelagic assimilation	mmol m ⁻³ day ⁻¹	0.023	0.008	0.053
P pelagic zooplankton excretion	mmol m ⁻³ day ⁻¹	0.00059	0.00008	0.00288
P pelagic decomposition of P-detritus	mmol m ⁻³ day ⁻¹	0.00031	0.00007	0.00112

Table 5. Mean, median and standard deviation of denitrification rates ($\text{mmol m}^{-2} \text{ day}^{-1}$) from measurements in BONUS COCOA. All data include data from Roskilde Fjord, Puck Bay, Öre estuary, Vistula estuary, and Tvärminne, while shallow areas include data only from Roskilde Fjord and Puck Bay.

	All data	Shallow areas (< 10m)
Mean	2.55	8.04
Median	0.26	5.94
Standard deviation	5.12	7.45

Data analysis

The experimentally determined multivariate data set from the shallow, illuminated stations was found to be similar to the multivariate data set produced by the SCM model (Fig. 4a), although some of the variation in the Curonian Lagoon was not matched by model data. In general, observed data was mostly similar to sub-basins in the three northern water districts (the Bothnian Bay, the Bothnian Sea and the Northern Baltic Sea). Depth, salinity and phosphate concentrations had low R^2 and Q^2 for individual variables which indicated variation not well explained by the model and that these variables were not well predicted by the model (Fig. 4a, bottom panel). A PCA model without these variables produced better fit and predictability ($R^2=0.94$ $Q^2=0.75$ compared to $R^2=0.64$ $Q^2=0.43$) (Fig. 4b). Without e.g. the salinity gradient, Puck Bay and Tvärminne were found in the middle of the data set (Fig. 4b). The position of Roskilde Fjord in relation to the model data can probably be attributed to high denitrification rates while high oxygen and nitrate concentrations as well as high N_{tot} content made some of the Curonian Lagoon measurements outliers compared to the model data.

A preliminary analysis on individual water districts (not shown) revealed possible model sub-basins with characteristics matching those observed at the study sites. For instance, stations in the Curonian Lagoon appeared to have similar characteristics as Svensbyfjärden (Bothnian Bay), Avan (Bothnian Sea), and Sjösaafjärden, Mellanfjärden and Stadsfjärden in the Northern Baltic Sea, while they were not similar to any sub-basins in the Southern Baltic Sea and on the West Coast. Only autumn values were included for stations in Roskilde Fjord and they therefore lacked seasonal variability. Sub-basins found to be similar were for example Tavleffjorden in the Bothnian Bay, Avan in the Bothnian Sea, and Sjösaafjord, Mellanfjärden and Stadsfjärden in the Northern Baltic Sea. As with Curonian Lagoon, these Roskilde fjord stations were not found to be similar to sub-basins in the Southern Baltic Sea and on the West Coast. The shallower illuminated stations at the Tvärminne study site shared characteristics with sub-basins from all water districts. These included Tavleffjorden (Bothnian Bay), Inre fjord (Bothnian Sea), Sjösaafjärden (Northern Baltic Sea), Borholmsfjorden (Southern Baltic Sea), and Inre Idefjorden (West Coast). Puck Bay stations were similar to Möröfjorden (Bothnian Bay), Inre fjord (Bothnian Sea), Sjösaafjärden (Northern Baltic Sea), Borholmsfjorden (Southern Baltic Sea) but not with sub-basins on the West Coast.

Hence, the results showed that there are indeed several sub-basins within the SCM model results that seem to have characteristics similar to the BONUS COCOA study sites. The rates from these sites may potentially be studied more in detail in following work comparing process rates. While observed data from Vistula Estuary was found to be similar to model data, other observed data from deeper depths at the Tvärminne site did in general not match well the model data from sub-basins within the same depth range (Fig. 5a and 5b). This station was partly separated from the model data set due to a combined impact from bottom water concentrations of oxygen, nitrate and ammonium. Results from analysis on individual

water districts, indicated that Tvärminne was most similar to two bays in the Bothnian Bay district; Yttre Lulefjärden and Inrefjärden. One possible explanation for the lack of match with deeper depths at Tvärminne is caused by the vertically integrated values that were made available from the SCM model. Hence, it is possible that these data are not representative for the characteristics of bottom water in these deeper stratified areas as also mentioned in connection with Fig. 8 below.

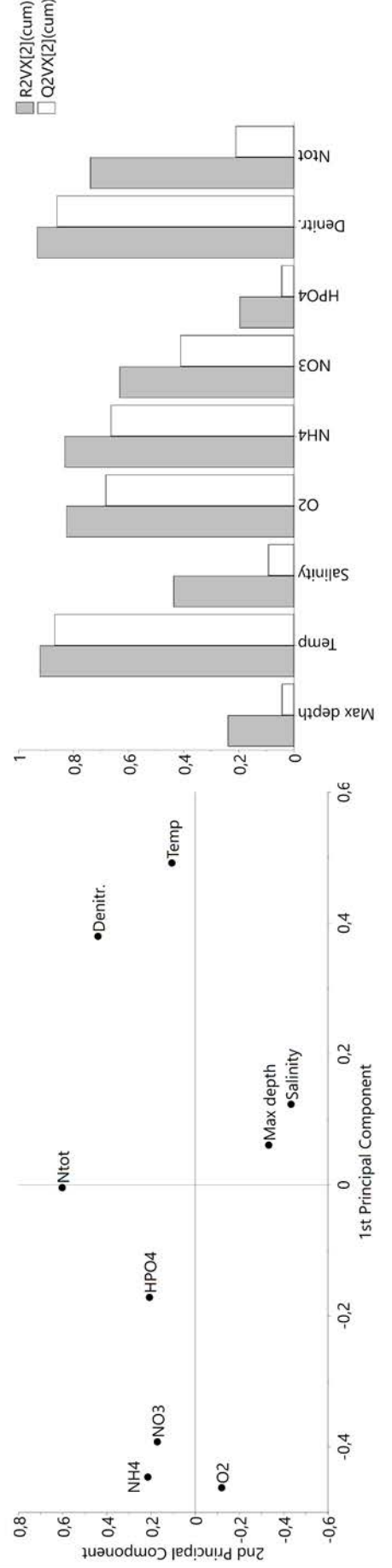
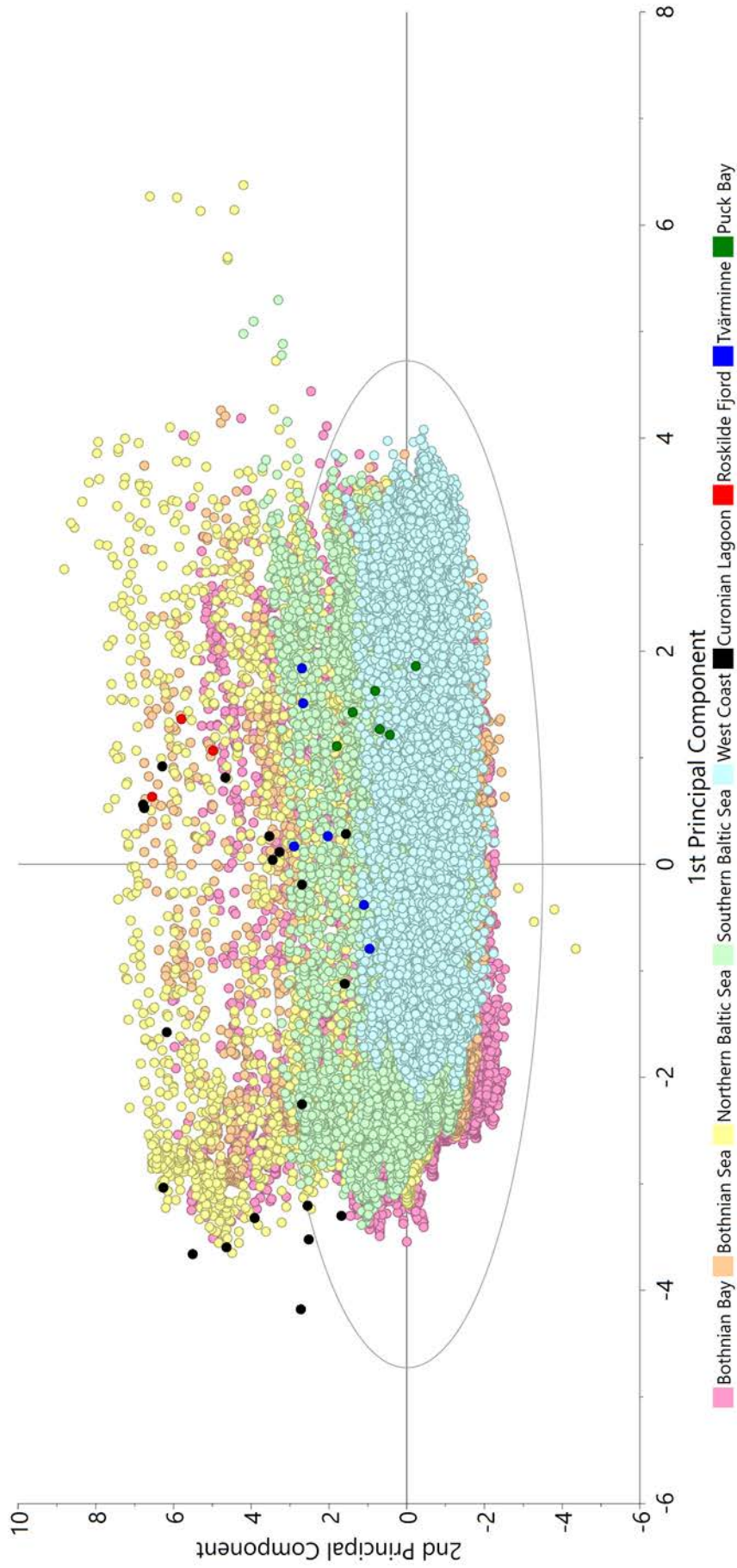


Figure 4a. Score- (top panel) and loading plot (bottom left panel) of the first two principal components from PCA analysis of model sub-basins with water depths <10 m along the Swedish coast together with observed data from four shallow study sites ($R^2=0.64$ and $Q^2=0.43$). Eight structural variables and denitrification rates were included in the PCA model. Also included are cumulative explained fraction of the variation of the variables (R^2 , grey bars) and cumulative predicted fraction of the variation of the variables (Q^2 , white bars; bottom left panel).

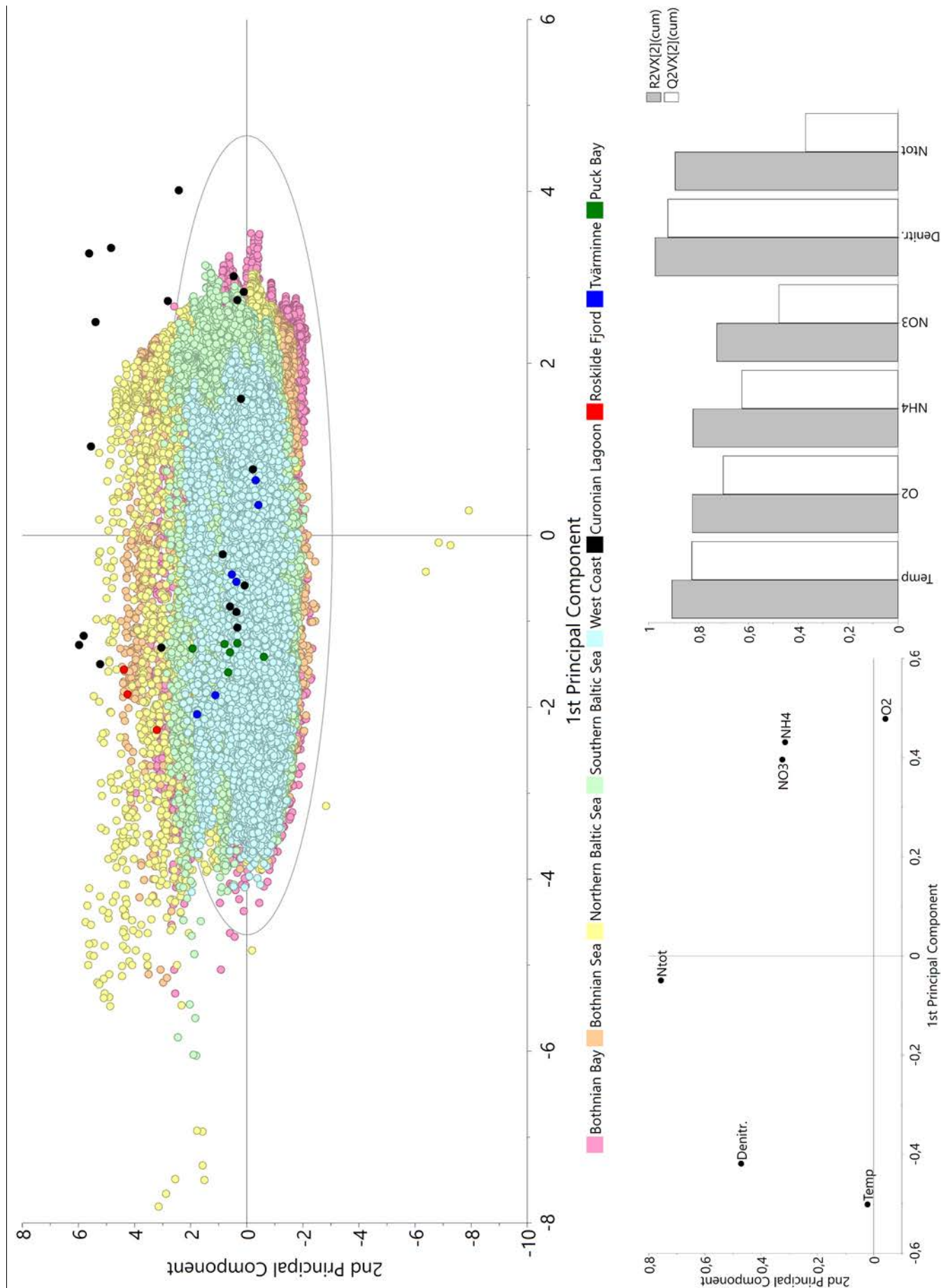


Figure 4b. Score- (top panel) and loading plot (bottom left panel) of the first two principal components from PCA analysis of model sub-basins with water depths <10 m along the Swedish coast together with observed data from four shallow study sites ($R^2=0.94$ and $Q^2=0.75$). Five structural variables and denitrification rates were included in the PCA model. Also included are cumulative explained fraction of the variation of the variables (R^2 , grey bars) and cumulative predicted fraction of the variation of the variables (Q^2 , white bars); bottom left panel).

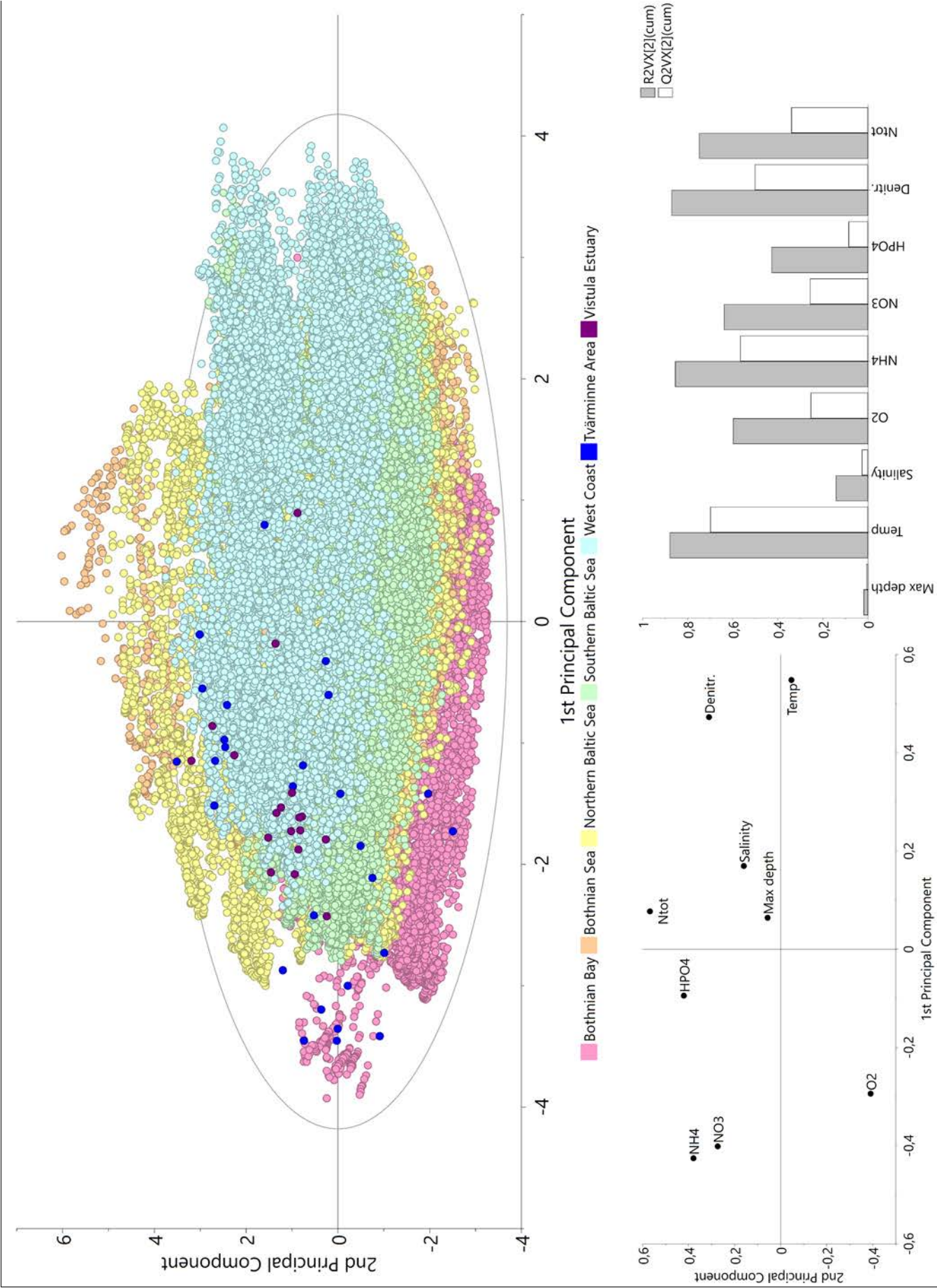


Figure 5a. Score- (top panel) and loading plot (bottom left panel) of the first two principal components from PCA analysis of model sub-basins with maximum depths within 22-34 m along the Swedish coast as well as observed data from Tvärminne and Vistula Estuary with maximum depths 22-34 m ($R^2=0.57$ and $Q^2=0.27$). Eight structural variables and denitrification rates were included in the PCA model. Also included are cumulative explained fraction of the variation of the variables (R^2 , grey bars) and cumulative predicted fraction of the variation of the variables (Q^2 , white bars; bottom left panel).

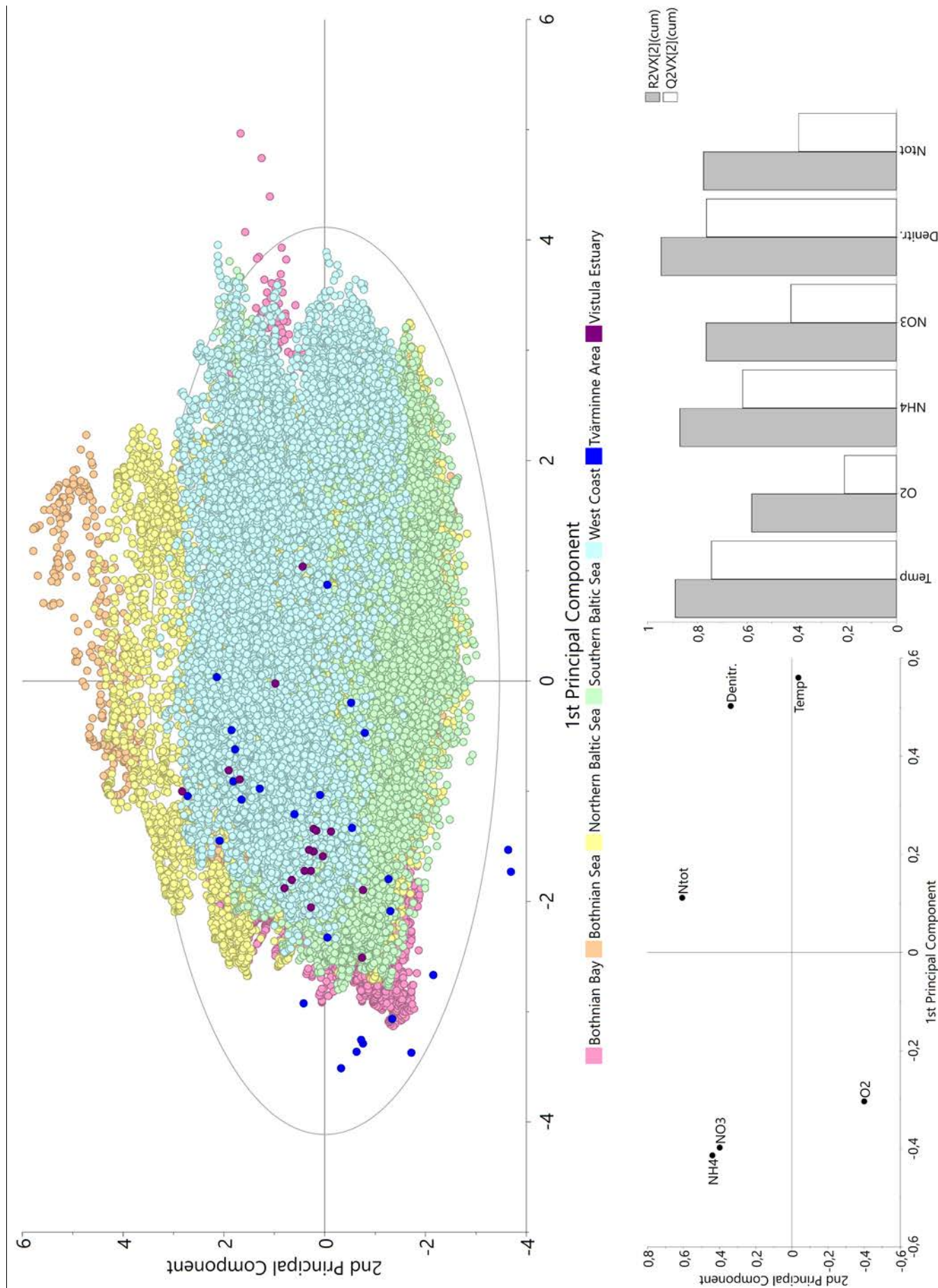


Figure 5b. Score- (top panel) and loading plot (bottom left panel) of the first two principal components from PCA analysis of model sub-basins with maximum depths within 22-34 m along the Swedish coast as well as observed data from Tvärminne and Vistula Estuary with maximum depths 22-34 m ($R^2=0.81$ and $Q^2=0.51$). Five structural variables and denitrification rates were included in the PCA model. Also included are cumulative explained fraction of the variation of the variables (R^2 , grey bars) and cumulative predicted fraction of the variation of the variables (Q^2 , white bars; bottom left panel).

Generally, no strong correlations of simple relations between observed denitrification and structural variables (latitude, longitude, depth, light, temperature, salinity, grain class, porosity, loss of ignition, sediment organic carbon, total nitrogen content in the sediment, sediment C/N-ratio, sediment Chl-a as well as bottom water concentrations of oxygen, ammonium, nitrate, and dissolved inorganic phosphorus and silicate) were found for data collected from all the learning sites. This might be explained by the low numbers of observations but also from the variation between learning sites as well as variations within learning sites. We found some non-significant correlation between denitrification rates and bottom water DIP and DSI (Fig. 6) but the reason behind the correlations is not clear. We may, however, note that the correlations for DIP and DSI are mainly caused by three data points with relatively high bottom water concentrations, which were observed in the Roskilde Fjord at 5 and 2 m depth. Potentially, this might be due to the activity of burrowing fauna that enhances nutrient release but further analysis of this question is left for future studies.

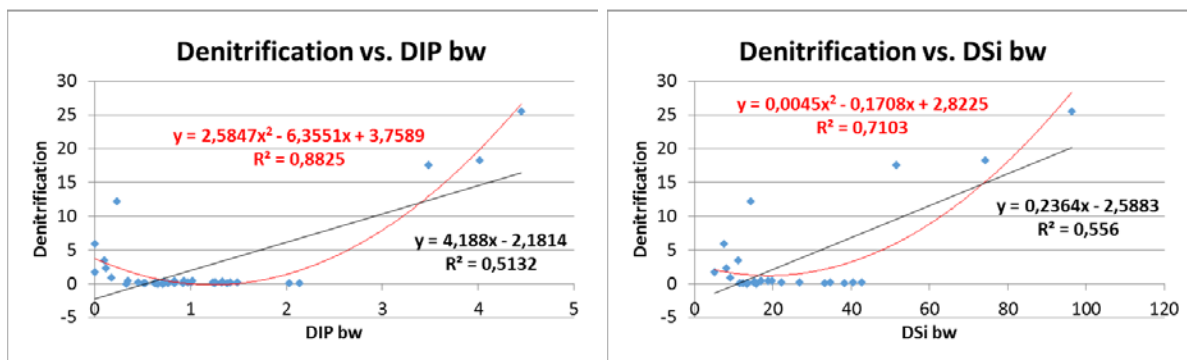


Figure 6. The denitrification rate vs. bottom water DIP (left) and DSI (right) (blue diamonds). The linear regression is shown by the black line and the quadratic regression by red line, respectively.

A correlation study based on model data from the shallow areas of the SCM model, however, show a significant correlation e.g. between the logarithm of denitrification rates and temperature (Fig. 7). There is still some spread in the data in Fig. 8 indicating that other factors also influence the results. As discussed by Deutsch et al. (2010) it has been shown that benthic denitrification can be controlled by temperature, nitrate availability, and supply of organic carbon, but, commonly a combination of various parameters is responsible for controlling the rate of denitrification in sediments. E.g. Piña-Ochoa and Álvarez-Cobelas

(2006) identified oxygen concentration, nitrate concentration, pore water dissolved organic carbon concentration, total phosphorus concentration, light regime, and plant occurrence as important factors.

The temperature dependence of denitrification is in the model explained by the formulations that drive denitrification in the model. Denitrification ($DENITB$) in the model formulations (Eq.8-Eq.11) is expressed as a function of oxygen (O_2) and temperature (T) and the nitrogen content in the sediment (NBT). The temperature dependence of denitrification is due to the exponential temperature dependence of organic matter mineralization ($DCOMP$). In the shallow areas the oxygen dependence becomes mainly an issue of temperature dependence, since the water is well mixed and saturated by air-sea exchange according to the water temperature (and slightly according to salinity as well) (e.g. Eilola et al. 2009). Further multiple factor analysis was discussed that may in combination with theoretical considerations potentially increase the correlations. This work is, however, out of the time frame of this report and will be left for the future outlook.

In the meantime we present a copy of the relations for the sediment nitrogen content ($mmol\ m^{-2}$), oxygen ($ml\ L^{-1}$) and temperature ($^{\circ}C$) dependent sediment denitrification (implicitly nitrification-coupled) ($DENITB_{NBT}$; $mmol\ m^{-2}\ day^{-1}$) that are used in the present version of the SCM model (Eq.8). The temperature dependent benthic decomposition of organic matter ($DCOMP$; Eq.9) is partly carried out by denitrifying bacteria also when oxygen is abundant in the overlying water. The denitrified fraction increases for declining oxygen concentrations according to Eq.10 and Eq.11. There is in addition potential denitrification driven by benthic processes in the SCM model under anoxic conditions when diffusion of nitrate from overlying water may support denitrification processes taking place in the sediment. Benthic decomposition of organic matter under anoxic conditions is first carried out by denitrifying bacteria until nitrate in the overlying water is depleted, and then by the sulfate reducing bacteria. For further details the reader is referred to Eilola et al. (2009). This process is however not significant in the oxygenated waters of the modelled shallow bays. The carbon content in the sediment is in the SCM model related to NBT according to a constant molecular relation (the Redfield ratio). Thus, anoxic (denitrification and sulfate reduction) and oxic decomposition of organic carbon is in the model described by the decomposition of organic nitrogen. This simplification might cause deviations between model and observations in regions where the bioactive organic carbon to nitrogen ratio deviates much from the Redfield ratio. Addition of carbon to the model is needed in order to explore this issue further.

$$DENITB_{NBT} = (1 - \delta_{NH_4}) \cdot (1 - \delta_{NO_3}) \cdot DCOMP_{NBT} \quad (Eq.8)$$

$$DCOMP_{NBT} = 0.0005 \cdot EXP(0.15 \cdot T) \cdot NBT \quad (Eq.9)$$

$$\delta_{NH4} = \left[1 + \left(\frac{O_2 + |O_2| + 0.07}{|O_2| + 0.07} \right)^{8.0} \right]^{-1} \quad (\text{Eq.10})$$

$$\delta_{NO3} = \frac{0.5}{1 + \text{EXP}(5.0 - 1.29 \cdot O_2)} - 0.004 \text{ if } O_2 > 0, \text{ else } \delta_{NO3} = 0 \quad (\text{Eq.11})$$

When comparing the available observations of denitrification and temperature from the BONUS COCOA study sites to the model data sets, most of these values are found within the possible outcomes of the SCM model (Fig. 7). It seems the observations from Puck Bay shallow areas are found within the higher range of temperature-specific denitrification rates compared to the SCM model data. This finding is in correspondence with the discussion in the beginning of this section about discrepancies between mean and median values calculated from model and observations for the shallow areas. Data from the deeper parts of Tvärminne and Vistula study sites, on the other hand, show some observations that are outside of the model results with lower temperature-specific denitrification rates. A likely explanation for the lack of match with observations from deeper depths is that the vertically integrated SCM data are not totally representative for the characteristics of bottom water in these deeper stratified areas. One reason is e.g. that the integrated model data include denitrification taking place on shallow areas of the deep basins of the SCM model as well, while the observations are taken at the bottoms of the deep study sites.

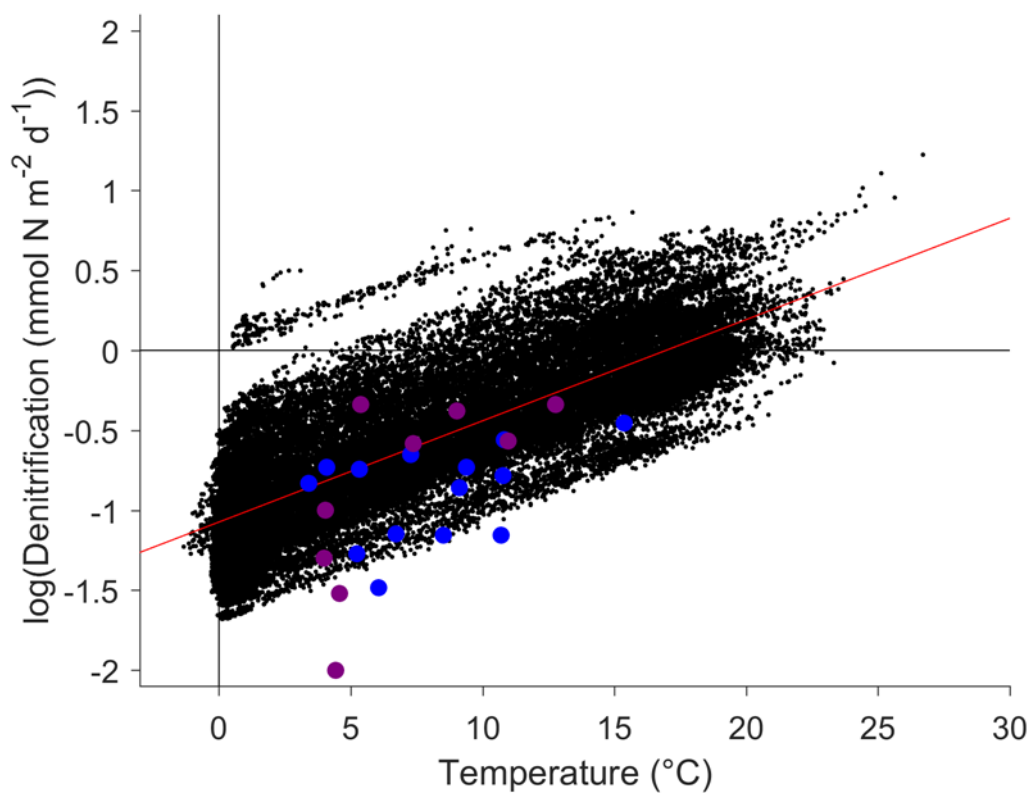
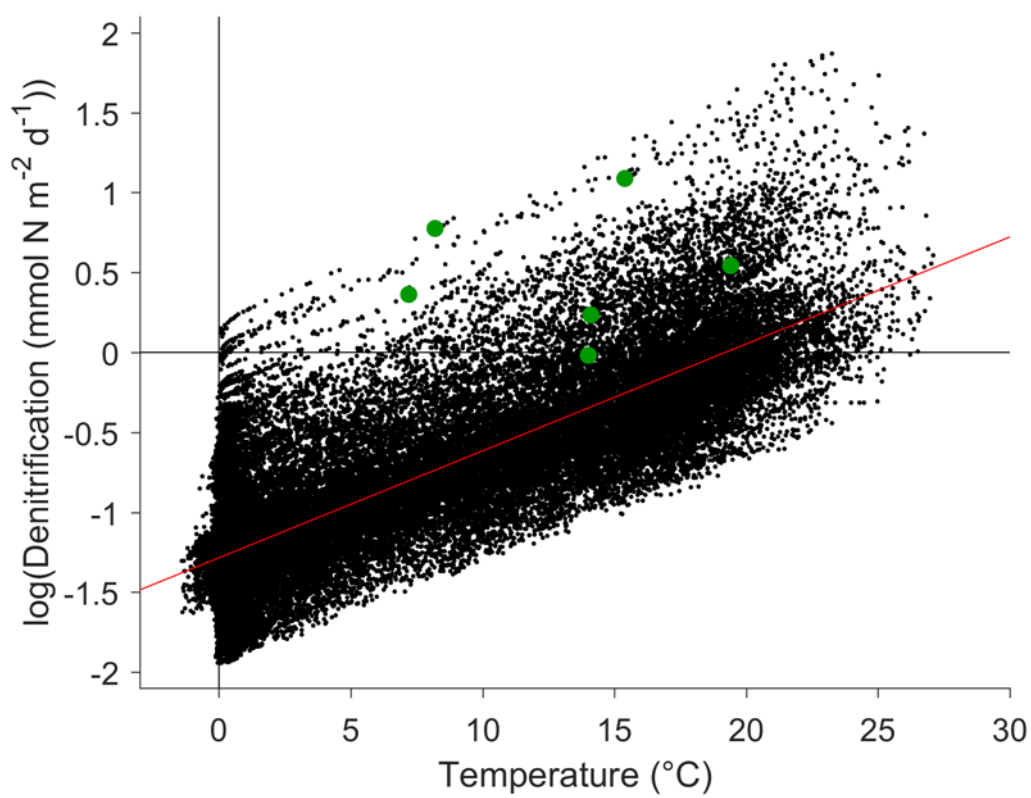


Figure 7. Denitrification plotted on a logarithmic scale versus temperature from the SCM model (black dots) for shallow sub-basins (<10m depth; upper panel) and deeper sub-basins (22-34 m depth; lower panel). Regression analysis was performed on the model data sets (red line). The regression of the shallow data set was significant ($p=0.000$), the coefficient of determination (R^2) was 0.65 and the equation $y=0.066x-1.266$. Superimposed on the graph are also experimentally determined data from the shallow parts of the Puck Bay study site (filled green circles). The regression of the deeper basins data set was significant ($p=0.000$), the coefficient of determination (R^2) was 0.65 and the equation was $y=0.062x-1.053$. Superimposed on the graph are also experimentally determined data from the deeper Tvärminne (filled blue circles) and Vistula (filled purple circles) study sites.

3.2 Theory

Importance of physical characteristics on nutrient retention

The apparent removal rate (V_s) indicates how efficiently the nutrients are removed by biological, chemical and geological processes from the water column in a specific sub-basin. The retention of nutrients is also affected by the physical conditions described by the mean depth and the water circulation (residence time) in Eq.4. We used the theoretical model to describe long term (20 years) mean conditions and results from the SCM model. A correlation study of Eq.4 for area specific permanent retention efficiency (R/A) calculated for all sub-basins of the SCM model (Fig. 8) show that a best 1:1 fit between theory and results from the dynamical SCM model is obtained when V_s for nitrogen and phosphorus are about 4.96 m yr^{-1} and 6.45 m yr^{-1} , respectively. The correlation coefficient ($r^2=0.80$) for N is higher than for P ($r^2=0.61$). Since the values of V_s are constant and the correlations are still relatively good the results indicate that a large fraction of the variability in nutrient retention is caused by variations in the mean depth, basin area and the water residence time. Actually, already e.g. Nixon et al. (1996) discussed the relations between P and N retention water depth and especially the mean residence time of water in the estuarine systems. The inverse correlation of P and N retention to the log scale of the ratio between the average depth and the residence time of the study areas was also indicated e.g. by the results from the Stockholm archipelago study by Almroth-Rosell et al. (2016).

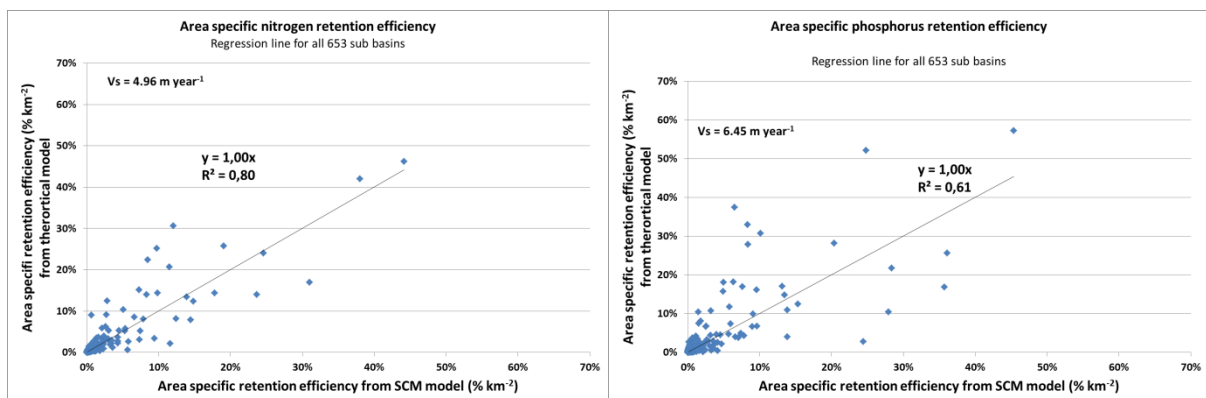


Figure 8. Best linear 1:1 fit for area-specific retention efficiency R/A ($\% \text{ km}^{-2}$) calculated from theoretical model (vertical axes) and compared to SCM model results (mean values for the period 1995-2014) from all sub basins along the Swedish coast (horizontal axes). Best fit

for nitrogen (left) was obtained with $V_s(N)=4.96 \text{ m yr}^{-1}$. Best fit for phosphorus (right) was obtained with $V_s(P)=6.45 \text{ m yr}^{-1}$.

Biogeochemical impact on nutrient retention

The biogeochemical impact on the internal losses is in the theory described by V_s . The average V_s for N and P for all sub-basins are 6.4 m yr^{-1} and 6.5 m yr^{-1} , respectively. This means e.g. that the amount of N and P removed every year by biogeochemical processes in a sub-basin corresponds to an average amount of nutrients in a water layer with a thickness of about 6.5 m. Actually, about 30% and 25% of the sub-basins has an apparent N and P removal, respectively, that annually exceeds the mean depth of the basin i.e. the ratio between V_s and the mean depth is larger than one (not shown). These sub-basins have on average a mean depth shallower than 6 m and in several of these basins the average amount of nutrients removed exceeds the standing stock several times. In these basins the import of nutrients from land, atmosphere or surrounding seas becomes relatively important. The spread of V_s values between the sub-basins of the SCM model is, however, large both for N and P (Figs 9 and 10). The large spread of V_s between different basins in Figs. 9 and 10 indicates that other parameters than mean depth, basin area and water residence time are important as well. The assumption of a steady state in Eq.1 may of course also have some impact on the results.

For the discussion we can mention results from the study by Wulff and Stigebrandt (1989) who estimated from budgets for the Baltic Sea in the period 1977-1981 that V_s for total P (N) varied from 5.6 (8.5) m yr^{-1} in the Baltic proper, 5.7 (6.5) m yr^{-1} in the Bothnian sea to 7.2 (2.0) m yr^{-1} in the Bothnian Bay. The results are not directly comparable to the present study since their budget method implicitly included the temporal retention in the sediments while the present report is discussing only the permanent retention. Their budgets also included the open sea areas while the present study focuses only on the Swedish coastal zone.

Regional differences in nutrient retention

There are regional differences in the V_s with the largest spread between basins for both N and P found in water districts 1-4 in the northern parts of the Baltic Sea (Fig. 9 and Fig. 10). The mean V_s for P show decreasing values from north to south with a small increase on the Swedish West coast. Nitrogen in the Baltic Sea shows the largest mean V_s in water district 4 and 7 while the maximum average V_s value is found on the Swedish West coast.

The mean permanent area-specific retention efficiency of N and P supplied to the sub basins are about $0.9 \% \text{ km}^{-2}$ and $1.0 \% \text{ km}^{-2}$, respectively (Fig. 11 and 12). This means that approximately 1 % of the nitrogen and phosphorus supplied to a sub-basin from land, atmosphere and surrounding seas is removed per square kilometer of a sub basin area. However, one should note that there is a large impact on the mean values from outliers which is indicated by the differences between median and mean values in the figures. Hence there are sub-basins which differ much from the main part of the sub-basins that generally have lower retention and V_s values. Only about 13% of the N- and P-retention values are larger than the mean values ($0.9 \% \text{ km}^{-2}$ and $1.0 \% \text{ km}^{-2}$), respectively (not shown). The median retention efficiency of N and P supplies to the sub basins are about $0.06 \% \text{ km}^{-2}$ and $0.05 \% \text{ km}^{-2}$, respectively (Fig. 11 and 12). For P, the average retention efficiency is largest in the northern Baltic Sea (Fig. 11). The values decrease towards southern Baltic Sea and the smallest retention efficiency is found on the Swedish west Coast. This is largely also true for the median values, but these show a slight increase again in the southernmost and West coast

districts. For N (Fig. 12) the median values show only relatively small variations, compared to P, with the highest retention efficiency on the West coast. The impact from outliers causes a higher mean retention especially in the Baltic Sea but also on the west coast.

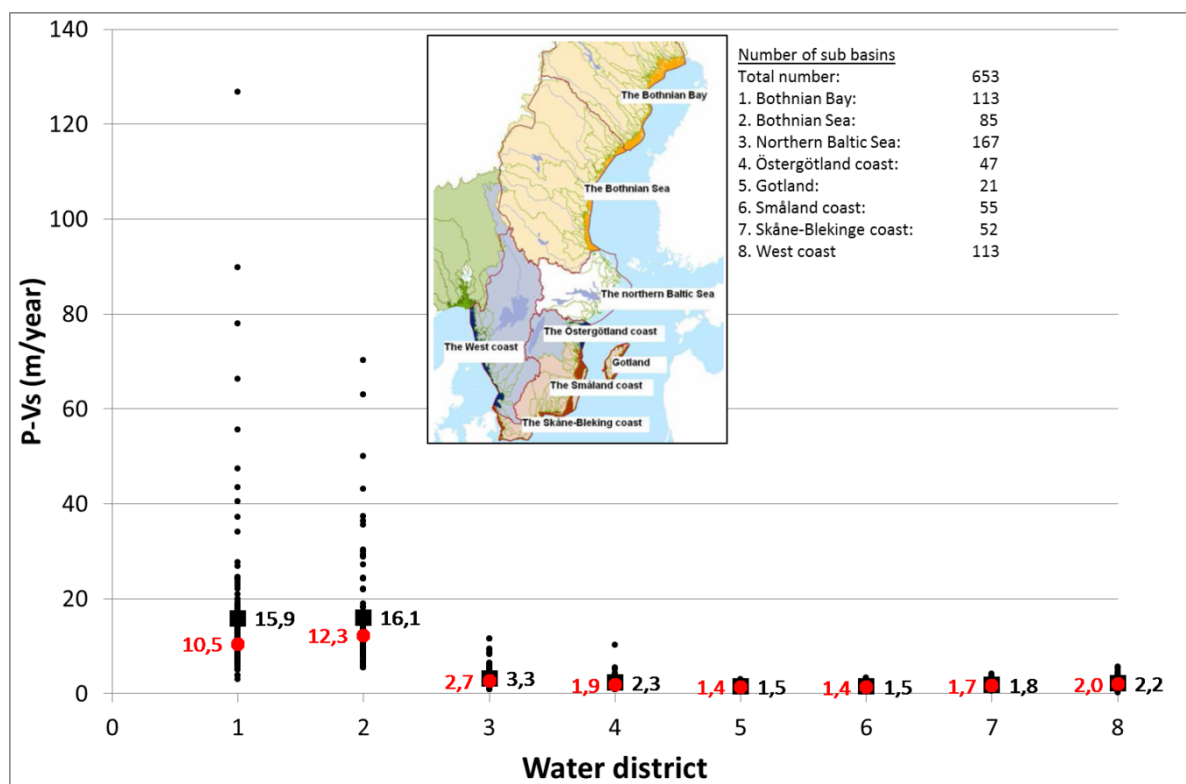


Figure 9. Apparent removal rate V_s (m yr^{-1}) for permanent removal of phosphorus in 653 sub-basins of the SCM model (mean for period 1995-2014). The results are presented for eight different water districts shown in the inserted map. The number of sub-basins in each district is shown in the inserted table. Mean values are shown by black squares and black numbers while the median numbers are shown by red circles and numbers.

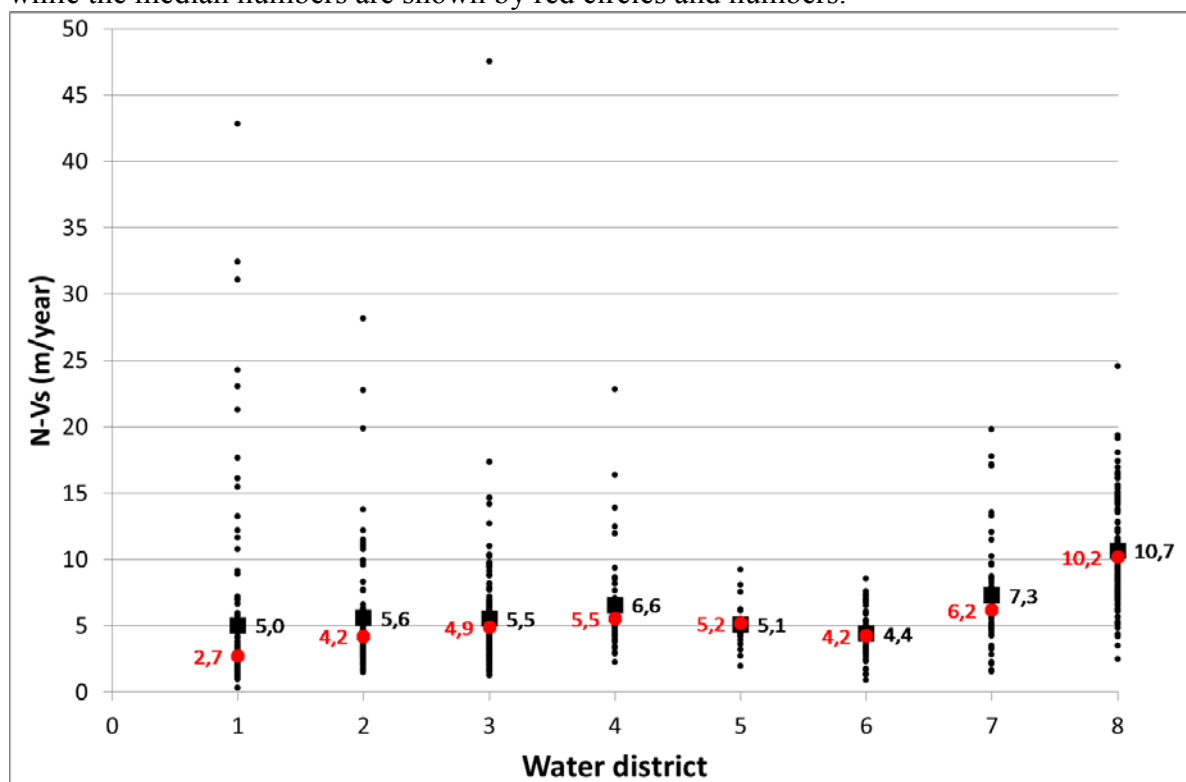


Figure 10. Similar as Fig. 9 but for nitrogen.

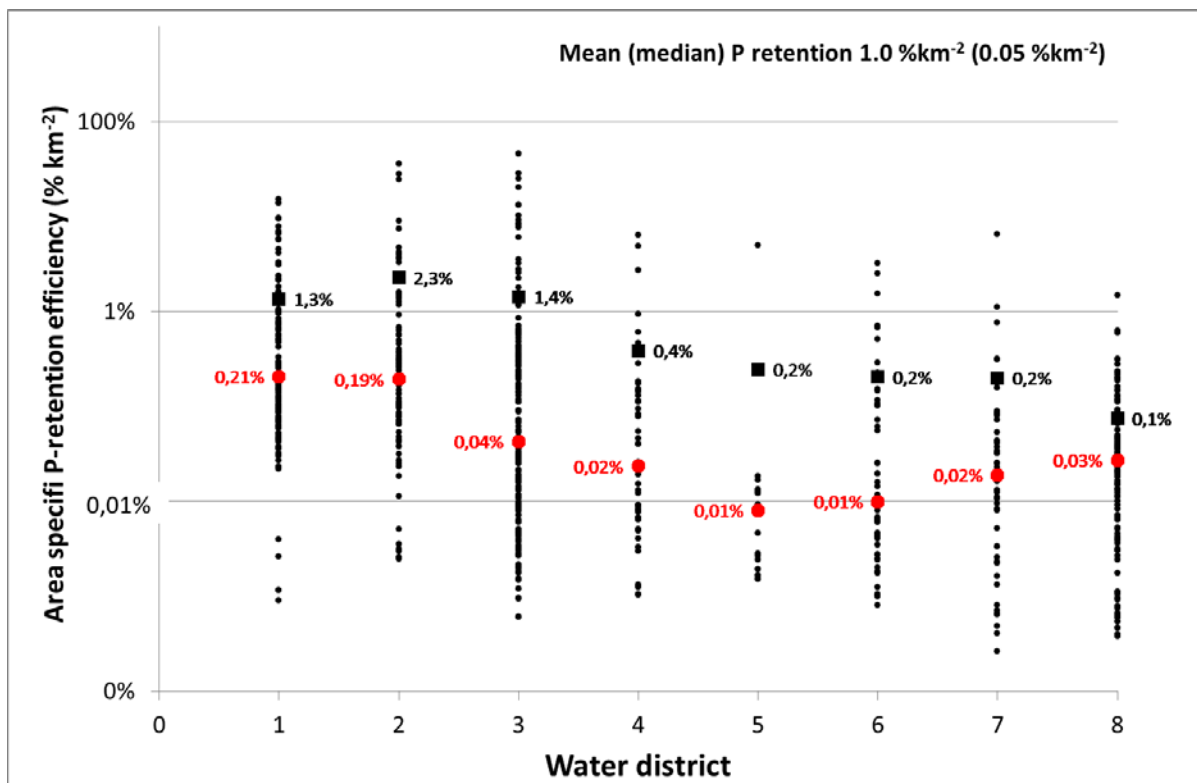


Figure 11. Area-specific phosphorus retention efficiency (R/A) (% km⁻²) of phosphorus in 653 sub-basins of the SCM model. The results are presented for eight different water districts (see Fig. 9). Mean values are shown by black squares and black numbers while the median numbers are shown by red circles and numbers. The mean and median values for all basins are shown in the upper right corner. Note the logarithmic scale on the vertical axes.

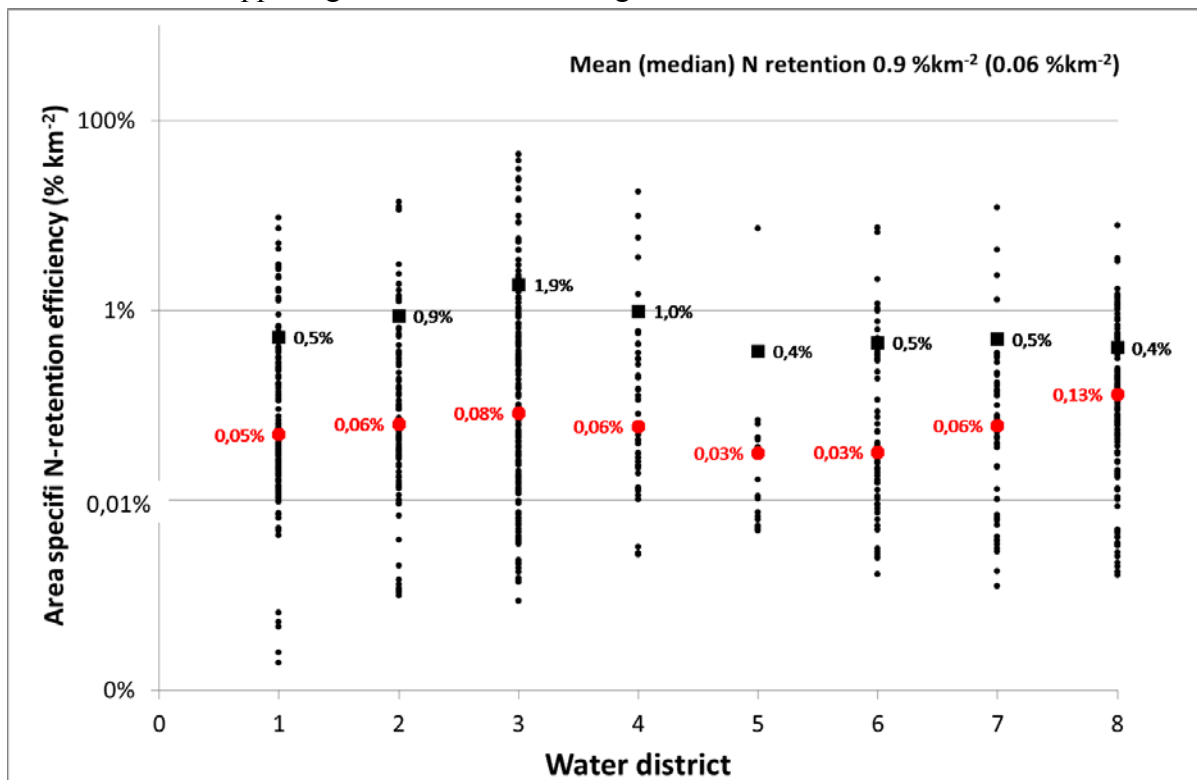


Figure 12. Similar as Fig. 11 but for nitrogen.

Theory related to monitoring

In order to relate the apparent removal rate to quantities related to monitoring we introduced Eq.6 which in combination with Eq.4 gives an estimation of the nutrient retention as a function of mean water depth, water residence time and the mean nutrient concentrations in the active sediment layer and in the water column. We also include information about the basin area when we calculate the area-specific retention efficiency R/A that becomes normalized per unit sediment area and therefore not dependent of the actual basin size. The results in Fig. 13 and Fig. 14 show that the correlation between the apparent removal rate theory and SCM model results improved ($P_r^2=0.78$, $N_r^2=0.94$) and reduce the spread from the linear trend which indicate that much of the variability in the model is captured by these factors. To some extent some outliers with very high area-specific retention efficiency increases the correlation. Therefore we also show the trend line and the corresponding correlation for a subset of basins with lower values (Figs. 13 and 14 in red). We may note that the correlation of the theoretical model is lower for nitrogen ($R^2=0.7$) in sub-basins with lower area-specific retention efficiency while for phosphorus the correlation is not changed as much.

The results indicate that the mean ratio of nutrients in the water and in the active layer of the sediment gives a signature for all the different biological, chemical and geological processes acting in each sub-basin. The theoretical study shows that we may get a first rough estimate of the area-specific nitrogen and phosphorus retention capacity in a sub-basin if we use mean water depth, water residence time, basin area and the mean nutrient concentrations in the active sediment layer and in the water column together with Eq.4 and Eq.6, where we set $Blr(P)=0.04 \text{ yr}^{-1}$ and $Blr(N)=0.4 \text{ yr}^{-1}$. When information about biogeochemical variables are missing we might potentially use only Eq.4 divided by the basin area to obtain the area-specific retention efficiency with $Vs(N)=4.96 \text{ m yr}^{-1}$ and $Vs(P)=6.45 \text{ m yr}^{-1}$ that then only depends on the physical conditions in the sub-basin.

The constants are of course depending on the SCM model that we used here. Further investigations can also give more information, e.g. about what are the characteristics of the sub-basins that are found to be outliers in the ensemble we have studied here. Future field campaigns could be planned based on the present theoretical pilot study to explore how standard monitoring programs could support studies of nutrient filtering in the shallow coastal regions of the Baltic Sea.

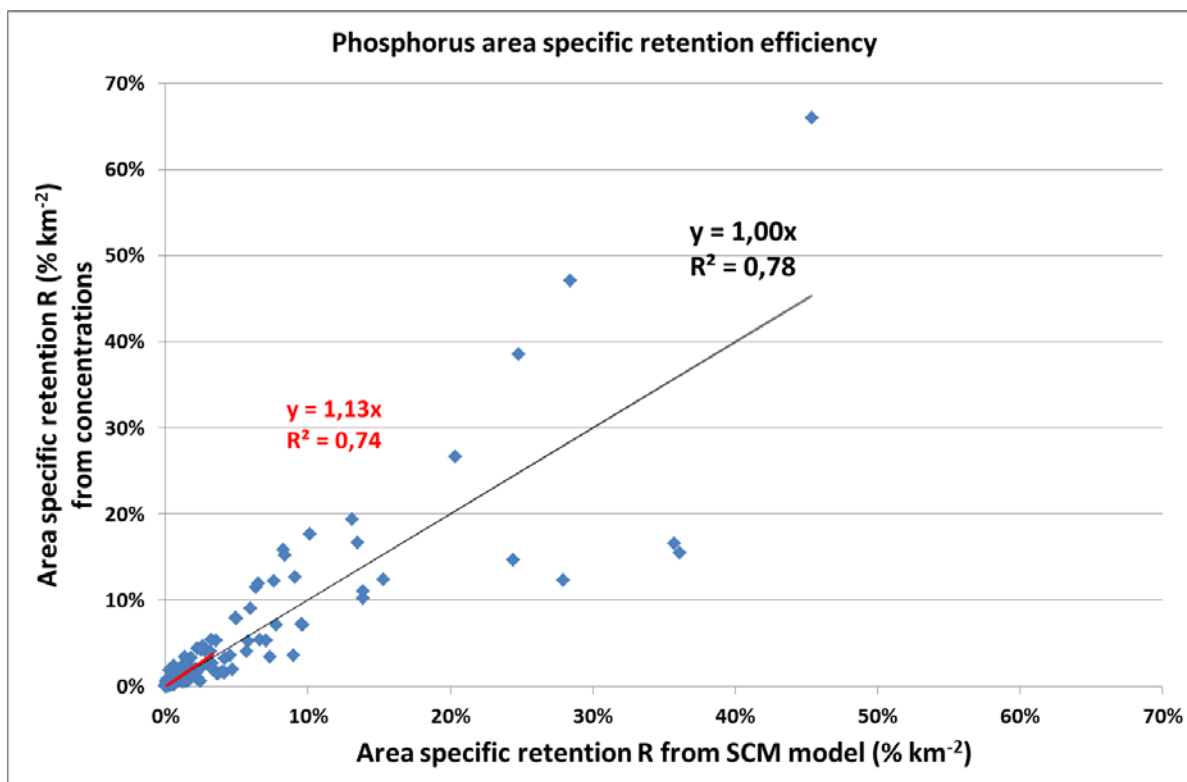


Figure 13. Best linear fit for area-specific phosphorus retention efficiency (R/A) calculated from theoretical model including information from the sediment and water column concentrations (Eq.4 and Eq.6 combined) and compared to SCM model results (R/A). Best fit for P on all data (653 sub basins) was obtained with $\text{Blr(P)}=0.04 \text{ yr}^{-1}$. The linear trend for a sub set (613 sub basins) of the data is shown by the red line and the red text.

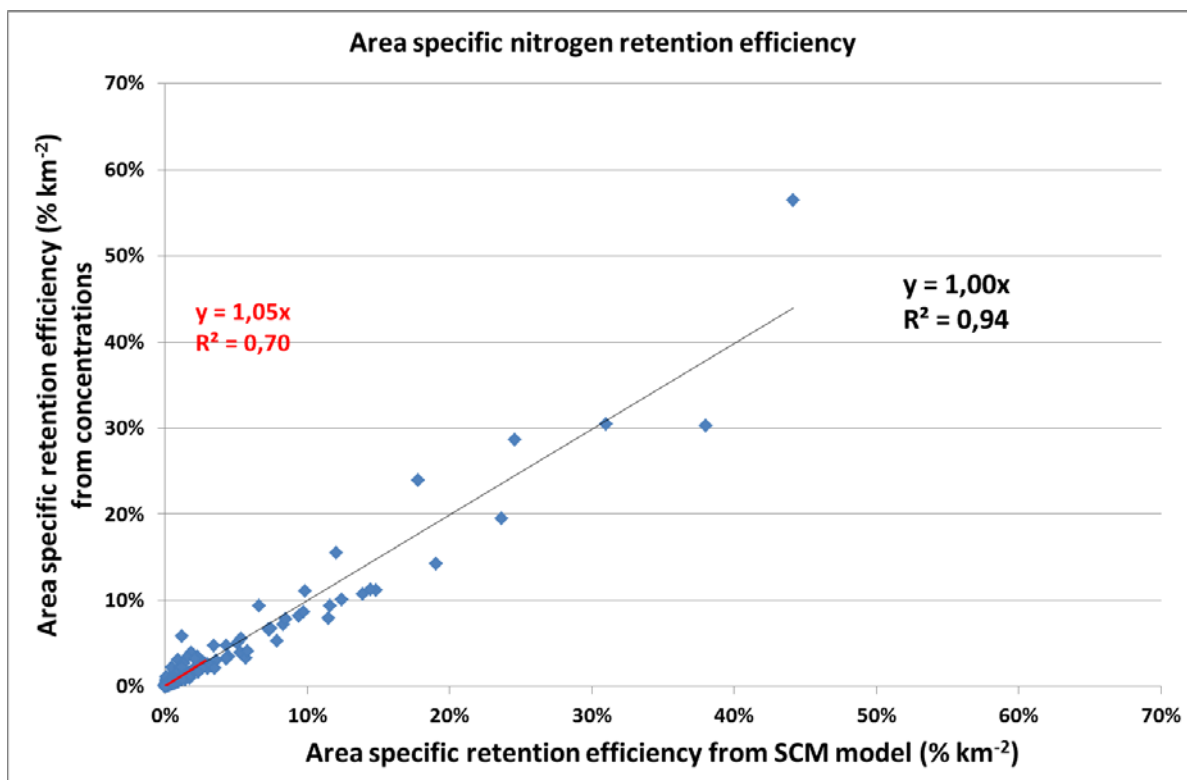


Figure 14. Similar to Fig.13 but for N. Best fit for N was obtained with $\text{Blr}(\text{N})=0.4 \text{ yr}^{-1}$.

3.3 Other evaluations not shown

The results shown above are the best 1:1 fit we found for the theoretical description of retention related parameters relative to the model data. The relations between process rates and state variables related to retention are, however, complex. As an example we present how Brr is calculated in the SCM model in relation to the state of the bottom water and sediment concentrations.

The sources and sinks (S) for sediment phosphorus (PBT) and nitrogen (NBT) in SCM model are calculated from:

$$S_{\text{NBT}} = \text{SINKI}_{\text{ORGN}} - \text{SEDOUT}_{\text{DIN}} - \text{DENIT}_{\text{NBT}} - \text{BURIAL}_{\text{N}}$$

$$S_{\text{PBT}} = \text{SINKI}_{\text{ORGP}} - \text{SEDOUT}_{\text{DIP}} - \text{BURIAL}_{\text{P}}$$

Here $\text{SEDOUT}_{\text{DIP}}/\text{PBT}$ is corresponding to Brr for phosphorus while $\text{SEDOUT}_{\text{DIN}}/\text{NBT}$ is corresponding to Brr for DIN (nitrate+ammonium), respectively. SINKI is the deposition of organic matter to the sediment, BURIAL is the permanent burial and DENIT the denitrification. As an example we show the formula (Eq. 12) for Brr for P as a function of salinity (SAL), temperature (T) and oxygen (O_2):

$$\frac{\text{SEDOUT}_{\text{DIP}}}{\text{PBT}} = 0.0005 \cdot \exp(0.15 \cdot T) \cdot \left(1.15 - \frac{1}{1 + 0.5 \cdot \exp(-1.5 \cdot (\text{O}_2 - 0.7)) - \frac{0.15}{1 + \left(\frac{5}{\text{SAL}}\right)^{20}}} \right) \quad (\text{Eq 12})$$

For the present report we investigated (not shown) in several attempts different simple regressions first and then also the possibility to use the process formulations used in the model to find robust statistical relations between modelled process rates and retention R or Vs but the results were poor. One major problem seemed to be caused by finding relations between the sedimentation rates and state variables. As we see from the theory presented above and in the results section there are other factors than the biogeochemical process rates that also influence the state of a certain water body.

Eq.7 shown in methods is dependent on many local factors such as the supplies to the sub-basin, the productivity and mineralization in the basin which depend on the temperature, salinity, oxygen and potentially other factors as well. The fact that the systems are dynamic and changing in time will also have some impact on Eq.7. Some of the rates in Eq.7 are measured momentarily at the BONUS COCOA study sites but the evaluation of the role of all potential drivers requires further research which is out of the scope of the present report and is therefore left for the future outlook.

3.4 The benthic primary production

One should note that the assimilation of nutrients taking place at the seafloor on illuminated sediments is not explicitly described in the SCM model. The SCM model does also not distinguish between different physical bottom types such as erosion, transport or

accumulation bottoms which is required for a good description of the benthic environment. This benthic production may be partly compensated for by the pelagic production and corresponding sedimentation taking place in the shallow areas of the model. The difference between the modelled organic matter depositions to the sediment to a case where the production could take place directly on the seafloor is uncertain. Pelagic nitrogen fixation is included in the SCM model but also evaluation of the importance of missing benthic nitrogen fixation needs further attention. Benthic micro algae do play an important role for total primary production capacity e.g. in the northern Baltic Sea (Ask et al. 2016). According to Sundbäck et al. (2004), microphytobenthic (MPB) nitrogen assimilation in littoral sediments often exceeds nitrogen removal by denitrification, partly because MPB activity suppresses denitrification. In quite many sub-basins light may reach the bottoms (Fig. 3) and benthic primary production may potentially dominate over the pelagic production. However, in order to fully evaluate and understand the relative role of benthic production on the permanent retention of nutrients supplied to a sub-basin, a model of benthic primary production is needed in the SCM.

4. Conclusions

We have made statistical analyses of observations from BONUS COCOA study sites together with results from the SCM model. We developed and evaluated a theory to relate process rates to monitoring data and nutrient retention.

The results showed that an experimentally determined multivariate data set from the shallow, illuminated stations was mainly found to be similar to the multivariate data set produced by the SCM model. The data from deeper depths from the Vistula Estuary was found to be similar to model data, while data from the Tvärminne site did in general not match well the model data from sub-basins within the same depth range likely because the model data included integrated characteristics for the entire water column and sediment area. The preliminary results showed that there are several individual sub-basins within the SCM model results that have characteristics similar to the BONUS COCOA study sites.

Generally no strong correlations of simple relations between observed denitrification and available structural variables were found for data collected from all the learning sites. We found some non-significant correlations between denitrification rates and bottom water DIP and DSi but the reason behind the correlations is not clear.

Mean denitrification rates from the SCM model basins were within the ranges of literature values and observations from BONUS COCOA study sites. An exception was the shallow areas of Roskilde Fjord and Puck Bay which showed quite high values when compared both to the SCM model results and also when compared with the other data sources. Anyway, we should not expect a perfect resemblance because the model output is an average daily rate for the entire area of each sub-basin while observations are made in specific points in the sub-basins of the BONUS COCOA study sites.

The theory of nutrient retention showed good correlations with model results. The spatial dimensions of a coastal area have large impact on the retention efficiency (Almroth-Rosell et al. 2016). This means that a large coastal basin or coastal area has more efficient nutrient retention than a small coastal area. In order to make the results independent of the size of a sub-basin we studied the area-specific retention efficiency (R/A). It was found that that we may get a first rough estimate of the area-specific nitrogen and phosphorus retention capacity in a sub-basin if we use mean water depth, water residence time, basin area and the mean nutrient concentrations in the active sediment layer and in the water column, together with Eq.4 and Eq.6, where we set $\text{Blr(P)}=0.04 \text{ yr}^{-1}$ and $\text{Blr(N)}=0.4 \text{ yr}^{-1}$. It was found that the mean ratio of nutrients in the water and in the active layer of the sediment gives a signature for all the different biological, chemical and geological processes acting in each sub-basin. The derived constants depend on the SCM model but could be tested against other models and monitoring efforts. Exploration and addition of functions driving the benthic loss rates might improve the correlations further.

Since the characteristics of the SCM model results corresponded well with the observations from study sites we may expect the relations obtained from the SCM model and theory should be fairly well representative for large parts of the Baltic Sea. Further model development including e.g. effects of benthic primary production and nitrogen fixation can deepen the understanding of retention processes even more. The present study used 20-year mean concentrations and fluxes and further investigations are needed to find out how appropriate the theoretical formula is on shorter time scales including the importance of the seasonal variability in nutrient retention caused e.g. by seasonal changes in nutrient loads. The biggest challenge is likely to find measurements of total nitrogen and phosphorus concentrations in the active sediment layer (Eq.6) from the different regions where monitoring in the coastal

zone is lacking. Future research may for instance continue to search for potential variables that could be used as proxy for the ratio between mean sediment concentrations and mean water column concentrations. The present analysis serve as a good start to further investigate how to cluster sub-basins into areas with similar characteristics. This would support the design of future monitoring needed to map environmental changes in the Baltic Sea.

5. Acknowledgement

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7. Appendix

Some model characteristics

As supplement we also show few examples of basic information related to the general characteristics of the SCM model. The model is described in more detail in D5.1 (Eilola et al. 2015) and in the paper by Almroth-Rosell et al. (2016). Some of the information is repeated below.

The SCM couples a 1-dimensional physical model to the biogeochemical model SCOBi (The Swedish Coastal and Ocean Biogeochemical model). In order to include horizontal variations in a larger region the area is divided into several dynamically interconnected sub-basins. The sub-basins are identical to the defined national water bodies according to the Water Framework Directive (WFD). Each sub-basin is described by the hypsographical curve and may exchange water and properties with other sub-basins through connecting sounds. The geometry of each sound is extracted from digital sea charts and the cross sectional area and the maximum depths are then manually compared and verified against ordinary sea charts.

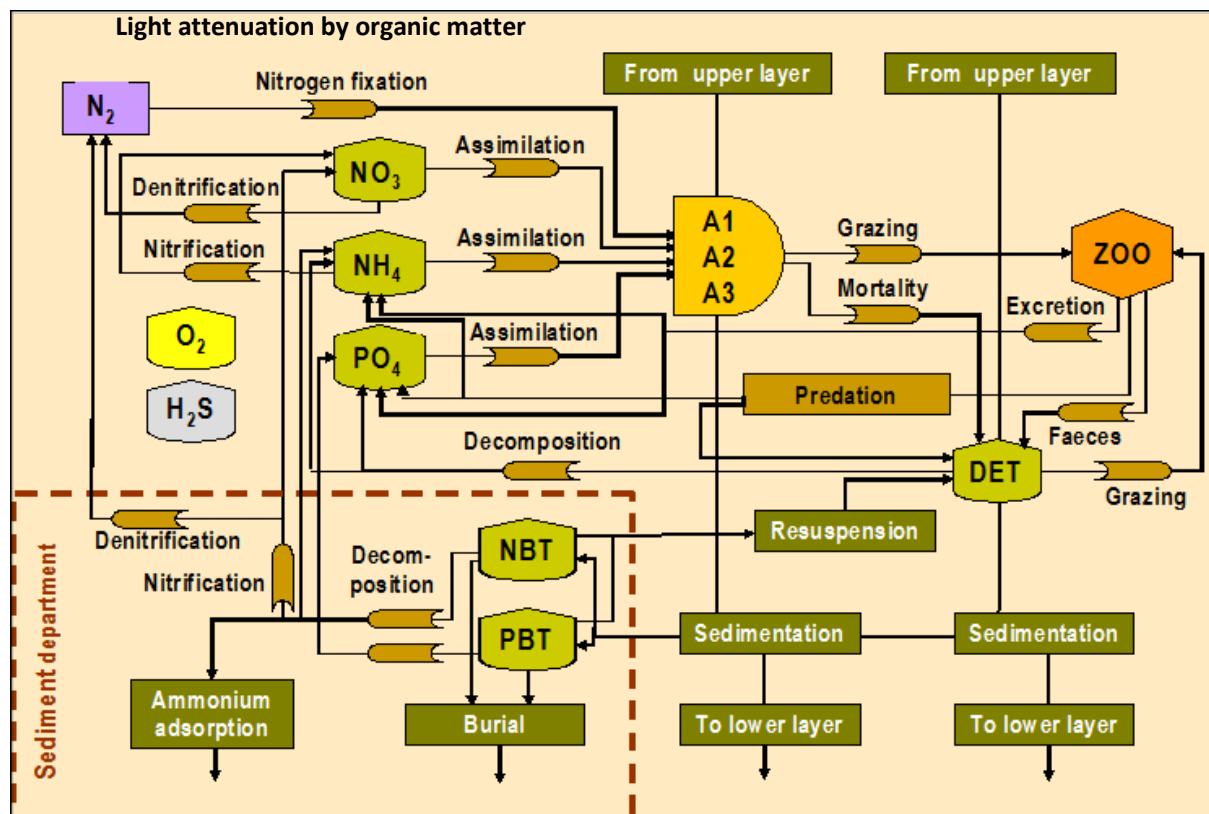


Figure A1. Components of the SCOBi model. The process descriptions of oxygen and hydrogen sulfide are simplified for clarity.

The SCOBi model (Fig. A1) describes the dynamics of nitrate, ammonium, phosphate, phytoplankton, zooplankton, detritus, and oxygen. Hydrogen sulfide concentrations are represented by “negative oxygen” equivalents ($1 \text{ ml H}_2\text{S l}^{-1} = -2 \text{ ml O}_2 \text{ l}^{-1}$). Phytoplankton consists of three algal groups representing diatoms, flagellates and others, and cyanobacteria (corresponding to large, small and nitrogen fixing cells). Processes like assimilation,

remineralisation, nitrogen fixation, nitrification, denitrification, grazing, mortality, excretion, sedimentation and burial are considered. The production of phytoplankton assimilates carbon (C), nitrogen (N) and phosphorus (P) according to the Redfield molar ratio (C:N:P=106:16:1) and the biomass is represented by chlorophyll (Chl) according to a constant carbon to chlorophyll ratio C:Chl=50. The carbon cycle is, however, not explicitly modelled. The molar ratio of a complete oxidation of the remineralised nutrients is $O_2:P=138:1$. The sediment processes include oxygen dependent nutrient remineralization and denitrification as well as burial of nutrients. Burial of nitrogen and phosphorus in the sediment and denitrification are the permanent nutrient sinks in the model. Light attenuation depends on background attenuation due to water and humic substances and a variable attenuation caused by the organic matter (phytoplankton and detritus) handled by the SCOB model. Sediment resuspension is not active in the present set-up of the SCM.

The residence times of all sub-basins of the SCM model together with the mean sediment nitrogen concentrations in the corresponding sub basins are shown in Fig. A2. The mean depth vary between 0.7m and 77m with an average of 11m and the residence time vary between 0.2 days and 495 days with an average of 14 days. The mean sediment N-concentration in the sub-basins vary between 4 mmol N m⁻² and 342 mmol N m⁻² with an average of 32 mmol N m⁻². The mean sediment N-concentrations increase with mean water depth up to about 40m-50m. But there is a large spread in mean concentrations especially in areas shallower than 30m in the model. The concentrations are similar for deeper basins but only a few sub-basins have mean depth larger than 50m.

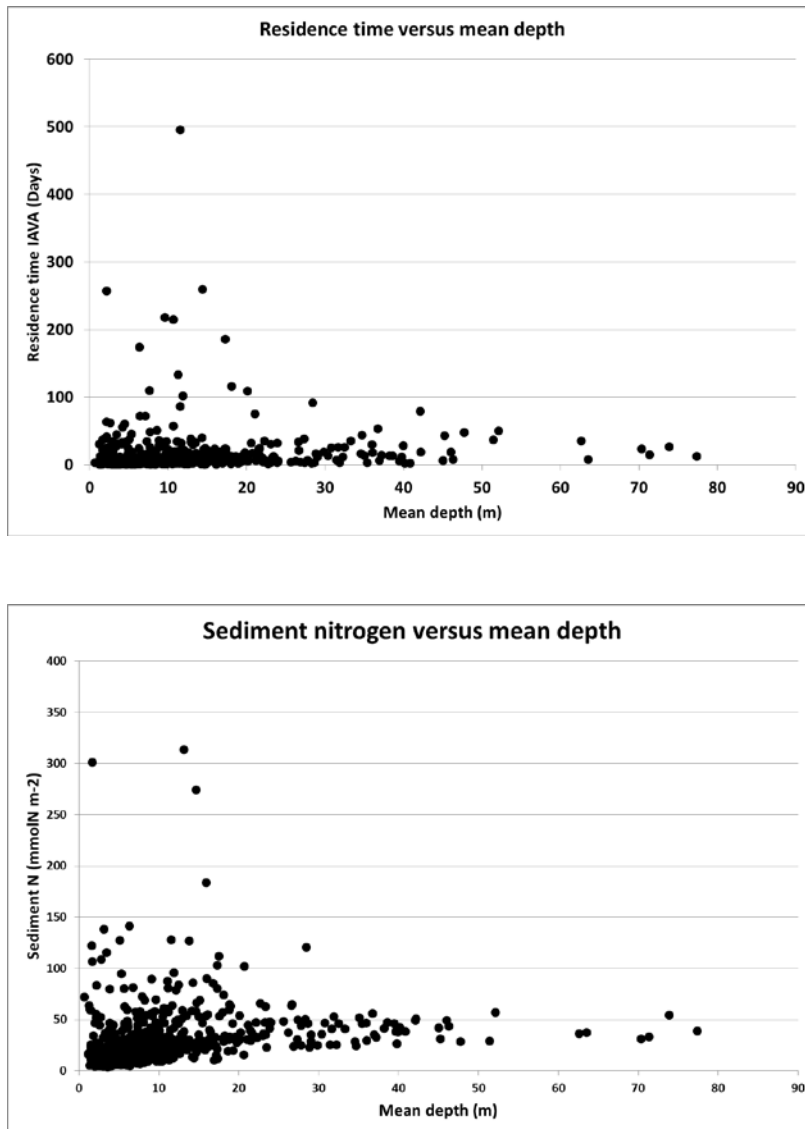


Figure A2. The relation between mean depth and IAVA residence time (days) in the 653 sub-basins of the SCM model is shown in the upper plot. The relation between sediment nitrogen concentrations (mmol N m⁻²) and mean depth is shown in the lower plot.

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