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Observation of surface ozone in the marine boundary layer along a cruise through the Arctic Ocean: From offshore to remote

Pengzhen He [a], Lingen Bian [b,*], Xiangdong Zheng [b], Juan Yu [a], Chen Sun [a], Peipei Ye [c], Zhouqing Xie [a,*]

[a] School of Earth and Space Sciences, Institute of Polar Environment, University of Science and Technology of China, Hefei 230026, China
[b] Chinese Academy of Meteorological Sciences, Beijing 100081, China
[c] School of Life Sciences, University of Science and Technology of China, Hefei 230026, China

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ABSTRACT

Ozone is an important reactive gas in the troposphere; it has been frequently used to estimate atmospheric oxidation capacity. However, there are few data of surface ozone over the Arctic Ocean, especially the central Arctic Ocean. Here, surface ozone in the marine boundary layer along the cruise path during the 5th Chinese Arctic Research Expedition (June to September, 2012) was investigated. The latitudes and longitudes covered in the cruise were 31.1°N–87.7°N and 9.3°E–90°E–168.4°W. The 1-h-averaged ozone varied from 9.4 ppbv to 124.5 ppbv along the cruise. The highest mixing ratios appeared in the East China Sea and the Sea of Japan while the lowest in the Chukchi Sea. The relatively high ozone levels over the East China Sea, the Sea of Japan, and offshore Iceland were caused by transport of precursors and/or ozone from the nearby continent. Ozone mixing ratio decreasing by ~2 ppbv/° with increasing latitude was observed during 31–45°N covering the East China Sea and the Sea of Japan, and during 62–69°N covering offshore Iceland. Over the entire Arctic Ocean, ozone levels were relatively low, varying from 9.4 ppbv to 36.1 ppbv with an average of 23.8 ± 4.6 (mean ± standard deviation) ppbv, which was not statistically different with data observed at Barrow observatory during the same period. Unlike ozone over contaminated areas, a slight increasing trend of ozone in 69–87°N was observed. This phenomenon may be ascribed to the role of both vertical transport and chemical processes due to solar radiation.

1. Introduction

Ozone is an important trace gas specie in the troposphere. It can not only affect human health in urban areas as a secondary air pollutant but also affect radiative forcing and climate change as a greenhouse gas (IPCC, 2007). As a reactive gas throughout the troposphere, ozone controls a variety of photochemical reactions in the atmosphere (Ravishankara et al., 1998). It plays an important role in oxidation of hydrocarbons, carbon monoxide (CO), dimethyl sulfide (DMS), and sulfur dioxide (SO_2) (Johnson et al., 1990; Stehr et al., 2002; Watanabe et al., 2005). Photolysis of ozone produces O^1D that reacts with water vapor, which is the primary source of hydroxyl radical (OH) (Finlayson-Pitts and Pitts, 2000). Earlier studies show that photochemical reactions involving precursor gases like CO, methane (CH_4) with sufficient nitrogen oxides (NO_x), and downward transport of ozone from ozone-rich stratospheric air are the dominant sources of global tropospheric ozone, which respectively account for ~80% and ~20% of producing processes of global tropospheric ozone (Crutzen et al., 1999; Ganguly and Tzanis, 2011; Lelieveld and Crutzen, 1994; Nair et al., 2011; Sprenger et al., 2007). Horizontal transport of ozone and/or its precursors from other locations in the troposphere can also change ozone level for a specific region or site (Nair et al., 2011). Surface ozone over land with high precursors, especially East Asia, remains high and can be transported to surrounding areas (He et al., 2008). However, ozone mixing ratios over polar regions remain low as NO_x is very low and photochemical production is limited (Helmig et al., 2007b; Johnson et al., 1990; Stehr et al., 2002). Since anthropogenic sources are few in polar regions, ozone in this environment mainly comes from downward transport and/or horizontal transport (Helmig et al., 2007b). Moreover, it is mainly destroyed by deposition to the surface, photolysis (Paluch et al., 1995) and chemical reactions with halogens like bromine and iodine (Foster et al., 2001; Stehr et al., 2002; Watanabe et al., 2005).

Surface ozone in the Arctic is particularly concerned not only because the Arctic is a place climate change accelerates (ACIA, 2004), but also because surface ozone episodically decreases rapidly during ozone depletion events (ODE) and mercury depletion events (MDE) in the Arctic springtime when sun rises, during which chemical reactions involving halogens especially Br ($O_3 + Br \rightarrow BrO + O_2$) play very important role in ozone depletion (Barrie et al., 1988; Bottenheim et al., 2009; Foster et al., 2001; Halfacre et al., 2014; Simpson et al., 2007). BrO during ODE has been found to be widespread and high-value based on satellite

* Corresponding authors. Tel./fax: +86 551 6360 1415.
E-mail addresses: blg@cams.cam.gov.cn (L. Bian), zqxie@ustc.edu.cn (Z. Xie).

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data (Platt and Wagner, 1998), and thus can be used as a marker for ODE (Sommar et al., 2010). The bromine explosion reaction sequence (net: $H^+ + Br^- + HO_2 + O_3 \rightarrow Br + H_2O + 2O_2$) during ODE highlights the important role of Br^- and Cl^- in halogen activations, and halogen activations could occur on the surface of sea salt aerosols (Saiz-Lopez et al., 2012; Simpson et al., 2007). Similarly, ozone destruction by halogen species after sunrise have been found in many other sea areas (Galbally et al., 2000; Stehr et al., 2002; von Glasow et al., 2002; Watanabe et al., 2005).

Station observation of surface ozone at Arctic sites Barrow, Alaska; Summit, Greenland; Alert, Canada; and Zeppelinfjellet, Norway, have lasted for decades (Helmig et al., 2007b). Annual ozone cycles in these Arctic stations show that the months with highest ozone mixing ratios are during December to May and the lowest ozone are found during June to August (Helmig et al., 2007b). Researches show that the decline of ozone level during summer months results from more ozone destruction than ozone production, which is typical for remote, low-NO_x environments (Ayers et al., 1992; Derwent et al., 1998; Janach, 1989). However, ship-based surface ozone observations in the Arctic marine boundary layer (MBL), especially the central Arctic MBL (over 80°N), are relatively few, and ship-based observations have the advantage of providing wider spatial distribution of surface ozone. Therefore, we carried out ship-based surface ozone observation along cruise of Chinese Arctic Research Expedition (CHINARE) since 1999. During the 5th CHINARE, the *Xuelong* icebreaker passed through the central Arctic Ocean and black carbon (BC) was measured along with surface ozone. As BC is released to the atmosphere by incomplete combustion of fossil fuels and biomass burning (Andreae and Crutzen, 1997) and BC along the cruise was found mainly affected by the terrestrial input (Xing et al., 2014), it was used as a marker for transport of air mass from land in this paper. The observations of surface ozone along this cruise path provide an opportunity to understand the variations of ozone in MBL via a ship-based study over a wide spatial range.

2. Experimental methods

2.1. The cruise

The cruise path of *Xuelong* icebreaker is shown in Fig. 1. The icebreaker departed from Shanghai in China on June 27, 2012, and it came back at the Yangtze estuary anchorage in Shanghai on September 23. The latitudes and longitudes covered were 31.1°N–87.7°N and 9.3°E–90°E–168.4°W. The research areas included the East China Sea, the Sea of Japan, the Sea of Okhotsk, the Northwest Pacific Ocean, the Bering Sea, the Arctic Ocean, and offshore Iceland. Over the Arctic Ocean, the icebreaker passed through the Chukchi Sea, the East Siberian Sea, the Barents Sea, the Norwegian Sea, the Greenland Sea, and the central Arctic Ocean. It was the first time for the *Xuelong* icebreaker to voyage through the Arctic Ocean along the Northeast Passage. And the icebreaker arrived at its most northerly site (87.7°N, 123.8°E) on August 30.

2.2. Equipment and data processing

All ozone data were measured every minute using an ultraviolet absorption ozone analyzer (model EC9810A, Ecotech Inc., Australia). Its minimum measuring limit is 0.5 ppbv, its accuracy is 1.0 ppbv, the baseline drift is <1.0 ppbv per month, and the response time is < 60 s per sampling in majority (95%) of cases. Sampling air flowed at a rate of 0.5 L/min, and the analyzer was calibrated before departure based on the NIST standard system. BC data were recorded every 5 min by an aethalometer (model AE31, Magee Scientific Co., USA). The instrument

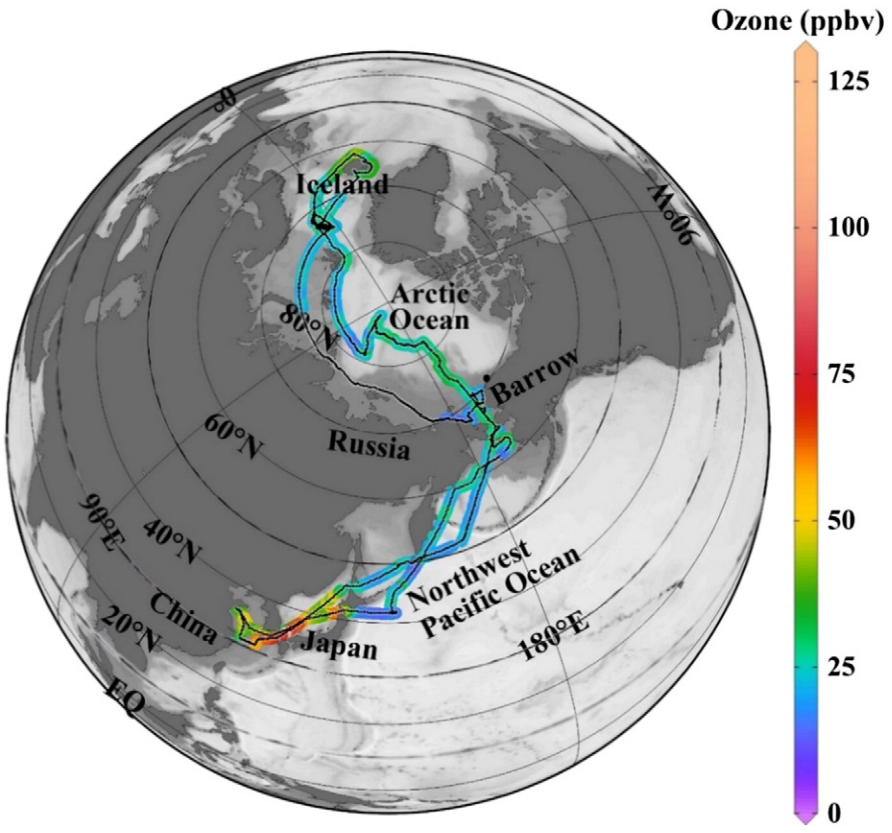

Fig. 1. Spatial variation of surface ozone along the cruise track of *Xuelong* icebreaker during the 5th CHINARE. The 1-h-averaged data were used to draw the distribution. The missing data along a cruise over the Arctic in the figure was caused by the analyzer being shut down as the icebreaker was in the exclusive economic zone of Russia. The black line along ozone data stands for the cruise track.