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Characteristics and emissions of isoprene and other non-methane hydrocarbons in the Northwest Pacific Ocean and responses to atmospheric aerosol deposition



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HIGHLIGHTS

· The ocean currents affected the NMHCs

promoted NMHCs formation.

by controlling the hydrographic features. • The Kuroshio-Oyashio Extension mainly

Variations in phytoplankton by aerosol

deposition accelerated isoprene produc-

The Northwest Pacific Ocean was a signif-

icant source of atmospheric NMHCs.

GRAPHICAL ABSTRACT



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ABSTRACT

Field investigations in the Northwest Pacific Ocean were carried out to determine the distributions of marine and atmospheric non-methane hydrocarbons (NMHCs), sources and environmental effects. We also conducted deck incubation experiments to investigate the effects of atmospheric aerosol deposition on NMHCs production. The marine NMHCs displayed an increasing trend from the South Equatorial Current to the Oyashio Current. The enhanced phytoplankton biomass and dissolved organic materials (DOM) content in the Kuroshio-Oyashio Extension contributed significantly to isoprene and NMHCs production compared with those in tropical waters and the North Pacific subtropical gyre. The Northwest Pacific Ocean was a significant source of atmospheric NMHCs, with average sea-to-air fluxes of 28.0 \pm 38.9, 65.2 \pm 73.3, 21.0 \pm 26.7, 48.7 \pm 62.6, 12.7 \pm 15.9, 14.2 \pm 16.8, and 41.7 \pm 80.4 nmol m⁻² d⁻¹ for ethane, ethylene, propane, propylene, i-butane, and isoprene displayed upward trends with increasing latitude. The deck incubation showed that the addition of aerosols and acidic aerosols significantly boosted phytoplankton biomass, altered community structure, and accelerated the production of isoprene. However, the other six NMHCs showed no obvious responses to atmospheric aerosol deposition in the incubation experiments. In summary, ocean current movements and atmospheric deposition could influence the production and release of isoprene in the Northwest Pacific Ocean.

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1. Introduction

Non-methane hydrocarbons (NMHCs) are ubiquitous trace gases in the marine atmosphere and play important roles in atmospheric chemistry and global climate change (Sahu et al., 2011). Atmospheric NMHCs serve as a crucial sink of hydroxyl (OH) radicals, and the associated reactions lead to the production of alkyl peroxy radicals. Alkyl peroxy radicals promote the production of nitrogen dioxide and ozone (O₃) and then modify the atmospheric oxidative capacity (Calvert, 1976; Poisson et al., 2000; Tran et al., 2013). In addition, the photochemical process of NMHCs is also crucial to secondary organic aerosol (SOA) formation in the marine boundary layer. SOA affects the Earth's radiation balance and energy budget as well as the regional air quality by forming cloud condensation nuclei (Carpenter et al., 2012; Ding et al., 2013; Krechmer et al., 2015). In addition, the SOA generated by NMHC oxidation can have an effect on organic carbon in marine aerosols and thus influence the global carbon cycle (O'Dowd and De Leeuw, 2007).

NMHCs are mainly derived from anthropogenic sources and natural sources (Kansal, 2009). The anthropogenic sources are related to biomass burning, forest fires, transportation and industrial processing. The natural sources include terrestrial vegetation and seawater emission, which account 69% to the total emissions of NMHCs (Liakakou et al., 2007; Kansal, 2009). Although terrestrial vegetation emission is the main pathway for NMHCs production in the atmosphere, ocean, one of the largest active reservoirs of organic carbon, also release NMHCs that influences atmospheric chemistry over the oceanic region (Sharkey et al., 2008; Singh and Zimmerman, 1992; Tanimoto et al., 2013). Oceans are considered to be a significant source of reactive trace gases (Tesdal et al., 2016; Tripathi et al., 2020). Isoprene dissolved in seawater mainly emitted from marine phytoplankton with varying production rates among phytoplankton species (Broadgate et al., 2004; Dani and Loreto, 2017; Kurihara et al., 2012). Earlier studies have reported that other NMHCs can be also produced by phytoplankton (Broadgate et al., 2004; Lee and Baker, 1992; McKay et al., 1996). However, additional evidence has confirmed that C2 - C4 NMHCs are mainly produced through the photochemical degradation of dissolved organic materials (DOM) (McKay et al., 1996; Riemer et al., 2000). Surveys of isoprene and C2 - C4 NMHCs in surface seawater have indicated that these NMHCs are supersaturated and can be emitted efficiently to the marine troposphere (Gist and Lewis, 2006; Plass-Dülmer et al., 1995, 1993). As reported in previous studies, the global estimates of marine NMHCs emissions show large variation in the range of 2-50 Tg C yr⁻¹ (Tran et al., 2013). Isoprene, the dominant compound of NMHCs, possess the annual emission of 1.9 Tg and thus taking part in the atmospheric chemical reaction and then influencing atmospheric oxidation balance over the ocean (Arnold et al., 2009).

The Northwest Pacific Ocean, which possesses a complex dynamic system, is influenced by various ocean currents (Fig. S1). The North Equatorial Current bifurcates into the Kuroshio Current and the Mindanao Current near the Philippine coast (Hu et al., 2015; Qiu et al., 2015). The northward-flowing Kuroshio Current, which is associated with high temperatures, high salinity and low nutrients, turns east near the coast of Japan and converges with the Oyashio Current to form the Kuroshio Extension. These currents are an important part of the North Pacific subtropical gyre. The Mindanao Current, combined with the South Equatorial Current, veers eastward to form the North Equatorial Countercurrent (Hu et al., 2015). This complex marine environment plays an essential role in local marine ecosystems and primary productivity (Chavez and Toggweiler, 1995; Chen et al., 2021; Meskhidze et al., 2005). In addition to ocean currents, the atmospheric aerosol deposition is a significant factor influencing the marine environment of the Pacific Ocean (Martino et al., 2014; Zhang et al., 2019). Total atmospheric deposition to the North Pacific Ocean has been reported to range from 31 to 92 Tg yr⁻¹ (Zender et al., 2003). Atmospheric aerosol deposition is an important source of nutrients and Fe of the North Pacific Ocean and the aerosol is mainly originated from the soils of the arid and semiarid regions of China and Mongolia in Central Asia (Letelier et al., 2019; Merrill et al., 1989; Zhao et al., 2006). Zhao et al.

(2015) reported that the Asian nitrogen deposition in the Northwest Pacific Ocean with the values of 28.6 Tg N yr⁻¹ and 15.7 Tg N yr⁻¹ for NH₃ and NO_x. The Northwest Pacific Ocean was regarded as Fe limitation area and the Fe supplied by aerosol deposition regulate the phytoplankton biomass and phytoplankton community (Behrenfeld et al., 2016; Buck et al., 2013; Nishioka et al., 2003; Tanita et al., 2021). A series of incubation and filed experiments conducted in the Pacific Ocean determined that Fe addition incused by aerosol deposition alter the phytoplankton community from pico-phytoplankton to micro-phytoplankton (Viljoen et al., 2018; Zhang et al., 2020).

Hence, we studied the effects of ocean currents on the characteristics and emissions of isoprene and C2 – C4 NMHCs through field investigations in the Northwest Pacific Ocean. The sea-to-air fluxes of NMHCs were quantified to verify the regional contribution to the global ocean. Meanwhile, the formation potentials of atmospheric NMHCs for ozone and SOA were estimated in this study. And the estimated SOA was used to assess the contribution to the aerosol samples collected on the same cruise. Additionally, we conducted deck incubation experiments to investigate the effects of atmospheric aerosol deposition on the release of isoprene and C2 – C4 NMHCs.

2. Materials and methods

2.1. Collection and chemical analysis of NMHCs

In this work, field investigations were conducted onboard the R/V 'Dong Fang Hong 2' from October 6 to December 7, 2017 to collect the samples for the NMHCs analysis. We investigated 55 stations along the 143°E longitudinal and equatorial transects in the Northwest Pacific Ocean (Fig. 1). Seawater samples were collected with Niskin bottles (12 L) installed in a conductivity-temperature-depth (CTD, Seabird 911) rosette. The samples were packed into 120-mL brown-colored glass vials. Then, 100 μ L of saturated HgCl₂ solution was added to each sample to prevent potential microbial activity before sample storage in the dark at 4 °C (Matsunaga et al., 2002; Wu et al., 2021). Atmospheric NMHCs samples were collected using 3-L fused-silica lined canisters (Restek, USA) on the upper deck of the ship.

The relevant characteristics of the marine samples were quantified by a gas chromatograph-mass spectrum detector (GC–MSD) (Agilent 7890A/5975C, USA) equipped with a purge-and-trap (P&T) system. The 100-mL sample was transferred to the gas extraction chamber and bubbled with high-purity helium gas (He, 99.999 %) at a flow rate of 80 mL/min for 15 min. The gas was passed through drying tubes containing anhydrous magnesium perchlorate and sodium hydroxide (on support) and then trapped onto a stainless steel trap tube that was cooled with liquid nitrogen. The collected gases were thermally desorbed with boiling water (100 °C) and introduced into the GC–MSD through an Rt-Alumina BOND/KCl capillary column (30 m \times 0.32 mm \times 5 μ m) for quantification. The detection limits and precisions of this method ranged from 0.5 to 1.0 pmol L⁻¹ and from 3 % to 6 %, respectively (Table S1).

A 200-mL air sample from the canister was successively injected into the three-level pre-concentrator (Nutech 8900DS, USA) to remove water vapor and carbon dioxide through the first two traps, successively. Then, the volatile gases were transferred into the third cryo-focusing trap. Finally, the third trap was heated instantaneously to 200 °C and the sample was released to the GC-MS system for analysis (Li et al., 2019, 2018). The detection limits and precisions of this method were lower than 3.0 pptv and 15 %, respectively (Table S1).

2.2. Collection and chemical analysis of aerosol

We collected the aerosol samples using a high-volume sampler (KB-1000) with quartz fiber filters (Whatman) in the cruise to analyze the organic carbon content of the aerosol. The aerosol samples used for the incubation experiments were obtained through Whatman 41 fiber filter in the Northwest Pacific Ocean in the autumn of 2018. To prevent shipborne



Fig. 1. Schematic map of the major surface currents and location of sampling stations (the red stations represent the atmospheric sampling stations in the same time). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

contamination, the aerosol sample was placed on the foredeck of the ship. The collection flow rate was controlled at 1.0 m³ min⁻¹ for 24–72 h during the sampling process. Upon completion of sampling, the filters were folded in half, stored in aluminum foil and kept frozen (-20 °C) until returned to the terrestrial laboratory for determination.

One-fourth of the aerosol filter was ultrasonically extracted with 10 mL Milli-Q water in centrifuge tubes for 40 min. The supernatants were placed into a 25-mL volumetric flask to obtain the main water-soluble inorganic ions. The water-soluble cations and anions were determined with an ion chromatograph (Metrosepa IC-940, Switzerland) coupled with a Metrosepa C Supp 4-150 and Metrosepa A Supp 7-250 anion column, respectively. One-eighth of the aerosol filter was put into a clean poly tetra digestion tank for digestion. After digestion, 2 mL concentrated nitric acid was added, and the sample was brought to 25 mL to obtain the metal samples. The trace metals were measured with inductively coupled plasma atomic emission spectrometry (Thermo, I6300). The total carbon in aerosols was determined with an elemental analyzer (2400II, PerkinElmer, USA). Onefourth of the aerosol filter was placed in a precleaned and pressed tin capsule (Chnos, China) and weighed before measurement. The samples were subsequently combusted subsequently at 980 °C in a combustion tube within the elemental analyzer, and the carbon-containing species were converted to CO2 for analysis.

2.3. Deck incubation experiments

Deck incubation experiments were carried out using seawater collected at station E142-5 (142°E, 3°N) during the 2019 Northwest Pacific cruise to assess the responses of NMHCs formation to atmospheric aerosol deposition. The investigation area was a low-nutrient low-chlorophyll-*a* (Chl-*a*) marine environment, with an initial Chl-*a* of 0.07 µg L⁻¹. The seawater utilized in these incubation experiments exhibited typical nitrogen limitation characteristics, with a ratio of dissolved inorganic nitrogen (DIN, the sum of NO_3^- , NO_2^- and NH_4^+) to phosphate of 6.3:1. In addition to nitrogen limitation, the marine environment in the study area was not sufficient to meet the Fe demands required for phytoplankton growth (Fig. S2, https://resources.marine.copernicus.eu).

We selected an aerosol sample of a certain interval (131.7°E, 12.4°N–29.0°E, 18.0°N) for pretreatment, and the concentrations of NO_3^- , NH_4^+ and Fe in the aerosol were 2.4, 0.9 and 0.09 µg m⁻³, respectively. Correspondingly, the aerosol dry deposition fluxes of NO_3^- , NH_4^+ and Fe reached 4.15, 1.56 and 0.23 mg m⁻² d⁻¹, respectively. Three groups (in duplicate)

were conducted in the incubation experiments, including the control, aerosol treatments and acidic aerosol treatments. Aerosol samples were added in the aerosol and acidic aerosol treatment groups at the start of the experiments, while no aerosol was added in the control. The aerosols were dissolved in Milli-Q water and Milli-Q water acidified with HCl (final pH = 2) to simulate atmospheric deposition and acidified atmospheric deposition processing (Krom et al., 2016). This pH represents the acidity of aerosols that have been in contact with anthropogenic emissions, including sulfur dioxide, nitrogen oxides, organic acids, which may enhance the solution and bioavailability of Fe (Longo et al., 2016; Shi et al., 2009, 2015). Then, the aerosol samples were sonicated for 1 h and the suspension was added to filtered seawater which was filtered through a 200-µm nylon mesh. The initial concentrations of NO₃⁻ and NH₄⁺ of the aerosol in the incubation system were 2.3 and 2.9 μ mol L⁻¹, respectively, and the theoretical initial concentration of Fe was 0.1 µmol L⁻¹. No variations in seawater pH were found between the treatment and the control. During the experiment, we continuously provided surface seawater to ensure constant water temperature of the incubation system.

2.4. Measurements of environmental parameters

The seawater samples were filtered by 47-mm filters (GF/F, Whatman) with a pressure of <15 kPa to obtain the Chl-*a* samples. Then the filters were kept frozen and measured with a fluorescence spectrophotometer (Hitachi, Japan) at the land laboratory (Parsons et al., 1984). For the phytoplankton species and abundance, the concentrated samples were identified and quantified using a microscope (Nikon YS100, Japan). As the biological elements of phytoplankton growth, nutrients are important indicators of the marine environment. The seawater was filtered through 47-mm filters (GF/F, Whatman) to obtain the nutrient samples, and then the filtrates were cryopreserved at the laboratory with an automatic analyzer (AA3, Seal) determination (Parsons et al., 1984). The meteorological and hydrological parameters, such as wind speed and temperature were obtained from the shipborne meteorological observation instrument and the CTD system, respectively.

2.5. Calculation of sea-to-air fluxes

The equation used herein to calculate the sea-to-air fluxes (F, nmol m⁻² d⁻¹) of NMHCs can be expressed as follows:

$$F = k \times (C_w - C_a \times H) \tag{1}$$

where k (m s⁻¹) represents the gas transfer velocity computed by Wanninkhof (1992), C_w (pmol L⁻¹) and C_a (pptv) are the NMHCs concentrations in the surface seawater and marine atmosphere, respectively, and H represents Henry's Law constant (Table S2, Sander, 2015).

2.6. Assessment of the environmental effects of NMHCs

The impacts of NMHCs on various tropospheric chemical reactions are related to their OH consumption rate $(L_{i,OH})$ (Eq. (2)). More reactive NMHCs species have increased contributions to O₃ and SOA formation (Panda et al., 2015). The O_3 formation potential (OFP, $\mu g m^{-3}$) and secondary organic aerosol formation potential (P_{SOAPi} , µg m⁻³) were determined to estimate the contribution of individual NMHCs in O₃ and SOA formation using Eqs. (3) and (4) (Carter, 1994):

$$L_{i,OH} = NMHC(i) \times k_{i,OH}$$
⁽²⁾

$$OFP(i) = MIR_i \times NMHC(i) \tag{3}$$

$$P_{SOAPi} = \Sigma NMHC_i \times SOAP_i \times FAC_{toluene} / 100$$
(4)

where $L_{i,OH}(s^{-1})$ represents the OH radical consumption rate of *i*; NMHC(*i*) represents the measured concentration of the NMHCs compound *i*; and $k_{i,OH}$ $(10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ represents the reaction rate constant of *i* with OH radicals (Atkinson and Arey, 2003). MIR_i (g O₃/g VOC) and $SOAP_i$ (relative to toluene = 100) are constants that represent the maximum incremental reactivity and SOA potential of *i*, respectively (Carter, 2010); FACtohuene represents the fractional aerosol coefficient of toluene, which has a value of 5.4 % (Grosjean and Seinfeld, 1989).

3. Results and discussion

3.1. Hydrological properties of the Northwest Pacific Ocean

The surface seawater temperature displayed an increasing trend from north to south, ranging from 20.4 to 30.3 °C. The temperature along the equatorial transect was stable at approximately 30.0 °C (Fig. S3). Relatively low salinity was found in the northwestern area of the equatorial transect, where the annual rainfall total reached 2 m (Spencer, 1993). The occurrence of upwelling in the eastern area of the equatorial transect contributed to higher salinity (Fig. S4). The concentrations of DIN, PO_4^3 – and SiO_3^2 in the investigation area varied from 0.30 to 4.31, 0.01–0.28, and $0.46\text{--}3.55~\mu\text{mol}~\text{L}^{-1},$ respectively. Abundant nutrients were found in the Kuroshio-Oyashio Extension, with average DIN, PO_4^3 - and SiO_3^2

Table 1

Comparisons of NMHCs (pmol L^{-1}) in surface seawater between this study and other stud

concentrations of 2.78 \pm 1.26, 0.12 \pm 0.04 and 2.36 \pm 0.84 μ mol L⁻¹, respectively. As an indication of phytoplankton biomass, Chl-a spanned a range of two magnitudes in the investigation. It ranged from 0.02 to 0.26 μ g L⁻¹, with an average value of 0.08 \pm 0.06 μ g L⁻¹. Stimulated by the abundant nutrients, Chl-a in the Kuroshio-Oyashio Extension was 3-5 times richer than that measured in the North Pacific subtropical gyre and tropical waters, and the average concentration reached 0.21 \pm $0.04~\mu g~L^{-1}.$ In addition, because the upwelling transported high nutrients (DIN: 1.35 ± 0.26 , PO₄^{3 -} : 0.04 ± 0.03, and SiO₂^{2 -} : 1.57 ± 0.20 μ mol L⁻¹) to the surface that promoted the growth of phytoplankton, we also found higher Chl-a concentrations (mean Chl-a: 0.21 \pm 0.02 µg L⁻¹) in the east side of the equatorial transect.

3.2. Variations in the phytoplankton community and NMHCs affected by ocean currents

In the surface seawater samples, the alkanes possessed the ranges of 1.0-31.7, 0.1-18.1, 0.1-11.0 and 1.1-11.2 pmol L⁻¹ for ethane, propane, i-butane and n-butane, respectively, with average values of 13.6 \pm 6.0, $9.0 \pm 4.1, 5.6 \pm 2.7$ and 6.2 ± 2.7 pmol L⁻¹. The average concentrations of alkenes exceeded those of the alkanes, with values of 24.3 ± 10.8 . 19.7 \pm 9.7 and 17.9 \pm 16.4 pmol L⁻¹ for ethylene, propylene and isoprene, respectively. As shown in Table 1, earlier studies reported the concentrations of propane and isoprene were comparable to our measurements in the Pacific Ocean (Li et al., 2019; Tsurushima et al., 1999). The investigations conducted in the Arctic Ocean and the Atlantic Ocean during summer showed that the ethylene and propylene were around 2-fold higher than those in this study (Plass-Dülmer et al., 1993; Tran et al., 2013; Tsurushima et al., 1999). The different sampling areas and seasons partly explained the differences between our results and those of previous measurements. In this study, significant distribution variations in marine NMHCs could be distinguished among the ocean currents.

The NMHCs concentrations in seawater showed increasing trends along the increasing latitude (Fig. 2). The highest isoprene value (57.8 pmol L^{-1}) emerged in the Kuroshio-Oyashio Extension, and it was 3-7 fold higher than that in the North Pacific subtropical gyre and tropical waters (Table 1). We found that the positive correlation between isoprene and Chl-a (Fig. 3), indicating the isoprene production from phytoplankton biomass. A study of phytoplankton performed during the same cruise reported that cyanobacteria and dinoflagellates were concentrated in the North Pacific subtropical gyre and tropical waters, with much higher abundances than those in the Kuroshio-Ovashio Extension (Chen et al., 2021). As for diatoms, it showed high values in the Kuroshio-Oyashio Extension, as much

	Ethane	Ethylene	Propane	Propylene	i-Butane	n-Butane	Isoprene
Northwest Pacific Ocean	13.6 ± 6.0	24.3 ± 10.8	9.0 ± 4.1	19.7 ± 9.7	5.6 ± 2.7	6.2 ± 2.7	17.9 ± 16.4
^a Pacific Ocean	6.7 ± 2.3	62.2 ± 7.6	10.0 ± 3.1	31.0 ± 3.9	-	-	-
^b Northwest Pacific Ocean	6.6 ± 5.8	51.9 ± 23.5	15.4 ± 4.3	17.2 ± 3.8	-	-	23.5 ± 8.6
^c Arctic and Atlantic Ocean	-	-	11 ± 32	80 ± 58	3 ± 20	24 ± 96	26 ± 31
^d Atlantic Ocean (23°N–2°S)	17 ± 6.0	129 ± 17	9.0 ± 4.6	44 ± 9	0.9 ± 0.5	4.2 ± 2.6	-
Kuroshio-Oyashio Extension	17.0 ± 3.9	34.6 ± 5.2	13.8 ± 3.0	26.6 ± 7.6	8.7 ± 2.3	9.2 ± 1.7	57.7 ± 10.6
	(12.1 - 21.5)	(27.1-38.8)	(11.4-18.0)	(16.6-33.7)	(6.1 - 11.0)	(6.8–10.6)	(45.5-69.1)
Subtropical Countercurrent	17.5 ± 3.6	30.1 ± 8.5	12.1 ± 1.8	25.1 ± 6.7	7.1 ± 1.6	8.1 ± 2.2	15.0 ± 6.8
	(6.8-20.8)	(10.9-49.5)	(9.1-14.1)	(5.6-29.5)	(3.0–9.3)	(3.9–10.8)	(6.6-30.0)
North Equatorial Current	7.2 ± 3.3	10.6 ± 3.1	4.2 ± 2.1	9.1 ± 4.4	2.6 ± 1.0	3.4 ± 1.5	13.3 ± 18.3
	(1.0-12.6)	(5.8-16.3)	(0.1 - 7.1)	(1.8-16.6)	(0.7-4.6)	(1.1-6.0)	(2.4-61.8)
North Equatorial Countercurrent	12.3 ± 5.9	19.9 ± 6.3	8.2 ± 4.5	17.1 ± 9.0	4.0 ± 1.6	4.2 ± 1.3	8.1 ± 5.3
	(4.6-18.9)	(12.4-27.6)	(4.4-14.8)	(5.7-27.6)	(1.9-5.8)	(2.3 - 5.1)	(5.0 - 16.1)
South Equatorial Current	14.2 ± 6.1	26.9 ± 9.3	9.1 ± 3.3	21.3 ± 9.6	6.0 ± 2.5	6.3 ± 2.4	16.3 ± 11.1
	(5.0–31.7)	(13.2–46.2)	(5.2–16.4)	(6.0–45.9)	(2.8–10.9)	(3.2–11.2)	(3.5–55.1)

^a Tsurushima et al. (1999).

^b Li et al. (2019).

^c Tran et al. (2013).

^d Plass-Dülmer et al. (1993).



Fig. 2. Horizontal distributions of Chl-a (µg L⁻¹) and concentrations of NMHCs (pmol L⁻¹) in the surface seawater of the Northwest Pacific Ocean.

as 3–5 times than that in other areas. The abundance of diatoms (20,679 \pm 9040 cells m $^{-3}$) was higher than that of cyanobacteria (8630 \pm 12,204 cells m $^{-3}$) and dinoflagellates (2594 \pm 604 cells m $^{-3}$) in the Kuroshio-

Oyashio Extension; thus, diatoms were the predominant phytoplankton, accounting for about 68 % of the total phytoplankton. The highest isoprene production rate of phytoplankton (3.8 pmol cell⁻¹) appeared at station



Fig. 3. The principal component analysis (PCA) with the concentrations of seven NHMCs and other environmental variables in the Northwest Pacific Ocean.

0701 and was 8–16 fold higher than the results in other areas. Diatoms were notably the most favorable contributors to isoprene production, which was similar to earlier investigations (Dani and Loreto, 2017; Meskhidze et al., 2015; Tripathi et al., 2020). Therefore, the Kuroshio-Oyashio Extension mainly promotes the growth of diatoms and thus facilitates the release of isoprene.

Similar to isoprene, the concentrations of other NMHCs in the Kuroshio-Oyashio Extension were almost 1.2-3.3 times higher than those in the North Pacific subtropical gyre and tropical waters (Table 1). NMHCs presented positive correlations with Chl-a in this study (Fig. 3), demonstrating that their production could be influenced by phytoplankton to some extent. Earlier studies reported that biological production could contribute to ethylene and alkane concentrations (Broadgate et al., 2004; Lee and Baker, 1992; McKay et al., 1996). In addition to biological production, the production of NMHCs was also related to abiotic pathways. The distributions of NMHCs were similar to the total absorption coefficients at 443 nm in the Northwest Pacific Ocean (Fig. S5, https://oceancolor.gsfc. nasa.gov/l3/). A recent study reported that the absorption coefficients at 443 nm provided by ocean color remote sensing could be used to reflect the temporal and spatial distributions of DOM (Juhls et al., 2019). Both high values of NMHCs and total absorption coefficients at 443 nm appeared in the Kuroshio-Oyashio Extension, demonstrating that the photochemical pathway could also contribute to NMHCs production. Similarly, owing to the abundant phytoplankton and DOM stimulated by the upwelling, elevated NMHCs were also found in the eastern area of equatorial transect. Therefore, the Northwest Pacific circulation, especially the Kuroshio-Oyashio Extension, significantly affected the marine environment including nutrient levels, DOM content and phytoplankton biomass and communities, thereby controlling variations in the concentration and distribution of NMHCs.

3.3. Emissions of NMHCs from the Northwest Pacific Ocean

On the study cruise, the supersaturation coefficients of ethane, ethylene, propane, propylene, i-butane, n-butane and isoprene with the ranges of 0.2-4.6, 4.0-34.0, 0.4-11.6, 1.2-30.9, 2.0-33.3, 2.2-22.1, and 1.0-27.3, respectively. Only a few supersaturation coefficients of ethane and propane were <1.0 and were concentrated at station 0722. The supersaturation coefficients of NMHCs at other stations were >1.0, illustrating a net input from the ocean to the atmosphere. Combined with the marine and atmospheric concentrations of NMHCs, the calculated sea-to-air fluxes had mean values of 28.0 \pm 38.9, 65.2 \pm 73.3, 21.0 \pm 26.7, 48.7 \pm 62.6, 12.7 \pm 15.9, 14.2 \pm 16.8, and 41.7 \pm 80.4 nmol m⁻² d⁻¹ for ethane, ethylene, propane, propylene, i-butane, n-butane, and isoprene, respectively. The results were 2-4 times higher than those in the Northwest Pacific Ocean (ethane:6.6 \pm 7.1, propane: 12.4 \pm 10.6 and propylene: 24.1 \pm 28.6 nmol m $^{-2}$ d $^{-1}),$ but comparable to the ethylene (74.7 \pm 81.9 nmol $m^{-2} d^{-1}$) and isoprene (43.4 ± 33.8 nmol $m^{-2} d^{-1}$) conducted by Li et al. (2019). However, compared with the results estimated in the coastal sea area, the sea-to-air fluxes of NMHCs in the Northwest Pacific Ocean were at a lower level as shown in Table 2 (Gist and Lewis, 2006; Li et al., 2021). From the results in this study, we found that the alkene fluxes significantly exceeded the results derived for alkanes. Owing to the abundant marine isoprene and high wind speeds, the highest average flux of

Table 2

Comparisons of sea-to-air fluxes (nmol $m^{-2} d^{-1}$) between this study and other studies.

	Ethylene	Propylene	Isoprene	Ethane	Propane	i-Butane	n-Butane			
Northwest Pacific Ocean	65.2 ± 73.3	48.7 ± 62.6	41.7 ± 80.4	28.0 ± 38.9	21.0 ± 26.7	12.7 ± 15.9	14.2 ± 16.8			
^a Northwest Pacific Ocean	74.7 ± 81.9	24.1 ± 28.6	43.4 ± 33.8	6.6 ± 7.1	12.4 ± 10.6	-	-			
^b Arctic and Atlantic Ocean	-	53 ± 31	4.6 ± 4.4	-	-	-	-			
^c China marginal sea	528.6	383.4	111.1	-	-	-	-			
^d North Sea coastal area	720	264	-	-	-	-	-			

^a Li et al. (2019).

^b Tran et al. (2013).

^c Li et al. (2021).

^d Gist and Lewis (2006).

isoprene (127 ± 150 nmol m⁻² d⁻¹) occurred in the Kuroshio-Oyashio Extension, where the flux was approximately 3 times higher than that in the Subtropical Countercurrent and North Equatorial Current and more than an order of magnitude higher in comparison with those in the North Equatorial Countercurrent and South Equatorial Current. Considering the supersaturation coefficients and emissions, it indicated that the Northwest Pacific Ocean was a vital source of NMHCs and emphasized the significant role of the Northwest Pacific Ocean in the global carbon cycle.

3.4. Variabilities and sources of atmospheric NMHCs

The average concentrations of atmospheric ethane, propane, i-butane and n-butane over the North Pacific subtropical gyre, with values of 3.64 ± 2.40 , 1.04 ± 0.23 , 0.30 ± 0.13 and 0.45 ± 0.15 ppbv, respectively, were generally higher than the corresponding unsaturated hydrocarbon concentrations (ethylene: 0.31 ± 0.14 ppbv, propylene: 0.31 ± 0.13 ppbv, and isoprene: 0.23 ± 0.02 ppbv). Positive correlations were found between the atmospheric NMHCs and sea-to-air fluxes. The sea-to-air fluxes of NMHCs showed that alkenes possessed high values than alkanes, which was contrary with the trends of atmospheric NMHCs. It illustrated that emission from seawater was not the only decisive factor controlling atmospheric concentrations of NMHCs. The $L_{i,OH}$ of alkenes ($0.06-0.63 \text{ s}^{-1}$) were calculated to be one order of magnitude higher than those of alkanes ($0.02-0.03 \text{ s}^{-1}$), suggesting that alkenes were more easily consumed by OH compared to alkanes. In addition, the ratios of alkene concentrations in day-time and nighttime (1.1-1.2) were lower than the ratios of alkene fluxes,

25

25

30

2.0

1.5

Total carbon

0.5

0.0

30

especially for isoprene whose flux ratio was 17. Isoprene was the most reactive compound (0.63 s^{-1}) and could more likely participate in atmospheric chemical reactions, leading to the lowest mean concentration.

The C2 - C4 NMHCs showed upward trends with increasing latitude, while no salient latitudinal gradient was found in the isoprene profile (Fig. 4). The source apportionment of the atmospheric NMHCs determined by the 72-h backward trajectories (Fig. S6) showed that the air mass originating from the ocean surface influenced all sampling stations. And positive correlations were found between the atmospheric NMHCs and sea-to-air fluxes. Enhanced emissions promoted the increase of the atmospheric NMHCs. In addition, the conceptual model simulations conducted in the tropical West Pacific Ocean showed that the atmospheric OH affected the concentrations and lifetimes of greenhouses gases (Rex et al., 2014). The OH minimum was conducive to the increase of the lifetimes of active gases. Spivakovsky et al. (2000) reported that the OH radical concentrations decreased from south to north, which reduced the C2 - C4 NMHCs consumption in the north area and resulting higher concentrations. Moreover, a minimum had been found in the tropical western Pacific Ocean centered at 17°N/158°E (Kuttippurath et al., 2023; Rex et al., 2014), which corresponded well with the increasing concentrations of NMHCs at station 0724 (18°N, 143°E). Consistent with the results in the study, alkanes showed a latitudinal increase from south to north in the western North Pacific and eastern Indian Ocean (Saito et al., 2000). Although higher Chl-a appeared around 19°N (Fig. 4), the concentration (3.2 pmol L^{-1}) and emission (8.7 nmol $m^{-2} d^{-1}$) of isoprene were relatively lower, which might be influenced by the phytoplankton species. The atmospheric isoprene was



Fig. 4. Latitudinal distributions of the NMHCs (ppbv) and total carbon (µg C m⁻³) in atmosphere as well as temperature (°C), salinity and Chl-a (µg L⁻¹) in surface seawater.

negatively affected subsequently. In addition, owing to the higher $\rm L_{i,OH}$ isoprene was easily removed by OH and then the isoprene was low and stable during the investigation.

3.5. Environmental effects of atmospheric NMHCs

We used the OFP and the SOAP metrics to speculate on the environmental impacts of NMHCs. According to the calculated results, isoprene accounted for 33 % of the total OFP owing to its stronger reactivity, with a value of 7.49 \pm 0.74 μ g m $^{-3}$. Propylene was the second contributor to OFP (6.80 \pm 2.83 μ g m $^{-3}$), followed by ethylene (3.52 \pm 1.56 μ g m $^{-3}$), ethane (1.37 \pm 0.90 μ g m $^{-3}$), n-butane (1.34 \pm 0.43 μ g m $^{-3}$), propane (1.00 \pm 0.22 μ g m $^{-3}$) and i-butane (0.95 \pm 0.40 μ g m $^{-3}$). Although the concentration of alkenes possessed lower concentrations than alkanes, their contributions to OFP were generally higher than alkanes. Thus, atmospheric reactivity and concentrations of NMHCs influenced the O₃ formation and hence environmental impacts.

The PSOAP values of ethane, ethylene, propane, propylene, i-butane, nbutane and isoprene were 2.64 ± 1.74, 2.76 ± 1.22, 0, 5.02 ± 2.08, 0, 1.89 ± 0.61 , and $7.29 \pm 0.70 \ 10^{-4} \ \mu g \ m^{-3}$, respectively. The isoprenederived SOA obtained in this study was within the range of biogenic isoprene SOA tracers (1.1 \times 10 $^{-4}$ –2.2 \times 10 $^{-2}$ μg m $^{-3}$) sampled over the global ocean (Fu et al., 2011) and comparable with the result $(6.23 \times 10^{-4} \,\mu g \,m^{-3})$ reported in the North Pacific Ocean and the Arctic Ocean (Ding et al., 2013). The results of the same cruise showed that the total carbon in the marine aerosol ranged from 0.1 to 1.7 μ g C m⁻³, with an average of 0.9 \pm 0.5 μ g C m⁻³ (Fig. 4). Based on the proportion of organic carbon to the total carbon in the Pacific Ocean (Hoque et al., 2017), we estimated the concentrations of organic carbon, with a range of 0.1–1.4 µg C m^{-3} in this study. Among the five NMHCs, the contribution of isoprene to the total organic carbon in aerosols accounted for 0.1 % to 0.6 %, which was in the range of 0.01 %-1.2 % estimated by Fu et al. (2011). The contribution of SOA generated from the oxidation of the five NMHCs to organic carbon was estimated to range from 0.1 % to 1.2 %. If more NMHCs were considered, the contribution of SOA generated from their oxidation would be higher. A study conducted during a round-the-world cruise reported that the SOA oxidized by >110 compounds contributed 1.8 % to 11.0 % to organic carbon (Fu et al., 2013). Therefore, the photooxidation of NMHCs released from seawater was conducive to the SOA production and it contributed to carbon budget in the Northwest Pacific Ocean.

3.6. Responses of NMHCs to atmospheric aerosol deposition

3.6.1. Variations in phytoplankton in the incubation experiments

The initial concentrations of NO_3^{-} and NH_4^+ in the aerosol and acidic aerosol treatments were 2-3 times higher than those in the control $(NO_3^{-}: 2.46 \pm 0.42 \text{ and } NH_4^+: 0.76 \pm 0.16 \mu mol L^{-1})$. Previous studies reported that atmospheric aerosol deposition led to the enhancement of DIN, which could alleviate nitrogen limitation (Jickells et al., 2017; Zhang et al., 2018). The NH_4^+ and NO_3^- concentrations decreased rapidly in the first few days as the nutrients were taken up for the growth of phytoplankton. The NH_4^+ in the control was under the detection limitation at the 3rd day and increased the concentration at the 8th day. As for NO_3^{-} , it was consumed totally at day 8 and then slightly increased in latter days in three incubation experiments. The increase in nutrient levels might be related to microbial degradation of DOM (Lønborg and Søndergaard, 2009; Repeta et al., 2016). As a proxy of phytoplankton biomass, Chl-a tremendously increased in the first 10 days until reaching the maximum, with values of 0.63 and 0.84 μ g L⁻¹ in the aerosol and acidic aerosol addition treatments, respectively (Fig. 5). The average concentrations of Chl-a in the aerosol and acidic aerosol addition treatments increased by 356 % and 457 % compared with the control, reflecting that the addition of both aerosols (T =4.160, p = 0.002) and acidic aerosols (T = 4.026, p = 0.002) was conducive to phytoplankton growth and favorable for marine ecosystems. The addition of acidic aerosols promoted the dissolution of Fe, which was more

conducive to increasing the phytoplankton biomass than the addition of aerosols alone (Jickells et al., 2005; Krom et al., 2016; Li et al., 2015).

The stimulation of aerosols and acidic aerosols shifted the phytoplankton community. Although dinoflagellate abundance increased during the incubation, its proportion decreased from 15 % to 9 % in the aerosol treatments. Diatoms became the dominant species in the incubation system and presented significant enhancement from 6 % to 91 % within the incubation period. In comparison, dinoflagellates were the dominant phytoplankton class in the acidic aerosol treatments and showed an increasing trend from 56 % to 92 %, while diatoms proportion decreased to 6 %. The incubation experiments performed in the DIN-limited area of the Northwest Pacific Ocean conducted by Zhang et al. (2020) highlighted that atmospheric aerosol deposition enhanced the change in phytoplankton from pico-size to micro-size. A survey conducted in the tropical and subtropical Pacific Ocean showed that DIN addition or combined DIN and Fe addition caused significant shifts from pico-phytoplankton to large phytoplankton (Li et al., 2015). Atmospheric deposition played a critical role in controlling the hydrological environment in the Northwest Pacific Ocean.

3.6.2. Variations in NMHCs emissions in the incubation experiments

The trends of isoprene concentrations measured in our experiments were almost synchronized with those of Chl-a. Isoprene displayed an increasing trend in the first 10 days of the experiments, with values of 28.3 \pm 0.4 and 22.8 \pm 1.3 pmol L⁻¹ on the 10th day in the aerosol and acidic aerosol treatments, respectively. Then, the isoprene level began to decline and stabilized on the 12th day (Fig. 5). The mean concentrations of isoprene in the aerosol and acidic aerosol treatments were approximately 1.7 and 1.4 times higher than those in the control, respectively, emphasizing that aerosol (T = 4.109, p = 0.002) and acidic aerosol (T = 2.872, p = 0.017) addition stimulated isoprene production. The differences between control and aerosol addition experiments did not follow the large increases in Chl-a (350-450 %) exhibited, which might be related to phytoplankton biomass and community. Positive correlations were found between isoprene and Chl-*a* in the aerosol addition ($R^2 = 0.51, p < 0.01$) and acidic aerosol addition treatments ($R^2 = 0.38$, p < 0.05). It suggested that the differences between phytoplankton species affected isoprene production. In contrast to the trends of Chl-a, the isoprene concentrations in the aerosol treatment were 8 %-70 % higher than those measured in the acidic aerosol treatment. The phytoplankton investigation results showed that diatoms and dinoflagellates became dominant phytoplankton in the aerosol and acidic aerosol treatments with increasing incubation time, respectively. Combined with the isoprene concentration and phytoplankton biomass in both treatments, we found that diatoms provided a favorable contribution to the elevated concentration of isoprene in the aerosol addition group compared to the dinoflagellates in the acidic aerosol treatment. This result reflected diatoms being the most predominant emitters of isoprene production, which was consistent with the results of the field investigations in this study.

Given other NMHCs, similar trends were found in the control and aerosol treatments as well as in the acidic aerosol treatments during the incubation period (Fig. 5). The ethane and propane showed no obvious trends in the early stage and then increased from the 12th day toward to the end of the incubation. The average concentrations were comparable among three incubation experiments and there were no significant differences between the control and the aerosol treatments (ethane: T = 0.770, p =0.459 and propane: T = 1.125, p = 0.281) as well as the acidic aerosol treatments (ethane: T = 1.526, p = 0.158 and propane: T = 1.592, p =0.136). The ethylene and propylene presented slightly increasing trends in first few days and then increased dramatically from the 12th day when the phytoplankton biomass displayed a decreasing tendency. No significant differences were found among three incubation experiments. Both the situations illustrated that atmospheric deposition had no pronounced effect on NMHCs production. In order to verify the role of Chl-a in NMHCs production during the incubations, correlation analysis was conducted and we found that there were no relationships between the NMHCs and Chl-a. It demonstrated that the enhancement of NMHCs was not due to the



Fig. 5. The variations of Chl-a (µg L⁻¹) and NMHCs (pmol L⁻¹) in the aerosol and acidic aerosol treatments during the deck incubation.

increased phytoplankton biomass caused by atmospheric deposition. The increases in NMHCs were more closely related to photochemical formation owing to the increasing release of DOM during the phytoplankton decline period.

4. Conclusions

We have investigated the responses of isoprene and other NMHCs production to ocean currents and atmospheric aerosol deposition using field investigations and deck incubation experiments in the Northwest Pacific Ocean. Our results indicated that the influx of the Oyashio Current enhanced the nutrient levels and subsequently boosted the phytoplankton biomass. Meanwhile, the transformation of major phytoplankton species from cyanobacteria to diatoms with increasing latitude accelerated the formation of optimal conditions for isoprene enrichment. This highlighted the favorable contributions of diatoms to isoprene production. Regarding other NMHCs, elevated concentrations were also found in the Kuroshio-Oyashio Extension owing to the abundant DOM, which promoted the photochemical production of NMHCs. The atmospheric NMHCs (except for isoprene) presented upward tendencies from south to north considering the source and removal. The sea-to-air fluxes and environmental effects calculated with atmospheric NMHCs suggested that the release from the North Pacific Ocean was a pathway for NMHCs production, which was conducive to O_3 and SOA formation. For the deck incubation experiments, we found that aerosol and acidic aerosol deposition was beneficial to increase the primary productivity and the biological production of isoprene. Moreover, diatoms, the dominant phytoplankton in the aerosol treatment, contributed more to isoprene production than the dinoflagellates in the acidic aerosol treatment, which was similar to the conclusion drawn by field investigation. The other six NMHCs did not show responses to atmospheric deposition. Therefore, ocean currents and atmospheric deposition affected the ocean environment and indirectly acted on the production and release of NMHCs.

CRediT authorship contribution statement

Ying-Cui Wu: Methodology, Investigation, Data curation, Validation, Writing – original draft. Xu-Xu Gao: Methodology, Investigation, Writing – review & editing. Hong-Hai Zhang: Methodology, Funding acquisition, Writing – review & editing. Yong-Zheng Liu: Software, Validation. Jian Wang: Data curation. Feng Xu: Data curation. Gui-Ling Zhang: Formal analysis, Writing – review & editing, Project administration. Zhao-Hui Chen: Writing – review & editing.

Data availability

Data reported in this study are available publicly at https://doi.pangaea.de/10.1594/PANGAEA.945550.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

- Arnold, S.R., Spracklen, D.V., Williams, J., Yassaa, N., Sciare, J., Bonsang, B., Gros, V., Peeken, I., Lewis, A.C., Alvain, S., Alvain, M., 2009. Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol. Atmos. Chem. Phys. 9, 1253–1262. https://doi.org/10.5194/acp-9-1253-2009.
- Atkinson, R., Arey, J., 2003. Atmospheric degradation of volatile organic compounds. Chem. Rev. 103, 4605–4638. https://doi.org/10.1021/cr0206420.
- Behrenfeld, M.J., O'Malley, R.T., Boss, E.S., Westberry, T.K., Graff, J.R., Halsey, K.H., Milligan, A.J., Siegel, D.A., Brown, M.B., 2016. Revaluating Ocean warming impacts on global phytoplankton. Nat. Clim. Chang. 6, 323–330. https://doi.org/10.1038/nclimate2838.
- Broadgate, W.J., Malin, G., Küpper, F.C., Thompson, A., Liss, P.S., 2004. Isoprene and other non-methane hydrocarbons from seaweeds: a source of reactive hydrocarbons to the atmosphere. Mar. Chem. 88, 61–73. https://doi.org/10.1016/j.marchem.2004.03.002.

- Buck, C.S., Landing, W.M., Resing, J., 2013. Pacific Ocean aerosols: deposition and solubility of iron, aluminum, and other trace elements. Mar. Chem. 157, 117–130. https://doi.org/ 10.1016/j.marchem.2013.09.005.
- Calvert, J.G., 1976. Test of the theory of ozone generation in Los Angeles atmosphere. Environ. Sci. Technol. 10, 248–256. https://doi.org/10.1021/es60114a002.
- Carpenter, L.J., Archer, D., Beale, R., Archer, S.D., 2012. Ocean-atmosphere trace gas exchange. Chem. Soc. Rev. 41, 6473–6506. https://doi.org/10.1039/c2cs35121h.
- Carter, W.P.L., 2010. Development of the SAPRC-07 chemical mechanism. Atmos. Environ. 44, 5324–5335. https://doi.org/10.1016/j.atmosenv.2010.01.026.
- Carter, W.P.L., 1994. Development of ozone reactivity scales for volatile organic compounds. J. Air Waste Manage. Assoc. 44, 881–899. https://doi.org/10.1080/1073161X.1994. 10467290.
- Chavez, F.P., Toggweiler, J.R., 1995. Physical estimates of global new production: the upwelling contribution. In: Summerhayes, C.P. (Ed.), Upwelling in the Ocean: Modern Processes and Ancient Records. John Wiley, NJ, pp. 313–320.
- Chen, Z., Sun, J., Chen, D., Wang, S., Yu, H., Chen, H., Wang, M., 2021. Effects of ocean currents in the Western Pacific Ocean on net-phytoplankton community compositions. Diversity 13, 428. https://doi.org/10.3390/D13090428.
- Dani, K.G.S., Loreto, F., 2017. Trade-off between dimethyl sulfide and isoprene emissions from marine phytoplankton. Trends Plant Sci. 22, 361–372. https://doi.org/10.1016/j. tplants.2017.01.006.
- Ding, X., Wang, X., Xie, Z., Zhang, Z., Sun, L., 2013. Impacts of siberian biomass burning on organic aerosols over the North Pacific Ocean and the Arctic: primary and secondary organic tracers. Environ. Sci. Technol. 47, 3149–3157. https://doi.org/10.1021/ES3037093.
- Fu, P.Q., Kawamura, K., Miura, K., 2011. Molecular characterization of marine organic aerosols collected during a round-the-world cruise. J. Geophys. Res. Atmos. 116, 13302. https://doi.org/10.1029/2011JD015604.
- Fu, P.Q., Kawamura, K., Chen, J., Charrière, B., Sempéré, R., 2013. Organic molecular composition of marine aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary aerosol formation. Biogeosciences 10, 653–667. https://doi.org/10. 5194/BG-10-653-2013.
- Gist, N., Lewis, A.C., 2006. Seasonal variations of dissolved alkenes in coastal waters. Mar. Chem. 100, 1–10. https://doi.org/10.1016/J.MARCHEM.2005.10.004.
- Grosjean, D., Seinfeld, J.H., 1989. Parameterization of the formation potential of secondary organic aerosols. Atmos. Environ. 23, 1733–1747. https://doi.org/10.1016/0004-6981 (89)90058-9.
- Hoque, M.M.M., Kawamura, K., Uematsu, M., 2017. Spatio-temporal distributions of dicarboxylic acids, ω-oxocarboxylic acids, pyruvic acid, α-dicarbonyls and fatty acids in the marine aerosols from the north and South Pacific. Atmos. Res. 185, 158–168. https:// doi.org/10.1016/J.ATMOSRES.2016.10.022.
- Hu, D., Wu, L., Cai, W., Gupta, A.Sen, Ganachaud, A., Qiu, B., Gordon, A.L., Lin, X., Chen, Z., Hu, S., Wang, G., Wang, Q., Sprintall, J., Qu, T., Kashino, Y., Wang, F., Kessler, W.S., 2015. Pacific western boundary currents and their roles in climate. Nat. 522, 299–308. https://doi.org/10.1038/nature14504.
- Jickells, T.D., An, Z.S., Andersen, K.K., Baker, A.R., Bergametti, C., Brooks, N., Cao, J.J., Boyd, P.W., Duce, R.A., Hunter, K.A., Kawahata, H., Kubilay, N., LaRoche, J., Liss, P.S., Mahowald, N., Prospero, J.M., Ridgwell, A.J., Tegen, I., Torres, R., 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. Science 308, 67–71. https://doi.org/10.1126/science.1105959.
- Jickells, T.D., Buitenhuis, E., Altieri, K., Baker, A.R., Capone, D., Duce, R.A., Dentener, F., Fennel, K., Kanakidou, M., LaRoche, J., Lee, K., Liss, P., Middelburg, J.J., Moore, J.K., Okin, G., Oschlies, A., Sarin, M., Seitzinger, S., Sharples, J., Singh, A., Suntharalingam, P., Uematsu, M., Zamora, L.M., 2017. A reevaluation of the magnitude and impacts of anthropogenic atmospheric nitrogen inputs on the ocean. Glob. Biogeochem. Cycles 31, 289–305. https://doi.org/10.1002/2016GB005586.
- Juhls, B., Overduin, P.P., Hölemann, J., Hieronymi, M., Matsuoka, A., Heim, B., 2019. Dissolved organic matter at the fluvial-marine transition in the Laptev Sea using in situ data and ocean colour remote sensing. Biogeosciences 16, 2693–2713. https://doi.org/ 10.5194/bg-16-2693-2019.
- Kansal, A., 2009. Sources and reactivity of NMHCs and VOCs in the atmosphere: a review. J. Hazard. Mater. 166 (1), 17–26. https://doi.org/10.1016/j.jhazmat.2008.11.048.
- Krechmer, J.E., Coggon, M.M., Massoli, P., Nguyen, T.B., Crounse, J.D., Hu, W., Day, D.A., Tyndall, G.S., Henze, D.K., Rivera-Rios, J.C., Nowak, J.B., Kimmel, J.R., Mauldin, R.L., Stark, H., Jayne, J.T., Sipilä, M., Junninen, H., St. Clair, J.M., Zhang, X., Feiner, P.A., Zhang, L., Miller, D.O., Brune, W.H., Keutsch, F.N., Wennberg, P.O., Seinfeld, J.H., Worsnop, D.R., Jimenez, J.L., Canagaratna, M.R., 2015. Formation of low volatility organic compounds and secondary organic aerosol from isoprene hydroxyhydroperoxide low-NO oxidation. Environ. Sci. Technol. 49, 10330–10339. https://doi.org/10.1021/ acs.est.5b02031.
- Krom, M.D., Shi, Z., Stockdale, A., Berman-frank, I., 2016. Response of the eastern Mediterranean microbial ecosystem to dust and dust affected by acid processing in the atmosphere. Front. Mar. Sci. 3, 133. https://doi.org/10.3389/fmars.2016.00133.
- Kurihara, M., Iseda, M., Ioriya, T., Horimoto, N., Kanda, J., Ishimaru, T., Yamaguchi, Y., Hashimoto, S., 2012. Brominated methane compounds and isoprene in surface seawater of Sagami Bay: concentrations, fluxes, and relationships with phytoplankton assemblages. Mar. Chem. 134–135, 71–79. https://doi.org/10.1016/J.MARCHEM.2012.04.001.
- Kuttippurath, J., Ardra, D., Raj, S., Feng, W., 2023. A seasonal OH minimum region over the Indian Ocean. Atmos. Environ. 295, 119536. https://doi.org/10.1016/j.atmosenv.2022. 119536.
- Lee, R.F., Baker, J., 1992. Ethylene and ethane production in an estuarine river: formation from the decomposition of polyunsaturated fatty acids. Mar. Chem. 38, 25–36. https:// doi.org/10.1016/0304-4203(92)90065-I.
- Letelier, R.M., Björkman, K.M., Church, M.J., Hamilton, D.S., Mahowald, N.M., Scanza, R.A., Schneider, N., White, A.E., Karl, D.M., 2019. Climate-driven oscillation of phosphorus and iron limitation in the North Pacific subtropical gyre. Proc. Natl. Acad. Sci. U. S. A. 116 (26), 12720–12728. https://doi.org/10.1073/pnas.1900789116.

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- Li, J.L., Zhai, X., Ma, Z., Zhang, H.H., Yang, G.P., 2019. Spatial distributions and sea-to-air fluxes of non-methane hydrocarbons in the atmosphere and seawater of the Western Pacific Ocean. Sci. Total Environ. 672, 491–501. https://doi.org/10.1016/j.scitotenv.2019. 04.019.
- Li, J.L., Zhai, X., Wu, Y.C., Wang, J., Zhang, H.H., Yang, G.P., 2021. Emissions and potential controls of light alkenes from the marginal seas of China. Sci. Total Environ. 758, 143655. https://doi.org/10.1016/j.scitotenv.2020.143655.
- Li, J.L., Zhai, X., Zhang, H.H., Yang, G.P., 2018. Temporal variations in the distribution and sea-to-air flux of marine isoprene in the East China Sea. Atmos. Environ. 187, 131–143. https://doi.org/10.1016/j.atmosenv.2018.05.054.
- Li, Q., Legendre, L., Jiao, N.Z., 2015. Phytoplankton responses to nitrogen and iron limitation in the tropical and subtropical Pacific Ocean. J. Plankton Res. 37, 306–319. https://doi. org/10.1093/plankt/fbv008.
- Liakakou, E., Vrekoussis, M., Bonsang, B., Donousis, C., Kanakidou, M., Mihalopoulos, N., 2007. Isoprene above the eastern Mediterranean: seasonal variation and contribution to the oxidation capacity of the atmosphere. Atmos. Environ. 41 (5), 1002–1010. https:// doi.org/10.1016/j.atmosenv.2006.09.034.
- Lønborg, C., Søndergaard, M., 2009. Microbial availability and degradation of dissolved organic carbon and nitrogen in two coastal areas. Estuar. Coast. Shelf Sci. 81, 513–520. https://doi.org/10.1016/j.ecss.2008.12.009.
- Longo, A.F., Feng, Y., Lai, B., Landing, W.M., Shelley, R.U., Nenes, A., Mihalopoulos, N., Violaki, K., Ingall, E.D., 2016. Influence of atmospheric processes on the solubility and composition of iron in saharan dust. Environ. Sci. Technol. 50, 6912–6920. https://doi. org/10.1021/acs.est.6b02605.
- Martino, M., Hamilton, D., Baker, A.R., Jickells, T.D., Bromley, T., Nojiri, Y., Quack, B., Boyd, P.W., 2014. Western Pacific atmospheric nutrient deposition fluxes, their impact on surface ocean productivity. Glob. Biogeochem. Cycles 28, 712–728. https://doi.org/10. 1002/2013GB004794.
- Matsunaga, S., Mochida, M., Saito, T., Kawamura, K., 2002. In situ measurement of isoprene in the marine air and surface seawater from the western North Pacific. Atmos. Environ. 36, 6051–6057. https://doi.org/10.1016/S1352-2310(02)00657-X.
- McKay, W.A., Turner, M.F., Jones, D.M.R., Halliwell, C.M., 1996. Emissions of hydrocarbons from marine phytoplankton—Some results from controlled laboratory experiments. Atmos. Environ. 30, 2583–2593. https://doi.org/10.1016/1352-2310(95)00433-5.
- Merrill, J.T., Uematsu, M., Bleck, R., 1980. Meteorological analysis of long range transport of mineral aerosols over the North Pacific. J. Geophys. Res. Atmos. 94, 8584–8598. https:// doi.org/10.1029/JD094iD06p08584.
- Meskhidze, N., Chameides, W.L., Nenes, A., 2005. Dust and pollution: a recipe for enhanced ocean fertilization? J. Geophys. Res. Atmos. 110, 1–23. https://doi.org/10.1029/ 2004JD005082.
- Meskhidze, N., Sabolis, A., Reed, R., Kamykowski, D., 2015. Quantifying environmental stress-induced emissions of algal isoprene and monoterpenes using laboratory measurements. Biogeosciences 12, 637–651. https://doi.org/10.5194/bg-12-637-2015.
- Nishioka, J., Takeda, S., Kudo, I., Tsumune, D., Yoshimura, T., Kuma, K., Tsuda, A., 2003. Size-fractionated iron distributions and iron-limitation processes in the subarctic NW Pacific. Geophys. Res. Lett. 30 (14), 1730. https://doi.org/10.1029/2002GL016853.
- O'Dowd, C.D., De Leeuw, G., 2007. Marine aerosol production: a review of the current knowledge. Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 365, 1753–1774. https://doi.org/10. 1098/rsta.2007.2043.
- Panda, U., Mahapatra, P.S., Das, T., 2015. Study of C2–C5 Non-methane Hydrocarbons and Their Ozone Formation Potential at Bhubaneswar, an Eastern Coastal Site in India. 30, pp. 195–202. https://doi.org/10.1007/s12647-015-0134-4.
- Parsons, T.R., Maita, Y., Lalli, C.M., 1984. A Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press, Oxford https://doi.org/10.1016/0198-0149(84) 90086-4.
- Plass-Dülmer, C., Khedim, A., Koppmann, R., Johnen, F.J., Rudolph, J., Kuosa, H., 1993. Emissions of light nonmethane hydrocarbons from the Atlantic into the atmosphere. Glob. Biogeochem. Cycles 7, 211–228. https://doi.org/10.1029/92GB02361.
- Plass-Dülmer, C., Koppmann, R., Ratte, M., Rudolph, J., 1995. Light nonmethane hydrocarbons in seawater. Glob. Biogeochem. Cycles 9, 79–100. https://doi.org/10.1029/ 94GB02416.
- Poisson, N., Kanakidou, M., Crutzen, P.J., 2000. Impact of non-methane hydrocarbons on tropospheric chemistry and the oxidizing power of the global troposphere: 3-dimensional modelling results. J. Atmos. Chem. 36, 157–230. https://doi.org/10.1023/A: 1006300616544.
- Qiu, B., Rudnick, D.L., Cerovecki, I., Cornuelle, B.D., Chen, S., Schönau, M.C., McClean, J.L., Gopalakrishnan, G., 2015. The pacific north equatorial current: new insights from the origins of the kuroshio and Mindanao currents (OKMC) project. Oceanography 28, 24–33. https://doi.org/10.5670/OCEANOG.2015.78.
- Repeta, D.J., Ferrón, S., Sosa, O.A., Johnson, C.G., Repeta, L.D., Acker, M., DeLong, E.F., Karl, D.M., 2016. Marine methane paradox explained by bacterial degradation of dissolved organic matter. Nat. Geosci. 9, 884–887. https://doi.org/10.1038/ngeo2837.
- Rex, M., Wohltmann, I., Ridder, T., Lehmann, R., Rosenlof, K., Wennberg, P., Weisenstein, D., Notholt, J., Krüger, K., Mohr, V., Tegtmeier, S., 2014. A tropical West Pacific OH minimum and implications for stratospheric composition. Atmos. Chem. Phys. 14, 4827–4841. https://doi.org/10.5194/acp-14-4827-2014.
- Riemer, D.D., Milne, P.J., Zika, R.G., Pos, W.H., 2000. Photoproduction of nonmethane hydrocarbons (NMHCs) in seawater. Mar. Chem. 71, 177–198. https://doi.org/10.1016/ S0304-4203(00)00048-7.

- Sahu, L.K., Lal, S., Venkataramani, S., 2011. Seasonality in the latitudinal distributions of NMHCs over bay of Bengal. Atmos. Environ. 45, 2356–2366. https://doi.org/10.1016/ j.atmosenv.2011.02.021.
- Saito, T., Yokouchi, Y., Kawamura, K., 2000. Distributions of C2–C6 hydrocarbons over the western North Pacific and eastern Indian Ocean. Atmos. Environ. 34, 4373–4381. https://doi.org/10.1016/S1352-2310(00)00249-1.
- Sander, R., 2015. Compilation of Herny's law constants (version 4.0) for water as solvent. Atmos. Chem. Phys. 15, 4399–4981. https://doi.org/10.5194/acp-15-4399-2015.
- Sharkey, T.D., Wiberley, A.E., Donohue, A.R., 2008. Isoprene emission from plants: why and how. Ann. Bot. 101 (1), 5–18. https://doi.org/10.1093/aob/mcm240.
- Shi, Z., Krom, M.D., Bonneville, S., Baker, A.R., Jickells, T.D., Benning, L.G., 2009. Formation of iron nanoparticles and increase in iron reactivity in mineral dust during simulated cloud processing. Environ. Sci. Technol. 43, 6592–6596. https://doi.org/10.1021/ ES901294G.
- Shi, Z., Krom, M.D., Bonneville, S., Benning, L.G., 2015. Atmospheric processing outside clouds increases soluble iron in mineral dust. Environ. Sci. Technol. 49, 1472–1477. https://doi.org/10.1021/es504623x.
- Singh, H.B., Zimmerman, P., 1992. Atmospheric distributions and sources of nonmethane hydrocarbons. In: Nriagu, J.O. (Ed.), Gaseous Pollutants: Characterisation and Cycling. Wiley, New York, p. 235.
- Spencer, R.W., 1993. Global oceanic precipitation from the MSU during 1979–91 and comparisons to other climatologies. J. Clim. 6, 1301–1326. https://doi.org/10.1175/1520-0442(1993)006<1301:GOPFTM>2.0.CO;2.
- Spivakovsky, C.M., Logan, J.A., Montzka, S.A., Balkanski, Y.J., Jones, D.B.A., Horowitz, L.W., Fusco, A.C., Prather, M.J., Wofsy, S.C., Mcelroy, M.B., 2000. Three-dimensional Climatological Distribution of Tropospheric OH: Update and Evaluation. 105, pp. 8931–8980. https://doi.org/10.1029/1999jd901006.
- Tanimoto, H., Kameyama, S., Iwata, T., Inomata, S., Omori, Y., 2013. Measurement of air sea exchange of dimethyl sulfide and acetone by PTR-MS coupled with gradient flux technique. Environ. Sci. Technol. 48 (1), 526–533. https://doi.org/10.1021/es4032562.
- Tanita, I., Shiozaki, T., Kodama, T., Hashihama, F., Sato, M., Takahashi, K., Furuya, K., 2021. Regionally variable responses of nitrogen fixation to iron and phosphorus enrichment in the Pacific Ocean. 126(9). J. Geophys. Res.: Biogeosci. 126, e2021JG006542. https://doi. org/10.1029/2021JG006542.
- Tesdal, J.E., Christian, J.R., Monahan, A.H., Salzen, K.V., 2016. Sensitivity of modelled sulfate aerosol and its radiative effect on climate to ocean DMS concentration and air–sea flux. Atmos. Chem. Phys. 16 (17), 10847–10864. https://doi.org/10.5194/acp-16-10847-2016.
- Tran, S., Bonsang, B., Gros, V., Peeken, I., Sarda-Esteve, R., Bernhardt, A., Belviso, S., 2013. A survey of carbon monoxide and non-methane hydrocarbons in the Arctic Ocean during summer 2010. Biogeosciences 10, 1909–1935. https://doi.org/10.5194/bg-10-1909-2013.
- Tripathi, N., Sahu, L.K., Singh, A., Yadav, R., Patel, A., Patel, K., Meenu, P., 2020. Elevated levels of biogenic nonmethane hydrocarbons in the marine boundary layer of the Arabian Sea during the intermonsoon. J. Geophys. Res. Atmos. 125, e2020JD032869. https://doi. org/10.1029/2020JD032869.
- Tsurushima, N., Watanabe, S., Tsunogai, S., 1999. Determination of light hydrocarbons dissolved in seawater. Talanta 50 (3), 577–583. https://doi.org/10.1016/S0039-9140(99) 00144-7.
- Viljoen, J.J., Philibert, R., Van Horsten, N., Mtshali, T., Roychoudhury, A.N., Thomalla, S., Fietz, S., 2018. Phytoplankton response in growth, photophysiology and community structure to iron and light in the polar frontal zone and Antarctic waters. Deep-Sea Res. I Oceanogr. Res. Pap. 141, 118–129. https://doi.org/10.1016/j.dsr.2018.09.006.
- Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res. 97, 7373–7382. https://doi.org/10.1029/92JC00188.
- Wu, Y.C., Li, J.L., Wang, J., Zhuang, G.C., Liu, X.T., Zhang, H.H., Yang, G.P., 2021. Occurance, emission and environmental effects of non-methane hydrocarbons in the Yellow Sea and the East China Sea. Environ. Pollut. 270, 116305. https://doi.org/10.1016/j.envpol. 2020.116305.
- Zender, C.S., Bian, H., Newman, D., 2003. Mineral dust entrainment and deposition (DEAD) model: description and 1990s dust climatology. J. Geophys. Res. Atmos. 108, 4416. https://doi.org/10.1029/2002jd002775.
- Zhang, C., Gao, H., Yao, X., Shi, Z., Shi, J., Yu, Y., Meng, L., Guo, X., 2018. Phytoplankton growth response to asian dust addition in the Northwest Pacific Ocean versus the Yellow Sea. Biogeosciences 15, 749–765. https://doi.org/10.5194/BG-15-749-2018.
- Zhang, C., He, J., Yao, X., Mu, Y., Guo, X., Ding, X., Yu, Y., Shi, J., Gao, H., 2020. Dynamics of phytoplankton and nutrient uptake following dust additions in the Northwest Pacific. Sci. Total Environ. 739, 139999. https://doi.org/10.1016/j.scitotenv.2020.139999.
- Zhang, C., Yao, X., Chen, Y., Chu, Q., Yu, Y., Shi, J., Gao, H., 2019. Variations in the phytoplankton community due to dust additions in eutrophication, LNLC and HNLC oceanic zones. Sci. Total Environ. 669, 282–293. https://doi.org/10.1016/j.scitotenv.2019.02. 068.
- Zhao, T.L., Gong, S.L., Zhang, X.Y., Blanchet, J.-P., McKendry, I.G., Zhou, Z.J., 2006. A simulated climatology of asian dust aerosol and its trans-Pacific transport. Part I: mean climate and validation. J. Clim. 19, 88–103. https://doi.org/10.1175/JCLI3605.1.
- Zhao, Y., Zhang, L., Pan, Y., Wang, Y., Paulot, F., Henze, D.K., 2015. Atmospheric nitrogen deposition to the northwestern Pacific: seasonal variation and source attribution. Atmos. Chem. Phys. 15, 10905–10924. https://doi.org/10.5194/acp-15-10905-2015.