Assessment of Urban Air Quality Using the Integrated Empirical Rate (IER) Model and the Airtrak System

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Abstract Novel modelling procedures for the management of photochemical smog formation by the use of air monitoring data are described. The technique is based on the evaluation of parameters invoked by the Integrated Empirical Rate (IER) model namely: "smog produced" (SP), extent of smog formation (E) and the photolytic rate coefficient for smog production in the air (R_{smog}). These properties of the air are measured by the Airtrak system. The IER model describes smog produced as a linear function of precursor emissions and sunlight exposure, enabling the age of precursor emissions to be determined and facilitating clear appraisal of the effectiveness of emissions control strategies.

Detailed evaluations using the IER model performed for three successive days of urban air monitoring data are presented in this paper. The variation of SP and extent parameters are also investigated and the method of representing the data for estimating the age of precursor emissions is elaborated. The role of the SP profile of the background air in determining the origin of a sampled air mass is examined.

1. INTRODUCTION

From time-to-time in summer episodes of photochemical smog with ozone concentrations that exceed the air quality guideline of 0.12 ppm are experienced in both urban and rural areas in the greater Sydney region (population 3.4 million). The Metropolitan Air Quality Study (MAQS) was undertaken by the NSW Environmental Protection Authority (EPA) to assess the airshed and to develop, implement, and evaluate a combined emission, meteorological, and photochemical modelling system that can be used to understand the reasons for high ozone concentrations and to assist in developing an effective emissions control plan for the Sydney airshed. During the summer of 1993/94 extensive ambient air quality monitoring was conducted by the EPA to provide a data base for model development and evaluation. The air quality monitoring network consisted of an extensive array of air quality monitoring stations plus Airtrak monitoring systems located at suitable locations. The Airtrak* system,(Johnson and Quigley [1989]), is an instrument which measures the photolytic rate coefficient (R_{smog}) for smog production of the air (due to the presence of reactive organic compounds) together with the O_3, and NO_x concentrations. In this paper Airtrak measurements provide the input data for assessment of photochemical smog formation. The IER model (Johnson [1983], Johnson et al [1990]) employs ambient monitoring data to photochemically characterise a given air parcel. The use of the IER approach avoids complexities inherent in the use of grid-based photochemical models and enables evaluations to be made without the need of an emissions inventory. The approach has the advantage that it can be readily applied to evaluate photochemical smog episodes case-by-case as they occur.

As an example of the Airtrak-IER approach we present a brief analysis and interpretation of data for three successive days monitored by an Airtrak system installed at Liverpool, in the south-west area of the Sydney airshed. In addition a brief outline is given of the Airtrak system and the IER model.

2. AIRTRAK MONITORING SYSTEM OVERVIEW

The Airtrak system samples continuously the air to determine the concentrations of nitric oxide (NO), total nitrogen oxides (NO_y), ozone (O_3), "Smog" and the photolytic rate coefficient for smog production (R_{smog}). The total nitrogen oxides (NO_y) concentration is measured by a conventional NO_x analyser and can include contributions from several species including NO, NO_2 , HNO_3 , PAN, and organic nitrates. SMOG concentration is defined as :

$$[SMOG]=[O_3]+[NO_y]-[NO] \qquad (1)$$

*The Airtrak system is manufactured and marketed by Mineral Control Instrumentation Ltd, P.O. Box 64, Unley, SA, 5061, Australia

and is measured directly by Airtrak via gas-phase titration technique. The R_{smog} parameter is measured continuously by measurement of the rate of consumption of nitric oxide by the sample when exposed to light in a special photolytic reactor. The R_{smog} value can be related to the concentration of reactive organic compounds in the sample by the relationship

$$ROC = \frac{R_{smog}}{a_{roc}} \qquad (2)$$

where a_{roc} is an activity coefficient for the ROC. Typical values of a_{roc} have been empirically determined but are not required for application of the IER technique.

3. IER MODEL OVERVIEW

The Integrated Empirical Rate (IER) photochemical model consists of functional relationships which were derived from the chemical interpretation of an extensive set of outdoor smog chamber data. A first description of the IER approach was published by Johnson [1983] and this has since been extensively elaborated.

Briefly the IER model requires ambient air monitoring data to photochemically characterise the air. To apply the model there is no need for information on precursor emissions fluxes or plume transport calculations. A feature unique to the IER model is that it provides information on whether the concentration of photochemical smog oxidants at locations under consideration are controlled by the emissions of nitrogen oxides or reactive organic compounds.

The model defines the formation of photochemical oxidants in terms of "Smog Produced" (SP), where SP represents the quantity of NO consumed by photochemical processes plus the quantity of O_3 produced.

According to the IER model SP increases approximately linearly with respect to cumulative sunlight exposure (the light-limited regime) until the available nitrogen oxides are consumed by reaction when the NO_x-limited regime occurs and SP production ceases.

During the light-limited regime the rate of SP increase is proportional to the photolytic rate coefficient R_{smog}, which is measured directly by the Airtrak system. SP is calculated by

$$[SP]^t = R^t_{smog} \int J_{NO_2} f(T^t) dt \qquad (3)$$

where J_{NO_2} is the rate coefficient for NO_2 photolysis (a measure of sunlight intensity), f(T) is a temperature function given as equation (4)

$$f(T) = \exp\{-1000\gamma(\frac{1}{T} - \frac{1}{316})\} \qquad (4)$$

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

In the light-limited regime the rate of smog formation is not significantly dependent on the concentration of nitrogen oxides. 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 into the air

$$[SP]^t_{max} = \beta[NO_x]^t_0 \qquad (5)$$

where $[NO_x]^t_0$ denotes the NO_x concentration that would exist at time t in the absence of atmospheric chemical reaction and where, from smog chamber data, the β coefficient can be assigned the value of 4.1.

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 towards attaining the NO_x-limited regime the photochemical reactions have progressed. This ratio is defined by the IER model as the parameter "Extent of smog produced" (E) and is given by equation (6):

$$E^t = \frac{[SP]^t}{[SP]^t_{max}} \qquad (6)$$

When $E^t = 1$, smog formation is in the NO_x-limited regime and the NO and NO_2 concentrations approach zero; when $E^t < 1$, smog production is in the light-limited regime .

From air quality monitoring data we can determine the regime of smog production by calculating the parameter G^t given by equation (7):

$$G^t = \frac{(1-PF)[O_3]^t}{(\beta - F)([NO_y]^t + P([O_3]^t - [NO]^t))} \qquad (7)$$

where F is the proportion of NO_x emitted into the air in the form of NO and P is a coefficient for loss of gas phase oxidised nitrogen into species and forms not detected as NO_y.

When $G^t < 1$ smog production is in the light-limited regime and, when $G^t \geq 1$, then the NO_x-limited regime exists.

For the light-limited regime we can calculate the following parameters:

$$[NO_x]^t_0 = \frac{[NO_y]^t + P([O_3]^t - [NO]^t)}{1 - FP} \qquad (8)$$

and

$$[SP]^t = \frac{[O_3]^t + F[NO_y]^t - [NO]^t}{1 - FP} \qquad (9)$$

In the NO_x-limited regime, where there is no new smog production, the concentration of NO_x expected in the absence of atmospheric chemical reactions is given by

$$[NO_x]_0^t = \frac{[O_3]^t}{\beta - F} \qquad (10)$$

The data provided by Airtrak can be interpreted via IER method to indicate the history and prospects for photochemical smog production for the air from which the sample was taken and to evaluate the effectiveness of various emissions control strategies.

4. EXAMPLE AIRTRAK DATA ANALYSIS

This section reports Airtrak monitoring data collected during the summer days of 10, 11, and 12 of February 1994 at Liverpool air quality monitoring in the south-west area of the Sydney airshed. These successive days cover three different categories of high, medium and low photochemically reactive air respectively. Six minute averages of Airtrak data recorded during these three days are presented in Figure 1. On the 10th of February, between 8:30 am and 9:40 am data is not available.

On the 10th of February between around 09:40 am and noon the ozone concentration was greater than 0.08 ppm. For the other time periods O_3 concentration was less then 0.06 ppm. On the 10th around 06 am and on the 11th around 06am and 06:00 pm, Figure 1A shows that plumes containing substantial NO_y and reactive organic compounds were detected. On the 11th at midday a plume with high R_{smog} (ie contains ROC) but no increase in nitrogen oxides was observed. On the 12th these plumes were not clearly pronounced.

The concentrations of NO, NO_y, O_3, and R_{smog} determined by Airtrak were used to calculate the various IER parameters. The modelling results are given in Figure 1C where the variation of smog produced and extent are plotted (on separate scales) against time. In addition Figure 1D shows the (R_{smog}/NOxo) ratio plotted against time demonstrating the presence of plumes enriched with emissions of ROC (ie high Rsmog/NO_x ratios). The IER modelling results show that the light-limited photochemistry persisted over the full three day period with the extent parameter values always less then 1 (Fig. 1C). On the 10th polluted air parcels were detected between 09:30 am and noon, and on the 11th other polluted air parcels were detected between 11:00 am and 3:00 pm. These parcels were characterised with a smog produced concentration greater then 0.08 ppm. In the morning before sunrise and after around 8:00 pm the air sampled by Airtrak during the 10th and 11th of February had the characteristics of background air where SP and extent values were less then 0.02 ppm and 0.2 respectively. On the 12th the concentration of smog produced was less then 0.03 ppm over the 24 hour period indicating that there was no pollution episodes detected on this day.

The analysis of the Airtrak data using the IER algorithm shows that the IER model provides a quick and robust way, expressed in terms of R_{smog}, , SP and extent, to assess and follow in real time the development of photochemical smog.

5. AGE OF PRECURSOR EMISSIONS

The IER parameters which describe the photochemical characteristic of an air parcel can also be used in several other ways. Here we demonstrate their use to evaluate the age of polluted air. The difference between the cumulative sunlight at the moment of sampling and the corresponding SP/R_{smog} ratio, gives insight on how much the air parcel has been exposed to sunlight and can allow the determination of the approximate time of precursor emissions to be determined. In addition, if a wind back trajectory is available for the given day, then an estimation of emissions location can be determined. An improved estimation of the age of precursor emissions would be made by firstly subtracting the background SP concentration allowing the anthropogenic emissions to be differentiated. This can be done by using $(SP-SP_{back})/R_{smog}$ where SP_{back} is the time series of smog produced for background air.

In the absence of any knowledge about the SP_{back} profile for the Sydney airshed and with the aim to further proceed in the selected Airtrak data analysis, we have adopted the following methodology: Two values of SP_{back} 0.015 ppm and 0.030 ppm were used in this study. The choice of these values were based on several Airtrak and conventional monitoring data collected during previous studies Johnson [1992]. The modelling results which are given in Figure 2 give for every selected day, four different plots designated by A, B, C, and D. The first, the second and the third were obtained by using SP/R_{smog} ,$(SP-0.015)/R_{smog}$, and $(SP-0.03)/R_{smog}$ respectively and the fourth plot represents the cumulative sunlight profile for the selected day and the previous day. The ordinate provides a scale for the cumulative sunlight exposure. The time increments are quantified on the abscissa which indicate how much time has elapsed before or after midnight of the selected day. The age of the emissions is evaluated for a given SP/R_{smog} value by reading the time corresponding to the same value on curve D. The negative values indicate that the air parcel has been carried over from the previous day. For example, let us consider the plot A at 11am on the 10th, (SP/R_{smog} was around -30 units), the calculations indicate that the average time of precursor emissions was some 11 hours before midnight eg. around 1:00 pm the previous day. The plots A, B, and C indicate the sensitivity of the method to the accuracy of the estimated SP_{back} concentration. Since the plot A does not have any SP_{back} correction, predictions of the age of the selected air parcels will be overestimated. For a given SP_{back} , if the calculated value at a given time is higher then the corresponding cumulative sunlight value, then the selected SP_{back} is not appropriate for that time. This can be seen on the following cases: on the 10th and 12th , between midnight and around 7:30 am and between around 6 pm hr and midnight the use of plot C was not appropriate. On the 11th the plot C was not appropriate between midnight and around 800 hr.

The relationships represented in Figure 2 show that what ever the value used for SP_{back} , on the 10^{th} , the air parcels sampled between around 9:30 am and noon would be emitted in the afternoon of the previous day. On the 11^{th} and for the range of the variability of the selected SP_{back} the three plots show that the pollution episodes experienced between 10:00 am and noon, originated from the previous day. On the 12^{th} and with the accepted SP_{back} range of confidence, all plots can be fitted to have the shape of the corresponding cumulative sunlight profile without showing any delay with the time. This finding allow us to say that on the 12^{th} the low levels of pollution were all from local sources of emission.

6. CONCLUSION

Three selected days of Airtrak data from the Liverpool area were implemented in the IER model to evaluate the air quality dynamics. These data show typical urban values for NO, NO_y, NO_2 , O_3, and R_{smog} . Airtrak measurements were in general agreement with measurements taken with conventional instruments. The IER parameters have produced information about ambient air quality including the age of the photochemical precursor emissions. This approach provides valuable and effective tool for assessing ozone precursor control strategies. In addition, the data analysis shows that it is important to characterise the properties of the background (clean) air.

7. REFERENCES

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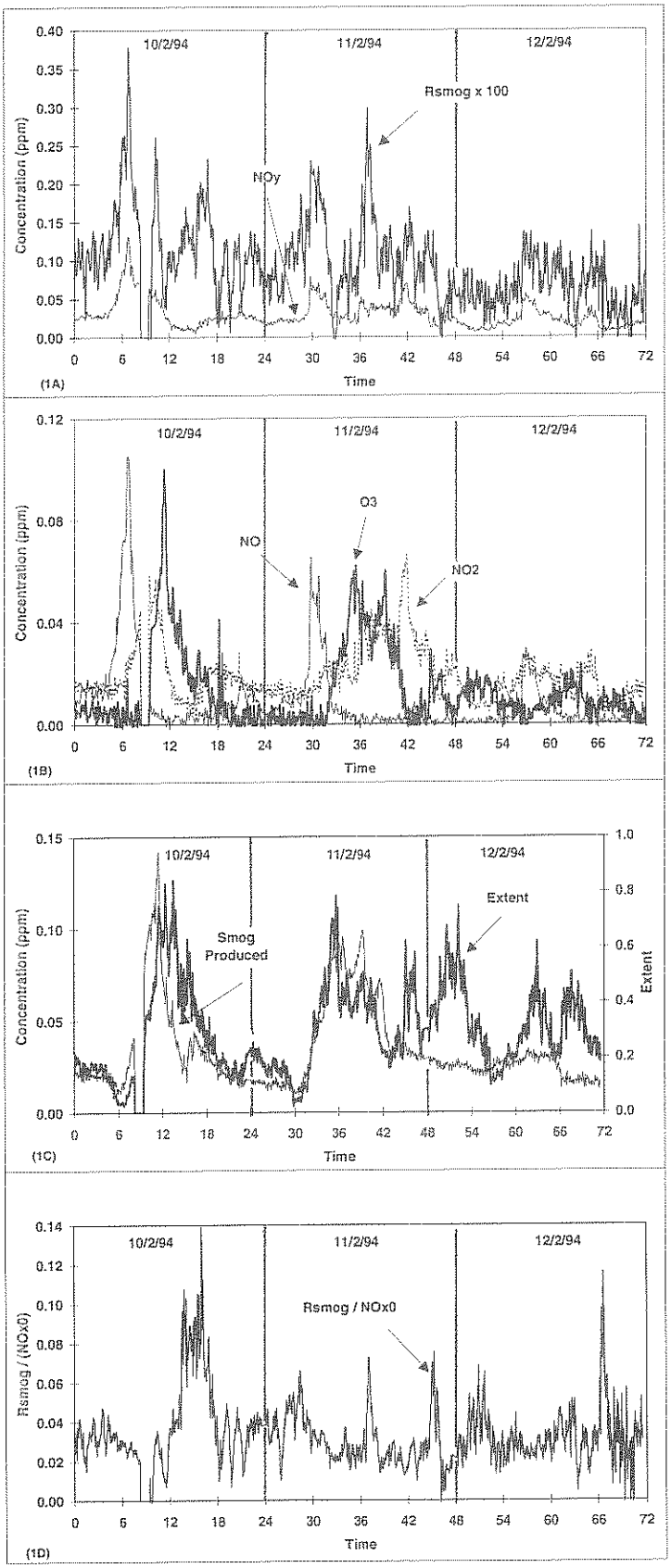

Figure 1: Air quality measured by Airtrak at Liverpool

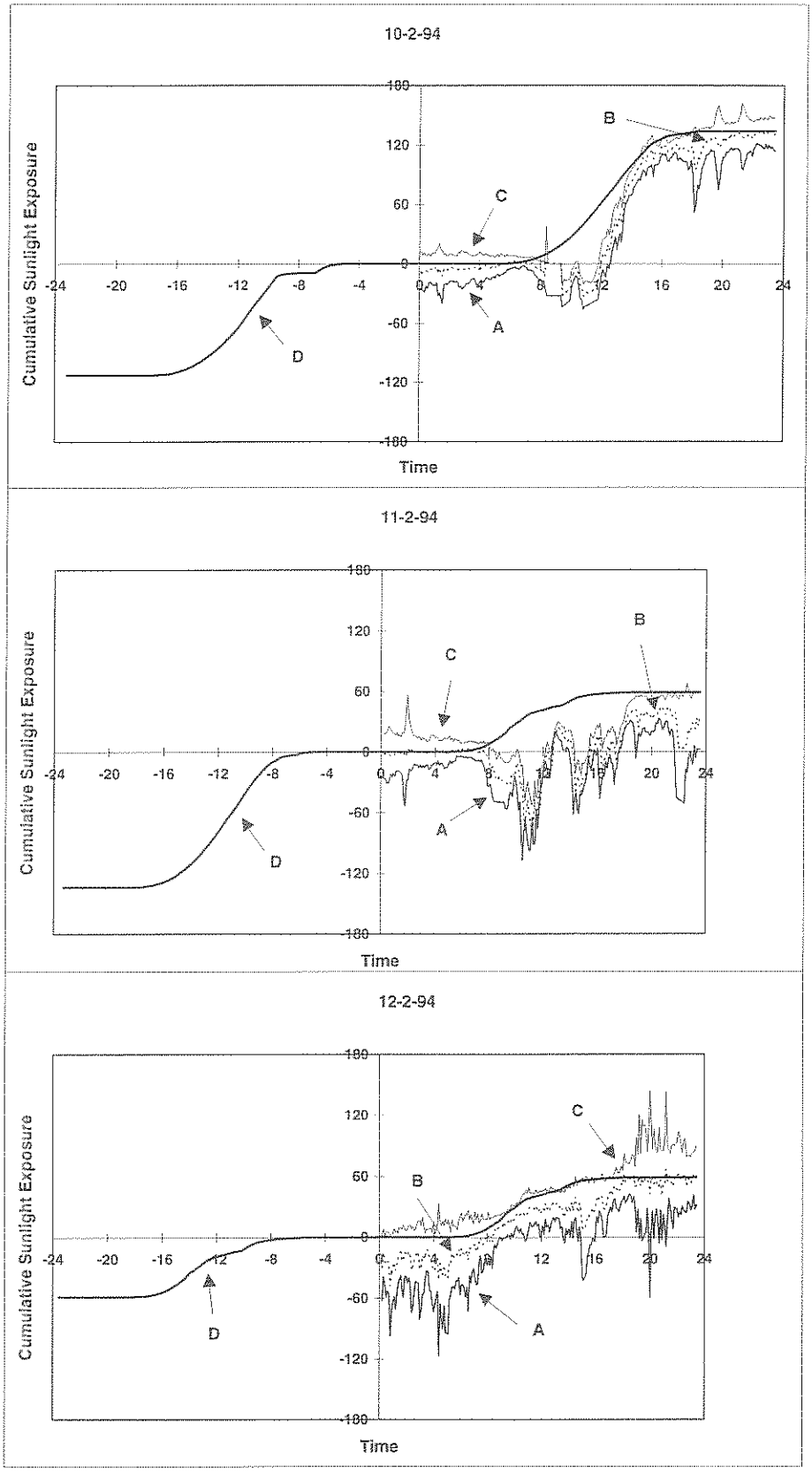

Figure 2: Age Evaluations for Precursor Emissions 10, 11 and 12 Feb 1994