Atmospheric deposition promotes relative abundance of main dimethylsulfoniopropionate producers in the western North Pacific

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Abstract

Haptophytes and Dinoflagellates are two cosmopolitan algae associated with dimethylsulfoniopropionate (DMSP) synthesis, which regulates the marine biogenic flux of dimethylsulfide (DMS) to the atmosphere and subsequently affects marine aerosols. Attempting to reveal the potential impact of atmospheric deposition on the growth of main DMSP producers, four bioassay experiments were conducted in the western North Pacific (WNP) by adding aerosols, nutrients and trace metals. Our results showed that the percentage of main DMSP producers increased substantially from coastal regions (<1%) to the open ocean (~17%) with the dominance of Dinophyceae and Haptophyceae, respectively. Aerosol additions largely increased the percentage of DMSP species in the open WNP. Specifically, atmospheric DIN and soluble Cu, and Fe promoted Chrysochromulina, and Phaeocystis and E. huxleyi, respectively. It is very likely that atmospheric deposition could lift the relative abundance of main DMSP producers in the vast oligotrophic oceans and contribute to the climate change.

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Highlights：

- **Simultaneous input of soluble metals with DIN from atmospheric deposition could further enhance the primary production.**
- **Dinophyceae and Haptophyceae were main DMSP producers in the coastal and oligotrophic oceans, respectively.**
- **Atmospheric deposition could elevate the proportion of main DMSP producers especially in oligotrophic oceans.**
- **DIN and Cu increased the proportion of *Chrysochromulina* whilst Fe benefited *Phaeocystis* and *E. huxleyi*.**

Abstract

Haptophytes and Dinoflagellates are two cosmopolitan algae associated with dimethylsulfoniopropionate (DMSP) synthesis, which regulates the marine biogenic flux of dimethylsulfide (DMS) to the atmosphere and subsequently affects marine aerosols. Attempting to reveal the potential impact of atmospheric deposition on the growth of main DMSP producers, four bioassay experiments were conducted in the western North Pacific (WNP) by adding aerosols, nutrients and trace metals. Our results showed that the percentage of main DMSP producers increased substantially from coastal regions (<1%) to the open ocean (~17%) with the dominance of

Dinophyceae and Haptophyceae, respectively. Aerosol additions largely increased the percentage of DMSP species in the open WNP. Specifically, atmospheric DIN and soluble Cu, and Fe promoted *Chrysochromulina*, and *Phaeocystis* and *E. huxleyi*, respectively. It is very likely that atmospheric deposition could lift the relative abundance of main DMSP producers in the vast oligotrophic oceans and contribute to the climate change.

Plain Language Summary

The DMSP synthesized by marine phytoplankton can be converted into DMS and contribute substantially to the sulfur budget in the atmosphere. Marine biogenic DMS actively participates in atmospheric chemistry and can be transformed into aerosols generating radiative effects. To understand the response of main DMSP producers to the atmospheric deposition of substances, we conducted *in situ* bioassay experiments at four sites of the western North Pacific (WNP), by adding aerosols and analogue amounts of nutrients and metals. Aerosol addition significantly elevated the relative abundance of main DMSP producers in the oligotrophic ocean with contained nitrogen, copper and iron promoting different species of Haptophyceae. The competitive and growing advantages of DMSP species are probably due to their larger size than Cyanobacteria and special mechanisms for assimilating insoluble metals. Dinophyceae as primary DMSP species in coastal regions failed to compete with Diatoms and Trebouxiophyseae for exogenous nutrients. With the intensive human activities and increasing deposition of atmospheric nitrogen and soluble metals, the production of DMSP and efflux of DMS may significantly rise and subsequently affect atmospheric chemistry and the climate.

Keywords: Atmospheric deposition; DMSP; Haptophyceae; Dinophyceae; Western North Pacific; Climate

1. Introduction

Atmospheric deposition is one of the most important exogenous sources of nitrogen, trace metals and other substances to the surface ocean which may profoundly affect primary production and regulate phytoplankton community structure (Chien et al., 2016; Duce et al., 2008; Gallisai et al., 2014; Li et al., 2021; Mahowald et al., 2018). Amplification of reactive N emissions by human activities may have led to a potential shift from N limitation to P limitation of primary production in lakes and the upper ocean (James et al., 2009; Kim et al., 2011). Atmospheric Fe deposition has been suggested to be a critical factor limiting the productivity in high nutrient low chlorophyll (HNLC) regions (Martin et al., 1990) and able to enhance the primary production in the vast area of Southern Ocean (Cassar et al., 2007). In contrast to soluble Fe, colloidal Fe was found to be enriched in the ocean surface as a result of atmospheric input, which could also be essential to phytoplankton growth (Wu et al., 2001). Copper is another key component of aerosols which exhibits ambiguous effect on marine phytoplankton depending on its concentration (Yang et al. 2020). Anthropogenic emissions are increasing Cu deposition sharply, and high Cu input to the ocean may change the phytoplankton community structure due to divergent physiological properties and tolerance of Cu toxicity of individual species (Paytan et al., 2009). Atmospheric input of other trace metals and substances may also be crucial to phytoplankton growth, determined by the elemental stoichiometry required by algal cells and the chemicals supplied in ambient seawater (Moore et al., 2013; Twining & Baines, 2013).

Marine phytoplankton can respond to the atmospheric deposition by producing biogenic substances which may be converted to the reactive gases entering the atmosphere or be released as primary organic aerosols. Dimethylsulfide (DMS) as the most abundant marine biogenic reactive gas accounts for more than half of natural flux of sulfur to the atmosphere, and its precursor dimethylsulfoniopropionate (DMSP) is a metabolite of phytoplankton (Lana et al., 2011; Meinrat O. Andreae & Paul J. Crutzen, 1997). DMS-oxidized aerosols play a crucial part in light extinction and formation of cloud condensation nuclei (CCN), in consequence altering the radiative balance of the Earth and regulating the climate (Leaitch et al., 2013; Rap et al., 2013). DMSP and its degradation products also act as potential contributors to methane production (Weller et al., 2013), which is a powerful greenhouse gas responsible for ~17% of the extra radiative forcing in the atmosphere via production of secondary aerosols (Allen, 2016). This phytoplankton feedback to the climate through DMSP production is the core of CLAW hypothesis (Charlson et al., 1987; Quinn & Bates, 2011), and the potential impact of atmospheric deposition on main DMSP producers is of particular interest in the surface ocean-lower atmosphere studies.

Haptophytes have long been recognized as the main producers of DMSP in the ocean since they are generally obligated to more than 30% of the global DMSP pool and nearly 40% in the Southern Ocean (Galí et al., 2015). As they are also dominant phototrophic picoeukaryotes in offshore waters, comprising 70% of nano-phytoplankton biomass, their capacity of DMSP production should be substantial (Liu et al., 2009; Massana, 2011). Three typical genera of Haptophyceae, *Emiliania huxleyi* (*E. huxleyi*), *Chrysochromulina* and *Phaeocystis* are commonly recorded as the important sources of DMSP in various oceans around the world (Galí & Simó, 2010; Holligan et al., 1993; Lizotte et al., 2012). The DMSP production in haptophytes-dominated assemblages in the HNLC regions has been found to be stimulated by the natural Fe sourced from vertical mixing or by artificial Fe fertilization (Royer et al., 2010; Turner et al., 2004). Besides, dinoflagellate species are gradually accepted as one of the most important producers of DMSP with even more diverse species and strains involved in DMSP synthesis (Caruana & Malin, 2014; Uchida et al., 1996), thereof *Gymnodinium* sp. release the highest amount of DMSP per cell (Belviso et al., 2000; Table S1).

The western North Pacific (WNP) is influenced significantly by the air masses transported from the East Asia which carry considerable anthropogenic pollutants as well as mineral dust. Nutrients composition and phytoplankton biomass and community structure vary remarkably from the coastal region to the open WNP, determined by riverine discharges, coastal upwells, ocean currents, atmospheric deposition and physical conditions. Previous studies have reported that severe dust events were correlated well and positively with the chlorophyll a (*Chl a*) concentrations in the south Yellow Sea (YS) and East China Sea (ECS, Tan et al., 2011). *In situ* bioassay experiments have shown that addition of mineral dust could significantly increase the *Chl a* concentrations and cell abundance of large-sized phytoplankton (>5 μm) in the subtropical gyre and Kuroshio Extension of the WNP (Zhang et al., 2018). In contrast, atmospheric deposition was not able to effectively enhance the *Chl a* in the N-replete coastal ECS due to the N-rich and P-deficient feature of aerosols, and the affluent metals they contained might strongly affect the phytoplankton composition and dominant groups (Li et al., 2021). High fluxes of atmospheric substances to the WNP have a great potential to affect the abundance of DMSP producers and subsequently alter the flux of marine biogenic DMS, but this process hasn't been clearly understood.

Here *in situ* bioassay experiments were performed in the coastal seas and subtropical gyre of the WNP, amending nutrients, trace metals and natural aerosols, aimed to investigate the potential impacts of aerosol deposition on two principal classes of DMSP-producing phytoplankton (Haptophyceae and Dinophyceae). Changes of *Chl a* and nutrient concentrations were monitored and dynamics of phytoplankton community structure was investigated using 16S and 18S rRNA high-throughput sequencing technique. Our results will help understand the change of phytoplankton community in response to the atmospheric deposition and the mechanism controlling variation of DMSP production in different oceanic regions.

2. Materials and methods

Four bioassay experiments were conducted during 2018-2019 using the surface seawater collected nearby Huaniao Island (H, 30°52'N, 122°40'E), at ~50 km east to Huaniao (H_O, 30°50'N, 123°10'E), in the north Taiwan Strait (TWS, T3, 26°17'N, 121°12'E) and the North Pacific Subtropical Gyre (NPSG, K8, 11°N, 155°E), respectively (Figure 1a). The detailed operations of water sampling, aerosol collection and addition, and incubation were introduced in Method S1. Nutrients, soluble metals and aerosols added to various treatments (each treatment in triplicate) followed the experimental design in Table 1. The amount of dissolved inorganic nitrogen (DIN), P, Cu or Fe added to each treatment was mimic to the concentration of each component in the aerosol addition treatment.

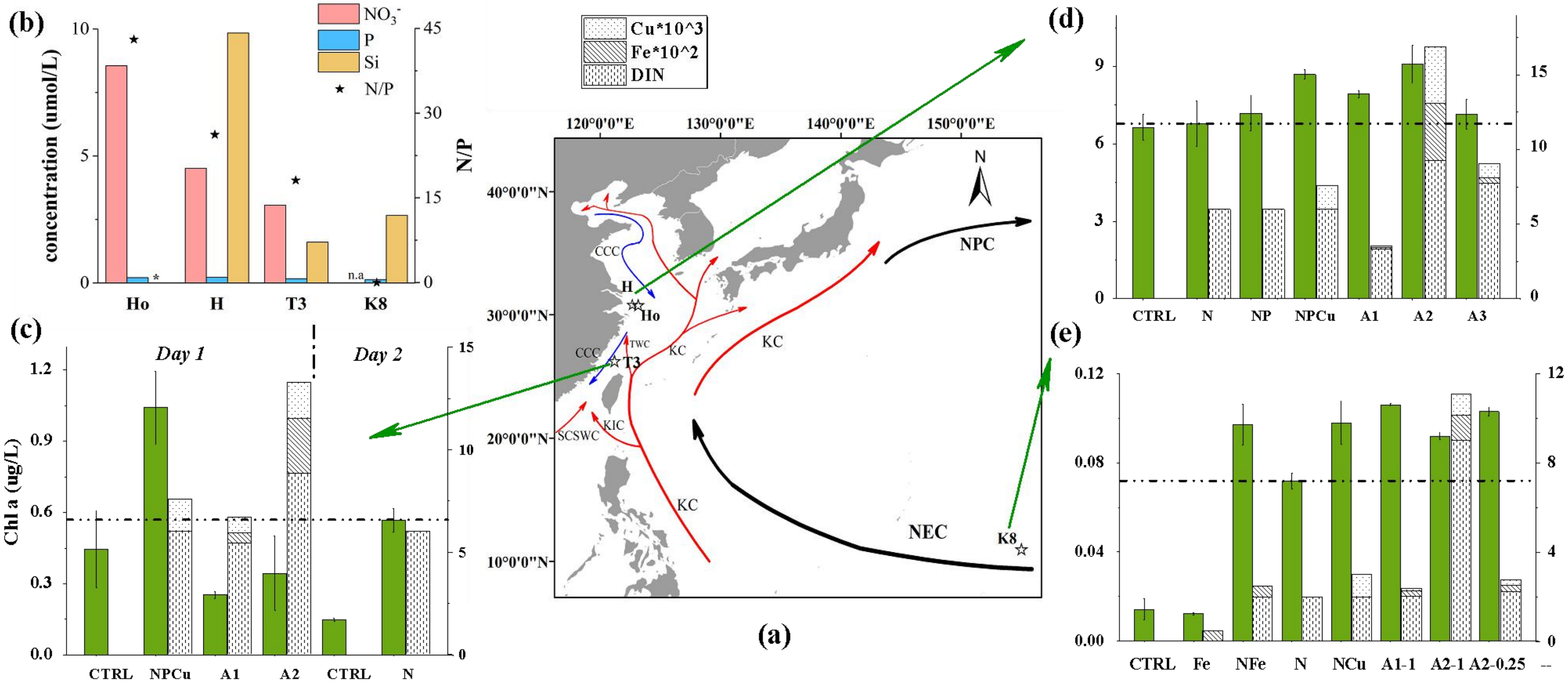
(a)
(b)
(c)
(d)
(e)
NO3-
P
Si
N/P
concentration (umol/L)
N/P
Ho
H
T3
K8
n.a
Day 1
Day 2
Chl a (ug/L)
CTRL
NPCu
A1
A2
CTRL
N
Cu*10^3
Fe*10^2
DIN
120°0'0"E
130°0'0"E
140°0'0"E
150°0'0"E
40°0'0"N
30°0'0"N
20°0'0"N
10°0'0"N
CCC
TWC
KC
KIC
SCSWC
NEC
NPC
N
CTRL
N
NP
NPCu
A1
A2
A3
concentration (umol/L)
CTRL
Fe
NFe
N
NCu
A1-1
A2-1
A2-0.25

Figure 1. Four sites (H, Ho, T3 and K8) in the western North Pacific where bioassay experiments were conducted (a), nutrient status (b) in the initial seawaters sampled from the four sites and peak concentrations of *Chl a* in the control (CTRL) and treatments by adding DIN, soluble Fe and Cu, and different aerosols (A) in the bioassay experiments conducted at Taiwan Strait (TWS) (c, 24 & 48 hrs incubation), Huaniao Island (HN) (d, 24 hrs incubation) and North Pacific Subtropical Gyre (NPSG) (e, 48 hrs incubation).

* NEC: the North Equatorial Current; NPC: the North Pacific Current; KC: the Kuroshio Current; KIC: the Kuroshio Intrusion Current; SCSWC: the South China Sea Warm Current; TWC: the Taiwan Current; CCC: China Coastal Current.

b: no data for Si concentration in Ho; n.a: NO_3^- concentration was below the detection limit in K8.

Table 1. The design of each treatment during the bioassay experiments.

	NO	Treatments	Name [1]	Additions
Distance to Huaniao (Ho)	1	control	HN-CTRL	N/A
	2	N	HN-N	NH_4^+ 3.6 μM, NO_3^- 2.4 μM
	3	N:P $_{Aerosol}$	HN-NP	NH_4^+ 3.6 μM, NO_3^- 2.4 μM, PO_4^{3-} 0.01 μM
	4	Cu	HN-NPCu	NH_4^+ 3.6 μM, NO_3^- 2.4 μM, PO_4^{3-} 0.01 μM, Cu^{2+} 1.6 nM [2]
	5	A1	HN-A1	Aerosol #1 (2016/4/4) 1.5 mg/L [3]
	6	A2	HN-A2	Aerosol #2 (2016/11/19) 1.5 mg/L
	7	A3	HN-A3	Aerosol #3 (2016/11/27) 1.5 mg/L
Nearby	1	control	HN-Cu-CTRL	N/A

Huaniao (H)	2	NCuFe	HN-Cu- NCuFe	NH_4^+ 5.4 µM, NO_3^- 3.6 µM, Fe^{2+} 11 nM, Cu^{2+} 1.6 nM [4]
	3	10XCu	HN-Cu-10xCu	Cu^{2+} 16 nM
TWS (T3)	1	control	TWS-CTRL	N/A
	2	N	TWS-N	NH_4^+ 3.6 µM, NO_3^- 2.4 µM
	3	Cu	TWS-NPCu	NH_4^+ 3.6 µM, NO_3^- 2.4 µM, PO_4^{3-} 0.01 µM, Cu^{2+} 1.6 nM
	4	A1	TWS-A1	Aerosol #1 (2018/4/11) 1 mg/L
	5	A2	TWS-A2	Aerosol #2 (2018/4/28) 1 mg/L
NPSG (K8)	1	Control	NPSG-CTRL	N/A
	2	N	NPSG-N	NH_4^+ 1 µM, NO_3^- 1 µM
	3	Fe	NPSG-Fe	Fe^{2+} 5 nM
	4	NFe	NPSG-NFe	NH_4^+ 1 µM, NO_3^- 1 µM, Fe^{2+} 5 nM [5]
	5	NCu	NPSG-NCu	NH_4^+ 1 µM, NO_3^- 1 µM, Cu^{2+} 1 nM [5]
	6	A1-1	NPSG-A1-1	Aerosol #1 (2018/4/15) 1 mg/L [3]
	7	A2-1	NPSG-A2-1	Aerosol #2 (2018/11/19) 1 mg/L
	8	A2-0.25	NPSG-A2-0.25	Aerosol #2 (2018/11/19) 0.25 mg/L [6]

* all the concentration of added Cu refers to soluble Cu (free Cu^{2+}), no chelate Cu.

[1] the abbreviative name in figures and tables.

[2] 6:4 of NH_4^+ / NO_3^- ratio was the most efficient in inducing a phytoplankton bloom (result of preliminary laboratory experiments); N/P/Cu was set on the basis of composition of aerosols (Huaniao, 2016).

[3] according to Mackey et al (2017), we assumed the additive concentration of aerosol was 1 or 1.5 (stronger deposition) mg/L.

[4] the concentration of Cu^{2+} was kept the same as HN experiment, and the N/Fe/Cu was set as the composition of aerosols (Huaniao, 2018, A2-1 used in SNPG).

[5] the amount of DIN and Fe^{2+} referred to (Browning et al., 2017; Moisander et al., 2012), Cu^{2+} was determined by A2-1 (Huaniao, 2018) in SNPG.

[6] 0.25 mg/L was designed according to the DIN concentration (1.24 μM NH_4^+ and 0.93 μM NO_3^-, similar to our DIN amendment) in A2.

Fifty mL seawater was sampled from each triplicate and filtered through a 0.45 μm PES filter for nutrient analysis (Bran+Luebbe GmbH, Norderstedt, Germany, 2005). Another 350~500 mL seawater was filtered through glass microfibre filters (0.7um, Whatman GF/F) under a vacuum pressure <0.02 MPa for *Chl a* measurement (Method 445.0, Elizabeth JA and Gray BC, 1997, EPA; Cary Eclipse, VARIAN, USA, 2009). The remaining 0.7~1.2 L seawater was filtered through 0.22 μm Durapore filter (Millipore) (P<0.02 MPa) for DNA extraction (PowerSoil total DNA extraction) and subsequent sequencing (Shanghai Majorbio Bio-pharm Technology Co. Ltd). We chose the primer 3ND/V4-euk-R2 (GGCAAGTCTGGTGCCAG / ACGGTATCTRATCRTCTTCG) and 338F/806R (ACTCCTACGGGAGGCAGCAG / GGACTACHVGGGTWTCTAAT) (Sun et al., 2014) for PCR of eukaryotic and prokaryotic algae. About 20 DMSP species were compiled and classified into five categories based on their richness (Table S3). Samples (water and membrane) were temporarily stored at -20℃ before succeeding analysis.

3. Results and Discussions

3.1 Response of *Chl a* concentration

The average concentrations of *Chl a* in initial seawaters decreased from the coastal region (~10 μg/L) to the remote WNP (~0.1 μg/L), tightly associated with nutrient levels. Coastal HN water was relatively eutrophic (with DIN 5~8 μM) and contained high DIN/PO_4^{3-} ratios (~26 at Ho and ~43 at H), while open NPSG appeared to be oligotrophic (DIN below the detection limit (BDL)); influenced by the Kuroshio Current, TWS possessed moderate nutrients (DIN 3 μM, Table S2, Figure 1).

The maximal elevation of *Chl a* concentration was associated with the nutrients requirement for phytoplankton growth in different oceanic regions. DIN additions supported the increases of ~0.4%, ~4.6% and ~204% *Chl a* per μM on Day 1 in HN, TWS and NPSG, respectively (N treatment vs. CTRL, Figure 1c-e), which was precisely coherent with the N/P ratios in initial seawaters. DIN input played a negligible role in N-replete HN (N/P > 26) but was indispensable in the extremely oligotrophic NPSG (undetectable initial DIN). Soluble Cu was found to stimulate additional ~13% and ~37% increase of *Chl a* per nM on the basis of DIN addition in

HN (Day 1) and NPSG (Day 2, N vs. NCu treatments), respectively. Only N:$P_{16:1}$ (0.375 μM PO_4^{3-}) treatment was designed in TWS experiment which contained an order of magnitude higher PO_4^{3-} than NPCu (0.01 μM PO_4^{3-}) treatment, but the maximum *Chl a* in NPCu (1.04 μg/L) was still significantly higher than that of N:$P_{16:1}$ (0.73 μg/L). This further confirmed the strong facilitation of Cu to phytoplankton growth in the WNP region. Similarly, Fe could also further enhance *Chl a* when DIN was satisfied in the oligotrophic water, in contrast to the negligible effect from Fe addition alone (NPSG-CTRL vs. NPSG-Fe treatment and NPSG-N vs. NPSG-NFe treatment). This suggested that DIN input played a fundamental role in the N-depleted NPSG and simultaneous input of soluble metals like Cu and Fe with DIN from the aerosol deposition could further strengthen the primary production. Besides, similar *Chl a* maximum was observed in the NPSG-NCu and NPSG-NFe treatments, suggesting that Fe and Cu might be able to function alternatively in promoting *Chl a*. As the additive amounts of N, P, Cu and Fe in all three bioassay experiments were mimic to the aerosol deposition, their effects on *Chl a* and interactions demonstrated the potential impact of atmospheric deposition on primary productivity.

The distinct effects of aerosol additions on *Chl a* were associated with the nutrient composition of initial seawater and specific aerosol types (Figure 1b & S1). For example, HN-A1 contained high Na^+, Mg^{2+} and Cl^- and adequate Al, Ca and Fe, and the corresponding air mass back trajectories pointed to the Gobi Desert and passed the YS and the ECS, which suggested a mixture of desert dust and marine source (Figure S1-1 & Table S4). Likewise, dust, anthropogenic and marine sources could be generally identified for the aerosols used in bioassay experiments (Table S4). At Huaniao Island, content of soluble metals in different types of aerosols resulted in various promoting effects (Li et al., 2021). In TWS, *Chl a* was vulnerable to aerosols even though they provided more DIN and trace metals than N and NPCu treatments. Given the perfect N/P ratio (~18, close to Redfield ratio) in TWS, the adapted phytoplankton community might be broken and rebuilt, causing lower *Chl a* concentrations than the control on Day 1 except Cu treatment. After 2 days, they grew better in aerosol treatments than in the control (Figure S2). Both crustal (A1-1) and anthropogenic (A2-0.25) aerosols favored the *Chl a* in NPSG, and their maximum *Chl a* concentrations were comparable to those of NCu and NFe treatments, suggesting that DIN, Cu and Fe could be the key factors in aerosols stimulating the primary production.

3.2 Dominant phytoplankton groups

Initial seawater

The community structure of algae in natural seawater was distinct owing to different sampling regions and times (Figure 2a, S3 & S4). Dinophyceae and Diatoms dominated in the surface seawater near HN, where Dinophyceae took control (42.1% of total OTUs) in April 2019 and Diatoms predominated (44%) in May 2018 (Table S2). *Skeletonema*, *Chaetoceros*, *Thalassiosira* belonging to Diatom and *Syndiniales*

Groups, *Amoebophrya* sp. in Dinophyceae were the richest. Chain-forming diatoms covering *Thalassionema* sp., *Pseudo-nitzschia* and *Skeletonema* sp. were reported to be the most dominant in the ECS nearly throughout the year except spring, and *Prorocentrum* belonging to Dinophyceae was found to bloom in spring (Guo et al., 2014).

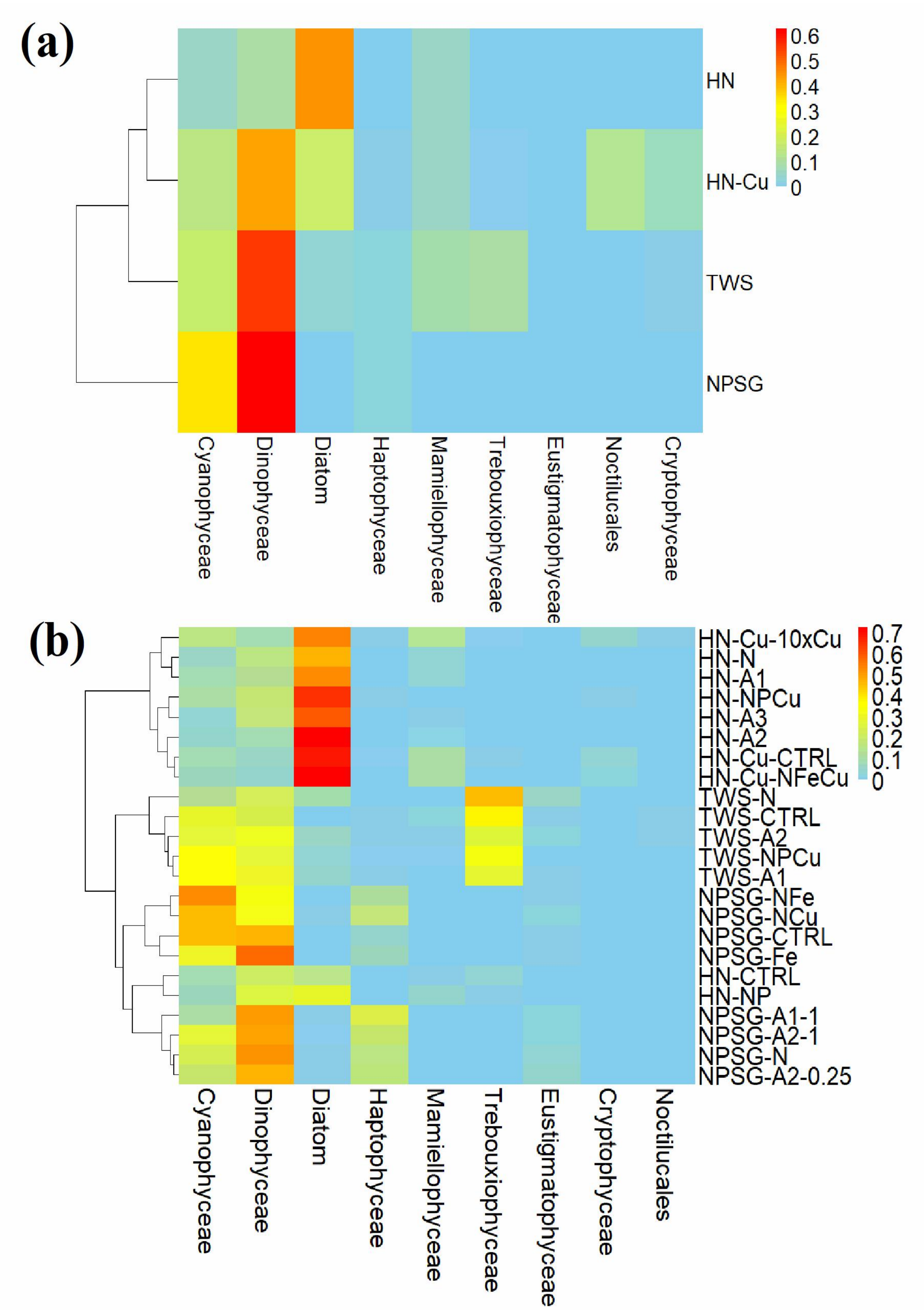

Figure 2. Clusters and relative abundances of dominant algae classes in the initial seawaters (a) and in various treatments (b) of the bioassay experiments in Huaniao Island (HN), Huaniao Lab (HN.Cu), Taiwan Strait (TWS) and North Pacific Subtropical Gyre (NPSG).

Dinophyceae (52.4%) and Cyanophyceae (20.9%) were mostly found in TWS (T3), followed by Trebouxiophyceae and Mamiellophyceae occupying merely 8.73% and 7.55%. *Syndiniales* Groups remained noticeable here, together with new dominators *Synechococcus* and *Nannochloris* ("no rank Trebouxiophyceae" in Figure S4-T3). Zhong et al. (2020) illustrated that the adjacent area of T3 was dominated by Diatom and *Synechococcus*. Diatoms were minor in our samples, which might be restricted by the relatively low Si/P ratio of 8.43 (<10) and Si/DIN ratio of 0.47 (<1) (Justić et al., 1995).

Dinophyceae and Cyanophyceae were more prevailing in NPSG than in TWS, together contributing to ~98% of total OTUs identified. *Erythropsidinium* and *Lepidodinium* classified as Dinophyceae and *Prochlorococcus* included in Cyanophyceae governed the community (Figure S4-K8). Dinophyceae and pico-cyanobacteria usually outcompeted in this oligotrophic environment (Brown et al., 2008; Rii et al., 2018), and Rii et al. (2018) reported that *Gyrodinium* was the most frequently detected Dinophyceae in the NPSG.

The proportion of diatoms decreased from 17-44% around HN to 3.27% and 0.18% in the TWS and the NPSG, respectively. In contrast, Cyanophyceae and Dinophyceae proportions increased significantly from 5% and 9% around HN to 40% and 57% in the NPSG, respectively (Figure S5).

In treatments

Figure 2b & S6 illustrated the overall community structure on class level for *Chl a* peaks in the bioassay experiments. Generally, Diatoms were outstanding in HN treatments, reaching 70% of total OTUs. Both Cyanophyceae and Dinophyceae were dominant groups in the treatments of TWS and NPSG, consistent to the initial phytoplankton composition at these two sites. The relative abundance of Trebouxiophyceae increased significantly in TWS with flourishing *Nannochloris*, who was fond of high temperature and high salinity habitat provided by Kuroshio intrusion (Figure 2b, Cho et al., 2007).

The additions of DIN, Cu and aerosols were all conducive to Diatoms growth relative to other phytoplankton in HN (Figure S6). Differently, DIN firstly boosted Trebouxiophyceae in TWS, and Cu and aerosols favored Cyanophyceae and Dinophyceae. Surprisingly, significant elevations of Haptophyceae were found in NPSG treatments, benefited from DIN, metals and aerosol additions, in spite that it was negligible in natural waters of the WNP (Figure 2a). Samples were commonly clustered by regions in Figure 2b, while “HN-CTRL” and “HN-NP” were located within NPSG treatments. The significant P depletion relative to DIN in these two HN treatments led to the remarkable decline of Diatoms and the increase of Dinophyceae percentages analogue to those of NPSG treatments. “NPSG-NCu” and “NPSG-NFe” had similar constitutions of phytoplankton, indicating interchangeable effects of Cu and Fe; the clustering of aerosols and N in NPSG inferred that DIN in aerosols was the most effective component in regulating phytoplankton composition.

3.3 Impacts on DMSP producers

The relative abundances of main DMSP producers in seawaters varied significantly in response to the inputs of DIN, Cu, Fe and aerosols (Table S3). It was clear that the total proportion of DMSP species climbed with the oligotrophication level by orders of magnitude (from <1% in HN to ~5 and ~20% in TWS and NPSG, respectively). Other Dinophyceae apart from *Gyrodinium* (*other Dino*) and *Phaeocystis* in Haptophyceae were the most abundant in HN; Dinophyceae were also the chief DMSP class and *E. huxleyi* was the prime Haptophyceae in TWS; *Gyrodinium*, *Phaeocystis* and *Chrysochromulina* all became abundant in NPSG. It appeared that DMSP species had little advantage in the interspecific competition with the predominant clades like Diatoms in the eutrophic region.

Atmospheric deposition supplies affluent DIN and trace metals such as Fe and Cu to the surface ocean. Trace metals are essential in regulating the productivity and community of marine phytoplankton in spite of their low concentrations (Sunda, 2012). Recent study has approved the essential roles of aerosol Fe and Cu in the eutrophic coastal sea, whose effects may exceed that of adequate P input in regulating the phytoplankton composition (Li et al., 2021). At coastal HN and TWS, aerosols principally supported Diatoms, Dinophyceae and Cyanophyceae so that the relative abundance of DMSP species especially Haptophyceae was defeated; Dinophyceae were the most important producers of DMSP at these sites. A significant percentage rise of DMSP producers was monitored in the late period of incubation in HN (90-1000%), probably because the mortality of dominant species (Diatoms) after the *Chl a* peak created chances for recovery of main DMSP producers. Differently, the percentages of main DMSP producers increased approximately 3-4 folds and 4-8 folds at day 1 and day 4-5 of TWS and doubled at the *Chl a* peak day of NPSG (Figure S7, Table S6). Generally, dust-dominated aerosols accelerated Haptophyceae while anthropogenic aerosols were more conducive to Dinophyceae (Table S3 & Appended).

DIN impact

Little effect of DIN input on DMSP species was observed (0.63% in CTRL vs. 0.54% in N, Table S3) as the dominant Diatoms were boosted (15-47% in CTRL and N, Figure S6a) on day 1 and 2 in HN treatments. In TWS, although aggressive Trebouxiophyceae depressed the percentages of Haptophyceae and *Gyrodinium*, DIN input favored *other Dino* resulting in approximately 5.79% lift per μM N for the whole DMSP group (column "Total" in Table S3). By contrast, DIN was greatly conducive to Haptophyceae in NPSG and exogenous N addition resulted in a large increase in relative abundance of DMSP genera (from ~5.3% to ~15.8%, Table S3), in which *Gyrodinium* (Dinophyceae), *Phaeocystis* and *Chrysochromulina* (Haptophyceae) were mostly promoted (CTRL vs. N). The percentages of DMSP genera were found to generally increase with the increasing DIN concentrations in the treatments for all three sites (Figure 3a-c). Specifically, this trend only occurred at day 3 with fluctuations in HN when the relative abundance of dominant diatoms declined (20~35%). DIN seemed to be an essential factor promoting the growth of marine DMSP producers. Practically, high N/P ratios and P deficiency caused by excess DIN input could create an appropriate environment for *Chrysochromulina* to outcompete other phytoplankton and bloom (Dahl et al., 2005; Maestrini & Graneli, 1991). Remarkably high N/P removal ratio by *Phaeocystis* was also determined when it reached a substantial abundance (Arrigo et al., 2002). These clades may not be able to compete with Diatoms and Trebouxiophyseae for DIN in the coastal regions but were largely stimulated by DIN input in the oligotrophic NPSG.

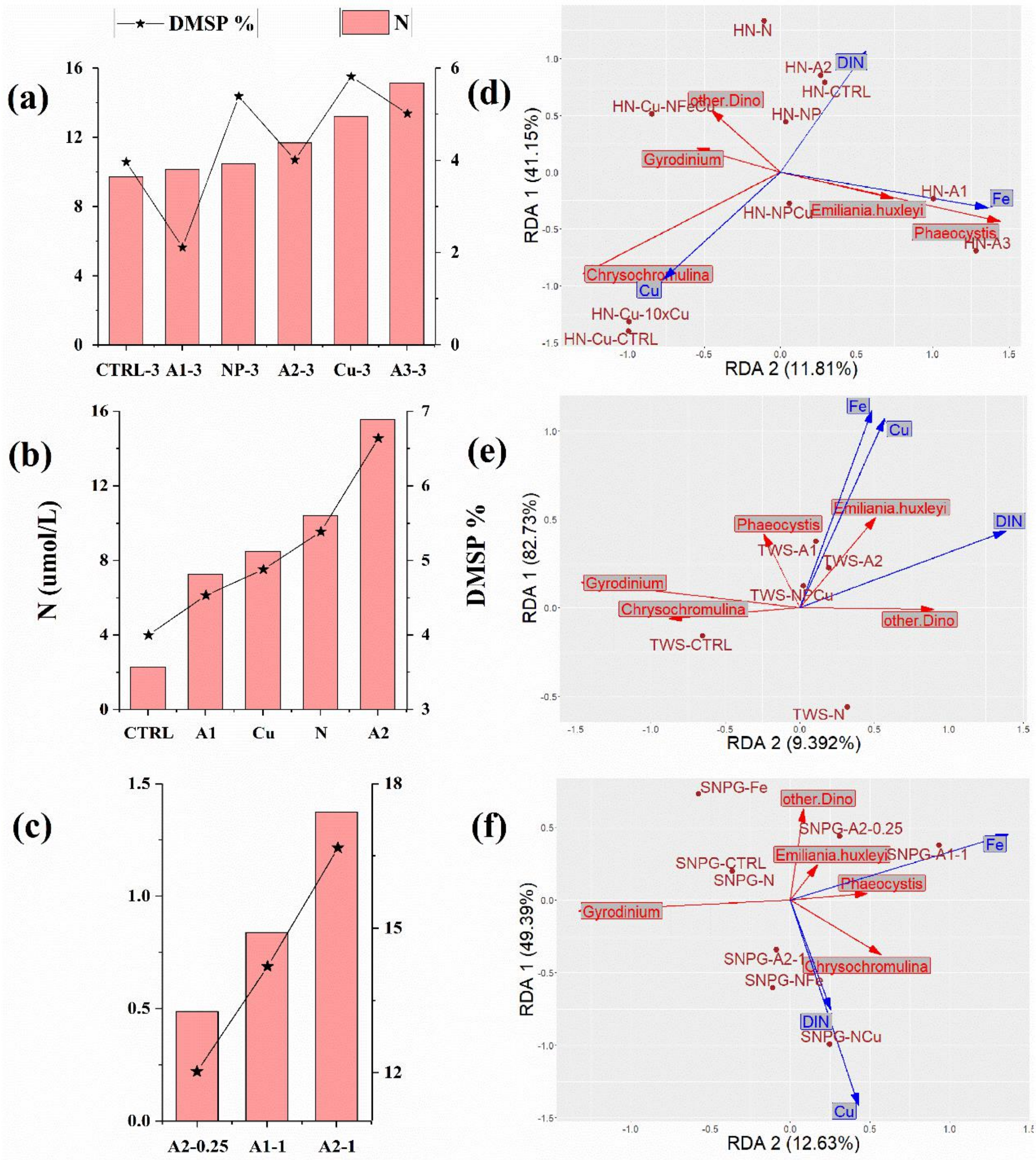

Figure 3. Increase of percentages of main DMSP producers with the increasing DIN concentrations in the late period (Day 3) of Huaniao Island (HN) (a) and on the *Chl a* peak days of Taiwan Strait (TWS) (b) and North Pacific Subtropical Gyre (NPSG) (c);

RDA plots of DMSP species, nutrients/metals and treatments in HN (d), TWS (e) and NPSG (f).

* as DMSP species struggled in the coastal HN, unlike relatively oligotrophic TWS and extreme sterile NPSG, we chose the late period of HN incubation to ensure their proportion. Three sites were illustrated separated because of their discrepant biomass and algae composition.

Metal impact

Atmospheric metals principally promoted Haptophyceae in our experiments. Haptophyceae was found to rise 4-7 and ~8% when adding soluble metals and aerosols (containing metals) to the NPSG surface water compared with the control. For the seawater collected near HN, Cu displayed noticeable stimulation to DMSP genera which increased to >2% in both HN-NPCu and HN-Cu-10xCu treatments (Table S3). Moderate Cu (1.6 nM) addition was beneficial to almost all main DMSP producers, but high Cu (16 nM) input only showed facilitation on *Chrysochromulina* (0.37% in HN-Cu-CTRL vs. 0.55% in HN-Cu-10xCu treatments). *E. huxleyi* was most frequently recorded in NPCu and aerosol treatments in TWS, and *Chrysochromulina* percentage was promoted by Cu addition in the NPSG region (N vs. NCu treatments). Overall, Haptophyceae increased 0.3% and 1.5% per nM Cu in HN (Day 1) and in NPSG (Day 2), respectively.

Redundancy Analysis (RDA) was used to investigate the relationships between added elements (including those in aerosols) and the relative abundances of main DMSP genera (Figure 3d-f). The statistic calculation verified that Cu strongly benefited *Chrysochromulina* meanwhile Fe was efficient in promoting *Phaeocystis* and *E. huxleyi* in HN (Figure 3d). In TWS, both Fe and Cu were found to stimulate the percentages of *Phaeocystis* and *E. huxleyi,* and DIN was potentially responsible for the percentage rise of *other Dino* (Figure 3e). DIN, Cu and Fe together mainly supported three Haptophyceae clades (*Chrysochromulina*, *Phaeocystis* and *E. huxleyi*) in NPSG (Figure 3f).

Chrysochromulina is an important DMSP species promoted by extremely high Cu input (16 nM) in HN and by atmospheric deposition of DIN and Cu in NPSG. It might be the most tolerant to high concentration of Cu among main DMSP producers, probably just second to some Diatoms (Croot et al., 1999). Additionally, a symbiotic association between *Chrysochromulina* and N-fixing cyanobacteria has been reported (Hagino et al., 2013). Cu was necessary in the synthesis of plastocyanin, which functioned in photosynthetic electron transport of cyanobacteria (Scanlan et al., 2009) and motivated them together. Meng et al. (2016) pointed out that mineral dust was valid in promoting Haptophyceae, thereof *Chrysochromulina* dominated. Aerosol Fe was also highly potential to benefit *Chrysochromulina*, since it was capable of directly digesting inorganic colloidal Fe with the acidic vacuoles (Barbeau et al., 1996; Nodwell & Price, 2001). Similar mechanism was found in the accumulation of Fe by

Phaeocystis through its colony mucus (Schoemann et al., 2005). Accordingly, *Phaeocystis* was closely associated with aerosol Fe in our experiments (Figure 3d-f). Coastal *E. huxleyi* (TWS) was less sensitive to Cu stress probably profited from a Cu‐efflux mechanism (Echeveste et al., 2018; Walsh & Ahner, 2014), and Fe was necessary in enhancing its carbon fixation and propagation (Rosario Lorenzo et al., 2018).

It could be inferred that main DMSP producers possess stronger competitiveness than Cyanobacteria for exogenous input of atmospheric materials in the oligotrophic oceans, quiet possibly benefited from their relatively larger cell sizes (5-20 μm, Franklin et al., 2010; Leadbeater & Manton, 1971) and generous nutrients uptake (Zhang et al., 2020). It was observed that Diatom (micro-phytoplankton), Dinoflagellate, *E.huxleyi* and pico-phytoplankton bloomed in sequence in response to their different maximal growth rates (Oguz & Merico, 2006). *E.huxleyi* could use the regenerated nutrients to grow after flourishing Diatom and Dinoflagellate in nutrient-rich coastal regions. Similarly, DMSP species rose significantly after the Diatom bloom in HN (Figure S7a), and surpassed Cyanobacteria (primarily comprised of pico- *prochlorococcus*) when aerosols were amended in NPSG (Figure S6c). Although Cyanobacteria growth (a dominant group in NPSG) could benefit from input of soluble Fe and Cu (NFe & NCu in Figure S6c), atmospheric deposition mainly stimulated Haptophyceae (aerosol treatments in Figure S6c). This probably resulted from the ability of utilizing colloidal Fe and particulate Cu by these DMSP species (Morris, 1971; Nodwell & Price, 2001; Schoemann et al., 2005), since most aerosol metals might not be directly bioavailable. In conclusion, atmospheric deposition could indeed elevate the proportion of main DMSP producers by supplying abundant nitrogen and metals, especially in those oligotrophic oceans.

4. summary

Haptophyceae are main producers of DMSP with *E. huxleyi*, *Chrysochromulina* and *Phaeocystis* three genera recorded as the most important DMSP sources in various oceans. *Gymnodinium* sp. belonging to Dinophyceae also contributes to a significant part of DMSP production. Our *in situ* bioassay experiments showed that there was an increasing trend in the relative abundance of these DMSP species from the most eutrophic HN (<1%) to TWS (4-7%) and to the oligotrophic NPSG (~17%). The percentage of DMSP producers in total phytoplankton biomass could be significantly promoted by input of DIN in NPSG (from ~5.3% to ~15.8%) but showed much less response in HN and TWS, which was probably attributed to the initially affluent DIN and overwhelming growth of other groups (e.g. Diatoms and Trebouxiophyceae) in the coastal region.

Atmospheric substances were suggested to exhibit stimulation on DMSP producers. Although aerosols had little effect in HN and TWS, metals (Cu & Fe) still showed preference to *Chrysochromulina*, *Phaeocystis* and *E. huxleyi*, and DIN was valid to elevate *other Dino*. These effects might be more prominent after bloom of predominant species triggered by episodic supplement of lacking nutrients. The remote NPSG offered a more pleasant environment for DMSP species, where atmospheric DIN and metals had remarkable promotion on them. Specifically, DIN, Cu and Fe mainly benefited *Phaeocystis* and *Chrysochromulina* whilst Fe alone promoted the relative abundance of *E. huxleyi*.

Overall, atmospheric deposition could hasten the growth of main DMSP producers in the oligotrophic oceans and subsequently enhance the production and emission of DMS from sea surface, generating climate effects on a large scale. With the intensive human activities and increasing deposition of atmospheric nitrogen and metals (e.g. Cu), these effects must be amplified. Even though DMSP species occupy only a small part of the entire phytoplankton community in coastal seas, the impact of atmospheric deposition on DMSP production should not be ignored in view of the much higher phytoplankton biomass (high *Chl a* concentration, Figure 1c-e) and stronger deposition.

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References

Allen, D. (2016). Attributing Atmospheric Methane to Anthropogenic Emission Sources. *Accounts of Chemical Research*, *49*(7), 1344–1350. https://doi.org/10.1021/acs.accounts.6b00081

Arrigo, K. R., Dunbar, R. B., Lizotte, M. P., & Robinson, D. H. (2002). Taxon-specific differences in C/P and N/P drawdown for phytoplankton in the Ross Sea, Antarctica. *Geophysical Research Letters*, *29*(19). https://doi.org/10.1029/2002GL015277

Barbeau, K., Moffett, J. W., Caron, D. A., Croot, P. L., & Erdner, D. L. (1996). Role of protozoan grazing in relieving iron limitation of phytoplankton. *Nature*, *380*(6569), 61–64. https://doi.org/10.1038/380061a0

Belviso, S., Christaki, U., Vidussi, F., Marty, J. C., Vila, M., & Delgado, M. (2000). Diel variations of the DMSP-to-chlorophyll a ratio in Northwestern Mediterranean surface waters. *Journal of Marine Systems*, *25*(2), 119–128. https://doi.org/10.1016/S0924-7963(00)00011-7

Brown, S. L., Landry, M. R., Selph, K. E., Jin Yang, E., Rii, Y. M., & Bidigare, R. R. (2008). Diatoms in the desert: Plankton community response to a mesoscale eddy in the subtropical North Pacific. *Deep-Sea Research Part II: Topical Studies in Oceanography*, *55*(10–13), 1321–1333. https://doi.org/10.1016/j.dsr2.2008.02.012

Browning, T. J., Achterberg, E. P., Rapp, I., Engel, A., Bertrand, E. M., Tagliabue, A., & Moore, C. M. (2017). Nutrient co-limitation at the boundary of an oceanic gyre. *Nature*. https://doi.org/10.1038/nature24063

Caruana, A. M. N., & Malin, G. (2014). The variability in DMSP content and DMSP lyase activity in marine dinoflagellates. *Progress in Oceanography*, *120*, 410–424. https://doi.org/10.1016/j.pocean.2013.10.014

Cassar, N., Bender, M. L., Barnett, B. A., Fan, S., Moxim, W. J., Levy, H., & Tilbrook, B. (2007). The southern ocean biological response to aeolian iron deposition. *Science*, *317*(5841), 1067–1070. https://doi.org/10.1126/science.1144602

Charlson, R. J., Lovelock, J. E., Andreae, M. O., & Warren, S. G. (1987). Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature*, *326*(6114), 655–661. https://doi.org/10.1038/326655a0

Chien, C. Te, Mackey, K. R. M., Dutkiewicz, S., Mahowald, N. M., Prospero, J. M., & Paytan, A. (2016). Effects of African dust deposition on phytoplankton in the western tropical Atlantic Ocean off Barbados. *Global Biogeochemical Cycles*. https://doi.org/10.1002/2015GB005334

Cho, S. H., Ji, S. C., Hur, S. B., Bae, J., Park, I. S., & Song, Y. C. (2007). Optimum temperature and salinity conditions for growth of green algae Chlorella ellipsoidea and Nannochloris oculata. *Fisheries Science*, *73*(5), 1050–1056. https://doi.org/10.1111/j.1444-2906.2007.01435.x

Croot, P. L., Karlson, B., Van Elteren, J. T., & Kroon, J. J. (1999). Uptake of 64Cu-oxine by marine phytoplankton. *Environmental Science and Technology*, *33*(20), 3615–3621. https://doi.org/10.1021/es9807901

Dahl, E., Bagøien, E., Edvardsen, B., & Stenseth, N. C. (2005). The dynamics of Chrysochromulina species in the Skagerrak in relation to environmental conditions. *Journal of Sea Research*, *54*(1 SPEC. ISS.), 15–24. https://doi.org/10.1016/j.seares.2005.02.004

Duce, R. A., LaRoche, J., Altieri, K., Arrigo, K. R., Baker, A. R., Capone, D. G., et al. (2008). Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science*. https://doi.org/10.1126/science.1150369

Echeveste, P., Croot, P., & von Dassow, P. (2018). Differences in the sensitivity to Cu and ligand production of coastal vs offshore strains of Emiliania huxleyi. *Science of the Total Environment*, *625*, 1673–1680. https://doi.org/10.1016/j.scitotenv.2017.10.050

Franklin, D. J., Steinke, M., Young, J., Probert, I., & Malin, G. (2010). Dimethylsulphoniopropionate (DMSP), DMSPlyase activity (DLA) and dimethylsulphide (DMS) in 10 species of coccolithophore. *Marine Ecology Progress Series*, *410*, 13–23. https://doi.org/10.3354/meps08596

Galí, M., & Simó, R. (2010). Occurrence and cycling of dimethylated sulfur compounds in the Arctic during summer receding of the ice edge. *Marine Chemistry*, *122*(1–4), 105–117. https://doi.org/10.1016/j.marchem.2010.07.003

Galí, M., Devred, E., Levasseur, M., Royer, S. J., & Babin, M. (2015). A remote sensing algorithm for planktonic dimethylsulfoniopropionate (DMSP) and an analysis of global patterns. *Remote Sensing of Environment*, *171*, 171–184. https://doi.org/10.1016/j.rse.2015.10.012

Gallisai, R., Peters, F., Volpe, G., Basart, S., & Baldasano, J. M. (2014). Saharan dust deposition may affect phytoplankton growth in the mediterranean sea at ecological time scales. *PLoS ONE*, *9*(10). https://doi.org/10.1371/journal.pone.0110762

Guo, S., Feng, Y., Wang, L., Dai, M., Liu, Z., Bai, Y., & Sun, J. (2014). Seasonal variation in the phytoplankton community of a continental-shelf sea: The East China Sea. *Marine Ecology Progress Series*, *516*, 103–126. https://doi.org/10.3354/meps10952

Hagino, K., Onuma, R., Kawachi, M., & Horiguchi, T. (2013). Discovery of an endosymbiotic nitrogen-fixing cyanobacterium UCYN-A in Braarudosphaera bigelowii (Prymnesiophyceae). *PLoS ONE*, *8*(12). https://doi.org/10.1371/journal.pone.0081749

Holligan, P. M., Fcrmindcz, E., Balch, W. M., Boyd, P., Peter, H., Finch, M., et al. (1993). A biogeochemical study of the coccolithophore, Emiliania huxleyi, in the North Atlantic. *Global Biogeochemical Cycles*, *7*(4), 879–900.

James, J. E., Tom, A., Jill, S. B., Ann-Kristin, B., Mats, J., Marcia, K., et al. (2009). Shifts in Lake N:P Stoichiometry and Nutrient Limitation Driven by Atmospheric Nitrogen Deposition. *Science*, *326*(5954), 835–837. https://doi.org/10.2307/1313296

Justić, D., Rabalais, N. N., Turner, R. E., & Dortch, Q. (1995). Changes in nutrient structure of river-dominated coastal waters: Stoichiometric nutrient balance and its consequences. *Estuarine, Coastal and Shelf Science*, *40*(3), 339–356. https://doi.org/10.1016/S0272-7714(05)80014-9

Kim, T. W., Lee, K., Najjar, R. G., Jeong, H. D., & Jeong, H. J. (2011). Increasing N abundance in the northwestern pacific ocean due to atmospheric nitrogen deposition. *Science*, *334*(6055), 505–509. https://doi.org/10.1126/science.1206583

Lana, A., Bell, T. G., Simó, R., Vallina, S. M., Ballabrera-Poy, J., Kettle, A. J., et al. (2011). An updated climatology of surface dimethlysulfide concentrations and emission fluxes in the global ocean. *Global Biogeochemical Cycles*, *25*(1). https://doi.org/10.1029/2010GB003850

Leadbeater, B. S. C., & Manton, I. (1971). Fine structure and light microscopy of a new species of Chrysochromulina (C. acantha). *Archiv Für Mikrobiologie*, *78*(1), 58–69. https://doi.org/10.1007/BF00409088

Leaitch, W. R., Sharma, S., Huang, L., Toom-Sauntry, D., Chivulescu, A., Macdonald, A. M., et al. (2013). Dimethyl sulfide control of the clean summertime Arctic aerosol and cloud. *Elementa*, *1*. https://doi.org/10.12952/journal.elementa.000017

Li, H., Chen, Y., Zhou, S., Wang, F., Yang, T., Zhu, Y., & Ma, Q. (2021). Change of dominant phytoplankton groups in the eutrophic coastal sea due to atmospheric deposition. *Science of the Total Environment*, *753*. https://doi.org/10.1016/j.scitotenv.2020.141961

Liu, H., Probert, I., Uitz, J., Claustre, H., Aris-Brosou, S., Frada, M., et al. (2009). Extreme diversity in noncalcifying haptophytes explains a major pigment paradox in open oceans. *Proceedings of the*

National Academy of Sciences of the United States of America, *106*(31), 12803–12808. https://doi.org/10.1073/pnas.0905841106

Lizotte, M., Levasseur, M., Michaud, S., Scarratt, M. G., Merzouk, A., Gosselin, M., et al. (2012). Macroscale patterns of the biological cycling of dimethylsulfoniopropionate (DMSP) and dimethylsulfide (DMS) in the Northwest Atlantic. *Biogeochemistry*, *110*(1–3), 183–200. https://doi.org/10.1007/s10533-011-9698-4

Mackey, K. R. M., Kavanaugh, M. T., Wang, F., Chen, Y., Liu, F., Glover, D. M., et al. (2017). Atmospheric and fluvial nutrients fuel algal blooms in the East China Sea. *Frontiers in Marine Science*, *4*(JAN). https://doi.org/10.3389/fmars.2017.00002

Maestrini, S. Y., & Graneli, E. (1991). Environmental conditions and ecophysiological mechanisms which led to the 1988 Chrysochromulina polylepis bloom: an hypothesis. *Oceanologica Acta*, *14*(4), 397–413.

Mahowald, N. M., Hamilton, D. S., Mackey, K. R. M., Moore, J. K., Baker, A. R., Scanza, R. A., & Zhang, Y. (2018). Aerosol trace metal leaching and impacts on marine microorganisms. *Nature Communications*, *9*(1). https://doi.org/10.1038/s41467-018-04970-7

Martin, J. H., Gordon, R. M., & Fitzwater, S. E. (1990). Iron in Antarctic waters. *Nature*, *345*(6271), 156–158. https://doi.org/10.1038/345156a0

Massana, R. (2011). Eukaryotic picoplankton in surface oceans. *Annual Review of Microbiology*, *65*, 91–110. https://doi.org/10.1146/annurev-micro-090110-102903

Meinrat O. Andreae, & Paul J. Crutzen. (1997). Atmospheric Aerosols: Biogeochemical Sources and Role in Atmospheric Chemistry. *Science*, *276*. Retrieved from http://web.gps.caltech.edu/classes/ge148c/Andreae and Crutzen (1997).pdf

Meng, X., Chen, Y., Wang, B., Ma, Q. W., & Wang, F. J. (2016). Responses of phytoplankton community to the input of different aerosols in the East China Sea. *Geophysical Research Letters*, *43*(13), 7081–7088. https://doi.org/10.1002/2016GL069068

Moisander, P. H., Zhang, R., Boyle, E. A., Hewson, I., Montoya, J. P., & Zehr, J. P. (2012). Analogous nutrient limitations in unicellular diazotrophs and Prochlorococcus in the South Pacific Ocean. *ISME Journal*, *6*(4), 733–744. https://doi.org/10.1038/ismej.2011.152

Moore, C. M., Mills, M. M., Arrigo, K. R., Berman-Frank, I., Bopp, L., Boyd, P. W., et al. (2013). Processes and patterns of oceanic nutrient limitation. *Nature Geoscience*, *6*(9), 701–710. https://doi.org/10.1038/ngeo1765

Morris, A. W. (1971). Trace metal variations in Sea water of the menai straits caused by a bloom of phaeocystis. *Nature*, *233*(5319), 427–428. https://doi.org/10.1038/233427a0

Nodwell, L. M., & Price, N. M. (2001). Direct use of inorganic colloidal iron by marine mixotrophic phytoplankton. *Limnology and Oceanography*, *46*(4), 765–777. https://doi.org/10.4319/lo.2001.46.4.0765

Oguz, T., & Merico, A. (2006). Factors controlling the summer Emiliania huxleyi bloom in the Black Sea: A modeling study. *Journal of Marine Systems*, *59*(3–4), 173–188. https://doi.org/10.1016/j.jmarsys.2005.08.002

Paytan, A., Mackey, K. R. M., Chen, Y., Lima, I. D., Doney, S. C., Mahowald, N., et al. (2009). Toxicity of atmospheric aerosols on marine phytoplankton. *Proceedings of the National Academy of Sciences of the United States of America*, *106*(12), 4601–4605. https://doi.org/10.1073/pnas.0811486106

Quinn, P. K., & Bates, T. S. (2011). The case against climate regulation via oceanic phytoplankton sulphur emissions. *Nature*, *480*(7375), 51–56. https://doi.org/10.1038/nature10580

Rap, A., Scott, C. E., Spracklen, D. V., Bellouin, N., Forster, P. M., Carslaw, K. S., et al. (2013). Natural aerosol direct and indirect radiative effects. *Geophysical Research Letters*, *40*(12), 3297–3301. https://doi.org/10.1002/grl.50441

Rii, Y. M., Bidigare, R. R., & Church, M. J. (2018). Differential responses of eukaryotic phytoplankton to nitrogenous nutrients in the North Pacific Subtropical Gyre. *Frontiers in Marine Science*, *5*(MAR). https://doi.org/10.3389/fmars.2018.00092

Rosario Lorenzo, M., Iñiguez, C., Egge, J. K., Larsen, A., Berger, S. A., García-Gómez, C., & Segovia, M. (2018). Increased CO2 and iron availability effects on carbon assimilation and calcification on the formation of Emiliania huxleyi blooms in a coastal phytoplankton community. *Environmental and Experimental Botany*, *148*, 47–58. https://doi.org/10.1016/j.envexpbot.2017.12.003

Royer, S. J., Levasseur, M., Lizotte, M., Arychuk, M., Scarratt, M. G., Wong, C. S., et al. (2010). Microbial dimethylsulfoniopropionate (DMSP) dynamics along a natural iron gradient in the northeast subarctic Pacific. *Limnology and Oceanography*, *55*(4), 1614–1626. https://doi.org/10.4319/lo.2010.55.4.1614

Scanlan, D. J., Ostrowski, M., Mazard, S., Dufresne, A., Garczarek, L., Hess, W. R., et al. (2009). Ecological Genomics of Marine Picocyanobacteria. *Microbiology and Molecular Biology Reviews*, *73*(2), 249–299. https://doi.org/10.1128/mmbr.00035-08

Schoemann, V., Becquevort, S., Stefels, J., Rousseau, V., & Lancelot, C. (2005). Phaeocystis blooms in the global ocean and their controlling mechanisms: A review. *Journal of Sea Research*, *53*(1-2 SPEC. ISS.), 43–66. https://doi.org/10.1016/j.seares.2004.01.008

Sun, Z., Li, G., Wang, C., Jing, Y., Zhu, Y., Zhang, S., & Liu, Y. (2014). Community dynamics of prokaryotic and eukaryotic microbes in an estuary reservoir. *Scientific Reports*, *4*, 6966. https://doi.org/10.1038/srep06966

Sunda, W. G. (2012). Feedback interactions between trace metal nutrients and phytoplankton in the ocean. *Frontiers in Microbiology*. https://doi.org/10.3389/fmicb.2012.00204

Tan, S. C., Shi, G. Y., Shi, J. H., Gao, H. W., & Yao, X. (2011). Correlation of Asian dust with chlorophyll and primary productivity in the coastal seas of China during the period from 1998 to 2008. *Journal of Geophysical Research: Biogeosciences*, *116*(2), 66–74. https://doi.org/10.1029/2010JG001456

Turner, S. M., Harvey, M. J., Law, C. S., Nightingale, P. D., & Liss, P. S. (2004). Iron-induced changes in oceanic sulfur biogeochemistry. *Geophysical Research Letters*, *31*(14). https://doi.org/10.1029/2004GL020296

Twining, B. S., & Baines, S. B. (2013). The Trace Metal Composition of Marine Phytoplankton. *Annual Review of Marine Science*, *5*(1), 191–215. https://doi.org/10.1146/annurev-marine-121211-172322

Uchida, A., Ooguri, T., Ishida, T., Kitaguchi, H., & Ishida, Y. (1996). Biosynthesis of Dimethylsulfoniopropionate in Crypthecodinium Cohnii (Dinophyceae). *Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds*, 97–107. https://doi.org/10.1007/978-1-4613-0377-0_9

Walsh, M. J., & Ahner, B. A. (2014). Copper export contributes to low copper levels and copper tolerance in Emiliania huxleyi. *Limnology and Oceanography*, *59*(3), 827–839. https://doi.org/10.4319/lo.2014.59.3.0827

Weller, D. I., Law, C. S., Marriner, A., Nodder, S. D., Chang, F. H., Stephens, J. A., et al. (2013). Temporal variation of dissolved methane in a subtropical mesoscale eddy during a phytoplankton bloom in the southwest Pacific Ocean. *Progress in Oceanography*, *116*, 193–206. https://doi.org/10.1016/j.pocean.2013.07.008

Wu, J., Boyle, E., Sunda, W., & Wen, L. S. (2001). Soluble and colloidal iron in the oligotrophic North Atlantic and North Pacific. *Science*, *293*(5531), 847–849. https://doi.org/10.1126/science.1059251

Zhang, C., Gao, H., Yao, X., Shi, Z., Shi, J., Yu, Y., et al. (2018). Phytoplankton growth response to Asian dust addition in the northwest Pacific Ocean versus the Yellow Sea. *Biogeosciences*, *15*(3), 749–765. https://doi.org/10.5194/bg-15-749-2018

Zhang, C., He, J., Yao, X., Mu, Y., Guo, X., Ding, X., et al. (2020). Dynamics of phytoplankton and nutrient uptake following dust additions in the northwest Pacific. *Science of the Total Environment*, *739*. https://doi.org/10.1016/j.scitotenv.2020.139999

Zhong, Y., Liu, X., Xiao, W., Laws, E. A., Chen, J., Wang, L., et al. (2020). Phytoplankton community patterns in the Taiwan Strait match the characteristics of their realized niches. *Progress in Oceanography*, *186*. https://doi.org/10.1016/j.pocean.2020.102366

Zou, H. X., Pang, Q. Y., Zhang, A. Q., Lin, L. D., Li, N., & Yan, X. F. (2015). Excess copper induced proteomic changes in the marine brown algae Sargassum fusiforme. *Ecotoxicology and Environmental Safety*, *111*, 271–280. https://doi.org/10.1016/j.ecoenv.2014.10.028

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Supporting Information methods for

Atmospheric deposition promotes relative abundance of main dimethylsulfoniopropionate producers in the western North Pacific

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Method S1. Water sampling, nutrient and aerosol amendments and incubation.

To avoid vessel and other metal contamination as much as possible, we sailed out a wooden boat (Huaniao) or reached the HDPE water pipe out about 3 meters from the gunwale tied on a fishing rod, with a ceramic plumb hanging on the end (cruise). On the island, we filled up the 50 L carboys using plastic buckets and funnels, while during the cruise, the air compressor (Jiebao, 8BAR) and diaphragm pump (Wilden, P100/PVDF+Teflon, USA) were introduced to pump water up. All sampled water was covered with black bags and filtered through 150 um nylon mesh tied to the faucet of carboys before experiments, removing larger zooplankton. After dividing into PP cubitainers (Paerl et al., 1990) or HDPE culture bottles and adding nutrient solutions or aerosol extracts, these marked treatments were soaked in the seawater (Huaniao: tied on the ropes fixed by fish rafts; cruise: floated in a cistern equipped with cyclic ballast seawater) and covered with a gray screen to weaken the sunlight intensity, simulating the light condition in the surface layer. In the laboratory, the illumination time and temperature were controlled to mimic the change of day and night. All the apparatuses used in the experiments, including pipes, carboys, cubitainers, measuring cylinder, etc. were dipped and washed with 0.2 M ultrapure HCl and then rinsed twice with MilliQ water in the laboratory before; and finally rinsed by sampled seawater when dividing initial water.

$(NH_4)_2SO_4$ (NH_4^+), $NaNO_3$ (NO_3^-), KH_2PO_4 (PO_4^{3-}) and Cu/Fe standard solution (ShijiAoke Biotechnology co. LTD, Beijing, China) were used for preparing the stock solutions of nutrients. Aerosols were previously sampled at Huaniao and analyzed by

Ion Chromatography (ICS3000, DIONEX, for determination of ions) and Inductively Coupled Plasma Optical Emission Spectroscopy (SPECTRO, Germany, for detection of total and soluble elements). Backward trajectories were applied for further analysis (HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model from the NOAA Air Resource Lab). Aerosol membranes were cut into small pieces and ultrasonicated within MilliQ water for 40 min, acquiring the supernate and stored at 4°C. Extracts were usually prepared just before division and addition.

References

Paerl, H.W., Rudek, J., Mallin, M.A., 1990. Stimulation of phytoplankton production in coastal waters by natural rainfall inputs: Nutritional and trophic implications. Mar. Biol. 107, 247–254. https://doi.org/10.1007/BF01319823

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Geophysical Research Letters

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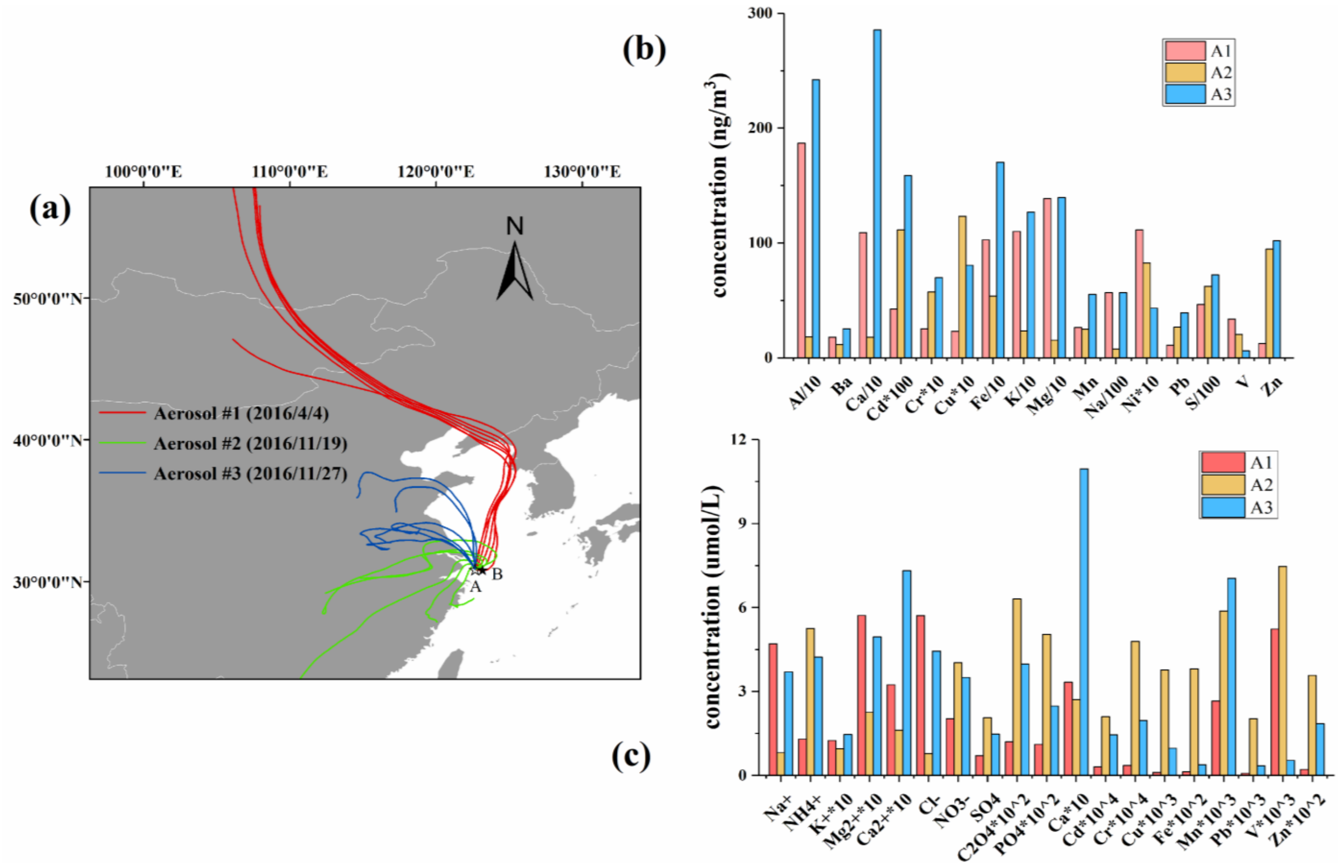

Figure S1-1. The (a) air mass back trajectories; (b) composition; (c) additive concentration of soluble elements of three aerosols used in Huaniao Island (HN). (a-A: aerosol sampling site; a-B: water sampling site)

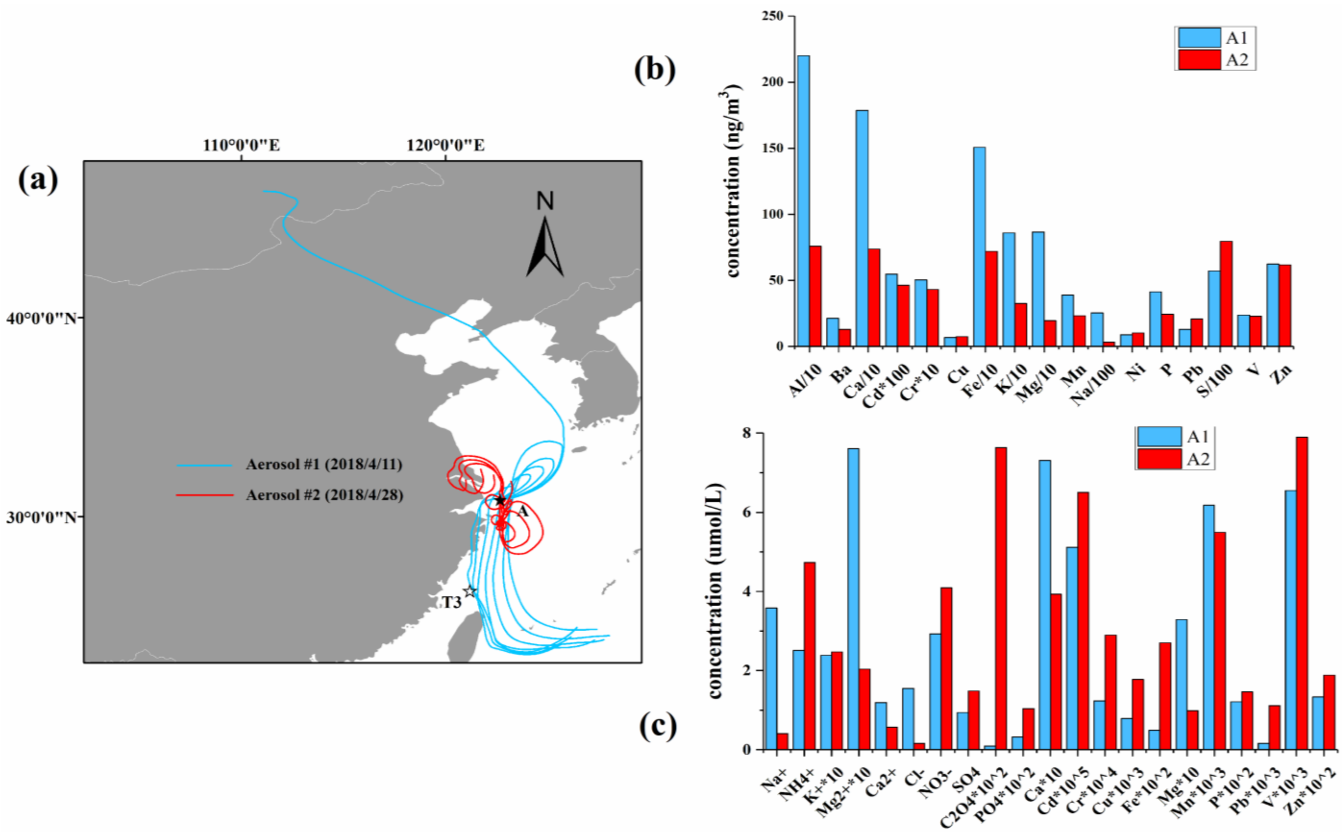

Figure S1-2. The (a) air mass back trajectories; (b) composition; (c) additive concentration of soluble elements of aerosols used in Taiwan Strait (TWS). (a-A: aerosol sampling site; a-T3: water sampling site)

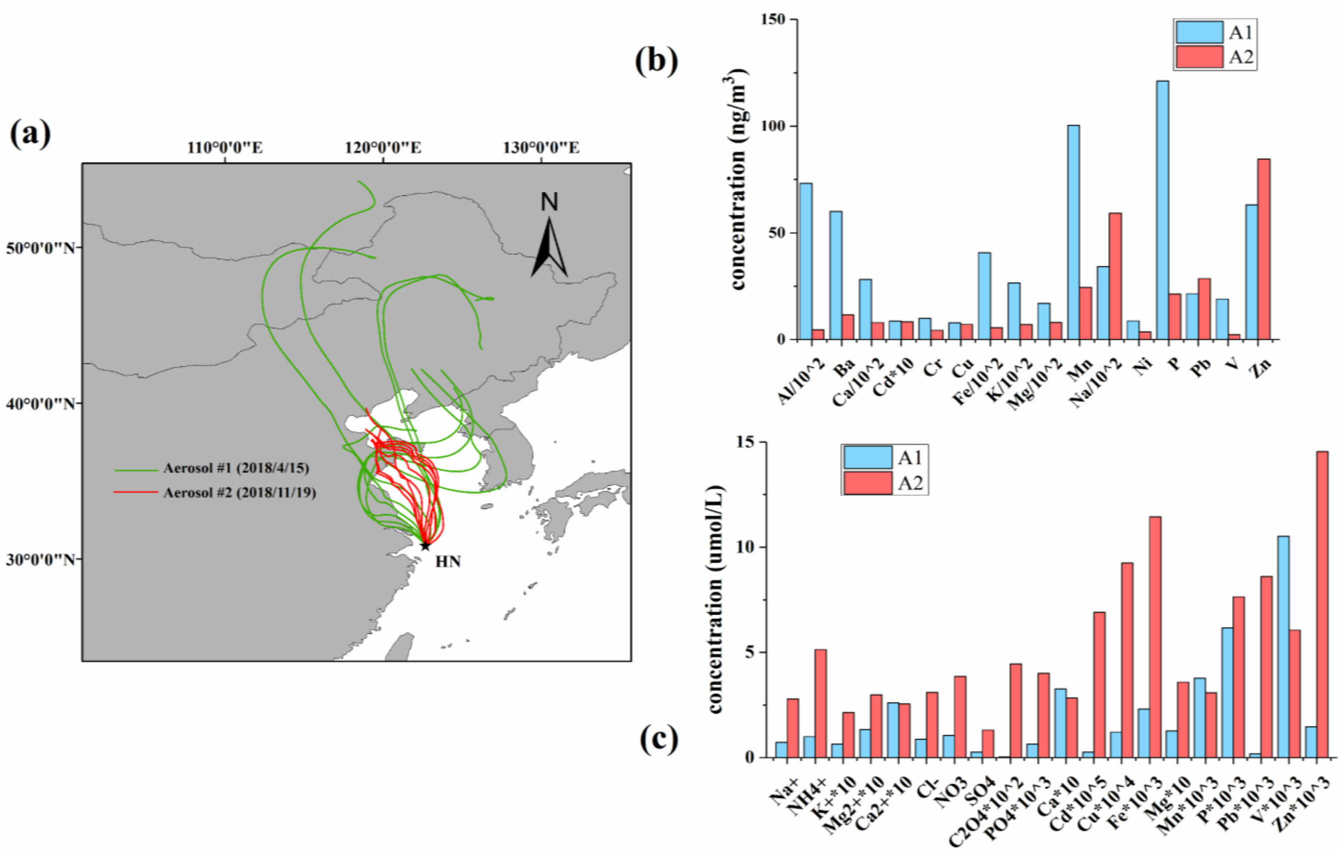

Figure S1-3. The (a) air mass back trajectories; (b) composition; (c) additive concentration of soluble elements of aerosols used in North Pacific Subtropical Gyre (NPSG).

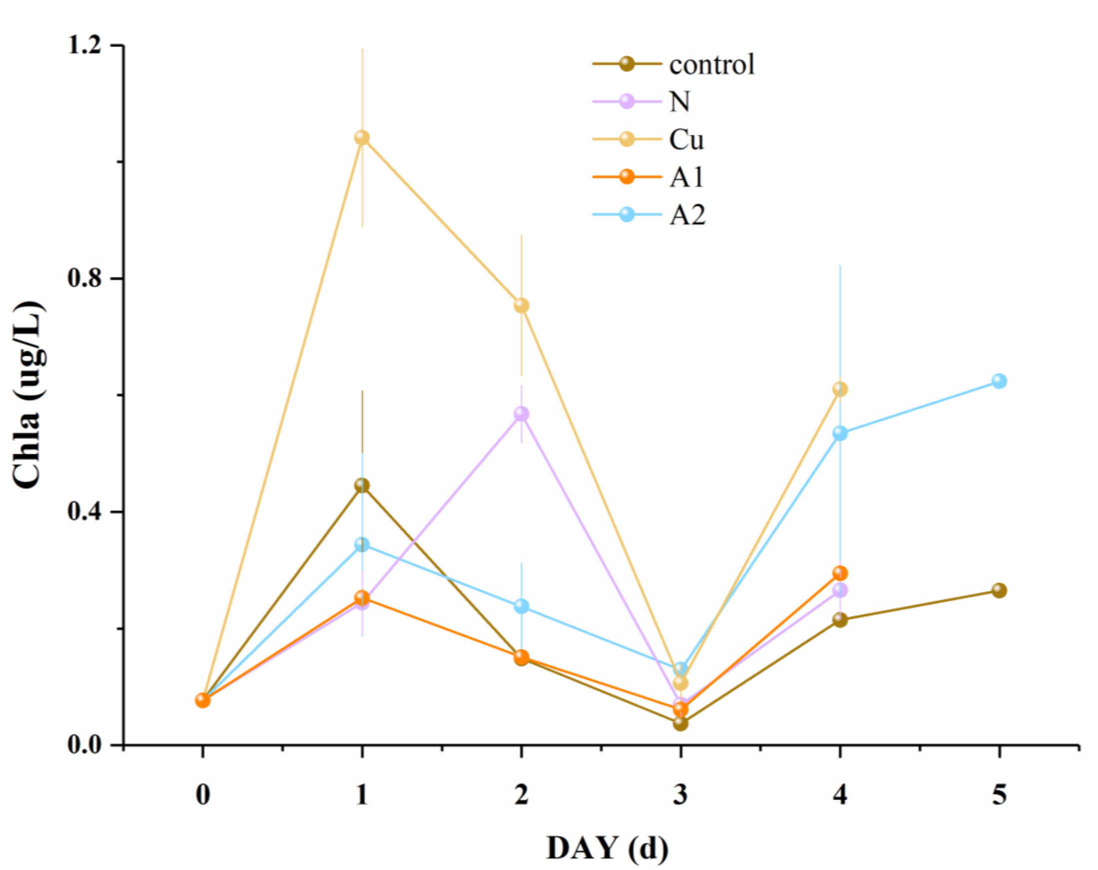

Figure S2. Variation of *Chl a* concentrations in different treatments of the bioassay experiment in Taiwan Strait (TWS).

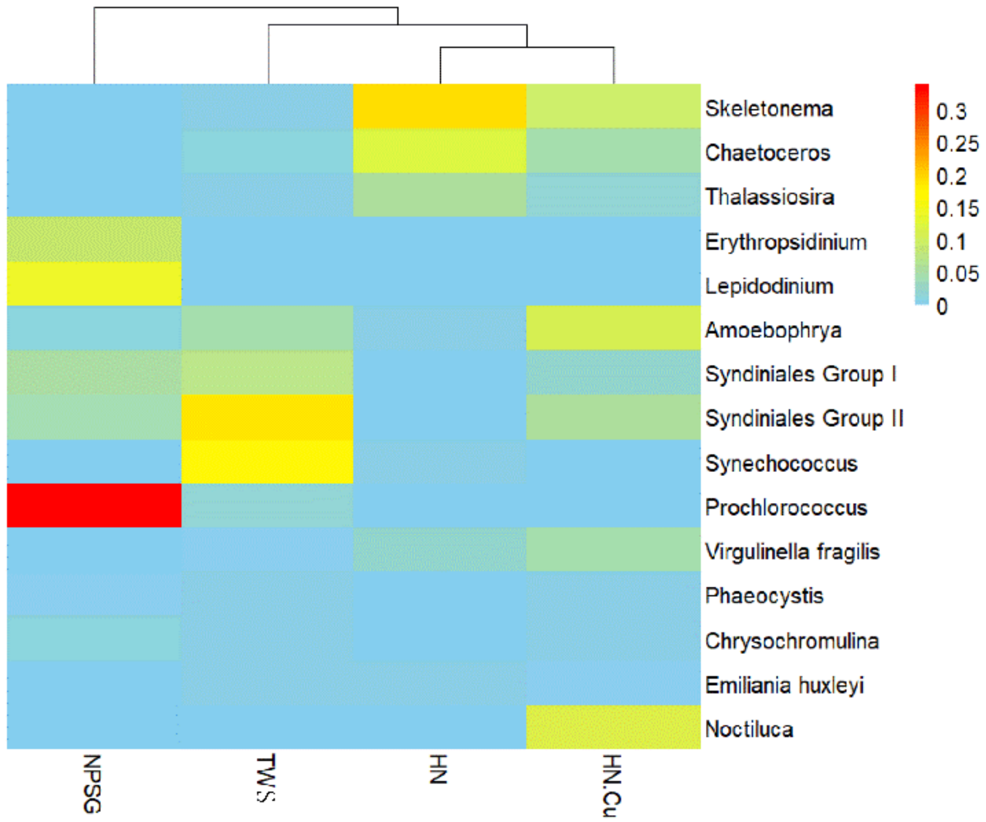

Figure S3. Relative abundance of different taxa on species level in the initial seawaters used for the bioassay experiments at Huaniao lab (HN.Cu), Huaniao Island (HN), Taiwan Strait (TWS) and North Pacific Subtropical Gyre (NPSG).

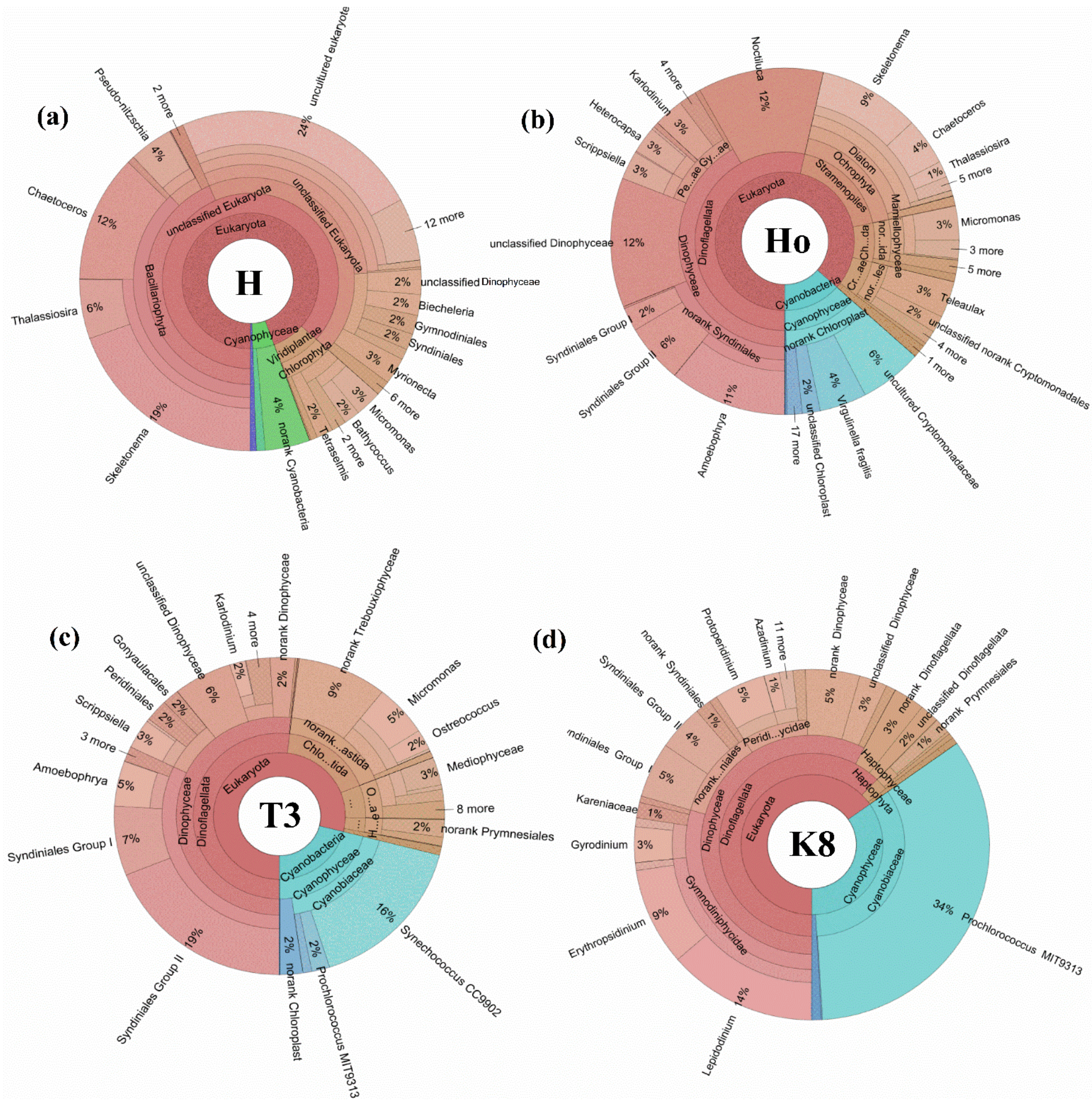

Figure S4. The community composition of initial seawaters in (a) Huaniao Island (H); (b) Huaniao Lab (Ho); (c) Taiwan Strait (T3); (d) North Pacific Subtropical Gyre (K8).

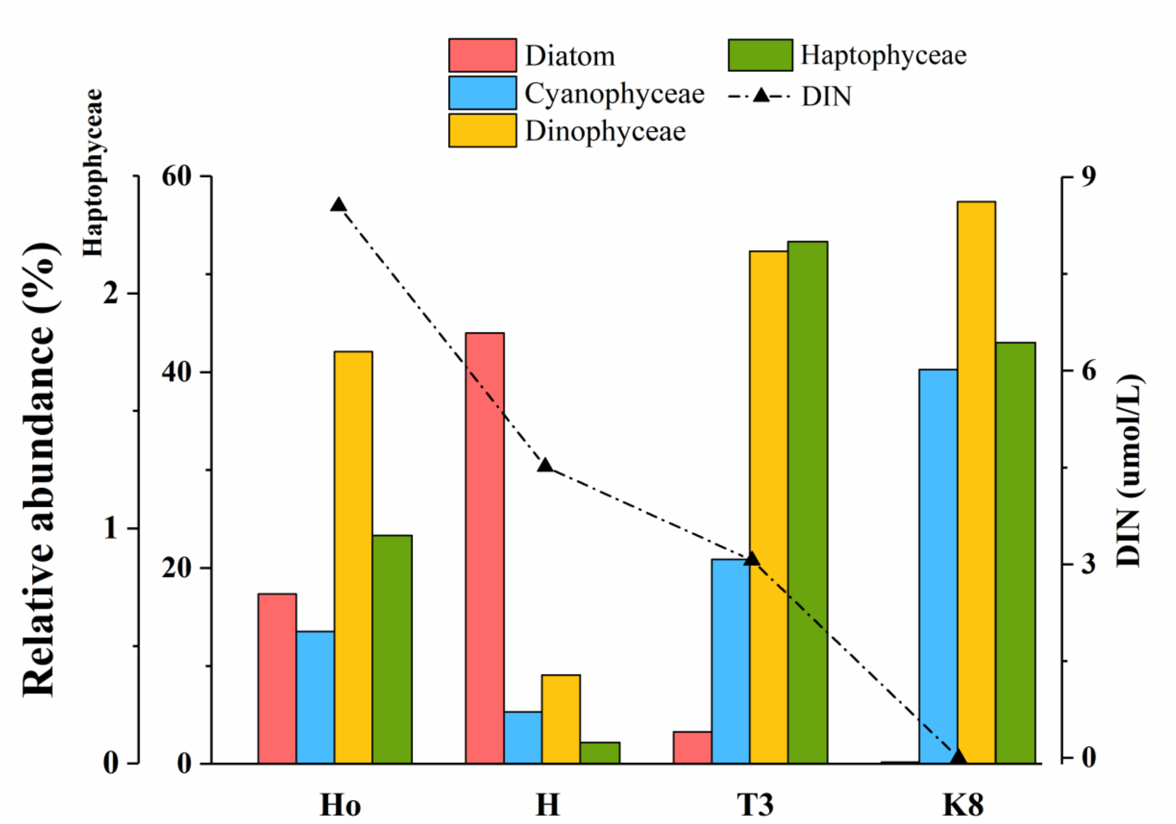

Figure S5. Relative abundances of prime algae classes and DIN concentrations in the initial seawaters sampled from Huaniao Lab (Ho), Huaniao Island (H), Taiwan Strait (T3) and North Pacific Subtropical Gyre (K8).

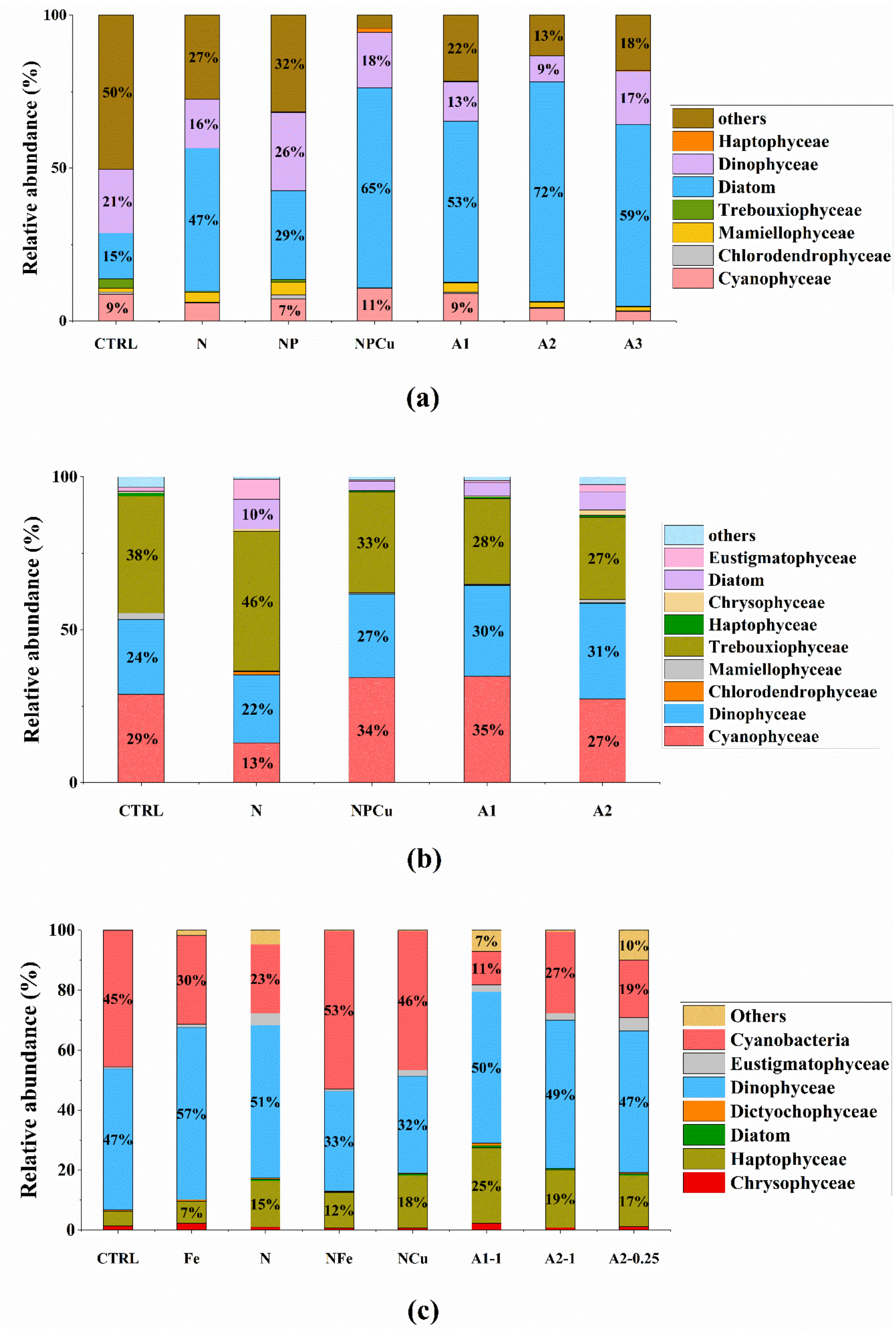

Figure S6. Relative abundances of dominant phytoplankton groups in different treatments during the bioassay experiments at (a) Huaniao Island (HN), (b) Taiwan Strait (TWS), and (c) North Pacific Subtropical Gyre (NPSG).

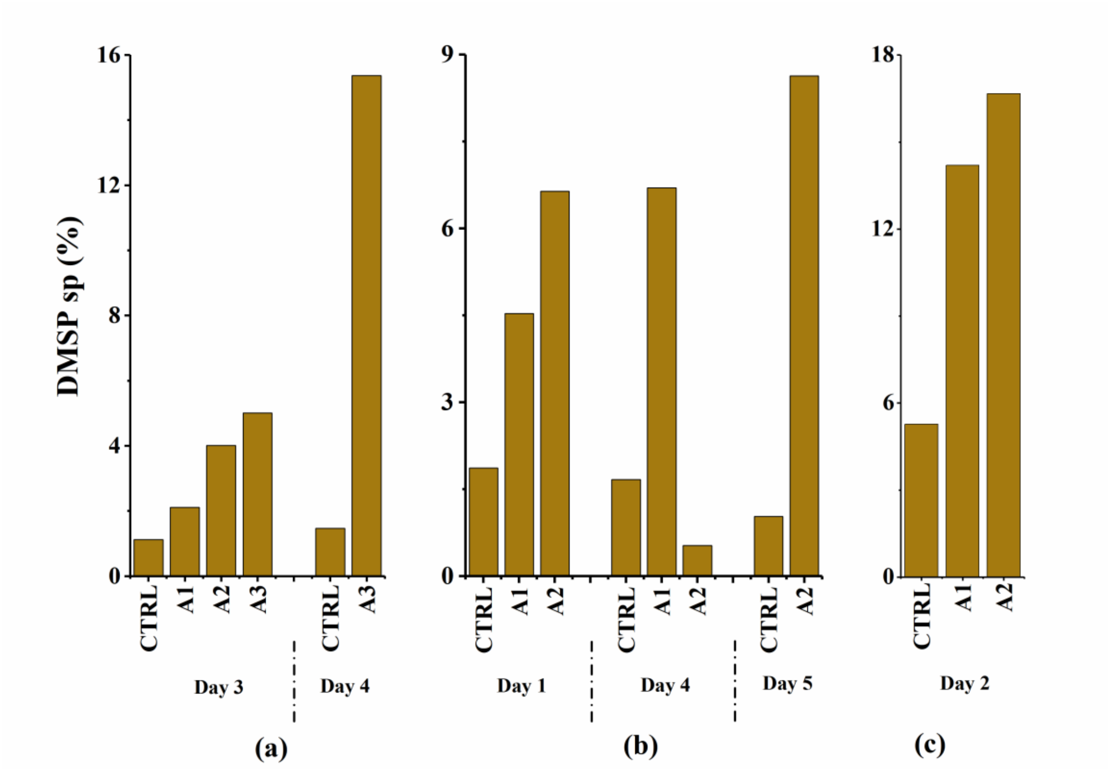

Figure S7. Percentages of DMSP species in the control (CTRL) and aerosol treatments in the late period (after 3 days) of HN (a), in both early and late periods (Day 1, 4 & 5) of TWS (b) and at the maximum *Chl a* (Day 2) of NPSG incubation (c)

Table S1. The release concentrations of DMSP by phytoplankton on cultures (Keller et al., 1989).

class	species	pg DMSP/cell	uM DMSP/cm3 CV
Dinophyceae	Gymnodinium sp.	24	124.63
Haptophyceae	*Chrysochromulina*	3.62	412.69
	Emiliania huxleyi	0.75	166.42
	Phaeocystis sp.	2.29	260.45

Table S2. Basic information of four bioassay experiments. (all aerosols used were sampled at Huaniao Island)

	date	water sampling	incubation	aerosols
HN	2018.5.4	30°52'N, 122°40'E; N/P=26.18	*in situ*	Aerosol #1 2016.4.4 Aerosol #2 2016.11.19 Aerosol #3 2016.11.27
HN Lab	2019.4.6	30°50'N, 123°10'E; N/P=43.03	laboratory	-
TWS	2018.7.14	26°17'N, 121°12'E; N/P=18.10	*in situ*	Aerosol #1 2018.4.11 Aerosol #2 2018.4.28
NPSG	2019.5.28	11°N, 155°E; DIN BDL *	*in situ*	Aerosol #1 2018.4.15 Aerosol #2 2018.11.19

* DIN concentration below the detection limit 0.1 umol/L.

Table S3. Relative abundance of high DMSP production associated species (primarily Dinophyceae and Haptophyceae) in different treatments of the bioassay experiments conducted at Huaniao Island (HN), Taiwan Strait (TWS) and North Pacific Subtropical Gyre (NPSG).

	Dinophyceae		Haptophyceae			Total
	Gyrodinium	*other Dino **	*Phaeocystis*	*Chrysochromulina*	*Emiliania huxleyi*	
HN-CTRL	0.00%	0.54%	0.03%	0.00%	0.06%	0.63%
HN-N	0.00%	0.53%	0.01%	0.00%	0.01%	0.54%
HN-NP	0.00%	0.89%	0.05%	0.01%	0.06%	1.01%
HN-NPCu	0.28%	1.50%	0.28%	0.07%	0.25%	2.38%
HN-A1	0.00%	0.32%	0.12%	0.00%	0.07%	0.51%
HN-A2	0.00%	0.15%	0.01%	0.00%	0.01%	0.17%
HN-A3	0.00%	0.29%	0.20%	0.00%	0.08%	0.57%
HN-Cu-CTRL	0.03%	0.92%	0.04%	0.37%	0.03%	1.39%
HN-Cu-NFeCu	0.05%	1.24%	0.01%	0.08%	0.01%	1.39%
HN-Cu-10xCu	0.03%	1.47%	0.05%	0.55%	0.05%	2.15%
TWS-CTRL	1.52%	1.87%	0.07%	0.54%	0.00%	4.00%
TWS-N	0.11%	5.21%	0.00%	0.02%	0.04%	5.38%
TWS-NPCu	0.53%	4.09%	0.07%	0.09%	0.11%	4.88%

TWS-A1	0.43%	3.80%	0.10%	0.02%	0.18%	4.53%
TWS-A2	0.28%	5.82%	0.09%	0.14%	0.32%	6.64%
NPSG-CTRL	2.16%	0.67%	0.39%	2.06%	0.00%	5.27%
NPSG-Fe	3.31%	1.01%	0.66%	1.78%	0.02%	6.78%
NPSG-N	6.91%	1.30%	2.60%	4.90%	0.05%	15.76%
NPSG-NFe	3.52%	0.40%	1.53%	4.52%	0.00%	9.98%
NPSG-NCu	2.97%	0.28%	2.09%	6.97%	0.00%	12.32%
NPSG-A1-1	1.03%	1.88%	3.54%	7.64%	0.12%	14.20%
NPSG-A2-1	5.64%	1.12%	2.23%	7.68%	0.00%	16.67%
NPSG-A2-0.25	2.58%	1.69%	2.36%	5.34%	0.05%	12.02%

* *other Dino* contains Symbiodinium sp., *Alexandrium minutum*, Prorocentrum sp., *Gyrodinium impudicum*, *Scrippsiella*, *Dinophysis acuminata*, *Heterocapsa pygmaea*, *Amphidinium carterae*, *Crypthecodinium cohnii*, *Heterocapsa triquetra*, *Gymnodinium nelson*, *Alexandrium tamarense*, *Thoracosphaera heimii*, Gymnodinium sp., *Gonyaulax spinifera*, etc. (Caruana and Malin, 2014)

Appended Table. Relative abundance of high DMSP production associated species (class) in the late period of HN incubation.

	CTRL	A1	A2	A3
Haptophyceae	24.17%	61.89%	24.69%	15.37%
Dinophyceae	72.41%	20.16%	62.61%	81.16%
other	3.43%	17.96%	12.70%	3.47%

Table S4. Concentration of important total elements and ions and classification of aerosols used in bioassay experiments.

	possible sources		HN			TWS		NPSG	
			A1	A2	A3	A1	A2	A1	A2
total elements (ng/m3)	dust	Al	1869.595	181.662	2419.583	2199.673	758.496	7325.567	456.758
		Ca	1090.186	178.837	2854.493	1786.467	737.002	2811.971	794.180
		Fe	1027.774	536.818	1701.107	1507.556	719.439	4073.124	550.022
		Mn	26.433	25.036	55.304	39.020	23.129	100.394	24.474
	vehicles	Cd	0.425	1.113	1.587	0.547	0.464	0.862	0.834
		Cu	2.311	12.336	8.061	6.670	7.331	7.843	7.095
		Zn	12.614	94.727	101.897	62.278	61.702	63.144	84.500
	industry	Pb	10.964	26.636	39.265	12.819	20.789	21.390	28.559
	vessels	V	33.816	20.394	6.170	23.678	22.924	18.988	2.284
ions (ug/m3)	marine	Na^+	10.589	0.872	5.437	3.658	0.721	3.262	5.542
		Mg^{2+}	1.342	0.254	0.760	0.810	0.374	0.628	0.619
		Cl^-	19.848	1.304	10.079	4.885	0.442	6.052	9.510
	anthropogenic	NH_4^+	2.285	4.448	4.859	4.014	6.524	3.510	8.000

NO_3^-	12.269	11.740	13.846	16.128	19.414	12.817	20.733
SO_4^{2-}	6.628	9.298	9.051	8.001	10.905	5.019	10.917
$C_2O_4^{2-}$	0.103	0.261	0.224	0.007	0.514	0.005	0.339
classification	dust + marine	urban pollution	soil dust (urban) + anthropogenic pollutants	dust + marine	urban pollution	dust	marine + anthropogenic pollutants

Table S5. Diversity index (Shannon & Simpson index) of different treatments.

Treatments	shannon	simpson
HN-CTRL	4.8233	0.9325
HN-N	4.3215	0.8995
HN-NP	5.4179	0.9559
HN-NPCu	3.7827	0.7937
HN-A1	3.8864	0.8348
HN-A2	4.4521	0.8466
HN-A3	4.3712	0.8846
HN-Cu-CTRL	3.7863	0.8310
HN-Cu-NFeCu	3.5111	0.8029
HN-Cu-10xCu	4.5050	0.9073
TWS-CTRL	3.7223	0.7931
TWS-N	3.6339	0.7732
TWS-NPCu	3.7053	0.8035
TWS-A1	4.0108	0.8354
TWS-A2	4.4927	0.8728
NPSG-CTRL	5.2044	0.9308
NPSG-Fe	4.8032	0.8763
NPSG-N	5.6090	0.9518
NPSG-NFe	4.9064	0.9167
NPSG-NCu	5.3510	0.9543
NPSG-A1-1	5.9617	0.9744
NPSG-A2-1	5.6555	0.9663
NPSG-A2-0.25	5.8608	0.9673

Table S6. Relative abundance of DMSP species in aerosol treatments in the early and late period of incubation in HN and TWS.

	early	DMSP species	late	DMSP species
HN	A1-D1	0.51%	A1-D3	2.11%
	A2-D1	0.17%	A2-D3	4.01%
	A3-D1	0.57%	A3-D3	5.01%
			A3-D4	15.36%
TWS	A1-D1	4.53%	A1-D4	6.70%
	A2-D1	6.64%	A2-D5	8.63%

References

Caruana, A.M.N., Malin, G., 2014. The variability in DMSP content and DMSP lyase activity in marine dinoflagellates. Prog. Oceanogr. 120, 410–424. https://doi.org/10.1016/j.pocean.2013.10.014

Keller, M.D., Bellows, W.K., Guillard, R.R.L., 1989. Dimethyl Sulfide Production in Marine Phytoplankton 167–182. https://doi.org/10.1021/bk-1989-0393.ch011

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Zhong, Y., Liu, X., Xiao, W., Laws, E.A., Chen, J., Wang, L., Liu, S., Zhang, F., Huang, B., 2020. Phytoplankton community patterns in the Taiwan Strait match the characteristics of their realized niches. Prog. Oceanogr. 186. https://doi.org/10.1016/j.pocean.2020.102366

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NPSG-A2-1	5.64%	1.12%	2.23%	7.68%	0.00%	16.67%
NPSG-A2-0.25	2.58%	1.69%	2.36%	5.34%	0.05%	12.02%

* *other Dino* contains Symbiodinium sp., *Alexandrium minutum*, Prorocentrum sp., *Gyrodinium impudicum*, *Scrippsiella*, *Dinophysis acuminata*, *Heterocapsa pygmaea*, *Amphidinium carterae*, *Crypthecodinium cohnii*, *Heterocapsa triquetra*, *Gymnodinium nelson*, *Alexandrium tamarense*, *Thoracosphaera heimii*, Gymnodinium sp., *Gonyaulax spinifera*, etc. (Caruana and Malin, 2014)

Appended Table. Relative abundance of high DMSP production associated species (class) in the late period of HN incubation.

	CTRL	A1	A2	A3
Haptophyceae	24.17%	61.89%	24.69%	15.37%
Dinophyceae	72.41%	20.16%	62.61%	81.16%
other	3.43%	17.96%	12.70%	3.47%

Table S4. Concentration of important total elements and ions and classification of aerosols used in bioassay experiments.

	possible sources		HN A1	HN A2	HN A3	TWS A1	TWS A2	NPSG A1	NPSG A2
total elements (ng/m3)	dust	Al	1869.595	181.662	2419.583	2199.673	758.496	7325.567	456.758
		Ca	1090.186	178.837	2854.493	1786.467	737.002	2811.971	794.180
		Fe	1027.774	536.818	1701.107	1507.556	719.439	4073.124	550.022
		Mn	26.433	25.036	55.304	39.020	23.129	100.394	24.474
	vehicles	Cd	0.425	1.113	1.587	0.547	0.464	0.862	0.834
		Cu	2.311	12.336	8.061	6.670	7.331	7.843	7.095
		Zn	12.614	94.727	101.897	62.278	61.702	63.144	84.500
	industry	Pb	10.964	26.636	39.265	12.819	20.789	21.390	28.559
	vessels	V	33.816	20.394	6.170	23.678	22.924	18.988	2.284
ions (ug/m3)	marine	Na^+	10.589	0.872	5.437	3.658	0.721	3.262	5.542
		Mg^{2+}	1.342	0.254	0.760	0.810	0.374	0.628	0.619
		Cl^-	19.848	1.304	10.079	4.885	0.442	6.052	9.510
	anthropogenic	NH_4^+	2.285	4.448	4.859	4.014	6.524	3.510	8.000

NO_3^-	12.269	11.740	13.846	16.128	19.414	12.817	20.733
SO_4^{2-}	6.628	9.298	9.051	8.001	10.905	5.019	10.917
$C_2O_4^{2-}$	0.103	0.261	0.224	0.007	0.514	0.005	0.339
classification	dust + marine	urban pollution	soil dust (urban) + anthropogenic pollutants	dust + marine	urban pollution	dust	marine + anthropogenic pollutants

Table S5. Diversity index (Shannon & Simpson index) of different treatments.

Treatments	shannon	simpson
HN-CTRL	4.8233	0.9325
HN-N	4.3215	0.8995
HN-NP	5.4179	0.9559
HN-NPCu	3.7827	0.7937
HN-A1	3.8864	0.8348
HN-A2	4.4521	0.8466
HN-A3	4.3712	0.8846
HN-Cu-CTRL	3.7863	0.8310
HN-Cu-NFeCu	3.5111	0.8029
HN-Cu-10xCu	4.5050	0.9073
TWS-CTRL	3.7223	0.7931
TWS-N	3.6339	0.7732
TWS-NPCu	3.7053	0.8035
TWS-A1	4.0108	0.8354
TWS-A2	4.4927	0.8728
NPSG-CTRL	5.2044	0.9308
NPSG-Fe	4.8032	0.8763
NPSG-N	5.6090	0.9518
NPSG-NFe	4.9064	0.9167
NPSG-NCu	5.3510	0.9543
NPSG-A1-1	5.9617	0.9744
NPSG-A2-1	5.6555	0.9663
NPSG-A2-0.25	5.8608	0.9673

Table S6. Relative abundance of DMSP species in aerosol treatments in the early and late period of incubation in HN and TWS.

	early	DMSP species	late	DMSP species
HN	A1-D1	0.51%	A1-D3	2.11%
	A2-D1	0.17%	A2-D3	4.01%
	A3-D1	0.57%	A3-D3	5.01%
			A3-D4	15.36%
TWS	A1-D1	4.53%	A1-D4	6.70%
	A2-D1	6.64%	A2-D5	8.63%

References

Caruana, A.M.N., Malin, G., 2014. The variability in DMSP content and DMSP lyase activity in marine dinoflagellates. Prog. Oceanogr. 120, 410–424. https://doi.org/10.1016/j.pocean.2013.10.014

Keller, M.D., Bellows, W.K., Guillard, R.R.L., 1989. Dimethyl Sulfide Production in Marine Phytoplankton 167–182. https://doi.org/10.1021/bk-1989-0393.ch011