

## Hypoxia Sustains Cyanobacteria Blooms in the Baltic Sea

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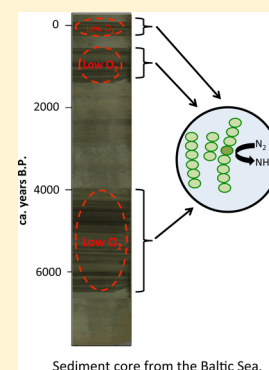
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### **S** Supporting Information

**ABSTRACT:** Nutrient over-enrichment is one of the classic triggering mechanisms for the occurrence of cyanobacteria blooms in aquatic ecosystems. In the Baltic Sea, cyanobacteria regularly occur in the late summer months and form nuisance accumulations in surface waters and their abundance has intensified significantly in the past 50 years attributed to human-induced eutrophication. However, the natural occurrence of cyanobacteria during the Holocene is debated. In this study, we present records of cyanobacteria pigments, water column redox proxies, and nitrogen isotopic signatures for the past ca. 8000 years from Baltic Sea sediment cores. Our results demonstrate that cyanobacteria abundance and nitrogen fixation are correlated with hypoxia occurring during three main intervals: (1) ca. 7000–4000 B.P. during the Littorina transgression, (2) ca. 1400–700 B.P. during the Medieval Climate Anomaly, and (3) from ca. 1950 A.D. to the present. Issues of preservation were investigated, and we show that organic matter and pigment profiles are not simply an artifact of preservation. These results suggest that cyanobacteria abundance is sustained during periods of hypoxia, most likely because of enhanced recycling of phosphorus in low oxygen conditions.



### ■ INTRODUCTION

The Baltic Sea, one of the largest brackish water bodies in the world, is vulnerable to hypoxia (dissolved oxygen < 2 mg/L) because of the limited bottom-water inflow of oxygenated waters from the adjacent Kattegat. Widespread hypoxia in the stratified water column<sup>1,2</sup> maintains a ready resupply of phosphorus from the sediments.<sup>3,4</sup> Together with enhanced denitrification, this leads to low surface water nitrogen/phosphorus (N/P) ratios following the spring bloom, favoring diazotrophic cyanobacteria blooms in the summer months. Unlike most phytoplankton, which require both high N and P conditions, diazotrophic cyanobacteria only require high P concentrations because they are “N-fixing” and can produce their own ammonia as a nutrient source from atmospheric N<sub>2</sub> gas.<sup>5</sup> Thus, diazotrophic cyanobacteria can flourish in the Baltic Sea during strongly N-limiting conditions and usually form blooms in the summer if the N/P ratio after the spring bloom is below the Redfield ratio of 16.<sup>1,6</sup> In addition to low N/P ratios, the prevalence of cyanobacteria is also influenced by other environmental factors, such as light attenuation, water temperatures (which must be >15 °C for blooms to occur), and vertical mixing.<sup>7</sup>

Cyanobacteria have been shown to provide a positive feedback to eutrophication, by supplying new N to the system and enhancing the downward flux of degradable organic matter from surface waters, which elevates oxygen consumption and the regeneration of phosphate.<sup>2</sup> Moreover, some species are toxic, and they are, therefore, problematic for recreation and

fisheries.<sup>2</sup> Because of these negative effects of cyanobacteria blooms, some scientists argue that efforts should be made to reduce their abundance and their contribution to the phytoplankton community.<sup>8</sup> Others argue that cyanobacteria are a characteristic, natural feature of the Baltic Sea.<sup>9</sup>

Cyanobacteria have been shown to be present in the Baltic Sea since around 7000 years B.P.,<sup>9,10</sup> but the triggers to past cyanobacteria blooms remain unclear. An improved understanding of the controls on cyanobacteria blooms will assist in developing solutions to reduce their occurrence in the future. In this study, we examine the presence of cyanobacteria pigments in sediment cores and compare these to proxies for past redox conditions to determine if there is a link between cyanobacteria and hypoxia in the Baltic Sea during the Holocene.

### ■ MATERIALS AND METHODS

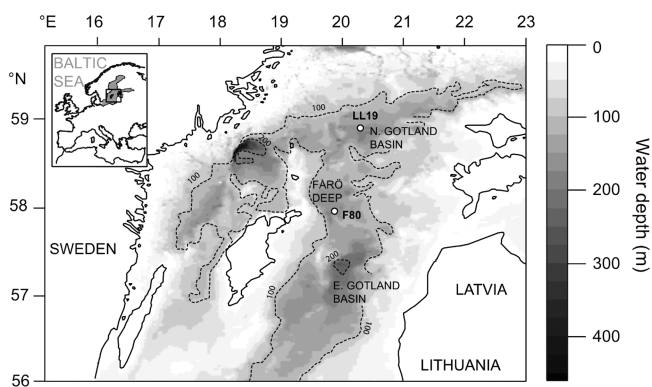
Sediment cores were taken with R/V Aranda in May/June 2009. Multi-cores (collecting the top 30 cm of the sediment) and gravity cores (collecting ~4.5 m of sediment) were obtained at two sites in the Baltic Sea (Figure 1): LL19 in the Northern Gotland Basin (58.8807° N, 20.3108° E, and 169 m water depth) and F80 in the Fårö Deep (58.0000° N, 19.8968° E, and 191 m water depth). These sites were selected because

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**Figure 1.** Map of the Baltic Proper showing the principle sub-basins, water depth, and locations of the cores collected in the Gotland Basin for this study: LL19 in the Northern Gotland Basin (58.8807° N, 20.3108° E, and 169 m water depth) and F80 in the Fårö Deep (58.0000° N, 19.8968° E, and 191 m water depth). Multi-cores (surface of ~40 cm) and gravity cores (~450 cm) were collected at both sites. Bathymetric and coastline data are presented in Miller cylindrical projection, taken from the General Bathymetric Chart of the Ocean (GEBCO) Digital Atlas.<sup>43</sup>

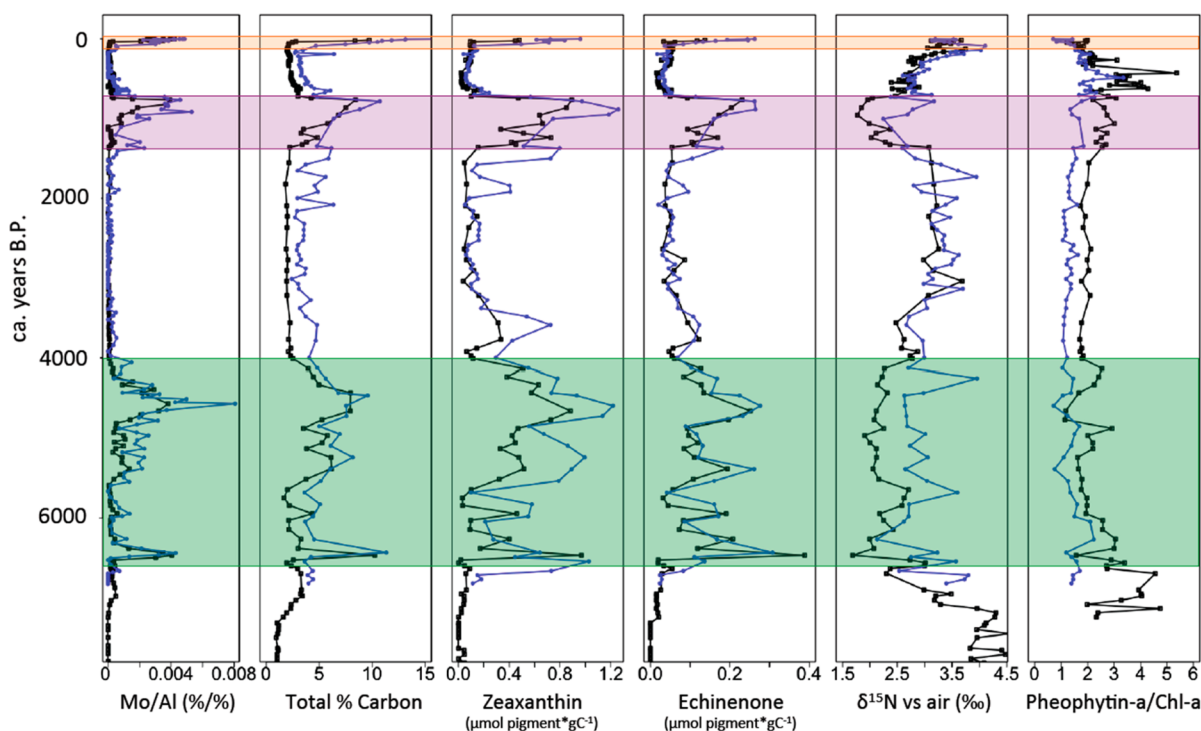
we expected continuous accumulation of sediment in these deep basins over the Holocene. Multi-cores were sampled immediately in a nitrogen-filled glovebox. Gravity cores were cut into 1 m sections and stored in the dark at 4 °C. Gravity cores were subsampled in a nitrogen-filled glovebox in a dark lab for pigment analyses. Sample resolution varied between 1 and 5 cm, and the sample selection for each analysis varied

slightly because of the availability of material. Subsamples were freeze-dried and homogenized with a mortar and pestle.

Multi-core and gravity core data were combined on the basis of overlaps in the geochemical profiles. The age models for both sites were constructed using a combination of <sup>210</sup>Pb dating for multi-cores and tuning of the gravity core  $C_{org}$  profiles to the loss on ignition (LOI) profile of core 372740-3 from the Gotland Deep.<sup>11</sup> Core 372740-3 was independently dated by identification of two Pb pollution isochrones<sup>12</sup> and 10 paleomagnetic secular variation features (see the Supporting Information for more details on the construction of the age models for LL19 and F80 and errors in absolute age estimates).

To determine the ratio of molybdenum/aluminum (Mo/Al, %/%), sediment samples were dissolved in HF (40%) and a HClO<sub>4</sub>/HNO<sub>3</sub> mixture in a closed Teflon bomb at 90 °C for 12 h. The acids were evaporated at 190 °C. The resulting gel was redissolved in HNO<sub>3</sub> and analyzed by inductively coupled plasma–optical emission spectroscopy (ICP–OES) for Mo and Al (precision and accuracy < 5%). For total percent carbon and  $\delta^{15}N$  measurements, samples were analyzed using a Carlo Erba NC2500 analyzer connected to a Finnigan MAT Delta V mass spectrometer. The reproducibility was better than 0.15‰ for  $\delta^{15}N$  and <1% for total percent carbon.

For pigment analysis, sediment samples were mixed with cold high-performance liquid chromatography (HPLC)-grade acetone/methanol/Milli-Q water (80:15:5%), sonicated, and stored in a freezer (−20 °C) overnight. Extracts were centrifuged and filtered (0.45 μm) and then were quantitatively analyzed by HPLC on a Shimadzu Prominence HPLC equipped with an online photodiode array detector (SPD-



**Figure 2.** Proxy profiles as a function of time in years B.P. for Northern Gotland Deep (LL19, black line) and Fårö Deep (F80, blue line). From left to right: molybdenum/aluminum (%/%) (euxinia proxy), total percent carbon (productivity proxy), zeaxanthin and echinenone (micromoles of pigment per gram of sediment normalized to total percent carbon) (cyanobacteria biomarkers),  $\delta^{15}N$  versus air (‰) (indicator of N fixation), and pheophytin *a*/chlorophyll *a* (mole ratio) (degradation proxy). The colored bars denote three intervals of hypoxia as determined by the occurrence of extensive laminated sediments: green, Littorina Transgression (7000–4000 years B.P.); purple, Medieval Climate Anomaly (1400–700 years B.P.); and orange, modern hypoxic period (~60 years B.P. at F80 and ~30 years B.P. at LL19; present = A.D. 2010).

**Table 1. Correlation Statistics between the Biomarkers: Mo/Al, Total Percent Carbon, Zeaxanthin, Echinenone, and  $\delta^{15}\text{N}$  ( $n = 154$ )<sup>a</sup>**

	Mo/Al	total percent carbon	zeaxanthin	echinenone	$\delta^{15}\text{N}$
Mo/Al		$r^2=0.63$ ; $p<0.001$	$r^2=0.55$ ; $p<0.001$	$r^2=0.60$ ; $p<0.001$	$r^2=0.09$ ; $p=0.001$
total percent carbon	<b><math>r^2=0.79</math>; <math>p&lt;0.001</math></b>		$r^2=0.58$ ; $p<0.001$	$r^2=0.66$ ; $p<0.001$	$r^2=0.07$ ; $p=0.001$
zeaxanthin	<b><math>r^2=0.63</math>; <math>p&lt;0.001</math></b>	<b><math>r^2=0.83</math>; <math>p&lt;0.001</math></b>		$r^2=0.73$ ; $p<0.001$	$r^2=0.18$ ; $p<0.001$
echinenone	<b><math>r^2=0.60</math>; <math>p&lt;0.001</math></b>	<b><math>r^2=0.72</math>; <math>p&lt;0.001</math></b>	<b><math>r^2=0.85</math>; <math>p&lt;0.001</math></b>		$r^2=0.24$ ; $p<0.001$
$\delta^{15}\text{N}$	<b><math>r^2=0.28</math>; <math>p&lt;0.001</math></b>	<b><math>r^2=0.54</math>; <math>p&lt;0.001</math></b>	<b><math>r^2=0.57</math>; <math>p&lt;0.001</math></b>	<b><math>r^2=0.60</math>; <math>p&lt;0.001</math></b>	

<sup>a</sup>Significant inverse relationships ( $p < 0.001$ ) between  $\delta^{15}\text{N}$  and other biomarkers were calculated for both sites: Northern Gotland Deep (LL19) (in bold) and Fårö Deep (F80) (not in bold).

M20A PDA) and an autosampler (Sil-10AF). The run program was programed as described by Reuss and Conley.<sup>13</sup>

Coefficients of determination ( $R^2$ ) were calculated between the complete data series of  $\delta^{15}\text{N}$  and each of the other sedimentary proxies (total percent carbon, echinenone, zeaxanthin, and Mo/Al) ( $n = 194$ ). Because the sample selection varied per analysis, data series were interpolated between age 15 and 7700 years B.P. and points were extracted at every 50 years ( $n = 154$ ) for calculation of the coefficients of determination and  $p$  values. Data were analyzed using the R statistical program (R 2.15.2).

## RESULTS AND DISCUSSION

Laminated sediments, indicative of hypoxic conditions, were observed during three intervals of the Holocene sedimentary record at the two sites: the Littorina Transgression, the Medieval Climate Anomaly (MCA), and the modern hypoxic interval. These intervals were also characterized by enhanced sedimentary Mo/Al (Figure 2). This proxy tracks the intensity of reducing conditions close to the sediment–water interface,<sup>14</sup> because of the conversion of seawater  $\text{MoO}_4^{2-}$  to particle-reactive thiomolybdates above a critical activity of hydrogen sulfide.<sup>15</sup> Hence, our records indicate intermittent euxinic (i.e., sulfidic) conditions in the bottom waters of the deep basins during the Holocene (Figure 2). The hypoxic intervals are also characterized by enhanced organic carbon ( $C_{\text{org}}$ ) contents, which we attribute to both enhanced preservation of organic matter under reducing conditions and enhanced primary productivity during the hypoxic intervals. Enhanced primary productivity was likely sustained by sedimentary phosphorus release under anoxic conditions, as shown by numerous studies.<sup>3,15–17</sup> The centennial-scale oscillations in hypoxia during the Littorina Transgression and MCA were recently suggested to be related to shifts in the North Atlantic Oscillation (NAO) and amplified by internal feedbacks in the phosphorus cycle of the Baltic Sea.<sup>16</sup> That study also showed that the replacement time of the Baltic Sea is sufficiently short for Mo/Al to be unaffected by reservoir effects and that Mo/Al varies in concert with organic carbon to total phosphorus ( $C_{\text{org}}/P_{\text{tot}}$ ) ratios, confirming the role of phosphorus regeneration in sustaining hypoxia.

During the hypoxic intervals, we observe higher carbon-normalized concentrations of cyanobacteria pigments in the sediments (zeaxanthin and echinenone; Figure 2). The pigment concentrations also vary in concert with the centennial-scale oscillations in Mo/Al. Furthermore,  $\delta^{15}\text{N}$  signatures are inversely related to total carbon, pigment concentrations, and Mo/Al, indicating enhanced N fixation during hypoxic intervals.<sup>17</sup> In combination, these results suggest that N-fixing cyanobacteria were more prevalent during intervals of hypoxic

conditions in the Baltic Sea and less so during the intervening oxic intervals (see Table 1 for statistics).

Organic matter is often better preserved in anoxic sediments because of the comparatively slow rate of microbial degradation in the absence of oxygen.<sup>18</sup> To examine if our cyanobacteria abundance trends are influenced by preservation artifacts, we calculated the molar ratio of pheophytin *a*/chlorophyll *a* (pheophytin *a*/chl *a*).<sup>19</sup> Pheophytin *a* is a degradation product of chlorophyll *a*; hence, low values of this ratio indicate good preservation of the initial material, and high values indicate poor preservation of the initial material. As shown in Figure 2, pheophytin *a*/chl *a* molar ratios show no systematic relationship (F80,  $r^2 = 0.026$  and  $p$  value = 0.031; LL19,  $r^2 = 0.026$  and  $p$  value = 0.029) with redox conditions, as represented by Mo/Al. These observations suggest that changes in the pigment concentration in the sediments are dominantly controlled by changes in the initial flux of the pigments to the sediments, i.e., by cyanobacteria abundance in the surface waters, and less by preferential preservation effects after sedimentation.

Three prominent intervals of frequent hypoxia and high cyanobacteria abundance occurred in the past ca. 7500 years. The first and longest of these, the Littorina Transgression (ca. 7000–4000 B.P.), followed the seawater intrusion through the Danish straits, which transformed the freshwater Ancylus Lake to the brackish Littorina Sea.<sup>20</sup> This intrusion of seawater increased the stratification of the water column of the Baltic Sea and has been hypothesized to be the primary cause of deep-water hypoxia during this interval.<sup>21</sup> It is likely that widespread hypoxia and euxinia in bottom waters stimulated sediment-bound P to be released into the water column,<sup>9,22,23</sup> and the low N/P conditions created an ideal environment for diazotrophic cyanobacteria to thrive.<sup>9</sup> The highest ratio between zeaxanthin and  $\beta$ -carotene (unpublished data), which is an indicator of the proportion of cyanobacteria in the phytoplankton community, was observed following seawater intrusion, as seen in previous studies (e.g., see refs 4 and 9). Additionally, this period coincides with the Holocene Thermal Maximum (HTM) when warmer surface waters may have favored cyanobacteria blooms. Around ca. 4000 B.P., the Littorina Sea stabilized and salinity decreased because of the reduction in the depth of the Danish straits, increasing vertical mixing and replenishing oxygen to the deep basins.<sup>24</sup> This shift reduced surface water phosphate concentrations and increased the N/P ratio, making conditions less favorable to diazotrophic cyanobacteria after ca. 4000 B.P.<sup>8</sup>

Hypoxia and high productivity was again observed ca. 1400–700 B.P. during the MCA (Figure 2). Several important factors may have contributed to hypoxia during this interval. First, northern Europe experienced milder winters because of a persistently positive phase of the NAO climate mode.<sup>25</sup> This increase in winter temperatures may have been sufficient to

increase thermal stratification, hence decreasing bottom-water oxygen concentrations and stimulating the release of P from the sediments. As during the HTM, the warmer temperature of the MCA may also have favored cyanobacteria.<sup>26</sup> Second, the population for many of the countries in the Baltic Sea watershed (i.e., Denmark, Germany, Poland, and Sweden) nearly doubled within 300 years,<sup>27</sup> leading to a change in land use<sup>28</sup> and increased terrestrial nutrient runoff.<sup>29</sup> The consequent spread of hypoxia in the Baltic Sea re-established the conditions required for diazotrophic cyanobacteria to thrive.

During the Little Ice Age (LIA), which followed the MCA, the NAO shifted to a more persistently negative phase.<sup>25</sup> This may have led to an increase in storm frequency<sup>30</sup> and cooler sea surface temperatures in the Baltic Sea.<sup>26,31</sup> In addition, the population decreased during the 14th century when the bubonic plague (Black Death) and famine hit Europe. For example, the Swedish population is estimated to have decreased approximately by one-third during this time,<sup>32</sup> leading to a 30–50% farm abandonment in some parts of Sweden.<sup>33</sup> This could potentially have caused a decrease in nutrient runoff into the Baltic Sea. In combination, these conditions were less favorable for hypoxia and cyanobacteria blooms.

The onset of modern hypoxic conditions in the late 20th century at both sites is directly linked to excess nutrient loading from agricultural activities and urban development in the past century.<sup>34,35</sup> From 1850 to 1980, N and P loads in the Baltic Sea increased on average 4.5-fold.<sup>36</sup> In the spring, algal blooms thrive in these highly nutrient-enriched waters. Sedimentation of the spring bloom, in addition to organic matter runoff, increases microbial respiration, resulting in hypoxia and creating an ideal environment for cyanobacteria blooms to form in the summer months.<sup>37</sup> Current climate change likely intensifies hypoxia<sup>26</sup> because of the reduction in vertical mixing of the water column, therefore favoring cyanobacteria blooms.<sup>38</sup>

## PERSPECTIVES

By reconstructing long-term trends, we conclude that multiple stressors, including climate variability, stratification, and anthropogenic activity, have influenced the occurrence of hypoxia in the Baltic Sea at different times during the Holocene. However, each hypoxic interval has been characterized by abundant cyanobacteria blooms, implying a close coupling between the two phenomena. Because of the limitations of sampling resolution, it remains difficult to determine the exact sequence of events at the onset of each hypoxic interval, i.e., the potential lead lag between hypoxia and cyanobacteria blooms. Theoretically, an external input of P could trigger cyanobacteria blooms by lowering surface water N/P ratios, leading to increased oxygen demand and hypoxia. Alternatively, hypoxia could be triggered by a change in stratification, leading to sedimentary P release and favoring cyanobacteria blooms. However, it is clear that once hypoxia is established, efficient phosphorus regeneration from sediments and cyanobacteria are closely coupled,<sup>39,40</sup> sustaining a “vicious” circle of eutrophication.<sup>2</sup>

Recent observations and models suggest that hypoxic and suboxic regions of many marine and freshwater systems are likely to expand and become shallower with warmer temperatures.<sup>41</sup> Hence, lakes,<sup>38</sup> marine waters above oxygen minimum zones,<sup>42</sup> and the Baltic Sea as reported here may all experience expanded hypoxia in the future. Coupled to the stress of anthropogenic nutrient loading and climate change, this global

expansion of hypoxia may be expected to drive an increase in the global prevalence of cyanobacteria blooms.

## ASSOCIATED CONTENT

### Supporting Information

Information on how the age models were constructed for the cores on the basis of two lead (Pb) isochrones identified from neighboring cores. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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