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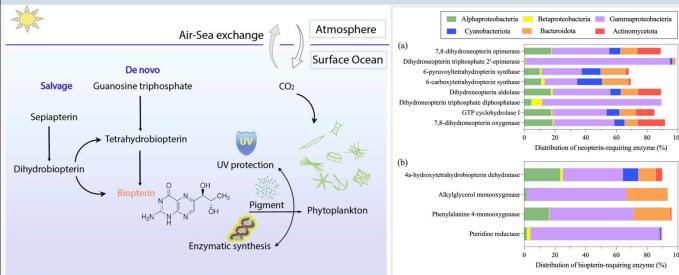
Spatial-temporal distribution and source of regulation of microbial pteridines in the euphotic layer of South China Sea

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ABSTRACT Originally discovered in photoautotrophic cyanobacteria, microbial pteridines are precursors involved in the metabolism of carbon and nitrogen cycles, and participate in phototaxis signal transduction (as photoreceptor), photochemical redox reaction, solar energy capture and ultraviolet radiation protection as coenzymes or cofactors. In this study, the vertical distribution of biogenic microbial pteridines in the euphotic layer of the South China Sea Basin was reported for the first time, and the marine environmental concentrations of neopterin (NP), bioprotein (BP) and isoxanthopterin (IP) were determined by high performance liquid chromatography fluorescence detector (HPLC-FLD), and the detection limits were NP: 0.48 nM, BP: 0.72 nM, and IP: 0.22 nM respectively. The results showed that the pteridines was mainly enriched in the surface layer (within 100 m), and the subsurface layer (at 100-200 m) was mostly below the detection limits. Noteworthily, NP was not detected in all samples, and the concentration of water column profile distribution of BP (0.01–0.6 pM) and IP (0.01–3 pM) was strongly negatively correlated with the nutrients at each station, indicating biomass-dependent attributes. Around the maximum layer depth of chlorophyll a, it was found that the corresponding depth IP content response value was high, and the geographical distribution of BP and IP was positively correlated with the abundance of cyanobacteria *Synechococcus* and *Prochlorococcus*, which may indicate that *Synechococcus* is an important source of BP contribution. In terms of seasonal distribution, the abundance of pteridines in the surface layer in summer was significantly higher than that measured in spring. The detection of pteridines in euphotic layer has the potential to reveal the biogeochemical cycling processes occurring in marine microbial communities and their biological roles.

Introduction



Left - Fig. 1. Synthesis and biological functions of microbial biopterins in the ocean

Right - Fig. 2. Common pterin-requiring enzymes in the most abundant marine taxa.

- Pteridines, aromatic compounds composed of fused pyrimidine and pyrazine rings, are essential biomolecules in most of microorganisms (Dunlap et al., 1985; Feirer and Fuqua, 2017).
- Pteridines are fundamental in biological growth and functioning (Fig. 1) serving as cofactors and coenzymes, including pigmentation, metabolic modulation, amino acid synthesis, and intracellular signaling (Feirer and Fuqua, 2017; Stravas et al., 2017).
- Enzymatic processes involved in pteridines (neopterin: Fig. 2a and bioprotein: Fig. 2b) are widely distributed in marine dominant prokaryotic microorganism taxa such as Cyanobacteriota, Proteobacteria, Actinomycetota and Bacteriodita etc. (<http://img.jgi.doe.gov, 2023>).

Material and method

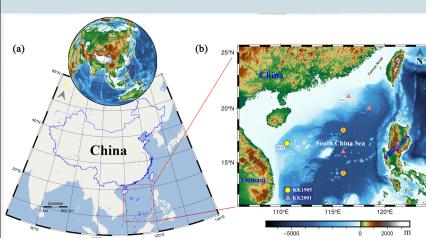
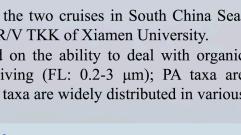


Fig. 3. Sampling geolocations in the basin of South China Sea

Fig. 4. Samples Processing flow-chart



- Samples in the euphotic layer (0–200 m) were collected from the two cruises in South China Sea: KK1905 (summer, Jul. 2019) and KK2001 (spring, Apr. 2020) by R/V TKK of Xiamen University.

- Prokaryotes can be divided into two functional groups based on the ability to deal with organic matter metabolism: particle-attached (PA: 3–10 μm) and free-living (FL: 0.2–3 μm); PA taxa are exclusively colonized on the surface of organic particles, while FL taxa are widely distributed in various water bodies (Zhang et al., 2020).

Results and discussion

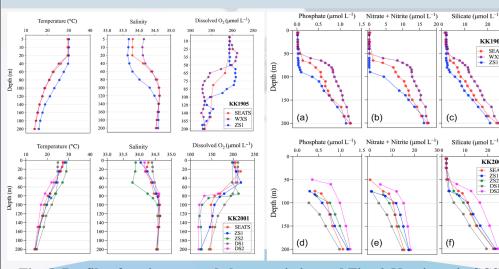


Fig. 5. Profile of environmental characteristics and Fig. 6. Nutrients in SCS

The vertical distribution of common environmental parameters include the following: temperature, salinity, and dissolved oxygen (DO), are shown in Fig. 5.

The surface layer within 50 m was nutrient-limited which absorbed by plankton, and gradually increased at a deeper concentration (>50 m) in both spring and summer.

Results and discussion

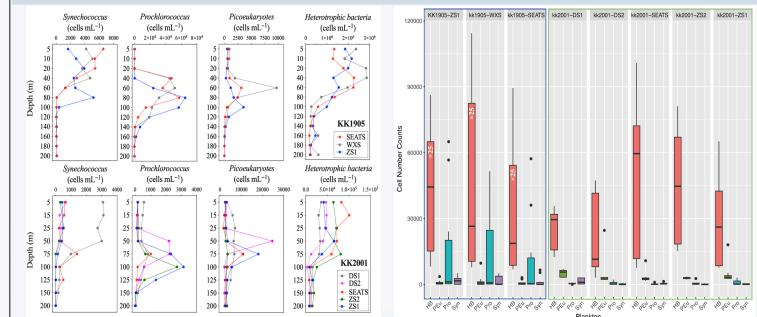


Fig. 7. Microbial community composition

- The vertical distribution of microplankton, Synechococcus (Syn) and Heterotrophic Bacteria (HB) were mainly distributed in the shallow euphotic layer within 100 m depth, while Prochlorococcus (Pro), and Picoeukaryotes (PEu) were widely distributed in the depth range of 40 to 150 m, showing high subsurface abundance (Fig. 7).

- The average abundance of microplankton in the summer was significantly higher than that of the spring (except PEu, Fig. 8), mainly related to the higher photosynthetically active radiation in summer.

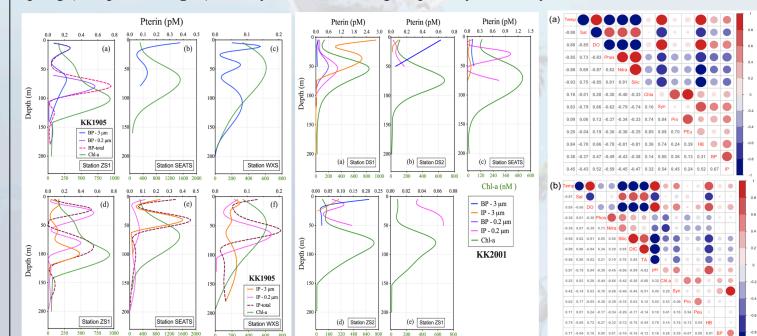


Fig. 8 . Comparison of average abundance

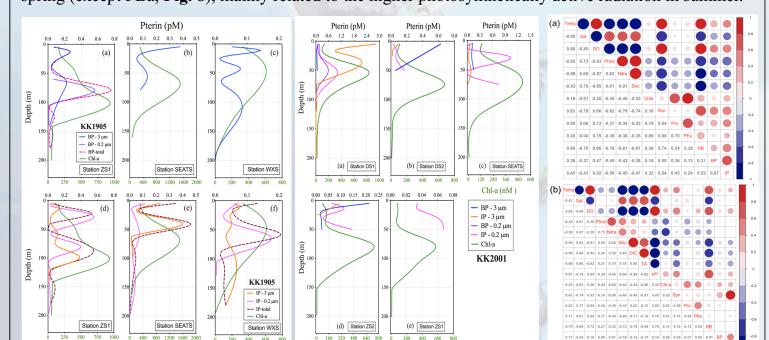


Fig. 9. Profile of bioprotein, isoxanthopterin and Chl-a for KK1905 and KK2001

- The depth of Deep Chlorophyll Maximum (DCM) observed in summer ranged from 60–100 m, the chl-a maximum was 1.44 nM (station SEATS), the DCM layer in spring ranged from 25–50 m, and the chl-a maximum was 0.82 nM (station DS1), as shown in Fig. 9.
- The concentration of bioprotein (BP: 0.01–0.6 pM) and isoxanthopterin (IP: 0.01–3 pM) in summer was higher than that in spring overall, the main source of BP was PA part (3–10 μm), and IP was distributed in both PA and FL, and the microplankton in the FL (0.2–3 μm) was the main source of contribution to pteridines in spring.

- The abundance of Syn positively correlated with BP ($R^2 = 0.39–0.50$) and IP ($R^2 = 0.54–0.89$) (Fig. 10 and Fig. 11). Syn is abundantly distributed on the surface of the ocean, and the high value of pteridines on the surface may indicate that Syn is one of their important sources.

Conclusion and Summary

- Bioprotein and isoxanthopterin have similar metabolic pathways, and may share some microbial sources.
- The sources of bioprotein are mainly the particle-attached microorganisms (ultra-micro and microplankton), while isoxanthopterin is distributed in microplankton of all different sizes, but free-living microorganisms as the main source.
- The coupling relationship between chlorophyll a and pteridines in vertical distribution showed that pteridines are important cellular metabolites of autotrophic phytoplankton.
- The main source of contribution of pteridines in the surface of the SCS may be the cyanobacterial *Synechococcus*, and the subsurface abundant *Prochlorococcus* is one of original sources.

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Fig. 10. Parameters correlation

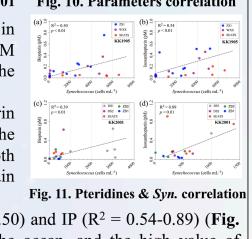


Fig. 11. Pteridines & Syn. correlation

