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# Upper Hunter Valley Particle Characterization Study

2<sup>nd</sup> Progress Report

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# 1 Aim

The objective of the Upper Hunter Valley Particle Characterization Study is to determine the major components and sources of particulate matter (as PM<sub>2.5</sub> – particles with a diameter of less than 2.5 micrometres) in the two main population centres in the Upper Hunter Valley, namely Singleton and Muswellbrook.

This 2<sup>nd</sup> Progress Report presents an update on the project, some preliminary results, and a description of the CSIRO analysis techniques.

## 2 Project description

This project will determine the major components and sources of PM<sub>2.5</sub> in the two main population centres in the Upper Hunter. This will be achieved by collecting PM<sub>2.5</sub> samples in Muswellbrook and Singleton. Because the sources of PM<sub>2.5</sub> and their relative contributions vary from season to season, samples will be collected over one full calendar year (January 2012 to December 2012). Two different types of samplers will be used to collect 24-hour samples every third day. Two samplers are required since different chemical analyses require different filter media. One sampler will collect particles on quartz fibre filters for the analysis of organic carbon, elemental carbon, soluble ions, anhydrous sugars, and pH, while the second sampler will collect particles on stretched Teflon filters for the analysis of elemental composition, and gravimetric mass. A range of analysis techniques will be employed to determine the concentrations in these species. The full chemical composition of all the samples from each site will be analysed using Positive Matrix Factorisation to determine the sources of PM (particulate matter) at the sites and the contribution each source makes to the particulate loading. This analysis will enable the study to provide:

- a description of the contributors to fine particles in the Upper Hunter
- an estimate of which sources are important and their relative contribution to fine particles in the Upper Hunter
- an indication of any weekly and seasonal changes in PM<sub>2.5</sub> particles in the Upper Hunter.

### 2.1 Sampling strategy

Samples are being collected at the two sites on a 1-in-3 day cycle during calendar year 2012. Sampling runs from midnight to midnight with both instruments sampling at the same time.

Timing on the samplers is Eastern Standard Time for the full duration of the study, i.e. the clocks will not be adjusted to daylight savings time.

Field blank samples are collected every 30 days.

Calibration and maintenance of the samplers will be undertaken every 3-6 months. Log sheets and diagnostic outputs from all samplers will flag any instruments problems (such as pump or timing errors), so that they can be addressed quickly during the study.

### 3 Project status

The sampling and shipping for analysis is progressing according to plan. Table 1 lists the status at the end of May of the sample collection and analysis. A teleconference between study participants (OEH, DoH, ANSTO, CSIRO) was held on 24 May to check on progress. There were no significant issues. The study is progressing well.

**Table 1 Status of sample collection and analysis**

SAMPLE DATE	COLLECTED & SHIPPED	CSIRO ANALYSIS STARTED	ANSTO ANALYSIS STARTED	SAMPLE DATE	COLLECTED & SHIPPED	CSIRO ANALYSIS STARTED	ANSTO ANALYSIS STARTED
04/01/2012	✓	✓	✓	19/03/2012	✓	✓	✓
07/01/2012	✓	✓	✓	22/03/2012	✓	✓	✓
10/01/2012	✓	✓	✓	25/03/2012	✓	✓	✓
13/01/2012	✓	✓	✓	28/03/2012	✓	✓	✓
16/01/2012	✓	✓	✓	31/03/2012	✓	✓	✓
19/01/2012	✓	✓	✓	03/04/2012	✓	✓	✓
22/01/2012	✓	✓	✓	06/04/2012	✓	✓	
25/01/2012	✓	✓	✓	09/04/2012	✓	✓	
28/01/2012	✓	✓	✓	12/04/2012	✓	✓	
31/01/2012	✓	✓	✓	15/04/2012	✓	✓	
03/02/2012	✓	✓	✓	18/04/2012	✓	✓	
06/02/2012	✓	✓	✓	21/04/2012	✓	✓	
09/02/2012	✓	✓	✓	24/04/2012	✓	✓	
12/02/2012	✓	✓	✓	27/04/2012	✓	✓	
15/02/2012	✓	✓	✓	30/04/2012	✓	✓	
18/02/2012	✓	✓	✓	03/05/2012	✓		
21/02/2012	✓	✓	✓	06/05/2012	✓		
24/02/2012	✓	✓	✓	09/05/2012	✓		
27/02/2012	✓	✓	✓	12/05/2012	✓		
01/03/2012	✓	✓	✓	15/05/2012	✓		
04/03/2012	✓	✓	✓	18/05/2012	✓		
07/03/2012	✓	✓	✓	21/05/2012	✓		
10/03/2012	✓	✓	✓	24/05/2012	✓		
13/03/2012	✓	✓	✓	27/05/2012	✓		
16/03/2012	✓	✓	✓	30/05/2012	✓		

## 4 Preliminary results

Figure 1 shows the time series of 24-hour average PM<sub>2.5</sub> concentrations measured at Singleton by the OEH Beta Attenuation Mass (BAM) monitor for the first 5½ months of 2012. The red symbols highlight the days when 1-in-3-day sampling was carried out by CSIRO and ANSTO for the current study. It shows that these are representative of the full period, including days with both high and low PM<sub>2.5</sub> concentrations. The equivalent time series for Muswellbrook is given in Figure 2.

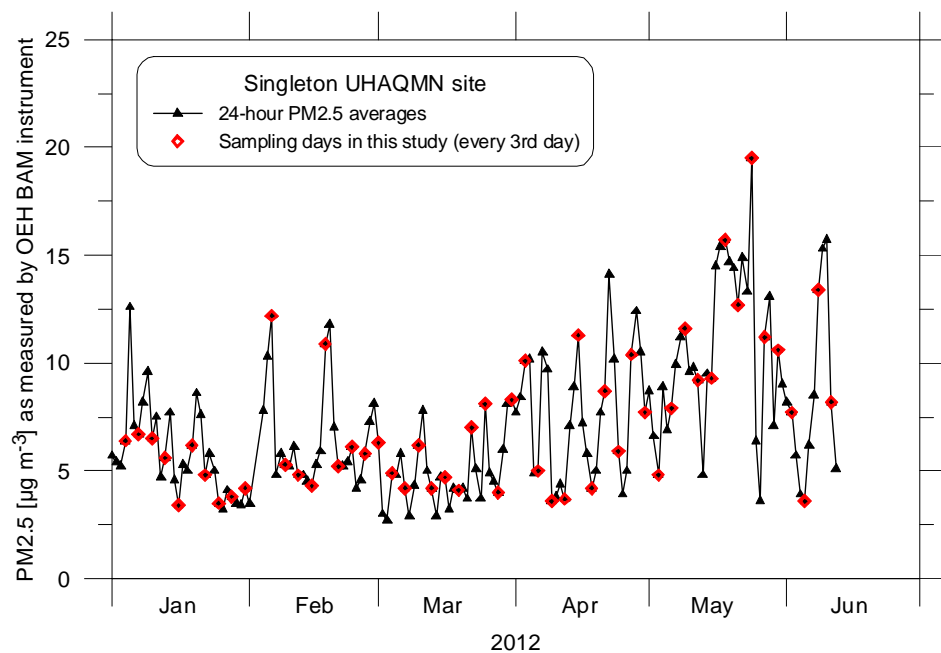


Figure 1 Time series of 24-hour average PM<sub>2.5</sub> concentrations measured by the OEH BAM (Beta Attenuation Mass) monitor at Singleton. The red symbols show the days when sampling for the current study was carried out.

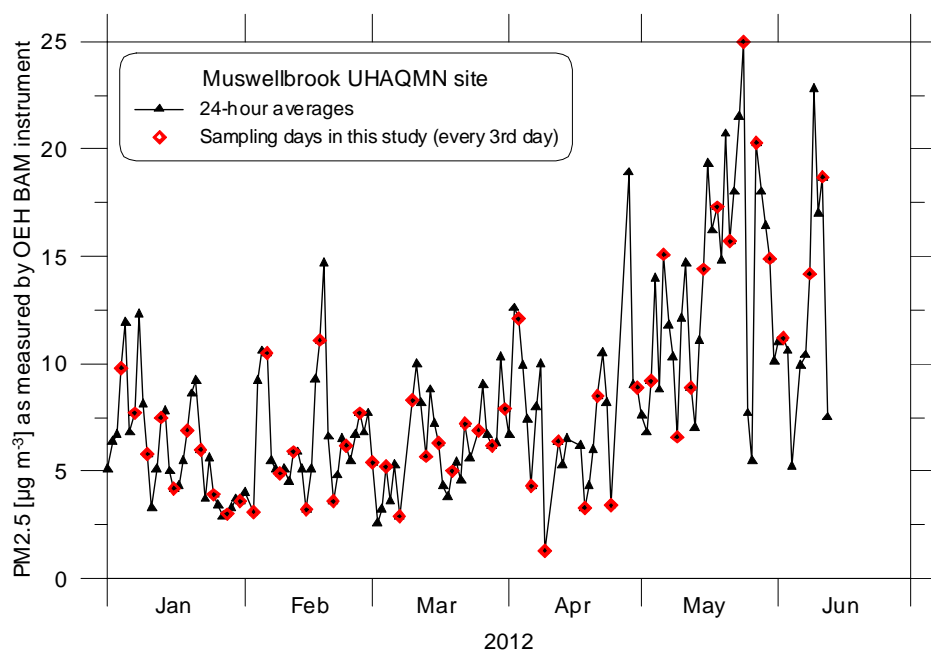
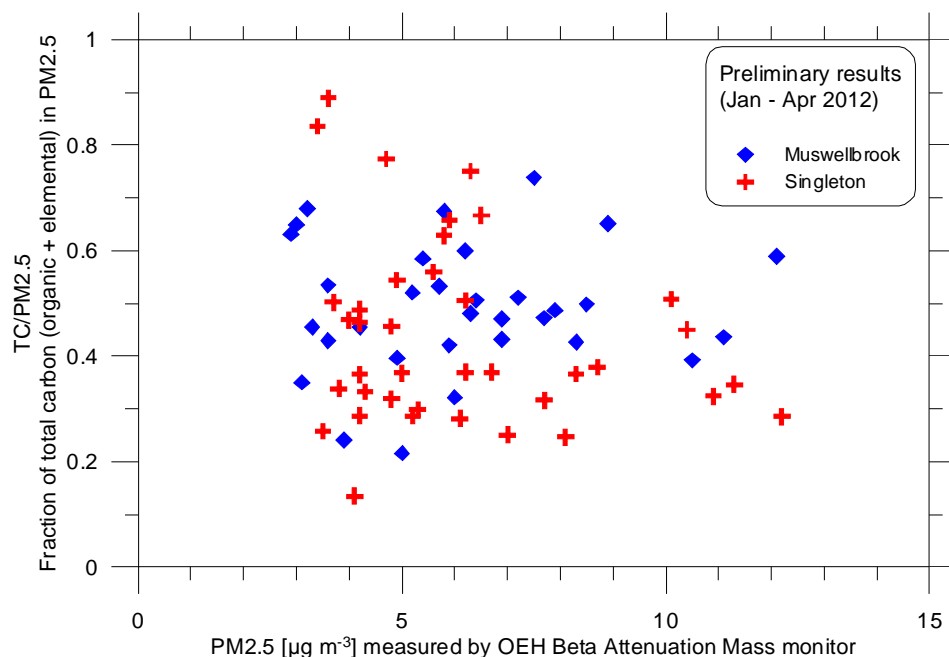


Figure 2 Time series as in previous figure but for Muswellbrook.

Preliminary results for the fraction of PM<sub>2.5</sub> that is carbonaceous (organic + elemental carbon) are shown in Figure 3. The average is about 0.5 at both sites although there is larger scatter at low PM<sub>2.5</sub> concentrations. Elemental carbon (EC) is emitted directly from the incomplete combustion of fossil fuels and biomass. Organic carbon (OC) includes a wide range of chemical species and is introduced to the atmosphere by a variety of processes, including directly during combustion and by chemical reactions of precursor volatile organic carbon gaseous compounds within the atmosphere to produce secondary organic aerosol. The other analyses of the samples in this project (including soluble ion and elemental analysis) aim to identify as much of the remaining fraction of PM<sub>2.5</sub> as possible.

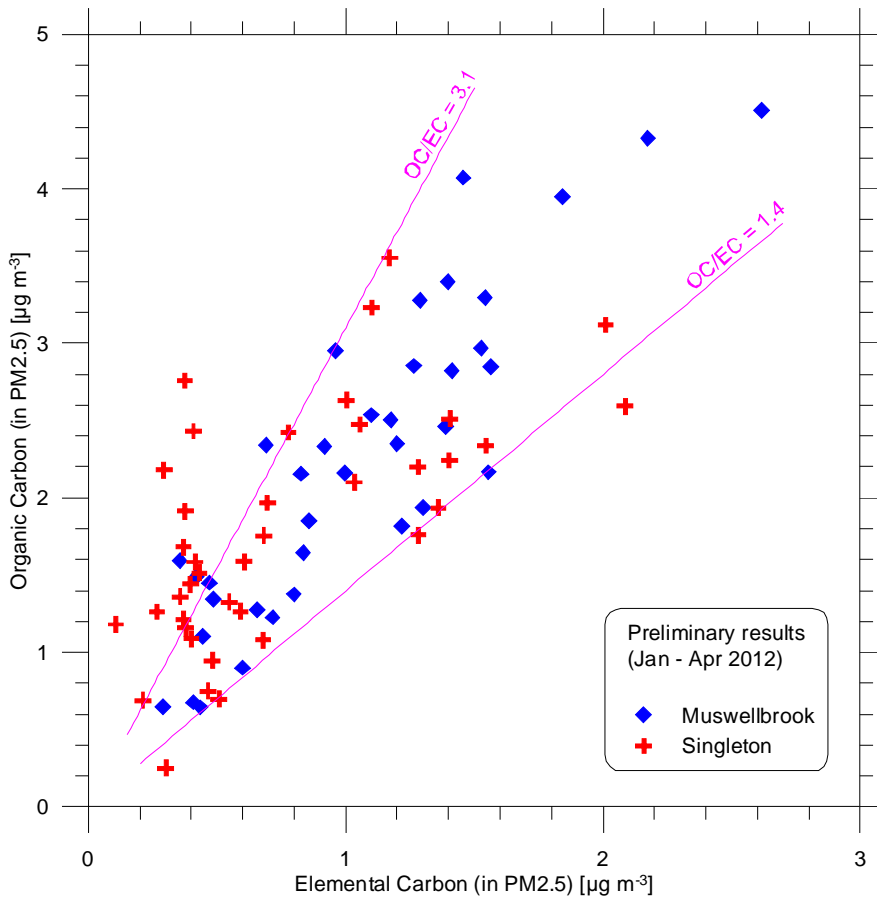


**Figure 3 Fraction of PM<sub>2.5</sub> that is carbonaceous (organic + elemental) versus PM<sub>2.5</sub> concentration from preliminary analysis of high-volume filters.**

The relationship between OC and EC in the PM<sub>2.5</sub> samples is shown in the scatter plot in Figure 4. On most days the ratio lies between 1.4 and 3.1 with an average of 2.0, but there are some days, mainly at Singleton and in January, with much higher ratios. The average of 2.0 in Figure 4 agrees with average values in the literature summarised by Na et al (2004) for sites with average PM<sub>2.5</sub> concentrations below 15 µg m<sup>-3</sup>. Keywood et al. (2007) measured OC/EC ratios in PM<sub>10</sub> in suburban Melbourne between 1.6 and 14.8 and reported a winter average of 4 and a summer average of 6.

The lower bound of about 1.4 in Figure 4 is consistent with PM<sub>2.5</sub> emissions from most sources (such as vehicles, biomass burning, coal combustion, natural gas combustion, paved road dust) having OC/EC ratios greater than 1, some much larger. The scatter in the figure reflects the day-to-day variation in the relative contribution of the various sources to the PM<sub>2.5</sub> loading in the two measurement locations. Further analysis is underway.





**Figure 4 Preliminary results for OC (organic carbon) versus EC (elemental carbon) concentrations in high volume PM2.5 samples.**

The sampling includes field blanks, which are filters that are installed in the sampler and then immediately removed, without any air having been drawn through the filter. This checks the whole filter handling and analyses procedures for possible contamination or artefacts. Table 2 lists the field blank values for OC and EC from the samples analysed to date and shows that the blanks are small compared to the observations in Figure 4.

**Table 2 Results for OC and EC from the field blanks for the High-Volume Sampler**

SITE	DATE	OC BLANK [ $\mu\text{g m}^{-3}$ ]	EC BLANK [ $\mu\text{g m}^{-3}$ ]
Muswellbrook	14/01/2012	0.151	0.00
"	20/02/2012	0.118	0.00
"	14/03/2012	0.163	0.00
"	26/04/2012	0.160	0.00
Singleton	11/01/2012	0.124	0.00
"	20/02/2012	0.149	0.00
"	02/04/2012	0.056	0.00
"	28/04/2012	0.304	0.00
<b>Average blank</b>		<b>0.15 ± 0.07</b>	<b>0.00</b>

## 5 CSIRO analysis techniques

### 5.1 High volume sampler

Samples are collected on the roof-top sampling platform about 4 m above the ground. An Ecotech 3000 High Volume sampler with a PM2.5 size-selective inlet is being used. The ambient flow rate through the inlet is  $67.8 \text{ m}^3 \text{ hr}^{-1}$ . The flow rate is controlled with a mass flow controller, and the ambient temperature and pressure are monitored during sampling so that both the ambient volumetric and standard flow rates can be determined. The flow rate is audited and calibrated using a calibration orifice plate every 3-6 months. Samples are collected on 250 mm x 200 mm quartz membrane filters (Pall-Gelman; prebaked at 600 °C for 4 hours). Samples are collected for 24 hours from midnight to midnight (Australian Eastern Standard time) on a 1-day-in-3-cycle. The filters are stored in a freezer before and after the sampling.

### 5.2 Carbon analysis

Elemental and organic carbon analysis is performed using a DRI Model 2001A Thermal-Optical Carbon Analyzer using the IMPROVE-A temperature protocol. Laser reflectance is used to correct for charring, since reflectance has been shown to be less sensitive to the composition and extent of primary organic carbon. Prior to analysis of filter samples, the sample is baked in an oven to 910 °C for 10 minutes to remove residual carbon. System blank levels are then tested until  $< 0.20 \text{ } \mu\text{g C cm}^{-2}$  is reported (with repeat oven baking if necessary). Twice daily calibration checks are performed to monitor possible catalyst degeneration. The analyser is reported to effectively measure carbon concentrations between 0.05 – 750  $\mu\text{g C cm}^{-2}$ , with uncertainties in OC and EC of  $\pm 10 \%$ .

### 5.3 Ion chromatography

A  $6.25 \text{ cm}^2$  portion of each filter is analysed for major water soluble ions by suppressed ion chromatography (IC) and for anhydrous sugars including levoglucosan by high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD). The filter portions are extracted in 10 ml of 18.2 mΩ de-ionized water. The sample is then preserved using 1% chloroform.

Anion and cation concentrations are determined with a Dionex ICS-3000 reagent free ion chromatograph. Anions are separated using a Dionex AS17c analytical column (4 x 250 mm), an ASRS-300 suppressor and a gradient eluent of 0.75 mM to 35 mM potassium hydroxide. Cations are separated using a Dionex CS12a column (4 x 250 mm), a CSRS-300 suppressor and an isocratic eluent of 20 mM methanesulfonic acid.

Anhydrous sugar concentrations are determined by HPAEC-PAD with a Dionex ICS-3000 reagent free ion chromatograph with electrochemical detection. The electrochemical detector utilizes disposable gold electrodes and is operated in the integrating (pulsed) amperometric mode using the carbohydrate (standard quad) waveform. Anhydrous sugars are separated using a Dionex CarboPac PA 10 analytical column (4 x 250mm) with a gradient eluent of 18 mM to 100 mM potassium hydroxide.

## 6 ANSTO analysis techniques

### 6.1 ANSTO PM2.5 ASP sampler

The ANSTO built ASP sampling unit is a PM2.5 cyclone type sampler based on the US EPA IMPROVE system used across North America in their National Parks air monitoring program. The cyclone operates at a flow rate of 22 L min<sup>-1</sup> using a mass flow controller which results in a PM2.5 particle size cut-off. The particles are collected on a 25mm diameter thin stretched Teflon filter. The filters and the sampling regime are specifically designed for the ANSTO ion beam analysis (IBA) system described below. Samples are collected over the same time period and on the same days as the CSIRO high volume sampler to enable comparison of data.

### 6.2 Black carbon analysis

Black carbon analysis is performed using the Laser Integrated Plate Method (LIPM). Light from a HeNe laser (wavelength 633 nm) is diffused and collimated to give a uniform beam across the Teflon filter. The transmitted signal intensity is measured using a photodiode detector on each filter before and after exposure. The Black Carbon (BC) concentration is estimated from these two transmission measurements assuming a mass absorption coefficient value of 7 m<sup>2</sup> g<sup>-1</sup> for carbon particles. Full details can be found in a publication by Taha et al. (2007).

### 6.3 Ion beam analysis (IBA) techniques

Each filter is analysed non-destructively on the ANSTO STAR 2MV accelerator using nuclear IBA techniques.

The simultaneous IBA techniques are applied here are:

1. Proton induced X-ray emission (PIXE) – for analysis of elements from aluminium to lead in concentrations from a few ng m<sup>-3</sup> upwards.
2. Proton induced gamma-ray emission (PIGE) – for analysis of light elements such as fluorine and sodium in concentrations above 100 ng m<sup>-3</sup>
3. proton elastic scattering analysis (PESA) – for analysis of hydrogen at levels down to 20 ng m<sup>-3</sup>.

A full description of these methods and how they are used can be found on the ANSTO WEB page at [www.ansto.gov.au/environment/iba](http://www.ansto.gov.au/environment/iba) together with key publications describing other fine particle studies at ANSTO.

## References

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