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Variability of Primary Productivity as an Initial Link in Carbon Flux Under the Influence of Hydrological Conditions in the Baltic Sea

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Abstract: Investigating variability in phytoplankton primary productivity as a key component of the "biological pump" is critical to quantifying flux in the marine environment. We hypothesized that under certain hydrological conditions, changes in phytoplankton productivity are greater with changes in photosynthetic efficiency (the ratio of primary production (PP) to the rate of electron transport in the phytoplankton photosystem, PP/ETR) than with changes in chlorophyll content. This study showed that increase of PP during sharp changes in hydrological parameters in the temporary frontal South-East Baltic (SEB) is achieved by increasing the efficiency of photosynthesis, i.e., the degree of use of light energy captured by chlorophyll *a* (Chl *a*). In the Gulf of Finland (GF), an increase in PP followed an increase in salinity from the Neva mouth to the sea and controls chlorophyll contents with low variability in photosynthetic efficiency. For SEB and GF, measurements of parameters of phytoplankton productivity and chlorophyll *a* content in late autumn (November) are carried out. The first stage of carbon flow (in biological pump), expressed in terms of primary production, was higher in the SEB than in the GF.

Keywords: primary productivity, carbon flux, photosynthetic efficiency, active chlorophyll fluorescence, frontal zone, Baltic Sea.

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1. Introduction

Primary productivity is a key parameter of the current state and dynamics of marine ecosystems, since it determines the trophic dynamics of marine organisms and the biogeochemical cycling of nutrients. The climatic role of the primary productivity of phytoplankton is also important as the main process of the biological pump [*Laws and Maiti*, 2019], which ensures the entry of atmospheric CO_2 into the sea (in the form of synthesized suspended and dissolved forms of organic carbon) with subsequent sedimentation into the deep layers of the water column and bottom sediments. Thus, the value of primary production (PP) can characterize the initial stage of the flux of carbon from the atmosphere (in the form of CO_2) into the upper layers of the water column (in the form of phytoplankton biomass or suspended organic matter).

Primary productivity at a particular point in the sea depends on the concentration of chlorophyll *a* (Chl *a*), the level of illumination and the activity of the photosynthetic apparatus, which is associated, first of all, with the efficiency of light absorption by pigments and its conversion into chemically bound energy. This energy is used to synthesize organic matter through photosynthesis. The efficiency of using captured solar energy in the processes of synthesis of organic matter depends on such environmental factors as the content of nutrients, temperature and salinity, as well as on the gradients of these factors. It was previously shown that photosynthetic efficiency increases significantly along gradients

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of hydrological conditions, including in frontal zones of different nature in the Kara Sea [*Mosharov et al.*, 2019].

For several decades, to assess the variability of primary productivity, a parameter such as the assimilation number (*AN*) has been used – *PP* normalized by Chl *a* [*Behrenfeld and Falkowsk*, 1997; *Eppley*, 1972]. Platt and Gallegos *Platt and Ch. L. Gallegos* [1980] introduced the "scaled rate" of photosynthesis, or P^B (production normalized by biomass), which is equivalent in size to *AN*. It was assumed that this value better characterizes the variability of productivity depending on the state of phytoplankton, environmental conditions or season than simply the rate of primary production, since it takes into account changes in phytoplankton biomass. However, it was later shown that *AN* depends on light and Chl *a* [*Cullen*, 1990]. With increasing Chl *a* concentration, cell size also increases [*Ciotti et al.*, 2002]. At the same time, the packaging of Chl *a* in cells increases, which leads to a decrease in the efficiency of light absorption and a decrease in *AN* [*Marra et al.*, 2007].

In the article [*Marra et al.*, 2007] extensive observations of primary productivity, Chl *a* concentrations and absorption characteristics of phytoplankton, as well as ocean optical properties were analyzed. As a result, it was shown that in many areas of the ocean, *AN* decreases with increasing Chl *a*, i.e., the variability of primary productivity in this case is not directly related to environmental conditions. The authors suggested that, across the wide range of trophic conditions found in the world's oceans, changes in productivity are more closely related to changes in the rate of light absorption by phytoplankton than to changes in Chl *a* concentrations.

However, methods for measuring the rate of light absorption by phytoplankton pigments (primarily Chl *a*) do not provide a reliable estimate. In our opinion, to understudy the variability of primary productivity and its relationship with environmental conditions, it is most effective to study productivity normalized to the rate of electron transport in the phytoplankton photosystem. First, the linear rate of photosynthetic electron transport (ETR) can be viewed as the net process of capturing and absorbing light energy and converting it into a chemically bound form for subsequent use in the synthesis of organic matter. ETR changes are a cumulative response to environmental factors such as light, temperature, and nutrients. Secondly, measuring this key photophysiological parameter is quite simple using modern fluorimeters – pulse amplitude modulation (PAM) fluorometer [*Schreiber et al.*, 1986] or fast repetition rate fluorometer (FRRf) [*Kolber et al.*, 1998]. Active fluorescence provides a non-invasive and rapid assessment of the conversion of photon flux to electron transport rate in photosystem II (PSII).

ETR is the rate of solar energy conversion into chemical energy, which provides the biosynthesis of organic matter by phytoplankton. *PP* is the result of this biosynthesis, expressed by the amount of synthesized organic matter using light energy captured in reaction centers with the participation of Chl *a*. Each of these parameters characterizes the intensity of stages of photosynthesis – light (assimilation and conversion of light energy into chemically bound and available for biosynthesis – Relative electron transport rate (rETR)) and dark (use of stored energy for the synthesis of organic matter, *PP*). The degree of use of light energy captured in the processes of synthesis of organic matter can be expressed through the ratio of *PP* and rETR values (photosynthetic efficiency, *PP*/rETR). *Lawrenz et al.* [2013] conducted the first analysis of the variability of the ETR and *PP* ratio based on 17 published results of expeditionary studies in different regions of the World Ocean. Our research in the Baltic Sea areas contributes to the general knowledge of these processes.

The hypothesis we want to test from this study is that primary productivity in areas of sharp hydrological gradients (frontal zones) is determined primarily by photosynthetic efficiency.

2. Materials and Methods

2.1. Study Area and Sampling

The studies were carried out in the south-eastern part of the Baltic Sea (SEB) and in the estuary of the river Neva in the Gulf of Finland (GF) during the 54th cruise of the R/V Akademik Sergei Vavilov from November 4 to November 13, 2022 (Figure 1). Water samples were collected using a Multi Water Sampler Hydrobios MWS 12 Slimline with a set of Niskin bathometers (Hydro-Bio, Altenholz, Germany). The temperature and salinity profile was obtained using a Sea & Sun CTD48Mc hydrophysical probe (Sea & Sun Technology, Trappenkamp, Germany).

Water samples were divided into subsamples, which were used to measure Chl *a* concentration, active fluorescence, and to experimentally measure the rate of primary production.

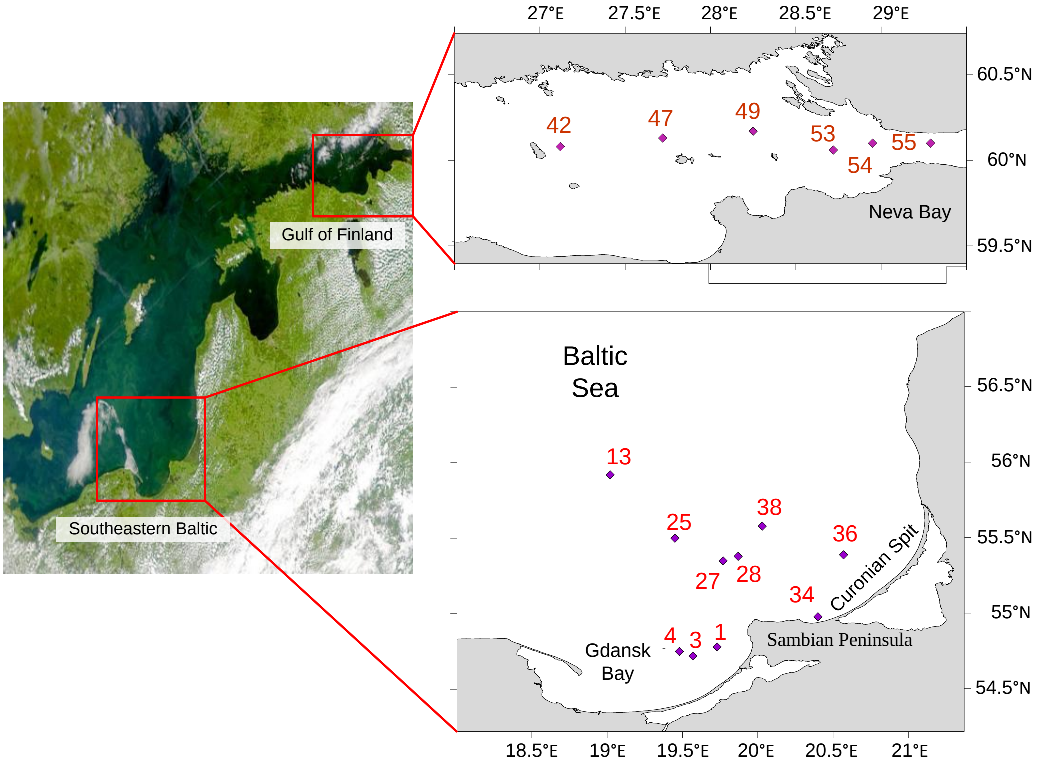


Figure 1. Research areas and station location.

2.2. Nutrient analysis

Samples to determine pH, nutrients (phosphates and nitrogen forms) and alkalinity were selected in 0.5 L plastic bottles without preservation and were treated immediately after sampling. For work in the areas with a considerable quantity of POM (bays and river–sea interfaces), the water samples were preliminarily filtered through a 1 µm Nuclepore filter. The dissolved inorganic phosphorous ($\mathrm{P-PO_4}$), nitrite nitrogen ($\mathrm{N-NO_2}$), nitrate nitrogen ($\mathrm{N-NO_3}$) and ammonium nitrogen ($\mathrm{N-NH_4}$) concentrations were measured by using standard procedures [*Grasshof et al.*, 1999].

2.3. Primary Productivity Parameters

Primary production was measured onboard using the ^{14}C uptake method [*Steemann Nielsen*, 1952]. The samples were incubated in polycarbonate flasks (50 ml) for 3 h in the original incubator with lighting and temperature maintenance. In the incubator, to simulate the light conditions corresponding to the sampling depths, each flask was illuminated by an individually adjustable LED panel (white light) with illumination level controlled using a LI-192SA quantum sensor. The light flux of each LED panel was regulated by changing the current.

After incubation, the samples were filtered through a 0.45 µm filter (Vladipor, Russia). The samples radioactivity was determined using a Triathler liquid scintillation counter (Hidex, Turku, Finland). The biomass-specific PP (AN, mgC/mgChl a per h) was calculated by dividing the PP value by the Chl a concentration in the corresponding depth.

Chl a concentration was determined by fluorometry [*Knap et al.*, 1994]. Seawater samples (500 ml) were filtered onto GF/F filters (Whatman) at a vacuum of <100 mmHg. Filters were placed in tubes with acetone (90%) and stored at +4 °C in the darkness up to 24 h. The extracts was measured with a MEGA-25 fluorometer (MSU, Moscow, Russia) [*Mosharov et al.*, 2019] before and after acidification with 1N HCl. Calibration of the fluorometer was carried out before and after each cruise using standard Chl a (Sigma). The concentration of Chl a and phaeophytin a was calculated according to [*Holm-Hansen and Riemann*, 1978].

The underwater irradiance profile in the PAR range (photosynthetically active radiation, 400–700 nm) was measured using a complex including Li-190R quantum sensor, Li-193 underwater sensor, and Li-1500 DataLogger (LI-COR, Lincoln, USA). The depth of the euphotic layer was determined from the depth of 1% surface PAR.

2.4. Measurement of Fluorescence Parameters

Active fluorescence of Chl a was measured with a fluorometer WATER-PAM (Walz, Germany). Prior to measurement, the samples were kept in the dark for at least 20 min [*Schreiber et al.*, 1995]. The minimum (F_0) and maximum (F_m) fluorescence of the samples was measured. The maximum quantum efficiency of PSII (F_v/F_m) was calculated as [*Krause and Weis*, 1991]:

$$F_v/F_m = (F_m - F_0)/F_m.$$

As shown earlier, the maximum F_v/F_m values for phytoplankton under optimal conditions correspond to 0.70, with a significant difference between taxa [*Juneau and Harrison*, 2005; *Suggett et al.*, 2009]. The F_v/F_m value indicates the potential photosynthetic capacity of phytoplankton.

Measuring the active fluorescence of phytoplankton cells after light adaptation at illumination level E allows us to calculate the effective quantum yield of PSII ($\Delta F/F'_m$) [*Genty et al.*, 1989]:

$$\Delta F/F'_m = (F'_m - F_t)/F'_m,$$

where F'_m is the maximum fluorescence of light-adapted cells, F_t is the fluorescence yield of light-adapted cells.

The rETR value at a certain light level is calculated as:

$$rETR = \Delta F/F'_m \times E \times 0,5,$$

where E is the actinic light level (µmol photons/m^2 per s), and the factor 0.5 is to correct for the partitioning of photons between PSI and PSII [*Lippemeier*, 1999; *Schreiber*, 2004].

2.5. Statistical analysis

Standard statistical methods of descriptive, correlation and t-test analyses were used. Averages in the text below are presented with a standard deviation (± SD). Correlation is given with the coefficient of correlation (r), number of measurements (n) and the probability of the null hypothesis (P). Statistical analyses were performed using PAST 4.12 [*Hammer et al.*, 2001].

3. Results

3.1. Research area Hydrological and Hydrochemical Peculiarities

Based on the results of the analysis of TS diagrams using CTD data, the hydrophysical characteristics of the studied areas were established. The upper layer of the water column in the GF was colder and less saline than in the SEB (Table 1). In the SEB, by November, as a result of autumn cooling and vertical convection of water, the seasonal thermocline deepened to 25–45 m. On the longitudinal section of the GF in November, the upper quasi-homogeneous layer (UML) deepened to 30–40 m and had a weakly pronounced increase in temperature with distance from the Neva Bay. The seasonal thermocline reached a depth of 50–55 m.

During our studies, the total daily solar radiation on the sea surface varied from 4 to 12 mol photons/m^2 per day. The depth of the euphotic zone, i.e., the penetration depth of 1% of surface illumination varied from 10 to 20 m (average 16.7 m) in the SEB and from 12 to 15 m (average 13.2 m) in the GF. Thus, during the study period, the UML was much deeper than the euphotic layer, which could contribute to the periodic removal of phytoplankton from the upper illuminated zone and a decrease in overall productivity.

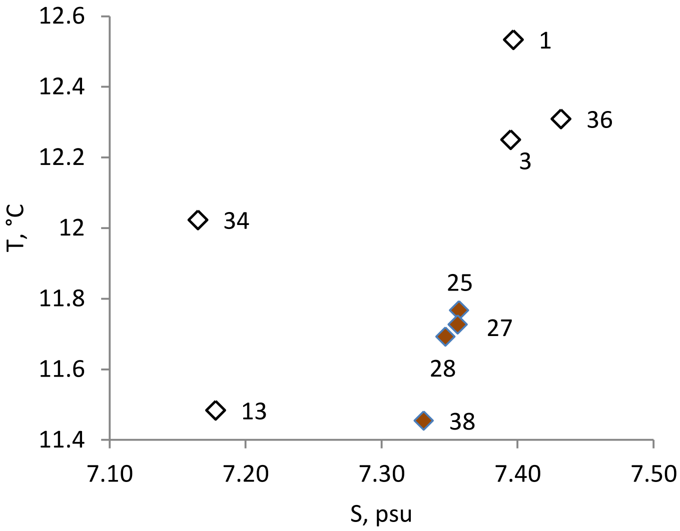


Figure 2. *TS* diagram for stations in the Southeastern Baltic Sea (surface). Dark diamonds are stations in the temporary frontal zone.

In terms of the relationship between temperature and salinity on the surface (Figure 2), stations 25, 27, 28, 38 differ significantly from other stations in this area. These measurements are quite similar to each other; the differences in *TS* characteristics between them are significantly less than with measurements outside this zone. It is possible that between the indicated group of stations and the remaining stations in this area, a temporary frontal zone may be observed [*Demidov et al.*, 2011], associated with the interaction of desalinated water from the Vistula Lagoon with sea water. In the section in the GF from the mouth of the Neva (station 55) to the central part (station 49), the surface salinity gradually increased from 2.8 to 4.9 psu, and the water temperature – from 7 to 8.5 °C.

Nutrient content varied significantly between the two study areas (Table 1). The phosphate content in the surface layer of water in the GF was five times higher, and DIN = ($NO_2 + NO_3 + NH_4$) was four times higher than in the SEB. All differences were statistically significant (*t*-test, $P < 0.05$). Surface phosphate concentrations in the SEB were uniform, and dissolved inorganic nitrogen (DIN) concentrations showed a slight increasing trend from the coast to the open sea (from 3.5 µM at station 1 to 5.4 µM at station 13). The surface concentration of DIN in the GF was maximum near the mouth (29.5 µM) and decreased in the central part by 2–4 times (7.5 µM at station 47 and 14.8 µM at station 42). The change in the phosphate content in the GF was insignificant (0.74–0.95 µM).

Nutrient content (dissolved inorganic nitrogen and phosphate concentrations) varied slightly within each study area. The nitrate significantly exceeded the level limiting phytoplankton growth. The phosphate content was below the limiting level in the SEB and higher in the GF.

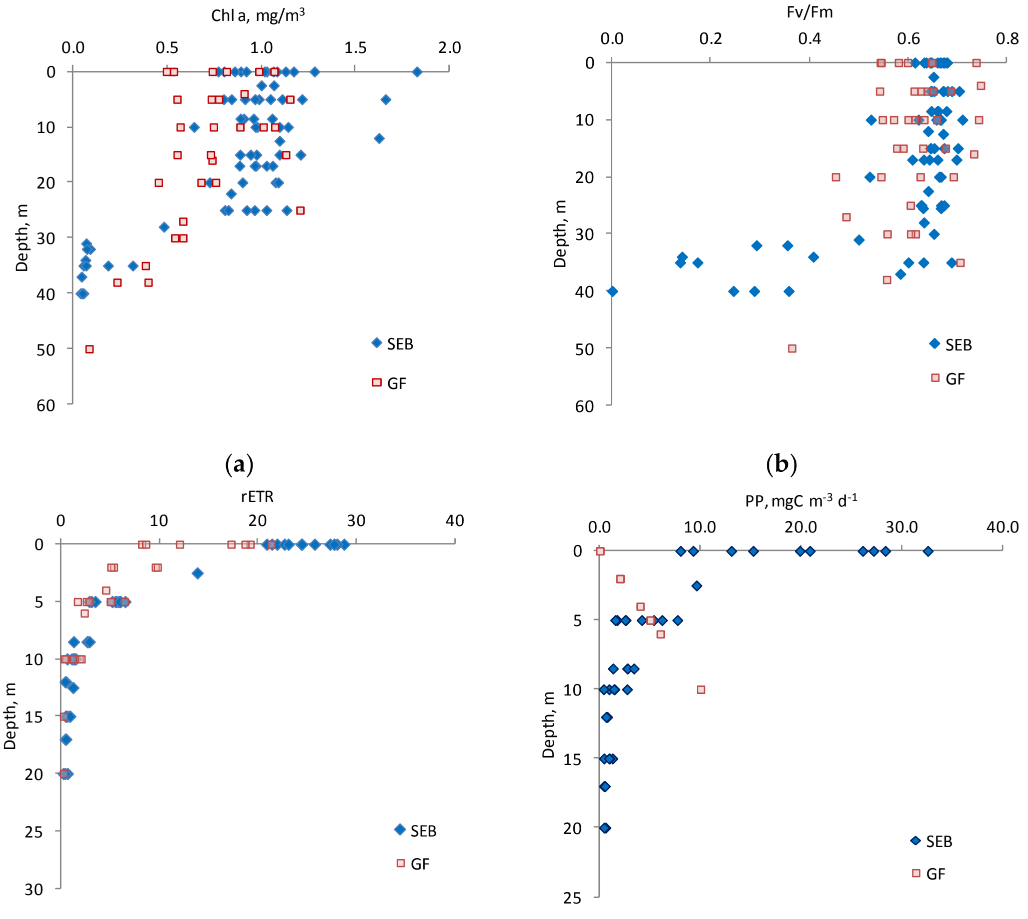
Table 1. Average surface values and standard deviations of hydrophysical and hydrochemical parameters for two regions of the Baltic: the southeastern part and the Gulf of Finland

Area	T	S	$P-PO_4$	DIN
SEB	11.9 ± 0.4	7.3 ± 0.1	0.17 ± 0.03	4.3 ± 0.7
GF	7.9 ± 0.6	4.2 ± 0.8	0.83 ± 0.09	17.2 ± 8.0

Note: T – surface temperature, °C; S – surface salinity, psu; $P-PO_4$ – concentration of phosphorus in phosphate, µM; DIN – dissolved inorganic nitrogen concentration (DIN = $NO_2 + NO_3 + NH_4$), µM.

3.2. Parameters of Primary Productivity

The vertical distribution of Chl *a* was relatively uniform within the upper 30 m layer of the water column in both the SEB and the GF (Figure 3a). The Chl *a* concentration here varied from 0.68 to 1.22 mg/m^3. In the layer below the thermocline (30 m), the Chl *a* concentration decreased significantly. In the SEB with a pronounced thermocline, this decrease was sharp and significant – on average 1.02±0.21 and 0.09±0.04 mg/m^3 above and below the thermocline, respectively. In the GF, the thermocline was less pronounced and the decrease in Chl *a* concentration with depth was not sharp – on average 0.77 ± 0.22 and 0.27± 0.15 mg/m^3, respectively. As can be seen in Figure 2, the variability of Chl *a* concentration within the upper mixed layer at different stations in the GF was greater than in the SEB (0.45–1.21 and 0.72–1.28 mg/m^3, respectively).



(a) (b)

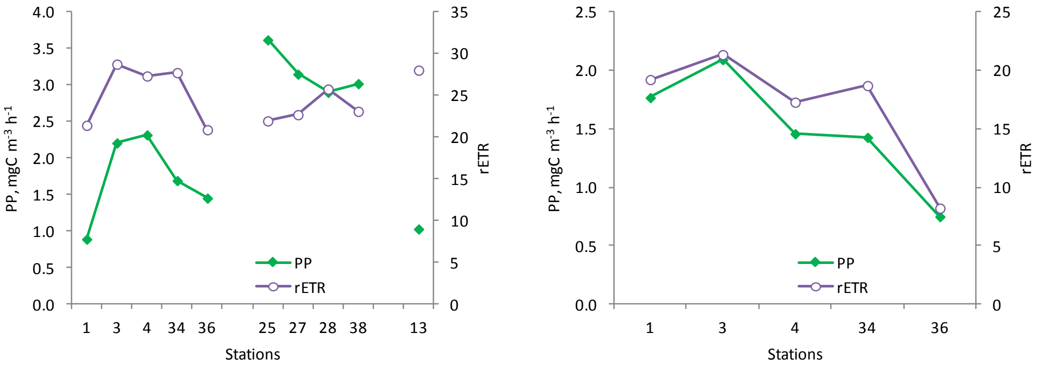
(c) (d)

Figure 3. Vertical distribution of the parameters of primary productivity: a) chlorophyll *a*, b) maximum quantum efficiency of PSII, F_v/F_m, c) relative electron transport rate (rETR), d) primary production (PP).

The maximum quantum yield of PSII (F_v/F_m), which characterizes the potential photosynthetic capacity of phytoplankton, was high at all stations of the SEB (0.61–0.68) and GF (0.54–0.74) (Figure 3b). The lowest surface F_v/F_m value (0.54) was recorded at station 55 near the mouth of the Neva. At most profile stations, a constant or slight decrease in F_v/F_m was observed with depth in the 0–30 m layer, with the main decrease being below 30 m.

The rETR value in PSII within the euphotic zone ranged from 0.24 to 28.7 a.u. in the SEB and between 0.21 and 21.3 a.u. in the GF. At all stations, rETR decreased exponentially with depth, which is associated with a decrease in underwater irradiance (Figure 3c). rETR values were more variable at the surface than in the water column (Figure 3a). The highest surface rETR values in the SEB (more than 27) were at coastal stations 3, 4 and 34. In the GF, surface rETR values were at an equally high level in the mouth zone (18.7–21.4 a.u.) and were minimal at the mouth of the Neva river (8.21 a.u.) (Figure 4b).

The bulk of *PP* (62–89%) was concentrated in the upper 5 m layer of the water column. A decrease in illumination with depth in the water column leads to an exponential decrease in *PP* (Figure 4d). Moreover, such a decrease was very sharp in the upper 5 m layer – *PP* values on the surface and at a depth of 5 m differed by 3–12 times at different stations of the SEB and GF. Surface *PP* varied from 8 to 32.6 mgC/m^3 per day in the SEB and from 6.1 to 16.7 mgC/m^3 per day in the GF. In the SEB, maximum values of surface *PP* (26.1–32.6 mgC/m^3 per day) were observed in the middle part of the study area (stations 25, 27, 28 and 38), and lower values with significant variability were observed in the coastal zone (Figure 3a). In the GF, the surface *PP* increased significantly from the mouth of the Neva towards the sea (Figure 4b).



(**a**) (**b**)

Figure 4. Distribution of surface values of primary production (*PP*) and electron transport rates in photosystem II of phytoplankton (rETR) in the Southeastern Baltic Sea (a) and in the Gulf of Finland (b).

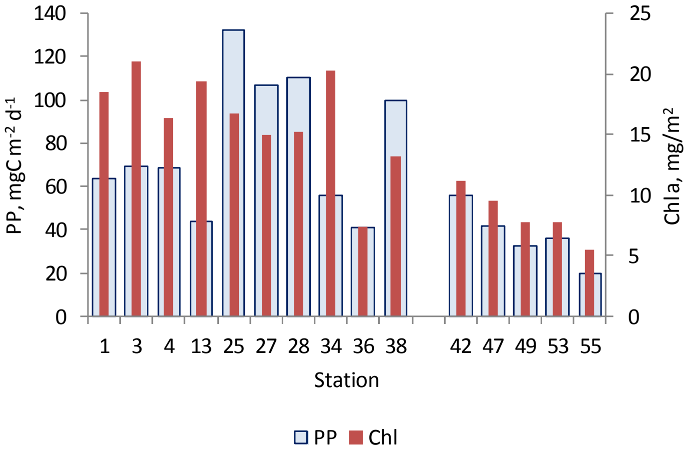


Figure 5. Depth-integrated Chl *a* and *PP* values in the Southeastern Baltic Sea (stations 1–38) and the Gulf of Finland (stations 42–55).

The maximum *AN* values for the water column, characterizing the specific photosynthetic activity of phytoplankton, were confined to the surface at both sites and varied at different stations from 0.69 to 3.92 mgC/mgChl per hour (on average 2.26 ± 0.69 mgC/mgChl per hour) in SEB and from 1.40 to 2.12 mgC/mgChl per hour (on average 1.78 ± 0.28 mgC/mgChl per hour) in GF. The highest values (more than 3 mgC/mgChl per hour) were detected in the middle part of the study area in the SEB (stations 25, 27 and 28). The lowest *AN* values (less than 1 mgC/mgChl per hour) were also found in the SEB at coastal stations 1 and 34.

The depth-integrated Chl *a* content in the euphotic layer varied three times (7.4–21.0 mg/m^2) at different stations of the SEB and two times (5.5–11.1 mg/m^2) in the GF (Figure 5). The average values of this parameter for SEB and GF differed twofold (16.3 ± 4.0 and 8.3 ± 1.2 mg/m^2, respectively). Similarly, the depth-integrated *PP* values differed by three times (41.2–132.2 mgC/m^2 per day) at different stations of the SEB and by two times in the GF (19.8–55.6 mgC/m^2 per day) (Figure 5). The average values of this parameter for each region differed twofold (79.1 ± 31.0 and 37.3 ± 13.2 mgC/m^2 per day, respectively). The differences between SEB and GF for the average values of Chl *a* and *PP* content were statistically significant (t-test, $P < 0.05$).

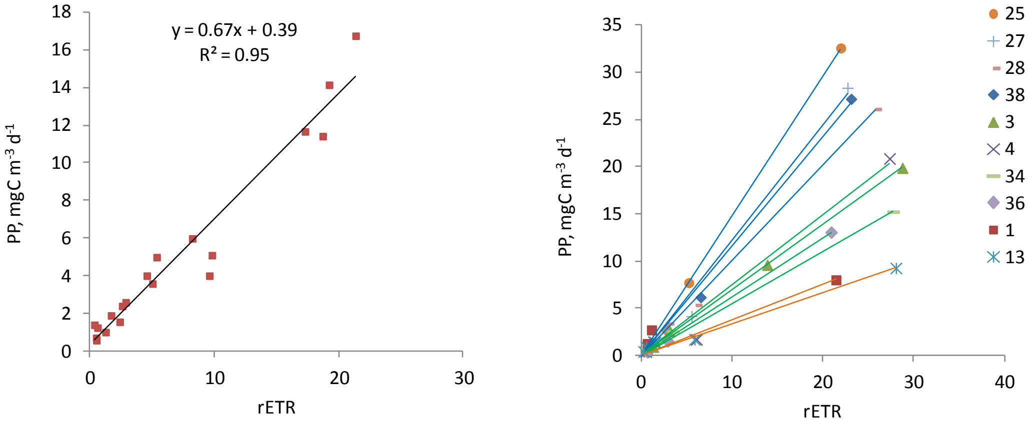
During the period of our research, the maximum photosynthetic activity of phytoplankton, expressed in terms of rETR and *PP*, was observed in the surface layer (see Figure 3). The average values of surface water productivity parameters are presented in Table 2. As can be seen from the table, the maximum quantum efficiency F_v/F_m (potential photosynthetic capacity of phytoplankton, characterizing its "health") is almost the same in both areas. However, the biomass of phytoplankton (based on Chl *a* content) and its production activity (rETR, *PP* and *AN*) were on average significantly higher in the SEB than in the GF.

Table 2. Productivity parameters (average and standard deviation) in surface waters (0 m) for two regions of Baltic Sea

Area	Depth	Chl *a*	% Phaeo	F_v/F_m	rETR	*PP*	*AN*
SEB	71 ± 32	1.07 ± 0.31	52 ± 4	0.65 ± 0.02	24.8 ± 3.1	20.4 ± 8.48	2.26 ± 1.15
GF	41 ± 15	0.83 ± 0.21	62 ± 7	0.64 ± 0.1	16.9 ± 5.1	12.0 ± 3.99	1.78 ± 0.28

Note: Chl *a* – concentration of chlorophyll *a*, mg/m^3; % Phaeo is the proportion of pheophytin in the sum of Chl *a* + pheophytin concentrations; F_v/F_m – maximum quantum efficiency, rETR – relative of electron transport rate in PSII, *PP* – primary production, mgC/m^3 per day, *AN* – assimilation number, mgC/mgChl per hour.

Analysis of the relationship between *PP* and rETR, measured in parallel at the same light levels for samples from the euphotic layer, shows a strong positive correlation for all pairs of values in the GF ($r = 0.95$, $n = 19$, $P = 0.05$) (Figure 6a) and the absence of such a general correlation in the SEB (Figure 6b). However, at each station, for samples from different horizons, a very high positive correlation between *PP* and rETR was observed in both regions.



(**a**) (**b**)

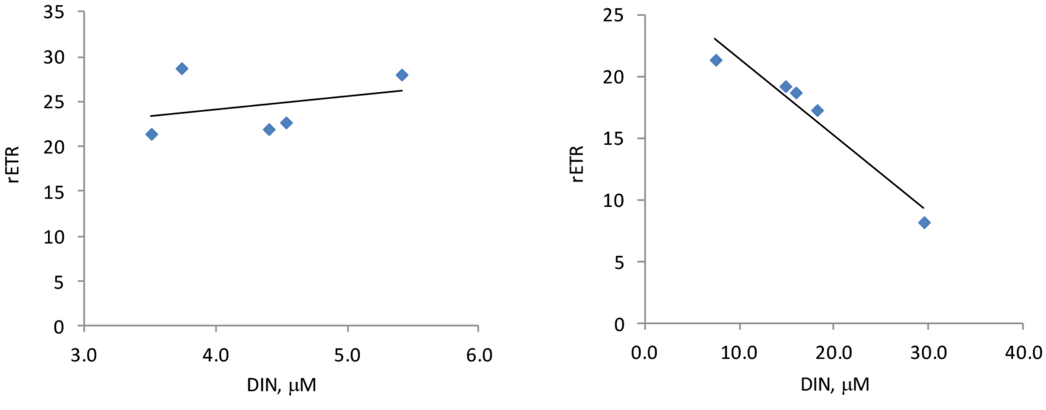
Figure 6. Relationship between primary production, *PP*, and relative electron transport, rETR, in Gulf of Finland (a) and Southeastern Baltic Sea (b). Different shapes of dots in figure (b) correspond to different stations according to the legend.

The minimum values of the regression coefficient *a* (0.33–0.38) were at station 1 (eastern part of the Gulf of Gdansk) and at station 13 (open sea) (orange lines in Figure 6b). Higher values of light energy efficiency (0.55–0.74) were observed at stations located in the coastal zone (stations 3, 4, 34, 36) (green lines in Figure 6b). The highest values (1.01–1.48) were found in the middle part of the study area with depths of 78–93 m (stations 25, 27, 28, 38) (blue line in Figure 6b), where *PP* values were also the highest.

It should be noted that the coefficients a in the regression equations based on parallel measurements of rETR and PP within the euphotic layer coincide for each station with the ratio of the surface values of these parameters (PP/rETR). This allows the ratio of surface values to be used to determine the efficiency coefficient for the entire euphotic layer.

Salinity and nutrients (DIN and phosphate) are considered to be the most important factors influencing the values and distribution of rETR and PP. The influence of the nutrient concentration on the current production capacity of phytoplankton is most effectively assessed for the surface at the same illumination. A strong negative correlation between surface values of rETR and DIN was found in the GF ($r = -0.97$, $n = 5$, $P < 0.05$) (Figure 7b) and no correlation between rETR and DIN in the SEB (Figure 7a). The same strong negative relationship was observed in the GF and between DIN and PP ($r = -0.68$, $n = 5$, $P < 0.05$), while in the SEB such a relationship was absent.

A strong positive correlation was established between rETR and salinity in the GF ($r = 0.95$, $n = 5$, $P < 0.05$) and a strong negative correlation in the SEB ($r = -0.63$, $n = 9$, $P < 0.05$). Also, a high positive correlation ($r > 0.8$, $n = 5$, $P < 0.05$) was between salinity and other production parameters (PP, AN and Chl a) in the GF.



(a) **(b)**

Figure 7. The relationship between the electron transport rate (rETR) and the content of mineral forms of nitrogen (DIN) in the Southeastern Baltic Sea (a) and in the Gulf of Finland (b).

The influence of nutrients on the photosynthetic efficiency coefficient was not revealed in this study. A strong negative relationship was found between photosynthetic efficiency (PP/rETR) and water temperature ($r = -0.83$, $n = 8$, $P = 0.05$) (Figure 8).

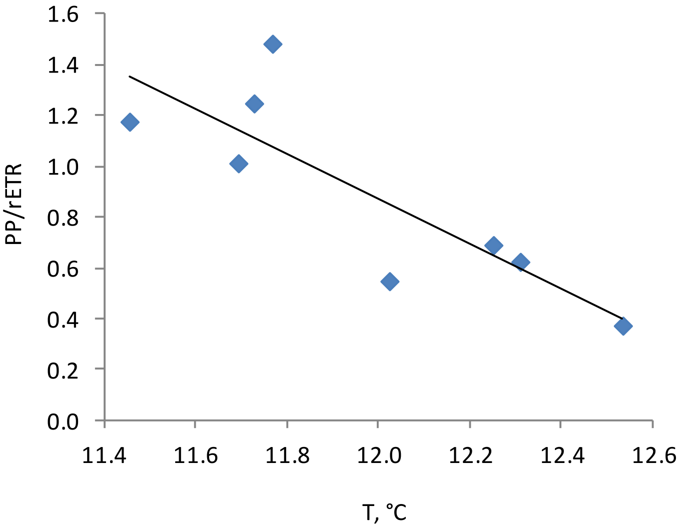


Figure 8. The relationship between photosynthetic efficiency (PP/rETR) and temperature (T) for stations in the Southeastern Baltic Sea.

4. Discussion

The bulk of Chl a was in the upper 25 m layer of the water column in both regions (see Figure 3). Likewise, the potential photosynthetic capacity of phytoplankton, expressed as F_v/F_m values, was uniformly high in the upper 40 m layer. However, the realization of productive potential was observed only in the surface layer of the water column. The rETR and PP values were maximum in the surface layer. The leading factor for PP is light energy. A decrease in illumination with depth in the water column leads to an exponential decrease in PP. Therefore, the main part of PP (62–89%) was concentrated in the upper 5 m layer of the water column. A similar distribution of PP values over depth and relatively high F_v/F_m values were shown for various areas of the Antarctic Peninsula at the end of summer [*Pereira Granja Russo et al.*, 2018].

The depth-integrated PP value in the SEB in November was lower than in the southern part of the open Baltic in summer – early autumn (381–617 mgC/m^2 per day [*Piontek et al.*, 2019]. The results of our PP measurements in the coastal zone of the SEB (Gdansk Bay and the northern coast of the Sambian Peninsula, stations 1, 2, 4 and 34) (6.7 ± 4.8 mgC/m^3 per day on average for the upper layer 0–10 m) correspond to the average long-term winter values for this area (4.6 ± 5.9 mgC/m^3 per day) [*Kudryavtseva and Aleksandrov*, 2019]. The PP values in the GF in November, obtained in our studies, were an order of magnitude lower than the results of PP measurements in July–August in the period 2003–2007 [*Golubkov et al.*, 2017]. There is no information for comparison for other seasons.

The highest values of depth-integrated PP (100–130 mgC/m^2 per day) were in the middle part of the SEB with depths of 78–93 m (stations 25, 27, 28, 38). The maximum values of AN, which characterizes the specific photosynthetic activity of phytoplankton, were confined to the surface layer. The surface concentration of Chl *a* at most stations (except for coastal stations 1, 34 and 38) was at the same level (0.77–1.03 mg/m^3), therefore variations in PP were determined by differences in photosynthetic activity. In the GF, the depth-integrated PP increased in the direction from the mouth of the Neva and was in the range of 19.8–55.6 mgC/m^2 per day, which corresponded to the PP level in the coastal zone of the SEB (41.2–69.1 mgC/m^2 per day). The rETR values are comparable to those for phytoplankton of the North Sea and South Atlantic (2–40 a.u.) [*Röttgers*, 2007].

Primary productivity parameters (rETR and PP) negatively correlated with the content of mineral forms of nitrogen (DIN) in water in the GF. It is likely that at very high DIN values in the GF, both light (light energy absorption, rETR) and dark (organic matter synthesis, PP) processes of photosynthesis are inhibited. The strong positive correlation between rETR and salinity in the GF suggests that the observed dependence of rETR on DIN is based on an increasing salinity trend (from the mouth to the outer estuary), reflecting the degree of mixing of river (biogen-saturated) and sea waters, at which DIN values decrease and, consequently, their inhibitory value decreases. In the SEB, at a lower range of DIN values, a similar inhibitory effect was observed only for rETR.

The surface PP values in the SEB were more variable (the difference between the minimum and maximum PP values is 4 times) than rETR (1.4 times), which may reflect a greater influence of environmental factors on the efficiency of using absorbed light energy in biosynthesis processes, than the solar energy conversion rate in this region. We observed a similar situation (PP was more variable than rETR) in the Kara Sea [*Mosharov et al.*, 2019]. In the GF, the variability of surface PP was negligible (1.4 fold) and comparable to that for rETR (1.2 fold).

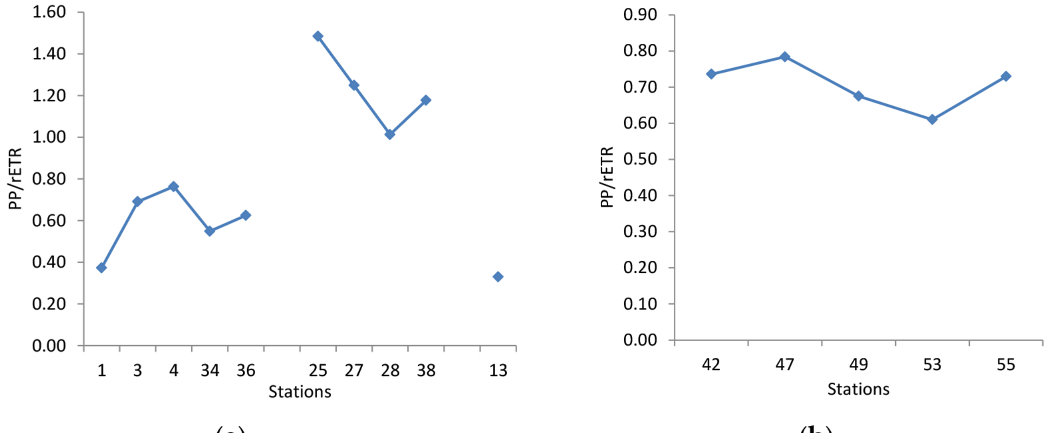
Empirical data obtained in different regions of the World Ocean demonstrate a linear relationship between ETR and the rate of C fixation and/or O^2 production [*Kromkamp et al.*, 2008; *Lawrenz et al.*, 2013; *Suggett et al.*, 2009], but deviations from linearity have also been reported [*Hancke et al.*, 2015; *Suggett et al.*, 2010]. This allows us to consider rETR and PP as values that reflect the intensity of different stages of photosynthesis – the light and dark stages, respectively. ETR is the rate of conversion of solar energy into chemical energy of the cell, which provides the processes of biosynthesis of organic matter by phytoplankton. Primary production is the result of this biosynthesis. The PP/rETR ratio (photosynthetic efficiency) can serve as an indicator of the efficiency of using energy stored in the reaction centers of the photosystem during the synthesis of organic matter at the dark stage [*Mosharov et al.*, 2019, 2022]. On the other hand, the value of the PP/rETR parameter can be used to calculate PP from the results of active fluorescence measurements.

In the SEB, photosynthetic efficiency is specific to each station, i.e., different regions are characterized by a certain ratio of the activity of the processes of assimilation of light energy (light stage of photosynthesis) and its use for biosynthesis (dark stage of photosynthesis), apparently associated with a different combination of natural factors.

The spatial distribution of photosynthetic efficiency values (PP/rETR) is shown in Figure 9. In the SEB, the maximum values of this parameter in the area with depths of 78–93 m are possibly associated with the formation of a temporary frontal zone. Depending on the wind regime, the Baltic Strait, connecting the Vistula Lagoon with the sea, can serve as a powerful source of fresh water [*Aleksandrov*, 2010]. The flow of water from the strait can spread both along the coast and at some distance from it, which can lead to the formation of a pronounced frontal zone [*Demidov et al.*, 2011]. At the same time, the strengthening and stabilization of the alongshore current is clearly evident, which corresponds to lower temperatures and higher salinity. The TS diagram for the SEB (see Figure 2) clearly shows that stations 25, 27, 28 and 38 are located in an area with a corresponding combination of temperature and salinity.

Our previous studies of photosynthetic efficiency on the Kara Sea shelf showed that areas with increased PP/rETR are characterized by sharp gradients of hydrophysical conditions corresponding to frontal zones of various origins [*Mosharov et al.*, 2019]. The maximum values of this parameter were observed in the zone of interaction between the river flow of the Yenisei River and sea water.

As the present study showed, an increase in photosynthetic efficiency in the central zone of the SEB with a significant thermohaline gradient led to a local increase in PP (see Figure 4a) at the same level of Chl *a* content and rETR value (see rres 4a and 5a). In the GF, with a pronounced increase in salinity from the mouth to the sea and the absence of sharp gradients, the PP/ETR values at different transect stations varied slightly (0.61–0.78) (Figure 9). At the same time, all indicators of phytoplankton productivity (Chl *a*, rETR and PP) increased almost synchronously with the increase in salinity (Figures 3b and 4). Thus, the local increase in PP in this region was due to both an increase in the abundance of phytoplankton and an increase in its light-catching activity. It is interesting to note that the values of photosynthetic efficiency in the GF correspond to the values in the coastal zone of the SEB.



(**a**) (**b**)

Figure 9. Distribution of surface values of photosynthetic efficiency PP/rETR in the south-eastern part of the Baltic (a) and the Gulf of Finland (b).

Earlier in 2021, we conducted studies of the seasonal variability of primary production and the formation of carbon flows in the eastern part of the Bay of Gdansk at the offshore site of the Kaliningrad Carbon supersite [*Mosharov et al.*, 2022]. A significant seasonal difference in photosynthetic efficiency and primary production values was shown, which determined the seasonal variability of the initial stage of carbon flux. The maximum photosynthetic efficiency was observed in summer and early autumn, and the minimum in late autumn in November. At the same time, seasonal differences reached 8 times. In the present study, conducted in November 2022, Station 3 was located adjacent to the

Carbon supersite, allowing estimates of interannual variability in primary production and, consequently, the magnitude of the carbon flux from the atmosphere to the sea. It was found that the PP/rETR value in November 2022 was twice as high as in November 2021.

5. Conclusions

In the south-eastern part of the Baltic Sea and in the Gulf of Finland, in the zone of interaction between river and sea waters, primary productivity increases with increasing salinity. With a significant thermohaline gradient in the central part of the SEB, an increase in PP occurs due to an increase in photosynthetic efficiency (PP/rETR) with minor fluctuations in the Chl *a* concentration and rETR in this region. On the other hand, in the GF, with a gradual increase in salinity from the mouth of the Neva to the outer estuary, PP values increase due to an increase in the Chl *a* concentration, while photosynthetic efficiency changes slightly.

Potential photosynthetic capacity of phytoplankton, measured by maximum quantum efficiency (F_v/F_m) (phytoplankton health), was high at all stations in both areas. The bulk of PP (62–89%) was in the upper 5 m layer. Chl *a* and F_v/F_m were evenly distributed in the upper 30 m layer in both areas. Thus, the high potential of phytoplankton productivity and, accordingly, the initial stage of carbon flow, which persists at the end of the growing season, is realized to varying degrees in the shelf zone of the SEB, reaching a maximum in the frontal zone with a sharp thermohaline gradient. The abundance of phytoplankton (in terms of Chl *a* content) and its production activity (rETR, PP) in the SEB is significantly higher than in the GF. Based on this, we can reasonably assume a higher carbon flux from the atmosphere to the upper layers of the water column (at the initial stage of the biological pump in the process of primary production) in late autumn in the central zone of the SEB, compared to the estuarine zone in the GF.

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References

Aleksandrov, S. V. (2010), Biological production and eutrophication of Baltic Sea estuarine ecosystems: The Curonian and Vistula Lagoons, *Marine Pollution Bulletin*, *61*(4–6), 205–210, https://doi.org/10.1016/j.marpolbul.2010.02.015.

Behrenfeld, M. J., and P. G. Falkowsk (1997), Photosynthetic rates derived from satellite-based chlorophyll concentration, *Limnology and Oceanography*, *42*(1), 1–20.

Ciotti, A. M., M. R. Lewis, and J. J. Cullen (2002), Assessment of the relationships between dominant cell size in natural phytoplankton communities and the spectral shape of the absorption coefficient, *Limnology and Oceanography*, *47*(2), 404–417.

Cullen, J. J. (1990), On models of growth and photosynthesis in phytoplankton, *Deep-Sea Research*, *37*, 667–683.

Demidov, A. N., S. A. Myslenkov, V. A. Gritsenko, V. Ya. Sultanov, M. N. Pisareva, K. P. Silvestrova, and A. A. Polukhin (2011), Specific features of water structure and dynamics within the coastal part of the Baltic Sea near the Sambian Peninsula, *Moscow University Bulletin. Series 5, Geography*, *1*, 41–47 (in Russian), EDN: OIPRSH.

Eppley, R. W. (1972), Temperature and phytoplankton growth in the sea, *Fishery Bulletin*, *70*(4), 1063–1085.

Genty, B., J.-M. Briantais, and N. R. Baker (1989), The relationship between the quantum yield of photosynthetic electron transport and quenching of chlorophyll fluorescence, *Biochimica et Biophysica Acta (BBA) - General Subjects*, *990*(1), 87–92, https://doi.org/10.1016/S0304-4165(89)80016-9.

Golubkov, S., M. Golubkov, A. Tiunov, and V. Nikulina (2017), Long-term changes in primary production and mineralization of organic matter in the Neva Estuary (Baltic Sea), *Journal of Marine Systems*, *171*, 73–80, https://doi.org/10.1016/j.jmarsys.2016.12.009.

Grasshof, K., K. Kremling, and M. Ehrhardt (Eds.) (1999), *Methods of Seawater Analysis*, 3rd ed., 577 pp., Wiley, https://doi.org/10.1002/9783527613984.

Hammer, Ø., D. A. T. Harper, and P. D. Ryan (2001), Past: paleontological statistics software package for education and data analysis, *Palaeontologia Electronica*, *4*, 1–9.

Hancke, K., T. Dalsgaard, M. K. Sejr, S. Markager, and R. N. Glud (2015), Phytoplankton Productivity in an Arctic Fjord (West Greenland): Estimating Electron Requirements for Carbon Fixation and Oxygen Production, *PLOS ONE*, *10*(7), e0133,275, https://doi.org/10.1371/journal.pone.0133275.

Holm-Hansen, O., and B. Riemann (1978), Chlorophyll a Determination: Improvements in Methodology, *Oikos*, *30*(3), 438, https://doi.org/10.2307/3543338.

Juneau, P., and P. J. Harrison (2005), Comparison by PAM Fluorometry of Photosynthetic Activity of Nine Marine Phytoplankton Grown Under Identical Conditions, *Photochemistry and Photobiology*, *81*(3), 649–653, https://doi.org/10.1111/j.1751-1097.2005.tb00239.x.

Knap, A., A. Michaels, A. Close, H. Ducklow, and A. Dickson (Eds.) (1994), *Protocols for the Joint Global Ocean Flux Study (JGOFS) Core Measurements. Reprint of the IOC Manuals and Guides No. 29*, UNESCO.

Kolber, Z. S., O. Prášil, and P. G. Falkowski (1998), Measurements of variable chlorophyll fluorescence using fast repetition rate techniques: defining methodology and experimental protocols, *Biochimica et Biophysica Acta (BBA) - Bioenergetics*, *1367*(1–3), 88–106, https://doi.org/10.1016/s0005-2728(98)00135-2.

Krause, G. H., and E. Weis (1991), Chlorophyll Fluorescence and Photosynthesis: The Basics, *Annual Review of Plant Physiology and Plant Molecular Biology*, *42*(1), 313–349, https://doi.org/10.1146/annurev.pp.42.060191.001525.

Kromkamp, J. C., N. A. Dijkman, J. Peene, S. G. H. Simis, and H. J. Gons (2008), Estimating phytoplankton primary production in Lake IJsselmeer (The Netherlands) using variable fluorescence (PAM-FRRF) and C-uptake techniques, *European Journal of Phycology*, *43*(4), 327–344, https://doi.org/10.1080/09670260802080895.

Kudryavtseva, E. A., and S. V. Aleksandrov (2019), Hydrological and Hydrochemical Underpinnings of Primary Production and Division of the Russian Sector in the Gdansk Basin of the Baltic Sea, *Oceanology*, *59*(1), 49–65, https://doi.org/10.1134/S0001437019010077.

Lawrenz, E., G. Silsbe, E. Capuzzo, P. Ylöstalo, et al. (2013), Predicting the Electron Requirement for Carbon Fixation in Seas and Oceans, *PLoS ONE*, *8*(3), e58,137, https://doi.org/10.1371/journal.pone.0058137.

Laws, E. A., and K. Maiti (2019), The relationship between primary production and export production in the ocean: Effects of time lags and temporal variability, *Deep Sea Research Part I: Oceanographic Research Papers*, *148*, 100–107, https://doi.org/10.1016/j.dsr.2019.05.006.

Lippemeier, S. (1999), Direct impact of silicate on the photosynthetic performance of the diatom Thalassiosira weissflogii assessed by on- and off-line PAM fluorescence measurements, *Journal of Plankton Research*, *21*(2), 269–283, https://doi.org/10.1093/plankt/21.2.269.

Marra, J., Ch. C. Trees, and J. E. O’Reilly (2007), Phytoplankton pigment absorption: A strong predictor of primary productivity in the surface ocean, *Deep Sea Research Part I: Oceanographic Research Papers*, *54*(2), 155–163, https://doi.org/10.1016/j.dsr.2006.12.001.

Mosharov, S. A., V. M. Sergeeva, V. V. Kremenetskiy, A. F. Sazhin, and S. V. Stepanova (2019), Assessment of phytoplankton photosynthetic efficiency based on measurement of fluorescence parameters and radiocarbon uptake in the Kara Sea, *Estuarine, Coastal and Shelf Science*, *218*, 59–69, https://doi.org/10.1016/j.ecss.2018.12.004.

Mosharov, S. A., I. V. Mosharova, O. A. Dmitrieva, A. S. Semenova, and M. O. Ulyanova (2022), Seasonal Variability of Plankton Production Parameters as the Basis for the Formation of Organic Matter Flow in the Southeastern Part of the Baltic Sea, *Water*, *14*(24), 4099, https://doi.org/10.3390/w14244099.

Pereira Granja Russo, A. D., M. S. de Souza, C. R. Borges Mendes, V. Maria Tavano, and C. A. Eiras Garcia (2018), Spatial variability of photophysiology and primary production rates of the phytoplankton communities across the western Antarctic Peninsula in late summer 2013, *Deep Sea Research Part II: Topical Studies in Oceanography*, *149*, 99–110, https://doi.org/10.1016/j.dsr2.2017.09.021.

Piontek, J., S. Endres, F. A. C. Le Moigne, M. Schartau, and A. Engel (2019), Relevance of Nutrient-Limited Phytoplankton Production and Its Bacterial Remineralization for Carbon and Oxygen Fluxes in the Baltic Sea, *Frontiers in Marine Science*, *6*, https://doi.org/10.3389/fmars.2019.00581.

Platt, T., and Ch. L. Gallegos (1980), Modelling Primary Production, in *Primary Productivity in the Sea*, pp. 339–362, Springer US, https://doi.org/10.1007/978-1-4684-3890-1_19.

Röttgers, R. (2007), Comparison of different variable chlorophyll a fluorescence techniques to determine photosynthetic parameters of natural phytoplankton, *Deep Sea Research Part I: Oceanographic Research Papers*, *54*(3), 437–451, https://doi.org/10.1016/j.dsr.2006.12.007.

Schreiber, U. (2004), Pulse-Amplitude-Modulation (PAM) Fluorometry and Saturation Pulse Method: An Overview, in *Advances in Photosynthesis and Respiration*, pp. 279–319, Springer Netherlands, https://doi.org/10.1007/978-1-4020-3218-9_11.

Schreiber, U., U. Schliwa, and W. Bilger (1986), Continuous recording of photochemical and non-photochemical chlorophyll fluorescence quenching with a new type of modulation fluorometer, *Photosynthesis Research*, *10*(1–2), 51–62, https://doi.org/10.1007/BF00024185.

Schreiber, U., W. Bilger, and C. Neubauer (1995), Chlorophyll Fluorescence as a Nonintrusive Indicator for Rapid Assessment of In Vivo Photosynthesis, in *Ecophysiology of Photosynthesis*, pp. 49–70, Springer Berlin Heidelberg, https://doi.org/10.1007/978-3-642-79354-7_3.

Steemann Nielsen, E. (1952), The Use of Radio-active Carbon (C14) for Measuring Organic Production in the Sea, *ICES Journal of Marine Science*, *18*(2), 117–140, https://doi.org/10.1093/icesjms/18.2.117.

Suggett, D. J., H. L. MacIntyre, T. M. Kana, and R. J. Geider (2009), Comparing electron transport with gas exchange: parameterising exchange rates between alternative photosynthetic currencies for eukaryotic phytoplankton, *Aquatic Microbial Ecology*, *56*, 147–162, https://doi.org/10.3354/ame01303.

Suggett, D. J., C. M. Moore, and R. J. Geider (2010), Estimating Aquatic Productivity from Active Fluorescence Measurements, in *Chlorophyll a Fluorescence in Aquatic Sciences: Methods and Applications*, pp. 103–127, Springer Netherlands, https://doi.org/10.1007/978-90-481-9268-7_6.