

Extent of photochemical smog reaction in the Sydney metropolitan areas

H. Duc^a, M.Azzi^b and S. Quigley^a.

^aEnvironment Protection Authority of New South Wales PO Box 29 Lidcombe, NSW 2141.

^bCSIRO, Division of Energy Technology PO Box 136, North Ryde, NSW 2113.

Abstract: The Sydney basin region experiences some high ozone episodes in summer, especially in the north west and south west of Sydney. Observation-based methods can be used to provide a means to access the potential extent of photochemical smog problem at various regions in the Sydney area. In this study, the observation-based Integrated Empirical Rates (IER) model is used to determine and understand the photochemical smog at various sites in Sydney using ambient measurements at the monitoring stations. Using the 1998/1999 summer air quality data, clustering and principal component analysis methods are then applied to delineate the various regions in the Sydney basin based on the extent of photochemical reaction and the ozone concentrations. This will help in determining and classifying the various regions having different photochemical characteristics, from which appropriate control policy may be used to reduce the photochemical smog.

Keywords: *Photochemical smog extent, region classification, observation-based method.*

1. INTRODUCTION

High ozone episodes, exceeding the EPA (NSW) standard, have occurred in the past and recently in the Sydney basin region, especially in the north west and south west of Sydney. It is desirable to formulate the control policy at the basin and local levels to reduce the ozone levels and the effects of photochemical smog on the population. Eventhough airshed model can be used to simulate results using different control scenarios and hence allows one to determine the best strategy to manage the photochemical smog problem. But the difficulties in obtaining an accurate emission inventory and setting up various data including meteorological information for a reasonable period of simulation can be a daunting task.

Observation-based methods can be used as an alternative to provide a means to access the potential extent of photochemical smog problem at various regions in the Sydney area. Observation-based method such as the Integrated Empirical Rate (IER) model has been used in conjunction with airshed model study to correlate and verify the Volatile Organic Compounds (VOC)/Nitrogen oxides (NO_x) emission control simulations (Blanchard, Stoeckenius [2001]). In this study, the IER model is used to determine and understand the photochemical smog at various sites in Sydney using ambient measurements at the monitoring stations.

2. THE INTEGRATED EMPIRICAL RATE (IER) MODEL

(a) Smog produced and smog chamber results

The photochemical smog formation is a complex process that involves hundreds of chemical reaction equations of many different species. To reduce the complexities and still have the ability to access fairly accurately and interpret air quality data, a semi-empirical model, resulted from smog chamber studies, has been formulated. The Integrated Empirical Rate (IER) model was developed by Johnson [1984] and is based on quantifying photochemical smog in terms of NO oxidation. The IER model defines Smog Produced (SP) as the quantity of NO consumed by photochemical processes plus the quantity of O₃ produced.

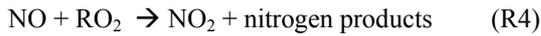
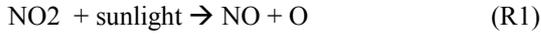
$$[\text{SP}]_0^t = [\text{NO}]_0^t - [\text{NO}]^t + [\text{O}_3]^t - [\text{O}_3]_0^t \quad (1)$$

where $[\text{NO}]_0^t$ and $[\text{O}_3]_0^t$ denote the NO and O₃ concentrations that would exist in the absence of atmospheric chemical reactions occurring after time $t=0$ and $[\text{NO}]^t$ and $[\text{O}_3]^t$ are the NO and O₃ concentrations existing at time t . $[\text{SP}]_0^t$ denotes the concentration of smog produced by chemical reactions occurring during time $t=0$ to time $t=t$.

As observed in the smog chamber, the key feature of the IER model is that SP increases

approximately linearly with respect to cumulative sunlight exposure during light-limited regime, until the available NO_x are consumed by reaction, then the NO_x-limited regime occurs and SP production ceases.

Following Blanchard et al. [1999], this linear relationship can be understood by examining the four main reactions in the ozone formation



In the first three reactions, the ozone is formed from the reaction with oxygen produced from the photolysis of nitrogen dioxides but is scavenged quickly by nitrogen oxides. The three reactions are in photo-stationary state. However, with the production of hydrocarbon radicals (eg. peroxy radical RO₂) from reactive organic compound (ROC) under sunlight, the nitrogen oxide is also consumed to produce nitrogen products such as nitric acid, peroxyacetyl nitrate (PAN) species, alkyl nitrates, and other organic nitrates. This reaction to consume nitrogen oxide is critical important for ozone formation as it allows ozone to attain higher concentration levels than those that would occur in the photo-stationary state.

From reactions (R1),(R2) and (R3), and assuming oxygen atoms are in steady-state in reactions (R1) and (R2) with the same rate of formation and loss, the rate of concentration change for ozone is $d[\text{O}_3]/dt = k_1[\text{NO}_2] - k_3[\text{O}_3][\text{NO}]$

where k1 and k3 are the rate constant of the reaction

From reactions (R1),(R3) and (R4), the rate of concentration change for nitrogen oxide is

$$d[\text{NO}]/dt = k_1[\text{NO}_2] - k_3[\text{O}_3][\text{NO}] - k_4[\text{RP}][\text{NO}]$$

Therefore from equation (1), the rate of smog production is

$$d[\text{SP}]/dt = d[\text{O}_3]/dt - d[\text{NO}]/dt = k_4[\text{RP}][\text{NO}]$$

This shows a linear relationship between smog produced and the peroxy radical concentrations. As the rate of peroxy radical formation is proportional to the sunlight intensity, it explains that the relationship between smog produced (SP) and cumulative sunlight is approximately linear as obtained by Johnson [1984].

For the NO_x-limited regime, where there is no new smog production, the concentration of SP is at its maximum and is proportional to the NO_x previously emitted in the air

$$SP_{\text{max}}(t) = \beta [\text{NO}_x]_0^t \quad (2)$$

$\beta=4.1$ from the smog chamber studies.

The IER model provides an alternative concept of smog description by treating smog produced as a function of the cumulative exposure of the reactants to sunlight rather than a function of time.

For the light-limited regime the concentration of smog produced, SP, at a given time t, can be written as:

$$[\text{SP}]^t = \int_0^t R_{\text{smog}}^t J_{\text{NO}_2}^t F(T^t) dt \quad (3)$$

where R_{smog} is the photolytic rate coefficient for smog production and J_{NO₂} is the rate coefficient for photolysis of NO₂, a measure of sunlight intensity. F(T) is the temperature function:

$$F(T) = \exp\{-1000\gamma(1/T - 1/316)\} \quad (4)$$

where γ is a temperature coefficient determined from smog chamber studies and has the value 4.7; T is given in °K.

The current concentration of SP compared to the SP concentration that would be present if the NO_x-limited regime existed is indicative of how far toward attaining the NO_x-limited regime the photochemical reactions have progressed. The ratio of the current concentration of SP to the concentration that would be present if the NO_x-limited regime existed is defined as the parameter "Extent" of smog production (E) and is given by:

$$E^t = [\text{SP}]^t / [\text{SP}]_{\text{max}} \quad (5)$$

When E=1, smog production is in the NO_x-limited regime and the NO₂ concentration approaches zero. When E<1, smog production is in the light-limited regime.

In the NO_x-limited regime we can derive an expression for the ozone concentration as follows:

$$[\text{O}_3]^t = (\beta - F) [\text{NO}_x]_0^t \quad (6)$$

where the coefficient F is the proportion of NO_x emitted into the air in the form of NO; usually $F \cong 0.9$.

(b) Relationship of IER variables to ambient monitored measurements

For IER model to be useful the IER approach should allow SP and $[\text{NO}_x]_0^t$ to be determined from ambient measurements of ozone and nitrogen oxides. Johnson and Azzi [1992] derived these key IER variables in terms of these ambient measurements as follows.

Current ambient measurements of NO, “NO₂” and “NO_x” in the NO_x analyser use NO reaction with ozone and chemiluminescence detection to measure ambient NO concentration accurately and thermal decomposition of all oxidised nitrogen to NO to measure total “NO_x” using the same ozone reaction and chemiluminescence detection. Besides nitrogen dioxides (NO₂), oxidised nitrogen species also include nitric acid (HNO₃), peroxyacetyl nitrates (PAN), and organic nitrates. The total measured “NO_x” therefore overestimates the NO_x concentration (defined as sum of NO₂ and NO). The “NO₂” concentration derived from the total “NO_x” also overestimates NO₂ by the same amount.

This total “NO_x” is therefore better represents NO_y rather than NO_x. The total “NO_x” is denoted as NO_y by Johnson and Azzi [1992] in the derivation of key IER parameters with respect to ambient measurements of ozone and nitrogen oxides. Blanchard [2000] indicates that even this total “NO_x” may underestimate NO_y, defined as the sum of reactive oxidised nitrogen NO_y = NO + NO₂ + HONO + HNO₃ + NO₃ + N₂O₅ + PAN + organic nitrates + aerosol nitrates, as aerosol nitrate is often removed by a pre-filter and lost due to deposition on inlet and instrument lines.

For the light-limited regime, the smog production can be calculated as:

$$[SP]^t = ([O_3]^t + [NO_y]^t - [NO]^t - (1-F)[NO_y]^t) / (1-FP) \quad (7)$$

where [NO_y]^t is the concentration of oxidised nitrogen conventionally measured by nitrogen oxides analysers and P is a coefficient for the loss of NO_x into species and forms not detected as NO_y. For urban air an appropriate value of P is 0.122. This loss of NO_x due to reaction with free radical to produce stable non-gaseous nitrogen products (SNGN) in the light-limited regime is defined as a function of the rate of SP formation with proportional constant P.

$$[SNGN]^t = P[SP]^t \quad (8)$$

For the NO_x-limited regime :

$$[SP]^t = \beta [O_3]^t / (\beta - F) \quad (9)$$

The value of [NO_x]₀^t for ambient air can also be determined from monitoring data.

For the light-limited regime:

$$[NO_x]_0^t = \{ [NO_y]^t + P([O_3]^t - [NO]^t) \} / (1-FP) \quad (10)$$

and for the NO_x-limited regime:

$$[NO_x]_0^t = [O_3]^t / (\beta - F) \quad (11)$$

In addition to the nitrogen oxides and ozone concentration of the air it is also necessary to know the photolytic rate at which new smog will be produced (see equation 3). The key parameters, which determine this rate, are the sunlight intensity and the value of R_{smog}, a photolytic rate coefficient. The values of R_{smog} for ambient air are related to the emissions of ROC (or VOC) and R_{smog} values can be routinely measured with the Airtrak system, which was especially developed for this purpose (Johnson et al. [1990]).

The IER chemistry formulation shows that the chemical rate dependent processes are significant only to the light-limited regime and that during this regime the rate of SP production is independent of the NO_x concentration of the air. Thus, when the ambient air is in the light-limited regime, SP formation is unchanged by the presence of additional NO_x from any NO_x – producing sources. During the NO_x-limited regime, mixing of additional NO_x from the plume into the surrounding air can cause resumption of SP formation.

The application of the IER model for VOC/NO_x control to reduce peak ozone levels in a particular region therefore can be accessed based on the calculation of the extent variable. At locations where the extent is substantially less than one during periods of high ozone concentrations (light-limited or VOC-limited), then a reduction of VOC input can lower the peak ozone concentrations. When the extent is at or closer to one for a number of hours during the period of high or peak concentrations (NO_x -limited), then reducing NO_x input can lower the peak ozone concentration at those locations.

3. THE ENHANCED SMOG PRODUCTION (SP) ALGORITHM

The original IER model is simple and useful in describing the photochemical smog production in terms of key variables such as SP, extent, and initial NO_x values. There are two concerns about the IER model. First, the linear relationship in equation (2) is simplified and is not accurate for low NO_x concentration. Secondly, the deposition of ozone and nitrogen oxides is not parameterised in the model (Blanchard [2000]).

Field studies and chemical mechanism have indicated that the efficiency of ozone production, defined as the number of ozone molecules produced for each NO_x molecule consumed, increases as NO_x concentrations decrease. To take this into account, Blanchard modified the linear equation (2) as

$$SP_{\max}(t) = \beta \left\{ [NO_x]_0^t \right\}^\alpha \quad (12)$$

where $\alpha = 2/3$ and $\beta = 1.9$ (ppm unit) or $\beta = 19$ (ppb unit)

Taking into account the nonlinearity of ozone production efficiency and the deposition loss, the new equations for estimating extent based on NO_y measurements

$$E(t) = \frac{SP(t)}{SP_{\max}} = \frac{O_3(t) - DO_3(t) - O_3(0) + [NO]_0^t - NO(t)}{\beta [NO_x]_0^t} \quad (13)$$

where $O_3(0)$ is the background ozone level, $[NO_x]_0^t$ (initial NO_x) is estimated as the sum of $NO_y(t)$ and the concentration $DNO_y(t)$ corresponding to the cumulative mass of NO_y lost to deposition since time 0 (sunrise). $DO_3(t)$ is ozone concentration lost due to deposition. The deposition can be parameterised based on the product the product of hourly concentration with diurnal varying deposition velocity, summed over the hours.

It is important to note that the IER model or SP algorithm is used only as a qualitative tool to access efficiency of VOC/ NO_x control rather than an absolute quantitative mean for control requirements. As the ozone formation in the environment of the smog chamber is simple and different from that in the ambient environment where other physical processes such as meteorology can play important role. And, as Blanchard [2000] pointed out, bias and imprecision in instrumentation typically can result in uncertainties in the order of 0.1 in the extent calculation.

4. ANALYSIS OF EXTENT OF REACTION IN THE METROPOLITAN AREAS

The application of IER model allows one to use routine ambient measurements of pollutants, ozone and nitrogen oxides, to calculate the extent of the photochemical reaction. The extent is an indicator of the sensitivity of instantaneous ozone production to changes in VOC or NO_x concentration. Blanchard [2000] interprets the extent calculated from the IER or SP algorithm as follows

- extent less than about 0.6 : strongly indicative of the light-limited or VOC-limited regime
- extent between about 0.6 and 0.9 : transitional to NO_x -limited regime
- extent greater than about 0.9 : strongly indicative of NO_x -limited regime.

Previous application of IER model (Blanchard [2000], Blanchard, Fairley [2001]) indicates that in the core urban areas, the ozone process is in the light-limited regime while and stations further away or downwind, the ozone formation is in the NO_x -limited regime, especially during smog episodes.

(a) Extent map for ozone season in Sydney metropolitan areas

The MAPPER (Measurement-based Analysis of Preferences in Planned Emission Reductions) program, written by Blanchard and Roth [1995], is used to determine the frequency distribution of extent for a number of monitoring stations in the Sydney region. The 1998/1999-summer period of 1/12/1998 to 1/3/1999 is considered. Hourly values of ambient ozone, nitrogen oxides are used to compute the extent of photochemical reaction for each hour. The original Johnson's IER equations are used with background ozone assumed to be 0. The results of the extent analysis for all hours at each site are shown in Figure 1 below, as percentiles of the distribution of the extent of reaction.

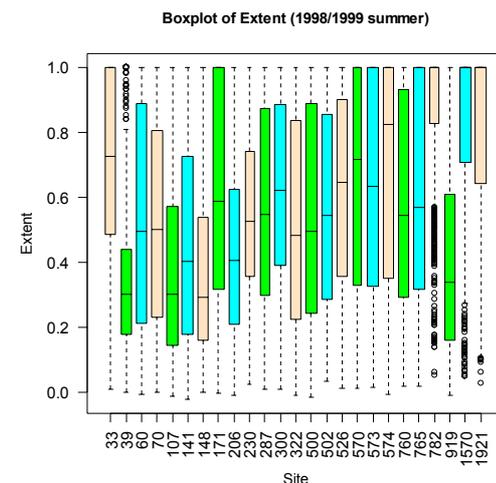


Figure 1 Percentiles distributions of extent of reaction for various sites.

From the table, in the Sydney basin, Rozelle, Earlwood and Woolooware is rarely in the NO_x -limited regime while Camden, Bargo, Oakdale and Wentworth Falls are in NO_x -limited regime most of the time. Sites that have higher frequency of high extent are Richmond, Vineyard, StMarys, Bringelly, Campbelltown and Randwick. In general, except Randwick, the more inland and further from the coast is the higher the extent and higher frequency of NO_x -limited regime occurs.

In the Hunter, Newcastle has less frequency of high extent and NO_x -limited occurrence than at Beresfield and Wallsend. In the Illawarra, Albion

Park is in NO_x-limited most of the time. Kembla Grange has higher frequency of high extent and NO_x-limited occurrences compared with Warrawong and Wollongong.

The result above is also similar to that obtained in Lake Michigan Ozone Study (Blanchard [2000]) and other urban studies in which the ozone formation is VOC or light-limited in the core urban areas and NO_x-limited at varying distances downwind. As extent indicates only if the present state of photochemical reaction is NO_x-limited or not. Extent alone is not sufficient to access the magnitude of photochemical smog process in high smog days or episodes.

(b) Classification of stations and regions

At low level of pollutant concentrations, near background levels, and little or no photochemical reaction, the extent can be equal to 1. For this reason, to better classify the degree of photochemical reaction, the ozone level or the SP (smog produced) concentration has to be taken into account (and possibly the length of time that the extent is high).

It is therefore more informative to categorise the smog potential using both the extent value and the ozone concentration such as

- category A : extent > 0.9 and ozone conc. > 8 pphm
- category B : 0.7 < extent < 0.9 and ozone conc. > 8 pphm
- category C : 0.6 < extent < 0.7 and 2 pphm < ozone conc. < 8 pphm
- category D : extent > 0.9 and ozone conc. < 2 pphm

Category A represents very high ozone episode, category B high ozone episode, category C medium smog potential and category D as background or no smog production.

For the 1998/1999-summer period of 1/12/1998 to 28/02/1999, the percentage of each category at each site is determined. This gives a profile of smog potential at each site, which is useful in assessing the likelihood of high smog episode. From the profiles at various sites, a classification to categorise sites, which are similar, into groups can be performed. Anh et al. [1996] has used this technique using cluster analysis to classify monitoring sites in Sydney based on the smog profiles for each hour of the day. Yu and Chang [2001] also used Ward's minimum variance clustering analysis of daily measured ozone and PM10 at monitoring sites to delineate and classify the air quality basins.

The classification based on the above smog profiles at each site, using hierarchical cluster analysis with average linkage agglomeration and squared Euclidean distance as a measure of similarity, is performed. In this clustering analysis using the profile of the percentage of four categories described above, the category D dominates the clustering result as percentage of background ozone is much higher than those of other categories. From the dendrogram, Bargo, Oakdale and Randwick are similar with respect to their background ozone distribution. Other sites are sub-grouped into 3 sub-groups with the first sub-group consists of Warrawong, Kembla Granges, Wollongong, Newcastle and Wentworth Falls.

It is more informative to remove category D of background ozone from our classification so that only very high, high and medium smog profiles are used in the cluster analysis. From the dendrogram, the sites which has high percentage of very high smog episode are grouped together (Oakdale, Bringelly, StMarys, Vineyard and Wentworth Falls). Next is the group with lesser percentage of very high smog but still have high percentage of high smog (Bargo, Richmond, Blacktown, Liverpool, Westmead, Lidcombe and Beresfield). Finally group 3, with no or very low frequency of high smog, consists of Randwick, Rozelle, Lindfield, Earlwood, Woolooware, Newcastle, Wallsend, Wollongong, Warrawong, Kembla Grange and Albion Park.

Three clusters of stations

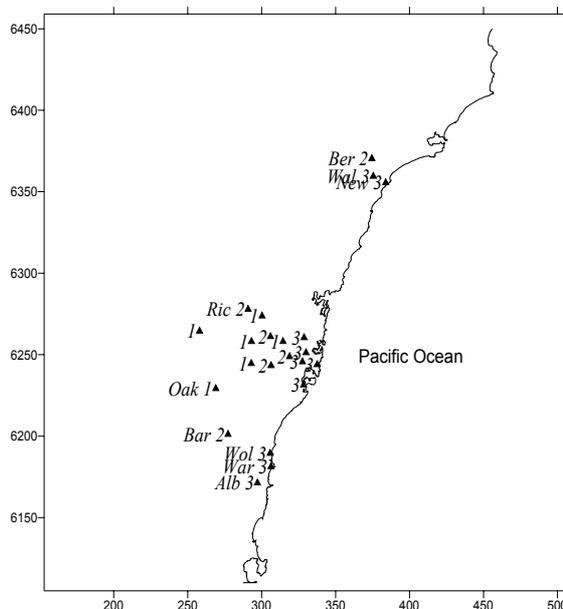


Figure 2 Three clustered groups of sites

For the above hierarchical clustering methods, the number of clusters can be determined using the cubic clustering criterion (CCC) or other

criteria such as the pseudo F statistic or the pseudo t^2 statistic. Both the CCC and the pseudo t^2 statistic indicate the optimum number of clusters is 3 corresponding to the above three branches (groups) of sites described above.

(c) Region determination

Using similar techniques as those of Yu and Chang [2001], the principal component analysis (PCA) on the ozone data (via correlation matrix) can be used to delineate the regions in the Sydney area. The correlation matrix is obtained using hourly observations at monitoring sites with missing values are handled by casewise deletion.

The results show that there are 4 principal components explaining most of the variances. The eigenvalues of the correlation matrix and the corresponding principal component scores for each site are obtained. The contour plot of component scores for each component is used to delineate the regions.

The principal component 1 corresponds to sites in the Eastern Sydney and the Lower Hunter (Randwick, Rozelle, Lindfield, Lidcombe, Earlwood, Woollooware, Westmead, Newcastle, Wallsend and Beresfield). Principal component 2 corresponds to sites in western Sydney (Campbelltown, Liverpool, Blacktown, Bringelly, Camden, Richmond, Bargo, StMarys and Vineyard). Principal component 3 corresponds to sites in the Illawarra (Wollongong, Warrawong, Kembla Grange and Albion Park). The last principal component corresponds to just one site, Wentworth Falls.

Note that the 3 regions, as delineated using the principal component analysis of ozone correlation between sites, may or may not correspond to the site classification using the previous analysis of smog extent.

5. DISCUSSION AND CONCLUSION

Statistical analyses of the extent of photochemical reaction as determined by the IER model for the 1998/1999 3-months summer period have been used to understand the ozone formation process in different regions of the Sydney metropolitan areas. It has been shown that the coastal sites from the Hunter in the north (Beresfield, Wallsend, Newcastle) to the Sydney basin (Randwick, Woollooware, Rozelle, Earlwood, Lindfield) and the Illawarra in the south (Wollongong, Warrawong, Albion Park) have low occurrences of high ozone and are mostly in the light-limited (or VOC-limited) photochemical regime. Sites in the Sydney basin, which are

further inland from the coast, have higher frequencies of high ozone and are mostly in the NO_x -limited regime.

This result is consistent with other urban studies in which the ozone formation is VOC or light-limited in the core urban areas and NO_x -limited at varying distances downwind.

6. REFERENCES

- Anh, V., M. Azzi, H. Duc and G. Johnson, Classification of air quality monitoring stations in the Sydney basin, Proceedings of the Asia-Pacific Conference on Sustainable Energy and Environmental Technology, Singapore, 1996, pp. 266-271, 1996.
- Blanchard, C.L., Roth, P.M., User's Guide: Ozone MAPPER, Measurement-based Analysis of Preferences in Planned Emission Reductions, version 1.1, 1995.
- Blanchard, C.L., Lurmann, F.W., Roth, P.M., Jeffries, H.E., Korc, M., The use of ambient data to corroborate analyses of ozone control strategies, Atmospheric Environment, 33, pp. 369-281, 1999.
- Blanchard, C.L., Ozone process insights from field experiments – Part III: extent of reaction and ozone formation, Atmospheric Environment, 34, pp. 2035-2043, 2000.
- Blanchard, C.L., Stoeckenius, T., Ozone response to precursor controls: comparison of data analysis methods with the predictions of photochemical air quality simulation models, Atmospheric Environment, 35, pp. 1203-1215, 2001.
- Blanchard, C.L., Fairley, D., Spatial mapping of VOC and NO_x -limitation of ozone formation in central California, Atmospheric Environment, 35, pp. 3861-3873, 2001.
- Johnson, G.M., A simple model for predicting the ozone concentration of ambient air, Proceedings of the Eight International Clean Air Conference, Melbourne 1984, Australia, pp. 715-731, 1984.
- Johnson, G.M., Quigley, S.M., Smith, J.G. Management of photochemical smog using the AIRTRAK approach, 10th International Conference of the Clean Air Society of Australia and New Zealand 1990, Auckland, New Zealand, pp. 209-214, 1990.
- Johnson, G.M., Azzi, M., Notes on the derivation: the Integrated Empirical Rate Model (V2.2). North Ryde, NSW, Australia: CSIRO Division of Coal and Energy Technology, 1992.
- Yu, T., Chang, L., Delineation of air-quality basins utilizing multivariate statistical methods in Taiwan, Atmospheric Environment, 35, pp. 3155-3166, 2001.