Variations of surface ozone at Ieodo Ocean Research Station in the East China Sea and influence of Asian outflows

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Abstract

Ieodo Ocean Research Station (IORS), a research tower (~ 40 m.a.s.l.) for atmospheric and oceanographic observations, is located in the East China Sea (32.07° N, 125.10° E). The IORS is almost equidistant from South Korea, China, and Japan and, therefore, it is an ideal place to observe Asian outflows without local emission effects. The average ozone concentrations were 51.8 ± 15.9 ppbv during June 2003–December 2010. The seasonal variation of ozone was distinct, with a summer minimum (37.8 ppbv) and a spring maximum (61.1 ppbv), and was largely affected by seasonal wind pattern over East Asia. The fractional contribution of ozone at IORS could be attributed to six well distinguished air masses that were classified by the cluster analysis of backward trajectories. Marine air from the Pacific Ocean represents a relatively clean background air with a lowest ozone level of 32.2 ppbv in summer. In spring and winter the influence of Chinese outflows was dominant with higher ozone concentrations of 61.6 and 49.3 ppbv, respectively. This study confirms that the influence of Chinese outflows was the main factor determining O$_3$ levels at IORS, of which extent was apt to be changed by meteorological state, particularly at a long-term scale.

1 Introduction

Ozone (O$_3$) and its photochemical derivative, OH, are primary oxidants and key players determining oxidation capacity within the troposphere (e.g., Berchet et al., 2013; Seinfeld and Pandis, 2006). A short-lived greenhouse gas, O$_3$ also affects climate change and air quality (e.g., Berchet et al., 2013; Brasseur et al., 1999; IPCC 2013; Jacobson, 2012). Exposure to high O$_3$ levels is known to increase human mortality rates (Bell and Dominici, 2008; Chang et al., 2010), reduce agricultural yields, and damage natural ecosystems (e.g., Bell et al., 2011; Karnosky et al., 2007; Schaub et al., 2005; Wang and Mauzerall, 2004). Tropospheric O$_3$ is primarily transported from the stratosphere upon tropopause folding and is produced by in situ photochemical processes involv-
ing carbon monoxide (CO) and hydrocarbons in the presence of nitrogen oxides (NO\textsubscript{x}) (e.g., IPCC 2013; Monks et al., 2009; Seinfeld and Pandis, 2006). Ozone is removed by deposition to the Earth’s surface and subsequent chemical destruction. As a result, the lifetime of O\textsubscript{3} ranges from about a week in summer to several months in winter, which permits O\textsubscript{3}, along with other pollutants, to be transported over long distances. In previous studies, ozone levels were observed to be enhanced episodically in polluted air masses from continental outflow in remote regions of the North Atlantic and North Pacific Oceans (e.g., Fischer et al., 2011; Lin et al., 2012; Parrish et al., 2009; Zhang et al., 2008).

Particularly, East Asia has experienced a rapid development in economy and industry, from which emissions of O\textsubscript{3} precursors such as NO\textsubscript{x} and VOCs have gradually increased (Huang et al., 2013; Monks et al., 2009; Zhao et al., 2013) and the emission of O\textsubscript{3} and its precursors in East Asia is expected to increase further in the near future (Zhao et al., 2013; Ohara et al., 2007). As a result, the study region became a hot spot for high O\textsubscript{3} and intensive measurements have been performed there to chart O\textsubscript{3} and the effects it has in conjunction with climate change. Over the North Pacific Ocean, ozone has been measured on remote islands (Kato et al., 2001; Parrish et al., 2012; Tanimoto et al., 2009; Wada et al., 2011), from ships (Ridder et al., 2012; Watanabe et al., 2005) and by aircraft (Dupont et al., 2012; Kotchenruther et al., 2001; Walker et al., 2010; Zhang et al., 2008).

The impact of continental outflow upon the background O\textsubscript{3} is substantial in Northeast Asia (Akimoto et al., 1996; Kondo et al., 2008; Tanimoto et al., 2009, 2008; Wada et al., 2011; Yamaji et al., 2006). This impact has similarly been detected near the western US (Fischer et al., 2011; Lin et al., 2012; Parrish et al., 2009). Walker et al. (2010) estimated that Asian anthropogenic outflow and lightning-derived NO\textsubscript{x} emissions contributed at least 7.2 and 3.5 ppbv to O\textsubscript{3} concentration, respectively, in the North Pacific Ocean and western North America. In addition, Zhang et al. (2008) assessed that O\textsubscript{3} in western North America was increased by Asian outflow 5–7 ppbv during spring 2006. The results of these studies indicate O\textsubscript{3} concentrations in the North Pacific-rim are
regularly affected by Asian outflow. Therefore, it is critical to understand the impact of continental outflows from East Asia on O$_3$ and oxidizing power over the North Pacific Ocean. Since IORS is located in the East China Sea (32.07° N, 125.10° E) (Fig. 1) and almost equidistant from nearby South Korea, China, and Japan; it is an ideal place to observe Asian outflows without local effects (Hwang et al., 2008; Shin et al., 2007). In this study, we present long-term measurements of O$_3$ at IORS, located in the boundary zone between the Yellow and East China Sea. Then, we describe their characteristic variations and evaluate the continental influence on the regional background concentrations of O$_3$.

2 Methodology

Ieodo Ocean Research Station is an unmanned research tower (~ 40 m a.s.l.) for atmospheric and oceanographic observations. It was built on rock 36 m below sea level by the Korea Institute of Ocean Science and Technology (KIOST) in 2003 (Moon et al., 2010; Shim et al., 2004). O$_3$ has been measured at IORS since June 2003. In addition, meteorological parameters have been monitored, which include air pressure, air temperature, relative humidity, wind speed and direction, and visibility. O$_3$ was measured by an UV photometric analyzer (49C, Thermo Inc., USA) using the absorption of UV radiation at 253.7 nm by O$_3$ molecules. The analyzer was installed in a dry lab of the main deck, which is 29 m above sea level. Ambient air was pulled underneath the main deck through a 7 m PFA tubing (6 mm-OD). The detection limit of the instrument was 1.0 ppbv. Calibration was done about once every two months with an internal ozonator. In addition, the ozone analyzer was inter-compared with an identical instrument, which was calibrated against the Primary Standard. The two instruments were run side-by-side using a common inlet. The correlation coefficient of the two measurements was 0.99 in the range between 10 and 90 ppbv and ambient measurements were scaled using the relationship between the two.
The data logger stored 10 min averages. There were power failures and system malfunction at IORS when it was hit by typhoon several times. Thus, raw data were first filtered manually and then the measurements bigger and smaller than $2\sigma$ (standard deviation) for the average for 10 neighboring values were eliminated. This method is widely used to remove local effects for long-term period measurement (Cvitaš et al., 2004). Statistical analysis was conducted using R (v.3.0.1) (R Core Team, 2014).

3 Ozone variations

The mean concentration of 10 min $O_3$ measurements was 51.8 ppbv with a maximum of 128.1 ppbv. The variation of monthly means is presented for eight years, from June 2003 to December 2010 (Fig. 2), during which $O_3$ increased $\sim$ 2.8 % year$^{-1}$ until 2009 and slightly decreased afterwards. The long-term trend of $O_3$ at IORS is consistent with recent findings of slowdown in the increase of $O_3$ concentrations observed in Japanese background stations at Mt. Happo and others (Parrish et al., 2012). Additionally, the vertical column density of tropospheric NO$_2$ was reported to be decreased over East Asia in 2009, as observed by satellites GOME-2 and SCIAMACHY (Itahashi et al., 2014). In the same context, emissions of NO$_x$ sharply increased in East Asia after 2000 mostly from China, but then slowed down in 2009 (Tanimoto et al., 2009; Zhao et al., 2013). Gu et al. (2013) pointed out that the stagnation of NO$_x$ emissions in 2009 were associated with an economic recession in China.

The $O_3$ concentrations of IORS were compared with those of other remote sites in East Asia and the North Pacific for the same period: Ryori, Yonagunijima, Minamitorishima in Japan, and Trinidad Head in the US (World Data Centre for Greenhouse Gases (WDCGG) http://ds.data.jma.go.jp/gmd/wdcgg/) (Fig. 1). The diurnal and monthly variations of eight-year averaged $O_3$ are presented here in Fig. 3. The averaged $O_3$ concentrations of IORS, Ryori, Yonagunijima, Minamitorishima and Trinidad Head were 51.8, 40, 39.0, 27.4, and 30.3 ppbv, respectively. The level of averaged $O_3$ concentrations decreased with increased distance from China. At IORS, $O_3$ mixing ra-
tios show the minimum at 9 a.m. and reached to the broad maximum at 5 p.m. The
daytime build-up of O$_3$ was 4.8 ppbv, which was much smaller than that in urban areas,
but implied in-situ photochemical production for O$_3$ in the marine boundary layer of the
remote site. The daytime build-up of O$_3$ at Ryori, located at the northeasterly edge of
mainland Japan, was 6 ppbv, significantly greater than at Yonagunijima (1.9 ppbv). At
Trinidad Head, the afternoon maximum was distinct, like those observed in metropolitan
cities (Tang et al., 2009). Considering O$_3$ destruction is generally observed under low
NO$_x$ conditions in the remote marine boundary layer (MBL) (Ayers et al., 1996), these
variations indicate that IORS including other remote sites in east Asia were influenced
by Chinese outflows. In the study region, the high concentration of O$_3$ was reported to
be attributed to transport of ozone or its precursors mainly from China (Tanimoto et al.,
2008).

The highest O$_3$ concentrations were mostly observed in spring with an apparent min-
imum in summer (Fig. 3b). This is a typical pattern that has been commonly observed
at the remote sites in Northeast Asia (Jaffe et al., 1996; Watanabe et al., 2005). At
IORS, the monthly averaged O$_3$ concentrations were the highest in April and Octo-
ber (62.4 ppbv) and lowest in July (38.3 ppbv) (Fig. 4a). This accords with what has
been observed in other remote sites during the past decade (Chan et al., 2002; Kondo
et al., 2008; Oltmans and Levy Ii, 1994; Tanimoto et al., 2009; Watanabe et al., 2005;
Weiss-Penzias et al., 2004). It is also noteworthy that outlier levels were the highest,
up to 128 ppbv, in July. The summer is characterized by heavy rain due to a mon-
soon system in the study region. Although temperature was high in summer (Fig. 4b),
O$_3$ level was reduced down to the minimum due to a washing out effect of the rains.
More importantly, IORS is mostly under influence of marine air masses coming from
the Pacific Ocean in summer (Fig. 5c). Based on meteorological characteristics, all
measured species were divided into five seasons: March–April, May–June (the pre-
monsoon period), July–August, September–November, and December–February and
their seasonal difference was examined. In Fig. 5f, wind direction is divided into four
sectors and their frequencies were given for each season.
All O₃ measurements showed bimodal distribution, with a little shoulder on the larger peak (Fig. 6a). In seasonal distributions, the smaller peak (24.5 ppbv) was the main mode of summer monsoon season. As shown in Fig. 5, southerly winds were dominant during July–August (82 %) under the influence of North Pacific High. This pattern reveals that the decrease in O₃ was associated with the aged marine air masses brought by the North Pacific High or tropical cyclones (Fig. 5c). In addition to aged air masses, precipitation had scavenged O₃ precursors, possibly leading to lowered O₃ concentrations (Hou et al., 2015). It was also observed that O₃ was decreased in Beijing and Shanghai during the summer monsoon season (Safieddine et al., 2013). In May–June, the mode concentration was the highest at 64.5 ppbv with the least frequency (Fig. 6c). It is a transition period from continental air mass to oceanic air mass and, as a result, the stagnant conditions which had developed under high temperature without prevailing wind (Fig. 5b), led to elevated O₃ concentrations. The mode concentration was the second highest (58.5 ppbv) in spring, which is characterized by the most effective transport of Chinese outflow by the passage of frontal system (Hou et al., 2014; Kondo et al., 2008; Lim et al., 2012). The mode frequency was the greatest in winter, which was due to prevailing northerly winds accounting for ~ 87 % of that period. The main mode of winter and fall, and the second mode of summer monsoon season displayed similar concentrations, which comprised the primary mode of O₃ distributions observed at IORS. O₃ levels are known to exhibit lower variability at remote sites and rural areas (McKendry et al., 2014; Oltmans and Levy Ii, 1994). However, the results of this study challenge those of previous studies. O₃ concentrations of IORS were highly dependent on air masses, upon which anthropogenic influence was in a wide variation. This finding emphasizes the significant role of continental outflows in determining O₃ concentrations in the Northeast Asian region.
4 Source signatures of O$_3$

4.1 Cluster analysis of air mass trajectories

Five-day backward trajectories arriving at 100 and 1500 m a.s.l. were calculated for 40 h every 00, 06, 12, and 24:00 UTC (03, 09, 18, and 21 LT) using the NOAA Air Resources Laboratory (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (version 4) (Draxler and Rolph, 2003, http://www.arl.noaa.gov/ready/hysplit4.html) with NCEP Final Analyses (FNL) six-hourly archived data. Isentropic trajectory was selected as it was believed to reflect a more realistic vertical motion for an adiabatic atmosphere. Forty hours were selected because it was long enough to capture regional transport patterns in the northwestern Pacific and short enough to keep trajectory errors. The results for 100 and 1500 m showed no meaningful differences and so the following discussion will be based on 1500 m.

Trajectories were divided into several groups using an agglomerative and hierarchical clustering algorithm with an average linkage function. Average linkage minimizes the within-cluster variance while maximizing between-cluster variance and has been identified as an effective method for categorizing different synoptic situations (Kalkstein et al., 1987). Within a cluster, the root mean square deviation (RMSD) of each trajectory from the cluster center was quantified and then summed to give the total root mean square deviation (TRMSD) (Cape et al., 2000). As a result, six trajectories were identified. The cluster analysis was performed using the Openair package in R (Carslaw and Ropkins, 2012, 2014). The distance matrix was calculated by the Euclidean distance.

The averaged backward trajectories of each cluster are presented in a map (Fig. 7a). Among the six clusters, W was the most dominant (23.0 %), followed by NW1 (19.9 %), N (17.9 %), SE (16.6 %), SW (13.4 %), and NW2 (9.2 %). The average O$_3$ concentration was the highest for W (59.8 ppbv) and lowest for SE (39.9 ppbv). For the four clusters of continental air masses, the mean O$_3$ concentrations were similar to the mean (51.8 ppbv) of the entire measurement set. In contrast, the marine air masses of SE and SW were characterized by low O$_3$ concentrations, particularly during summer.
4.2 Source signature by CWT (Concentration Weighted Trajectory) analysis

The CWT (Concentration Weighted Trajectory) method was employed to figure out the potential source of O$_3$ observed at IORS. The concentration of O$_3$ for each grid-cell was calculated using the following equation (Carslaw, 2013):

\[
\ln\left(\frac{C_{ij}}{\tau_{ij}}\right) = \frac{1}{N} \sum_{l=1}^{N} \ln(c_l) \cdot \tau_{ijl}
\]

where, $i$ and $j$ indicate the indices of grid, $N$ shows the entire number of backward trajectories, $l$ represents the index of trajectory, $c_l$ signifies the concentration of O$_3$ observed upon arrival of trajectory $l$, and $\tau_{ijl}$ is the residence time of trajectory $l$ in the grid-cell ($i$, $j$) (Carslaw, 2013; Cheng et al., 2013). In Fig. 8, the average O$_3$ concentrations were presented over each grid-cell. The O$_3$ concentration was notably higher for NW1 when air mass passed through the Beijing region. The trajectory of NW2 was similar to that of NW1 except for vertical movement, which is typical for air masses laden with Asian dusts (e.g., Kang et al., 2013).

Because the trajectory length is inversely proportional to the residence time of air in a grid-cell, the clusters N and W represent stagnant conditions, which was favorable for O$_3$ to build up. These two trajectories were the most frequently observed at IORS. Although the air masses of SW and SE originated from the Pacific Ocean, they were likely to pick urban emissions up when passing through the Southeastern China and South Japan, respectively. The result of CWT analysis confirms that the outflows from nearby lands were the source of O$_3$ observed at IORS, of which the Chinese influence was the most dominant.

4.3 Influence of Asian continental outflows

For all clusters, the monthly variations of O$_3$ concentrations were compared (Fig. 9a). In general, six clusters were similar in their annual pattern of O$_3$, with higher concentra-
tions in spring and fall and lower concentrations in summer. In contrast, for NW1, which passes through the Beijing metro area, O\textsubscript{3} concentrations stayed high over 60 ppbv during July–August without considerable decrease (Fig. 9a). Although the summer concentrations in SE were low, below 30 ppbv, in spring and fall the O\textsubscript{3} concentration were high and comparable to those of NW1.

The influence of Chinese outflows, represented by NW1, NW2, and W, was highest in winter, with a maximum occurrence (86\%) in December. The study region is under influence of Asian monsoon and is characterized by winds southerly in summer, and northerly in winter. The occurrence of maritime air, SE and SW, was the most frequent in summer monsoon season. The westerlies prevalent in this region are coupled with the steady occurrence of W through the year, implying a constant influence of Chinese outflows. The cluster N was commonly observed in before and after summer monsoon season, during which a stagnant condition often developed under the influence of migratory anticyclone systems. This condition is also favorable for a build-up in O\textsubscript{3}, leading to the highest concentrations in these seasons. The model results of Zhao et al. (2009) also showed that the high concentration of O\textsubscript{3} can be expanded under a high pressure system in East Asia, like the cases of clusters W and N.

The annual variation of each cluster was examined (Fig. 10a). As the O\textsubscript{3} measurement began in June 2003, the measurements of 2003 were not included in this analysis. The yearly O\textsubscript{3} concentrations increased from 48.7 ppbv in 2004 to 54.8 ppbv in 2009 and then decreased to 49.2 ppbv in 2010 (Fig. 2). This pattern was not reflected in NW1 and NW2, for which annual means were the highest in 2004 and lowest in 2010. Marine air masses, including SE and SW, showed the most visible change during this period. Particularly, their annual frequencies increased in 2010, while those of clusters W, N, NW1 decreased (Fig. 10b). It is not certain for a higher and lower frequency of NW2 and W in 2004 than in other years. These results imply that marine air masses were likely to play a significant role in decreasing O\textsubscript{3} concentration in 2010. The causes underlying increased occurrence of marine air masses needs to be further investigated. These results suggest that a decrease in O\textsubscript{3} concentrations after
2009 was not only associated with the decrease in NO\textsubscript{x} emission from China, but also a change in meteorological character in the study region. Considering that Chinese influence is implicit in N and SW, Chinese emission was the predominant factor determining the concentrations of O\textsubscript{3} at IORS. The impact of Korean and Japanese emissions were incorporated in N and SE, apparent in spring and fall, respectively.

5 Conclusion

Surface O\textsubscript{3} concentrations were determined at Ieodo Ocean Research Station (IORS) in the East China Sea (32.07° N, 125.10° E) from June 2003 and December 2010. The IORS is a 40 m research tower roughly equidistant from Korean, Chinese, and Japanese shores. The average concentration of O\textsubscript{3} for the entire period was of 51.8 ± 15.9 ppbv. It is higher than those of remote sites in the Northeast Asia and implies the steady influence of continental outflows. Particularly, the seasonal differences were prominent, with spring maximum (61.1 ppbv) and summer minimum (37.8 ppbv), which are greatly dependent on synoptic scale circulation of the atmosphere which, except for summer, expedites effective transport of Asian outflows into the Northwest Pacific region. The diurnal variation of O\textsubscript{3} showed a broad maximum in late afternoon, resulting in 4.8 ppbv of daytime build-up.

The cluster analysis of backward trajectories identified the six air masses affecting O\textsubscript{3} concentrations at IORS. Among the six, four types of air masses originated from Asian continents, carrying their outflows (NW1, NW2, W, and N) and the other two were aged marine air from the Pacific Ocean (SE, SW). They primarily determined the maximum (61.6 ppbv) and minimum (32.2 ppbv) O\textsubscript{3} concentrations in spring and summer, respectively. Particularly, the three clusters of NW1, NW2, and W, coming directly from mainland China, comprised 53% of all air masses which arrived at IORS, their contribution increasing up to ~ 86% in winter. The clusters N and W were the most frequent under stagnant condition before and after summer monsoon. In summer, the
occurrence of marine air reached the maximum (~ 74%). These results confirm that Chinese emissions were the dominant source of O$_3$ observed at IORS.

The annual O$_3$ concentrations increased until 2009, and then slightly decreased in 2010, which is in good accordance with NO$_x$ observed in East Asia, where, a slowdown of NO$_x$ emission occurred in 2009 as a result of economic recession in China. In addition, the cluster analysis of air masses highlighted the increased contribution of marine air masses also played a role in decreasing mean concentration of O$_3$ in 2010.

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References


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Jaffe, D. A., Honrath, R. E., Zhang, L., Akimoto, H., Shimizu, A., Mukai, H., Murano, K., Hatakeyama, S., and Merrill, J.: Measurements of NO, NOy, CO and O3 and estimation of


Figure 1. Geographical locations of (a) Ieodo Ocean Research Station, Korea, (b) Ryori, Japan, (c) Yonagunijima, Japan, and (d) Minamitorishima, Japan.
Figure 2. Monthly mean $O_3$ concentrations at IORS, from June 2003 to December 2010, with smoothed trend (thick line) and estimated 95% confidence interval (gray shade).
Figure 3. Comparison of diurnal and monthly variations of O$_3$ concentrations at remote sites in the Northwest Pacific region including IORS, Yonagunijima, Ryori, and Minamitorishima. All the data were averaged for 8 years (2003–2010).
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**Figure 6.** Frequency distributions of 10 min averaged $O_3$ concentrations at IORS for (a) all data, (b) spring, (c) dry summer, (d) wet summer, (e) fall, and (f) winter with mode concentrations given.
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Figure 8. Concentration Weighted Trajectory (CWT) analysis of O$_3$ concentrations.
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Figure 10. Annual variations of (a) $O_3$ concentrations for six clusters, (b) their frequency.