OPEN

SUBJECT AREAS:

ATMOSPHERIC
CHEMISTRY

OCEAN SCIENCES

CLIMATE CHANGE

CRYOSPHERIC SCIENCE

Received

14 May 2013

Accepted

9 July 2013

Published

24 July 2013

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Secondary organic aerosols over oceans via oxidation of isoprene and monoterpenes from Arctic to Antarctic

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Isoprene and monoterpenes are important precursors of secondary organic aerosols (SOA) in continents. However, their contributions to aerosols over oceans are still inconclusive. Here we analyzed SOA tracers from isoprene and monoterpenes in aerosol samples collected over oceans during the Chinese Arctic and Antarctic Research Expeditions. Combined with literature reports elsewhere, we found that the dominant tracers are the oxidation products of isoprene. The concentrations of tracers varied considerably. The mean average values were approximately one order of magnitude higher in the Northern Hemisphere than in the Southern Hemisphere. High values were generally observed in coastal regions. This phenomenon was ascribed to the outflow influence from continental sources. High levels of isoprene could emit from oceans and consequently have a significant impact on marine SOA as inferred from isoprene SOA during phytoplankton blooms, which may abruptly increase up to 95 ng/m³ in the boundary layer over remote oceans.

Secondary organic aerosols (SOA) are produced from atmospheric reactions of anthropogenic and biogenic volatile organic compounds (VOCs) with oxidants like ozone (O₃), nitrogen oxides (NO_x) and OH radicals^{1–4}. As an important component of atmospheric aerosols, SOA affects air quality and earth's radiation budget by scattering and absorbing sunlight and acting as cloud condensation nuclei (CCN)^{1,5}. A recent study in the Amazon discovered that SOA serves as CCN by condensing on primary biological aerosols instead of by forming new particles⁶. Biogenic VOCs (BVOCs) are identified as dominant global SOA precursors over anthropogenic VOCs^{7,8}. On the global scale, isoprene and monoterpenes are main BVOCs and have important contribution to SOA⁹. Emissions of isoprene and monoterpenes from oceans had also been discovered^{10,11}. However, the contributions of oceanic isoprene and monoterpenes to marine aerosols were debatable. Meskhidze and Nenes¹² suggested that SOA formed by the oxidation of isoprene emitted by phytoplankton could significantly affect the chemical composition and number of marine CCN. However, later model studies deemed that oceanic isoprene and monoterpenes did not have a remarkable influence on marine aerosols, because the estimated emissions were much less than other BVOCs like dimethylsulphide (DMS)^{13–15}. Nevertheless, there are great uncertainties about the estimation of global BVOCs emissions. For instance, estimated global oceanic isoprene emissions by “top-down” methods were two orders of magnitude higher than those by “bottom-up” methods¹⁶. Moreover, biogenic SOA over oceans can be produced by the oxidation of BVOCs emitted from oceans, or transported from continents, which should be considered when evaluating the contribution of marine BVOCs to SOA.

Some special SOA tracers can assist in obtaining the information of precursors and SOA formation processes. For instance, pinic acid and pinonic acid as monoterpene SOA tracers were discovered in many places^{2,5,17–20}. Despite its large emission, isoprene was deemed to be a negligible SOA precursor for a long time because of the high vapor pressure of its discerned productions²¹, until Claeys, et al.¹ found 2-methyltetrols (2-methylthreitol and 2-methylerythritol), SOA tracers for isoprene, in the Amazon rain forest. From then on, 2-methyltetrols and other isoprene SOA tracers like 2-methylglyceric acid were successively detected in many sites, such as Finland²², Hungary²³, the US²⁴, China¹⁹ and the Arctic⁵. Nevertheless, all of these studies were conducted in continents. Information about marine SOA from isoprene and monoterpenes was gained only recently through samples collected during a round-the-world cruise in October 1989 to March 1990²⁵ and during a France–Canada–USA joint Arctic campaign, MALINA, in the southern Beaufort Sea in summer 2009²⁶. However, these two cruises were

both confined to the Northern Hemisphere. Significant influence of lands makes it difficult to estimate the contribution of oceanic BVOCs to marine aerosols. More studies about SOA over oceans, especially over remote oceans, are needed for a better understanding of global VOCs emissions and SOA budget.

During the 3rd Chinese Arctic Research Expedition (CHINARE 08) and the 26th Chinese Antarctic Research Expedition (CHINARE 09/10), we collected aerosol samples in the marine boundary layer from the Arctic to the Antarctic, across more than 150° latitudes. Via these samples, this study provides information on the chemical compositions and spatial distribution of isoprene and monoterpene SOA tracers over a large latitudinal range, especially in the Antarctic where the influence of continental ecosystems is negligible. Moreover, this study also estimates secondary organic carbon (SOC) from isoprene and monoterpenes over oceans.

Results

As summarized in Table 1, all types of SOA tracers varied with a wide range during the two cruises. The average values were higher than median values due to the existence of samples with especially high tracer concentrations. The abbreviations of the tracers are listed in Table 1. The sum of isoprene SOA tracers ranged from 0.018 to 36 ng/m³, with an average of 8.5 ± 11 ng/m³. The sum of monoterpene SOA tracers ranged from 0.045 to 20 ng/m³, with a mean of 3.0 ± 5.0 ng/m³. The average levels of marine isoprene and monoterpene SOA tracers were one to two orders of magnitude lower than those in continental samples, while the maximum levels were close to those over the continents^{17,18,27}. Based on 5-day air mass back trajectories (BTs), our samples were split into three groups: ocean origin (OO), land origin (LO) and Antarctic origin (AO). Air mass of OO samples only transported over oceans during the past 5 days, whereas air mass of AO and LO samples passed through continental Antarctica and other continents, respectively. As presented in Figure 1, the concentrations of all types of SOA tracers in the LO samples were much higher than those in the OO samples and the AO samples, indicating significant influence of continental sources on SOA over oceans. The spatial distribution and composition of isoprene and monoterpene SOA tracers are discussed respectively in the following sections.

Isoprene SOA tracers. The results were listed in Table 2 and shown Figure 2a. In order to make a comparative study, the literature reports over oceans up to date, including two cruises in the Northern Hemisphere^{25,26}, were also summarized together. The sum of isoprene SOA tracers in the Northern Hemisphere (14 ± 11 ng/m³) was much higher than that in the Southern Hemisphere (3.3 ± 6.4 ng/m³). The BTs indicated that most samples in the Northern Hemisphere were affected by continents, including samples collected over the Arctic Ocean; while 64% of samples in the Southern Hemisphere belonged to the OO or AO samples. The concentrations over the west North Pacific were much higher than those from the round-the-world cruise²⁵ (Table 2). This difference was likely associated with the seasonal variations of primary productivity. The round-the-world cruise samples were collected in autumn, winter and early spring, while our samples were collected in summer when the emissions of BVOCs increased greatly owing to the peak primary productivity. As this region is notably affected by continents, enhanced input of SOA from adjacent lands resulted in higher concentrations in our samples. The highest levels of isoprene SOA tracers were found in the middle latitudes of the Northern Hemisphere (30°N–60°N), with a mean of 25 ± 7.7 ng/m³. Isoprene SOA tracers in all the samples collected over the East China Sea, Sea of Japan and Sea of Okhotsk were above 20 ng/m³, much higher than those in samples collected in other regions. This indicates that the three seas have the greatest influence of isoprene on aerosols over oceans. The BTs reveal that these samples were affected by air mass from the Eurasian continent and Japan (Figure S1a–f). The airflow from continents may bring massive isoprene SOA. Samples collected in the low latitudes (30°S–30°N) and high latitudes of the Northern Hemisphere (60°N–90°N) also contained high-level isoprene SOA tracers, with the average levels of 9.2 ± 6.7 ng/m³ and 5.3 ± 3.7 ng/m³, respectively. Isoprene SOA tracers over the Arctic Ocean showed similar concentrations to the results from the MALINA cruise²⁶ (Table 2). However, isoprene SOA tracers in most samples collected in the middle (60°S–30°S) and high latitudes (90°S–60°S) of the Southern Hemisphere were one to two orders of magnitude lower than those in the other regions. This is probably due to the small land area in the middle latitudes and the lack of higher plants in the continental Antarctica. Nonetheless, Sample N33 (Table S1) collected over the South Indian Ocean had high-level isoprene

Table 1 | Summary of isoprene and monoterpene SOA tracers (ng/m³) during the CHINARE 2008 and CHINARE 09/10

	Abbr.	average	median	min	max	SD ^a
isoprene SOA tracers						
<i>cis</i> -2-methyl-1,3,4-trihydroxy-1-butene	MTHB1	0.071	0.013	ND ^b	0.78	0.15
3-methyl-2,3,4-trihydroxy-1-butene	MTHB2	0.081	0.019	ND	1.8	0.24
<i>trans</i> -2-methyl-1,3,4-trihydroxy-1-butene	MTHB3	0.22	0.060	ND	2.8	0.45
2-methylglyceric acid	MGA	0.79	0.11	ND	6.8	1.5
2-methylthreitol	MTL1	2.1	0.89	ND	11	2.8
2-methylerythritol	MTL2	5.2	1.8	0.015	24	6.5
C ₅ -alkene triols ^c		0.37	0.079	ND	3.8	0.72
2-methyltetrols ^d	MTLs	7.3	2.8	0.018	34	9.3
sum of isoprene SOA tracers		8.5	3.1	0.018	36	11
monoterpene SOA tracers						
<i>cis</i> -pinonic acid	PNA	0.09	0.032	ND	0.69	0.16
pinic acid	PA	0.21	0.019	ND	2.9	0.48
3-methyl-1,2,3-butanetricarboxylic acid	MBTCA	0.97	0.017	ND	8.0	1.9
3-hydroxyglutaric acid	HGA	1.2	0.20	ND	10	2.2
3-hydroxy-4,4-dimethylglutaric acid	HDMGA	0.56	0.047	ND	6.1	1.3
sum of monoterpenes SOA tracers		3.0	0.62	0.045	20	5.0
SOC_{isoprene} ^e (ngC/m³)		52	20	0.12	220	65
SOC_{monoterpene} ^f (ngC/m³)		13	2.7	0.19	84	22

^aSD is one standard deviation. ^bND means not detect. ^cSum of *cis*-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene and *trans*-2-methyl-1,3,4-trihydroxy-1-butene. ^dSum of 2-methylthreitol and 2-methylerythritol. ^eSOC from isoprene. ^fSOC from monoterpene.

Figure 1 | Comparison of the average concentrations of SOA tracers among land origin, ocean origin and Antarctic origin samples. The Table 1 for abbreviations of the tracers.

SOA tracers, the concentrations of which are similar to those of samples in coastal regions (Figure 2a). It may be caused by more oceanic emission due to the enhanced sea-air exchange in the westerlies.

Among the measured isoprene SOA tracers, MTLs were the dominant species ($7.3 \pm 9.3 \text{ ng/m}^3$) and accounted for $79 \pm 22\%$ of all the tracers, followed by MGA ($0.79 \pm 1.5 \text{ ng/m}^3$). The average concentration of C_5 -alkentriols was $0.37 \pm 0.72 \text{ ng/m}^3$. This composition

Table 2 | Sum of SOA tracers (ng/m^3) from isoprene and monoterpenes at different locations

locations	isoprene SOA tracers		monoterpene SOA tracers		reference
	Range	Mean	Range	Mean	
East Antarctica	0.24–6.0	1.3	0.075–0.62	0.28	This study
Prydz Bay	0.28–6.0	1.9	0.075–0.51	0.24	This study
West Antarctica	0.018–0.81	0.27	0.048–1.7	0.26	This study
Southern Ocean	0.26–24	12	0.046–1.9	0.66	This study
Australian adjacent sea	0.34–10	4.2	0.046–1.9	0.66	This study
Southeast Asia	3.1–22	11	0.045–0.48	0.19	This study
	*	22		5.3**	Fu, et al. ²⁵
North Indian Ocean	–	5.1	–	2.7**	Fu, et al. ²⁵
Western North Pacific	1.2–35	18	0.15–17	8.6	This study
	0.11–0.51	0.36	0.60–2.9**	1.3**	Fu, et al. ²⁵
Eastern North Pacific	0.17–8.3	3.6	0.020–1.5**	4.1**	Fu, et al. ²⁵
North Atlantic	0.20–0.54	0.37	0.55–0.79**	0.67**	Fu, et al. ²⁵
East China Sea	–	36	–	20	This study
Sea of Japan	22–27	24	5.5–18	11	This study
Sea of Okhotsk	–	35	–	9.9	This study
Bering Sea	3.9–23	12	0.87–11	3.9	This study
the Arctic Ocean	1.4–13	4.6	0.73–5.6	1.9	This study
	0.16–32	4.0	***	0.63**	Fu, et al. ²⁶
90°S–60°S	0.023–6.0	0.87	0.048–0.62	0.20	This study
60°S–30°S	0.018–24	3.1	0.046–1.7	0.30	This study
30°S–30°N	1.2–22	9.2	0.045–1.9	0.56	This study
30°N–60°N	13–36	25	3.6–20	11	This study
60°N–90°N	1.4–13	5.3	0.73–5.8	2.0	This study
Southern Hemisphere	0.018–24	3.3	0.045–1.9	0.31	This study
Northern Hemisphere	1.2–36	14	0.13–20	5.8	This study

* " " means only one sample in this region.

**The monoterpene SOA tracers are the sum of PNA, PA, MBTCA and HGA.

***The range of monoterpene SOA tracers reported by Fu, et al.²⁶ was not compared here because four tracers (3-(2-hydroxyethyl)-2,2-dimethylcyclobutanecarboxylic acid, 3-acetylglutaric acid, 3-acetyladipic acid and 3-isopropylglutaric acid) counted in the sum of monoterpene SOA tracers in the reference were not measured in this study.

Figure 2 | Spatial distributions of SOA tracers over oceans. (a) sum of isoprene SOA tracers; (b) sum of monoterpene SOA tracers. Circles represent the results from this study. Squares represent data obtained from the around-the-world cruise²⁵. Triangles represent the average levels during the MALINA cruise²⁶. The monoterpene SOA tracers are the sums of PNA, PA, MBTCA and HGA for the around-the-world and MALINA cruises. Base maps used in (a) and (b) are from ArcGIS software.

was similar to previous results over most oceans during the round-the-world cruise and the southern Beaufort Sea where MTLs were the predominant isoprene SOA tracers^{25,26}. The average values of MGA/MTLs ratio were 0.33, 0.18 and 0.59 for LO, OO and AO samples, respectively. Based on chamber experiments, MGA and MTLs have quite different formation mechanisms. MGA is formed under high- NO_x conditions; while MTLs are apt to emerge under low- NO_x conditions²⁸. Furthermore, the formation of MGA is enhanced in

the particulate phase under low relative humidity (RH); while different RH does not cause obvious difference in MTLs productivities²⁹. Marine atmosphere is normally in low- NO_x conditions with mixing ratios of below 100 pptv³⁰, and high-RH conditions, so it favors the formations of MTLs instead of MGA. NO_x levels are much higher over continents than over oceans due to anthropogenic and natural emissions such as fossil fuel combustion and biomass burning^{31,32}, as such the ratios for the LO samples were higher than those for the OO

samples. Despite the lack of local air pollution, NO_x mixing ratios could reach up to 1000 pptv³³ over the Antarctic inland, because of the emissions from photochemical reactions in snow^{33–35}. Air mass from the continental Antarctica brought high levels of NO_x and caused high MGA/MTLs ratios of the AO samples. However, despite these levels being significantly higher than those over oceans, it was much less than those over continents (tens of pptv)^{36–38}. Change in NO_x level cannot fully explain the relative high MGA/MTLs ratios of the AO samples, which may be impacted by other factors as well. It has been found that MTLs yields are positive correlated with ambient temperature, while MGA yields present no significant difference with varied temperature³⁹. Cold conditions in the Antarctic may cause the decreased productivities of MTLs, and then yielded higher MGA/MTLs ratios of the AO samples than those of the LO samples.

Monoterpene SOA tracers. Similar to isoprene SOA tracers, the sum of monoterpene SOA tracers in the Northern Hemisphere ($5.8 \pm 6.0 \text{ g/m}^3$) was one order of magnitude higher than that in the Southern Hemisphere ($0.31 \pm 0.48 \text{ ng/m}^3$). As shown in Table 2 and Figure 2b, the middle latitudes of the Northern Hemisphere had the highest monoterpene SOA concentrations ($11 \pm 5.2 \text{ ng/m}^3$), followed by the high latitudes of the Northern Hemisphere ($2.0 \pm 1.8 \text{ ng/m}^3$). Different with the isoprene SOA tracers, concentrations of monoterpene SOA tracers in the low latitudes were very low in this study.

Among the measured monoterpene SOA tracers, HGA was the dominant species ($1.2 \pm 2.2 \text{ ng/m}^3$) and accounted for $47 \pm 28\%$ of all the tracers. It was followed by MBTCA ($0.97 \pm 1.9 \text{ ng/m}^3$) and HDMGA ($0.56 \pm 1.3 \text{ ng/m}^3$). The fact that HGA played as the main monoterpene SOA tracer was also found in previous studies, including over both oceans²⁵ and continents^{5,17,19,24,27}. According to previous studies, PNA and PA could be further photodegraded to MBTCA^{27,40}. Therefore, the compositions of monoterpene SOA tracers may reflect seasonal variations. PNA and PA were not detected in Hong Kong in summer, while MBTCA showed a high level¹⁹. MBTCA was the dominant monoterpene SOA tracer during summer, and PNA and PA were the dominant species during fall-winter in the Pearl River Delta²⁷. In this study, most of our samples were collected in summer. The ratios of MBTCA/(PNA + PA) varied with a wide range during our cruises, with a median value of 0.70 and an average value of 2.6. High levels of the ratio were found mostly in the high and middle latitudes because of the long day length there in the summer.

According to previous studies, the emission factor of isoprene is much higher than that of monoterpenes^{8,41}, while the SOA yield from monoterpenes is 16 times higher than that from isoprene⁴². As such, in different areas the quantitative relationship of the two types of SOA tracers is quite different. Monoterpenes were the dominant SOA precursors in Hong Kong¹⁹, the US^{17,24} and the Arctic⁵; while isoprene was the major one in the Pearl River Delta²⁷. During the round-the-world cruise, isoprene SOA tracers were dominant over most oceans of the Northern Hemisphere, except for the North Atlantic and Western North Pacific²⁵. During our cruises, isoprene was the predominant precursor over most oceans, too. The mean ratio of monoterpene SOA tracers to isoprene SOA tracers was 0.57 ± 0.73 , with a median level of 0.35. Higher concentrations of monoterpene SOA tracers than isoprene SOA tracers were observed in Samples N14, N18, N20, N29 and N30, which were collected over coastal regions of Antarctica (including Drake Passage) and Sample B30 collected over the Bering Sea (Table S1). The emission ratio of monoterpenes to isoprene might increase in these regions. During a ship-board study on the Southern Atlantic Ocean¹¹, the concentrations of monoterpenes in some regions were just slightly less than isoprene. It might be related to the distinct phytoplankton compositions in different oceans¹¹.

Discussion

For SOA over oceans, previous studies focused more on methane-sulfonic acid (MSA) formed by the oxidation of dimethyl sulfate (DMS) and dimethyl- and diethylammonium salts (DMA^+ and DEA^+) originating from biogenic amines^{43,44}. Knowledge about the contributions of isoprene and monoterpenes to SOA over oceans is limited and controversial. SOA or SOC originating from isoprene and monoterpenes can be estimated by the tracer-based approach¹⁷, which is described as $[\text{SOA}] = \sum[\text{tracer}]/f_{\text{tracer}/\text{SOA}}$ or $[\text{SOC}] = \sum[\text{tracer}]/f_{\text{tracer}/\text{SOC}}$ where $\sum[\text{tracer}]$ is the sum of SOA tracers for a certain precursor, $f_{\text{tracer}/\text{SOA}}$ and $f_{\text{tracer}/\text{SOC}}$ are the tracer/SOA and tracer/SOC conversion factors, respectively. SOA and SOC from isoprene are calculated by MGA and MTLs with the tracer/SOA conversion factor of 0.063 and the tracer/SOC conversion factor of $0.155 \mu\text{g}/\mu\text{gC}$, respectively, according to laboratory experiments¹⁷. SOA and SOC from monoterpenes are estimated by the five measured tracers²⁷ with the tracer/SOA conversion factor of 0.168 and the tracer/SOC conversion factor of $0.231 \mu\text{g}/\mu\text{gC}$, respectively¹⁷. During our cruises, isoprene SOA ranged from 0.29 to 540 ng/m^3 , with an average of $130 \pm 160 \text{ ng/m}^3$; while monoterpene SOA ranged from 0.27 to 120 ng/m^3 , with an average of $18 \pm 30 \text{ ng/m}^3$. SOC from isoprene ranged from 0.12 to 220 ngC/m^3 , with a mean of $52 \pm 65 \text{ ngC/m}^3$; while SOC from monoterpenes ranged from 0.19 to 84 ngC/m^3 , with a mean of $13 \pm 22 \text{ ngC/m}^3$. Spatial variations were also noted. Isoprene and monoterpene SOAs over coastal regions, where air mass was directly affected by continents, displayed a high level. As the short lifetimes of isoprene and monoterpenes⁴⁵ and the high SOA yield, especially for monoterpenes¹⁶, they were probably oxidized over continents and then transported as particulates.

Isoprene SOA estimated by the tracer-based approach in most samples over remote oceans without phytoplankton blooms both in the low latitudes²⁵ and the high latitudes was below 5 ng/m^3 , with an average of about 3 ng/m^3 ; while monoterpene SOA was below 4 ng/m^3 , with a mean of about 1 ng/m^3 . These regions are not directly influenced by continents, and these selected samples belonged to the OO or AO samples, so the SOAs were derived from oceans. If we apply the average levels of SOAs over remote oceans, 4–7 days as the lifetimes of tropospheric particles⁴⁶, 600–1000 m as the boundary layer height¹², the isoprene SOA yield of 2% and the monoterpene SOA yield of 32%⁴², the estimated sea-air fluxes are $13\text{--}38 \mu\text{g m}^{-2} \text{ d}^{-1}$ for isoprene and $0.27\text{--}0.78 \mu\text{g m}^{-2} \text{ d}^{-1}$ for monoterpenes. These isoprene fluxes were similar to the model result of $\sim 10\text{--}100 \mu\text{g m}^{-2} \text{ d}^{-1}$ over the North Atlantic⁴⁷. Consequently, the global oceanic emissions of isoprene and monoterpenes are about $1.5\text{--}4.4 \text{ TgC yr}^{-1}$ and $0.031\text{--}0.091 \text{ TgC yr}^{-1}$, respectively. This isoprene emission was in the range of emissions estimated by Myriokefalitakis, et al.¹³ (0.88 TgC yr^{-1}), Arnold, et al.¹⁴ (1.7 TgC yr^{-1}) and Gantt, et al.¹⁵ (0.92 TgC yr^{-1}), and Luo and Yu¹⁶ (0.32 TgC yr^{-1} by “bottom-up” method and 11.6 TgC yr^{-1} by “top-down” method). The monoterpene emission was comparable to the estimation by Myriokefalitakis, et al.¹³ (0.18 TgC yr^{-1}) and by Luo and Yu¹⁶ using “bottom-up” method ($0.013 \text{ TgC yr}^{-1}$), but was two to three orders of magnitude smaller than the value simulated by Luo and Yu¹⁶ using the “top-down” method (29.5 TgC yr^{-1}). Unlike previous estimates based on marine chlorophyll-*a* concentrations^{13–16}, this study calculated the emissions using the measured oxidation products of isoprene and monoterpenes. Since our estimates were obtained over remote oceans without blooms while coastal regions usually contained more chlorophyll-*a* (Figure 3), the real global emissions of isoprene and monoterpenes may be even greater than our results.

High concentrations of SOA tracers were found over the Arctic Ocean. Although massive phytoplankton under the Arctic sea ice⁴⁸ might emit large amount of isoprene and monoterpenes, this region was also significantly affected by surrounding continents (Figure S1g). We cannot distinguish the influence of phytoplankton from

Figure 3 | Maps of oceanic Chlorophyll-*a* concentrations. Chlorophyll-*a* concentrations for (a) December, 2009 and (b) March, 2010. The maps were acquired from the NASA Oceancolor website (<http://oceancolor.gsfc.nasa.gov>).

continental ecosystems. Monoterpene SOA concentrations around the Antarctic continent were consistent with the average level over remote oceans. However, several high concentrations of isoprene SOA were found over the coastal regions of Antarctica, especially in the Prydz Bay. The estimated isoprene SOA in the bay ranged from 3.9 to 95 ng/m³, with a mean of 29 ± 38 ng/m³. Therefore, the isoprene fluxes were estimated as 18–1200 $\mu\text{g m}^{-2} \text{d}^{-1}$. Due to the lack of higher plants, the massive isoprene SOA amount was not derived from Antarctic inland. Nevertheless, high chlorophyll-*a* concentrations (up to 30 mg/m³, Figure 3) indicated the existence of phytoplankton blooms¹² in the Prydz Bay during our sampling episodes. Phytoplankton blooms regularly occurred in the Antarctic pack ice zone^{49,50} might supply abundant isoprene. These concentrations of isoprene SOA were comparable to those of MSA, a major SOA species derived from the oxidation of DMS in the marine atmosphere, which was about 36–300 ng/m³ (average value: 139 ng/m³) over the Prydz Bay in austral summer⁵¹, and the peak value of MSA (~250 ng/m³) around Antarctic during blooms reported by O'Dowd, et al.⁵². In addition, the maximum isoprene flux was even higher than the peak value of DMS (477 $\mu\text{g m}^{-2} \text{d}^{-1}$) around Antarctic⁵². This study suggested that, despite finite sea-air fluxes in normal conditions, oceanic emissions of isoprene are able to abruptly increase and become important sources of organic aerosols over oceans during phytoplankton blooms.

Methods

Total suspended particles (TSP) as well as field blanks were collected between East China Sea and the Arctic Ocean (33°N–85°N) during the CHINARE 08 cruise from July to September, 2008, and between East China Sea and Antarctica (26°N–69°S) during the CHINARE 09/10 cruise from November 2009 to April 2010. A high volume air sampler was placed on the upper-most deck of the icebreaker *Xuelong*, and TSP samples were collected by glassfiber filters which were prebaked at 450°C for 4 h. Each sampling lasted for 1–3 days, and the air volumes ranged from 372 to 2752 m³ (at 0°C and 1 atm). Samples were then wrapped with aluminum foil, zipped in plastic bags, and stored in freezers at –20°C until analysis. Details of sampling information are listed in Table S2 in the supplementary materials.

A punch (9 × 11.5 cm) of each filter was taken and analyzed for SOA tracers. Details of the analytical procedure was described elsewhere^{27,39}. Briefly, each sample was extracted by sonication with 30 mL of mixed solvent (dichloromethane:hexane 1:1, V/V) twice, and then extracted with another 30 mL of mixed solvent (dichloromethane:methanol 1:1, V/V) twice. Before extraction, levoglucosan-¹³C₆ and lauricid-D₂₃ were spiked as internal standards. Each extract of samples was combined, filtered and concentrated. Then each of the concentrated extracts was divided

into two parts. One part was methylated and analyzed for three monoterpene SOA tracers (PNA, PA and MBTCA) by a gas chromatography–mass selective detector (GC-MSD). The other part was silylanized and analyzed for the other two monoterpene SOA tracers (HGA and HDMGA) and six isoprene SOA tracers (MTHB1, MTHB2, MTHB3, MGA, MTL1 and MTL2). PNA and PA were quantified by authentic standards. Owing to the lack of standard reagents, the other three monoterpene SOA tracers (MBTCA, HGA and HDMGA) were quantified using PA^{27,39}; isoprene SOA tracers were all quantified using erythritol^{1,27}. For samples collected during the CHINARE 08, the MDLs were 0.011 ng/m³ for PNA, 0.004 ng/m³ for PA and 0.048 ng/m³ for erythritol, calculated by three times of the standard deviation of field blanks under the average sampling volume of 1311 m³. For samples collected during the CHINARE 09/10, the MDLs were 0.008, 0.002 and 0.007 ng/m³ for PNA, PA and erythritol, respectively, under the average volume of 2189 m³.

Field blanks and laboratory blanks were extracted and analyzed in the same way as ambient samples. Recoveries of the target compounds in six spiked samples (authentic standards spiked into solvent with prebaked filters) were $104 \pm 2\%$, $68 \pm 13\%$ and $62 \pm 14\%$ for PNA, PA and erythritol, respectively. The relative differences for all target compounds in paired duplicate samples ($n = 6$) were all <15%. The results in this study were not recovery corrected.

Air mass BTs were calculated for the samples using HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) transport and dispersion model from the NOAA Air Resources Laboratory (<http://www.arl.noaa.gov/ready/hysplit4.html>). 5-day BTs for the start and end of each sampling episode were traced with 6 h steps at 100, 500, and 1000 m above sea level. Satellite maps of chlorophyll-*a* in the surface seawater were obtained by Moderate Resolution Imaging Spectroradiometer (MODIS) from NASA satellites (<http://oceancolor.gsfc.nasa.gov>).

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Acknowledgements

This research was supported by grants from the National Natural Science Foundation of China (Project Nos. 41025020, 41176170), the Chinese Arctic and Antarctic Administration (Projects Nos. CHINARE2013-01-01, CHINARE2013-03-04, CHINARE2013-04-01) and the Fundamental Research Funds for the Central Universities. We wish to thank Ming Li and Xiang Ding for their help in sampling and analysis. The authors acknowledge the NOAA Air Resources Laboratory (ARL) for making the HYSPLIT transport and dispersion model available on the Internet (<http://www.arl.noaa.gov/ready.html>).

Author contributions

Q.H.H. and Z.Q.X. contributed equally to design the study and write the manuscript. X.M.W. and P.Z. contributed to the discussion of results and manuscript refinement. Q.H.H., H.K. and Q.F.H. contributed to the sample collection and analysis.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Hu, Q.-H. *et al.* Secondary organic aerosols over oceans via oxidation of isoprene and monoterpenes from Arctic to Antarctic. *Sci. Rep.* **3**, 2280; DOI:10.1038/srep02280 (2013).

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