A Pilot Study of Air Quality in Darwin, N.T.
for the
Northern Territory Government,
Department of Lands Planning and Environment

Final Report

CSIRO Atmospheric Research
Aspendale, Victoria, Australia

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1. Air quality in Darwin, Pilot Study design.

Work described in this report was carried out for a pilot study of air quality in Darwin. This was a joint activity of the Northern Territory Government Department of Lands Planning and Environment (DLPE), the Northern Territory University (NTU) and CSIRO Atmospheric Research (CAR). The purpose of the study was to provide scientifically rigorous measurements of selected Air NEPM components in the Darwin area from March 2000 to October 2000, a period including both wet and dry season conditions. At the request of DLPE the study was extended, with particle and gas measurements carried through until 13th December. The main sampling instrumentation was decommissioned on 18th December. Measurements undertaken in the study include airborne mass for particles with aerodynamic diameter less than 10 μm (PM10), airborne lead (in PM10), NO_2, SO_2 and ozone. PM10 determinations include measurement using a tapered element oscillating mass balance (TEOM) as well as gravimetric mass and airborne PM10 lead loadings determined using filter collections. TEOM analyses provided continuous PM10 loadings with a 30-minute time resolution and the filter collections were operated on a one-day-in-six cycle. Passive gas samples were taken as duplicates on a six-day (integral) cycle.
The site at Berrimah was selected by DLPE for the main sampling location to satisfy the requirements of a representative urban location with a secure site and controlled environment for the continuous monitor. An additional filter sampler was operated at the NTU Casuarina campus on a six-day cycle for gravimetric PM10 and particulate lead. Initially this sampler was operated on a one-day-in-six cycle but, because of relatively low lead concentrations in Darwin and the low integrated flow rate with the filter sampler, this was altered on 23rd July to also include a five-day-in-six collection. In this final report, all gas and particle data are reported to the end of October and also data for the November-December study extension period where these have been analysed. Gas concentration data to the end of January 2001 are included. All data will be available in electronic form on completion of the analyses for the study extension period.

2. Equipment & installation

Continuous mass loading was determined at the CSIRO site in Berrimah using a Rupprecht and Patashnick TEOM 1400A series mass balance. This was operated at the "standard" conditions of 50 ºC for the inlet conditioning and a sample flow rate of 3 l min^{-1}. A Rupprecht and Patashnick PM10 size selective inlet was mounted on the roof at the sampling site with the sample flow directed vertically downward to the TEOM mass balance, which was located inside an air-conditioned laboratory, maintained at 19 ºC. A standard Ecotech flow splitter was used to divide the sample

flow after the size selective inlet to the sample line (3 l min^{-1}) and a bypass flow to which a filter sampler was connected (13.67 l min^{-1}). Flow rates were maintained at a constant value by mass flow controllers in the TEOM control chassis. This system was installed at Berrimah on 21st and 22nd February 2000. Data were obtained from 23rd February to 13th December 2000. The inlet sample line in the laboratory was lagged to prevent excessive cooling of the sample flow before the TEOM inlet heater. Subsequent problems indicative of condensation occasionally falling as water droplets into the TEOM (sudden jump in mass and subsequent decay) prompted installation of a second layer of lagging (24th March) and a small heater was constructed at CAR and sent to Darwin for installation on the inlet line. The second layer of lagging and reduction of the absolute humidity with the onset of drier conditions meant that the condensation problem was not evident after about mid-April and that the auxiliary heater was not necessary. Another problem that was encountered was acoustic noise from the sample pump. The pump that was used to provide the main TEOM sample flow (16.7 l min^{-1}) had baffling on the outlet to reduce acoustic noise, but this was insufficient to reduce the noise to a level that was considered low enough to prevent impact on normal office work nearby. An acoustic baffle box was constructed and tested for noise reduction at CAR, it was also tested to ensure that the pump was operating within its design thermal range. The baffle box was shipped to Darwin on 13th May, and installed. This reduced acoustic noise to an acceptable level.

A standard CAR passive sampler mount plate was installed by NTU at Berrimah in late February and an Ecotech MicroVol aerosol sampler was installed at the NTU Casuarina Campus and became operational on 7th March.

3. Operation

The sampling program operated substantially as planned although there were a number of problems. As detailed in Section 2, some minor difficulties occurred with the TEOM and were corrected. A small amount of data loss also occurred in the early stages of the project when the collected mass on the TEOM filter reduced the sample flow rate below the accepted threshold. The NTU MicroVol flow controller malfunctioned between 24th March to 5th May and this unit was replaced for the 11th May sample with a new sampler sent from CAR. Samples obtained during the period when the sensor output was low show low mass loadings and data obtained before 11th May should be considered suspect. An error in the shipping schedule for the passive samplers meant that no ozone samplers were exposed over the March to May period but duplicate NO_2 and SO_2 samples were obtained as planned. The replacement MicroVol showed flow problems from mid September and was replaced with a new unit on 2nd October.

4. Data summary

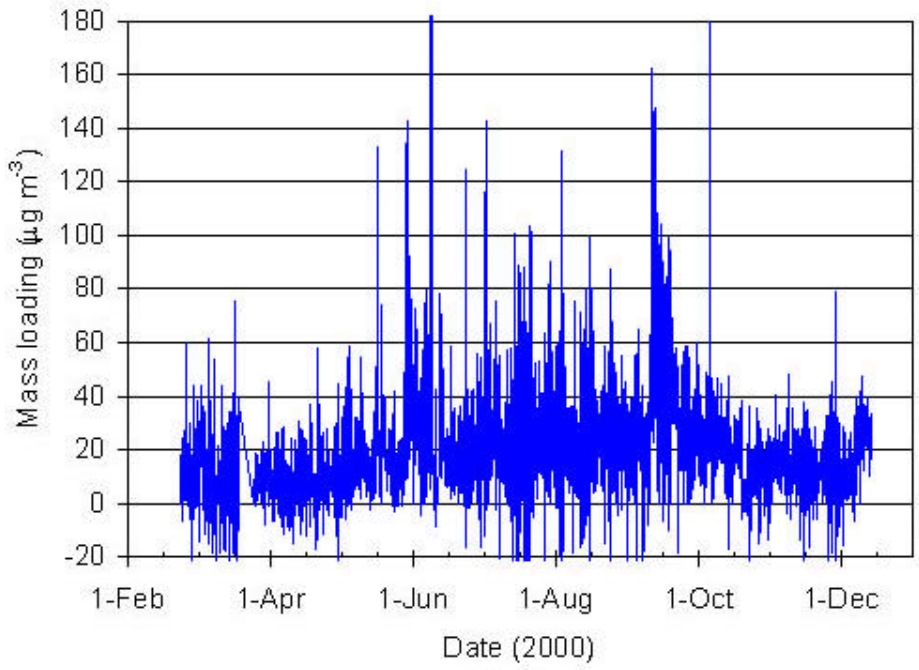
4.1 TEOM PM10 data

Analyses of PM10 data were carried out approximately weekly. Data were recorded as 30-minute, 1-hour, 8-hour and 24-hour mass loadings and integrated collected mass, using the standard TEOM protocol. Data were down loaded to the local PC every six days by the NTU operator and then transmitted to CAR. Primary editing at CAR involved visual inspection of the data and operator comments. Any data that

were known, or appeared, to be invalid were flagged in the data file. Frequently, this included short periods of several hours after changing TEOM filter elements and also included the events that appear to be due to condensation in the inlet line. Mass loadings recorded by the TEOM have a number of "built-in" corrections. These include conversion to the Australian standard measurement conditions of 1 atmosphere and 0 ºC (these parameters are set in the operation firmware) and an empirical correction required for US EPA PM10 equivalence. This latter correction is:

$$PM10 = 1.03 \times \text{mass loading} + 3.0\ \mu g\ m^{-3}.$$

The presence of this correction also needs to be taken into account when comparing the TEOM-derived mass loadings with those from other samplers. Small corrections for the sample and bypass flow must also be included to allow for departures from the nominal 3.0 and 13.67 l min^{-1} flows, as measured using a reference flow meter.



Values of 24-hour mean PM10 were derived from the edited 30-minute loadings for each day. In keeping with normal practice, negative masses were included in the running averages. Figure 1 shows hourly mean mass loadings and the 24-hour mean loadings are shown in Fig. 2 (for days where more than 15 hours of accepted data were collected in the 24-hour period).

Figure 1. PM10 mass loading hourly samples from the Berrimah TEOM, 23rd February – 12th December 2000 (1 atmosphere, 0 ºC, US EPA equivalent)

Mass loadings follow the expected general pattern of increase from the wet season into the dry season with occasionally stronger events. There were two main periods where the 24-hour mean PM10 mass loading exceeded the Air NEPM standard of 50 µg m^{-3}, both associated with local observations of smoke. The first occurred at the end of May, when a single day just exceeded the 50 µg m^{-3} level; the second was in

early September when 5 consecutive days exceeded 50 μg m^{-3}. During this second period the loading reached 69 μg m^{-3} on 11th September and 70 μg m^{-3} on the following day. Another smoky period was also observed near the end of the measurements in December, during a late dry period, although 24-hour loadings reached only about 30 μg m^{-3}.

4.2 Gravimetric mass determinations.

Gravimetric mass loadings as 24-hour integrals were determined from filter collections on the TEOM bypass flow line and also using an Ecotech MicroVol system with a 10-μm size selective inlet operating at the NTU Casuarina Campus. Samples in both cases were collected on pre-weighed (dried) stretched PTFE substrates.

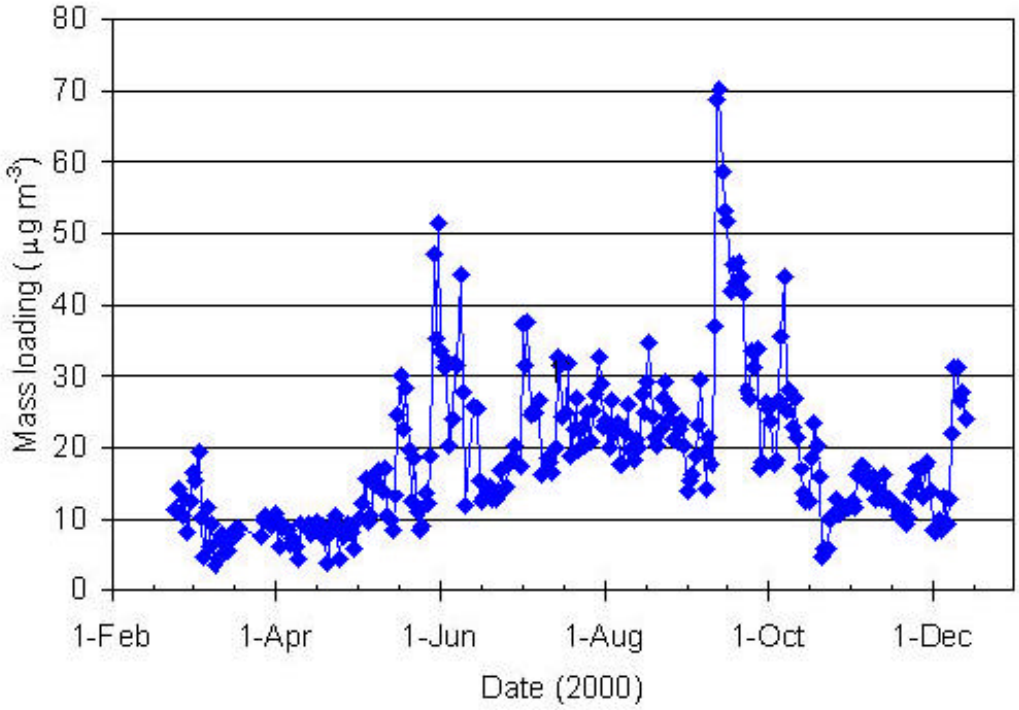


Figure 2. PM10 24-hour mean mass loadings at Berrimah, 23rd February – 12th December 2000 (1 atmosphere, 0 ºC, US EPA equivalent).

On return to CAR Aspendale the collected samples were conditioned for 24 hours at low relative humidity (RH < 20%) and weighed dry using a Mettler UMT2 Ultra-microbalance. Mass loadings from the two filter samplers and from the TEOM for the filter sample periods, without US EPA equivalence correction, are plotted in Fig. 3. MicroVol data for the period prior to 12th May have been excluded.

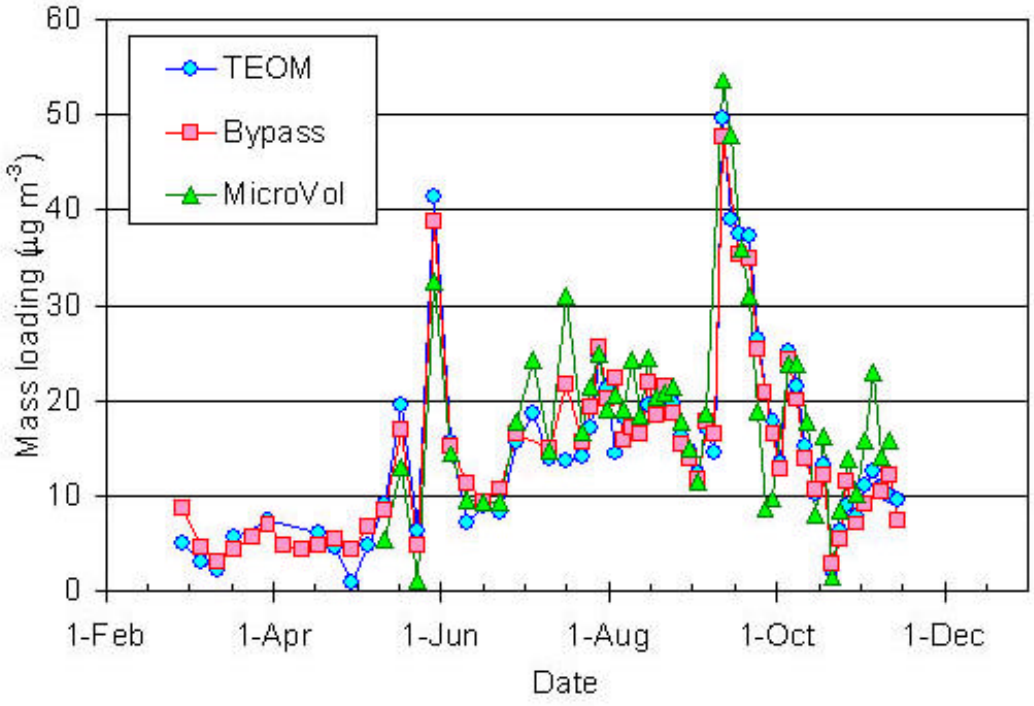


Figure 3. Comparison of integrated mass loading derived from TEOM system, gravimetric determination using the TEOM bypass flow sampler and gravimetric determination using a MicroVol filter sampler at the NTU Casuarina site. All data shown for 1 atmosphere, 0 ºC. For this figure TEOM data are not corrected to US EPA equivalence.

4.3 Comparison of TEOM and gravimetric mass loadings.

Atmospheric mass loadings, derived by integrating the TEOM data for the sample periods of the bypass filter, are also shown in Fig. 4 as a function of the corresponding mass loadings derived using the bypass filter. For this comparison the US EPA equivalence correction was removed from the TEOM data so that, in effect, both estimates of atmospheric mass loading are based on observed mass and the corrected flow at 0 °C, 1 atmosphere. Small empirical corrections for the actual flow rates, determined using a bubble flow meter when the sampler was commissioned in Darwin, are also included. Four outliers with suspected weighing errors have been deleted from Fig. 4. The relationship between the mass loadings is

$$\text{PM10 (TEOM)} = 1.04 \times \text{PM10 (bypass)} - 0.8\ (\mu g\ m^{-3}),$$

with $R^2 = 0.95$. This relationship indicates quite clearly that volatilisation losses of aerosol mass due to heating the inlet to 50 °C in the TEOM inlet is not a problem in Darwin and also raises the question of whether the US EPA equivalence correction of

$$\text{PM10 (reported)} = 1.03 \times \text{PM10 (observed)} + 3.0\ (\mu g\ m^{-3})$$

for the TEOM is appropriate in this location. Empirical equivalence correction is an issue that perhaps should be addressed in establishing an Australian standard procedure for the TEOM. It should be noted that the comparison reported here is not with a co-located Hi-Vol sampler but a low-volume sampler (13.67 l min^{-1}) using the same size-selective inlet.

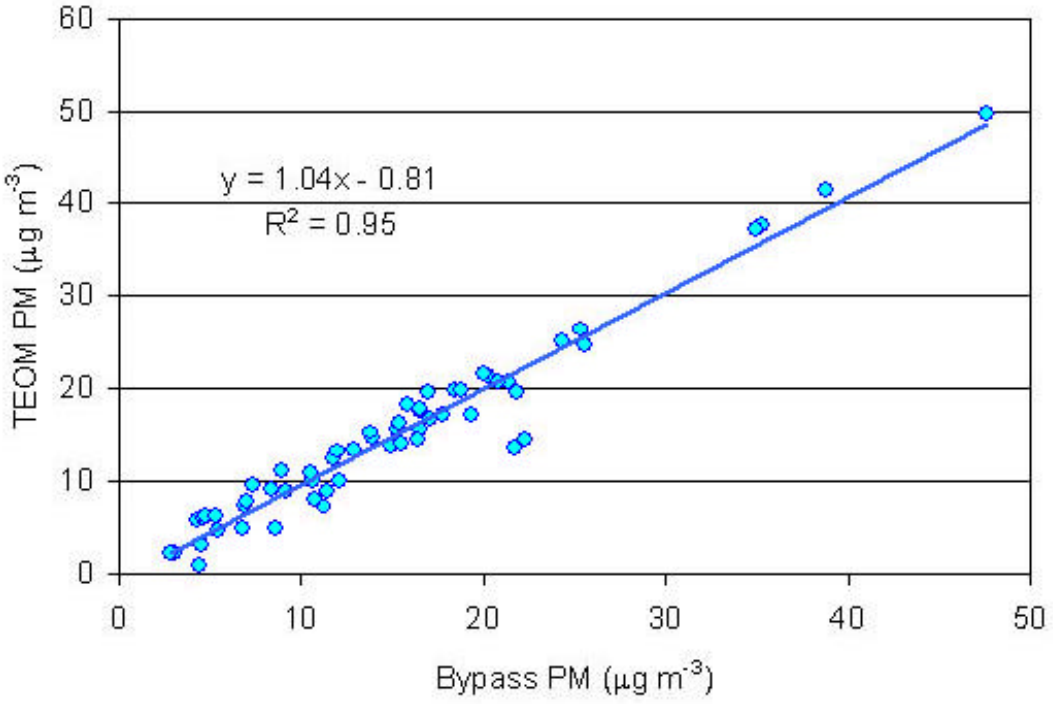


Figure 4. Averaged PM10 mass loading derived from TEOM mass loadings as a function of gravimetric determination using the TEOM bypass flow sampler, for filter sample periods (1 atmosphere, 0 ºC, TEOM data not corrected to US EPA equivalence).

4.3.1 Comparison of MicroVol and TEOM bypass samples

The time series of mass loadings for the discrete filter sampling periods is shown in Fig. 3. This indicates a strong coherence between the different samplers, including the MicroVol sampler, which was located at the NTU Casuarina site. The relationship between the samplers is further examined in Fig. 5, which gives the bivariate relationship between mass loadings of PM10 from the MicroVol at Casuarina and the TEOM bypass filters at Berrimah. Overall the agreement between the two samplers is quite strong, given their 7-km separation. The relationship is given by

$$\text{PM10 (NTU)} = 1.05 \times \text{PM10 (Berrimah)} - 0.9 \ (\mu g\ m^{-3}),\ (r^2 = 0.79).$$

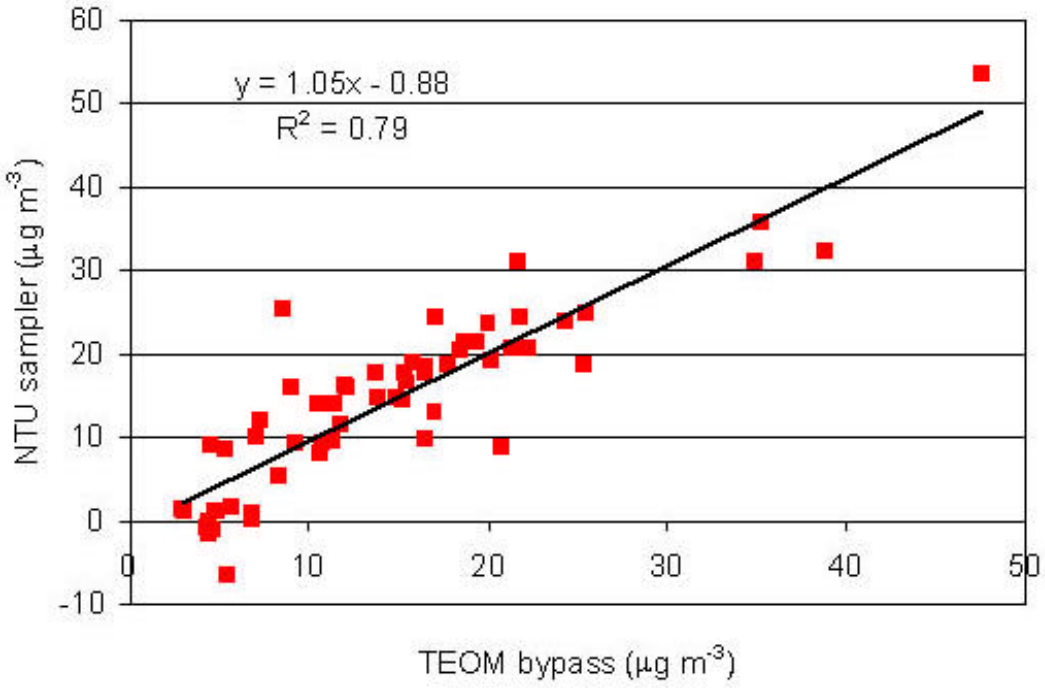


Figure 5. PM10 mass loadings from gravimetric determination on filter samples collected at the NTU Casuarina site and filter samples collected with the TEOM bypass sampler at Berrimah (1 atmosphere, 0 ºC, TEOM data not US EPA equivalent).

4.4 Particulate lead loadings.

Airborne lead in the PM10 fraction was determined at Berrimah using samples collected via the TEOM bypass flow and at the NTU Casuarina site using an Ecotech MicroVol sampler with a PM10 size selective inlet. Initially, samples were taken for 24-hour averages, however from 23rd July the sample period was extended to five days. This change in sampling duration was made because of the very low levels of lead encountered. Exposed filters were first shipped to CAR for determination of gravimetric mass after which they were returned to NTU for determination of lead.

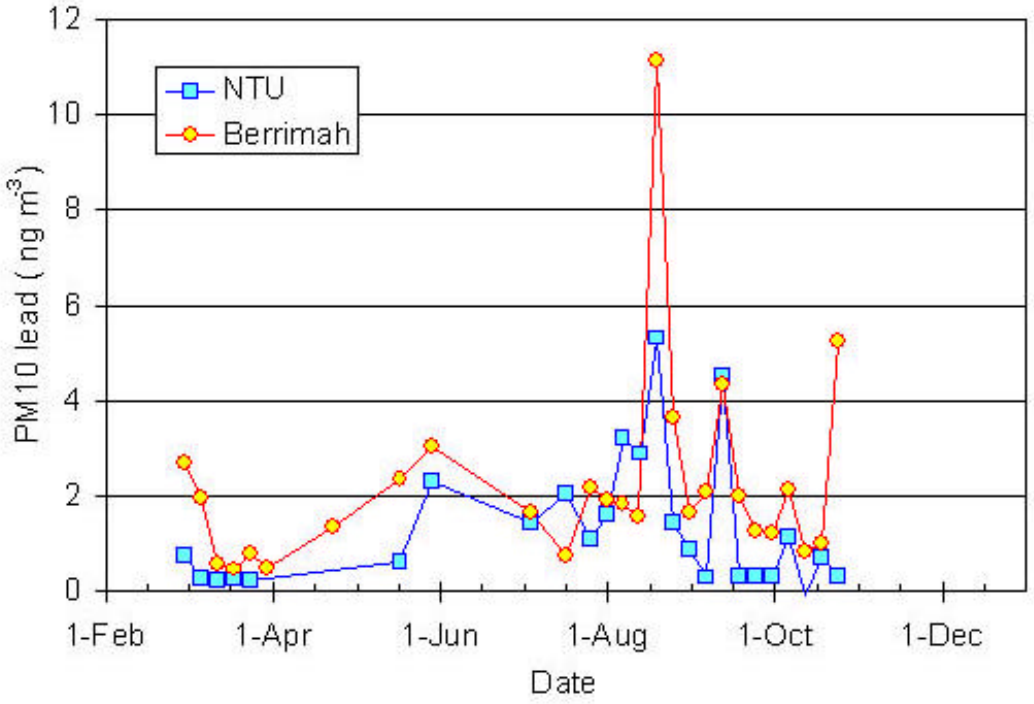


Figure 6. Atmospheric lead loadings in PM10 at the Berrimah and NTU Casuarina sites.

At NTU the filters were digested using nitric acid and then analysed using inductively-coupled plasma – mass-spectrometry (ICP-MS). This procedure has a detection limit of around 2 ng lead per filter. Atmospheric PM10 lead loadings for the Berrimah and Casuarina sites are shown as a time series in Fig. 6. Where samples returned loadings per filter less than the minimum detection level, a value corresponding to one half this minimum detection limit has been plotted. The maximum lead loading observed was 11.1 ng m^{-3}, at the Berrimah site. These concentrations are well inside the Air NEPM standard of 0.5 µg m^{-3} (500 ng m^{-3}) for 24-hour average lead loading. It can also be compared, for example, to Perth in 1994 - 1995 (Gras 1996) where the mean lead loading (in PM2.5) was 85 ng m^{-3}.

4.5 PM10 Zinc and Iron

Zinc and iron, both elements usually associated with mineral aerosol, are also determined using the ICP-MS method. Time series of PM10 zinc loadings at the Berrimah and Casuarina sites are shown in Fig. 7 and a corresponding series of iron loadings in Fig. 8. Iron loadings at the two sites are reasonably similar with a broad dry season maximum and evidence of individual events. Surprisingly, concentrations of zinc at the two sites are quite different. Frequently, airborne concentrations of zinc at the Casuarina site were significantly larger than at Berrimah. Clearly, this points to an intermittent local source for airborne zinc near the NTU Casuarina site.
For the 1994 -1995 period in Perth, the mean PM2.5 iron loading was 36 ng m^{-3} and the corresponding zinc loading was 12 ng m^{-3}. The higher iron values and pattern of temporal variation in Darwin are consistent with a coarse mode (dust) source for the mineral fraction.

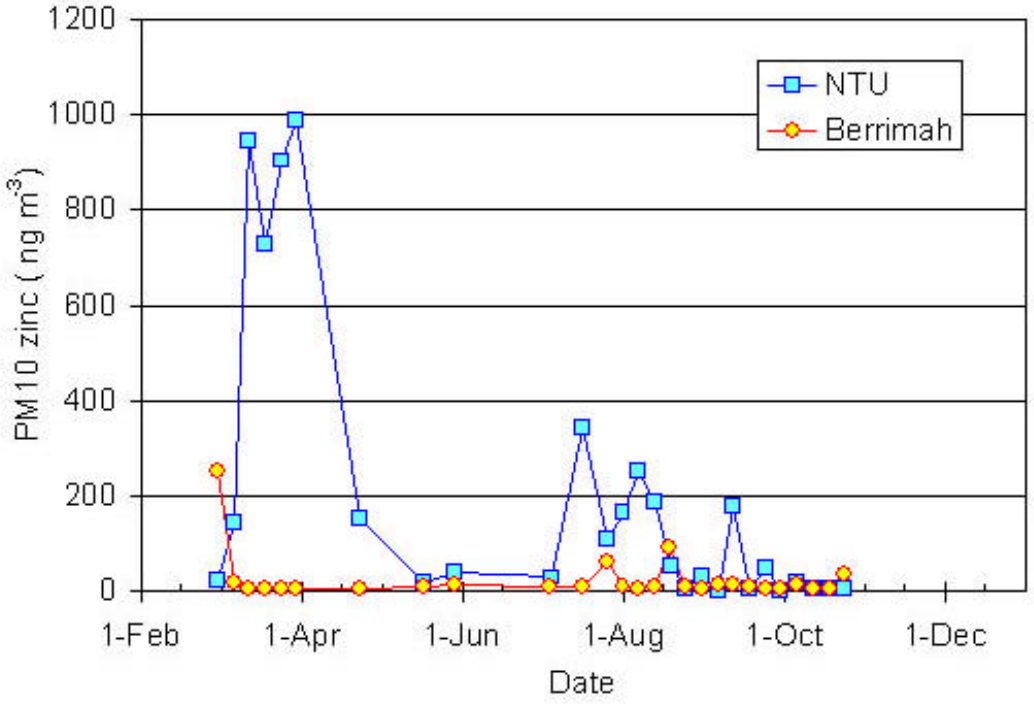


Figure 7. Atmospheric zinc loadings in PM10 at the Berrimah and NTU Casuarina sites.

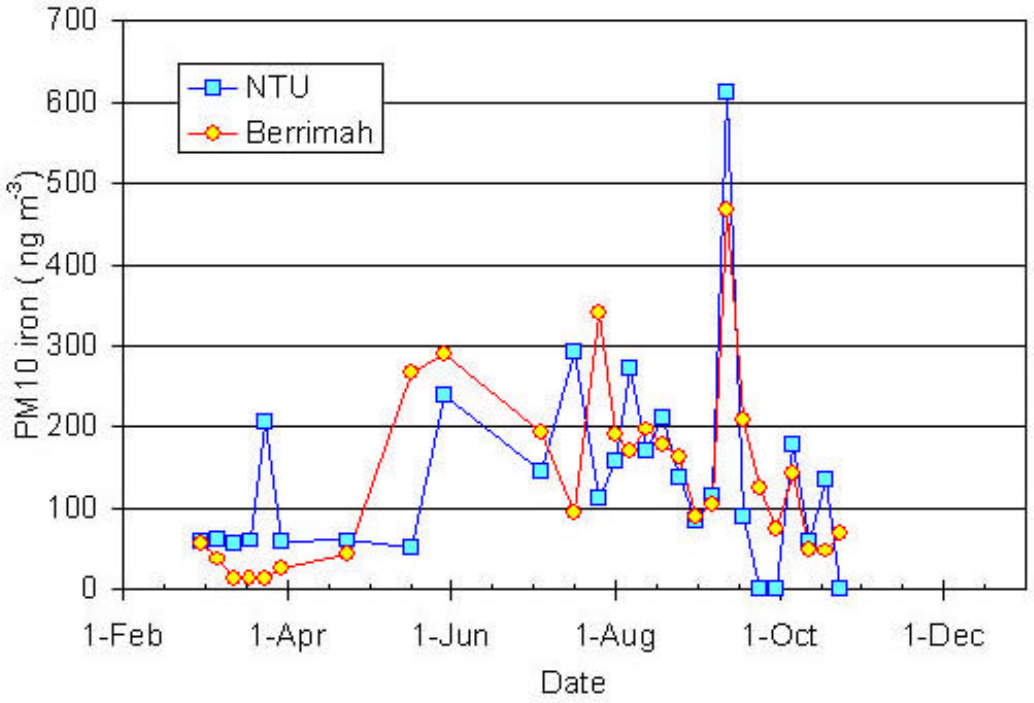


Figure 8. Atmospheric iron loadings in PM10 at the Berrimah and NTU Casuarina sites.

4.6 Diurnal variation of PM10 loading at Berrimah.

Diurnal variation in PM10 mass loadings for the Berrimah site, derived from the edited 30-minute "US-EPA equivalenced" TEOM data, are given in Fig. 9 as a function of time of day. Values plotted are the median concentrations at the particular time of day for the indicated month.

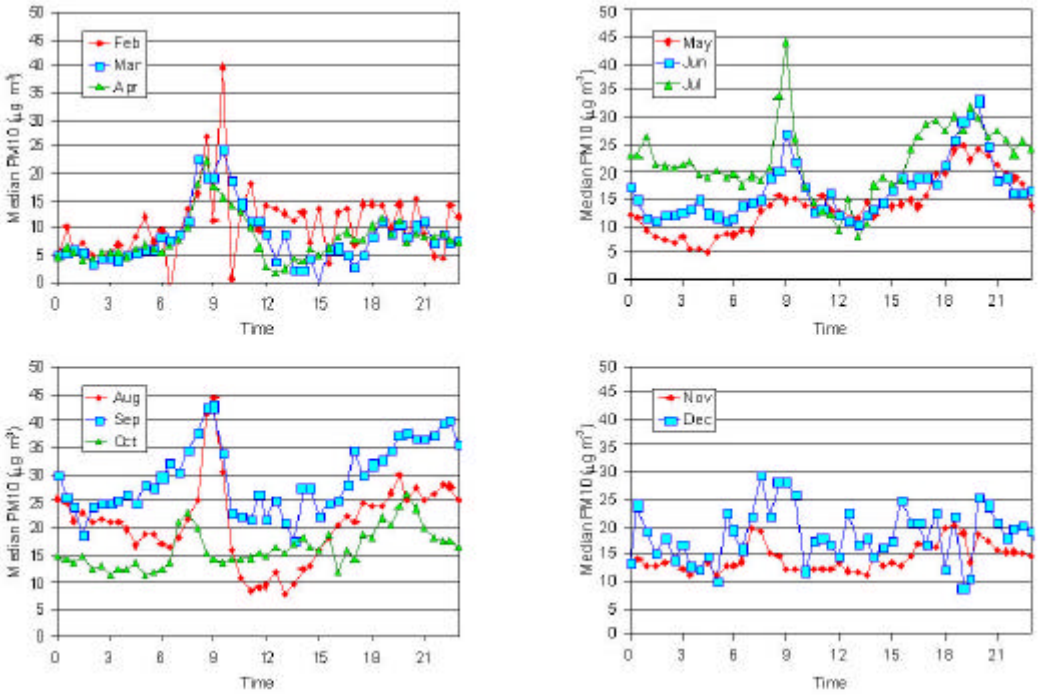


Figure 9. Diurnal variation in PM10 loading as monthly medians of the 30-minute "equivalenced" TEOM data.

Plots from February and December are noisier than the other months due to their shorter sampling periods. These diurnal variations in mass loading demonstrate a number of features that are typically related to local sources and atmospheric stability. This includes the persistent early morning peak at around 08:00 to 09:00 corresponding with the start up of local sources before the onset of convective mixing, and minimum around midday or early afternoon due to the maximum ventilation associated with convective mixing. With progression into the dry season both the early morning and evening mass peaks become more pronounced. This is particularly obvious for the period July to September and is consistent with increased nocturnal stability and reduced ventilation during this period and the seasonal increase in regional aerosol loading. By the end of the sampling period, as shown by the November-December data, the diurnal cycle had returned to a pattern more like that observed at the end of the previous wet season in February-March although the concentrations in general appear to be still elevated. Maximum concentrations both at night and during the day were observed in September. Comparison between typical wet and dry season diurnal cycles can be seen clearly in Fig. 10, which shows the median concentrations for February, March, November and December representing "wet" season and medians for July, August and September representing the "dry" season. For Fig. 10 data from all days of the week are included.

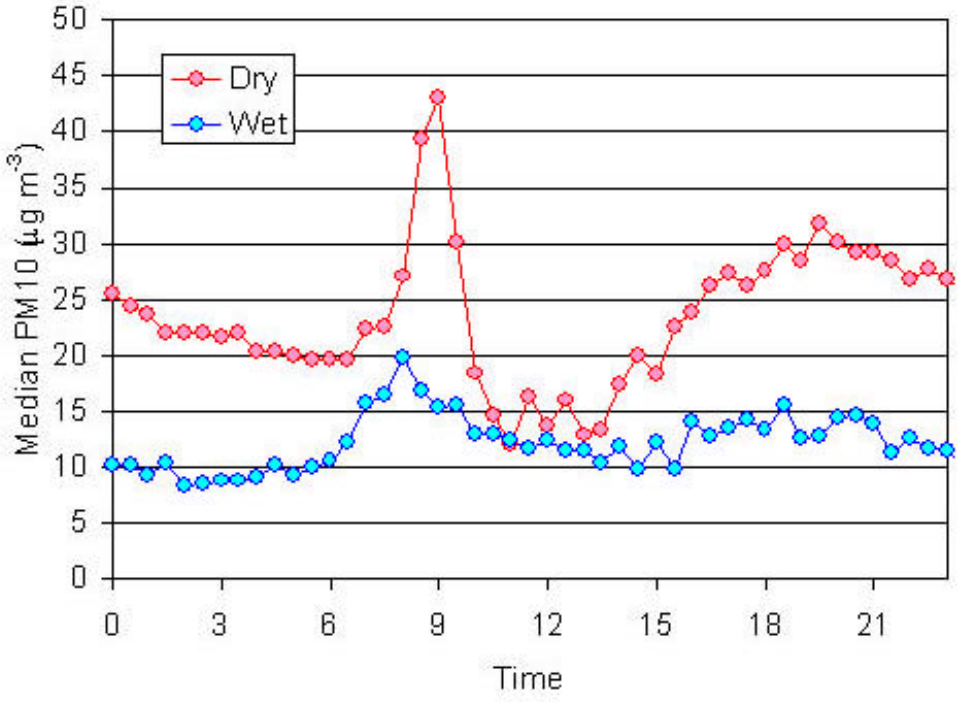


Figure 10. Diurnal variation in 30-minute PM10 loading, using "equivalenced" TEOM data medians representing the dry season (July, August & September) and the wet season (February, March, November & December).

With this level of temporal filtering the main difference appears in the nocturnal concentrations and early morning peak, which is most probably associated with the differences in atmospheric stability and ventilation. Daytime concentrations are quite similar. More noticeable differences can be seen in the monthly medians such as shown in Fig. 9 and even more extreme differences could be expected for individual fumigation events. Individual 30-minute loadings for the 10th to 20th September are plotted in Fig. 11. As is evident in Figs. 1 and 2, this was a period with significant mass loadings. The wide range in loadings from day to day for the 10th to 20th September period can be seen in Fig. 11, but the effect of increased ventilation during the day is also still quite evident. This can be interpreted as an indication that the increased loadings are due to advection to the measurement location mainly at low altitude. During the day the advected material is diluted by mixing. Advection at higher altitudes and mixing down with convection would result in increased loadings during the day. The mass loading data also show some weekday – weekend differences indicating an impact of local (mainly traffic) sources on the mass loading. This can be seen clearly in Fig. 12. Data used in Fig. 12 were separated into weekend (midnight Friday to midnight Sunday) and weekday (midnight Sunday to midnight Friday). The dry season is represented by data from July, August and September, as for Fig. 10. In order to reduce noise in the weekend series for the wet season, data from February to the end of April and October 16 to the end of the record in December were used. All four series shown in Fig. 12 are medians for the selected conditions. The most consistent weekday-weekend difference is in the magnitude of

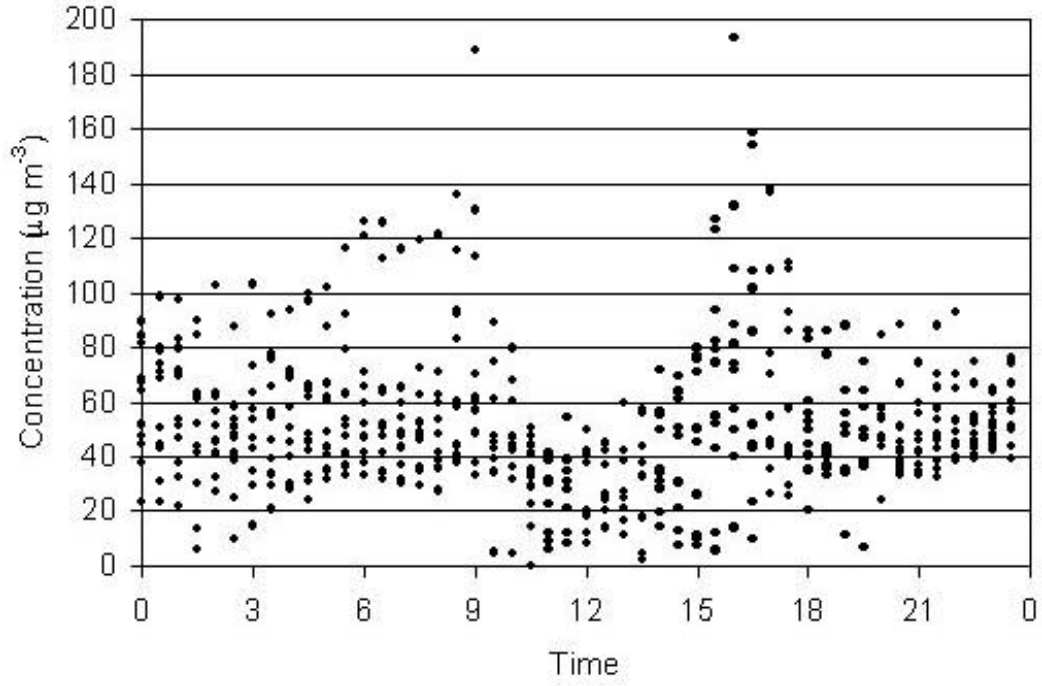


Figure 11. Diurnal variation in PM10 loading as individual 30-minute "equivalenced" TEOM data for the period 10th to 20th September.

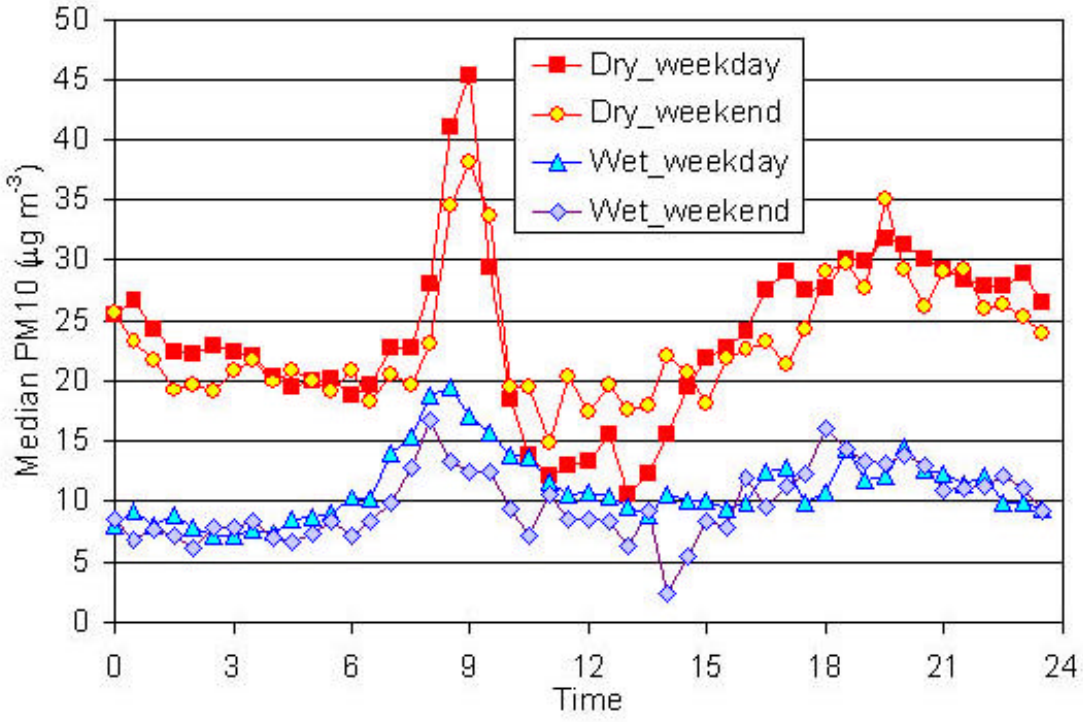


Figure 12. Diurnal variation in 30-minute PM10 loading, using "equivalenced" TEOM data showing weekend – weekday differences for both "dry" and "wet" seasons.

the morning peak, which is clearly greater during weekdays during both the "wet" and "dry" periods.

4.7 Sulfur dioxide, nitrogen dioxide and ozone passive samplers

All concentration data obtained from the duplicate passive samplers at the Berrimah site up to the end of January 2001 are shown in Fig. 13. This represents all data that have been analysed. The concentration of SO_2 was very low throughout the study averaging 0.5 ppbv, with a root-mean-squared (rms) difference of 0.3 ppbv between the paired samples and an overall sample standard deviation of 0.3 ppbv. The maximum concentration (single sample) was 1.3 ppbv. The Air NEPM 24-hour average standard for SO_2 is 80 ppbv. The Berrimah SO_2 concentrations are very similar to the average concentration of 0.8 ppbv obtained at Charles Point, for a 5-year period from 1993 to 1998 using the same passive sampling approach (Ayers, Parry and Gillett, unpublished data).

NO_2 concentrations were generally relatively low, ranging from1 ppbv to 8 ppbv, with an overall mean of 4.3 ppbv. The rms difference between paired samples was 0.8 ppbv. Concentrations show a clear seasonal variation with greater NO_2 during the dry season. Some measurements of NO_2 concentrations have been made at Charles Point. Typical values obtained (in September 1998) were about 1 ppbv with peaks associated with smoke plumes up to several ppbv (M. Meyer, CSIRO Atmospheric Research, personal communication 2001). As well, passive sampling for NO_2 was carried out at Charles Point for the 1993 – 1998 period returning an overall mean concentration of 0.5 ppbv. The longest averaging time specified in the Air NEPM for NO_2 is one hour, and for this, the standard is 120 ppbv. Neither SO_2 nor NO_2 concentrations observed throughout the study suggest cause for concern.

Ozone data are available only from 4th June 2000 and all of the available data are included in Fig. 13. As plotted in Fig. 13, ozone concentrations include an empirical calibration factor based on six months' observation at two sites in Melbourne. At these sites ozone was determined simultaneously using passive samplers and Victorian EPA active ozone monitors. As shown in Fig. 13 ozone concentration shows a complicated but systematic pattern of variation with time, most values being less than 25 ppbv and a period in July-August with concentrations less than 10 ppbv. This latter period of lower ozone concentrations coincides with that where NO_2 concentrations were greatest, but titration of the ozone by NO alone is insufficient to explain the apparent decrease at this time. Ozone concentration was determined at Charles Point from about 1993-1997. These unpublished data show a seasonal cycle in ozone concentration with a dry season maximum of about 25 ppbv (July to October) and a minimum around February to April of about 12 ppbv (M. Meyer, CSIRO Atmospheric Research, personal communication 2001). Concentrations for ozone in the Air NEPM are specified only up to a four-hour average, for which the limit is 80 ppbv. Direct extrapolation of the Berrimah data to shorter measuring periods cannot be justified in the absence of additional data on the frequency distribution of ozone concentrations, but some data from Charles Point may be indicative in this respect. For example, for the period 1993 –1997 maximum hourly concentration data are available for Charles Point, for the month of May. For these

data the maximum hourly concentration reached was 61 ppbv (M. Meyer, CSIRO Atmospheric Research, personal communication 2001).

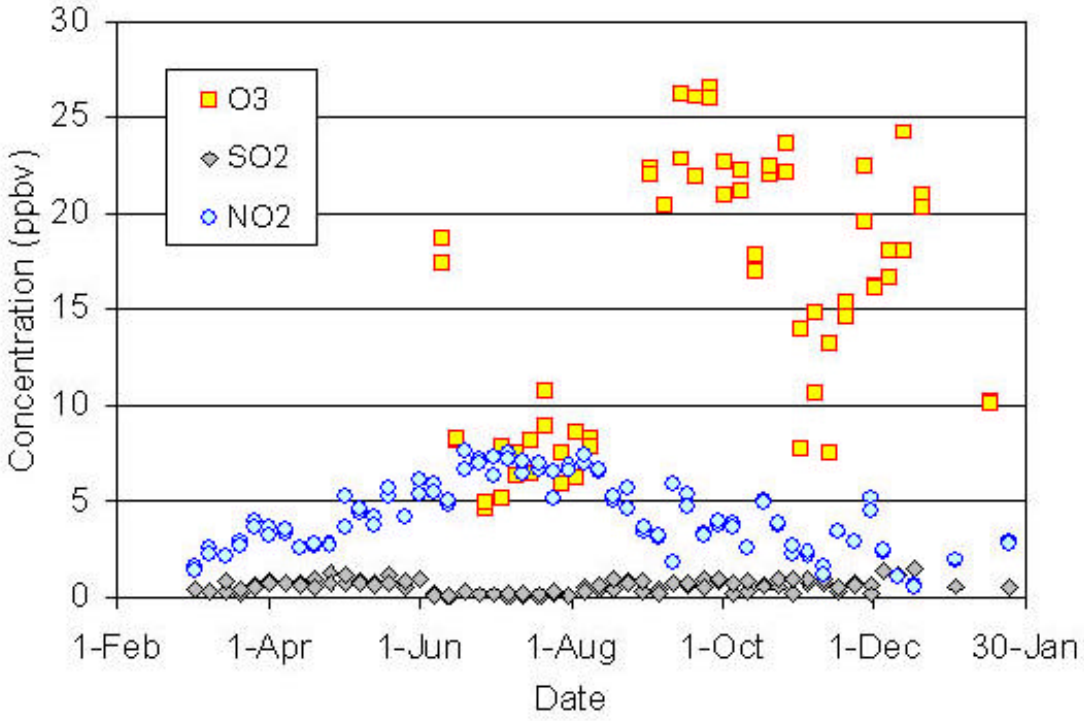


Fig. 13 Time series for concentrations of NO_2, SO_2 and O_3 at the Berrimah site. Data are plotted for the middle of the 6-day sample period.

5. Summary

Initial problems with the TEOM included occasional condensation on the sample filter due to the large difference between ambient and laboratory temperatures. This was overcome by better thermal insulation on the inlet line and auxiliary heating. Any longer-term sampling program should benefit substantially from operation at a more elevated but stabilised laboratory temperature, possibly around 25 ºC. An acoustic noise problem with the sample pump was solved by using a heavily damped and baffled pump box. Other problems included several failures of the flow system in the MicroVol samplers installed at NTU. These appear to have been random, possibly induced by environmental conditions. No ozone samples were collected before 4th June, but ozone and NO_2 sampling continued through until the end of January 2001 to obtain a wet season reference. All data obtained during the study and the extension will be available in electronic form on completion of the analyses.

Aerosol PM10 mass loadings show both a systematic seasonal variation and the presence of a number of enhanced events lasting from one to several days. Mass loadings were minimum in the wet season, when observed values were typically less than 10 µg m^{-3}, increasing significantly to around 20 µg m^{-3} in the dry season. Two main factors contributing to this pattern are expected to be seasonal burning in the surrounding region and increased nocturnal stability reducing ventilation. Even in the absence of additional sources this could be expected to lead to some increase in

loadings. A quite consistent diurnal pattern is evident in the mass loading with a daytime minimum and two maxima. These are a narrow peak at around 08:00 to 09:00 and a broader nocturnal peak. Daytime loadings appear to be similar in the wet and dry season but nocturnal and morning peaks in the dry season have about twice the mass loading as those in the wet season. A number of visually smoky periods were observed during the study. In two of these smoky periods observed PM10 concentrations exceeded the NEPM standard of 50 $\mu g\ m^{-3}$ over a 24-hour period. Such events occurred on six days. The maximum 24-hour PM10 loading was 70 $\mu g\ m^{-3}$ (including the US EPA equivalence correction). The presence of a vehicle contribution to the PM10 mass is evident from weekday – weekend differences in the morning peak (around 09:00) in both the wet and dry seasons.

Overall, very good agreement was observed between mass loadings derived through the TEOM system and samples taken with the same size selective inlet but collected on filters, subsequently dried and subjected to gravimetric determination. This close agreement calls into question the practice of using a US EPA empirical equivalence correction that is "built in" to the TEOM system in Australian conditions. For low mass loadings in Darwin, this "correction" apparently results in a significant overestimation. Mass loadings determined by filter sampler at the NTU Casuarina campus were strongly correlated with those observed at Berrimah, although the distance between the two site locations is about 7 km (the regression analysis gives $r^2 = 0.79$). This points to a largely common variance, or regional pattern, to the temporal variation in mass loading. The PM10 metal concentrations that were determined (lead, iron and zinc) were generally low. The maximum lead concentration of 11.1 ng m^{-3} being well inside the Air NEPM standard of 0.5 $\mu g\ m^{-3}$. The pattern of iron concentrations is consistent with a coarse-mode soil source and some anomalous zinc loadings up to 1 $\mu g\ m^{-3}$ were measured at the Casuarina Campus.

NO_2 concentrations averaged 4.3 ppbv and ranged from 1 ppbv to 8 ppbv. Changes in concentration are consistent with a seasonal increase during the dry season. Concentrations observed in this study are consistent with dry season concentrations previously observed at Charles Point with the expectation of local sources in the present study. SO_2 concentrations throughout the study were very low, having an overall mean of 0.5 ppbv and an rms difference between paired samples of 0.3 ppbv. Neither NO_2 nor SO_2 concentrations suggest reason for concern when judged against the new Air NEPM concentration limits. Ozone concentrations are similar to those previously seen at Charles Point although the cause of relatively lower concentrations in July-August is unclear. The season maximum observed was around 26 ppbv for 6-day samples, considerably short of the Air NEPM 80 ppbv limit for a 4-hour average.

Reference

Gras J.L., 1996. The Perth Haze Study, Final Report. CSIRO Atmospheric Research, Aspendale, Australia.