Ozone concentrations, flux and potential effect on yield during wheat growth in the Northwest-Shandong Plain of China

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ARTICLE INFO

Article history:
Received 10 October 2014
Revised 8 December 2014
Accepted 15 December 2014
Available online 5 May 2015

Keywords:
Ozone concentration
Ozone flux
Deposition velocity
Eddy covariance
Yield loss estimation
Cropland ecosystem

ABSTRACT

Ozone (O₃) concentration and flux (Fₒ) were measured using the eddy covariance technique over a wheat field in the Northwest-Shandong Plain of China. The O₃-induced wheat yield loss was estimated by utilizing O₃ exposure-response models. The results showed that: (1) During the growing season (7 March to 7 June, 2012), the minimum (16.1 ppbV) and maximum (53.3 ppbV) mean O₃ concentrations occurred at approximately 6:30 and 16:00, respectively. The mean and maximum of all measured O₃ concentrations were 31.3 and 128.4 ppbV, respectively. The variation of O₃ concentration was mainly affected by solar radiation and temperature. (2) The mean diurnal variation of deposition velocity (Vₑ) can be divided into four phases, and the maximum occurred at noon (12:00). Averaged Vₑ during daytime (6:00–18:00) and nighttime (18:00–6:00) were 0.42 and 0.14 cm/sec, respectively. The maximum of measured Vₑ was about 1.5 cm/sec. The magnitude of Vₑ was influenced by the wheat growing stage, and its variation was significantly correlated with both global radiation and friction velocity. (3) The maximum mean Fₒ appeared at 14:00, and the maximum measured Fₒ was −33.5 nmol/(m²·sec). Averaged Fₒ during daytime and nighttime were −6.9 and −1.5 nmol/(m²·sec), respectively. (4) Using O₃ exposure-response functions obtained from the USA, Europe, and China, the O₃-induced wheat yield reduction in the district was estimated as 12.9% on average (5.5%–23.3%). Large uncertainties were related to the statistical methods and environmental conditions involved in deriving the exposure-response functions.

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Introduction

Ground-level ozone (O₃) is a secondary pollutant with adverse effects on plant growth, photosynthesis, and crop yields (Heck et al., 1982; Cape, 2008; Feng et al., 2008). The O₃ concentration is determined by its photochemical reactions with NOₓ (NO + NO₂) and VOCs (Volatile Organic Compounds) as well as horizontal and vertical large-scale transport (Crutzen et al., 1999; Cape, 2008). According to long-term observations across the globe, ground O₃ concentration levels have been increasing in the past several decades (Monks, 2000; Vingarzan, 2004). In China, fast-paced industrialization and ever-increasing numbers of fossil-fueled vehicles have produced significant amounts of VOCs and NOₓ, which have led to rapidly increasing atmospheric O₃ concentrations (Wang et al., 2009; Li et al., 2014). The elevated O₃ concentration is threatening crop production in China (Aunan et al., 2000; Wang and Mauzerall, 2004; Wang et al., 2007; Zhu et al., 2011).

Two kinds of metrics, O₃ concentration or exposure-based indices, and flux-based indices, were applied to assess the effect...
of O₃ on plants and ecosystems (Musselman et al., 2006; Pleijel et al., 2007). The former are metrics related to the atmospheric environment that do not consider the status of vegetation and ecosystems, e.g., stomatal conductance, leaf area index, and growing stages. Plant response to O₃ is closely related to the amount absorbed into leaf tissue, so stomatal O₃ uptake is considered a better metric than ambient O₃ concentration to evaluate the O₃-induced yield loss (Pleijel et al., 2004; Paoletti and Manning, 2007). One of the well-established methods to quantify stomatal O₃ uptake is to measure total O₃ flux (Fₒ) over an ecosystem and then partition Fₒ into stomatal (Fₛ) and non-stomatal uptake (Fₙₛ) by using resistance models (Gerosa et al., 2003; Lampaud et al., 2009).

Currently, the eddy covariance method is considered the best micrometeorological technique for measuring ecosystem fluxes (Grünhage et al., 2000; Baldocchi, 2003). Due to a lack of robust and high performance fast-response gas analyzers that can be deployed in the field on a long-term basis, several short-term O₃ flux measurements have been carried out in the past few decades (Gerosa et al., 2003; Lampaud et al., 2009). In China, studies of the effects of O₃ on plants have mainly centered on OTC (open top chamber) or FACE (free-air concentration enhancement) experiments (Feng et al., 2003; Zhu et al., 2011; Feng et al., 2012). To our knowledge, there have been few investigations on O₃ flux at the ecosystem level in China.

One purpose of studying O₃ concentration and flux over a cropland ecosystem is to assess the yield loss caused by O₃. To quantify these losses, some O₃ exposure/flux-response models have been generated using OTC or FACE experiments (Heck et al., 1982; Mills et al., 2007; Feng et al., 2012; Wang et al., 2012). Although flux-based indices have advantages over exposure-based indices owing to their linkage to stomatal uptake of plants, there are some practical limitations that hinder their use in current research. Such limitations include the lack of continuous stomatal O₃ flux estimations and suitable flux-based assessment models. In contrast, yield loss estimations utilizing O₃ exposure-response functions are relatively easy (Wang and Mauzerall, 2004; Van Dingenen et al., 2009; Avnery et al., 2011).

The Northwest-Shandong Plain of China is an important grain production base, and wheat is a high O₃-sensitivity crop (Mills et al., 2007). To investigate the current O₃ status over the cropland ecosystem and to assess the effect of O₃ on crop yield, O₃ concentration and flux over a wheat field were measured by using the eddy covariance technique. The objectives of the study were to investigate: (1) the relationship of O₃ concentration with environmental factors and the diurnal and seasonal variations of O₃ concentration; (2) the relationships of O₃ deposition velocity and flux with environmental factors or other fluxes as well as their diurnal and phenological variations; and (3) the O₃-induced wheat yield loss at current O₃ levels by using exposure-response functions.

1. Materials and methods

1.1. Site description

The observations were conducted over a winter wheat (Triticum aestivum L.) field at the Yucheng Comprehensive Experiment Station of the Chinese Academy of Sciences (36°50’ N, 116°34’ E, 28 m asl; Shandong Province, China). The site is located in the Yellow River alluvial plain of the North China Plain, characterized by loamy soil texture as well as a semiarid and warm temperate climate. The mean annual temperature and precipitation are 13.4°C and 567 mm, respectively. The main growing season of winter wheat is from March to early June. The experimental site is fairly flat, and fetch requirements for eddy covariance measurements are well satisfied within 200 m of the instrument locations. The canopy height of the winter wheat increased from 0.05 m to 0.75 m during the field experiment from 7 March to 7 June, 2012.

1.2. Data collection

The absolute concentration of ambient O₃ was measured with a slow-response portable UV-absorption based O₃ analyzer (Model 205, 2B Technologies Inc. CO., Boulder, Colorado, USA; hereafter referred to as M205). It has a detection limit of 1 ppbV and its output rate was set to 2 sec. Ozone flux was measured with the eddy covariance method in combination with observations from the Chinese Terrestrial Ecosystem Flux Observational Research Network (ChinaFLUX) (Yu et al., 2006). The instrumentation includes a 3D sonic anemometer (CSAT3, Campbell Scientific Instruments, Logan, Utah, USA) and an open-path CO₂/H₂O gas analyzer (LI-7500, LI-COR Biosciences, Lincoln, Nebraska, USA). The O₃ fluctuation was measured with a fast-response O₃ analyzer (Enviscope GmbH, Frankfurt am Main, Germany), hereafter referred to as ENVI. The measurement principle is based on the chemiluminescence reaction of O₃ with an ozone-sensitive dye layer on an aluminum plate placed in the cell. Although its response time can reach 0.1 sec, the sensitivity is affected by the consumption of dye and environmental conditions, particularly the air humidity (Güsten et al., 1996; Muller et al., 2010). More information about the analyzer can be found in Zahn et al. (2012). Air was drawn into the two analyzers through two PTFE (Teflon) tubes that were 3 m long with a 4 mm interior diameter. The mean delay time (2.8 sec) was calculated by the maximum covariance method. The ENVI’s output signal (in mV) was calibrated by the ambient O₃ concentration. Micrometeorological and radiation variables were also measured, including air temperature and relative humidity (HMP45C, Vaisala Co., Finland), wind speed (A100R, Vector Instruments, UK), net radiation (CNR1, Kipp & Zonen, the Netherlands), and photosynthetically active radiation (LI-190SB, LI-COR Biosciences, USA).

All sensors were installed at 2.2 m height. The sampling frequency was 10 Hz. Two gas intake tubes were mounted next to the sonic anemometer center with 0.2 m horizontal separation. Due to the continuous consumption of organic dye, ENVI’s sensitivity slowly decreased with time. To maintain high sensitivity, we replaced the organic dye disc every 3 to 4 days. 10 Hz raw data from the eddy covariance (EC) system and 30-min mean data were recorded by a data-logger (CR5000, Campbell Scientific Instrument, Logan, Utah, USA).

1.3. Eddy covariance O₃ flux calculation and data post-processing

The eddy covariance method is based on the statistics involved in vertical turbulent exchange of scalars. Because the ENVI's
signal output is a relative measure of O₃ and its stability is affected by the consumption of O₃-sensitive dye and environmental conditions, it needs to be simultaneously calibrated using the absolute O₃ concentration. In this study, the "Ratio Method" was used to calibrate the ENVI’s signal output (X), which means that X (in mV) is proportional to the absolute ambient O₃ concentration over a 30 min period. Based on this assumption, the ozone deposition velocity ($V_o$, cm/sec), defined as the O₃ flux divided by O₃ concentration, can be calculated by (Muller et al., 2010):

$$V_o = \frac{-\overline{wX}}{\overline{X}}$$

(1)

where, $w$ is vertical wind speed. The overbar denotes time average and the prime signs indicate the fluctuation of each variable. The role of the minus sign in Eq. (1) is to maintain a negative. $V_o$ can be understood as the normalized O₃ flux, and is often used to compare deposition characteristics at different surfaces (Wesely and Hicks, 2000; Fowler et al., 2009). The raw O₃ flux $F_{o,raw}$ (nmol/(m²·sec)) can be given as:

$$F_{o,raw} = \overline{\rho_o \cdot \overline{wX}}$$

(2)

where, $\overline{\rho_o}$ is the mean O₃ density (nmol/m³) derived by combining M205 output (ppbV) and atmospheric temperature and pressure.

In practice, O₃ flux was processed by EddyPro® software (LI-COR, Lincoln, NE, USA) with a series of corrections. Double rotation was utilized to correct the tilt errors (Wilczak et al., 2001). (LI-COR, Lincoln, NE, USA) with a series of corrections. Double rotation was utilized to correct the tilt errors (Wilczak et al., 2001). AOT40 was utilized to correct the tilt errors (Wilczak et al., 2001). With the help of a series of corrections. Double rotation was utilized to correct the tilt errors (Wilczak et al., 2001). (LI-COR, Lincoln, NE, USA) with a series of corrections. Double rotation was utilized to correct the tilt errors (Wilczak et al., 2001). Rotation was utilized to correct the tilt errors (Wilczak et al., 2001). AOT40 was utilized to correct the tilt errors (Wilczak et al., 2001).

1.4. Calculation of O₃ concentration-based indices

In this study, two concentration-based indices were used to assess wheat yield loss during the growing season (3 months). The M7 index (ppbV) is the 7-hr (9:00–16:00) mean O₃ concentration and the AOT40 index (ppmV·hr) is the accumulated hourly ozone concentration above a 40 ppbV threshold. They are calculated according to Van Dingenen et al. (2009):

$$M7 = \frac{1}{N} \sum_{i=1}^{N} C_{O3}[9–16]$$

(3)

$$AOT40 = \sum (C_{O3} > 40 \text{ ppbV})$$

(4)

where, $C_{O3}$ (ppbV) is hourly-mean O₃ concentration. Gaps in O₃ concentrations caused by instrument malfunction and power shortage were filled using two methods. If missed data spanned less than 4 sequential gaps, the linear interpolation method was used, otherwise, the mean diurnal variation method was applied (Falge et al., 2001).

1.5. Data statistical methods

Statistical analysis was performed with MATLAB® 2011 (Mathworks) and Microsoft Office Excel 2003 for Windows. We used the standard deviation (std) to indicate the temporal variance of an individual variable. Outliers were removed prior to subsequent analysis. The main screening criteria are: 0 to 200 ppbV for O₃ concentration and ~35 to 0 nmol/(m²·sec) for O₃ flux. Data that correspond to periods of instrument malfunction, instrument calibration, and replacement of the disc were removed.

2. Results and discussion

2.1. Response of O₃ concentrations to environmental factors

2.1.1. Mean diurnal variations of O₃ concentration

Fig. 1a displays the mean diurnal variation of 30-min averaged O₃ concentration for the entire growing season. To compare its variation with other environmental factors, we also present mean diurnal variations of global radiation (Q) and air temperature (T) (Fig. 1b). The lowest value (16.1 ppbV) of mean O₃ concentration occurred around 6:30, approximately a half hour later than mean sunrise time. It then continuously increased in the morning and early afternoon. The highest value (53.3 ppbV) appeared at 16:00, 4 hr later than the global radiation peak (~12:00) and slightly later than the air temperature peak (Fig. 1b). O₃ then rapidly fell until roughly 20:00. During the night, O₃ always had a downtrend until the next morning. Daytime (6:00–18:00) and nighttime (18:00–6:00, hereafter) mean O₃ concentrations were 39.5 ± 22.1 and 20.7 ± 14.1 ppbV (mean ± std, hereafter), respectively. The mean O₃ concentration during the growing season was 31.3 ± 22.3 ppbV.

The diurnal variation of O₃ concentration depends on the balance of many factors affecting O₃ formation (e.g., local photochemical reactions and horizontal or vertical transport) and destruction (e.g., deposition or chemical reactions) (Crutzen et al., 1999; Cape, 2008; Lin et al., 2008). In the early afternoon, in spite of the gradual decrease of radiation, the increasing temperature resulted in higher levels of chemical precursors, which then led to the rise in O₃ concentration. In the evening, the slow decrease of O₃ concentration may result from the balance between transported O₃ from the upper atmosphere and weak decomposition. The extreme value occurred when the production and destruction velocities of O₃ were equal. Diurnal variation patterns (particularly the peak times) are not the same in different areas. Our results agree well with the typical diurnal patterns for O₃ concentration at low-elevation locations (Kelly et al., 1984; Lin et al., 2008). However, it differed from the patterns from high-elevation sites. For example, the maximum value at the Waliguan site in the Qinghai-Tibet Plateau (3810 m asl) took place at night or early morning, and there was little diurnal variation. This is caused by the extremely low levels of O₃ precursors in the closed natural background condition (Ma et al., 2002; Wang et al., 2006). The difference in O₃ concentration during the day and night showed that O₃ was produced by local photochemical reactions at this site (Crutzen et al., 1999; Xu et al., 2008).

2.1.2. Seasonal variation of O₃ concentration

Fig. 2 shows the daily and 7-hr averaged O₃ concentrations (M24 and M7) during the entire growing season. The overall seasonal change showed an increasing trend, in spite of the lower value that occurred at end of March. The ensemble-averaged O₃
concentrations in March, April, May, and from 1 to 7 of June were 21.6 ± 12.5, 25.6 ± 15.7, 42.1 ± 24.3, and 43.8 ± 27.5 ppbV, respectively. The maximum of the 30-min mean O₃ concentrations was 128.4 ppbV at 16:30, 27 May 2012. The variation of M7 was similar to M24, and the final M7 during the growing season was 45.1 ppbV. The seasonal changes of O₃ concentration may be related to emissions of VOC and NOₓ, which are also affected by radiation and temperature (Dueñas et al., 2002; Cape, 2008).

2.1.3. Relations of O₃ concentration and environmental variables
For a given location, the O₃ concentration variation was dependent on meteorological variables, such as global radiation, temperature, and wind speed (Dueñas et al., 2002; Cape, 2008; David and Nair, 2011). Because the variations of O₃ concentration and radiation were out-of-phase (Fig. 1), the correlation between O₃ concentration and the 3-hr-ahead global radiation were the most significant, see Fig. 3a. The out-of-phase phenomenon may be explained by the time required for the following processes. First solar radiation heats the surface, which results in more emissions of NOₓ and VOCs from the surface. These emissions are then transported above the crop canopy by turbulent motions. Fig. 3b presents the relationship between O₃ concentration and air temperature, which was fitted by a quadratic equation. As air temperature change is primarily driven by solar radiation, temperature can be regarded as an indirect influencing factor for O₃ formation.

2.2. Response of O₃ deposition velocity and flux to environmental variables

2.2.1. Mean diurnal variations of deposition velocity and flux to environmental variables
Fig. 4 shows the mean diurnal variation of 30-min averaged Vd and friction velocity (u*) during the growing season. The diurnal variation of mean Vd can be roughly divided into four stages: (1) rapid increase in the early morning (~7:00–10:00); (2) stable variation around noon (~10:00–15:00) with a range of 0.45–0.55 cm/sec and a maximum at approximately 12:00; (3) relatively fast decrease in the later afternoon (~15:00–19:00); and (4) slight gradual changes during the night (~19:00–7:00) with a range of 0.05–0.15 cm/sec. During the observation period, average Vd during the daytime and at nighttime were 0.42 and 0.14 cm/sec, respectively. The diurnal variation of Vd is affected by many factors, e.g., radiation, turbulent intensity, and atmospheric humidity (Fowler et al., 2009; Turnipseed et al., 2009; Zona et al., 2014). In the morning, the increasing radiation results in stronger turbulence (described by friction velocity u*) (Fig. 4b), which facilitates O₃ transport to the underlying surface. Elevated radiation can also cause stomata to open, allowing easy access for O₃. Thus, Vd increased rapidly during the morning. Around noon, u* remained strong with stable variation, and wheat stomata were predominantly opened at this time. Vd showed a stable variation with strong deposition velocity during this period because of these factors. Vd displays a downward trend and reaches a relatively low level in the afternoon due to the weak turbulent exchange and gradually closing stomata. At night, though the wheat stomata are almost completely closed, the slow Vd may result from the reaction of O₃ with other chemicals (e.g., NO from soil) or absorption by soil and stems (Zona et al., 2014). The diurnal variation was similar to that measured on a barley field (Gerosa et al., 2004) and on ponderosa pine (Kurpius et al., 2002). The average Vd was comparable with the results from

![Fig. 1](image1.png) - Mean diurnal variations of (a) 30-min averaged O₃ concentrations as well as (b) global radiation (Q) and air temperature (T). Top and bottom of vertical lines represent mean ± std.

![Fig. 2](image2.png) - Seasonal changes of 7-hr (9:00–16:00) and daily-averaged O₃ concentrations (M7 and M24) during the growing seasons (7 March to 7 June, 2012).
vineyard and cotton surfaces in the USA, which were 0.5 and 0.8 cm/sec, respectively (Padro, 1996).

Fig. 5a compares the mean diurnal variations of average $V_d$ in different periods or months. To compare these with the crop growth status, the crop heights ($h_c$) and Leaf Area Index (LAI) are shown in Fig. 5b. Clearly, there were large differences in the values and diurnal variation of $V_d$ due to the differences in the surface status. At the beginning of the observation period (March), the wheat was short ($h_c$ ranged from 10 to 30 cm,) and most of the surface was bare soil (LAI was between 0.3 and 1). $V_d$ showed a symmetrical diurnal cycle during this period with the maximum of 0.4 cm/sec at midday. In the vegetative stages (April to May), $h_c$ increased from 30 to 75 cm and LAI varied between 1 and 2.7. During this period, the maximum $V_d$ appeared around noon and reached as high as 0.7 cm/sec. At the end of the growth stage (from 1 to 7 of June), most leaves were senescent and stomata were nearly closed. $V_d$ reached its peak in the early morning and the mean $V_d$ was the smallest (~0.35 cm/sec) during this period.

There is large variability in $V_d$ between different surfaces and different crop growing stages. Generally, abiotic surfaces with very little organic matter (e.g., desert or snow) have a deposition velocity on the order of 0.1 cm/sec or less (Güsten et al., 1996; Wesely and Hicks, 2000). The relatively large daytime $V_d$ (~0.4 cm/sec) in March ($V_d3$) might be driven by the chemical reaction of O$_3$ with NO and other gases emitted from soil as well as stomata uptake of O$_3$ (Zona et al., 2014). The phenological variation of $V_d$ was similar to that observed in some previous studies (Gerosa et al., 2003, 2004). For example, mean $V_d$ over barley in Italy gradually increased from seedling growth to stem elongation and reached its maximum soon after anthesis (i.e., the grain filling period) when photosynthesis was at the highest level (Gerosa et al., 2004). In our study, the $V_d$ in April and May was the same magnitude as the $V_d$ over the barley field. During this period the maximum of averaged $V_d$ could reach approximately 0.8 cm/sec around noon (see $V_d4$ and $V_d5$ in Fig. 5a). During the latter part of the growing season of barley, $V_d$ decreased gradually with the maturation of the barley and leaf senescence. The midday $V_d$ also noticeably decreased during this period, leading to an earlier maximum and skewing the diurnal variation pattern towards morning (Gerosa et al., 2004). A similar diurnal variation pattern was found in our study (see $V_d6$ in Fig. 5a).

**Fig. 3** – Relationships of daytime O$_3$ concentration with (a) global radiation (Q) and (b) air temperature (T). Global radiation was shifted forward by 3 hr.

**Fig. 4** – Mean diurnal variations of (a) deposition velocity ($V_d$) and (b) friction velocity ($u^*$).
2.2.2. Relationship between V\textsubscript{d} and environmental variables

The previous studies showed that the main controlling factors of V\textsubscript{d} were radiation, air temperature, friction velocity, vapor pressure deficit, soil moisture, and phenology (Wesely and Hicks, 2000; Kurpius et al., 2002; Turnipseed et al., 2009; Zona et al., 2014). In our study, we found that there were obvious positive correlations between V\textsubscript{d} and both global radiation (Q) and friction velocity (u\textsuperscript{*}). During the growing stage (Fig. 6), u\textsuperscript{*} could be considered an indirect influencing factor of O\textsubscript{3} deposition. On the one hand, the increase of radiation can cause leaf temperature rise, which will result in the opening of stomata to reduce temperature. The opening of stomata will simultaneously let other gases (e.g., CO\textsubscript{2} and O\textsubscript{3}) enter plants. On the other hand, radiation increases can also strengthen atmospheric turbulent exchange, i.e., u\textsuperscript{*} becomes large, which allows for greater proximity to stomata via vertical and horizontal transport. In fact, V\textsubscript{d} is synthetically affected by numerous factors and complex processes, which can be verified by the relatively scattered relationships.

2.2.3. Mean diurnal variations of ozone flux and its uncertainty

According to Eq. (2), the magnitude and variation of F\textsubscript{o} are determined by O\textsubscript{3} concentration and V\textsubscript{d}. Fig. 7 shows the diurnal variations of mean F\textsubscript{o} in (a) the growing season and (b) for different periods. Since there is no known biological source of O\textsubscript{3}, F\textsubscript{o} was always directed downward. Because of the rapid increase of O\textsubscript{3} concentration and V\textsubscript{d} in the morning, F\textsubscript{o} showed a faster increase until 11:00. From 11:00 – 16:00, there was relatively slow variation in F\textsubscript{o}, and maximum flux appeared at approximately 14:00, which was between the peak times of O\textsubscript{3} concentration and V\textsubscript{d}. Beginning at 16:00, F\textsubscript{o} showed a rapid decrease because of the drastic decline of O\textsubscript{3} concentration. At night, F\textsubscript{o} displayed small and smooth changes due to weak changes in concentration and V\textsubscript{d}. The mean F\textsubscript{o} during daytime and nighttime were ~6.9 and ~1.5 nmol/(m\textsuperscript{2}·sec), respectively. The maximum measured F\textsubscript{o} was ~33.5 nmol/(m\textsuperscript{2}·sec). Due to the differences in O\textsubscript{3} concentrations and V\textsubscript{d} during different months, there were obvious differences in the magnitude and diurnal variation pattern of F\textsubscript{o} in different months (Fig. 7b). The ensemble-averaged F\textsubscript{o} in March, April, May, and from 1 to 7 of June 2012 were 2.3 ± 2.0, 5.1 ± 3.7, 5.5 ± 5.3, and 4.5 ± 3.1 nmol/(m\textsuperscript{2}·sec), respectively.

Although eddy covariance is the best technique for ecosystem flux measurements, it still has some uncertainties. Different corrections or choice of parameters will result in an altered flux (Massman and Lee, 2002). Particularly, due to the sensitivity drift...
of the fast-response O$_3$ analyzer, choice of calibration models becomes an added uncertainty source for eddy covariance O$_3$ flux measurements (Muller et al., 2010). Further, to assess the effects of O$_3$ on plants and ecosystems, F$_{st}$ and F$_{ns}$ are usually partitioned by resistance models (Gerosa et al., 2004; Lamaud et al., 2009). The ratio of F$_{st}$ to F$_o$ usually varies from 1/2 to 1/3 in terrestrial ecosystems, and it is affected by physiological activity and meteorological conditions (Gerosa et al., 2004, 2005; Fowler et al., 2009; Lamaud et al., 2009). The estimation of F$_{st}$ and additional relevant research will be carried out in the future.

2.3. Estimation of wheat yield loss based on O$_3$ concentration and its uncertainties

To estimate O$_3$-induced wheat yield loss, exposure indices must be calculated, and then exposure-response functions can be used to estimate the loss due to ozone. Fig. 8 shows the changes of daily-AOT40 (AOT40$_{day}$) and the daily-accumulative AOT40. Clearly, the AOT40 was mostly driven by the AOT40$_{day}$ during the later part of the growing season (April and May). According to Eqs. (3) and (4), the M7 was equal to 45.1 ppbV and AOT40 was 10.2 ppmV·hr during the growing seasons (3 months).

The exposure-response functions were commonly generated by OTC or FACE experiments. For example, the National Crop Loss Assessment Network (NCLAN, USA) obtained the M7-based functions using 10-year OTC experiments (Heck et al., 1982; Wang and Mauzerall, 2004). Mills et al. (2007) summarized numerous AOT40-based response functions for some crops obtained by several OTC experiments in Europe and the USA. In China, AOT40-based models have recently been created for the Yangtze River Delta (Feng et al., 2003; Wang et al., 2012). Table 1 shows the yield loss estimations calculated by different ozone exposure-response functions. Note that some functions were corrected with unified units and outputs (Relative Yield Loss (%), RYL). The current O$_3$-induced wheat yield reduction in the Northwest-Shandong Plain of China was estimated as 12.9% on average, with considerable variability (5.5%–23.3%). In spite of the large differences in the yield loss estimation by different functions, our results still have a certain reference value.

A large discrepancy in the yield loss estimations by two indices and models was reported by Van Dingenen et al. (2009) and Avnery et al. (2011). Wheat yield losses obtained by the M7-based models were significantly lower than those of the AOT40-based models. The inconsistency may be due to the differences in statistical methods used for deriving the exposure-response functions (Van Dingenen et al., 2009). For example, yield loss by AOT40 is relative to that in the charcoal-filtered (i.e., zero-O$_3$) air treatment (Mills et al., 2007), while the yield losses calculated by the M7 models

![Fig. 7](image1)

**Fig. 7** – Diurnal variations of mean ozone flux (F$_o$) over wheat field (a) during the entire growing season and (b) during different periods. F$_o3$, F$_o4$, F$_o5$, and F$_o6$ are the ensemble-averaged F$_o$ of March, April, May, and from 1 to 7 June 2012, respectively.

![Fig. 8](image2)

**Fig. 8** – Changes in daily and continuously-accumulated O$_3$ concentrations above 40 ppbV (AOT40$_{day}$ and AOT40) during wheat growing season.
were relative to that at $M7 = 0.025$ ppmV (Heck et al., 1982). Adding the yield loss (7.8%) at $M7 = 0.025$ ppmV compared to that at $M7 = 0$ ppmV, the yield loss estimation using $M7$ should be equal to 14.1%. This value is comparable to the estimations that utilize AOT40 models.

Another source of uncertainty is that the yield response functions may also vary with different wheat cultivars, plant locations, and other environmental conditions when using the same index (Heck et al., 1982; Wang and Mauzerall, 2004; Zhu et al., 2011; Wang et al., 2012). In addition, functions were obtained from OTC experiments and the indices were obtained from natural ecosystems, which may also result in some uncertainties (Wang et al., 2012). Fortunately, more FACE experiments were utilized to study the effects of O3 on crop yield loss, which may improve the assessment accuracy (Zhu et al., 2011; Feng et al., 2012).

### Table 1 - Relative yield loss (RYL) estimation with different O3 exposure-response functions.

<table>
<thead>
<tr>
<th>O3 exposure-response function</th>
<th>Relative yield loss (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>RYL$^a = 0.313 \times M7$−7.8</td>
<td>6.3</td>
<td>Heck et al. (1982)</td>
</tr>
<tr>
<td>RYL = $\exp(-(M7/137)^2)$/$\exp (-25/137)^2)$</td>
<td>5.5</td>
<td>Mauzerall (2004)</td>
</tr>
<tr>
<td>RYL$^b = 1.296 \times AOT40$</td>
<td>13.2</td>
<td>Feng et al. (2003)</td>
</tr>
<tr>
<td>RYL$^b = 1.61 \times AOT40$</td>
<td>16.4</td>
<td>Mills et al. (2007)</td>
</tr>
<tr>
<td>RYL$^b = 2.2795 \times AOT40$</td>
<td>23.3</td>
<td>Wang et al. (2012)</td>
</tr>
</tbody>
</table>

$M7$: 7-hr (9:00–16:00) mean O3 concentration; AOT40: accumulated hourly ozone concentration above a 40 ppbV threshold.

$^a$ The function was corrected with the same unit (ppbV).

$^b$ AOT40 unit and output were corrected.

### 3. Conclusions

In this study, O3 concentration and flux over a winter wheat field in the Northwest-Shandong Plain were measured via the eddy covariance technique. Slow-response and fast-response were derived as follows:

1. During the observation period (7 March–7 June, 2012), there was an obvious diurnal variation pattern in O3 mean concentration, with the minimum (16.1 ppbV) and maximum (53.3 ppbV) mean concentrations occurring around 6:30 and 16:00, respectively. Daytime and nighttime averages of concentrations were 39.8 ± 23.1 and 20.7 ± 14.1 ppbV, respectively. The variation of O3 concentration was mainly affected by solar radiation and temperature.

2. The diurnal variation of $V_d$ can be divided into four phases. The maximum (0.57 cm/sec) of mean $V_d$ occurred at noon (12:00). Average $V_d$ during daytime and nighttime were 0.42 and 0.14 cm/sec, respectively. The magnitude of $V_d$ was influenced by the wheat growing stage, and its variation was significantly correlated with both global radiation and friction velocity.

3. O3 flux is determined by the O3 concentration and $V_d$, $F_{o}$ was always directed downward and the maximum of mean $F_{o}$ appeared at 14:00. The mean $F_{o}$ during daytime and nighttime were −6.9 and −1.5 nmol/(m$^2$·sec), respectively.

4. Using O3 exposure-response functions for wheat yield loss obtained from the USA, Europe, and China, the O3-induced wheat yield reduction at current O3 levels in the Northwest-Shandong Plain of China was estimated as 12.9% on average, with considerable variability (5.5%–23.3%). The uncertainties were related to the statistical methods and environmental conditions involved in deriving the exposure-response functions in the respective studies.

### Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 31070400), the National Basic Research Program of China (No. 2010CB833501-01), the Innovation Project of the Institute of Geographic Sciences and Natural Resources Research, CAS (Grant No. 201003001), and the Max Planck Society (Germany).

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