



Brief Report

Potential Implications of the Sesquiterpene Presence over the Remote Marine Boundary Layer in the Arctic Region

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Abstract: We present reactive VOC observations over the North Pacific and the Arctic Ocean from airborne and shipborne measurements, investigating, in particular, distributions of biogenic volatile organic compounds that may be emitted from phytoplankton. In contrast to terrestrial observations, isoprene (C₅H₈), the most dominant BVOC emission from the terrestrial ecosystem, was mostly present under the lower detection limit along with monoterpenes (C₁₀H₁₆), the second largest emission from the terrestrial ecosystem. However, we consistently detected sesquiterpenes (C₁₅H₂₄) over the Arctic Ocean for the two Arctic cruises. The results of the analysis of sorbent cartridge samplings conducted over the Arctic Ocean on Korean icebreaker R/V Araon in 2016 and 2017 illustrate that few tens ppt levels of sesquiterpenes were present over the Arctic Ocean. Moreover, the concentration variation was positively correlated with the quantitative indicators of ocean biological activities, such as chlorophyll-*a*, dissolved DMS, and the ratio of dissolved O₂ and Ar. This suggests that further investigations on sesquiterpene's emission and atmospheric transformation processes over the marine boundary layer are required.

Keywords: arctic ocean; BVOC; sesquiterpenes; Araon; DMS

1. Introduction

The planetary boundary layer is the interface between the surface and atmosphere of the Earth. As most of the reactive trace gases controlling oxidation capacity and reactivity are emitted by the surface processes, it is important to properly constrain emission distributions of various reactive trace gases over the boundary layer for the proper representations of reactivity throughout the troposphere. However, oceanic emissions of reduced gases have rarely been investigated relative to terrestrial emission sources. Even dimethyl sulfide (DMS), one of the most studied reactive gases [1,2], has significant uncertainty in grasping its global distributions over the remote marine boundary layer due to limited accessibility [3].

It has also been speculated that biologically derived volatile organic compounds (BVOCs) such as terpenoids (isoprene, monoterpenes, and sesquiterpenes) are also produced through physiological processes of phytoplankton, subsequently emitted to the atmosphere. Bonsang et al. [4] first presented dissolved isoprene over the Mediterranean Sea and the Pacific Ocean. Using the multiple profiles of dissolved isoprene in the seawater column, isoprene emission rates were estimated using Henry's constant. The analysis suggests that the estimated bottom-up isoprene emission is negligible compared with the emission from the terrestrial ecosystem [5–7]. Guenther et al. [8] developed the hypothesis from laboratory study results and sparse in situ observations to establish a model

Citation: Park, K.; Rodriguez, B.; Thomas, J.; Gu, D.; Zhang, M.; Sarkar, C.; Guenther, A.; Kim, S. Potential Implications of the Sesquiterpene Presence over the Remote Marine Boundary Layer in the Arctic Region. *Atmosphere* **2023**, *14*, 823. https://doi.org/10.3390/ atmos14050823

Academic Editor: Evangelos Tolis

Received: 17 March 2023 Revised: 24 April 2023 Accepted: 28 April 2023 Published: 3 May 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/license s/by/4.0/). framework. The model is based on the representation of a relationship of dissolved organic matter in the seawater deduced from an ocean color remote sensing dataset and radiation flux. In the model frame, only two categories—other reactive VOCs (other than isoprene and monoterpenes) and oxygenated VOCs (OVOCs)—were assessed in global emissions, which concluded a substantially less contribution (less than 0.5% in the carbon mass unit) to the global VOC budget from oceanic sources compared with terrestrial sources.

Laboratory studies have confirmed isoprene emission from various phytoplankton monocultures [9]. The studies reported that the isoprene emission rates could be parameterized as a function of temperature and solar radiation similar to that described for the isoprene emission of terrestrial plants. However, various laboratory studies also have illustrated inconsistent emission dependency upon the phytoplankton types. Bonsang et al. [10] reported a wide range of chlorophyll-normalized measurable isoprene production rates from major phytoplankton types. Therefore, this rather small set of experimental results causes substantial uncertainty in global emission estimation, which ranges from 0.27 Tg C yr⁻¹ to 11.6 Tg C yr⁻¹ [11]. The top-down estimates tend to be higher than the bottom-up ones, based on the limited isoprene observations over the remote boundary layers. At the same time, more frequent surveys are performed in coastal regions, which show higher productivity compared to the open ocean. Furthermore, ship-borne observations tend to aim for revealing elevated concentration events rather than measuring background concentration when bloom subsides. For example, among the published topdown estimates, [12] presented the highest estimates for isoprene and monoterpene emissions based on one shipborne observation conducted during the Organic over Ocean Modifying Particles in both Hemisphere (OOMPH) summer cruise from Cape Town, South Africa, to Punta Arenas, Chile. According to this observation, both isoprene and α -pinene were observed up to a few hundred ppt, which is particularly high compared to the limited number of observations conducted in the open ocean.

In summary, the large outstanding uncertainty in VOC emission estimates becomes one of the missing constraints in global estimates of organic aerosol contributions from marine environments ranging from 8 Tg C yr⁻¹ to 75 Tg C yr⁻¹[13]. Although it is still substantially less than isoprene emission from the terrestrial ecosystem (535 Tg C yr⁻¹), considering limited reactive VOC sources in the remote marine boundary layer, this uncertainty needs to be better constrained. Therefore, more comprehensive observational constraints such as boundary layer distributions of BVOCs will enhance our understanding of global secondary organic aerosol distributions, ultimately becoming the basis for assessing climate forcing from aerosol through both direct and indirect mechanisms.

This motivates us to present a comprehensive VOC distribution from anthropogenic and biogenic sources over the Pacific and the Arctic. Specifically, we will discuss airborne observed VOCs over the marine boundary layer during the NASA INTEX-B field mission in 2006. In addition, VOC observational results during the trans-Pacific and Arctic cruise on Korean icebreaker R/V Araon in 2016 and 2017 are presented. This work provides a snapshot of the distribution of reactive VOCs over the marine boundary layer of the greater Pacific Ocean.

2. Methods.

2.1. VOC Analysis

In this study, we present the VOC dataset, particularly terpenoids, from two different sampling and analysis methods. One is the whole air sampling method with gas chromatography and mass spectrometry. The technical details are thoroughly described in Colman et al. [14]. The method utilized 2-L electro-polished stainless-steel canisters for air sampling. After the transport to the laboratory at the University of California Irvine, USA, the sample is introduced to the GC-MS system with four columns to analyze more than 50 compounds ranging from C2 to C10 compounds with different functional groups. Most compounds are quantified within 5% of analytical precision and 3 pptv of the lower

detection limit. This sampling and analytical method have been deployed on the NASA DC-8 Airborne Laboratory. The dataset is open to the public, and we present observations conducted during the INTEX-B campaign over the East Pacific Ocean in 2006.

The sorbent cartridge air samples were collected during the R/V Araon's Arctic Cruises in 2016 and 2017. A time-of-flight mass Spectrometer (ToF-MS) with Select-eV technology (Markes BenchTOF Select-eV) was used to quantify the collected VOCs. Hatch, et al. [15] summarize the advantages of ToF-MS compared to the more widely used quad-rupole MS, including better sensitivity, chromatographic separation, and deconvolution of co-eluting compounds due to higher scan rates, mass resolution, and accuracy. The select-eV technology allows the switch between conventional electron ionization (70 eV) and a much softer ionization, down to 10 eV, without losing sensitivity [16]. Samples were analyzed using both conventional ionization to generate spectra that can be compared with standard libraries, including NIST, and with softer ionization to detect molecular ions with much higher sensitivity, and, also, to provide additional information regarding molecular structures for unknown compounds. Nagalingam et al. [17] have described this analytical technique.

2.2. The INTEX-B and the 2016 and 2017 R/V Araon Campaigns

The Intercontinental Chemical Transport Experiment (INTEX)—B campaign was conducted from March to June in 2006. It aimed at characterizing pollution outflow from Mexico City and East Asia. In this study, we present the airborne observation data over the marine boundary layer (<400 m) of the North Pacific. Spatially, the extent of coverage over the marine boundary layer is unprecedented, so we can comprehensively evaluate the distribution of terpenoids, particularly isoprene [18]. The data is publicly available at https://www-air.larc.nasa.gov/missions/intex-b/intexb.html (accessed on 1 March 2023).

The Araon Arctic cruise is an annual campaign conducted by the Korea Polar Research Institute (KOPRI). We conducted ambient VOC samplings using a handheld pump and sorbent cartridges. We sampled six standard liters over a sampling time of 30 min. A potassium iodide (KI) doped Pall filter was used as an ozone scrubber. During Araon's 2016 campaign (5–21 August 2016), we conducted blank sampling at the frequency of one for every ten samples. For the 2017 cruise (6–25 August 2017), we conducted the blank sampling more often, with a frequency of one for every two ambient samples. Blank sampling was conducted using an identical procedure to that of air sample collection for VOCs analysis, with the only difference being that the pump was turned off.

3. Results

3.1. Isoprene Distribution over the North Pacific during the INTEX-B Campaign

The flight track of NASA DC-8 during the INTEX-B campaign for the second phase is presented in Figure 1.

The flight track presents substantial aerial coverage over the East North Pacific with color-coded altitudes. The research flight was planned to sample from the boundary layer to the upper troposphere and lower stratosphere (UTLS). As presented, there have been several boundary layer samplings for each science flight, and most of the time, the boundary layer runs maintained an altitude of 400 m or below. This flight pattern allows us to assume that the air sampled on the boundary layer run represents the air-sea interface layer well.



Figure 1. The NASA DC-8 flight tracks during the INTEX-B over the North Pacific. Altitude and sea ice content are presented with color coding. The sea ice concentration is obtained from the near-real-time NOAA/NSIDC climate data record of passive microwave sea ice concentration, version 1.

Most anthropogenic tracers, such as CO, benzene, and toluene, were observed at the level of the Northern Hemispheric background (Figure 2). The average distribution of chlorophyll concentration in May 2006 is also presented in Figure 2. The distribution map was a compilation of the MODIS/AQUA sensor data provided by the NASA Earth Observing Laboratory website. The flight track also represents the low-productivity pacific gyre region to the more productive mid-latitude open ocean. In addition, the relatively more productive continental shelf region was also sampled during the science flights.



Figure 2. The distributions of various trace gases observed on NASA DC-8 during the INTEX-B campaign, along with chlorophyll-*a* observed by MODIS/AQUA.

The distributions of DMS and isoprene over the East North Pacific are presented in Figure 2. Overall, DMS was quantified in the lower level (<30 ppt), and isoprene was detected lower than the detection limits all over the study area. During the INTEX-B campaign, OH was also quantified by the laser-induced fluorescence technique [19], and the daytime high was measured at ~ 1×10^6 molecules cm⁻³. In certain environments, isoprene and DMS lifetime is expected to be 2.7 h and 64 h, respectively. This estimated lifetime

warrants the assumption that the air sampled on the NASA DC-8 aircraft contains similar concentration levels of these gases, considering the boundary layer samplings were conducted below 400 m altitude.

3.2. Sesquiterpene Distributions over the Arctic Ocean

The Arctic Ocean off the coast of Alaska, including the Chuckchi Sea and the Bering Sea, is known for its highly productive area [20]. Thus, this region will allow us to survey the impacts of biological activities over the surface ocean to reactive gas distributions over the marine boundary layer. To understand the link between VOCs distributions and ocean productivity, we present three different measurement parameters reflecting the productivity of the surface ocean. First, fluorescence is a measure of the abundance of chlorophyll-*a* regardless of its biological activities (proxy of bulk phytoplankton biomass), measured by an underway fluorometer (Turner 10-AU, San Jose, CA, USA). Second, biological oxygen supersaturation (Δ O₂/Ar) accurately represents biological oxygen production, which removes the effect of physical processes influencing dissolved oxygen concentration, such as bubble injection, water temperature, and air pressure [21]. Because the physical characteristics (i.e., solubility and diffusivity) of argon and oxygen are similar while argon is biologically inert, the following definition of Δ O₂/Ar enables us to quantify biological oxygen production:

$$\Delta O_2/Ar (\%) = \{(O_2/Ar)_{\text{measured}}/(O_2/Ar)_{\text{saturated}} - 1\} \times 100$$
(1)

where, $(O_2/Ar)_{measured}$ and $(O_2/Ar)_{saturated}$ are the ratios of O_2/Ar in the sampled and air-saturated water, respectively.

Lastly, Dissolved DMS (nM) reflects the abundance and the biological activities of DMS emitting phytoplankton. The high-frequency DMS and O₂/Ar ratio are measured by the underway membrane inlet mass spectrometry system in the ship, and the nominal depth of seawater supply was 7 m.

The distributions of fluorescence, dissolved DMS concentration, $\Delta O_2/Ar$, and sesquiterpene observed during the Araon's 2016 and 2017 cruises are shown in Figures 3 and 4. As is consistent with the satellite chlorophyll observations averaged over August 2016 and 2017 in the figure, the Chuckchi Sea area consistently illustrates higher fluorescence, DMS, and $\Delta O_2/Ar$ values. Correspondingly, sesquiterpenes were detected up to a few hundred ppt. The exclusively detected sesquiterpene species were longifolene in 2016 and cubenene in 2017. Isoprene or monoterpene species were not identified in the mass spectrum. A previous study [17] demonstrated that the analytical technique introduced in this study is capable of detecting a wide range of naturally present monoterpene species. In both years, the region where the elevated sesquiterpene was observed illustrated higher productivity. This observation becomes clear by comparing the time series of sesquiterpene levels with dissolved DMS, fluorescence, and $\Delta O_2/Ar$ as presented in Figures 5 and 6. The comparison suggests that observed atmospheric sesquiterpenes are likely from oceanic biological activities.



Figure 3. The spatial distributions of the atmospheric sesquiterpene and other oceanographic parameters observed during 2016 on R/V Araon's Arctic research cruise.



Figure 4. The spatial distributions of the atmospheric sesquiterpene and other oceanographic parameters observed during 2017 on R/V Araon's Arctic research cruise.



0 08/03 08/05 08/07 08/09 08/11 08/13 08/15 08/17 08/19 08/21 08/23 Date Figure 5. The temporal variation of the atmospheric sesquiterpene and other oceanographic param-

eters observed during 2016 on R/V Araon's Arctic research cruise. The blue dots are observed oceanographic parameters (DMS, $\Delta O_2/Ar$, and Fluorescence) and the red triangles are measured longifolene concentration.



Figure 6. The temporal variation of the atmospheric sesquiterpene and other oceanographic parameters observed during 2017 on R/V Araon's Arctic research cruise. The blue dots are observed oceanographic parameters (DMS, ΔO_2 /Ar, and Fluorescence) and the red triangles are measured longifolene concentration.

To our best knowledge, this is the first report of the presence of sesquiterpenes over the marine boundary layer. As stressed, terpenoid measurements have rarely been conducted in the open ocean. Even considering the rarity, it is worth speculating why this is the first report. Sesquiterpenes are rarely quantified terpenoid species, even in terrestrial ecosystems [22]. This is mainly due to the difficulties in proper samplings and quantifications of sesquiterpenes, as they are considered semi-volatile organic compounds. For the GC application, both sampling and sensitivity have been considered a limitation for sesquiterpene quantifications. In addition, the ToF-GC system demonstrates higher sensitivity toward the higher mass compounds. We think that the combination of the establishment of the sampling methods and the advanced analytical system allow us to quantify sesquiterpenes in the remote marine boundary layer.

4. Discussion and Outlook

Remarkably, sesquiterpenes have been observed at such high concentration levels over the Chukchi Sea for 2 years. The observed mixing ratio levels are comparable with reported values from terrestrial ecosystems. In terms of tropospheric reactive gas loading, the observed levels are not expected to be a substantial contribution. Longifolene, a dominant observed sesquiterpene observed in 2016, is a reactive isomer among sesquiterpenes. Its reaction constants with OH and ozone are $k_{OH} = 4.70 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and k_{O3} $< 7.01 \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹ [23], with which we can assess the lifetime of longifolene for 16 h and 4.6 days, towards reactions with OH (5×10^5 molecules cm⁻³) and ozone (20 ppb), respectively. The atmospheric oxidation rates of alpha-cedrene towards OH is marginally faster ($k_{OH} = 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) than that of longifolene [24]. However, the reaction constant with ozone is around 5.6 times faster ($k_{03} = 3.9 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$ s-1) than that of longifolene. Therefore, the lifetimes of the detected sesquiterpenes are expected to be around ~ 10 h. Mao et al. [19] presented OH reactivity observations over the Pacific with missing OH reactivity (~50%); in other words, the fraction of observed OH reactivity that the observed trace gas dataset cannot account for during INTEX-B. The analysis shows that the degree of missing OH reactivity positively correlates with underpredicted formaldehyde and over-predicted hydroxyl radical in the constrained box model framework. Therefore, the authors concluded that the quantified missing OH reactivity most likely originated from reaction products of reactive VOCs with an oxidation product of formaldehyde. As formaldehyde is a universal oxidation product for most of the terpenes [25], it is entirely plausible that Mao et al. [19] does not account for the marine sesquiterpenes [19], and that their oxidation products may help to reconcile missing OH reactivity. Indeed, multiple studies have demonstrated that multi-generation oxidation products could have higher OH reactivity than those from the precursors' [26–28]. Although the detected sesquiterpenes are not particularly reactive, and, thus, not significantly contributing total OH reactivity (~0.05 s⁻¹), such as β-caryophyllene (~minutes [23]), it is also plausible that the reactive sesquiterpenes may be co-emitted with the detected sesquiterpenes but never actually sampled due to the short atmospheric lifetime.

It should also be noted that the high aerosol yields of sesquiterpenes (see [29]) illustrates isoprene aerosol yields of a few percent. On the other hand, monoterpenes are assessed as high as ~40% and ~100% for sesquiterpenes [30]. Therefore, we argue that the potential roles of aerosol formation from sesquiterpenes should be investigated by deploying a comprehensive atmospheric chemistry observational suite encompassing gas and aerosol chemical compositions, since cloud formation in the Arctic region is critical to understanding the regional climate change [31].

Author Contributions: Conceptualization, K.P., M.Z. and S.K.; methodology, S.K. and D.G.; validation, A.G., S.K. and K.P.; sampling and formal analysis, B.R., J.T., D.G. and C.S.; data curation, K.P.; writing—original draft preparation, K.P. and S.K.; writing—review and editing, K.P., S.K., M.Z. and A.G.; supervision, S.K.; project administration, K.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by Korea Institute of Marine Science & Technology Promotion (KIMST) funded by the Ministry of Oceans and Fisheries (20210605, Korea-Arctic Ocean Warming and Response of Ecosystem, KOPRI).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All datasets used in this paper are available upon request from the corresponding authors (keyhongpark@kopri.re.kr; saewung.kim@uci.edu).

Acknowledgments: We would like to express our appreciation to the captain and crew members of R/V Araon for their assistance during the Arctic Ocean research cruises. We also extend our thanks to the three reviewers who provided constructive comments for the improvement of the manuscript. This research was supported by Korea Institute of Marine Science & Technology Promotion (KIMST) funded by the Ministry of Oceans and Fisheries (20210605, Korea-Arctic Ocean Warming and Response of Ecosystem, KOPRI).

Conflicts of Interest: The authors declare no conflict of interest.

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