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# Variations of Annual Turnover Cycles for Nutrients in the North Sea, German Bight Nutrients Turnover Cycles in The North Sea



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#### Abstract

The long term behavior of water chemical composition in the North Sea, German Bight is much influenced by the atmospheric, hydrographical as well as biological processes. We analyze the long term trends in annual turnover cycles of the silicate, phosphate, nitrate and nitrite for the period of 1966-2009. We provide a straightforward numerical procedure for determination of the nutrients depletion phases. It uses the rates of cumulative concentrations to distinguish among different phases of nutrients cycle. The silicate is one of the key nutrients used by diatoms. The amount of silicate also depends on the mixing of coastal and more marine water at Helgoland. We show that seasonal dynamics of silicate undergone a strong change since 1987 until 2009. It is characterized by an earlier onset of nutrients depletion and build-up phases. Also a shortening of nutrient depletion phases for both silicate and phosphate is observed during period 1966-1984/1985 For phosphate the start of depletion and build-up phases generally evolves towards later time of the year in the interval 1984-2009. Among other nutrients nitrate exhibits higher interannual and interseasonal variability over the whole time analyzed. The depletion cycle length for most of the nutrients (with exception of silicate) is negatively correlated with total annual concentrations. The annual sunshine hours are qualitatively compared with the onset and termination of depletion for phosphate and a good match between the variation of depletion phase and annual sunshine is observed.

Keywords: Nutrients cycles; Depletion rates; Silicate concentration; Long-term data; Nutrients limitation

## Introduction

Wide-scale shifts in biological and abiotic variables has been reported to occur for the North and Wadden Sea in 1979, 1988 and 1998 [1]. In line with these results other studies report on large scale changes in various levels of ecosystem that took place in the late 1970s and 1980s [2-4].

The coastal region of the North Sea is characterized by the seasonal fluctuations of the climate and environmental conditions and biological population variability. This happens to the large extend due to the interplay between different water bodies: low salinity coastal and offshore marine waters. In addition coastal area is mainly driven by the atmospheric forcing and therefore is more sensitive to the climate change [5]. The ecosystem along the coast is largely affected by the local influence of increased nutrients concentrations [6]. Also the GB ecosystem is heavily impacted by anthropogenic perturbations.

Although numerous observations and statistical analysis of long term data support the clear evidence of the regime shifts in hydrographical, atmospheric and physicochemical variables [7] it remains unclear how these changes affect the base of marine food webs. And more general, is the coastal ecosystem affected by the wide-scale climate variations, can it be placed in the framework of the overall pattern on climate-ocean variability observed for the North Sea. For example, in spite of the fact that most of the parameters indicating water climate altered markedly no significant change of timing of seasonal diatom blooms at Helgoland has occur in years 1975-2005 [8]. At the same time analysis of phytoplankton species diversity and algal density shows a marked increase in the number of large diatoms [8]. The average cell size has increased from 0.1ng to 1-2ng. As a consequence of the increased percentage of large diatom cells the rate of primary production and resource reduction will be altered as well. The increase of numbers of cells with hard silicate shell introduces higher silicates demand in the ecosystem that it was found during previous period. To our knowledge the effects of increase of the cell sizes on the annual pattern of silicate turnover has not been studied so far. From the other hand there is a pronounced upward shift in silicate concentrations observed in late 1970s at HR.

Many long-term studies in the coastal North and Wadden Sea region highlight the importance of nutrients and water chemical composition on the local ecosystem developments [9]. In the GB the increase of biodiversity in mid 1990s of phyto-and zooplankton documented at Helgoland [8] by no means influences the routes of energy and nutrients transfer in the marine food web. One of the topics of interest is to investigate how the incline of percentage of large size diatoms [8] contributes to the change of nutrient depletion rates. In this paper we analyze the long-term trends in the nutrient cycles for the silicate, phosphate, nitrate, nitrite and ammonia from HR data. The HR data set is, in this sense, one of the valuable observational data that provide biological and physicochemical parameters measured at high frequency and for more than 45 years time [10]. We provide a numerical method for a straight forward discrimination of different phases of nutrient annual cycles. The method is based on the local extrema calculations of the cumulative nutrient concentrations. The lengths of depletion cycles are estimated based on our procedure for four chemical parameters from HR data: nitrate, silicate, phosphate and nitrite. Sun radiation is one of the major environmental factors that determine the life cycle and productivity of shelf pelagic organisms. Specifically, the amount of sun radiation and its long-term development are vital for understanding the light limitation patterns [11,12] as well as changes in the onset and termination of the annual phytoplankton bloom. In addition sun radiation is responsible for the amount of heat transfer from air to the sea surface and therefore is one of the regulators of sea surface temperature and biomass production. It is also evident, that the intensity of sunshine radiation impacts the underwater light climate, therefore it is a key factor that determines the start and the end of phytoplankton bloom, termination and beginning of the nutrients accumulation. To our knowledge the long-term trends of sunshine annual cycles are not studied for the local area near HR. In this work we study long term trends of sunshine annual cycles and their relation to the changes in nutrient depletion patterns.

## Data Sampling and Study Site

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HR is situated in the GB and located about 60km away from the German coast and rivers Elbe and Weser. The HR water masses are a mixture of North Sea and coastal waters. Depending on the prevalent water transport Helgoland area is influenced either by the low saline riverine input or the influx of saline water masses of the North Sea. The hydrography is largely determined by the topography of the inner GB and wind conditions [13]. The Elbe coastal water do not reach Helgoland but due to mixing with other coastal water bodies indirectly influence the HR water composition. The daily water sampling procedure is maintained at HR  $(54^{\circ}11.3' \text{ N}, 7^{\circ} 54.0' \text{ E})$  since 1962 up to present time. The dissolved inorganic nutrients, temperature, salinity and Secchi depth are measured 5 days a week and therefore resolved on the scale from 5 days to 45 years [10]. The water sample is well mixed as a result of tidal currents and is a sample of an entire water column.

The sunshine daily data for the period 1966-2009 are retrieved from Deutscher Wetterdients as a part of free available meteorological records at the Helgoland Station. The 20-days means are used to approximate the sunshine radiation.

### Methods

Analysis of nutrients cycles is usually hindered by the presence of large scale variations in the observational data sets, high inter annual and interseasonal variability of chemical parameters. In particular, the different phases of the annual nutrient turn over such as decline, depletion and build-up are not easily distinguished because of a significant influence of various environmental processes. These fluctuations are related to daily and long term variability of meteorological conditions, river discharge dynamics and hydrographical situation. Also noise in the data alters the actual timing and distribution of nutrient levels during every phase. Possible source of noise are the errors and outliers which are inevitable due to the measuring procedure [10]. To avoid outliers and weekend gaps that are present in the long term records the data are first preprocessed by interpolation and smoothing. A smoothing procedure is performed in Matlab. It uses local regression with six points weighted linear least squares and a 1<sup>st</sup> degree polynomial model. The method assigns lower weight to outliers in the regression and zero weight to data outside six mean absolute deviations.

Since remineralization processes do not always terminate in February but might have different time cycle from one year to another the February medians [10] are not used here as a proxy of the observed annual changes of nutrients. The peaks of nutrient concentrations can be distributed over several months and the distribution is not the same for each year. Therefore, it is more reliable to use other temporal descriptors of the seasonal changes of nutrients. To differentiate the seasonal dynamics we separate annual circle into two periods: the HLis observed from late autumn and could last until early spring, the LL phase is characterized by a low concentration of nutrients due to rapid growth of biomass and high microalgal activity and the depletion rates.

In our study we refer to two major descriptive estimations: total annual concentrations and HL mean values. We will compare both quantities with evolution of depletion phases and overall seasonal shape of nutrients.

The numerical procedure based on cumulative concentration profiles is used for approximating the onset and termination of

depletion cycle that separate HL from LL phases. The resulting cumulative profiles are calculated for every year from the following expression:

$$\theta_{o}^{j} = \frac{S_{1}^{j}}{\sum_{i=1}^{N} S_{i}^{j}} - \Delta \qquad .....(1)$$
  
$$\theta_{k}^{j} = -\theta_{o}^{j} + \frac{\sum_{i=1}^{k} S_{i}^{j}}{\sum_{i=1}^{N} S_{i}^{j}} - k\Delta \qquad .....(2)$$

where k=1, ....N are days counts,  $S_i^j$  is the concentration measured on ith day ofjth year,  $\Delta = 1/N$  is the time interval (in this case one day), N is the number of days per year and  $\theta_k^j$  is the cumulative concentration measured on  $k^{th}$  day of jth year. The term  $\theta_0^j$  is an initial constant offset. The calculated profile  $\theta_k^j$  is shown in Figure 1a for 1977. Two points in Figure 1a mark the beginning and the end of depletion phase as shown in Figure 1b for the annual silicate. Effectively, the first of the extrem a points in Figure 1a indicates the decline of the concentrations in the first half year. This point is associated with the onset of nutrient limitation period that lasts for several months and ends when the concentrations in the second half of the year begin to increase and reach around 40% of its maximum in the first half of the year.



concentration for the silicate in 1977. The cumulative curve is calculated (1)-(2). (b) The annual normalized silicate profile. The lines indicate on set and termination of depletion.

## Results

#### Nitrate

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The levels of nitrate changed substantially during the last 44 years. Also annual cycle undergone large variations with the shift of timing of the maxima and the seasonal pattern (Figure 2a). To simplify the discussion the seasonal pattern is divided according to LL period (June-October) and HL period (February-June). The HL means of nitrate substantially increase over the period 1966-1984 (Figure 2b). The calculated HL means increase from ~17 in 1966 to ~42 in 1987 [1]. Over the interval 1966-1987 the highest annual concentration is observed in 1987 with the total annual levels above 5000 (Figure 2a). Since 1981HL means never drop to the recorded values before 1980 (exception are years 1998

and 2009). The nitrate concentrations are negatively correlated with salinity data and salinity itself is anticorrelated with the peaks of Elbe discharge [10]. It is likely that higher current velocities and river discharge rates are the consequences of the artificial deepening of the bed of the lower river that is made at the end of 1970s [10]. This explains the higher HL means and annual nitrate concentrations found after 1980s at HR. In years of 1981, 1987 and 1994 anomalously high discharge rates of Elbe are documented. These events are well reflected in the observed HLs (Figure 2b). After 1994 an overall decline in HL means and annual nitrate concentrations is observed.



**Figure 2: (a)** Total annual concentrations of nitrate at Helgoland for 1966-2009 period. (b) The HL means are shown for nitrate for the same time period.

The nutrient limitation phase for nitrate lasts till end of December and in some years (1970-1974) shifts even to the late January nitrate (Figure 3a). In general the timing for the onset of depletion is highly variable and fluctuates within the ranges of 10-30 days (Figure 3a).



Meanwhile the onset and termination of depletion show quite apparent shifts for two time periods 1966-1980 and 1995-2009 for intermediate interval of 1981-1995 sharp variations

of nutrient intra- and inter annual patterns and the time of SD and ED are evident. The first time period (1966-1980) is distinguished by both shift of SD from April in 1966 to May-June in 1981 and advance of ED from late December in 1966 to October-November in 1981. The second time period (1995-2009) features an overall widening of the depletion phase with the exception of years with outliers such as 2001, 2005-2007, 2009. The SD in this case is advances from July in 1995 to May in 2008. In 2009 there is a jump of the onset of depletion towards later time in July. The ED is shifted towards later period in the year from late November in 1995 to the end of December in 2009. Overall the tendency towards the later timing of ED is detected although the trend is not significant. The duration of depletion period can be calculated by substracting the SD from ED yield. The depletion length (Figure 3b) shows high interannual variability with differences between years sometimes exceeding 2 months period. For example, in 2000 and 2002 the depletion phase lasts for about 240 days meanwhile in 2001 it continues only for about 160 days. It is interesting to note that trends associated with the shift of depletion cycle such as observed for two time periods 1966-1980 and 1995-2009 are related with the change in annual concentrations. We show that depletion phase correlates negatively (linear regressions for years 1966-2009 provides the fit,  $y = -23.66 * X + 7942 r^2 = 0.118, p < 0.05$ ) with the annual concentrations of nitrate.

#### Silicate

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Annual levels of silicate show large magnitude variations over the entire time period from concentrations reaching ~37.09 during HL season to the concentrations hitting zero in summer (Figure 4). Due to the fact that the HL period has a fewer influence of biological processes the HL means reflect the impact of environmental and meteorological processes on the observed levels. For the first twenty years (1966-1986) the silicate levels substantially reduce. The HL mean (Figure 4b) declines rapidly from value of ~20 in 1966 to ~5 in 1970. In later years until 1986 the HL means stay always below 12. Simultaneously gradual decline of total annual concetrations is observed for years 1966-1986. In 1987 the sudden jump of both annual concentrations and HL means is detected. After 1987 the levels of silicate are substantially higher than observed in the previous decades. In the subsequent years 1986-2002 there is a general decrease of HL and annual concentrations (exceptions are 1995 and 2000). After 2003 the HI means increase again until 2008. In 2009 the HL drops down to ~11. During period 1987-2000 not only HL means are higher than attained in the time before 1987 but annual concentrations are measured higher throughout the year. The silicate levels stay higher even from May to October than the concentrations estimated for the same season before 1987 and after 2000.



Rather the timing of accumulation and depletion events varies from one year to another in the range of several weeks or months (Figure 5a). The onset of depletion from 1966 to late 1980s mostly occurs in May. Exceptions are years 1972, 1978 and 1986 with earlier onset of depletion in March-February. The year 1981 is characterized by later onset of depletion that happens in June. After 1987 until 1990 the timing for both BD and ED is quite variable. These variations can be partly explained by strong fluctuations in seasonal and annual silicate levels during these years. During later period 1990-1995 the BD shifts gradually from April to May. In 1996 the BD advances to late May. In the following period until 2009 the BD progresses consistently towards later time in Spring. Contrary to relatively smooth pattern of BD the timing of ED changes greatly even for short time periods. It fluctuates from early termination that occurs in August to late termination that starts in December.

It is indicative that large interannual variations for the ED are influenced by the biomass and composition of the late summer and autumn blooms. The analysis of long term phytoplankton data from HR indicate year-to-year changes of

species composition and biomass distribution. These changes do not affect the timing of BD since it is related with the onset of spring bloom and the environmental factors that drives the start of spring bloom every year.

The depletion length for silicate does not show significant correlation (p>0.05) with annual concentrations data as for the nitrate. The average depeltion period over 44 years is about 188days. However, specific time periods can be distinguished with the increase of depletion phase (1969-1974), duration of depletion does not change and keeps at about 180 days (1975-1981), high variability of depletion (1986 - 1995), since 1996 until 2000 the phase increase, after 2000 it decrease to 140 days and the period of 2001-2009 is characterized by overall increase of depletion (exception: 2005).

#### **Phosphate**



River systems is a major source for phosphate at Helgoland. According to analysis in Ref. [10] phosphate shows high significant negative correlation with salinity. Phosphate concentrations exhibit high variability over the 44 years period that is mostly explained by the river discharge events which are positively correlated with the phosphate concentrations (Figure 6a). The peaks of phosphate levels are observed during the first half of the year in January - May and in the second half of the vear in November- December. The HL meanssteadily increase during initial interval of 1966-1981 from the level of ~0.79 in 1966 to ~1.3 in 1981 (Figure 6b). The sudden increase of HL mean in 1981 can be explained by the Elbe river discharge event in December of 1981. The decline of HLs is observed since 1983. Since 1995 the annual concentrations exhibit large magnitude fluctuations over short time scales of one or two years. The variability is especially well observed for the latest years: the total concentration of phosphate in 2007 changes about threefold of 2006 value. Also it is indicative that in the period

before 1983 when the peaks of levels are detected both in winter and autumn the peaks of phosphate for the period 1987-2009 occur mostly in autumn period.





The SD for the phosphate occurs most of the times during April-May (Figure 7a). The ED indicates the end of summers limitation and the start of phosphate accumulation phase. The yield marks the time of ED in September- October with exception of few outliers. As an example here we study in more detail two depletion cycles for the consequitive years 2006 and 2007. The concentrations in 2006 start to decline much earlier in February and begin to recover already in September, in the following 2007 the depletion initiates in April and terminates in November. Variation of timing of depletion is likely to be related to the amount of phosphate available during HL and LL period and to the rates of nutrients uptake and recycling from the phytoplankton. In the year of 2006 the January maximum is below 0.7 whereas the situation drastically changes in 2007 (January maximum reaches ~1.6). The uptake from phytoplankton forces an earlier initiation of a depletion phase in 2006. In the second half of the year the nutrients recovery is much faster in 2006 than in 2007 therefore the ED occurs two months earlier in 2006. Both BD and ED advance in time: SD shifts from May in 1966 to April at the end of 1980s, the ED shifts from October in 1966 to September in 1980s. In most cases an early commencement of depletion occurs for the years with low levels of phosphate in winter period. The period from 1985 to 2009 is associated with a gradual widening of the depletion phase. As for nitrate the depletion length (Figure 7b) for phosphate highly significantly correlated with the annual concentrations (the linear regression fit:  $y = -312 * X + 245, r^2 = 0.0963, p < 0.05$  ).

#### Nitrite

Concentration of nitrite is not related to particular water bodies but depend on nitrification processes and on turn-over rates in the biological systems. The peaks of concentrations are mostly detected from January to June and from September to December (HL period). Lowest concentrations are observed from April to October (LL period). Nitrite HL means vary from 0.8 to 3 over the entire time period as shown in (Figure 8b). The whole period of 1995-2000 is characterized by high annual concentrations of nitrite (Figure 8a). After 2000 the annual concentration



drop down to lower values (exception: 2006). The event of sudden rise of annual levels is most probably related to higher rate of nitrification processes.

The variations of the length of depletion cycle (Figure 9) is highly significantly correlated with the annual concentrations of nitrite fit .  $(y = -0.7322 * X + 317.45, r^2 = 0.257, p < 0.0001)$  The length of depletion shows a substantial shift from a short limit below 200 days observed at the beginning of time series to a depletion cycle over 250 days per year in 2001-2005.





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#### Sunshine seasonal activity

The importance of light on phytoplankton development and underwater climate is emphasized in several studies of the coastal and shelf areas of Wadden and North Sea [11-12]. Untill now elaborate analysis of changes in the light conditions near Helgoland area has not been done yet. Some important questions concerning seasonal variations of the light conditions and their impact on biomass production and rates of nutrients consumption are not investigated in details.

In Figure10a the yeilds for 6 hours-per-day levels of sunshine at Helgoland are evaluated from the annual sunshine pattern for 1966-2009. Apart from a few outliers the SD and ED fits well the long term trend observed for period 1966-1975. The mean length of a high sunshine season (as expressed by 6-hours-per-day yeilds) changes from 125 days as observed in 1966 to 175 days in 2009 per year (Figure10b). The time 1976-1987 is characterized by shortening of high sunshine season. For the subsequent time period 1988-2009 the duration of high sunshine season increases but features high interannual variations. Similar pattern is observed for the phosphate depletion phase, both SD and ED yields keep close to the sunshine yeilds.



**Figure 10:** (a)Yelds show the begining /end of season with mean sunshine exceeding 6 hours per day for 1966-2009 at Helgoland. The isolines is marked with squares /triangles. For the same time period the SD/ED yield for phosphate is indicated by diamonds /triangles. (b) Length  $\Delta$  (in days) of the season with mean sunshine exceeding 6 hours per day. Daily values for sunshine are obtained from Deutscher Wetterdients (http:// www.dwd.de/).

#### Discussion

In the end of 1980s more saline and nutrient reach water influenced the North Sea due to increased inflow from the Atlantic water masses [14]. This change is accompanied with the simultaneous increase phytoplankton biomass that is observed in the North Sea and east Atlantic from the CPR [3]. The observational studies are confirmed by statistical analysis of long-term biological and meteorological global data sets from the North Sea and also local data from the GB that report two major regimes shifts in 1979 and 1988 [1,15]. The shifts are more pronounced for biological parameters and triggered by environmental factors. The strong change of phytoplanktonzooplankton interactions and community influences the nutrient recycling and chemical composition overall in the North Sea and in the coastal areas especially. We show that for all the nutrients the prominent alternation in annual turnover take place in the late 1980s. The commencement of LL is shifted towards later time, whereas the termination of LL phase is advanced during first period from 1966 to end of 1980s. In the second interval of time series from mid of 1990s to 2009 the widening of time period with low nutrient concentrations is evident: the onset of depletion phase starts earlier and terminates also later. It is likely that the major role in reshaping of the seasonal pattern of nutrients recycling is determined by strong changes in phytoplankton-zooplankton interactions [6].

The high variability of depletion length of silicate in years 1986-1995 coincide with variations in annual silicate and might be a result of the North Atlantic inflow events documented for the period 1976-1994 [3]. Some instabilities related with break down of northwards transport of the coastal waters and increased fresh water discharges into the German Bigth [13] could explain alternations in silicate seasonal and annual patterns during period since late 1980s until 1995.

The high interannual variability of the phosphate levels observed from HR data and from the reference data obtained in area around Helgoland [10] after 1990 might be a consequence of alternating hydrographical situation in the GB and higher influence of coastal water bodies from the Elbe region in some years. This needs to be verified with the numerical models.

Although, the differences of phytoplankton species and seasonal patterns are not substantial among different sites the nutrient limitation patterns are strongly site-dependent and linked to the local hydrography and light conditions [12]. The silicate limitation occurred between April and June since 1998 till 2005. A phosphate limitation lasted for about five months and fluctuated between March and April of years 1998-2005. The limitation pattern provides information about the important phytoplankton growth factors. However, they can not alone undermine the complexity of phytoplankton-nutrient interactions at particular site. To give an example it remains unclear why the years 2000 and 2003 with similar limitation patterns are still distinguished by the late (December) and early (July) onset of the silicate build-up. A prolonged depletion phase in 2000 might be due to increased nutrient uptake, change of biodiversity towards more silicate demanding species or influence of riverine loads. These or other factors that analysis in Ref. [12] does not take into consideration can maintain different nutrient turnover in the second half of the year. Also analysis of species sizes and compositions should be added for estimation of nutrients uptake rates.

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Although the length of depletion phase is found to be negatively correlated with annual concentrations for the phosphate, nitrate and nitrite, no significant correlation is found between the timing of SD, ED and HL means and annual concentrations. The SD depends on several factors such as initiation of phytoplankton bloom, winter nutrient levels and the rates of nutrients uptake and recycling from the phytoplankton. Similarly, the ED is conditioned by the decline of phytoplankton biomass in late summer and autumn, availablity of nutrients and the increase of concentrations during build-up phase. Therefore, both SD and ED are affected indirectly by HL means, nutrients annual levels, winter river discharge events and biomass distribution during spring and late summer blooms.

The maxima of year-to-year variation of ED can reach a period of several months. One of the important questions is to investigate the causes of these variability. Since silicate is the main nutritional source for the diatoms it is likely that ED is positively correlated with late summer and autumn blooms of diatoms. Higher biomass and consumption rates from the diatoms population leads to a later start of accumulation of the silicate. The relation between late summer and autumn biomass and changes of the silicate accumulation needs to be investigated further in order to confirm this hypothesis.

# Conclusion

We investigate the long term behavior of the main nutrients for the period 1966-2009. The depletion phases of nutrients are calculated based on the extrem points of the cumulative chemical concentrations. The depletion cycles for most of the chemical parameters (with the exception of silicate) show significant negative correlations with the annual concentrations.

The spring onset of the phytoplankton blooom could be triggered by several key factors such as temperature, tidal mixing and sun radiation could. In turn, the spring bloom initiates the nutrients depletion and transition to LL phase. Keeping this in mind, we made a comparison of the depletion phase timing and mean hours of sunshine is made. We discover a good match between the onset and termination of phosphate depletion phase and the sunshine expressed by 6-hours-perday yields. Comparison of other nutrients depletion cycles does not show any similarity to the sunshine data. The nitrate accumulation phase spans much later time period that the phosphate accumulation period, therefore BD occurs during late spring and summer months. Nitrite cycles manifest higher seasonal variability that is related to nitrification processes but are hardly regulated by light conditions only. For silicate there exists a possibility that other processes, biological and physical, impact the rates and initiation of depletion.

Our observations shows that the sunshine yields in Spring shifts from May-June as detected in 1987-1990 to March-April in the latest period from 2001 to 2009. The influence of this trend on the biomass production and seasonality of the phytoplankton blooms should be investigated further.

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