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Phytoplankton taxonomic composition, nutrients utilization and biogeochemistry in the upper mixed layer in the coastal area of the Terra Nova Bay, Ross Sea, Antarctica

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Within BioAPRoS project (Biogenic Aerosol and Primary production in the Ross Sea) two research campaigns were conducted in the coastal area of Terra Nova Bay (TNB) in front of the Italian Base Mario Zucchelli Station, Ross Sea, Antarctica, spanning from 13/11/2018 to 30/01/2019 (BioAPRoS18), and from 01/12/2019 to 30/01/2020 (BioAPRoS19), an area classified as Marginal Ice Zone (MIZ) during this period. The goal was to study nutrient dynamics, phytoplankton biomass and taxonomic composition in the upper mixed layer (UML), exploring assimilation preferences of different phytoplankton assemblages and their biogeochemical effects. The findings were compared with similar 1990s campaigns in the same region. In line with the previous outcome, UML was persistent and always very shallow (5–18 m). Nutrient concentrations showed decreasing trends from spring to summer synchronously opposite to Chl_a, highlighting pronounced consumption of nutrients during phytoplankton growth. Discrepancies emerged during phytoplankton summer bloom; in BioAPRoS18 N/P was about 40 due to $\Delta N/\Delta P$ removal ratio of 11.8, a typical already known condition, while BioAPRoS19 showed an unprecedented N/P around 6 with $\Delta N/\Delta P$ of 17.6. Also, differences in Si/P and Chl_a/Si ratios emerged. Diatoms were the primary group in both campaigns, but they exhibited highly differentiated composition. In BioAPRoS18 pennate diatoms, notably *Fragilariopsis curta*, were prevalent as in '90s campaigns, while BioAPRoS19 experienced the dominance of centric diatoms, especially *Dactyliosolen tenuijunctus*, never occurred before. These differences in nutrients dynamics and taxonomic composition between the two diatom assemblages, most likely indicate different assimilation modalities of N and P, with *Dactyliosolen tenuijunctus* favouring N assimilation over P, unlike *Fragilariopsis curta*. Biological and biogeochemical characteristics of TNB, a

pivotal marine ecosystem, are then displaying shifts after relative stability since the 1990s that could be the result of current climate change. These trends necessitate in-depth investigations and monitoring to comprehend and manage these shifts effectively.

KEYWORDS

Terra Nova Bay, Ross Sea Antarctica, *Dactyliosolen tenuijunctus*, *Fragilariopsis* spp., nutrient utilization strategies, biogeochemistry

1 Introduction

The Ross Sea holds immense ecological significance, encompassing diverse marine systems like polynyas, marginal ice zones, coastal and offshore areas. It is characterized by high biodiversity and is among the most productive regions in the Antarctic Ocean (Arrigo and McClain, 1994; Nelson et al., 1996; Smith and Gordon, 1997; Arrigo et al., 1998; Saggiomo et al., 2002; Vaillancourt et al., 2003; Arrigo et al., 2008; Smith and Kaufman, 2018; Smith, 2022), such that the Commission for the Conservation of Marine Living Resources (CCAMLR) in 2016 designated the Ross Sea a Marine Protected Area.

The investigation site, Terra Nova Bay (TNB) located along the Victoria Land coast between the Drygalsky Glacial tongue and Cape Washington (Figure 1), is one of the most productive sectors in the Ross Sea (Lazzara et al., 2000; Saggiomo et al., 2002). An essential aspect of the Ross Sea ecology involves the extent and dynamics of ice, closely connected to water column stabilization due to the UML

formation. This process significantly impacts the temporal variability of seasonal production (Innamorati et al., 2000; Mangoni et al., 2017).

The homogenization of the water column, resulting from Circumpolar Deep Water (CDW) upwelling, leads to a substantial rise in nutrients concentration in the surface layer during early spring. Typically, during this time, at TNB, concentrations of $\text{NO}_2^- + \text{NO}_3^-$, PO_4^{3-} and $\text{Si}(\text{OH})_4$ can reach values of 35, 2, 80 μM respectively, with ratios approximating the theoretical values (Redfield et al. 1963; Catalano et al., 1997, 2000; Innamorati et al., 2000).

In spring, increasing irradiance, temperatures and CDW upwelling trigger ice melting, causing a dilution of surface waters and the formation of a less dense surface layer (UML) separated from the underlying waters, this process being particularly pronounced in the Marginal Ice Zones (MIZ). This strong water column stabilization enables phytoplankton to better utilize available irradiance and nutrients; moreover, the presence of ice further increases nutrient concentrations, including iron, a limiting factor in Antarctic waters (Martin et al., 1990; Sedwick and

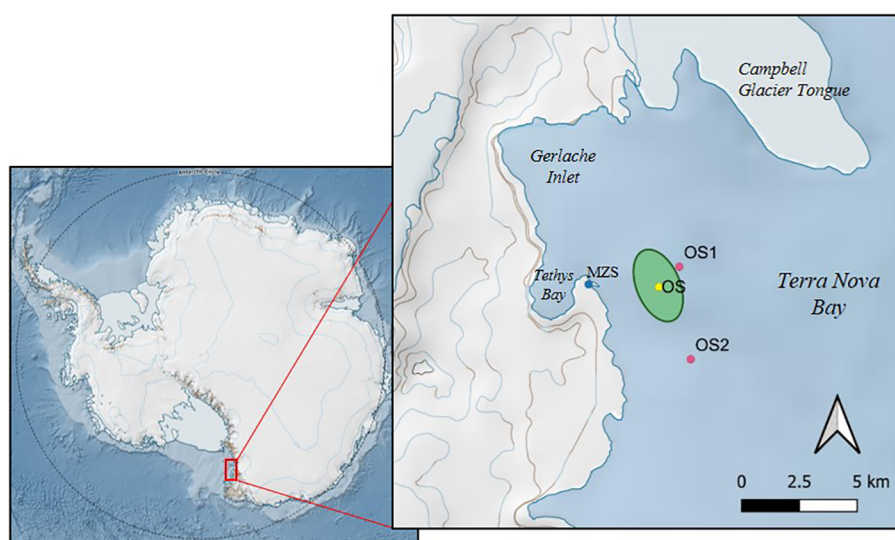


FIGURE 1

Sampling stations of BioAPROS campaigns. OS station of BioAPROS18, in some cases, in response to sea ice conditions has been moved within the green area; OS1 and OS2 are the sampling stations of BioAPROS19. (This map was obtained with QGIS and Quantartica, developed by Norwegian Polar Institute).

DiTullio, 1997; Sedwick et al., 2000; Alderkamp et al., 2012). These conditions - strong summer irradiation, stable UML and nutrients availability - contribute to rapid phytoplankton growth between December and the end of January early February, with chlorophyll *a* reaching 8-10 mg m⁻³ (Innamorati et al., 2000; Mangoni et al., 2004).

Phytoplankton assemblage dynamics in the Ross Sea alternate between diatoms and the Haptophyte *Phaeocystis antarctica* dominance, playing distinct role in terms of eco-physiology, biogeochemistry and food web functions (Smith et al., 2014). Biogeochemically, diatoms require silicon for frustules and assimilate N and P at lower ratio than that of Redfield (Arrigo et al., 2000; Sweeney et al., 2000; Dunbar et al., 2003). *P. antarctica* prevails in the offshore and southern waters (Arrigo et al., 2000; Liu and Smith, 2012), flourishing in the spring mixed water column and in polynya waters (Smith and Asper, 2001; Arrigo et al., 2003; Smith et al., 2010) due to its adaptation to low light conditions. In TNB, *Phaeocystis* dominance in the mixed water column under the UML has been observed (Goffart et al., 2000; Nuccio et al., 2000), while Mangoni et al. (2019) reported an unusual *Phaeocystis* bloom in the UML of TNB. The diatoms growth primarily occurs in the summer stratified waters of the MIZ (Garrison et al., 2005; Smith et al., 2014) and it is well documented in TNB by many authors (Goffart et al., 2000; Nuccio et al., 2000; Mangoni et al., 2004; Saggiomo et al., 2021). Despite interannual variability in ice melt and diatom bloom timing, there is a general consensus on the overall constancy of the diatoms bloom composition: centric diatoms (*Thalassiosira*, *Chaetoceros*, *Dactyliosolen*) dominate open waters (Leventer and Dunbar, 1996; Saggiomo et al., 2021), while pennate diatoms, particularly *Fragilariopsis curta* - known as “ice algal” species (Nelson and Smith, 1986) - predominate in the summer surface layer of TNB waters (Andreoli et al., 1995; Goffart et al., 2000; Nuccio et al., 2000). The relevant presence of this species has been observed into the annual sea-ice environment, during the spring-summer transition (Guglielmo et al., 2000, 2004; Lazzara et al., 2007).

The growth of diatoms leads to a substantial decrease in nutrients concentrations, in fact at TNB the concentrations of NO₃⁻ + NO₂⁻, PO₄³⁻ and Si(OH)₄ in the UML fall down to values around 5, 0.05 and 15 μM respectively (Catalano et al., 2000; Innamorati et al., 2000; Saggiomo et al., 2002). These values remain high compared to other seas, also due to Iron deficiency acting as limiting factors for the phytoplankton growth, especially in the offshore Ross Sea areas (Martin et al., 1990; Sedwick and DiTullio, 1997). Additionally, nutrient ratios N/P, Si/N and Si/P undergo modifications due to differential nutrient utilization strategies, as distinct nutrient utilization strategies and biogeochemical consequences are linked to phytoplankton taxonomic composition. Ross Sea studies on inorganic elements removal ratios ($\Delta C/\Delta N$, $\Delta C/\Delta P$, $\Delta N/\Delta P$, $\Delta C/\Delta N$, $\Delta C/\Delta Si/\Delta N$) reveal pronounced variations based on dominant species (Catalano et al., 1997; Arrigo et al., 2000; Sweeney et al., 2000; Smith and Asper, 2001; Saggiomo et al., 2002; Dunbar et al., 2003). Particularly, *Phaeocystis antarctica*-dominated assemblages exhibit significant higher $\Delta N/\Delta P$ ratios (17.5-19.7) than Redfield, while diatom-dominated assemblages display lower ratio (10.1-15.2), underscoring the close connection between phytoplankton

composition and biogeochemical properties in Ross Sea waters (Arrigo et al., 2000; Sweeney et al., 2000; Smith and Asper, 2001; Dunbar et al., 2003). A shift in the initial N/P ratio towards strong P deficiency during *Fragilariopsis curta* blooms is evident at TNB (Innamorati et al., 2000; Nuccio et al., 2000), showing that this phytoplankton assemblage assimilates greater quantities of P than N compared with the theoretical ones of Redfield (Catalano et al., 1997, 2000; Saggiomo et al., 2002).

This study is focused on the relationships between phytoplankton assemblage composition, studied through both pigment composition and optical microscopy, their nutrients assimilation preferences, and the resulting biogeochemical effects at TNB.

Analysis covers the temporal evolution of NO₃⁻, NO₂⁻, PO₄³⁻ and Si(OH)₄ concentrations in the UML, alongside phytoplankton biomass and taxonomic composition dynamics during austral springs and summers 2018-19 and 2019-20, from the ice melt until the end of January. The findings are compared with data from three '90s campaigns (1989-90, 1994-95, 1997-98), highlighting similarities, differences and the potential influence of climate change.

2 Materials and methods

2.1 Campaign description

This study is part of the BioAPRoS (Biogenic Aerosol and Primary Production in the Ross Sea) project funded by the Italian National Antarctic Research Programme (PNRA). Two campaigns were carried out during the austral summers 2018/19 (13 November 2018, 30 January 2019, BioAPRoS18) and 2019/20 (1 December 2019, 30 January 2020, BioAPRoS19) in the coastal area of Terra Nova Bay (TNB) in front of the Italian base Mario Zucchelli Station (MZS) (Figure 1). Sampling was carried out from aboard a motorboat using 5 L Niskin bottles within the UML at depths of 0.5, 5, 10 and 15 m. The samples from 15 m were included in the data set of this study only on the days when this depth was included within the UML (1 sample in BioAPRoS18 and 5 for BioAPRoS19). During BioAPRoS18 the ice cover prevented sampling in open waters until 26 December and in three dates (13, 23 November, 1 December) water samples were collected at 0.5 and 5 m depth with a Niskin bottle from a hole previous drilled in the ice. From 26 December samples were collected in open waters at station OS. Since floating ice blocks were almost always present in the area, the position of the OS station was, depending on the case, slightly moved within a range of 1000 m to allow sampling operations.

In total, 46 samples in the BioAPRoS18 campaign and 57 samples in BioAPRoS19 were analyzed for chlorophyll *a*, pigments, nutrients and microscopic counts of phytoplankton.

Sampling area, modalities and periods of these two campaigns are the same as a series of campaigns carried out in 1990, 1995 and 1998 (Innamorati et al., 1991, 1994; Lazzara et al., 1997; Innamorati et al., 2000; Lazzara et al., 2000; Nuccio et al., 2000).

In the following representation, for the sake of simplicity, the days of the various campaigns have been reported by counting them from 1 November to 28 February, therefore with progressive numbers from 1 to 120.

2.2 Upper mixed layer depth determination

In situ measurements were carried out in the upper 25 m of the water column with specially assembled prototypes of minimal low-cost instrumentation easy to use even in extreme conditions. In the first campaign, a FTB Idromar multiparametric probe equipped with temperature and pressure sensors as well as chlorophyll *a* fluorescence and backscattering meters (Dr Haardt) was used. In the second campaign the ACHAB (Antarctic Low-Cost Hydro Arduino Bio-optic) profiler was used, a low-cost Arduino based probe specifically developed within the BioAPRoS project to measure temperature, pressure, chlorophyll *a* fluorescence and backscattering (Turner Designs Cyclops7). The identification of the UML and its depth was carried out through the bathymetric profiles of temperature variation (Δt) with 1 m window. The results were compared and validated by the feature of the backscattering profiles. The identification of the UML depths was also carried out with C-GLORSv7 product distributed as a part of Copernicus Marine Service (CMS). It is a reanalysis product (built to be as close as possible to the observations) that simulates the effect of ice melting during the austral summer season thanks to the coupling between NEMO (1/4° horizontal resolution, 75 vertical levels) and LIM2 sea-ice models.

2.3 Nutrient analysis

Seawater subsamples were filtered on prewashed Wathman GF/F filters (diameter 47 mm), poisoned with HgCl₂ and stored in 250 mL plastic bottles at 4°C. The dissolved inorganic nutrients (NO₃⁻, NO₂⁻, PO₄³⁻ and Si(OH)₄) were analyzed with a Bran +Luebbe AA3 Autoanalyzer following standard procedures (Grasshoff et al., 1999; Saggiomo et al., 2010). Detection limits for the determination of NO₃⁻, NO₂⁻, PO₄³⁻ and Si(OH)₄ were 0.02, 0.02, 0.01 and 0.1 μM respectively with precision of ±0.02 μM for NO₂⁻ and PO₄³⁻; ± 0.3 μM for NO₃ and ±1.5 μM for Si(OH)₄. Since the concentrations of ammonia were not analyzed, it was not possible to obtain the concentrations of total dissolved inorganic nitrogen (DIN). The sum of nitrites and nitrates (NO₂⁻ + NO₃⁻) summarized as total oxidised nitrogen (TNO_x) was therefore used as its estimate since ammonia, in the Ross Sea, generally constitutes a small fraction, about 2-10% of the DIN (Knox, 1994).

Nutrients analytical procedure for the campaigns of the '90s are reported in Innamorati et al. (2000).

2.4 Chlorophyll and pigments analysis

1-2 L of seawater were filtered on 47 mm Wathman GF/F filters. Filters with collected material were stored dry at -80°C. After about 4 months, each filter was homogenized manually in 10 mL 90% acetone and left to extract at 4°C for 24 hours before carrying out both Hight Performance Liquid Chromatography (HPLC) and spectrophotometric analyzes. HPLC analysis of pigments was carried out following Vidussi et al. (1996) and Barlow et al. (1997) by means of a Class VP system (SHIMAZDU) using

ACME C8 column (Phase) with UV/VIS and fluorometric detectors to quantify chlorophyll *a* (Chl_a), other chlorophylls, carotenoid pigments, phaeopigments and phaeophorbids. The pigments recognition and calibration procedures were performed following Montura and Repeta (1997) using DHI pigment standards and B-Apo-8-Carotenol as internal standard. Spectrophotometric analyzes was carried out with a SHIMATZU UV 2600 spectrophotometer and Chlorophaeopigments concentrations (Chl) were calculated from the absorbance values using the monochromatic equation (Lazzara et al., 2010). This procedure was added in order to compare the data of the last campaigns with those of the '90s in which only spectrophotometric measurements were made (Innamorati et al., 2000). In this work phytoplankton biomass are expressed in terms of Chl_a; in addition, for comparison purpose, the phytoplankton biomass/nutrient ratios are also obtained using Chl as for of the '90s campaigns. The global quantitative relationships between HPLC Chl_a and spectrophotometric Chl are:

$$\text{for BioAPRoS18: Chl} = 1.38\text{Chl}_a; R^2 = 0.984$$

$$\text{for BioAPRoS19: Chl} = 1.47\text{Chl}_a; R^2 = 0.947$$

2.5 Microscopic analysis of phytoplankton

300 mL of seawater samples for microscopic analysis were stored in dark glass bottles, to better preserve the siliceous structures of diatoms, with buffered formalin (final concentration 4%) until their analyzes in Italy. Phytoplankton counting and identification was carried out after sedimentation of variable sample volumes (10-25 mL) with inverted microscopes (Zeiss IM35 or Zeiss Axiovert at 400x) following standard methods (Zingone et al., 2010). From 500 to 17,000 cells were counted in each sample.

2.6 Nutrient utilization and their ratios

In the summer period the water column in TNB is characterized by the constant presence of the separation between the uppermost layer (UML) and the deeper ones. The effectiveness of this separation barrier increases as the temperature and salinity difference enhances, due to melting of ice and heating, resulting in reduction or blockage of vertical transport (Catalano et al., 2000). Nutrient dynamics within the UML were analyzed together with the N/P, Si/N, Si/P ratios (with N = TNO_x = NO₃⁻ + NO₂⁻, and P = PO₄³⁻; Si = Si(OH)₄). Nutrient concentrations dynamic in the UML can be associated to those of Chl_a, representing an estimate of phytoplankton biomass. How these relationships change following the evolution of phytoplankton biomass Chl_a/N and Chl_a/P dynamics has been considered. In addition, in order to compare these dynamics with that of previous campaigns, the logarithms of the ratios Chl/N and Chl/P and their model II regression line (Sokal and Rohlf, 1995) are calculated and plotted together with the 95% confidence ellipses of the points to better evaluate their distribution.

The stability of UML can allow, through the measurement of the nutrient dynamics, to evaluate the nutrients removal ratios in the UML and can provide an insight into how the phytoplankton community assimilated nutrients into cellular pools (and subsequently used). The quantitative estimate of the phytoplankton nutrient removal ratios ($\Delta N/\Delta P$, $\Delta Si/\Delta N$ and $\Delta Si/\Delta P$) in the UML was carried out by using the angular coefficient of the regression line between each pair of nutrients (model II regression; Sokal and Rohlf, 1995).

3 Results

3.1 UML

UML depth in the sampling periods was similar for both campaigns and the *in situ* measures ranged from 5 m to 18 m. UML was more superficial at the start and near the end of the sampling period (Figure 2).

The fluorescence maximum in both campaigns was always within the UML, between the depths of 5 and 15 m (Figure 3).

3.2 Chlorophyll *a*

Sampling period of BioAPRoS18 started in mid-November when the ice cover was still present and Chl*a* was low; at the end of December (from 27/12 to 30/12/2018) in ice free waters a maximum of about 4.5 mg m⁻³ was present (Figure 4A). Subsequently after a brief decrease there was a sharp Chl*a* increase, reaching the absolute maximum of about 9 mg m⁻³ at the end of January when sampling was stopped. BioAPRoS19 (Figure 4B) started on 14/12/2019 when Chl*a* was nearly 1 mg m⁻³ in both stations and after a brief decrease reached its maximum of approximately 5.5 mg m⁻³ in OS1 and 6.5 mg m⁻³ in OS2 at 21/01/2020. Immediately after reaching their maximum, Chl*a* began to decrease until the end of samplings which occurred on 30/01/2020.

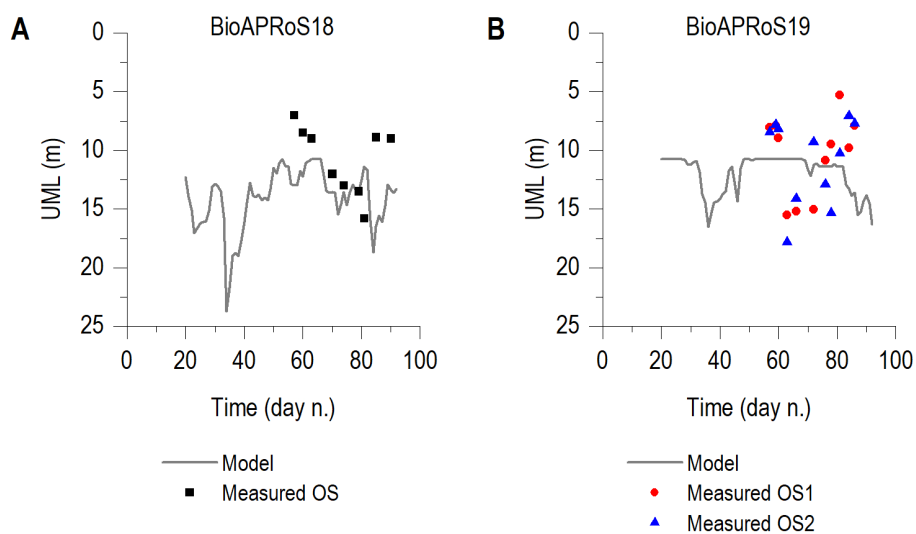


FIGURE 2
UML depth in BioAPRoS18 (A) and BioAPRoS19 (B). Single points from *in situ* measurements, lines from model.

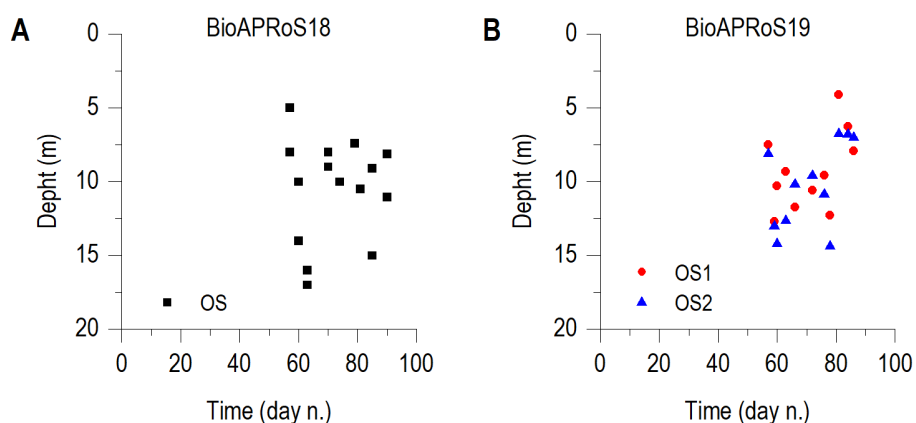


FIGURE 3
Depth of the fluorescence maximum in BioAPRoS18 (A) and BioAPRoS19 (B).

3.3 Nutrients

In both campaigns the high initial concentrations showed a sharp decrease, reaching their minima at the same time with the *Chla* maxima (Figure 5).

In the ice-free UML TNO_x ($\text{NO}_3^- + \text{NO}_2^-$) maxima were around $22 \mu\text{M}$ in both BioAPRoS campaigns (Figures 5A, B). The minimum concentrations in BioAPRoS18 were $1.75 \mu\text{M}$ (Figure 5A) while in BioAPRoS19 were lower, $0.17 \mu\text{M}$ (Figure 5B). Maxima PO_4^{3-} were about $1.7 \mu\text{M}$ in BioAPRoS18 (Figure 5C) and about $1.5 \mu\text{M}$ in BioAPRoS19 (Figure 5D), minima were quite similar, 0.19 for BioAPRoS18 (Figure 5C) and 0.22 for BioAPRoS19 (Figure 5D). Maximum $\text{Si}(\text{OH})_4$ concentrations were about $90 \mu\text{M}$ in BioAPRoS18 (Figure 5E) and $80 \mu\text{M}$ in BioAPRoS19 (Figure 5F) and minima were different, about $20 \mu\text{M}$ (Figure 5E) and $0.99 \mu\text{M}$ respectively (Figure 5F).

3.4 In-water nutrient ratios

From Figures 6A and 6B it is evident how the two campaigns had a very different trend of the N/P ratio. The N/P ratios under the ice cover in the first sampling days of BioAPRoS18 and at the beginning of BioAPRoS19 were about 13-14. In the first UML sampling in ice free water of BioAPRoS18 N/P ratio decreased up to 9 in correspondence with a short *Chla* increase and rose steeply reaching the value of 40 simultaneously at the *Chla* maximum (Figure 6A), reaching a condition of P deficiency. In BioAPRoS19 the N/P ratio (Figure 6B) underwent a continuous decrease up to the *Chla* maximum and values between 9 in OS2 and 4 in OS1 were reached, revealing a condition of N deficiency.

The Si/P ratio (Figures 6C, D), similarly to that of N/P, showed opposite trends in the two campaigns. The initial values were similar, both around 40, but in BioAPRoS18 (Figure 6C) they increased up to 150 at the *Chla* maximum, while in BioAPRoS19 (Figure 6C) decreased to a minimum of 4.3 in OS1 and 14 in OS2.

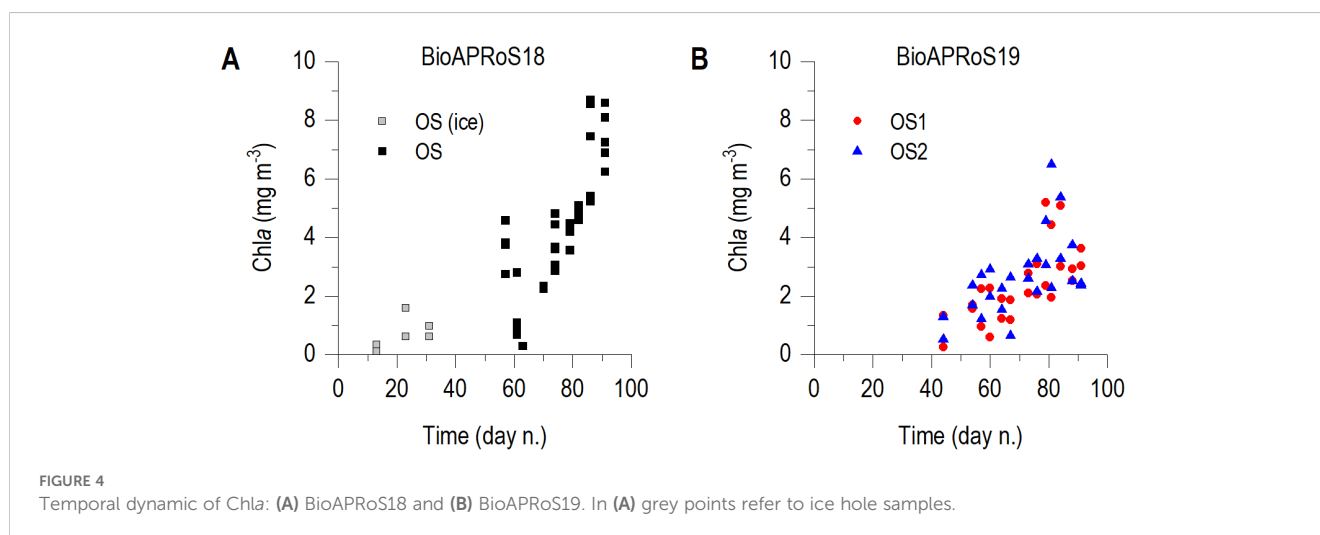
Si/N ratio in BioAPRoS18 had a biphasic trend (Figure 6E). The values of around 3, recorded during the period of ice cover,

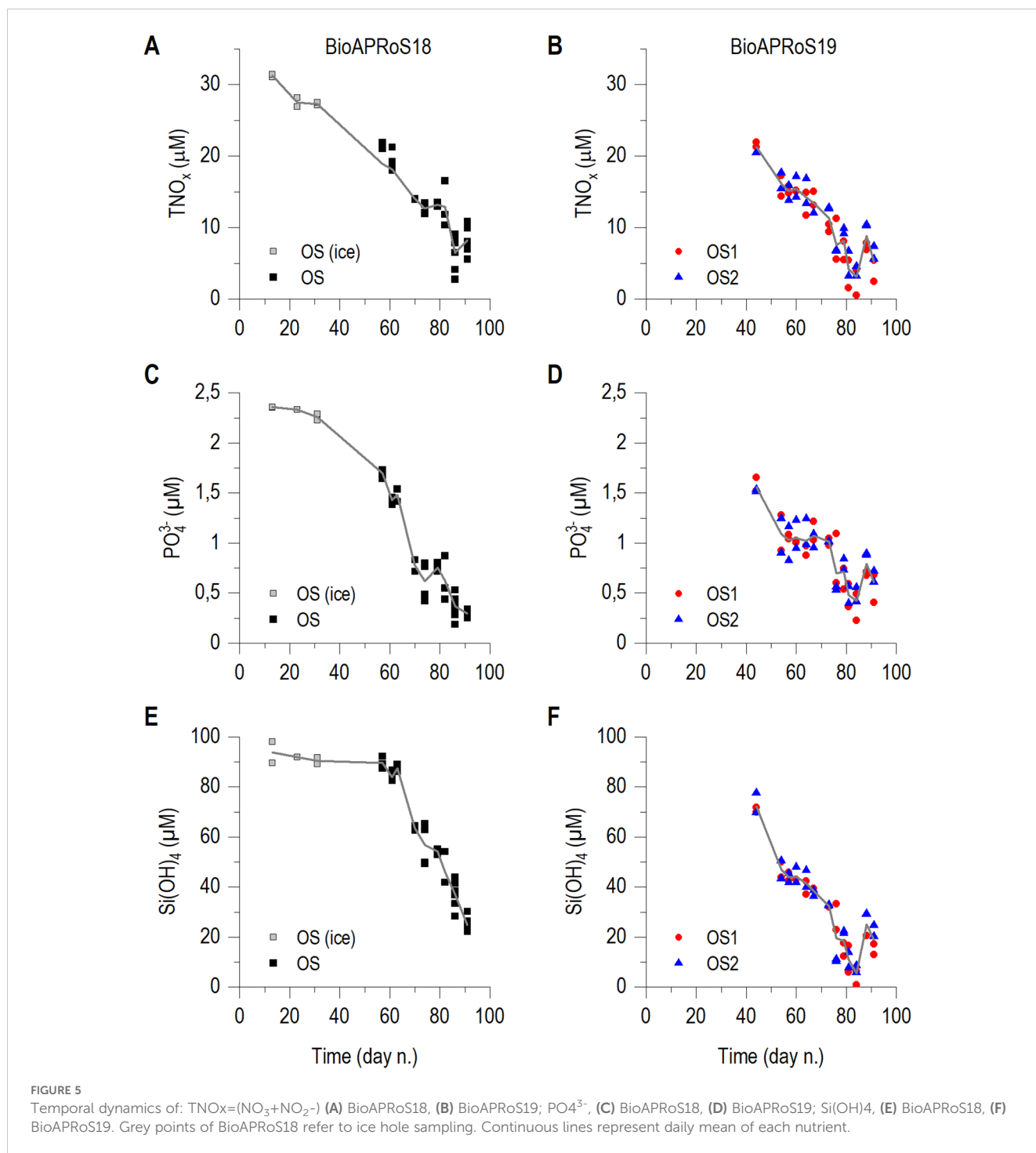
increased up to 5 and reached its maximum by exceeding 10 simultaneously with the blooming of the end of December. Subsequently Si/N decreased to about initial values of around 3. In BioAPRoS19 (Figure 6F) Si/N remained similar, initially around 2.8 and slightly increased in the last sampling days.

3.5 *Chla*/nutrient ratios

Chla/N ratio in the two campaigns showed a marked similarity for both temporal trend and maximum value, reaching about $1.2 \mu\text{g Chla } \mu\text{MN}^{-1}$ (Figures 7A, B). *Chla*/P ratio increased from very low values up to about $22.5 \mu\text{g Chla } \mu\text{MP}^{-1}$ in BioAPRoS18 (Figure 7C), while stopped at about $15 \mu\text{g Chla } \mu\text{MP}^{-1}$ in BioAPRoS19 (Figure 7D). Major differences were found in the *Chla*/Si ratio (Figures 7E, F). In both campaigns there was a first phase with fairly constant values of *Chla*/Si, with a subsequent increase which in BioAPRoS18 reached $0.25 \mu\text{g Chla } \mu\text{MSi}^{-1}$ (Figure 7E), while in BioAPRoS19 exceeded 1 and up to $3 \mu\text{g Chla } \mu\text{MSi}^{-1}$ (Figure 7F).

In Figure 8 in order to compare BioAPRoS results to that of '90s campaigns are plotted the value of *Chl*/P vs *Chl*/N together with the 95% confidence ellipses and the relative regression lines. Figure 8A shows the data of two BioAPRoS campaigns. The points of the two campaigns located at the bottom left, *i.e.* which have the lowest *Chl*/(NP)^{1/2} ratio and belonging to the first sampling days, are very close to N/P = 16 (Figure 8A). Moving to the top right there are the data with a major value of the ratio *Chl*/(NP)^{1/2}, corresponding to the *Chl* maxima. In this graph area the distribution of data points and the regression lines clearly diverge. Those of BioAPRoS18 lead to N/P values typical of the condition of P deficiency, while those of BioAPRoS19 lead toward N deficiency (Figure 8A). By comparing these distributions of points and related regression lines with those of the campaigns of the '90s (Figure 8B), the similarity with BioAPRoS18 emerges. In the latter campaigns there was evidence of a strong P deficiency in correspondence with *Chl* maxima, while in BioAPRoS19 the situation was opposite with an evident condition of N deficiency in conjunction with *Chl* maxima.





3.6 Phytoplankton taxonomic composition

Pigments analysis (Figures 9A, 9B) synthetically shows how in both campaigns there was a strong dominance of diatoms deduced by the prevailing concentration of the Fucoxanthin (Fuco). The averages ratio Fuco/Chla were 0.65 and 0.50 in BioAPRoS18 and BioAPRoS19, respectively. The presence of *Phaeocystis antarctica*, estimated by Hex-Fuco (19-Hexanoyloxifucoxanthin), was significant only around the end of December in BioAPRoS18.

As already pointed out, excluding a short bloom of *Phaeocystis antarctica* in the last days of December 2018 (Figure 9A), the only

sampling period in which their density and dominance were significant, diatoms were the most abundant group by far, even if the taxonomic composition in the two campaigns were significantly different. In BioAPRoS18 pennate dominated, never being less than the 85% of total diatoms, especially in correspondence of the *Chla* maxima (in the second half of January). The genus *Fragilariopsis* represented the bulk of the assemblage, mainly with *Fragilariopsis curta* followed by *Fragilariopsis cylindrus/nana* both reported in Figure 10 as *Fragilariopsis* spp. In BioAPRoS19 blooms of *Phaeocystis* were not detected and diatoms composition was more differentiated: in the pennate diatoms a greater presence of *Pseudo-*

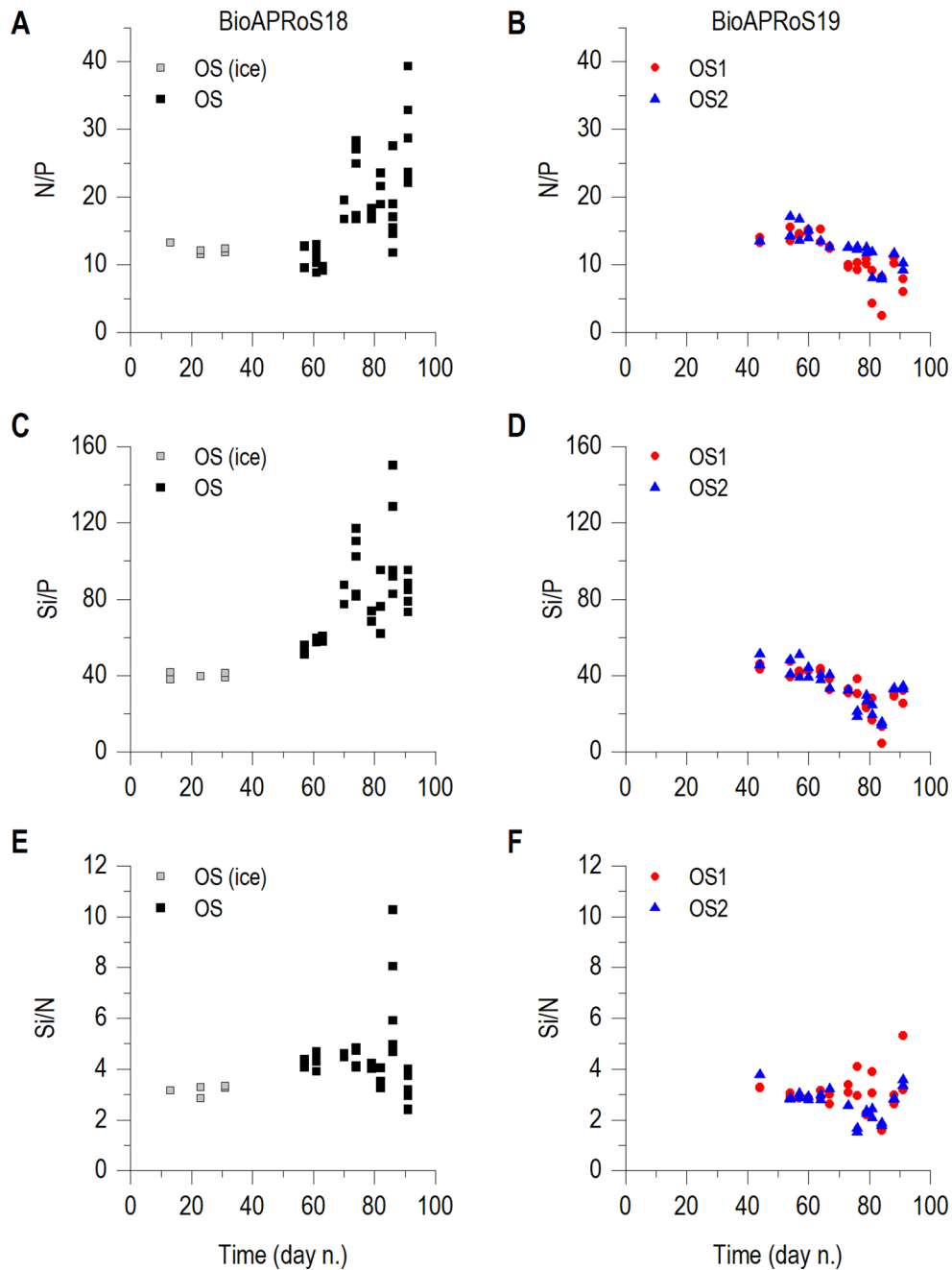
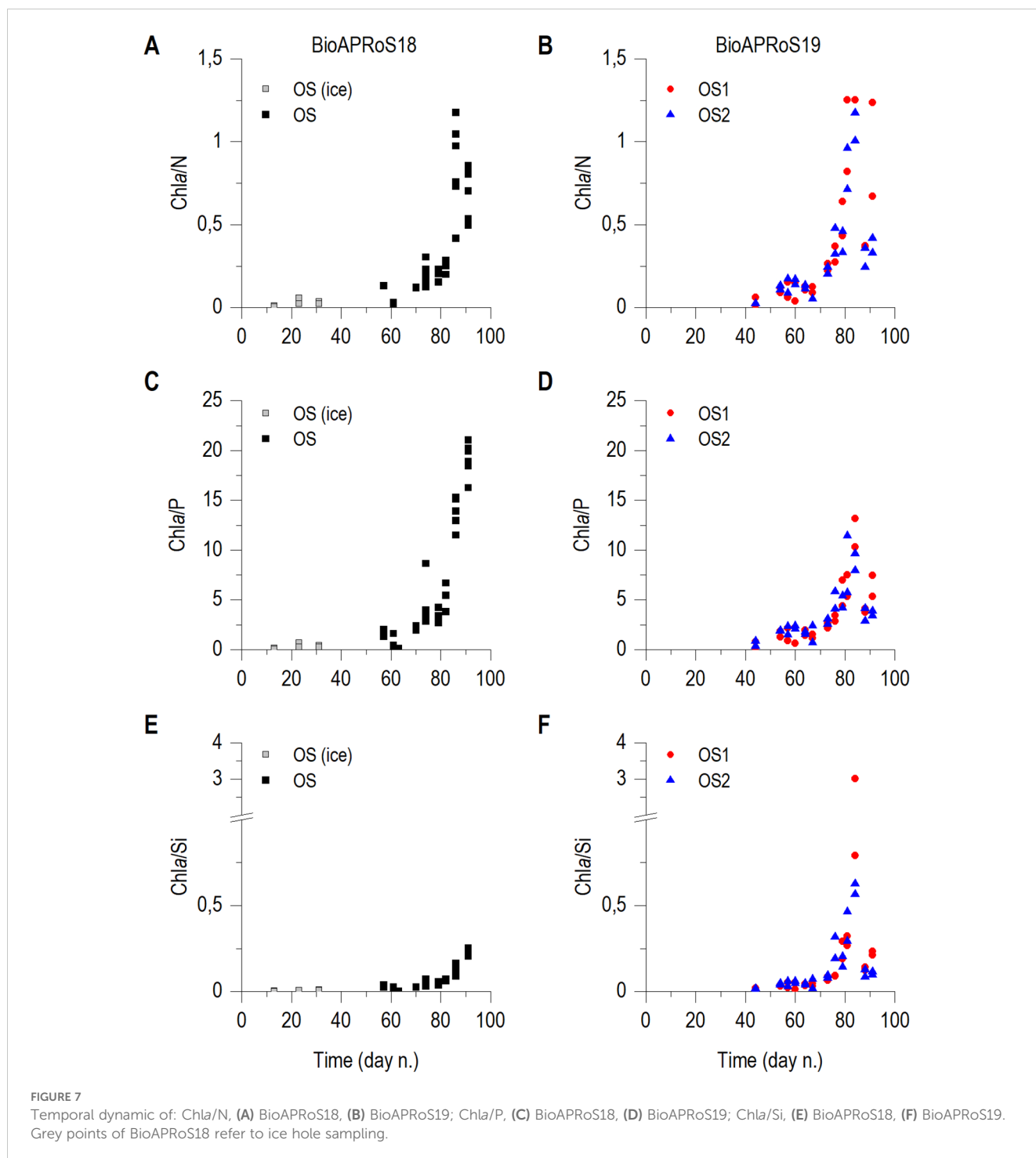


FIGURE 6 Temporal dynamic of: N/P, (A) BioAPRoS18, (B) BioAPRoS19; Si/P, (C) BioAPRoS18, (D) BioAPRoS19; Si/N, (E) BioAPRoS18, (F) BioAPRoS19. Grey points of BioAPRoS18 refer to ice hole sampling.

nitzschia (*P. subcurvata*, mainly prevailing in early summer, *P. turgiduloides* prevailing in late summer) together with *Fragilariopsis curta* (never dominant) was detected from late spring to summer, and especially a consistent presence of centrics with *Chaetoceros* spp. (mainly *C. bulbosus*) in late spring and an elevated bloom of *Dactyliosolen tenuijunctus* in January corresponding to the *Chla* maxima (Figure 10) were observed.

3.7 Nutrients removal ratios

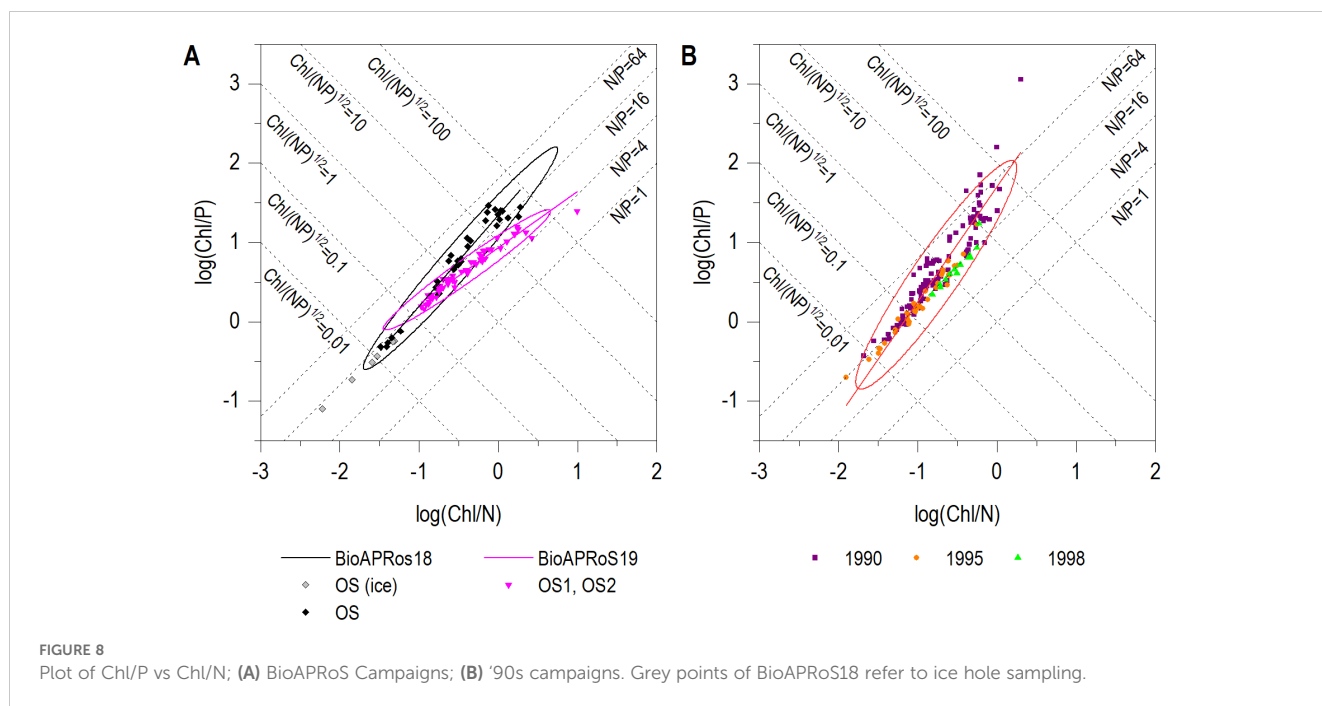
Table 1 shows the removal ratios of nutrients of BioAPRoS campaigns together with the '90s ones, calculated using the slope of the regressions between nutrient pairs. In all cases determination coefficient, R^2 of the regressions between nutrient concentrations show high significance ($p < 0.01$).



The histograms of Figure 11A show the $\Delta N/\Delta P$ in TNB during the two BioAPRoS campaigns compared to that of the '90s. The removal ratio $\Delta N/\Delta P$, was quite similar between BioAPRoS18 and the campaigns of the '90s (Figure 11A) ranging from 11.32 to 12.28. During BioAPRoS18 $\Delta N/\Delta P$ was 11.78 and the same ratio in 1990-1998 had an average of 11.50. Data of BioAPRoS19 were, instead very different in both stations, 17.71 and 17.53 in OS1 and OS2 respectively.

Also, the $\Delta Si/\Delta P$ of BioAPRoS19 differed considerably from those of the '90s, respectively with an average of 58.63 respect to 31.59 (Figure 11C) with BioAPRoS18 having an intermediate value of 47.05.

The $\Delta Si/\Delta N$ of BioAPRoS19 was consistent with those of the other campaigns (Figure 11B); while the 1990 stations had lower values of the ratio around 1.3, the other averages were around 3.14, with BioAPRoS19 OS2 exceeded 3.5. In any case these values of $\Delta Si/\Delta N$ are typical of phytoplankton assemblage dominated by diatoms.



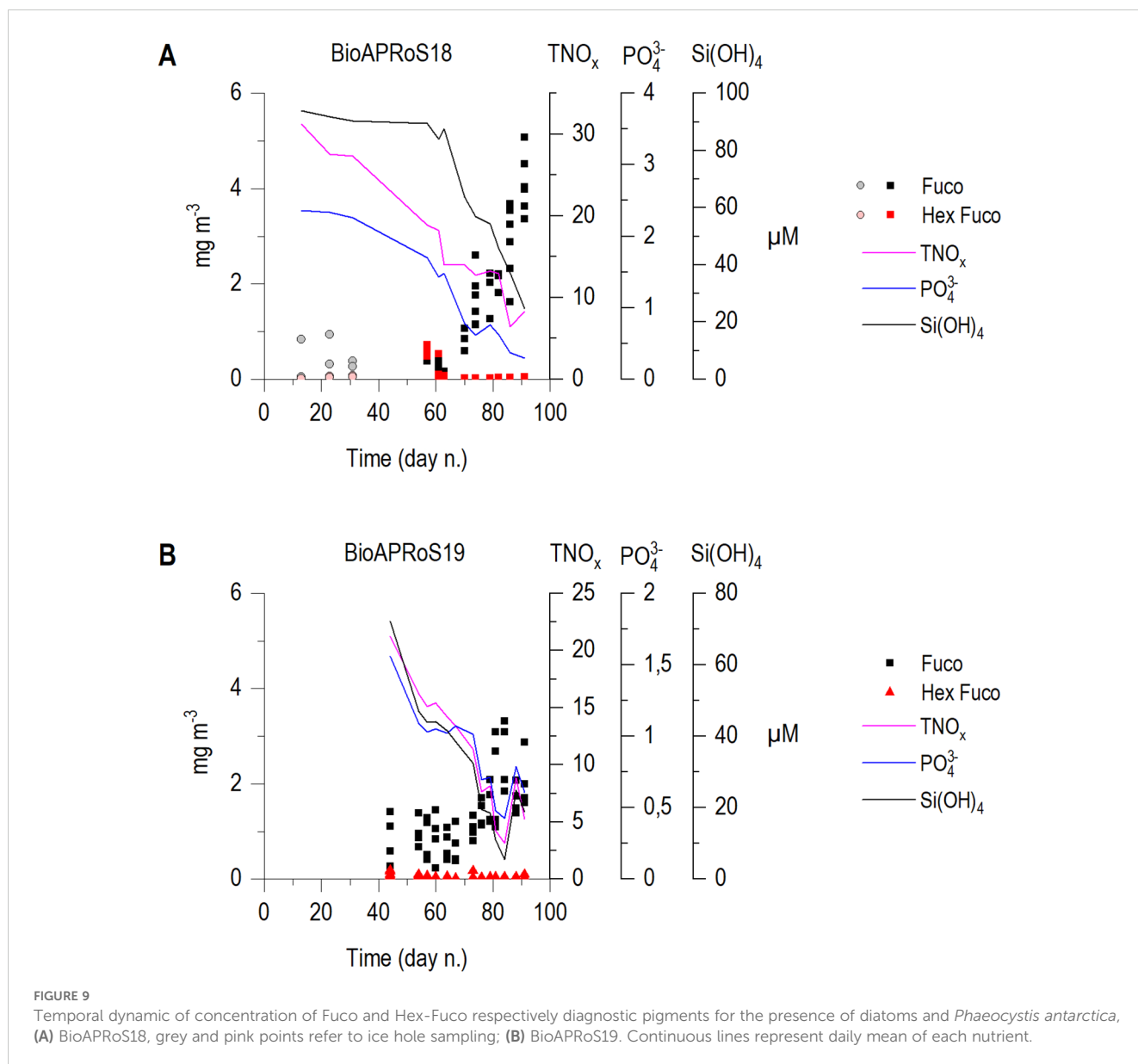
4 Discussion

The area in front of the Italian base at TNB experienced significant ice-driven dynamics, classifying it as Marginal Ice Zone (MIZ) during both spring and summer. The upwelling of Antarctic Deep Water in spring brings high concentrations of nutrients and warmer water to the surface layers, which, along with ice melting and warming due to increased solar irradiance, leads to the segregation of the UML. In line with the findings reported by Mangoni et al. (2004), in the coastal sampling stations of the BioAPROS campaigns, the UML was persistent and always very shallow, never exceeding the depth of 20 m (Figure 2). UML thickness was at the minimum depth during the beginning of the sampling period (late November early December) and reached the maximum depths in mid-January, shortly before the maximum of Chl a concentration observed within the UML (Figure 3).

The growth dynamics we have tried to represent with our sampling frequency (almost daily sampling), being higher or similar to phytoplankton growth rate (Smith et al, 1996), allows us to follow with a certain accuracy the temporal evolution of nutrient concentrations, phytoplankton biomass and its taxonomic composition in a largely segregated UML system (Catalano et al., 1997). UML spring summer phytoplankton growth is supported by favourable conditions of light, temperature and large nutrient availability (Figure 5). Under these conditions, variations in nutrient concentration appear to be essentially regulated by phytoplankton consumption. Only at the end of the cycle, at the end of summer, when nutrients become scarce, some other processes can supply the surface layers with nutrients in relation to weakening of the UML or *on-site* degradation of accumulated particulate and dissolved organic matter (Smith and Kaufman, 2018). These processes can modify the dynamics of phytoplankton biomass within the UML as highlighted by Mangoni et al. (2017). Innamorati et al. (2000) especially associate weakening of

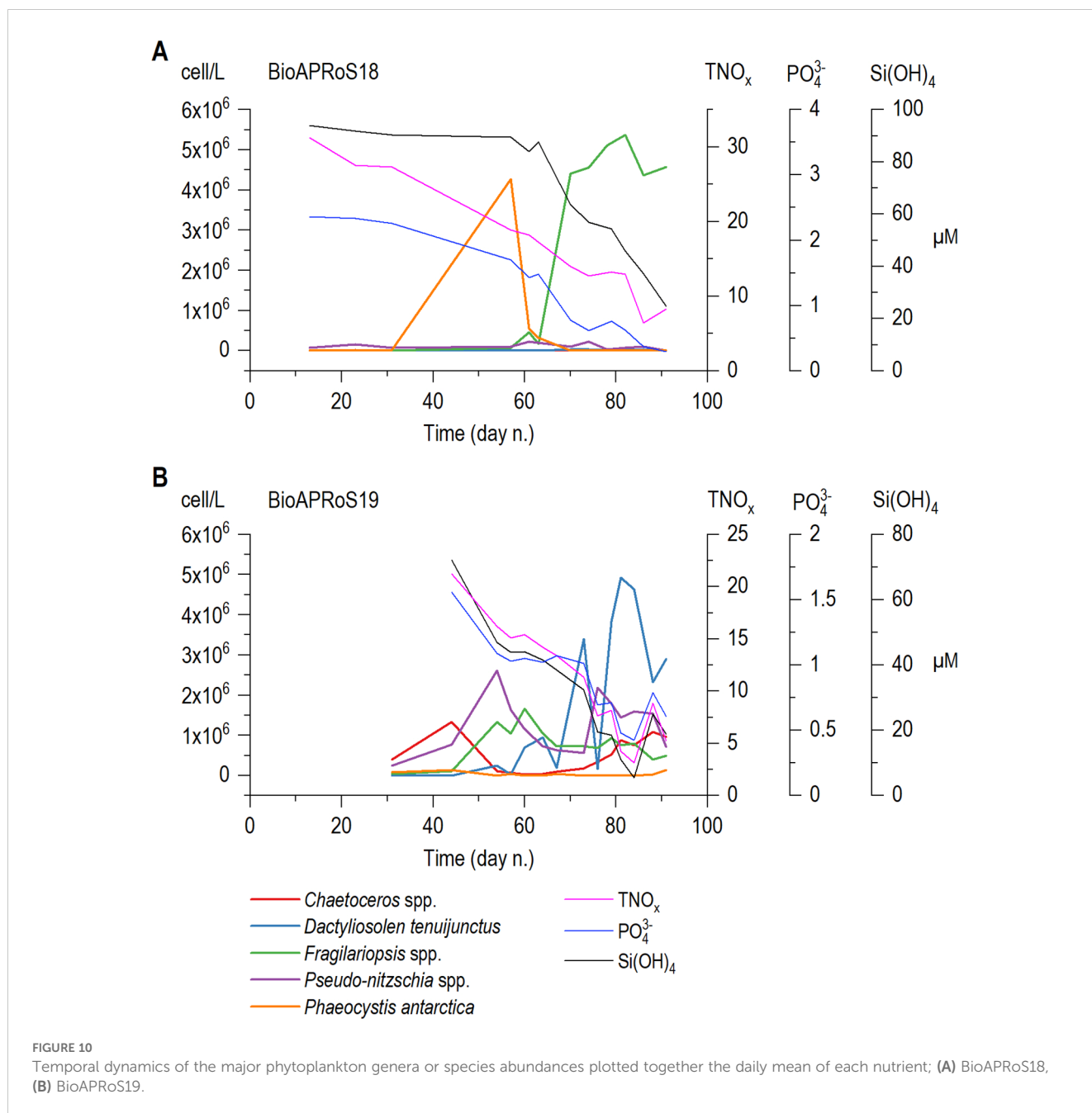
the UML and replenishing of nutrients with the appearance of a second maximum of Chl a , not seen in the two more recent campaigns. These contributions can alter and affect the measurements of phytoplankton consumption/utilization of nutrients. In these cases, given the sensitivity of the system, we should expect a positive response of phytoplankton dynamics, which however has not been recorded (Figure 4).

Both BioAPROS campaigns exhibited comparable temporal nutrient dynamics and concentrations within the UML. Maximum nutrient concentrations were detected as the ice cover vanished, followed by their minimum level during the Chl a peaks (Figures 4, 5). Recent campaigns maximum and minimum nutrient concentrations mirror those reported for 1987/88, 1989/90 and 1994/95 at TNB by Innamorati et al. (2000) and Catalano et al. (2000). UML Nutrients dynamics was synchronously opposite to that of Chl a highlighting a pronounced consumption of nutrients during the growth of phytoplankton biomass (Figures 4, 5). Although Chl a values correspond to those reported by Innamorati et al. (2000) for '90s campaign, their temporal dynamics exhibited some deviations. The previous campaigns maximum occurred approximately a month earlier, between end of December-mid January, followed by a second rise in early February not observed in the BioAPROS campaigns. Innamorati et al. (2000) outlined that phytoplankton biomass declines at TNB during summer primarily derive from reduced nutrients availability. As shown in Figure 8, the ratio Chl/(NP) $^{1/2}$ approaches 100 in both BioAPROS and '90s campaigns. This threshold poses a limitation of nutrients exploitation at TNB, which is still lower than the more efficient nutrient utilization in other seas (Innamorati and Giovanardi, 1992). Thus, the presence of other limiting factors beyond general nutrient scarcity can be assumed. Iron deficiency leads to the failure to exploit the still high concentrations of macro-nutrient. Although iron limitation has



been postulated (Martin et al., 1990) and verified (Sedwick et al., 2000; Feng et al., 2010; Smith and Kaufman, 2018) to be a limiting factor in The Ross Sea, it seems more pertinent to offshore Ross Sea areas than TNB coastal zones (Sedwick and DiTullio, 1997; Sedwick et al., 2000; Arrigo et al., 2003) strongly influenced by the melting of the ice. However, the role of iron in the UML of coastal TNB requires further investigation. In summer, following robust phytoplankton growth, together with the lower nutrient concentrations a strong imbalance in their ratios occurs, which has been defined as an important limiting factor at TNB (Innamorati et al., 2000). Notably, the N/P ratio undergoes significant changes during the spring-summer period. Initially and early spring UML, N/P ratio was near the theoretical Redfield value (Figure 8A). Over time, during the phytoplankton bloom, in BioAPRoS18 and particularly in the '90s campaigns (Figure 8B), this ratio rises to remarkably high levels, leading to a pronounced P deficiency (Catalano et al., 2000; Innamorati et al., 2000; Sweeney

et al., 2000; Saggiomo et al., 2002). In BioAPRoS18 the N/P ratio rose up to 40 and higher values was reached in '90s (Figures 8, 6A). Conversely, in the BioAPRoS19, N/P ratio fluctuated from the beginning of the season up to the *Chl a* maximum, culminating at approximately 4 (Figure 6B), a condition of N deficiency unprecedented in previous observations at TNB. Modification of the in-water nutrients ratios in the UML likely arises from the distinct ways in which the phytoplankton assimilate these nutrients. A confirmation is evident in the dynamics of Si(OH)_4 . The concentration of Si(OH)_4 remained constant during the short initial bloom of *Phaeocystis* in BioAPRoS18 (Figures 5E, 9A, 10A) and starts to decrease only when diatoms become dominant in the phytoplankton community. In BioAPRoS19, where the community has always been dominated by diatoms, Si(OH)_4 shows a continuous decrease (Figure 5F). This dynamics underscores the system sensitivity to changes: even a slight shift in assemblage composition over a few days results in an immediate alteration in



UML nutrient concentration, confirming the prevalent role of the phytoplankton and its taxonomic composition in UML nutrient removal following their preferences.

Based on this awareness, nutrient removal ratios $\Delta N/\Delta P$, $\Delta Si/\Delta N$ and $\Delta Si/\Delta P$ were estimated. Specifically, $\Delta N/\Delta P$ ratio deviated from its theoretical value, assuming a lower value of about 11.8 during BioAPRoS18, similarly to the average of 11.5 measured during the '90s campaigns (Table 1; Figure 11). These values align with those reported by Catalano et al. (1997); Catalano et al. (2000); Saggiomo et al. (2002) for TNB, as well as by Arrigo et al. (2000); Sweeney et al. (2000); Smith and Asper (2001); Dunbar et al. (2003) for diatom dominated phytoplankton assemblage of the Ross Sea. This phenomenon, termed luxury consumption, signified that P

removal surpasses theoretical N removal, a pattern often observed in diatoms. It is to be expected that the strategies of phytoplankton nutrients assimilation determine alteration in the original in-water N/P ratios. A $\Delta N/\Delta P$ removal ratio of about 11.5 determines a P deficiency state over time. Conversely, the nutrients ratios dynamic during BioAPRoS19 displayed an opposite trend. The $\Delta N/\Delta P$ ratio average was 17.6, surpassed the theoretic reference of 16 (Table 1; Figure 11), indicating a greater preference for N over P utilization. This accounts for the occurrence of N deficiency, an unprecedented event in previous years in TNB.

In BioAPRoS19, along with the previously unobserved N deficiency, an equally unprecedented bloom of *Dactyliosolen tenuijunctus* was identified (Figure 10B). In both BioAPROS

TABLE 1 $\Delta N/\Delta P$, $\Delta Si/\Delta N$ and $\Delta Si/\Delta P$ obtained from model II angular coefficient regressions between nutrients.

Year	1990	1990	1990	1995	1995	1998	2018-19	2019-20	2019-20
Station	BTN	SMN	Merg	Tib	BTN	A	OS	OS1	OS2
$\Delta N/\Delta P$	12.28	11.67	11.44	11.32	11.42	10.84	11.78	17.71	17.53
Num	25	25	20	18	23	17	36	26	25
R ²	0.78**	0.92**	0.92**	0.97**	0.90**	0.85**	0.87**	0.92**	0.92**
$\Delta Si/\Delta N$	1.85	1.78	1.55	3	3.39	2.74	3.79	3.16	3.69
Num	24	26	22	18	23	17	36	26	25
R ²	0.85**	0.82**	0.92**	0.93**	0.92**	0.94**	0.82**	0.96**	0.93**
$\Delta Si/\Delta P$	26.38	25.86	27.73	32.14	37.54	39.82	47.05	55.16	62.1
Num	24	24	22	18	22	16	38	26	26
R ²	0.82**	0.89**	0.94**	0.92**	0.93**	0.88**	0.93**	0.92**	0.91**

The number of data (Num), the determination coefficient (R²) and their significance level (** = P < 0.01) are reported.

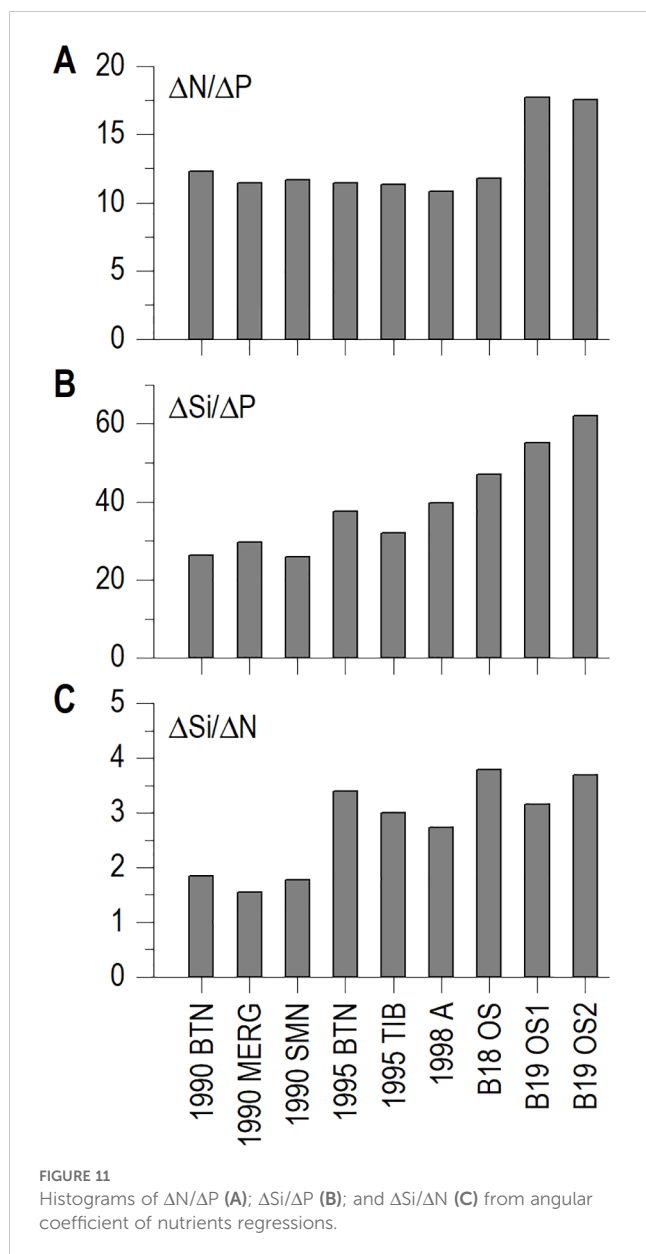
campaigns diatoms dominated; however, the phytoplankton bloom described since the '90s in TNB was typically dominated by pennate diatoms, mainly *Fragilariopsis curta*, as reported by Nuccio et al. (2000); Mangoni et al. (2017); Saggiomo et al. (2021). The same phytoplankton composition was also observed during the Chla maximum in BioAPRoS18 (Figure 10A). In BioAPRoS19, alongside the pennate diatoms (mostly *Pseudo-nitzschia* spp.), the centric *Dactyliosolen tenuijunctus* dominated during the peak phase. *Dactyliosolen tenuijunctus* was previously found in TNB as the prevailed species in the November sea-ice column (Saggiomo et al., 2017), in limited quantities during the ice melting period (Nuccio et al., 2000; Mangoni et al., 2017), together with other centric diatoms, primarily in offshore waters (Saggiomo et al., 2021). The dominance of *Dactyliosolen tenuijunctus*, along with a notable presence of *Pseudo-nitzschia* spp. and *Chaetoceros* spp., and the reduced presence of *Fragilariopsis*, confirm the peculiar nature of the blooming phytoplankton assemblage of BioAPRoS19. A similar *Dactyliosolen tenuijunctus* bloom was recently documented by Lee et al. (2022) in the neighboring Amundsen Sea during austral summer 2020. The authors classified this event as an extraordinary occurrence, possibly associated to the ongoing effects of climate change. It is plausible that the *Dactyliosolen tenuijunctus* bloom could be connected through horizontal transport between the Amundsen Sea and the Ross Sea. Various waters fluxes in the coastal area of TNB lead to the growth and accumulation of centric diatoms assemblage, more typical of offshore waters (Saggiomo et al., 2021).

It is well known that grazing by krill and Copepods plays an important role in Antarctica and in the Ross Sea, through which about half of the phytoplankton primary production is transferred to higher trophic levels (Smith et al., 2017). Their intervention on the phytoplankton community is always very important on the biomass present, but it can also be important on the taxonomic composition due to the diet selectivity (Hopkins, 1987; Crescenti et al., 2000). This selectivity is essentially expressed on a dimensional basis and with the general preference of the diatoms over the *Phaeocystis* (Meyer and ElSayed, 1987; Hopkins 1987,

Haberman et al., 2003; Nejtgaard et al., 2007; Smith et al., 2017). As far as it is known regarding grazing selectivity among diatoms, Meyer and El Sayed (1987) report that krill have a higher filtration efficiency for *Nitzschia* and *Chaetoceros* than for *Fragilariopsis*. On the contrary, we could not find information about the selectivity of grazing on *Dactyliosolen tenuijunctus*, therefore, it is very difficult to evaluate the role of grazing in selecting species dominance in TNB diatom assemblages. However, considering the size dominance of grazing process, it does not seem that this could be a strong discriminant between the dominance of *Dactyliosolen tenuijunctus* or *Fragilariopsis curta*.

By merging the described nutrients and phytoplankton dynamics, it can be assumed that the blooms of *Fragilariopsis curta* were associated with a condition of P deficiency due to their reliance of N and P with a $\Delta N/\Delta P$ ratio within the 10.8-12.3 range, indicating a preferential assimilation of P over N. The BioAPRoS19 campaign in TNB stands out, not only for the different taxonomic composition of phytoplankton highlighted by the unexpected *Dactyliosolen tenuijunctus* bloom but also for its distinctive nutritional dynamics. Differing from all previous campaigns in TNB, the N/P ratio, at the Chla peak, showed a state of N deficiency, driven by the $\Delta N/\Delta P$ ratio exceeding 17.5. This highlights elevated N disappearance respect to P, an opposite condition compared to the *Fragilariopsis curta*-dominated assemblage, indicating different nutrients assimilation modalities. An analogous increase in the $\Delta N/\Delta P$ ratio was also noted in waters dominated by *Phaeocystis antarctica*, typically offshore and along the southern part of the Ross Ice Shelf in the Ross Sea. In these waters $\Delta N/\Delta P$ ratio can rise beyond Redfield value, reaching approximately 19 due to the nutritional preferences of *Phaeocystis antarctica* (Arrigo et al., 2000; Sweeney et al., 2000; Smith and Asper, 2001; Dunbar et al., 2003). However, no *Phaeocystis* blooms were detected during BioAPRoS19, except for a very slight increase in its abundance in the final days of sampling. Instead, a short *Phaeocystis antarctica* bloom emerged between mid-December and the end of December during BioAPRoS18.

Typically, at TNB, in relation to the diatoms dominance, $\Delta Si/\Delta N$ ratio consistently exceeds 1.5, often surpassing 3, particularly



during the BioAPRoS campaigns. The Si concentrations in the two campaigns at blooming time are different, higher in BioAPRoS18 than in BioAPRoS19 (Figures 5E, F; 10). Also Si/P dynamics differ markedly between the two BioAPRoS campaigns (Figure 6): in BioAPRoS18 it increased in correspondence with the peak of *Chla*, whereas in contrast, it decreased in BioAPRoS19. Notably, in latter campaign, $\Delta Si/\Delta P$ values surged to over 50, the highest recorded. Petrou et al. (2019) described changes in Si utilization by Antarctic diatoms in relation to the acidification of the Southern Ocean.

The assemblage dominated by *Dactyliosolen tenuijunctus* exhibited not only an elevated $\Delta N/\Delta P$ ratio but also greater $\Delta Si/\Delta P$ ratio (Figure 11). This can be explained by a greater N requirement, lower need of P by *Dactyliosolen tenuijunctus* unlike *Fragilariopsis curta*. Consequently, biogeochemical differentiation emerges between the two BioAPRoS campaigns which involves the concentrations and the relationships not only between N, P but also with Si, of which, most probably, the phytoplankton

assemblage is the main protagonist. The series of campaigns of the '90s and further sampling of BioAPRoS18 exhibit a general stability in phytoplankton assemblage composition and biogeochemical characteristics (Catalano et al., 2000; Innamorati et al., 2000; Nuccio et al., 2000; Mangoni et al., 2017; Bolinesi et al., 2020; Saggiomo et al., 2021). The variations that arise from the comparison of this series of campaigns include a slight increasing trend of $\Delta Si/\Delta P$ from 1990 to 2018, and lower $\Delta Si/\Delta N$ in 1990, as well as the temporal differences in the dynamics of the phytoplankton biomass. The temporal discrepancies appear to correlate with the period of ice cover melting and disappearance, which, in turn, are connected to the annual weather variability. Conversely, the results of BioAPRoS19 show distinct conditions compared to previous year and entirety of the '90s. Specifically, in contrast to previous campaigns with the dominance of *Fragilariopsis curta*, where N/P reached high values (Figure 8A), the appearance of a different phytoplankton composition with distinct nutrient requirements resulted in a state of N deficiency related to higher $\Delta N/\Delta P$. Literature has long highlighted the differing nutritional needs of the Ross Sea pennate diatoms assemblage and those dominated by *Phaeocystis antarctica*. This study, enabled by microscopic analyzes of the phytoplankton assemblage composition, further distinguished the nutritional requirements between the two assemblages dominated by *Fragilariopsis curta* and *Dactyliosolen tenuijunctus*.

These findings suggest at least two considerations. The first refers to the importance of deepening the study of the photo-physiological, ecological and biogeochemical behaviour of the different species, made possible by the recent development of bio-optical models for the estimation of pelagic primary production (Bonamano et al., 2020). The second refers to the conditions of the TNB ecosystems. The Ross Sea and TNB are among the planet most significant marine ecosystems, exerting a profound global influence, in fact these regions support high primary production and play a crucial role in generating the conveyor belt system that fuels ocean currents (Rahmstorf, 2006). TNB ecosystems, which remained fairly stable since the '90s, could potentially undergo shifts in their biological and biogeochemical characteristics, echoing concerns raised by Mangoni et al. (2017) and by Smith et al. (2012) for the entire Ross Sea. The insights gained so far underscore the need for in-depth research and ongoing monitoring into the context of planetary climate change.

5 Conclusions

The results of recent BioAPRoS18 and BioAPRoS19 campaigns compared with those carried out in the '90s at BTN show many similarities and some important differences. UML formation modalities and characteristics, nutrient concentrations and their ratios (like Redfield) in spring-early summer and their strong consumption associated with phytoplankton growth in summer are similar. At summer *Chla* maxima, reached with some temporal deviations between recent and '90s campaigns, nutrient concentrations were at their minima. At this stage in BioAPRoS18, a recurrent condition of P deficiency already observed at TNB, and

elsewhere in the Ross Sea, was detected due to preferential assimilation of P over N ($\Delta N/\Delta P$ about 11.5). Associated with this condition, the recurrent bloom of pennate diatoms like *Fragilariopsis curta*, was present. Conversely, the BioAPRoS19 campaign exhibited different nutritional dynamics, marked by N deficiency ($\Delta N/\Delta P = 17.6$) and a bloom of centric *Dactyliosolen tenuijunctus*, which shows different nutrient requirements among diatoms species and which was never detected in this area. Furthermore, during the bloom of the two phytoplankton assemblages differences also emerged in the Chla/Si and Si/P ratios, probably linked to their preferences in the utilization of Si.

These results highlight the importance of studying ecological and biogeochemical role of the different phytoplankton species, the potential for shifts in the TNB ecological and biogeochemical characteristics. Given their global influence on ocean currents, primary production, and carbon storage, understanding these ecosystems is vital in the context of planetary climate change. The study offers insights into the complex interactions between nutrient availability, phytoplankton dynamics, and the effects of changing ice cover, contributing to our understanding of the intricate relationships within these critical marine environments.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

LM: Conceptualization, Data curation, Writing – original draft, Resources. CN: Data curation, Supervision, Validation, Writing – review & editing, Resources. CM: Data curation, Visualization, Writing – review & editing, Formal analysis, Resources. SBE: Data curation, Funding acquisition, Project administration, Writing – review & editing, Resources. GM: Data curation, Writing – review & editing, Resources. LV: Formal analysis, Writing – review & editing, Data curation, Resources. SBo: Writing – review & editing, Data

curation, Resources, Validation. AM: Writing – review & editing, Data curation, Resources. VP: Writing – review & editing, Data curation, Resources. MM: Writing – review & editing, Data curation, Resources. LL: Writing – review & editing, Data curation, Resources, Supervision.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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