

Chapter 5: Photochemical Oxidants (as Ozone)

5.1 Nature, Sources and Health Effects

Photochemical oxidants, commonly known as photochemical smog, is a term used for a complex mixture of chemicals produced in the atmosphere under the sunlight. Ozone is the principal component of photochemical oxidants and it is used as a surrogate for photochemical smog.

Ozone is a colourless, highly reactive gas with a sharp odour. It occurs naturally in the stratospheric ozone layer, 15–20 km above ground level, where it protects the Earth from harmful ultraviolet radiation from the Sun. In the lower atmosphere, at ground level, however, O₃ is a major health and environmental concern.

At ground level, O₃ is a secondary pollutant. It is not emitted directly but is formed, in the presence of sunlight, as a result of reactions involving oxides of nitrogen and volatile organic compounds (VOCs). Sources of VOCs are many and varied, but include motor vehicles, refineries, petrochemicals and vegetation (biogenic). In many regions of Australia, biogenic sources make major contributions to the level of VOCs and possibly to the level of O₃ in ambient air, particularly at background levels.

Ozone has adverse health effects on various parts of the respiratory system. Prolonged short-term exposures have been linked with significant decreases in lung function and increased respiratory symptoms, as well as aggravation of pre-existing respiratory diseases such as asthma. Ozone also has adverse effects on vegetation and building materials.

5.2 AAQ NEPM Standards

The ambient air quality standards for O₃ are:

- 0.10 ppm averaged over a 1-hour period; and
- 0.08 ppm averaged over a 4-hour period.

The goal is to meet both standards with one allowed exceedence day per year within a 10-year time frame.

5.3 Monitoring Results

Ozone data have been provided for 43 sites. Annual data availability by site for the years 1991–2001 is shown in Table A2-3 of Appendix 2. No data have been provided for the sites in Adelaide for 1997–2001. This is because from 1996 to 2001 SA used a network of non-conventional prototype instruments for measuring ozone.

5.3.1 2001 status

The 2001 summary statistics and air quality status for daily maximum 1-hour and daily maximum 4-hour O₃ concentrations are given in Table A3-3 of Appendix 3. For each monitoring station the following statistics are shown:

- quarterly and annual data availability (Q1, Q2, Q3, Q4 and ANN);
- highest daily maximum 1-hour concentration (M1HR);
- date of the highest daily maximum 1-hour concentration (DM1HR);

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- time of the highest daily maximum 1-hour concentration (TM1);
- second-highest daily maximum 1-hour concentration (2M1HR);
- date of the second-highest daily maximum 1-hour concentration (D2M1HR);
- time of the second-highest daily maximum 1-hour concentration (T2M1);
- highest daily maximum 4-hour concentration (M4HR);
- date of the highest daily maximum 4-hour concentration (DM4HR);
- time of the highest daily maximum 4-hour concentration (TM4);
- second-highest daily maximum 4-hour concentration (2M4HR);
- date of the second-highest daily maximum 4-hour concentration (D2M4HR);
- time of the second-highest daily maximum 4-hour concentration (T2M4);
- number of days when daily maximum 1-hour concentration exceeded the 1-hour standard (E1HR);
- number of days when daily maximum 4-hour concentration exceeded the 4-hour standard (E4HR);
- performance against the 1-hour standard and goal (P1HR);
- performance against the 4-hour standard and goal (P4HR).

The daily maximum 4-hour concentration for a given calendar day is the highest of the 24 possible 4-hour concentrations computed for that day. In counting exceedences and identifying the second-highest daily maximum 4-hour concentrations, the possibility of overlap has to be considered. Sometimes, in non-urban areas with no pronounced diurnal variation in hourly O₃, overlapping daily maximum 4-hour concentrations from two consecutive days may have some hourly concentrations in common. However, at the NEPM standard level this was not an issue for the sites included in this report. The AAQ NEPM allows one exceedence per year; therefore, the second-highest daily maximum 1-hour and 4-hour concentrations are of significance.

Due to insufficient data (data availability of <75% for one or more quarters), a valid analysis at four sites in Victoria, two sites in NSW, one site in Queensland and one site in ACT could not be carried out, and they are shown as 'not demonstrated'.

As shown in Table A3-3, the highest and the second-highest concentrations occurred in the early to late afternoon during the months from late spring to early autumn, with a peak in summer.

Widespread exceedences of both 1-hour and 4-hour levels of 0.10 and 0.08 ppm respectively have been experienced in NSW at several sites. The highest 1-hour concentration was 0.175 ppm at Bringelly and the highest 4-hour concentration was 0.137 ppm at Lidcombe, both located in the suburbs of Sydney. The only other jurisdiction with particularly high levels was WA, where two 4-hour exceedences of 0.08 ppm were recorded at Rolling Green. Rolling Green is a rural, non-NEPM, station where important data are collected for the air quality management plan of Perth. In Victoria, only one 4-hour exceedence of 0.08 ppm was reported.

The locations of all O₃ monitoring sites, not just NEPM sites, and the 2001 status of air quality against the NEPM standards are shown on a map in Figure 5-1.

It is apparent from Table A2-3 that the number of sites and the data availability vary from jurisdiction to jurisdiction. The number of monitoring stations is the largest in NSW, and WA has provided data from a number of non-NEPM stations. No comparable data are available for Adelaide for the years 1997–2001. An important implication is that extensive monitoring is more likely to capture the high

ambient levels that can occur on the fringes of urban areas. In particular, a well-designed network is needed to account for the distribution of emissions and the mechanisms associated with air quality, and to provide regional representativeness.

The sea breeze is recognised as an important mechanism associated with high O₃ levels in coastal cities. In a simplified picture, under typical meteorological conditions conducive to photochemical activity, primary emissions drift offshore with gentle morning winds and return as O₃ in the afternoon. With the onset of a sea breeze, associated with low mixing depth, high O₃ concentrations are sometimes experienced very close to the coastline. As the sea breeze moves inland, given adequate time for continuing chemical reactions, under some conditions maximum concentrations can occur in the outer suburbs or the outskirts of large cities.

In Melbourne, drainage flow and sometimes mesoscale circulations (e.g. Melbourne eddy) transport precursors over Port Phillip Bay. The bay breeze dynamics are crucial because the flow is radial. Small changes in the location of the precursors can mean the difference between transport to the eastern or western side of the bay. The interaction between the synoptic flow and the bay breeze or sea breeze determines how far the flow penetrates inland. Sometimes frontal passages or pressure troughs interact with the mesoscale flows. In this context, it appears that data provided for Melbourne do not cover the inland outer suburbs where high O₃ levels can be expected. This gap was addressed in the monitoring plan for Victoria, which proposed two new NEPM sites in the outer east and outer northwest of Melbourne.

5.3.2 Annual statistics for 1991–2001

Annual statistics and percentiles are presented in Tables A4-15 to A4-24 of Appendix 4. The number of days with daily maximum 1-hour O₃ concentrations greater than 0.10 ppm for the years 1991–2001 for each site is shown in Table A4-15. The number of days when the 4-hour level was greater than 0.08 ppm is shown in Table A4-20. There have been more days when the 4-hour concentration was greater than 0.08 ppm, as this is the more stringent level. NSW reported two or more days with 4-hour concentrations greater than 0.08 ppm in every year of data except 1995 and 1996.

The highest and the second-highest daily maximum 1-hour and 4-hour O₃ concentrations by site are given in Tables A4-16 and A4-17, and Tables A4-21 and A4-22. Second-highest daily peak 1-hour concentrations indicate that since 1997 all jurisdictions except NSW have not experienced daily maximum 1-hour concentrations greater than 0.10 ppm more than once.

Annual 98th and 95th percentiles for each site are shown in Tables A4-18 and A4-19, and Tables A4-23 and A4-24.

The highest and the second-highest daily maximum 1-hour O₃ concentrations in capital cities for 1991–2001 are plotted in Figures 5-2 and 5-3, respectively. Figures 5-4 and 5-5 show the 4-hour concentrations. The relevant NEPM standard is shown as a red line on Figures 5-2 to 5-5 for comparison. It is emphasised that the NEPM standards were made in 1998 and therefore they were not in place during most of the data period of these graphs. Figures 5-3 and 5-5 show that during this period the second-highest concentrations were greater than the 1-hour 0.10 ppm and the 4-hour 0.08 ppm levels in all capital cities except Canberra and Adelaide. For Adelaide, only limited data to 1996 were available. The number of days with daily maximum 1-hour O₃ concentrations greater than 0.10 ppm and 4-hour O₃ concentrations greater than 0.08 ppm are shown in Figures 5-6 and 5-7. There seems to be a significant decrease in the number of days with 1-hour concentrations greater than

0.10 ppm and with 4-hour concentrations greater than 0.08 ppm, and in the daily peak concentrations in 1995 and 1996 in Sydney and Melbourne. This may be due to meteorological conditions not being conducive to photochemical activity over SE Australia during this period. Overall, the graphical presentations suggest no downward trend over the decade.

The NEPC is currently reviewing the practicability of setting a long-term goal of achieving a 1-hour average standard for photochemical oxidants of 0.08 ppm measured as O₃ within the major urban airsheds. The number of days with daily maximum 1-hour O₃ greater than 0.08 ppm in the capital cities is shown in Figure 5-8, and in Table A4-25, for 1991–2001. In the last five years some decrease is apparent in Brisbane, Perth and Melbourne, but the number of such occurrences remain high in Sydney.

Annual average O₃ concentrations, based on hourly data, are shown in Table A4-26.

5.3.3 Trends

Observed air quality and trends are the result of many factors, in particular:

- monitoring
- meteorological variables
- emissions.

To minimise the impact of monitoring, it is important to ensure adequate spatial coverage by carefully positioned monitoring stations that provide data with a greater than 90% data recovery rate. To help interpretations, all statistics in this report which are based on insufficient data (one or more quarters with less than 75% data) are labelled with a trailing hyphen. Also, all trend analysis results presented in this report are site-specific, with no claim for comprehensive coverage of any region.

The impact of year-to-year changes in meteorology on observed changes in O₃ levels, particularly on the highest percentiles, is very significant. The impact during extreme weather years is easier to identify than the subtle ongoing effects. Possible climatic influences include the ENSO (El Nino-Southern Oscillation) phenomenon. Time series containing more than one ENSO cycle may be needed to understand trends.

The main purpose of air quality trend analysis is to link observed changes in air quality to trends in emissions, with a view to assessing the success of various emission-control strategies. Accurate assessments of the link between emissions and air quality would only be possible after allowing for other confounding factors such as meteorology. There is a further complication in identifying the link for secondary pollutants. For example, O₃ is formed in air under suitable atmospheric conditions as a result of complex reactions involving precursor emissions of NO_x and VOCs. In this report, trend analysis is carried out on O₃ levels as observed at the sites for which data have been provided, without removing the influences of meteorology. Meteorologically adjusted trends and linking the results to emission controls would involve sophisticated analysis as recommended in Chapter 10.

Site-specific trend analysis has been performed for 26 sites with reasonably long data records. Comprehensive coverage is intended to provide an opportunity to explore spatial variations in trends for this pollutant of concern.

Box plots and estimated trend lines for daily maximum 1-hour O₃ concentrations are shown in Figures 5-9 to 5-42. These figures show box plots for all 26 sites, but trend lines for only some. Box plot statistics are shown in Table A4-27 of Appendix 4. Trend analysis results for each site and for all eight

indicators are summarised in Table 5-1. Overall, statistically highly significant or significant trends are rare.

The most comprehensive coverage is provided by the network in NSW, where relatively high O₃ levels are experienced. Trend analysis is carried out on 11 NSW sites to enable examination of spatial variations. At each of the 11 sites the direction of trend or tendency is upward for almost every indicator shown in Table 5-1. However, these are mostly statistically non-significant upward tendencies. It is noted that at most of these sites at low percentile levels, in particular at the 50% level, the upward tendency becomes a statistically significant upward trend.

Analysis results for four sites in Victoria show a downward tendency or trend, in general, with higher significance at the lower percentile levels.

The trend or tendency for Queensland sites is also downward at three sites. Trend results for two different periods are presented for Rocklea. At the fourth site (Flinders View) an upward tendency is apparent for the top four indicators and the 50% levels.

In SA, Netley shows an upward tendency, while significant downward trends are observed at Northfield. It is noted that the trend period ends at 1996 and 1993 respectively for these sites.

Monitoring data from three sites in WA show a mostly upward tendency, with a statistically significant upward trend at low percentile levels at Caversham.

Data from Civic, ACT, show statistically non-significant upward tendencies for the peak and low percentile levels.

Trend analysis results in annual statistics for daily maximum 4-hour O₃ by site are listed in Table 5-2. Box plots are not included, as the distributions are similar to the 1-hour box plots shown in Figures 5-9 to 5-42. Nevertheless, site-specific box plot statistics are shown in Table A4-28 of Appendix 4. Overall, trend results for daily maximum 4-hour O₃ are similar to the pattern of daily maximum 1-hour O₃, with perhaps some increase in the significance level of 4-hour trends. The trend results that are different (significance level or direction) are highlighted in red in Table 5-2.

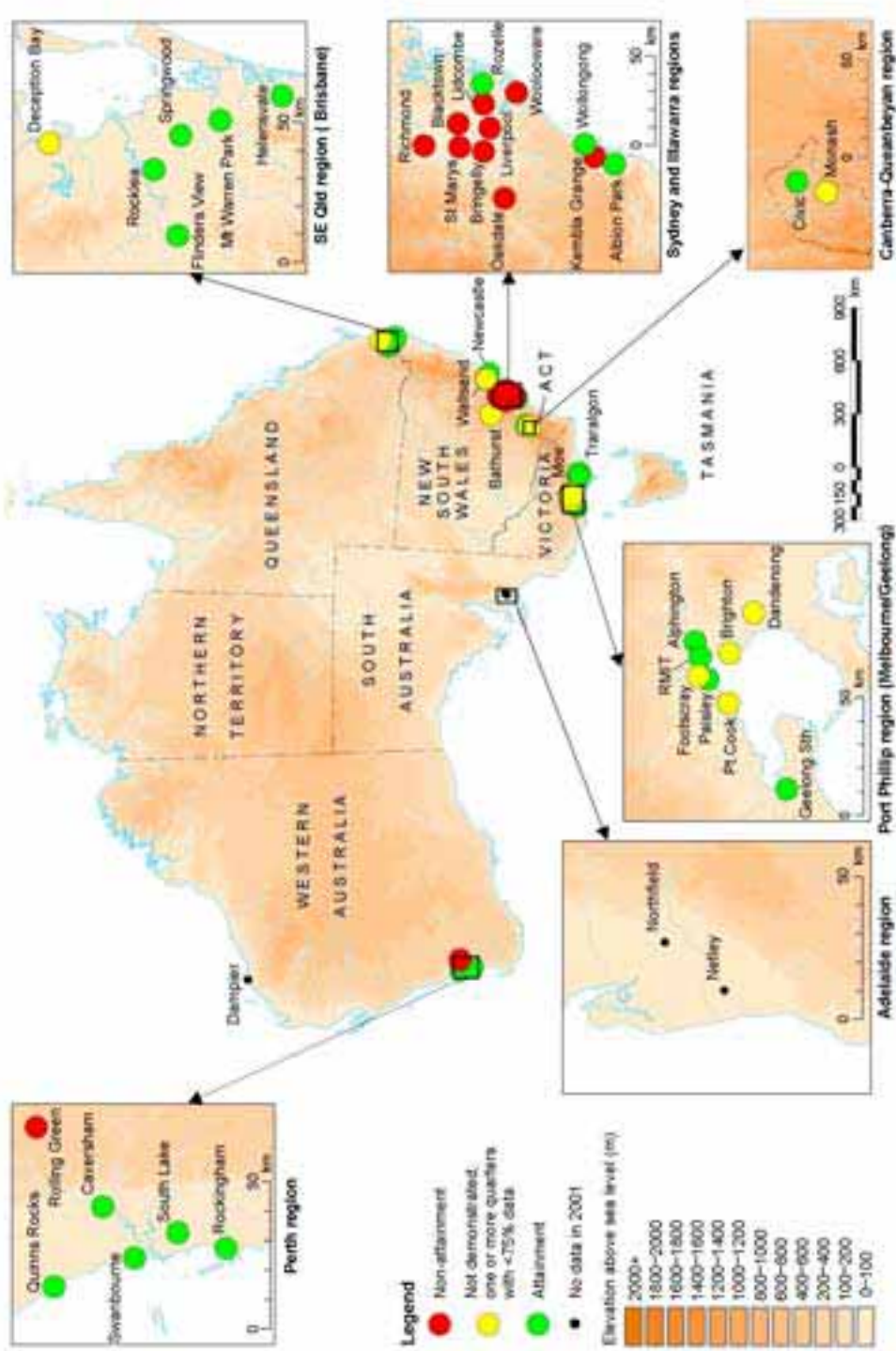


Figure 5-1. Ozone monitoring sites and 2001 status, where 'attainment' means that the second-highest daily maximum concentration for 1 hour is ≤ 0.10 ppm and for 4 hour is ≤ 0.08 ppm (All sites with data, not just NEPM sites, are shown.)

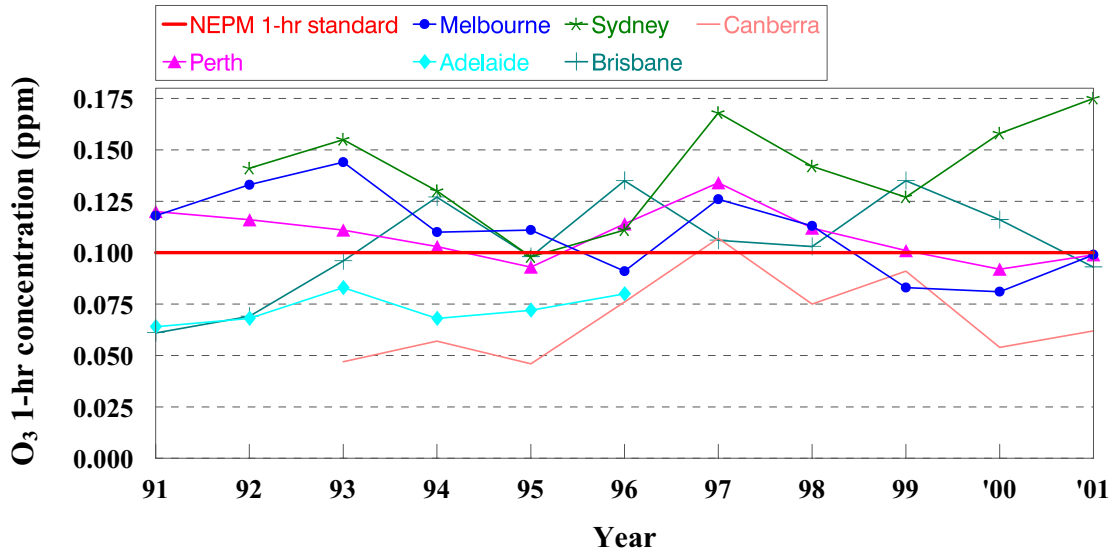


Figure 5-2. Highest daily maximum 1-hour O₃ concentrations in Australian capital cities, 1991–2001
(For each year, data from all operational sites in each capital city are used in selecting the highest daily maximum 1-hr O₃ concentration.)

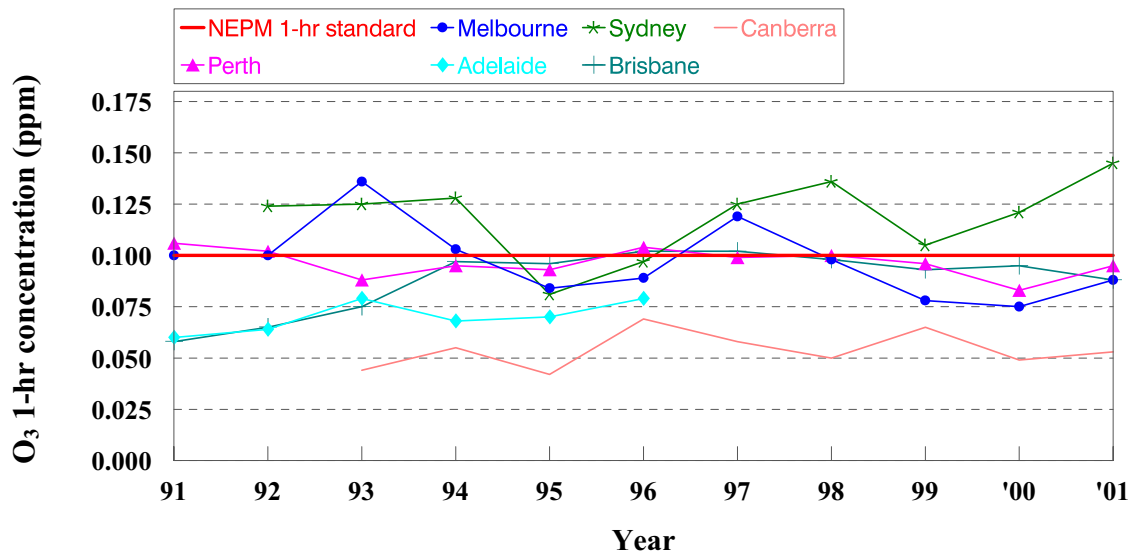


Figure 5-3. Highest second daily maximum 1-hour O₃ concentrations in Australian capital cities, 1991–2001
(For each year, data from all operational sites in each capital city are used. The highest second daily maximum 1-hr O₃ concentration is the highest of the second-highest station daily maxima.)

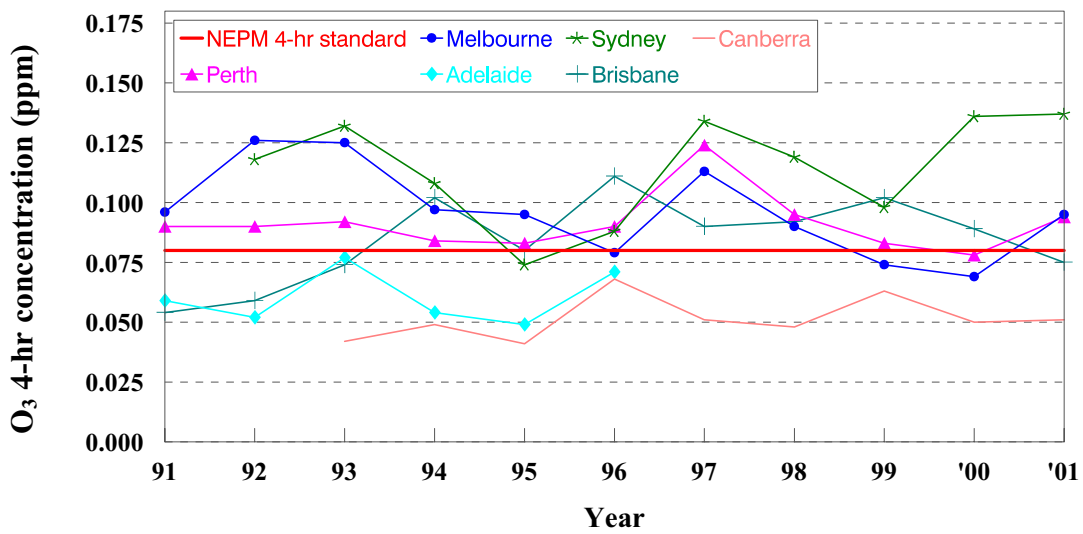


Figure 5-4. Highest daily maximum 4-hour O₃ concentrations in Australian capital cities, 1991–2001
(For each year, data from all operational sites in each capital city are used in selecting the highest daily maximum 4-hr O₃ concentration.)

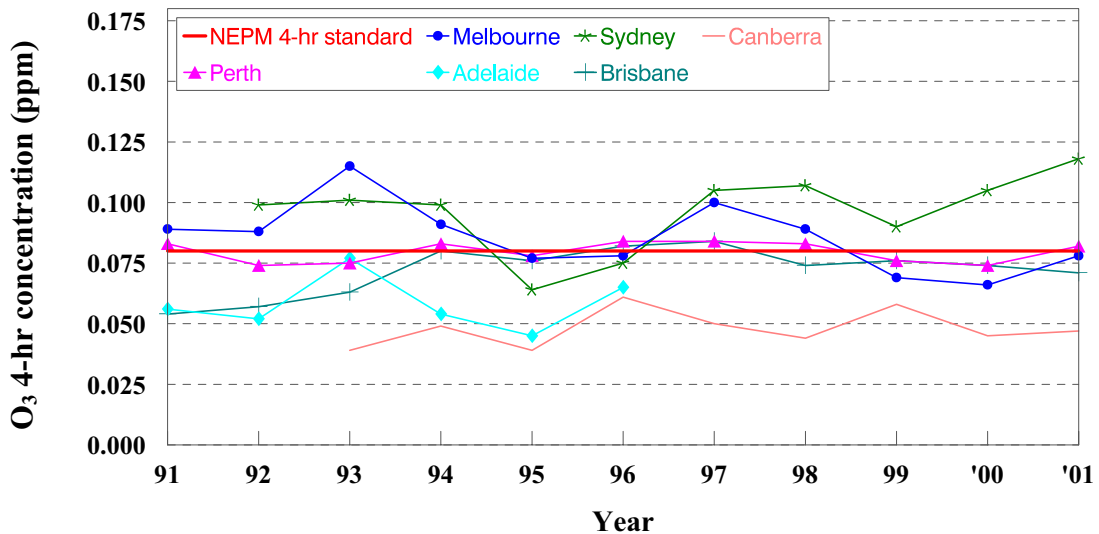


Figure 5-5. Highest second daily maximum 4-hour O₃ concentrations in Australian capital cities, 1991–2001
(For each year, data from all operational sites in each capital city are used. The highest second daily maximum 4-hr O₃ concentration is the highest of the second-highest station daily maxima.)

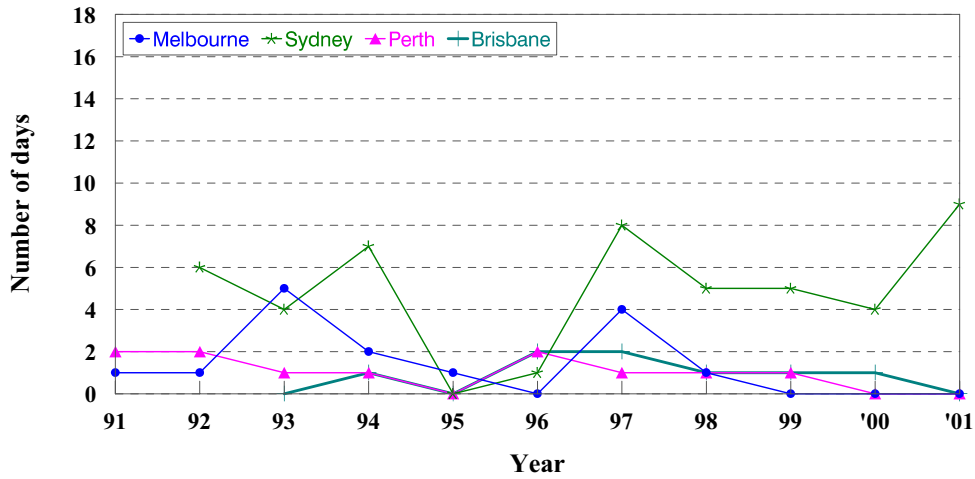


Figure 5-6. Number of days with daily maximum 1-hour O₃ > 0.10 ppm at any one site in each capital city, 1991–2001

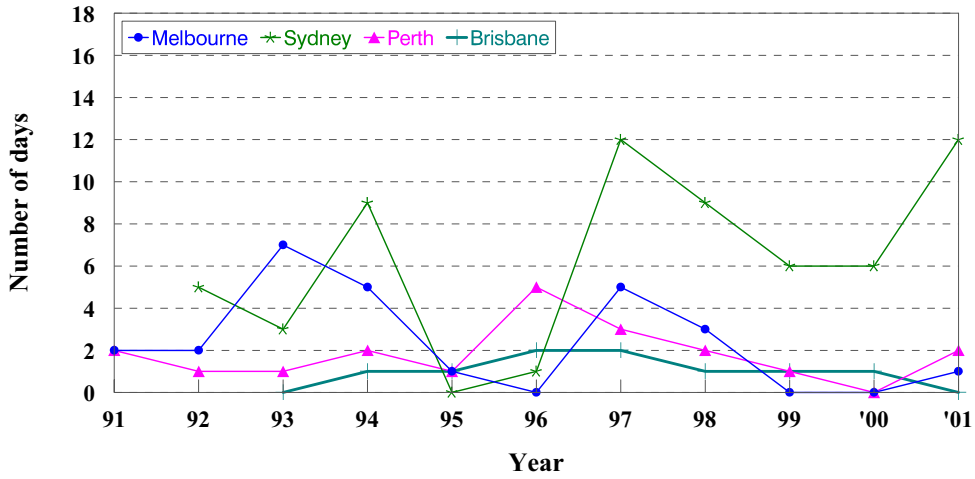


Figure 5-7. Number of days with daily maximum 4-hour O₃ > 0.08 ppm at any one site in each capital city, 1991–2001

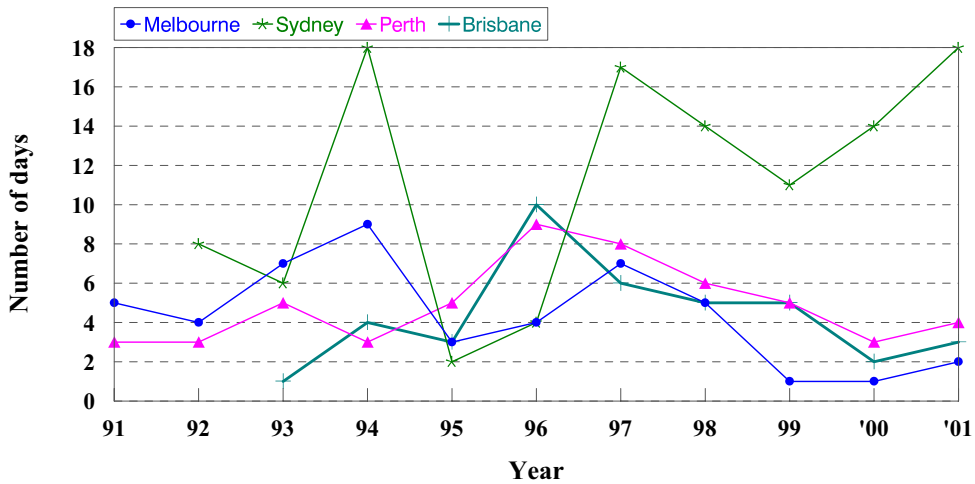


Figure 5-8. Number of days with daily maximum 1-hour O₃ > 0.08 ppm at any one site in each capital city, 1991–2001

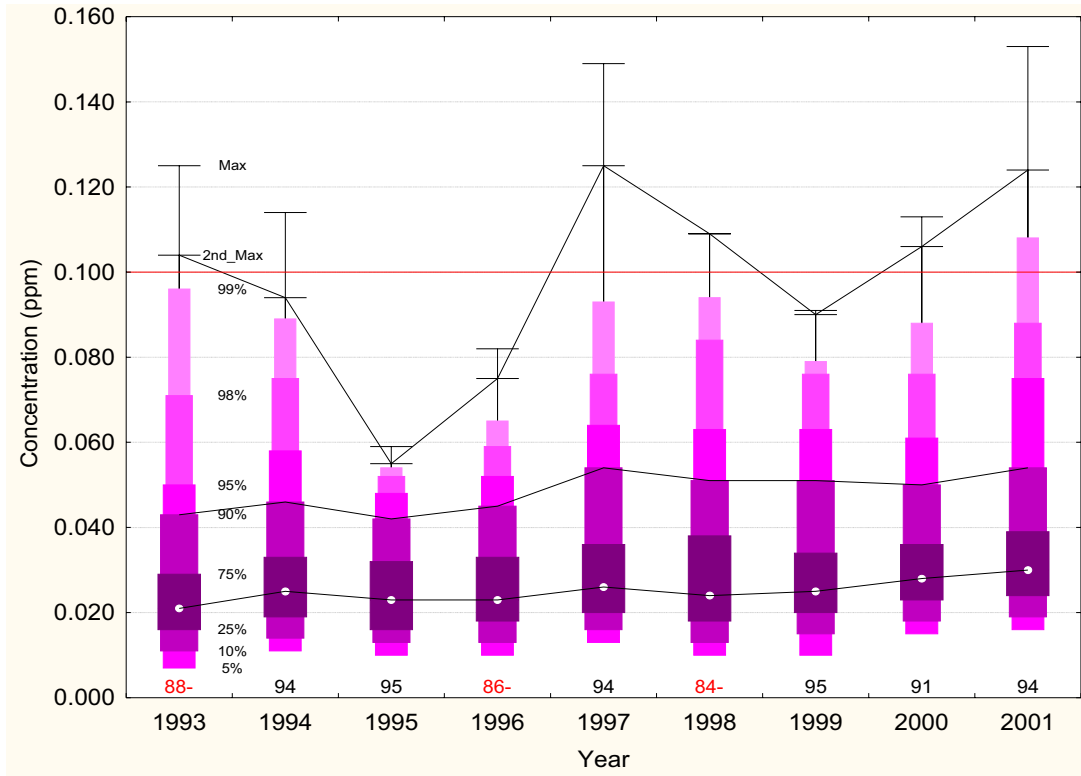


Figure 5-9. Box plots for daily maximum 1-hour O₃ concentrations at Blacktown, NSW

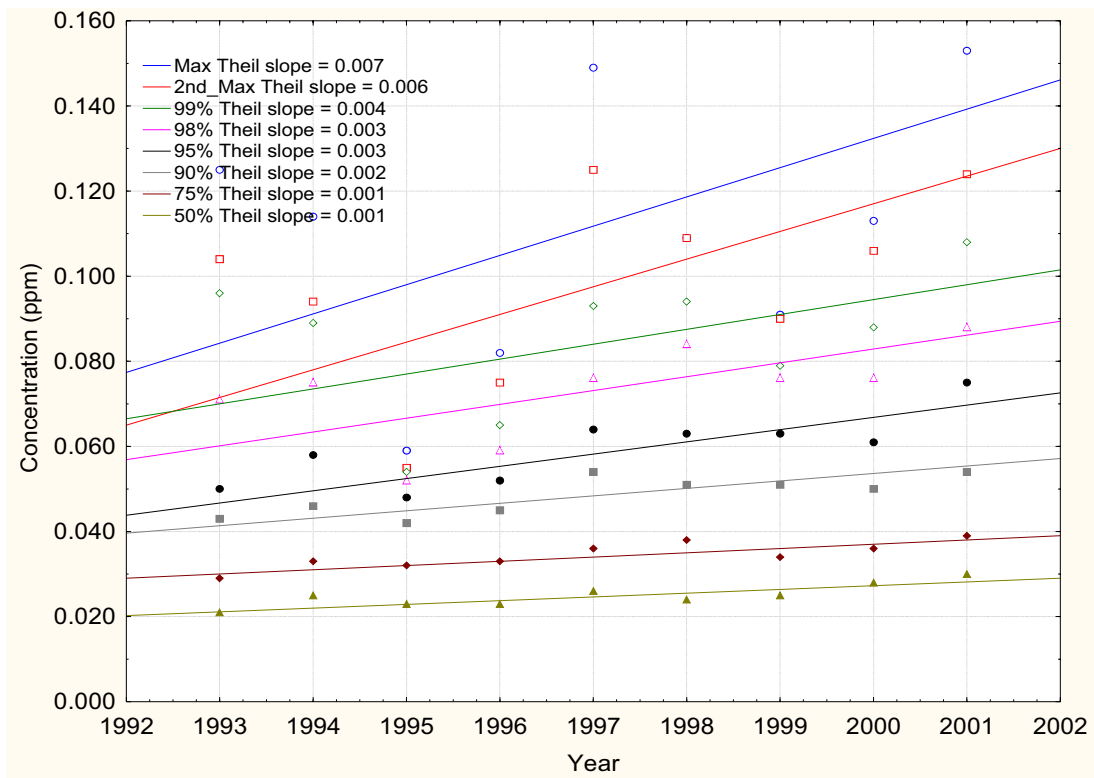


Figure 5-10. Trend analysis for daily maximum 1-hour O₃ concentrations at Blacktown, NSW