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Threshold exceedances and cumulative ozone exposure indices at tropical suburban site

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[1] This study provides the first analysis of threshold exceedances and cumulative ozone exposure indices from Pune, a tropical suburban site in India. We used the directives on ozone pollution in ambient air provided by the United Nations Economic Commission for Europe, and by the World Health Organization to assess the air quality from in situ measurements of surface ozone (during the years 2003–2006). We find that the exposure-plant response index (Accumulated exposure Over a Threshold of 40 ppb (AOT40)) and target values for protection of human health (8-h > 60 ppb) are regularly surpassed. This is a concern for agricultural and human health. Air-mass classification based on back-air trajectories shows that the excess of AOT40 values is quite plausibly due to long-range transport of background ozone and its precursors to the measurement site. **Citation:** Beig, G., S. D. Ghude, S. D. Polade, and B. Tyagi (2008), Threshold exceedances and cumulative ozone exposure indices at tropical suburban site, *Geophys. Res. Lett.*, *35*, L02802, doi:10.1029/2007GL031434.

1. Introduction

[2] High surface ozone arising from photochemical formation and accumulation is now a major environmental concern in many regions of the world [*Klumpp et al.*, 2006a, 2006b], with current concentrations being high enough to harm human health and agricultural productivity over wide areas [*Chameides et al.*, 1999; *Benton et al.*, 2000; *Klumpp et al.*, 2006a, 2006b]. It is now well known that high amounts of volatile organic compounds (VOCs) from industrial and traffic emission lead to fairly high concentration of surface ozone in the boundary layer of industrial cities [*Sillman et al.*, 1990]. This not only deteriorates air quality near the region of emission, but is also likely to have far-reaching impacts at remote places [*Lal et al.*, 1998; *Jacob et al.*, 1999]. Some recent studies have shown that rapid forest decline, reduction in life span of various materials [*Lee et al.*, 1996] and decrease in winter crop yields [*Wang et al.*, 2005; *Mills et al.*, 2007] is due to an increase in ozone concentration at ground level. Epidemiological and toxicological evidence indicates that increased ozone has led to associated health problems [*Avol et al.*, 1998; *Delfino et al.*, 1998]. A considerable part of the population of industrial cities is regularly exposed to peak air pollution in excess of current limit values, as given by the United Nations Economic Commission for Europe (UNECE) and the World Health Origination (WHO) guidelines for air pollution. The European Environment Agency (EEA) uses two indicators related with tropospheric ozone for the assessment of the air quality (available at http://www.eea.eu.int/): (1) Number of days when limit values for ozone are exceeded. The policy issue is protecting the population. (2) Exposure of crops and forests to ozone. The policy issue is protecting the environment.

[3] A few scattered surface ozone measurements are available over the Indian region [*Naja and Lal*, 2002; *Jain et al.*, 2005; *Ghude et al.*, 2006; *Beig et al.*, 2007]. However, all these studies seldom describe threshold exceedances and cumulative ozone exposure indices. Estimations made by chemical transport models show that, because of increasing anthropogenic emissions, ozone production is raised massively, over the Indian region [*Berntsen et al.*, 1996]. Since emissions of ozone precursors from Asian countries (East Asia, Southeast Asia, the Indian Subcontinent) are rising and may continue to rise for several decades [*Akimoto*, 2003] we must carefully evaluate the contribution of each region to air pollution, so that adaptation and mitigation strategies can be developed. In view of this necessity, the present study is aimed at assessing and evaluating air quality at the tropical suburban site Pune. Since no Ozone Pollution Directive is yet established for the Indian region, we have evaluated ozone concentrations in excess of current limit values based on current UNECE and WHO guidelines. This approach enabled us to determine where these limits are exceeded significantly and whether the objectives for human health and the protection of vegetation can be met.

2. Method

2.1. Site Overview

[4] Measurements are carried out at Pune (18.54°N, 73.81°E), a well industrialized suburban city of India. The observational site is at a considerable distance from the main traffic junctions of the city, in a relatively silent zone surrounded by hills. Moderate commuter traffic is observed on the nearby road, which is at 150 m away. The nearest major traffic junction is located around 5 km away from the site. Major industries are situated towards the northeast and east, about 25 km away. The site experiences a strong influence of the southwest monsoon (June–September). This period is dominated by rain and westerly airflow which brings clean marine air from the Arabian Sea. The pre-monsoon (March–May) is governed by high temperature (∼40°C) and gusty winds, while the post-monsoon (October–November) is dominated by easterly airflow and clear skies, while light surface winds and very low relative humidity exist during winter (December–February). For further detail see *Beig et al.* [2007].

2.2. Evaluation of Surface Ozone Concentration

[5] Ozone is measured with an analyzer ($O_3$42M, Environment S.A., France) based on the absorption of UV

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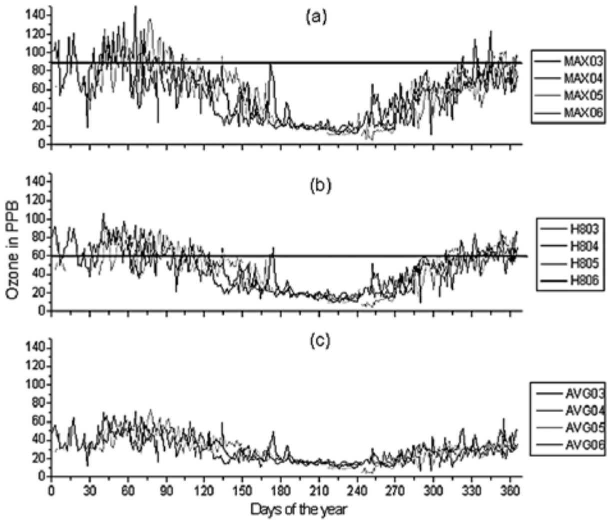

Figure 1. Daily (a) maximum, (b) 8-h average for a fixed period of 11–18 h, and (c) 24-h average surface ozone concentration during March 2003–December 2006 at Pune. Black horizontal grid line through 90 ppb (Figure 1a) and 60 ppb (Figure 1b) is information threshold (1-h > 90 ppb) and health protection threshold (8-h > 60 ppb) respectively.

radiation at 253.7 nm. Calibration is regularly done with the help of an inbuilt ozone generator and instrument zero is checked automatically every 8 hours. More details are given by *Beig et al.* [2007]. Following the Ozone Directive [*European Union*, 2002], at least 75% of valid data are required to calculate mean values and 90% to compute cumulative indices and the number of threshold exceedances. Here, we have used monthly data covering between 85% and 100% of the time (with of few exceptions with 80% coverage) to compute AOT40 values over a one month period. These monthly AOT40 values are added when AOT40 over a 3 months period is calculated.

[6] A cumulative ozone exposure index, AOT40 (Accumulated exposure Over a Threshold of 40 ppb), is calculated as the sum of the differences between the hourly ozone concentrations exceeding 40 ppb and 40 ppb using only the hourly values measured for daylight hours between 07 and 19 h. AOT40 is an exposure-plant response index function set by the United Nations Economic Commission for Europe (UNECE) and the United States Environmental Protection Agency (USEPA). AOT40 values of 3000 ppb*h during the 3 month growing season, and of 10,000 ppb*h during 6 months are the critical levels corresponding to 5% loss in crop and forest yield established by UNECE and WHO [*World Health Organization* (*WHO*), 2000]. An 8-h mean of 60 ppb corresponds to the critical level for human health [*WHO*, 2000].

3. Threshold Exceedances and Cumulative Ozone Exposure

3.1. Limit for the Protection of Human Health

[7] The daily maximum, daily 8-h mean (over a fixed period of 11–18 h), and daily average surface ozone concentration during 2003–2006 are shown in Figures 1a, 1b, and 1c respectively. Elevated ozone concentrations have been observed on a large number of days indicating significant ozone pollution. The target value for human health protection (8-h mean > 60 ppb) is surpassed significantly. The poor air quality threshold (1-h > 80 ppb) and the threshold for information to the public (90 ppb as 1-h mean) is also regularly exceeded. Strong ozone pollution exceeding the threshold values for human health has generally been observed from November to April, while low ozone concentration below the human health threshold and comparable to the background level is observed during monsoon.

[8] The annual number of days exceeding the various threshold values (as described above) is given in Table 1. Since data are missing for a few days from 2003–2006, we have taken average values to obtain a general idea about the average number of days exceeding the threshold values. We have found no significant difference in comparison with 2004 (when 95% of hourly data were available for every month). The human health protection threshold is exceeded up to an average of 84 days per year (28%). It is remarkable that this is more than the 25 days per year permitted by the directive for the target value averaged over 3 years. Exceedance above 80 ppb is registered up to an average of 57 days per year (19%), while the threshold for information to the public is exceeded for around 32 days per year (11%). Monthly means, monthly means of maximum ozone, and monthly 8-h average ozone concentrations varied between 13–47 ppb, 16–89 ppb and 14–72 ppb, respectively (Table 2). It is remarkable that daily mean ozone values above 60 ppb have been observed on some days in February and March, while the monthly 8-h mean concentration is above 60 ppb during the period December–March (Table 2). This means that there is a significant ozone pollution at the monitoring site.

3.2. Protection of Vegetation and Forest

[9] The EU ozone directive defines an accumulated ozone exposure of 3000 ppb*h for 3 months period as a critical level for the protection of vegetation. Therefore, daily AOT40 values in general should not exceed ~33 ppb*h (3000/90). Days when this limit is exceeded are here defined as plant exceedance days (PED). We have observed 167 plant exceedance days per year during 2003–06 (or ~55% of the time).

[10] AOT40 values for the different months are given in Table 2. Since data (more than 85%) for January were available only in 2004, the January AOT40 values for 2003–2006 are the same as for 2004. As can be seen from Table 2, the UNECE/WHO threshold and EU long term

Table 1. Annual Number of Days Exceeding Threshold Values

Year	8 h > 60 (11–18 h)	1 h > 80	1 h > 90	PED[a]	Number of Days
2003	54	30	14	116	224
2004	122	90	53	196	365
2005	88	66	41	189	294
2006	71	42	21	168	333
2003–06 (mean)	84 (28%)	57 (19%)	32 (11%)	167 (55%)	304
2004	(33%)	(25%)	(15%)	(54%)	365

[a]PED, Plant Exceedance Days.

Table 2. Monthly Mean Distribution of Daily Average, 8-h Average for a Fixed Period of 11–18 h, Daily Maximum Ozone and AOT40 at Pune

	Daily Average, ppb(v)		8-Hr Average, ppb(v)		Daily Maximum, ppb(v)		AOT40,[a] ppb(v)*h	
Months	(03–06)	2004	(03–06)	2004	(03–06)	2004	(03–06)	2004
Jan	35	40	61	66	73	80	6478	6478
Feb	46	54	72	77	89	91	7380	9702
Mar	47	53	64	72	82	94	8781	9257
Apr	40	41	56	58	72	76	4914	5466
May	31	25	43	35	55	42	1990	998
Jun	22	21	28	24	34	30	432	78
Jul	17	16	19	18	21	20	0	0
Aug	13	14	14	15	16	17	0	0
Sep	15	18	21	25	27	31	103	63
Oct	22	24	35	40	44	48	1339	2081
Nov	28	26	53	51	63	61	3822	3428
Dec	33	34	64	66	75	78	5760	6634

[a]AOT40, 7–19 h.

objective (2002) for the protection of vegetation (3000 ppb*h for 3 months) are exceeded even for individual months, mostly from November to April. The same thresholds are exceeded up to an average of approximately 5100 ppb*h during the post-monsoon (ON), 19600 ppb*h in winter (DJF), and 15700 ppb*h during the pre-monsoon (MAM). The AOT40 cumulative ozone exposure was 1.7 times higher during post-monsoon, 6.5 times higher during winter, and 5.2 times higher during pre-monsoon than the AOT40 critical limit for the protection of vegetation. Over a six month period (November–April), AOT40 cumulative ozone exposure exceeded up to an average ~36000 ppb*h, clearly 3.6 times higher than the critical level for the protection of forests. Note, however, that the AOT40 limit values in the EU Directive are defined as 5-year means in order to compensate for annual variations, while the statements here are based on an average value between 2003 and 2006.

3.3. Classification of Air Masses

[11] *Beig et al.* [2007] have related monthly mean ozone concentration during monsoon and winter to the air masses arriving at the site that traveled over different regions and prevailing meteorological conditions. To investigate whether the exceedances of AOT40-values are mostly due to background ozone increases or due to more local emissions of ozone precursors, seasonal (Table 2) and diurnal variations in ozone (Figure 2) have been analyzed using a classification based on back-air trajectories. As can be seen from Figure 2, minimum ozone concentration and small diurnal variation is observed during monsoon (JJAS). 5-day twice in a week back trajectories during this period show that the suburban site Pune is mostly dominated by influx of cleaner marine air (southwesterly) from the Indian Ocean (Figure 3). This drastically reduces the possible presence of ozone and precursor pollutants transported from a distant source region. Moreover, there is also less solar radiation for photochemical reactions on cloudy days, during monsoon months. Since air masses originate almost over the same location and follow the same paths, they will generally carry the same clean air to the monitoring site. Therefore, the variability of hourly mean concentration over the diurnal cycle will generally be small. However, it should be noted that this variability can give only general information about the nature of air masses arriving at the site. Other day-to-day changes such as due to micrometeorological circulation systems may also largely determine the variability. Small amplitude of the diurnal cycle and small variation in hourly mean concentration associated with monsoonal air trajectories (wind flow) implies that the ozone concentration is mainly dominated by the local emission of precursor pollutants and local meteorological conditions.

[12] On the other hand, northeasterly and easterly winds prevail at the observational site during November–March. A clear diurnal variation is observed during this period with a minimum in the morning and a maximum in the afternoon. This behavior fits relatively well to what is expected when photochemical ozone formation is involved in the presence of precursor pollutants at urban and suburban sites. However, large diurnal variations of hourly mean concentration suggest that the photochemical ozone formation could be

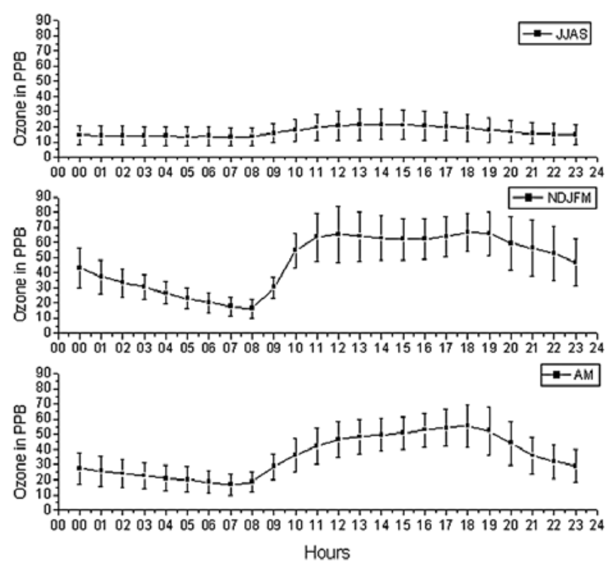

Figure 2. Diurnal variation of averaged surface ozone during 2003–2006 (top) June–September, (middle) January–March, and (bottom) April–May.

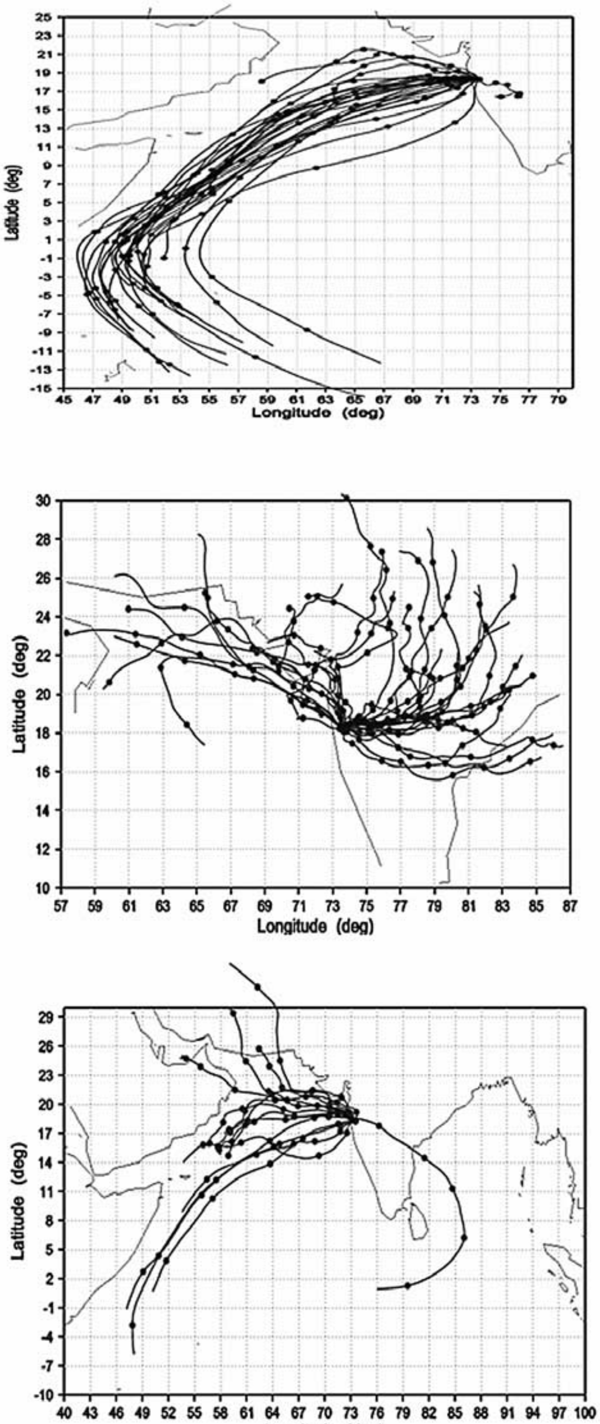

Figure 3. 5-day twice in a week back air-trajectories during (top) June–September, (middle) November–March, and (bottom) April–May for the year 2004.

affected by ozone and precursor pollutants transported from different distant sources. Figure 3 shows that most of the air masses arriving at the site during November–March have traveled from the Northern region, Indo-Gangetic Planes (IGP), or the Eastern region of India by means of regional long-range transport and therefore, are regionally polluted. Since the air masses originate over different parts of the Northern Plains of India and generally follow different paths, variability in the diurnal cycle of hourly mean concentration could be large compared to that observed during monsoon (JJAS). *Beig and Ali* [2006] have also shown that ozone and precursor pollutants from the IGP region spread to other regions including the receptor site, Pune. The large amplitude of the diurnal cycle associated with back-air trajectories arriving at the site indicates that the long-range transport of ozone and precursor pollutants contributes significantly to ozone increase during this period. On the other hand, during April and May, air masses arriving at the site travel mostly from the Arabian Sea (Figure 3, bottom) and are less polluted. Monthly mean ozone concentration (Table 2) and the amplitude of the diurnal variation appear to be reduced during this period. This indicates that the contribution to the increase in ozone concentration due to transport of background ozone and precursor pollutants at the monitoring site is less significant. As a result, observed ozone concentration is likely to be due to the local emission rather than the transport of background ozone and precursor pollutants. It is therefore quite plausible that long-range transport of background ozone and its precursors may be contributing significantly to the exceedances of AOT40 values at the measurement site during November–March period, less significantly during April–May, and almost negligibly during the June–September (monsoon) period.

4. Summary and Conclusion

[13] In this study, we have shown that, according to UNECE and WHO ozone directives, the current ozone concentrations at the tropical Indian suburban site Pune are high enough to exceed 'Critical Levels' for the protection of human health, vegetation and forest.

[14] The concentrations measured during the study period exceeded the target values and long-term objectives for the protection of human health. The human health protection threshold is exceeded for up to an average of 84 (28%) days per year, while the 1-h threshold for information to the public is surpassed up to an average of 32 (11%) days per year at Pune. The AOT40 (3000 ppb*h) EU long-term objective and WHO threshold for the protection of vegetation is exceeded mostly between post-monsoon, winter, and pre-monsoon up to an average of approximately 5100, 19600 and 15700 ppb*h respectively. This corresponds to an increase by a factor of 1.7 during pre-monsoon, 6.5 during winter, and 5.3 during pre-monsoon when compared to the AOT40 critical limit for the protection of vegetation. Over a six-month period (November–April) the threshold is clearly exceeded 3.6 times when compared to the target value for the protection of forest. Air-mass classification based on back-air trajectories shows that the exceedances of the AOT-40 values are quite plausibly due to long-range transport of background ozone and precursor pollutants to the monitoring site.

[15] This study, suggests that surface ozone is much above critical levels and is a significant concern for human health and agricultural productivity. According to new literature of critical levels [*Mills et al.*, 2007] the situation

is even worse. The implementation of measures to reduce emissions of precursors may lower the risk of peak ozone concentrations in the short term. Since emissions of ozone precursors are rising and may continue to rise for several decades [*Akimoto*, 2003] in the Indian region, the situation can be expected to aggravate in the future. With continued economic development in India, in any case, this region will have an increasingly large impact regionally on human health and plant life. More than 40 percent of the population in the Indian region depends on an economy related to agriculture. Detailed studies are needed to develop adaptation and mitigation strategies to minimize the ozone impact on productivity in the region.

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References

Akimoto, H. (2003), Global air quality and pollution, *Science*, *302*, 1716–1719.

Avol, E. L., W. C. Navidi, E. B. Rappaport, and J. M. Peters (1998), Acute effects of ambient ozone on asthmatic, wheezy, and healthy children, *Res. Rep. 82(III)*, pp. 1–18, Health Eff. Inst., Boston, Mass.

Beig, G., and K. Ali (2006), Behavior of boundary layer ozone and its precursors over a great alluvial plain of the world: Indo-Gangetic Plains, *Geophys. Res. Lett.*, *33*, L24813, doi:10.1029/2006GL028352.

Beig, G., S. Gunthe, and D. B. Jadhav (2007), Simultaneous measurements of ozone and its precursors on a diurnal scale at a semi-urban site in Pune, *J. Atmos. Chem.*, *57*, 239–253, doi:10.1007/s10874-007-9068-8.

Benton, J., J. Fuhrer, B. S. Gimeno, L. Skarby, D. Palmer-Brown, G. Ball, C. Roadknight, and G. Mills (2000), An international cooperative programme indicates the widespread occurrence of ozone injury on crops, *Agric. Ecosyst. Environ.*, *78*, 19–30.

Berntsen, T., I. S. A. Isaksen, W. Wang, and X. Liang (1996), Impacts of increased anthropogenic emissions in Asia on tropospheric ozone and climate, *Tellus, Ser. B*, *48*, 13–32.

Chameides, W. L., et al. (1999), Is ozone pollution affecting crop yields in China?, *Geophys. Res. Lett.*, *26*, 867–870.

Delfino, R. J., A. M. Murphy-Moulton, and M. R. Becklake (1998), Emergency room visits for respiratory illnesses among the elderly in Montreal: Association with low-level ozone exposure, *Environ. Res.*, *76*, 67–77.

European Union (2002), Directive 2002/3/EC of the European Parliament and of the Council relating to ozone in ambient air, *Off. J. Eur. Community.*, *L67*, 14–30.

Ghude, S. D., S. L. Jain, B. C. Arya, P. S. Kulkarni, A. Kumar, and N. Ahmeed (2006), Temporal and spatial variability of surface ozone at Delhi and Antarctica, *Int. J. Climatol.*, *26*, 2054–2062.

Jacob, D. J., J. A. Logan, and P. P. Murti (1999), Effect of rising Asian emissions on surface ozone in the United States, *Geophys. Res. Lett.*, *26*(14), 2175–2178.

Jain, S. L., B. C. Arya, A. Kumar, S. D. Ghude, and P. S. Kulkarni (2005), Observational study of surface ozone at New Delhi, India, *Int. J. Remote Sens.*, *26*(16), 3515–3526.

Klumpp, A., et al. (2006a), Ozone pollution and ozone biomonitoring in European cities. Part I: Ozone concentrations and cumulative exposure indices at urban and suburban sites, *Atmos. Environ.*, *40*, 7963–7974.

Klumpp, A., et al. (2006b), Ozone pollution and ozone biomonitoring in European cities. Part II: Ozone-induced plant injury and its relationship with descriptors of ozone pollution, *Atmos. Environ.*, *40*, 7437–7448.

Lal, S., M. Naja, and A. Jayaraman (1998), Ozone in the marine boundary layer over the tropical Indian Ocean, *J. Geophys. Res.*, *103*, 18,907–18,917.

Lee, D. S., M. R. Holland, and N. Falla (1996), The potential impact of ozone on materials in the U.K., *Atmos. Environ.*, *30*, 1053–1065.

Mills, G., A. Buse, B. Gimeno, V. Bermejo, M. Holland, L. Emberson, and H. Pleijel (2007), A synthesis of AOT40-based response functions and critical levels of ozone for agricultural and horticultural crops, *Atmos. Environ.*, *41*, 2630–2643.

Naja, M., and S. Lal (2002), Surface ozone and precursor gases at Gadanki (13.5°N, 79.2°E), a tropical rural site in India, *J. Geophys. Res.*, *107*(D14), 4197, doi:10.1029/2001JD000357.

Sillman, S., J. A. Logan, and S. C. Wofsy (1990), The sensitivity of ozone to nitrogen oxides and hydrocarbons in regional ozone episodes, *J. Geophys. Res.*, *95*, 1837–1852.

Wang, H., C. S. Kiang, X. Tang, X. Zhou, and W. L. Chameides (2005), Surface ozone: A likely threat to crops in Yangtze delta of China, *Atmos. Environ.*, *39*, 3843–3850.

World Health Organization (WHO) (2000), *Air Quality Guidelines for Europe*, 2nd ed., *Reg. Publ. Eur. Ser.*, vol. 91, 288 pp., WHO Reg. Off. for Eur., Copenhagen.

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