A case study of photochemical pollution in a sub-tropical city

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INTRODUCTION AND METHODOLOGY

A multi-level approach has been adopted to assess the air-shed carrying capacity of Brisbane, a medium size sub-tropical city in north-eastern Australia. A balance of deterministic and stochastic approaches is required to achieve an adequate description of system characteristics and predictability over a range of time and length scales. Our goal is a coherent set of methodologies for determining long-term trends in a system of evolving spatial complexity and providing useful short-term forecasts of maximum regional ozone concentrations.

The Brisbane conurbation is based on a central core population of 1.3 million that is likely to grow considerably (5% per annum) over the next twenty years, mainly by an expansion of the outlying suburbs. It has a small industrial base but a very extended residential structure, with a coastal strip of some 80 km extending from the Sunshine Coast in the north to the Gold Coast in the south. In the past 16 years the traffic volume in the region has doubled and the population increased by 40%. The topographical setting is complex with several local ranges of hills of elevation to 730 m and a set of more extended ranges to the south and west.

With most population within 30 km of the coast and the prevalence of meso-scale circulations in a sub-tropical climate, Brisbane has been attributed the highest photo-chemical pollution potential of any of the major Australian cities. The high temperatures experienced from early spring to late autumn and the considerable degree of vegetation cover in the region may increase biogenic emissions of reactive organic compounds (ROC's) and hence accelerate the rate of formation of photochemical smog. Bushfires often occur in spring and early summer both within the air-shed and in neighbouring agricultural regions, producing a considerable influx of particulates and hydrocarbons.
As part of an assessment of sustainable development of the south-east Queensland region, the Brisbane City Council and Queensland Department of Environment and Heritage have commissioned a series of investigations of the Brisbane air-shed. The study has targeted the following objectives:

(a) Identify the major photochemical and meteorological characteristics of high ozone days to facilitate the choice of days for detailed analysis.
(b) Determine the spatial extent of the air-shed to rationalise the existing and future expanded monitoring.
(c) Quantify the statistical characteristics of the historical air quality database for use in various prediction tasks.
(d) Utilise a semi-empirical photo-chemical methodology to estimate highest ozone levels in areas distant from the existing monitoring stations.
(e) Construct a full emissions inventory for use in detailed air-shed modelling of future development scenarios.

This progress report concentrates upon the items (a)-(d); item (e) will be completed by 1996. Both historical and episodic analyses have utilised the Integrated Empirical Rate (IER) description of photochemical formation (Johnson et al [1]). Based on an extensive set of smog chamber studies in similar conditions in Sydney, this recognises two essential stages. At first the photochemical activity is governed by the cumulative photolytic exposure and the concentrations and reactivity of background ROC distributions. Ozone production may then be limited by the availability of nitrogen oxides (NO\textsubscript{X}).

Three variables characterise an air parcel. The smog produced (SP) corrects the photochemical concentrations to account for the reactions that have occurred previously (e.g. the scavenging of ozone by local traffic sources). The extent of reaction (E) describes how far the reactions have proceeded to the second, NO\textsubscript{X}-limited stage. The amount of nitrogen oxides emitted into the air parcel can also be estimated (NO\textsubscript{X}-emit). The IER methodology can predict the photochemical age of an air parcel if the ROC/NO\textsubscript{X} ratio is estimated from suitable (Airtrak) monitoring or the emissions inventory. If wind-fields are sufficiently accurate, the source of any significant concentrations can be identified.

ANALYSIS OF HISTORICAL INFORMATION

There is a 16-year database of half-hourly measurements of ozone, nitrogen dioxides, scattering coefficient and meteorological parameters at three sites in the Brisbane river valley, with more limited measurements in outlying suburbs. Surface wind measurements are now sufficiently extensive to forecast plume trajectories, although upper-level measurements rely upon six-hourly pilot balloons and a morning radiosonde flight at the river-mouth airport. Daily spectrophotometer measurements of ozone burden are also recorded there.
High photochemical activity has been characterised by hourly ozone levels over 60 ppb, SP levels over 100 ppb or the extent parameter higher than 50%. Significant events usually occur in clusters of 2-5 days, during quasi-stationary synoptic conditions. These form a small subset of the 67 different types of synoptic states recognised from a principal component analysis of surface and upper-level meteorological parameters. The subset is characterised by light synoptic winds with an off-shore component, moderate to high temperatures and a seabreeze. The frequency of occurrence of significant events varies considerably from year-to-year and between sites. The limited information from outer suburbs has higher extent levels, as expected, but includes several morning episodes that indicate recirculation of the previous day's emissions. Highest hourly levels of ozone at the three river-valley sites usually coincide with the passage of the seabreeze front. Interpolated surface wind-fields give rise to closed or spiral particle trajectories on high event days. This is especially apparent in late winter and early spring.

NUMERICAL MODELLING OF WINDFIELDS AND OZONE FORMATION

Three representative days have been chosen from ozone clusters in late winter, spring and mid-summer for detailed windfield analysis using the Lagrangian Atmospheric Dispersion Model (LADM) of CSIRO (Physick [2]). This nested scheme considers topographic influences for scales of 10, 5, 2.5 and 1 km, with temperature and wind profiles set by the morning radiosonde measurements at the river-mouth. Forward and backward trajectories for surface pollutants emitted at the points of highest traffic density show a very high degree of recirculation, caused by the regular succession of drainage flows and seabreezes. The insert of Figure 1 shows that the much of the surface pollutants that gave rise to the highest hourly event on the winter ozone day resided overnight west of Ipswich; the residence time within the Brisbane air-shed is 40 hours.

The retention of urban emissions in the local air-shed appears very sensitive to synoptic conditions. The synoptic wind must act to delay the onset of the seabreeze until early afternoon, allowing temperatures in the inland basin to rise well over 30°C in the mid-afternoon. A narrow window of west to north-west synoptic winds encourages significant recirculation. LADM was also used in simulations of pollutant flow, using the IER approach to investigate the interaction and development of the emissions from urban sources and major industries in the region. Maximum levels of SP and ozone occur during the late afternoon in the outer suburbs, with values up to 50% higher than in the inner city.

PHOTOCHEMICAL ANALYSIS FOR HIGH OZONE DAYS

Four types of days were discriminated by detailed IER analysis of 30
significant events. The most common and least severe is that associated with a seabeach front, characterised by moderate values of E. The second type occurs mainly at the more inland sites in the mid-morning, with E ≈ 1 (presumably recirculated afternoon emissions). For the rarer third type, the SP and E parameters are high at each site, suggesting a stagnation of the overall air mass. The final type of day requires substantial enhancements of background ROC concentrations to explain the rapid formation of ozone on late winter days.

Recirculation of surface pollutants as a cause of high ozone concentrations has been substantiated on several occasions by the close agreement of the chemical age of air with the transit times predicted by LADM for peak afternoon emissions to reach the monitoring location next day.

LONG-MEMORY MODELS OF OZONE FORMATION

This section outlines how long memory modelling might be used to describe the underlying dynamics of the complex ozone formation process, to identify important scales and scaling behaviour and to indicate how this information could form the basis of a multi-level real time multivariate forecasting procedure. Work is still in the preliminary stages but the findings appear very encouraging.

A number of time series for the sixteen year period have been analysed. In particular the series for maximum daily ozone, hourly wind speed and maximum of the IER parameters have auto-correlation functions that converge to zero at an extremely slow rate; their power spectra contain an integrable pole at the origin, and the dimensions of the records are higher than the topological dimension. This behaviour indicates convincingly that each data record is an observed sample of a long-range dependent process. The value of the fractional power indicates the appropriate degree of differencing to transform a time-series into a stationary one for further modelling of its short-term behaviour. The short-term fluctuations of the time-series of length T, can be modelled conveniently by an AR model, yielding a combined spectral density of the form:-

\[
f(\omega) = \frac{\sigma^2}{2\pi} \frac{1}{|P(e^{i\omega})|^2} \frac{1}{|1-e^{i\omega}|^{2d}}, \quad \omega \in [0,2\pi)
\]

where \(\sigma^2\) is the variance of the innovations, \(P(e^{i\omega})\) is a polynomial of low degree and \(0 < d < 0.5\). In this range the value of \(d\) is equal to the Hurst exponent \(H\). A basic parameter of fractal processes, the value of \(H = \frac{1}{2}\) corresponds to Brownian motion; \(H < \frac{1}{2}\) as 'persistence' and \(H > \frac{1}{2}\) as 'persistence' reversal. We now outline a method to estimate all parameters of Equation (1) simultaneously and a method to examine the multifractal nature of a time series. Following Anh and Lunney [3], the time series \(X(t)\) can be
tapered as
\[ X_{\varepsilon,\alpha}(t) = X(t) \frac{\sin \varepsilon^{1+\alpha} t}{\varepsilon^{1+\alpha} t}, \quad 0 < \varepsilon < \frac{1}{2}. \]
The time series \( X(t) \) with \( f(\omega) \) as in Equation (1) has the spectral representation
\[ X(t) = \lim_{\varepsilon \to 0} \int_{-\pi}^{\pi} e^{i\omega t} \frac{Z_{\varepsilon,\alpha}(\omega)}{2 \varepsilon^{1+\alpha}} \, d\omega, \]
and the covariance representation
\[ R(k) = \lim_{\varepsilon \to 0} \int_{-\pi}^{\pi} e^{i\omega k} \frac{|Z_{\varepsilon,\alpha}(\omega)|^2}{2 \varepsilon^{1+\alpha}} \, d\omega, \]
where \( Z_{\varepsilon,\alpha}(\omega) \) is the Fourier transform of \( X_{\varepsilon,\alpha}(t) \) and is characterised by
\[ \supremum_{0 < \varepsilon < \frac{1}{2}} \int_{-\pi}^{\pi} \frac{|Z_{\varepsilon,\alpha}(\omega)|^2}{2 \varepsilon^{1+\alpha}} \, d\omega < \infty. \]
The periodogram can then be written as
\[ I_{\varepsilon,\alpha}(\omega) = \frac{|Z_{\varepsilon,\alpha}(\omega)|^2}{2 \varepsilon^{1+\alpha}}. \]
The asymptotic maximum likelihood estimator of the parameters of \( f(\omega) \) can now be obtained by solving
\[ \min_{-\pi}^{\pi} \left[ \log f(\omega) + \frac{I_{\varepsilon,\alpha}(\omega)}{f(\omega)} \right] \, d\omega. \]
The following estimation procedure provides a computationally efficient method to calculate all parameters in Equation (1).
1. After correcting for the mean obtain the sequence
\[ X_{\varepsilon,\alpha}^1(t) = \begin{cases} X_{\varepsilon,\alpha}(t), & t = 1, \ldots, T \\ 0, & t = T+1, \ldots, T^1 \end{cases} \]
and then compute the periodogram
\[ I_{\varepsilon,\alpha}(\omega_j) = \frac{\varepsilon^{\alpha}}{\pi T} \left| \sum_{t=1}^{T} X_{\varepsilon,\alpha}^1(t) e^{i\omega_j t} \right|^2, \quad \omega_j = \frac{2\pi j}{T^1}, \]
where $T^1$ should be a power of 2 for the efficient use of the fast Fourier transform.

2. To obtain an initial value of $d$, regress

$$\log I_{\varepsilon,\alpha}(\omega_j) \text{ on } \log \left[ 4 \sin^2 \left( \frac{\omega_j}{2} \right) \right] \text{ for } j = 2, \ldots, (T^1)^{\frac{1}{2}}$$

3. Using the fast Fourier transform the covariance function for any $d$ can be computed.

$$\gamma_d(k) = \frac{1}{T^1} \sum_j I_{\varepsilon,\alpha}(\omega_j) \left| 1 - e^{i\omega_j} \right|^{2d} e^{ik\omega_j}$$

4. Use the Durbin - Levinson recursion to estimate the AR(h) parameters and prediction variance. The optimal order, $h$, can be calculated using the concept of minimum description length (Anh & Kavalieris,[4]).

5. Using a downhill simplex minimisation algorithm, for a series of values $d$, minimise $T \log \sigma^2_d + (h+1) \log T$.

6. These steps (1) - (5) are then repeated for a set of values of $\alpha$ ranging from $0 < \alpha < 1$.

It is shown in Anh and Lunney [5] that the dimension of the process for each value of the scaling parameter $\alpha$ is $2 - d(\alpha)$ and there exists an $\alpha_0$ where the gradient of the curve $2 - d(\alpha)$ ceases to be zero or negative and becomes positive.

Figure 2 shows the periodograms of the maximum daily ozone series and the residuals after fitting the spectral density of Equation (1). Figure 3(a) shows the dimension for various values of $\alpha$ for this ozone data and clearly shows multifractal behaviour. The scaled dimension for the NO$_x$ series is shown in Figure 3(b) and indicates fractal behaviour with dimension 1.56. Further results of these analyses are shown in Table 1. The identification of statistical causal factors after pre-whitening of the data series using standard cross-spectral techniques will allow the design of a multivariate forecasting system that provides a day ahead ozone forecast as well as a measure of the predictability error for the given set of meteorological conditions. It is also hoped that the use of the IER variables that are more closely tied to the precursors of photochemical activity may increase the predictability horizon. The forward prediction of photochemical evolution within each air parcel that passes through each of the monitoring sites offers a new method of spatial extrapolation of site results and predictions to likely affected parts of the airshed. It is also anticipated that the long memory or fractal characteristics of a system could be used to test potential deterministic models.
Table 1: Characteristics of photo-chemical pollution in Brisbane.

<table>
<thead>
<tr>
<th>ISSUE</th>
<th>KNOWLEDGE PRE-STUDY</th>
<th>STUDY FINDINGS</th>
<th>COMMENTS</th>
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</thead>
<tbody>
<tr>
<td>Severity of problem.</td>
<td>Few hours per year of concern.</td>
<td>Existing monitoring may underestimate the frequency and spatial extent, especially in developing outer suburbs.</td>
<td>Changing emission patterns, emission controls and expanding residential areas complicate assessment.</td>
</tr>
<tr>
<td>Photochemical potential of region.</td>
<td>Considered high due to the land/seabreeze circulations.</td>
<td>Recirculation on event days much more important and wide-scale than anticipated.</td>
<td>Expanded conventional monitoring network and two photochemical sites implemented.</td>
</tr>
<tr>
<td>Photochemical activity-trends</td>
<td>Few apparent trends</td>
<td>Trends likely to be obscured by inter-annual variability of required synoptic conditions, and long-term memory.</td>
<td>Requires deconvolution of long-term memory, and better assessment of traffic trends.</td>
</tr>
<tr>
<td>Causes of high ozone days</td>
<td>Traffic and thunderstorm activity?</td>
<td>Traffic, meso-scale meteorology, topographic steering, and high HC/NO, ratios are key agents.</td>
<td>Greater evaporative losses and influence of bushfires, especially in Spring.</td>
</tr>
<tr>
<td>Relevant time-scales</td>
<td>&lt; 1 day</td>
<td>Hours to several days; recirculation possible of up to 40 hrs, dependent on synoptic conditions.</td>
<td>System parameters have different fractal dimensions and predictability.</td>
</tr>
<tr>
<td>Spatial extent</td>
<td>Inner suburbs, but perhaps more widespread.</td>
<td>Outer suburbs likely to be more severely affected during certain conditions, and may experience more frequent exceedances.</td>
<td>Minimum size of air-shed from Moreton Island to Toowoomba and Gold Coast to Caboolture.</td>
</tr>
<tr>
<td>Classification of events</td>
<td>Several classes of events for inner city region.</td>
<td>Importance of NW synoptic winds and later seabreeze arrival.</td>
<td>Better definition of sufficient conditions is required.</td>
</tr>
<tr>
<td>Identification of precursors</td>
<td>Little known</td>
<td>Formation rate strongly dependent on ROC levels.</td>
<td>Role of humidity and biogenic emissions uncertain.</td>
</tr>
<tr>
<td>Identification of causal parameters for early detection of likely extreme events</td>
<td>Mixing height was conjectured to be important.</td>
<td>The seven day traffic cycle extremely important. Cross-spectral analysis with the ozone series shows: (a) High correlation at low frequencies for 850 mb temperatures. (b) Correlation at high frequencies of scattering coefficient. (c) Correlation at synoptic frequencies for surface wind speed and pressure</td>
<td>7 day cycle in ozone data show Thursday and Friday as higher ozone days. This corresponds to peak traffic flow for most major roads. Still investigating possible lead times but preliminary investigations look encouraging.</td>
</tr>
<tr>
<td>Limits of predictability</td>
<td>Unknown</td>
<td>Good within a cluster; prediction of clusters a key issue.</td>
<td>Tropical climate and relatively small urban population may make the system simpler.</td>
</tr>
</tbody>
</table>

ACKNOWLEDGMENT
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Figure 1: Predicted LADM trajectories from various sources north and south of the inner city area for the winter ozone day. The insert shows the back trajectory for air of high ozone content arriving at Deception Bay at 1300 hours.

Figure 2: A comparison of the periodogram of the maximum daily ozone series (a) with the spectral density of the residuals after the removal of the estimated model (b).
Figure 3: The relationship between dimension and scaling parameter for (a) the daily maximum ozone series and (b) the daily maximum NO\textsubscript{x} series.

REFERENCES


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