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OCEANOGRAFI Nr 99/2009

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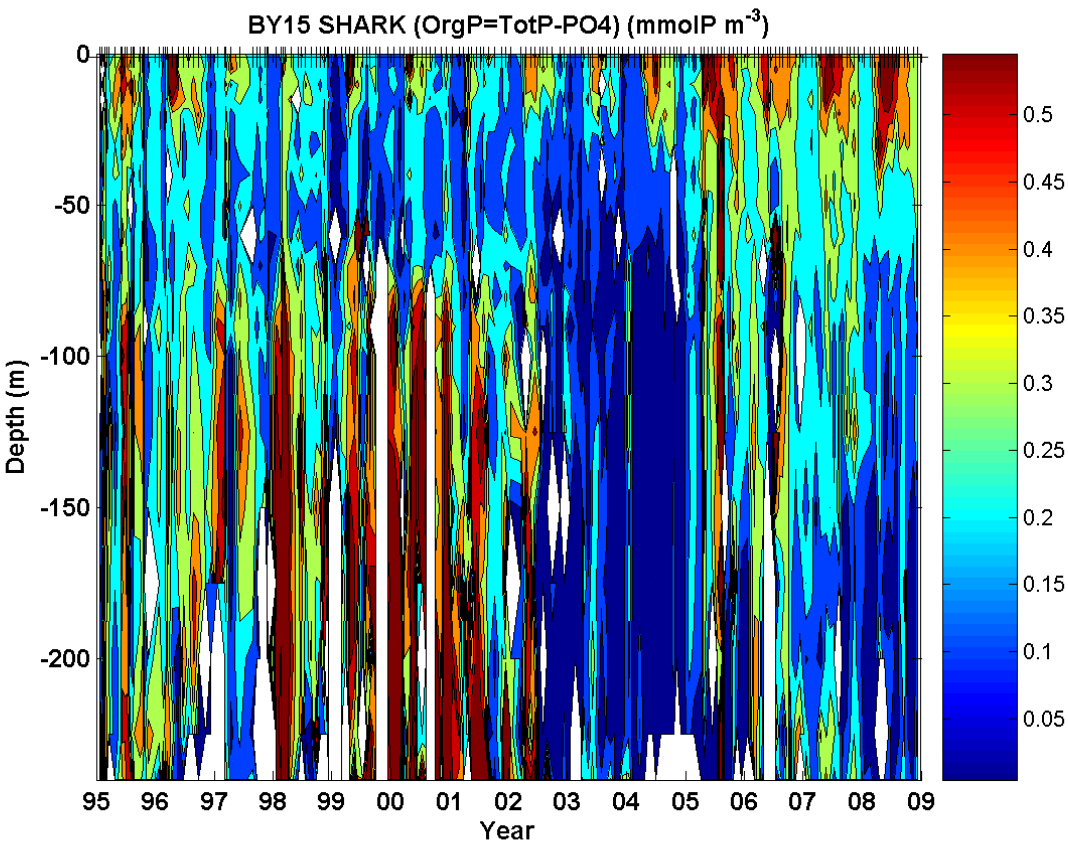

Cover picture:
Observations (mmol m^{-3}) of organic phosphorus defined as total P – inorganic P at the Gotland Deep station BY15 during the period 1995-2008 (data from SHARK). White areas lack observations. The upper black tic marks indicate dates of observations

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On the dynamics of organic nutrients, nitrogen and phosphorus, in the Baltic Sea

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Abstract

In this report we study the dynamics of organic nutrients, nitrogen and phosphorus, in the Baltic Sea. The results indicate that much of the characteristics of the surface layer dynamics of organic nutrients can be described by the Redfield ratio especially in the Baltic proper. There is however deviations from the Redfield ratio that are discussed and needs to be further investigated. The seasonal variations at all investigated stations indicate that the increase and decrease of the organic phosphorus and nitrogen concentrations in spring and autumn takes place with stoichiometric values different from the Redfield ratio. It is also found that organic phosphorus concentrations start to decrease earlier in summer than organic nitrogen that may continue to increase during summer and early autumn. There is a clear trend with decreasing DIN:DIP ratios in late winter at the Gotland Deep during the period 1995-2008 while there is an improved correlation of the Redfield model during the later part of the period when we have extremely low DIN:DIP ratios. Also the results from the Bothnian bay show that the variability of organic matter is fairly well described by the Redfield model despite the extremely high late winter N:P ratios observed in this region. Hence, the seasonal variability of organic matter seems to be rather independent of the ratio of inorganic nutrients. The variability of the inorganic N to P ratios in late winter and early spring across the Baltic Sea is much larger than seen from the variability of the organic matter. This suggests that other sources than DIN and DIP as sources for new nutrients in spring are used. This is true both in the Baltic proper, where an additional nitrogen source for organic matter production in spring is needed besides inorganic nitrogen, and in the Bothnian Bay, where an additional phosphorus source is needed. Nitrogen fixation by cyanobacteria that grow later in the summer in the southern Baltic Sea can not explain the additional nitrogen source needed in early spring. Future model experiments may reveal more information about the dynamics of organic matter in the Baltic Sea.

Contents

1. Introduction

The aim of the present report is to summarize some characteristics of the dynamics of organic nutrients nitrogen and phosphorus in the Baltic Sea as seen from observations at some standard monitoring stations. The results may serve as a basis to improve our understanding and also to provide a background for future model validations of the dynamics these nutrients.

The pools of organic nutrients in the forms of nitrogen and phosphorus in the Baltic Sea are large. For phosphorus the organic concentrations are of the same order of magnitude as the inorganic fractions and for nitrogen the organic concentrations are relatively much larger. The variability of the observed organic nutrients is large at all depths as seen in the examples from the Gotland Deep in Fig.1.

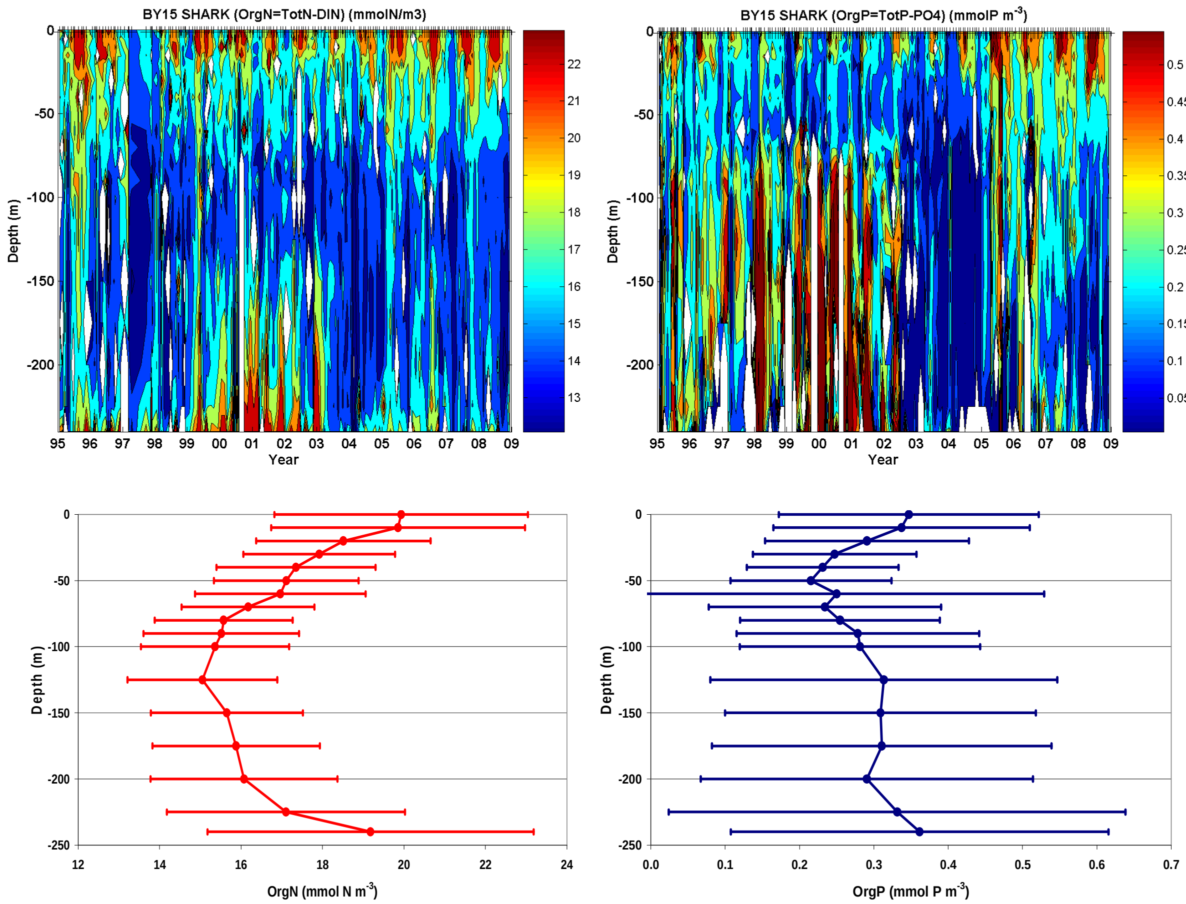

Figure 1. Upper: Observations (mmol m^{-3}) of organic nitrogen (left) and phosphorus (right), defined as total N (P) – inorganic N (P), respectively, at the Gotland Deep station BY15 during the period 1995-2008 (data from SHARK). White areas lack observations. The upper black tic marks indicate dates of observations. **Lower:** Corresponding mean values of organic nitrogen (left) and phosphorus (right) (mmol N m^{-3}) and $\pm$1 standard deviation given by error bars.

One may note from Fig.1 that the concentration of organic matter in the deep water is of the same order of magnitude as found in the surface layers and that there is a large average pool of nitrogen that is usually not exhausted as seen from the observations. The variability of phosphorus however often shows occasions when the variability at all depths ranges from very low to high values. The deepwater variability is not obviously correlated to the local production of organic matter in the surface layer and the seasonal patterns do not show any clear transport patters from the surface towards the depth. This is also indicated by the average organic nutrient concentrations and standard deviations that in general are larger in the surface and the bottom layer than in the intermediate waters. The monthly observations can of course miss some events with high speed sinking organic matter but it seems the impact from deep water dynamics such as inflows and resuspension events, like after the hurricane “Gudrun” in 2005, mainly influence the deep water variability. Further investigations about the dynamics of organic nutrients in the deepwater are out of the scope of the present investigation and are therefore left for future work.

Below we will focus on the surface layer dynamics and the composition of organic matter as it is seen from the seasonal variations of the total concentrations of organic nitrogen and organic phosphorus in the Baltic proper. We will also briefly investigate possible differences between the northern and the southern parts of the Baltic Sea. The discussion is based on the standard Redfield molar composition ratio of fresh organic matter N:P=16:1. Redfield (1934; 1958; 1963) showed that major plant nutrients, such as nitrate and phosphate, change concentrations in seawater in a fixed stoichiometry that is the same as the average N and P stoichiometry of planktonic organisms. The implication that Redfield draw was that organisms control the nutrient concentrations in their distributions. Even though there are no physical or biochemical constraint on the elemental composition of primary production, it seems that the overall average N:P composition of marine particulate matter largely follows the Redfield ratio (see review by Geider and La Roche (2002)). In the shallow semi-enclosed Baltic Sea one should also remember that the supplies from land and the benthic-pelagic nutrient fluxes highly influences the observed patterns of nutrient concentrations in the water (e.g. Eilola & al, 2009).

Area description

The Baltic Sea is a strongly stratified semi-enclosed basin. Its horizontal and vertical salinity gradients are the result of the large freshwater supply from rivers and net precipitation and of the reduced water exchange with the world ocean (Fig. 2).

The climate of the 20th century is characterized by an average salinity of about 7.4 and a freshwater supply including river runoff and net precipitation of about 16 100 $m^3\ s^{-1}$. The average in- and outflows of the Baltic Sea amount to 16,100 $m^3\ s^{-1}$ and 32,200 $m^3\ s^{-1}$, respectively (applying the well-known Knudsen formulae with surface and bottom layer salinities of 8.7 and 17.4, respectively).

The large-scale horizontal circulation is characterized by cyclonic gyres and the vertical circulation is driven by the inflow of high-saline water from the Kattegat. The bottom water is usually only replaced after so-called Major Baltic Inflows. However, small and medium-strength inflows are important as well since they may renew intermediate layers of the Baltic proper halocline. During inflow events the high-saline water spills over the shallow sills of the Baltic Sea entrance area into the Arkona Basin and Bornholm Basin. Both dense bottom flows and cyclonic eddies renew the deep water of the eastern Gotland Basin. From the Gotland Deep the flow continues via the Northern Deep either into the northwestern Gotland Basin or into the Gulf of Finland. The mean ages of inflowing Kattegat water varies from about 10 years in the

Arkona deep water to more than 40 years in the northern Baltic surface waters (Meier, 2007). Present knowledge about the renewal of the Baltic Sea deep water is summarized e.g. by Meier et al. (2006).

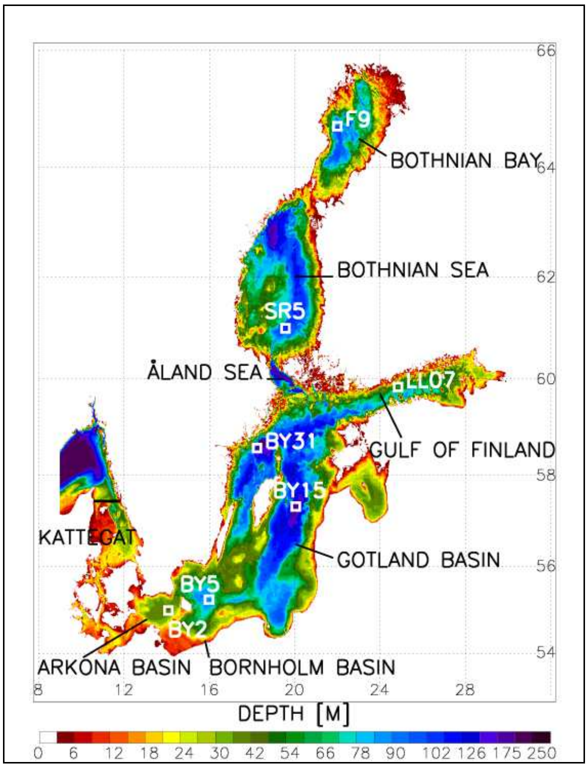

Figure 2. *Overview of the RCO model domain. The black line indicates the open boundary in the northern Kattegat. The color bar shows depths in meter. Some standard monitoring stations are indicated by white squares.*

2. Method

Data

The data used in the present investigation are from the Swedish Oceanographic Data Centre (SHARK) at the Swedish Meteorological and Hydrological Institute, see http://www.smhi.se. Data from the monitoring stations BY5, BY15, BY31 are used as representative for the Baltic proper and for the comparison with the northern Baltic Sea we use data from station F9 (Fig.2).

Organic phosphorus (OrgP) is defined as Total phosphorus – dissolved inorganic phosphorus (DIP) and organic nitrogen (OrgN) is defined as Total nitrogen – dissolved inorganic nitrogen (DIN) where DIN=NO3+NO2+NH4. Simultaneous observations of all parameters at same dates were a requirement for the computations. Only non negative values of OrgP were used in the data analysis.

Surface layer proxy data

An investigation of available OrgN and OrgP data from 1980-2008 at BY 15 in the upper 10 m (Fig.3) shows that values from 10 m depth has quite similar characteristics as the whole data set. The mean values and standard deviations of the data sets are shown in Table 1. This suggests that we may use a subset from 10 m depth as a good proxy for the surface layer characteristics of organic matter dynamics.

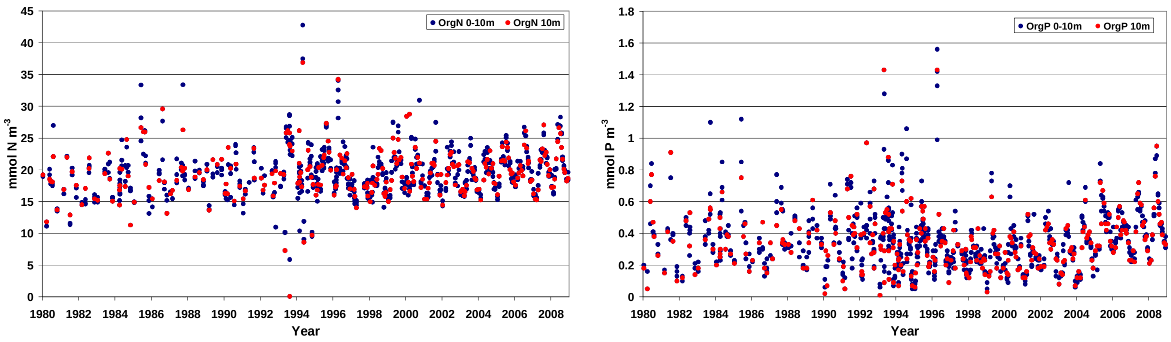

Figure 3. All available OrgN (left) and OrgP (right) data from the upper 10 m at BY15 (blue dots) and all data from 10 m depth (red dots).

Table 1. Statistical properties of OrgN and OrgP (mmol m^{-3}) in the surface layer of BY15.

	OrgN		OrgP	
	0 - 10 m	10 m	0 – 10 m	10 m
Mean value	18.8	19.5	0.36	0.35
Standard deviation	4.1	3.8	0.19	0.19

Annual anomalies

In order to compare the variations of organic nitrogen and phosphorus and discuss its possible coupling to the stoichiometric composition of fresh organic matter according to the Redfield ratio we will study the deviations from annual means in each year.

Thus in each year we first compute the annual mean (M_i) from all available OrgN and OrgP data in year “i” and then we compute the anomalies (Ax_i) for all data x_i relative to the annual mean in each year.

$Ax_i = x_i - M_i$

For this investigation we extracted only data sets that were complete and available from same dates for N and P respectively. Below the linear equation of the regression between OrgN and OrgP is given by

$$OrgN = m \times OrgP + b \qquad \text{Equation 1}$$

where OrgN and OrgP denote the anomalies relative to the annual means. Note that the Redfield ratio model is obtained when *m*=16 and *b*=0. Below this is called the Redfield model.

In order to reduce the impact from outliers and scarce data sets from the beginning of the period, the subset period 1995-2008 with larger amounts of data available with higher sampling frequency is analyzed specifically. Due to the scarce data cover in the Bothnian Bay only observations from the period 1991-1999 were used.

3. Results

In Fig.4 the inter-annual variations of the annual anomalies at BY15, BY31, BY5 and F9 are shown for observed OrgN as well as for OrgN estimated from OrgP by assuming that the organic matter is composed according to the Redfield molar ratio N:P=16:1.The results from the Redfield model seems to largely follow the variations within the limits of the standard deviation of the observed OrgN at all stations.

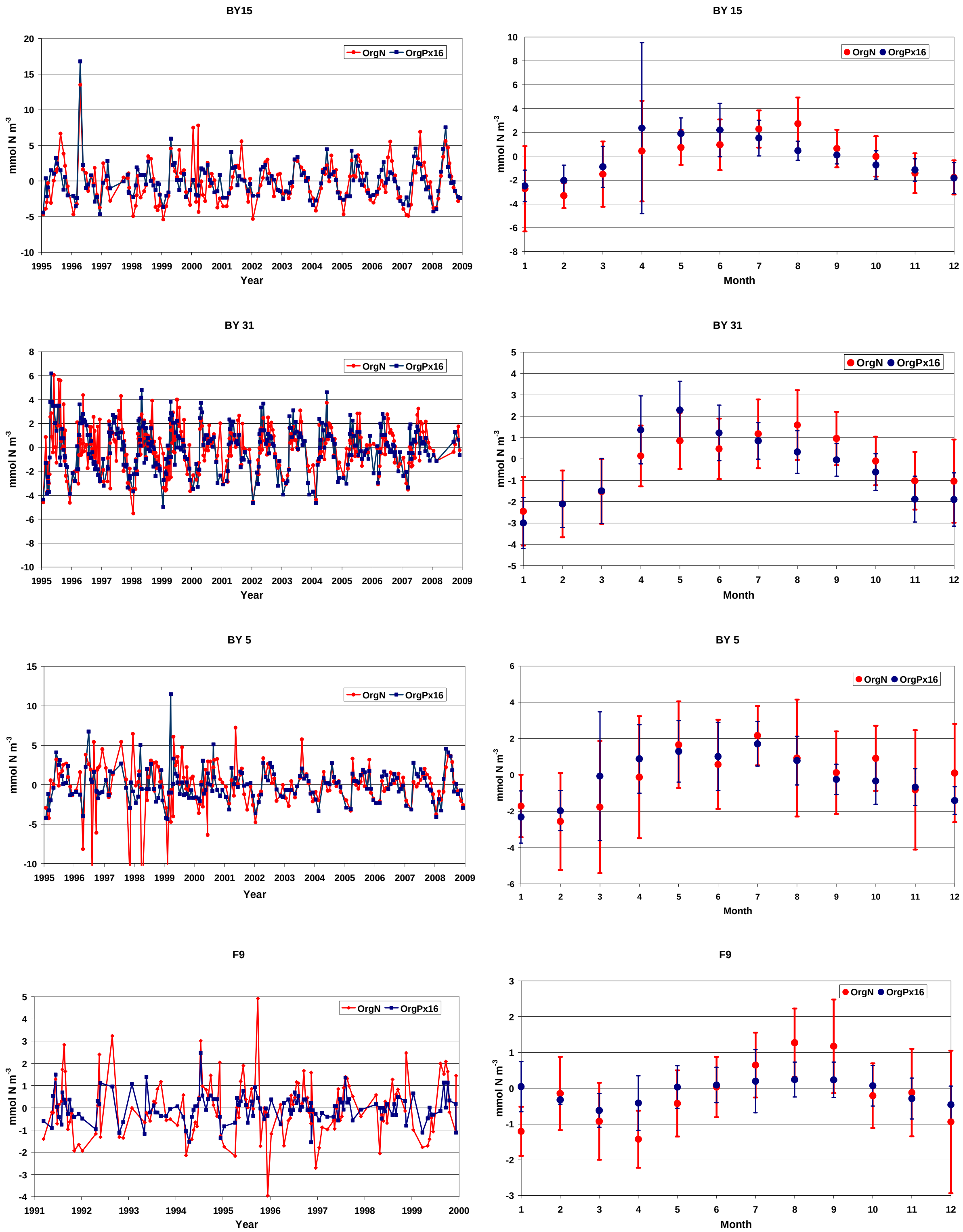

Figure 4. Annual anomaly variations (Left) of OrgN (mmol N m^{-3}) (red) and the corresponding estimate of OrgN based on the Redfield model, OrgN=OrgP x 16, (blue). The right panel show the corresponding monthly means and ±1 standard deviation. The stations listed from above and down are BY15, BY31, BY5 and F9.

An investigation about the seasonal variability of the correlation between the anomalies of OrgN and OrgP in the BY15 data set shown in Fig.5 is given in Table 2. The results indicate that the correlation is quite significant on annual basis and during the spring and early summer with the highest correlation (R^2=0.71) found in late spring. The correlation in late summer and autumn is much lower though it is still significant on less than the 5% level.

Table 2. The regression coefficients m, b, R^2, and the *p*-value of significance of the anomalies at BY 15 of OrgN and OrgP in the period 1995-2008. The standard deviation of m and b is given in italics in the brackets.

	m	**b**	$\mathbf{R^2}$	***p***
Annual	12.7 (*1.1*)	0.00 (*0.17*)	0.45	< 0.0001
Jan-Mar	13.7 (*3.9*)	-0.75 (*0.56*)	0.24	0.001
Apr-Jun	12.6 (*1.3*)	-0.90 (*0.30*)	0.71	< 0.0001
Jul-Sep	9.7 (*3.8*)	1.68 (*0.33*)	0.12	0.016
Oct-Dec	7.5 (*3.2*)	0.39 (*0.35*)	0.13	0.025

The regression line from BY15 in Fig.5 shows that on an annual basis the annual anomalies of OrgN are significantly correlated to the annual anomalies of OrgP by a factor of 12.7 which is lower than the standard value of the Redfield number. There is a large spread that is indicated by the relatively low R^2 value of 0.45.

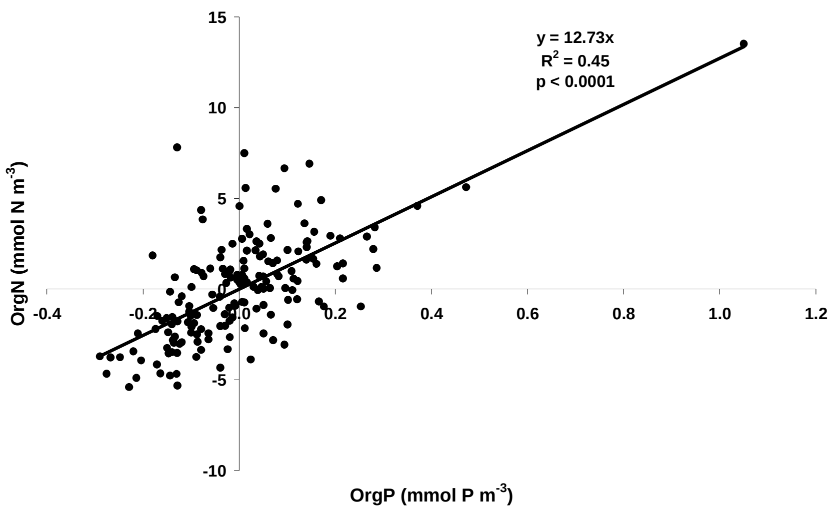

Figure 5. The regression analysis at BY 15 between OrgN and OrgP for the period 1995-2008.

We may see from Fig.4 that the anomaly of OrgP is generally at all stations biased to an earlier increase in spring and a faster decrease in autumn than OrgN which might partly explain the negative value of *b* during spring and the positive *b* during late summer and autumn seen at BY15.

In order to investigate average characteristics and to reduce the impact of single measurements, a five point running mean and the correlation of the running means was computed for BY15 (not shown). Because of the monthly standard monitoring program, except in years with gaps in the data, this filtering approximately makes an average of the actual month and the two months before and after the actual month. From these results it seems that the average characteristics of the anomalies of OrgN and OrgP are significantly correlated with a higher correlation coefficient (R^2=0.55) than seen from the single data points (Fig.5). The relation between the running mean anomalies of OrgN and OrgP (m=14.7 *(std=1.0)*) is higher than the ratio seen from the single data points (m=12.7).

Statistical characteristics

If we investigate the statistical behaviour of the predicted time series of OrgN at BY15 by using the best fit value (m=12.73) of the linear correlation relation between OrgN and OrgP (Fig.5) we find that the variability of the prediction becomes lower than observed (Table 3). The observed OrgN has a standard deviation of 2.93 mmol N m^{-3} while the predicted curve has a standard deviation of 1.94 mmol N m^{-3} which underestimates the standard deviation by about 1.0 mmol N m^{-3}. If we require that the predicted data should have the same standard deviation as the observed data (Fig.6) the m value becomes 19.2 which is larger than the Redfield value. Improving the standard deviation of the data set does however not improve the time lag between OrgN and OrgP in spring and autumn. The Redfield model (*std*=2.44 mmol N m^{-3}) used in Fig.4 underestimates the standard deviation by about 0.5 mmol N m^{-3}.

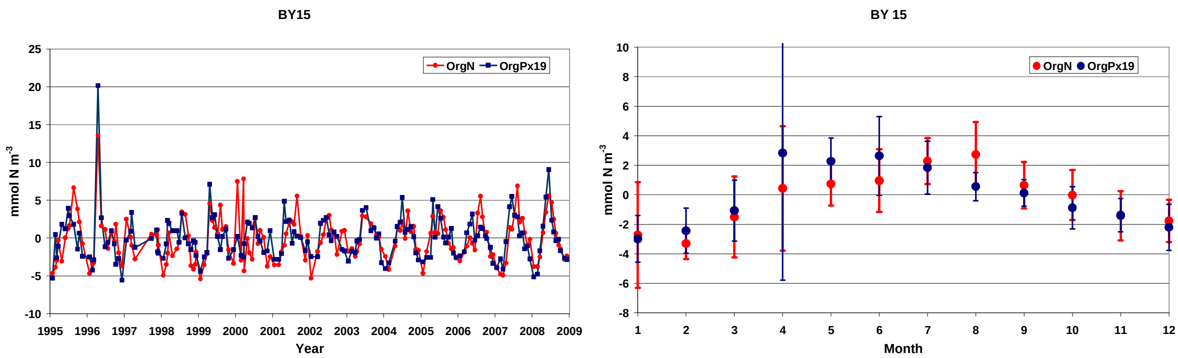

Figure 6. Annual anomaly variations (Left) of OrgN (mmol N m^{-3}) (red) and the corresponding estimate of OrgN based on the best fit of the standard deviation at BY15 (blue). The right panel show the corresponding monthly means and ±1 standard deviation.

At station BY31 the Redfield model (*std*=1.91 mmol N m^{-3}) estimates well the standard deviation of the data (*std*=1.86 mmol N m^{-3}) while a prediction with the best linear fit value (m=10.18) show much lower variability (*std*=1.22 mmol N m^{-3}). The best fit of the standard deviation is obtained when m=15.6.

At station BY5 the observed standard deviation of OrgN is 2.98 mmol N m^{-3} while the standard deviation of the Redfield model is 2.08 mmol N m^{-3}. Applying the best linear fit value (m=9.38) gives *std*=1.22 mmol N m^{-3}. The best fit of the standard deviation is obtained when m=23.0.

At station F9 the observed standard deviation of OrgN is 1.32 mmol N m^{-3} while the standard deviation of the Redfield model is much lower, 0.62 mmol N m^{-3}. Applying the best linear fit value (m=13.5) gives *std*=0.53 mmol N m^{-3}. The best fit of the standard deviation is obtained when m=34.0 which is quite high relative to the Redfield ratio.

Table 3. The standard deviation of observations, the Redfield model and of the best linear fit model. The last column show the m-value of the best fit to the standard deviation.

	Observed Std	**Redfield model Std**	**Best linear fit Std**	**Standard deviation fit m-value**
BY 5	2.98	2.08	1.22	23.0
BY 15	2.93	2.44	1.94	19.2
BY 31	1.86	1.91	1.22	15.6
F 9	1.32	0.62	0.53	34.0

Improved correlation of the Redfield model in later years

There is a period with quite high scatter in the data from BY5 lasting until about year 2001. The correlation of the regression (R^2=0.63) is much higher in the later period 2002-2008 than for the entire period 1995-2008 (R^2=0.17). The m-value (12.7) in the later period is in agreement with the findings from the BY15 regression line. The reason for the scatter in the early period at BY5 is unclear. The standard deviation at BY5 during the period 2002-2008 is 1.83 mmol N m^{-3} which is much lower than for the whole period 1995-2008 (*std*=2.98 mmol N m^{-3}). Actually the standard deviation of the Redfield model during the same period 2002-2008 is 1.80 mmol N m^{-3}, which is close to the observed value. Also BY15 and BY31 stations show less variability during the later period (2.56 and 1.55 mmol N m^{-3}, respectively) than in the entire period (2.93 and 1.86 mmol N m^{-3}, respectively). Also the standard deviation of the BY15 Redfield model during the period 2002-2008 (2.21 mmol N m^{-3}) is more in accordance with the observed value.

4. Discussion

The results indicate that much of the characteristics of the surface layer dynamics of organic N and P can be explained by the Redfield ratio especially in the Baltic proper. There is however differences that need to be further explored between the observed variability of organic nitrogen and the predicted time series based on dynamics of organic phosphorus and based on the usage of the Redfield ratio.

The observation that the anomaly of OrgP is biased towards a faster decrease in autumn than OrgN can be due to the faster remineralisation rate and higher degree of recirculation of phosphorus than that of nitrogen in organic matter (eg. Savchuk, 2002). This may cause deviations from the Redfield ratio when looking at the total organic nutrient pool which is done in the present report. It might also be due to increased nitrogen fixation in late summer but it seems hard to use this explanation in the Bothnian Bay where we do not expect any larger amounts of nitrogen fixing cyanobacteria.

The observation that the anomaly of OrgP is biased towards a faster increase in spring than OrgN is perhaps harder to explain. This could be explained if we simply assume that the N:P ratio of newly built organic matter is variable and lower than the Redfield ratio. If we assume that the composition of new organic matter depend on the available inorganic fractions in spring of DIN and DIP this would produce organic matter composed with N:P ratio in the range 4-10 at BY15 and 100-400 at F9 as seen from Fig.7. This is however far from the observed variability of the organic pools of N and P discussed above.

One may note from Fig.7 that there is a clear trend with decreasing DIN:DIP ratios at BY15 from about 10 to about 4 during the period. The trend seems to correspond mainly to an increase of the DIP concentration but also to a decrease of the DIN concentrations during the period. One may note that the improved correlation of the Redfield model during the later part of the time period corresponds to a period when we have extremely low DIN:DIP ratios. The reason for this is not obvious. Also the results from the Bothnian Bay show that the variability organic matter is fairly well described by the Redfield model despite the extremely high N:P ratio observed in this region. Hence, the seasonal variability of organic matter seems to be rather independent of the ratio of inorganic nutrients. This suggests that other sources than DIN and DIP as sources for new nutrients are used.

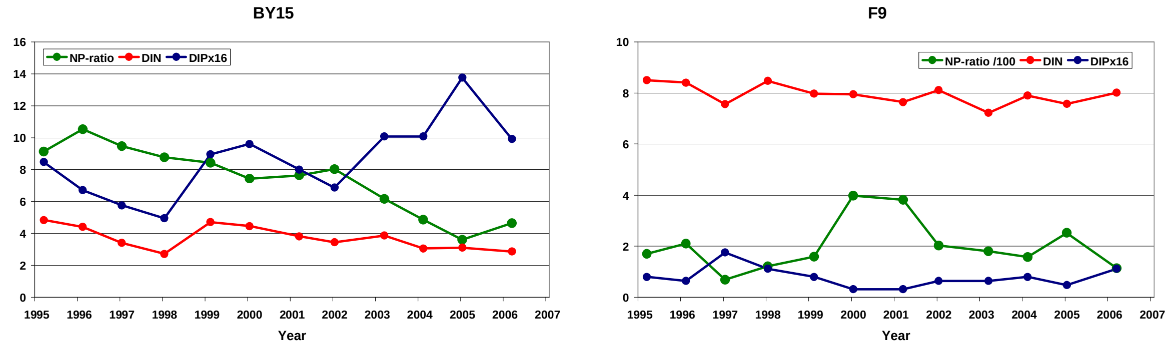

Figure 7. Left: The maximum observed surface layer (10 m) DIN to DIP ratio (green) in early spring and corresponding DIP (x16) (mmolPm^{-3}) (blue) and DIN (mmolNm^{-3}) (red) values at the Gotland Deep station BY15 (Left). Right: The minimum observed surface layer (10 m) DIN to DIP ratio (divided by 100) in early spring and corresponding DIP (x16) (mmolPm^{-3}) and DIN (mmolNm^{-3}) values at the Bothnian Bay station F9.

Another explanation for the faster increase of OrgP in spring might be that the nitrogen content in the newly built organic matter is to larger degree than phosphorus based on nutrients mineralized or assimilated from the existing pool of organic nutrients available in early spring. The total pool of organic nitrogen in spring would then change less than the pool of organic phosphorus since nitrogen are transformed from older organic matter into fresh organic matter. This process should then be independent of latitude in the Baltic Sea in order to explain the similarity between the southern stations and F9.

One might perhaps expect that the much lower DIN:DIP ratios at BY15 in the later period correlates with increased biomasses of cyanobacteria in the following summer. The results from an investigation by Karlson et al. (2009; submitted manuscript) did however not support this hypothesis (cf. Fig.8). The data set used in their study (1999-2007) showed no correlation between excess DIP (=DIP-DIN/16) in winter and total summer cyanobacteria biomass. The explanation for this might be that during the studied period phosphate in surface water is already available in high concentrations during all years. Thus the cyanobacteria growth is likely regulated by other factors. In fact, a correlation between the cloud free fraction of the sky in July and cyanobacteria biomass was observed. One may also note from Fig.8 that cyanobacteria have its major impact in summer time on the dynamics of organic nitrogen. Hence, nitrogen fixation by cyanobacteria that grow later in the summer can not explain the additional nitrogen source needed in early spring in the southern Baltic Sea.

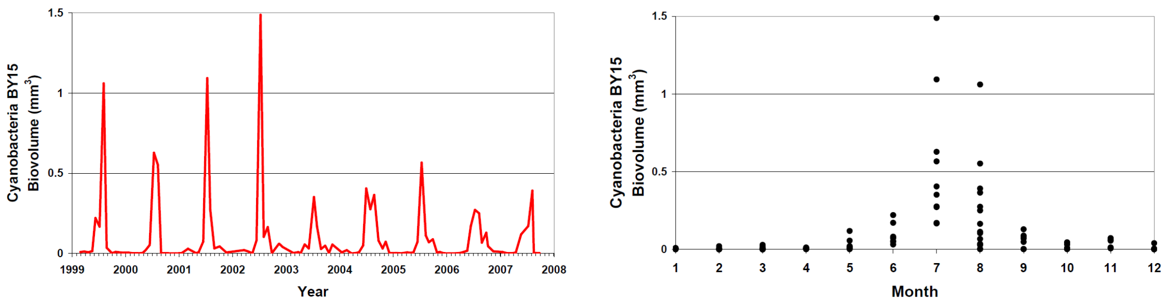

Figure 8. All observations in the period 1999-2007 of cyanobacteria biovolume from tube sampling 0 – 10 m at BY15. Data provided by Dr. Bengt Karlson at SMHI. The time series is to the left and the monthly scatter to the right.

The variability of organic nitrogen and phosphorus at station F9 is significantly (p<0.0001) correlated to the uptake and release of DIN (Fig.9) and DIP (not shown) though the spread is large, R^2=0.34 and 0.12, respectively. The monthly means in Fig.9 show that there is a larger seasonal variability of the inorganic nitrogen than of the organic nitrogen. This might be due to a decrease of OrgN caused by sinking organic matter in summertime and an additional release of inorganic nutrients from sediments in late autumn and winter which therefore is not reflected in a decrease of the pool of pelagic organic matter. The inorganic phosphorus concentrations at F9 are often close to the detection limits since DIP varies below and around about 0.05 mmol m^{-3}. This limits the analysis of the phosphorus dynamics at this station. One should also mention that the number of observations in different months (N_m) at F9 (N_m =7, 2, 6, 6, 20, 16, 11, 15, 14, 11, 11, 8, respectively) differ much and that the February mean value is based on only two observations.

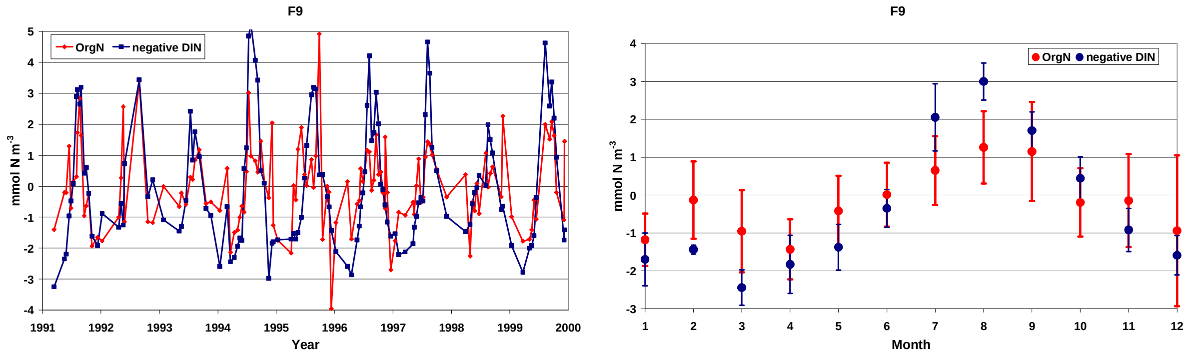

Figure 9. Station F9. Left: Annual anomaly variations of OrgN (mmol N m^{-3}) (red) and the negative (=inverse) anomaly variation of corresponding DIN (mmol N m^{-3}) (blue). The right panel show the corresponding monthly means and ±1 standard deviation.

It is however obvious from Fig.10 that the variability of DIPx16 and also of TotPx16 is much lower than observed from the variability of DIN. Hence, the variability of phosphorus in combination with the Redfield ratio can not explain the inorganic nitrogen dynamics in the Bothnian Bay. Future investigations using complementary information from model experiments might give more information of possible mechanisms that can explain the dynamics of organic matter in the north.

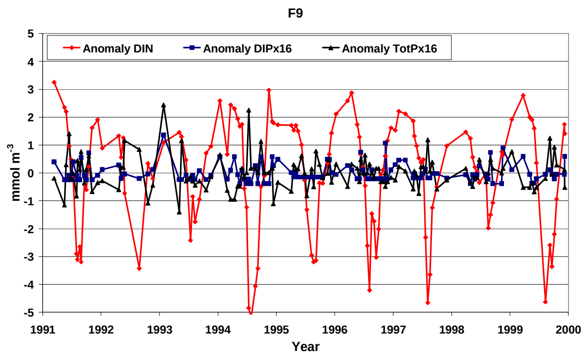

Figure 10. Station F9. Annual anomaly variations (mmol m^{-3}) of DIN (red), 16xDIP (blue) and 16xTotP (black).

There is an unexplained variability of the data sets of organic nutrients that may be due to many other causes. Uncertainties in the measurement methods of nutrient concentrations may have errors which were obvious for example when TotP-DIP became negative in the computations. These values were however not many and were removed manually from the data set. Using a vertically integrated value for the entire surface layer, hence including more of the sinking matter, could give somewhat different results. The choice of using the annual averages of observations as a basis for the estimation of anomalies might have some impact and using another time frame for the analysis than the annual mean value could give slightly different results. It is also likely that the limited number of observations may have an impact. The variability of the organic matter at a single spatial station may be due to advective processes that import a mixture of organic matter that already has degraded and the composition of older organic matter may differ much from the newly produced organic matter. The importance of different factors influencing the variability may be further investigated e.g. by models but these tasks are out of the scope of the present report.

5. Concluding remarks

The results indicate that much of the characteristics of the surface layer dynamics of organic nutrients can be described by the Redfield ratio. There is however a need for additional nutrient sources besides the inorganic nutrients to explain the variability of organic nutrients. In the south there is a need for an additional nitrogen input during the spring and early summer and in the north there is a need for additional phosphorus. Future model experiments may reveal more information about the dynamics of organic matter in the Baltic Sea.

6. Acknowlegements

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