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Lower Hunter Particle Characterisation Study

1st Progress Report

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1 Introduction

The Lower Hunter Particle Characterisation Study (LHPCS) was initiated in 2013 and is being undertaken to provide the EPA and communities in the Lower Hunter with scientific information about the composition and likely sources of fine airborne particles in their local environment. The study represents a collaboration between the NSW Environment Protection Authority (EPA), the NSW Office of Environment and Heritage (OEH), NSW Health, the Commonwealth Scientific and Industrial Research Organisation (CSIRO) and the Australian Nuclear Science and Technology Organisation (ANSTO). Following the establishment of governance arrangements and an independently peer reviewed study design, the one year airborne particle sampling program commenced on 2 March 2014.

This 1st Progress Report outlines the design of the project, the methodology, the commissioning phase and documents the samples collected during the first quarter (Autumn period) of the one year sampling program.

1.1 Study Objectives

The Lower Hunter Particle Characterisation Study aims to determine the composition of $PM_{2.5}$ and PM_{10} air particles, and to identify major sources contributing to $PM_{2.5}$ and PM_{10} concentrations in the region to inform EPA's control programs[1].

Specific sub-objectives are as follows:

- Determine the composition and major sources contributing to $PM_{2.5}$ concentrations at sites representative of regional population exposures.
- Establish airborne particle composition and major sources contributing to $PM_{2.5}$ and PM_{10} concentrations at sites indicative of population exposures in areas near to the Newcastle Port.

1.2 Background

Responding to community concern about particle pollution in the Lower Hunter region of NSW, the Minister for the Environment met with community representatives in April 2013 and gave in-principle support for a study into the major components and sources of fine particles. This particle characterisation study was intended to focus on fine particles as $PM_{2.5}$, which is the metric the World Health Organisation recommends for management of the health risks of particle pollution. On 10 July the Minister announced commencement of the study.

A similar study was completed for the Upper Hunter. The Upper Hunter Valley Particle Characterisation Study was commissioned by the Office of Environment and Heritage (OEH) and NSW Health and carried out by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) and the Australian Nuclear Science and Technology Organisation (ANSTO). This study, successfully completed in September 2013, provided valuable information on the composition and sources of $PM_{2.5}$ concentrations in Muswellbrook and Singleton (Hibberd *et al.*, 2013).

[1] $PM_{2.5}$ and PM_{10} refer to airborne particulate matter with an equivalent aerodynamic diameter of 2.5 micrometres and 10 micrometres respectively.

NSW Environment Protection Authority (EPA) consulted with the Newcastle community on 13 August about the scope of the Lower Hunter particle characterisation study. At the request of the community, the EPA expanded the study scope to include sampling and characterisation of PM_{10} in addition to $PM_{2.5}$.

EPA is the sponsor and primary funder of the study, with the Climate and Atmospheric Sciences (CAS) Branch of OEH directing and managing the study and NSW Health to provide guidance and support for the initiative. For consistency with OEH's ambient air quality monitoring network and the Upper Hunter study, the study will be referred to as the *Lower Hunter Particle Characterisation Study* (LHPCS).

The study is being undertaken as a collaborative project by selected research partners to maximise opportunities for co-investment. CSIRO and ANSTO were chosen as the most suitable research partners based on their expertise in the field, prior experience and demonstrated performance on the Upper Hunter Valley Particle Characterisation Study, and their track-record for co-investment and collaborative research.

1.3 Study Scope and Overview

The study comprises $PM_{2.5}$ sampling at four sites in the Lower Hunter region over a one year period, including two sites representative of wider community exposures in the region (Newcastle and Beresfield) and two sites indicative of public exposures in areas neighbouring the Newcastle Port (Stockton and Mayfield). PM_{10} sampling and analysis is also being undertaken for the Stockton and Mayfield sites in response to community requests that PM_{10} be addressed.

Existing or planned ambient air quality monitoring sites were preferred locations since they allow timely establishment of study sampling sites. These sites also have continuous particulate matter and gaseous monitoring records and meteorological data that can be used during the source apportionment analysis. Selected study sites coincide with the existing OEH Beresfield Air Quality Monitoring (AQM) Station, the OEH Newcastle AQM Station, the Orica Fullerton Street Stockton AQM Station, and the CSIRO Energy Centre AQM Station in Mayfield West. Sampling is being conducted over the period 1 March 2014 to 28 February 2015.

A summary of the monitoring sites, equipment and filter types and sampling schedules for the study is given in Table 1.

Table 1 LHPCS monitoring sites, equipment, filter types and sampling schedule

MONITORING SITE:	EQUIPMENT, SIZE FRACTION AND FILTER TYPE	SAMPLING SCHEDULE
OEH Newcastle AQM Station	Two ANSTO Aerosol Sampling Program (ASP) $PM_{2.5}$ cyclone samplers – one collecting on Teflon filter and one on a quartz filter.	1-in-3 days
OEH Beresfield AQM Station	Two ANSTO ASP $PM_{2.5}$ samplers – one collecting on Teflon filter and one on a quartz filter.	1-in-3 days
CSIRO Energy Centre (Mayfield) AQM Station	One GENT Stacked Filter Unit (SFU) sampling 'coarse' ($PM_{2.5\text{-}10}$) particles on a Nuclepore filter and 'fine' ($PM_{2.5}$) particles on a quartz filter. One ANSTO ASP $PM_{2.5}$ sampler collecting fine particles on a Teflon filter to be relocated to this site from the nearby Steel River AQM station. (Separately funded program, with sampling done by OEH, analysis by ANSTO, and funded by the EPA.)	1-in-3 days
Orica Fullerton Street Stockton AQM Station	One GENT SFU sampling 'coarse' ($PM_{2.5\text{-}10}$) particles on a Nuclepore filter and 'fine' ($PM_{2.5}$) particles on a quartz filter. One ANSTO ASP $PM_{2.5}$ cyclone sampler collecting fine particles on a Teflon filter already in operation at this site. (Separately funded program with sampling and analysis undertaken by ANSTO, funded by Orica).	1-in-3 days

Sample analysis for the $PM_{2.5}$ component will include Ion Beam Analysis (IBA) techniques and Ion Chromatography (IC) on the Teflon filters and organic and elemental carbon (OC/EC) analysis using a DRI Model 2001A Thermal-Optical Carbon Analyzer for the quartz filters.

The use of ANSTO ASP $PM_{2.5}$ cyclone samplers at each of the four sites provides the basis for gravimetric analysis to determine $PM_{2.5}$ concentrations. Combining results from the gravimetric analysis of the coarse and fine fractions from the GENT SFU sampling will allow PM_{10} concentrations to be determined.

Chemical analysis of the $PM_{2.5\text{-}10}$ component will include IBA and IC on the Nuclepore filters in addition to black carbon (BC) being determined through the use of the Laser Integrated Plate Method (LIPM), which is a light absorption technique. Given that organic carbon is primarily in the fine fraction, the use of quartz filters to support OC/EC analysis of the coarse fraction is not required.

The chemical composition of all the samples will subsequently be input into receptor modelling using a mathematical technique called Positive Matrix Factorisation (PMF) to identify factors and the contribution of each factor to the total $PM_{2.5}$ and PM_{10} concentration. The key source of emissions in each factor will be identified using a range of information including source characteristics, wind data and the pattern of seasonal variation in the factor.

2 Study Design

2.1 OEH Regional Air Quality Monitoring Stations

OEH operates air quality monitoring stations at Beresfield, Newcastle and Wallsend to characterise regional air quality. PM_{10}, $PM_{2.5}$, ozone (O_3), oxides of nitrogen (NO_x), sulfur dioxide (SO_2), carbon monoxide (CO) and meteorology (wind speed, wind direction, air temperature and relative humidity) are continuously measured at these stations (Table 2)

Table 2. OEH Monitoring Stations in the Lower Hunter Region

Monitoring Site		MGA X (km)	MGA Y (km)	O_3	NO NO_2 NO_x	PM_{10}	$PM_{2.5}$	SO_2	CO
Beresfield	Francis Greenway High School	374.534	6370.275	✓	✓	✓ (TEOM)	✓ (TEOM/ BAM)(a)	✓	
Newcastle	Athletics Field	383.917	6355.512	✓	✓	✓ (TEOM)	✓ (BAM) (c)	✓	✓
Wallsend	Swimming Pool	375.529	6359.445	✓	✓	✓ (TEOM)	✓ (TEOM/ BAM)(b)	✓	

✓ indicates that the pollutant is monitored at the monitoring station; MGA: Map Grid of Australia (GDA94)
TEOM – tapered element oscillating microbalance (continuous monitoring instrument)
BAM – beta attenuation monitor (continuous monitoring instrument)
(a) Beresfield $PM_{2.5}$ TEOM replaced with a BAM on 24 February 2012
(b) Wallsend $PM_{2.5}$ TEOM replaced with a BAM on 29 November 2012
(c) $PM_{2.5}$ BAM monitoring was commissioned at the Newcastle Air Quality Monitoring Station in December 2013.

Annual time series of PM_{10} and $PM_{2.5}$ for the period October 2012 – September 2013 are shown in Figure 1 and Figure 2. Data are included from the OEH monitoring stations and the site at Stockton run by Orica.

The figures show stronger regional variations in PM_{10} than $PM_{2.5}$ concentrations. The PM_{10} and $PM_{2.5}$ levels recorded at Stockton were generally higher and characterised by some localised peaks not evident at the regional air quality monitoring stations. Peaks in PM_{10} and $PM_{2.5}$ levels recorded at the Stockton monitoring station have been noted to coincide with north-easterly (onshore) airflows and westerly and north-westerly (off-shore) airflows (TAS, 2013).

$PM_{2.5}$ levels measured at the Stockton monitoring station are comparable to levels measured at the OEH Beresfield and Wallsend stations for much of the year, with average and median levels being in the same range. Higher peaks were however observed to occur on occasion at Stockton resulting in 3 days exceeding the national advisory reporting standard of 25µg/m³ compared to 1 day at the OEH stations.

The reasons for higher PM_{10} concentrations and marginally higher $PM_{2.5}$ levels being recorded at the Stockton monitoring station are not currently known. Potential reasons may include: greater marine aerosol (sea salt) contribution due to the proximity of Stockton to the coast; proximity to industrial activity on Kooragang Island; and different configuration or models of monitoring instrumentation in use. Procedures for dealing with negative data and data averaging may also be different to those implemented by OEH. This will be investigated further during the course of the LHPCS.

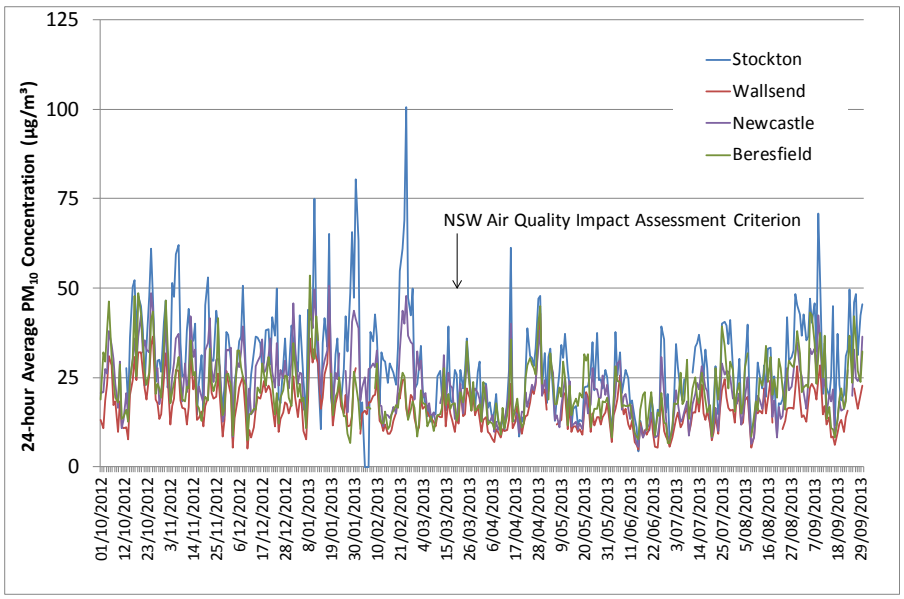

Figure 1 One year of 24-hour average PM_{10} concentrations recorded at the OEH Lower Hunter monitoring stations and the Orica Fullerton Street Stockton monitoring station (Oct 2012 – Sept 2013)

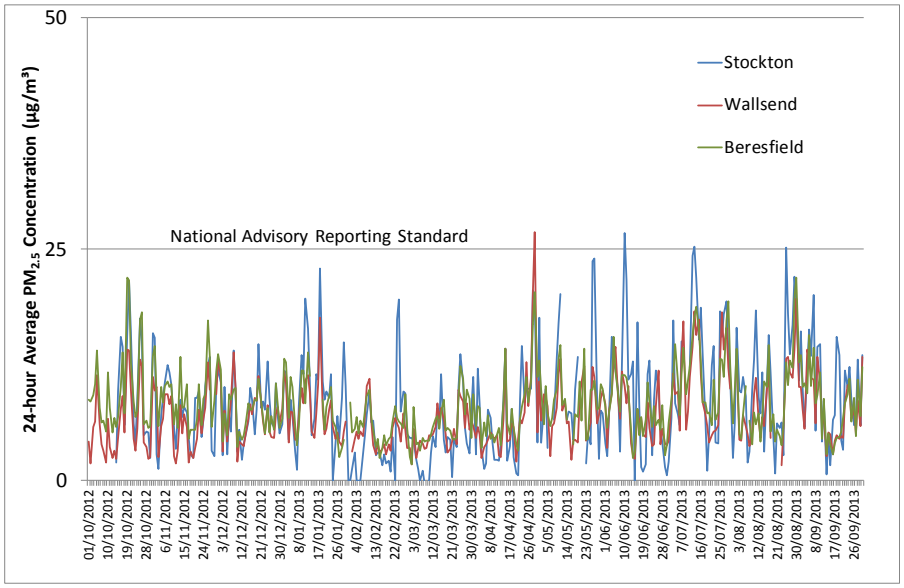

Figure 2 One year of 24-hour average $PM_{2.5}$ concentrations recorded at the OEH Lower Hunter monitoring stations and the Orica Fullerton Street Stockton monitoring station (Oct 2012 – Sept 2013)

2.1.1 COMPOSITION AND SOURCES OF $PM_{2.5}$

ANSTO has been conducting $PM_{2.5}$ characterisation at several east coast sites since 1998, including several sites within NSW and a background (pristine environment) site at Cape Grim in Tasmania. One of the NSW sites is located within the Newcastle LGA at Mayfield. Key sources of long-term average $PM_{2.5}$ concentrations (1998-2008) determined by ANSTO are shown in Figure 3. The following sources were identified: 'Secondary Sulfate' formed from reactions of sulfur dioxide with ammonium in the atmosphere, 'Auto' referring to motor vehicle emissions, 'Smoke' for smoke emissions, 'Sea' representing fresh sea salt, 'Soil' indicating soil dust and 'Industry' emissions. Sources of sulfur dioxide emissions in the region include coal-fired power generation, industry, vehicles and shipping.

The ANSTO ASP $PM_{2.5}$ sampler located at Mayfield was relocated to the nearby Steel River monitoring station in 2012. Sampling and analysis at the Steel River monitoring site is funded by EPA for two years, with sampling being undertaken by OEH and analysis by ANSTO.

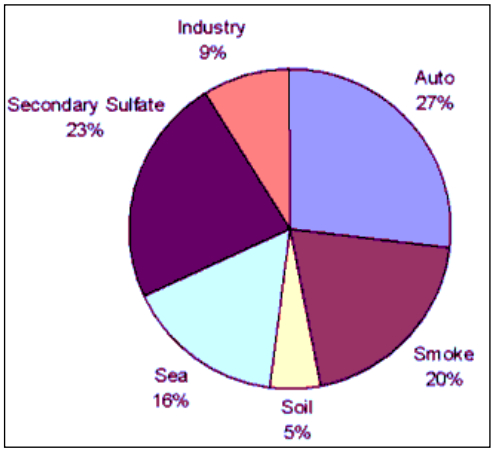

Figure 3 Percentage source contributions to $PM_{2.5}$ concentrations at Mayfield (1998-2009)

2.2 Sampling Sites

Site selection is an important component of the design of the study with emphasis placed on representative sampling locations with characteristics that match the study objectives (refer to Section 1.1). Reference was made to information from emissions inventories, meteorology data, and available air quality monitoring and airborne particle speciation data to determine candidate locations for sampling. This information was used in conjunction with the program objectives to determine appropriate site selection. Furthermore, sampling sites identified to meet the study objectives were selected to coincide with existing ambient air quality monitoring sites where possible. This was to ensure timely establishment of sites and enable reference to longer-term, continuous particulate matter and gaseous monitoring records and to detailed meteorological monitoring records from such sites.

The study sampling sites selected are as follows (Figure 4):

- OEH Newcastle AQM Station (the 'Newcastle site'),
- OEH Beresfield AQM Monitoring Station (the 'Beresfield site'),
- Orica Fullerton Street Stockton AQM Station (the 'Stockton site'), and
- CSIRO Energy Centre Meteorological Monitoring Station in Mayfield (the 'Mayfield site')

The Steel River Industrial Park Air Quality Monitoring Station was initially selected as a potential sampling site near the Newcastle Port. Due however to the proximity of this station to a major road preference was given for the location of the fourth site at CSIRO Energy Centre located in Mayfield West, a short distance from the Steel River monitoring station. Furthermore, the CSIRO Energy Centre site had been selected as one of three preferred sites for the Newcastle Local Air Quality Monitoring Network due to be established during the latter half of 2014. The Orica Fullerton Road Stockton monitoring site is another of the selected sites for this network.

Figure 4 Overview of sampling sites for Lower Hunter Particle Characterisation Study

The manner in which each site contributes to the study objectives being met is explained below and further contextual information on each site provided.

The Newcastle and Beresfield sites were selected as sampling sites representative of more general population exposures within the Lower Hunter. The Newcastle site is located at the Newcastle athletics track, off Smith Street, Newcastle. It is situated in a residential area, next to a school and close to the commercial centre of Newcastle and is at an elevation of 5m. The site is not located in proximity to any major roads, nor any other significant local emission sources. The air quality monitoring at this site was commissioned in November 1992, with PM_{10}, NO, NO_2, NO_x, SO_2, CO and O_3 being continuously measured, in addition to wind speed and direction, air temperature and relative humidity. PM_{10} is measured using a TEOM[2]. Although $PM_{2.5}$ has not previously been measured at the site, a continuous monitor (BAM)[3] was installed at the site in December 2013 prior to the commencement of the sampling program for this study. (BAMs are in use for $PM_{2.5}$ monitoring across the OEH NSW Air Quality Monitoring Network).

The Beresfield site is located in Francis Greenway High School, on Lawson Avenue, Beresfield (Figure 5). It is situated in a residential area north-west of Newcastle and is at an elevation of 14 metres. Air quality monitoring was commissioned at this site in May 1993, with PM_{10}, $PM_{2.5}$, NO, NO_2, NO_x, CO and O_3 being continuously measured, in addition to wind speed and direction, air temperature and relative humidity. SO_2 is not measured at this site. PM_{10} is measured using a TEOM, with $PM_{2.5}$ measured with a BAM. The Beresfield site is located about 300 metres from the main railway line along which diesel-electric trains are in use, including passenger and freight trains and coal trains transporting coal from mines in the Hunter to the Newcastle Port for shipping.

The Newcastle and Beresfield sites were selected over the Wallsend Air Quality Monitoring Station for a number of reasons. Higher PM_{10} concentrations are usually recorded at Newcastle and Beresfield, with higher $PM_{2.5}$ concentrations also observed at Beresfield when compared to Wallsend. Airflow patterns at

[2] Australian Standard AS3580.9.8-2008 Methods for sampling and analysis of ambient air, Method 9.8: Determination of suspended particulate matter – PM_{10} continuous direct mass method using a tapered element oscillating microbalance analyser.

[3] Australian Standard AS3580.9.11-2008 Methods for sampling and analysis of ambient air, Method 9.11: Determination of suspended particulate matter – PM_{10} beta attenuation monitors.

Newcastle and Beresfield are more representative of the greater Lower Hunter region, whereas airflow at Wallsend is significantly influenced by the local terrain. The Newcastle site is in an area characterised by greater population densities compared to Wallsend. The location of the Beresfield site relative to the Newcastle site will support the evaluation of the change in contribution of the sea salt component of $PM_{2.5}$ with increasing distance from the coast.

Figure 5 Beresfield site (rail line indicated by dashed black line)

Figure 6 Locations of the Newcastle, Stockton and Mayfield sites

The Stockton and Mayfield sites were selected to represent residential areas situated in proximity to the Newcastle Port. The Stockton site is situated between the Stockton residential area and the northern arm of the Hunter River, and across the river from industries situated on Kooragang Island (Figure 6). Being situated on a peninsula, the Stockton site is also in close proximity to the ocean. Air quality monitoring was

commissioned at this site in October 2012, with PM_{10}, $PM_{2.5}$, NO_2, NO_x and NH_3 being continuously measured, in addition to wind speed and direction. PM_{10} is continuously measured using a TEOM, with $PM_{2.5}$ measured with a BAM. There is also an existing ANSTO $PM_{2.5}$ ASP sampler located on the roof of the Stockton Air Quality Monitoring Station, which is being used as part of the LHPC Study.

The Mayfield site at CSIRO Energy Centre is situated within the Steel River Estate at 10 Murray Dwyer Circuit, Mayfield West. The site is located south of the south arm of the Hunter River in close proximity to the Mayfield West residential areas and industrial operations at the Newcastle Port including the coal terminals on Kooragang Island. Although no air quality monitoring has previously been undertaken at the site, a meteorological station was in operation and the site is situated near to the Steel River Air Quality Monitoring Station at which TSP and PM_{10} is sampled on a 1-in-6 day schedule and SO_2 and NO_x continuously monitored. The existing ANSTO $PM_{2.5}$ ASP sampler located at the Steel River monitoring station was relocated to the CSIRO Energy Centre site for inclusion in the LHPC Study.

The CSIRO Energy Centre site in Mayfield and the Stockton Air Quality Monitoring Station have been selected as locations for the establishment of air quality monitoring stations as part of the planned Newcastle Local Air Quality Monitoring Network being established during the latter half of 2014.

2.3 Sampling Equipment

Two types of samplers were selected for use in the study:

- GENT Stacked Filter Units (SFUs) sampling 'coarse' ($PM_{2.5-10}$) and 'fine' ($PM_{2.5}$) particles
- ANSTO's low volume Aerosol Sampling Program (ASP) $PM_{2.5}$ cyclone samplers

GENT Stacked Filter Units

The GENT stacked filter unit (SFU) sampler (Figure 7) is capable of collecting air particulate matter samples in coarse (2.5–10 µm) and fine (<2.5 µm) size fractions. The SFU includes a holder for two sequential filters. The initial filter is an 8 µm pore 47 mm Nuclepore filter and the second filter is an 0.4 µm pore Nuclepore filter. At a flow rate of 16 litres/minute, the SFU acts as a dichotomous sampler, with the flow through the 8 µm pores resulting in the collection of ~2.2 µm particles with 50% efficiency. The <2.2 µm particles are then collected on the 0.4 µm filter (Hopke *et al.*, 1997).

GENT SFU samplers have been used to support ion beam analysis and particle characterisation in a number of published studies (Cohen *et al.*, 2004, 2012; Santoso *et al.*, 2008).

ASP $PM_{2.5}$ Sampler

The ANSTO built ASP sampling unit (Figure 7) is a $PM_{2.5}$ cyclone type sampler based on the US EPA IMPROVE system used across North America in their National Parks air monitoring program (Cohen *et al.,* 1996; Malm *et al.*, 1994). The unit was specifically designed for use with multi-elemental ion bean analysis methods. The cyclone operates at a flow rate of 21 L min^{-1} using a mass flow controller which results in a 2.5 µm particle size cut-off. The particles are most typically collected on a 25mm diameter thin stretched Teflon filter masked to 17 mm diameter to increase sample thickness and improve deposit uniformity.

ANSTO ASP $PM_{2.5}$ samplers are currently being used by ANSTO for the on-going Australian East Coast particle sampling and characterisation project (Section 2.1.1) and were successfully used in the Upper Hunter Valley Particle Characterisation Study (Hibberd *et al.*, 2013).

Figure 8 and Figure 9 show the Newcastle monitoring station before and after installation of the ASP samplers, and Figure 10 shows the GENT and ASP samplers on the roof of the Stockton Air Quality Monitoring Station, with a view across the river from this site to Kooragang Island.

Figure 7 Left – GENT sampler installed at the Mayfield site; Right – Detail of an ASP sampler at Beresfield

Figure 8 OEH Newcastle Air Quality Monitoring Station before installation of the LHPCS samplers

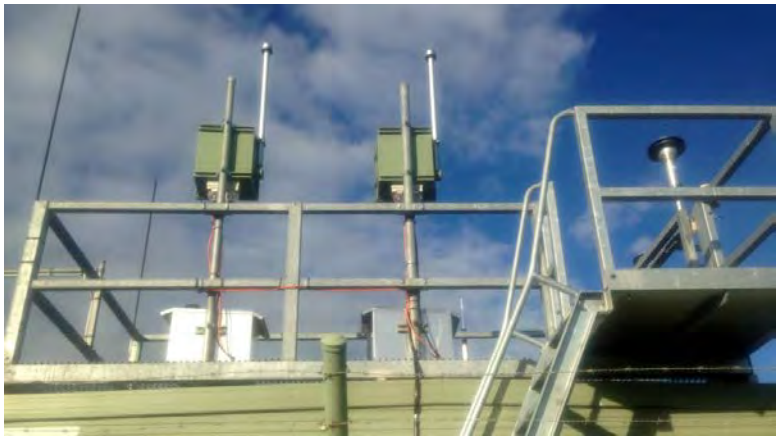

Figure 9 ASP samplers on the roof of the OEH Newcastle Air Quality Monitoring Station

Figure 10 View across the river to Kooragang Island from the Stockton Air Quality Monitoring Station with the GENT and ASP samplers visible on the roof of the station

Filter Types

Appropriate filter types were selected based on the analytical techniques to be applied in the study, which include Ion Beam Analysis (IBA) techniques, Ion Chromatography (IC), organic and elemental carbon (OC/EC) analysis using a DRI Model 2001A Thermal-Optical Carbon Analyzer, and the Laser Integrated Plate Method (LIPM) for measuring black carbon (BC). Teflon and Nuclepore filters are appropriate for IBA, LIPM and IC analysis, whereas quartz filters are required for OC/EC with the DRI Analyser.

Samplers and types of filters being used in the LHPCS are as follows:

- Two purposely installed ANSTO ASP $PM_{2.5}$ cyclone samplers at the **Newcastle site**, one collecting particles on a Teflon filter (for IBA, LIPM and IC analysis) and the other on a quartz filter (for EC/OC analysis).
- Two purposely installed ANSTO ASP $PM_{2.5}$ cyclone samplers at the **Beresfield site**, one collecting particles on a Teflon filter (for IBA, LIPM and IC analysis) and the other on a quartz filter (for EC/OC analysis).
- One GENT SFU at the **Mayfield site**, collecting $PM_{2.5\text{-}10}$ particles on a Nuclepore filter (for IBA, LIPM and IC analysis) and $PM_{2.5}$ particles on a quartz filter (for EC/OC analysis).
- Relocation of the existing ANSTO ASP $PM_{2.5}$ sampler collecting particles on Teflon filters from the Steel River monitoring station to the **Mayfield site**. Results from the IBA conducted on these filters by ANSTO (funded by EPA) will be integrated into the study, with further (IC) analysis conducted on the filters by CSIRO.
- One GENT SFU at the **Stockton site**, collecting $PM_{2.5\text{-}10}$ particles on a Nuclepore filter (for IBA, LIPM and IC analysis) and $PM_{2.5}$ particles on a quartz filter (for EC/OC analysis).
- Integration of results from the IBA conducted on the ASP $PM_{2.5}$ sampler Teflon filters from the **Stockton site** filters by ANSTO (funded by Orica) into the study, with further (IC) analysis conducted on the filters by CSIRO.

Field Blanks

Quartz field blanks are being used every 6 days for the ASP $PM_{2.5}$ sampler and every 12 days for the GENT stacked filter, with the blanked values propagated in the analysis.

2.4 Analysis Techniques

The same analytical techniques as were implemented during the Upper Hunter Valley Particle Characterisation Study are planned for implementation within the LHPCS. Descriptions of these techniques were given by Hibberd *et al.* (2013) and are summarised in the following sections.

2.4.1 Mass measurements

The mass of $PM_{2.5}$ on the sample filters will be determined gravimetrically. The filters will be weighed before and after the sampling period to determine the particulate mass collected and then divided by the total volume of air that passed through the filter to obtain the $PM_{2.5}$ concentration. The weighing will be performed under controlled temperature (22 ± 2°C) and relative humidity conditions. Relative humidity conditions of 50±10% were specified for use in the Upper Hunter Valley Fine Particle Characterisation Study. However, the contribution of liquid water to the mass on the filter is expected to be higher in the LHPCS than was evident for the Upper Hunter Valley Fine Particle Characterisation Study due to the proximity of the LHPCS sampling sites to the coast. The study team will therefore investigate whether weighing should be done at lower relative humidity, and will record the actual relative humidity in the weighing environment. The contribution of liquid water will therefore be more explicitly investigated and reported in the study report. The use of ANSTO ASP $PM_{2.5}$ cyclone samplers at each of the four sites provides the basis for gravimetric analysis to determine $PM_{2.5}$ concentrations. Combining results from the gravimetric analysis of the coarse and fine fractions from the GENT SFU sampling will allow PM_{10} concentrations to be determined. All filters will be neutralized prior to being weighed.

2.4.2 Ion beam analysis (IBA) techniques

The Teflon filters will be analysed non-destructively on the ANSTO STAR 2MV accelerator using nuclear IBA techniques including:

- Proton induced X-ray emission (PIXE) – for analysis of elements from aluminium to lead in concentrations from a few ng/m³ upwards, as described in Cohen (1993).
- Proton induced gamma-ray emission (PIGE) – for analysis of light elements such as fluorine and sodium in concentrations above 100 ng/m³, as described in Cohen (1998).
- Proton elastic scattering analysis (PESA) – for analysis of hydrogen at levels down to 20ng/m³, as described in Cohen (1996).

The elements whose concentrations are to be determined are:

Hydrogen (H)	Chromium (Cr)
Sodium (Na)	Manganese (Mn)
Aluminium (Al)	Iron (Fe)
Silicon (Si)	Cobalt (Co)
Phosphorous (P)	Nickel (Ni)
Sulfur (S)	Copper (Cu)
Chlorine (Cl)	Zinc (Zn)
Potassium (K)	Selenium (Se)
Calcium (Ca)	Bromine (Br)
Titanium (Ti)	Lead (Pb)
Vanadium (V)	

2.4.3 Ion chromatography

IC analysis will be conducted by CSIRO. A 6.25 cm² portion of each quartz filter will be 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 will be extracted in 10 ml of 18.2 mΩ de-ionized water. The sample will then be preserved using 1% chloroform.

Teflon filters will also be analysed by CSIRO for water soluble ions by IC after IBA has been carried out by ANSTO. The Teflon filters will first be wetted with 100 µl of methanol, extracted in 5 ml of 18.2 mΩ de-ionized water and then preserved with 1% chloroform.

Anion and cation concentrations will be determined with a Dionex ICS-3000 reagent free ion chromatograph (Hibberd *et al.*, 2013). Anions will be separated using a Dionex AS17c analytical column (2 x 250 mm), an ASRS-300 suppressor and a gradient eluent of 0.75 mM to 35 mM potassium hydroxide. Cations will be separated using a Dionex CS12a column (2 x 250 mm), a CSRS-300 suppressor and an isocratic eluent of 20 mM methanesulfonic acid.

Anhydrous sugar concentrations will be determined by HPAEC-PAD with a Dionex ICS-3000 chromatograph with electrochemical detection (Hibberd *et al.*, 2013). 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 MA 1 analytical column (4 x 250mm) with a gradient eluent of 300 mM to 550 mM sodium hydroxide.

The species whose concentrations are to be determined are:

Chloride (Cl^-)	Methanosulfonate (MSA^-)
Nitrate (NO_3^-)	Sodium (Na^+)
Sulfate (SO_4^{2-})	Ammonium (NH_4^+)
Oxalate ($C_2O_4^-$)	Magnesium (Mg^{2+})
Formate ($HCOO^-$)	Calcium ($Ca^{2+)}$
Acetate (CH_3COO^-)	Potassium (K^+)
Phosphate (PO_4^{3-})	Levoglucosan ($C_6H_{10}O_5$, an anhydrous sugar - woodsmoke tracer)

Levoglucosan and mannosan are unique tracers for the combustion of cellulose found in trees and plants (Iinuma *et al.*, 2007). The ratio of levoglucosan to mannosan is an indication of the type of wood combusted. Potential limitations in the use of levoglucosan as a marker species for wood smoke burning arise from its limited atmospheric lifetime (Hoffmann *et al.*, 2009; Hennigan *et al*., 2010). Options to include other biomass markers will therefore be investigated for inclusion in the chemical analysis.

2.4.4 Organic carbon (OC) and Elemental carbon (EC) analysis

Different sources emit different types of carbon. Thus the carbon on the samples will be analysed to obtain the two separate components – organic carbon and elemental carbon. The latter is approximately equivalent to black carbon, which is measured using light absorption techniques (US EPA, 2012). The sources of carbon (OC and EC) include a wide range of types of combustion.

Elemental and organic carbon analysis will be performed using a DRI Model 2001A Thermal-Optical Carbon Analyzer following the IMPROVE-A temperature protocol (Chow et al., 2007). Laser reflectance will be used to correct for charring, since reflectance has been shown to be less sensitive to the composition and extent of primary organic carbon (Hibberd *et al.*, 2013). 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 will then be tested until < 0.20 µg C cm^{-2} is reported (with repeat oven baking if necessary). Twice daily calibration checks will be

performed to monitor possible catalyst degeneration. The analyser is reported to effectively measure carbon concentrations between 0.05 – 750 µg C cm^{-2}, with uncertainties in OC and EC of ± 10% (Hibberd *et al.*, 2013).

Use of the IMPROVE-A temperature protocol provides four OC fractions, namely OC1 at 140°C, OC2 at 280°C, OC3 at 480°C, and OC4 at 580°C. As in the Upper Hunter Valley Fine Particle Characterisation Study, the variations in the proportions of the OC fractions will assist in ascribing Positive Matrix Factorisation factors for both local domestic woodheater smoke and emissions from more distant planned burns and bushfires, the latter having much lower levoglucosan levels.

2.4.5 Black carbon (BC) analysis

Chemical analysis of the coarse ($PM_{2.5-10}$) component measured at the Mayfield and Stockton sites will include IBA and IC on the Teflon filters in addition to black carbon being determined using the Laser Integrated Plate Method (LIPM). (Given that organic carbon is primarily in the fine fraction, the use of quartz filters to support OC/EC analysis is not required for the coarse fraction.)

For LIPM measurements, 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 BC concentration is estimated from these two transmission measurements assuming a mass absorption coefficient value of 7 m^2 g^{-1} for carbon particles. Full details can be found in a publication by Taha *et al.* (2007).

2.4.6 Positive matrix factorisation (PMF) and Source Apportionment

The chemical composition of all the samples will be input into receptor modelling using a mathematical technique called Positive Matrix Factorisation (PMF) to identify factors and the contribution of each factor to the total $PM_{2.5}$ and PM_{10} concentration.

PMF is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices – factor contributions and factor profiles. These factors are then interpreted to determine what sources are represented by these factors. This is done using measured source profile information, wind direction analysis, and emissions inventories (Norris *et al*., 2008). The method is described in greater detail by Paatero (1997). PMF is widely used in air pollution studies for source apportionment, including in Australia (e.g. Hibberd *et al.*, 2013; Chan *et al.*, 2008; Cohen *et al.*, 2011; Cohen *et al.*, 2012; Belis *et al.*, 2013).

In the study, the chemical composition data of all samples from each site will be analysed collaboratively by CSIRO and ANSTO using PMF. Both the US EPA developed software package EPA PMF 3.0 (Norris *et al*., 2008) and the PMF2 DOS version (Paatero, 2004a, b) will be used. Once factors are obtained, further analysis will be undertaken to identify the sources in each factor. This uses information about known sources and other knowledge of atmospheric chemistry as well as wind sector and seasonal analysis to identify the most likely source of emissions for each factor and hence the contribution that each source makes to the total $PM_{2.5}$ or PM_{10} concentrations. Previous studies have shown that the more robust results are derived by including all the samples in the PMF analysis and using the time series of the factor contributions to assist in source identification (Hibberd *et al.*, 2013; Cohen *et al.*, 2011; Cohen *et al.*, 2012).

2.5 Supporting Analysis

2.5.1 Emission Events Log and Air Quality Monitoring Data Analysis

An emissions events log is being maintained recording any significant local releases or regional emission events (e.g. large bushfires and dust storms) observed during the sampling period for use during the source apportionment analysis.

Trend analysis will be conducted on the continuously monitored PM_{10}, $PM_{2.5}$ and gaseous pollutant concentrations from the Newcastle, Beresfield, Wallsend and Stockton monitoring stations (and from other monitoring stations with available data). Meteorological data recorded at the monitoring stations will similarly be subject to detailed analysis to support source apportionment.

2.5.2 Case Study Analysis

In addition to the above PMF analysis and source apportionment, several case study days will be identified from the data including both high $PM_{2.5}$ and PM_{10} days (with the decision on the days to be made in discussion with the Project Management Team). These case study days will be the subject of further detailed analysis using a number of techniques with the aim of reducing uncertainties in the source apportionment and, for some high PM_{10} days, to identify the causes of peak events. The techniques will include chemical transport modelling using CSIRO's CTM (Chemical Transport Model) for the case study days to assist in understanding the origins of the air masses generating secondary particles identified in the PMF.

Event analysis will also include material balance comparisons, including comparisons between co-measured species, and predicted versus measured species (e.g. ammonium). Ion balances will be constructed to verify the data and determine the degree of neutralisation of acid aerosols by ammonia.

2.5.3 Wind sector analysis

To determine the directions from the sampling site which are likely to include the sources of the factors (identified in the PMF), the conditional probability function (CPF) technique will be used. This couples the source contribution estimates from PMF with the wind directions measured at the sampling site (e.g. Kim and Hopke, 2004). The CPF estimates the probability that a given source contribution from a given wind direction will exceed a pre-determined criterion. It is defined as

$$CPF = m\Delta\theta/n\Delta\theta \qquad (1)$$

where $m_{\Delta\theta}$ is the number of occurrences from wind sector $\Delta\theta$ (typically about 20°) that exceed the criterion and $n_{\Delta\theta}$ is the total number of data from the same wind sector. Wind speeds below 0.5 m s^{-1} are excluded from the analysis as they are considered to represent calm conditions.

Daily fractional mass contribution from each source will be used rather than the absolute source contribution. The criterion is typically set as the upper 25^{th} percentile of the fractional contribution from each source. The same daily fraction is assigned to each hour of a given day to pair with the hourly wind data. This is a limitation of the method due to the sampling being 24-hour samples. However, using 24-hour average wind directions to match the sampling period for the PM produces poorer results from the CPF analysis than using the method outlined above because of the information lost by averaging the wind data.

3 Report on March-May 2014 Sampling

3.1 Commissioning

Monthly meetings of the Project Management Team have been held since October 2013 to coordinate design and roll-out of the study. These monthly meetings will continue until the study is finalised.

The purpose and design of the study was presented to the independent Air Pollution Expert Advisory Committee in December 2013. The study design was peer reviewed by two independent experts prior to being finalised and the one year sampling program initiated.

The sampler installation was undertaken during February 2014 with some test samples collected from 22 February 2014 and all samplers operating for the commencement of the study on 2 March 2014.

An initial audit of procedures, documentation, instrument siting, and filter changing was undertaken on 24 March 2014. Overall it was concluded that the procedures reviewed were fit for purpose with minor amendments to sampler placement recommended in some cases to ensure compliance with Australian Standards. The recommendations from the audit report have been implemented, principally clarifications and correction of typographical errors in the documentation of procedures for filter collection and shipping, and small adjustments to sampler positioning at Stockton.

Power outages and timing errors led to some samples at Mayfield and Stockton not being collected in mid-March, with resultant sample losses indicated in the subsequent subsection.

There have been no significant issues with filter shipping. Analysis of filter samples has commenced but no results are ready to be reported.

A briefing of the Newcastle Community Consultative Committee on the Environment (NCCCE) on the study was held on 9 April 2014, with study progress reported to the NCCCE on a monthly basis.

3.2 Sampling Report

The LHPCS aims to achieve a 95% valid sample collection rate. Table 3 lists the status of the sample collection for the first 3 months of the study, with the sample collection rates achieved for each sampler-filter train noted. The missing samples were due to power outages and timing errors as noted above. Contingency measures have since been implemented to reduce the potential for these disruptions so as to maximise sample collection rates.

Overall, a sample collection rate of 98% was achieved during the March to May 2014 (Autumn) period.

Table 3 Status of sample collection

SITE	BERESFIELD $PM_{2.5}$		NEWCASTLE $PM_{2.5}$		MAYFIELD PM_{COARSE} & $PM_{2.5}$			STOCKTON PM_{COARSE} & $PM_{2.5}$		
SAMPLE DATE	ASP TEFLON	ASP QUARTZ	ASP TEFLON	ASP QUARTZ	ASP TEFLON $PM_{2.5}$	GENT NUCLEPORE PM_{COARSE}	GENT QUARTZ $PM_{2.5}$	ASP TEFLON $PM_{2.5}$	GENT NUCLEPORE PM_{COARSE}	GENT QUARTZ $PM_{2.5}$
02/03/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
05/03/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
08/03/2014	✓	✓	✓	✓	✓	✓	✓	×	✓	✓
11/03/2014	✓	✓	✓	✓	✓	✓	✓	×	✓	✓
14/03/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
17/03/2014	✓	✓	✓	✓	×	×	×	✓	✓	✓
20/03/2014	✓	✓	✓	✓	×	✓	✓	✓	✓	✓
23/03/2014	✓	✓	✓	✓	×	✓	✓	✓	✓	✓
26/03/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
29/03/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
01/04/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
04/04/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
07/04/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
10/04/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
13/04/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
16/04/2014	✓ C	✓ C	✓ C	✓ C	✓ C	✓ C	✓ C	✓ C	✓ C	✓ C
19/04/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
22/04/2014	✓	✓ C	✓	✓ C	✓	✓ C	✓ C	✓	✓ C	✓ C
25/04/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
28/04/2014	✓	✓ C	✓	✓ C	✓	✓	✓	✓	✓	✓
01/05/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
04/05/2014	✓	✓ C	✓	✓ C	✓	✓ C	✓ C	✓	✓ C	✓ C
07/05/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
10/05/2014	✓	✓ C	✓	✓ C	✓	✓	✓	✓	✓	✓
13/05/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
16/05/2014	✓ C	✓ C	✓ C	✓ C	✓ C	✓ C	✓	✓ C	✓.C	✓
19/05/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
22/05/2014	✓	✓ C	✓	✓ C	✓	✓	✓ C	✓	✓	✓.C
25/05/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
28/05/2014	✓	✓ C	✓	✓ C	✓	✓	✓ C	✓	✓	✓ C
31/05/2014	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Sample collection rate	100%	100%	100%	100%	90%	97%	97%	94%	100%	100%

Notes: ✓ - Filter sample collected; × - Filter sample not collected; C – control (unexposed) filter included

3.3 Daily PM Results from the Monitoring Sites

Figure 11 shows the time series of 24-hour average $PM_{2.5}$ concentrations measured at the Newcastle, Beresfield and Stockton monitoring sites using the standard TEOM and BAM equipment for the first three months of the study. The green bars highlight the days when 1-in-3-day sampling was carried out for the current study. It shows that these are representative of the full period, including days with both high and low concentrations. Stockton data for the first half of March has not been included because of quality assurance issues (the data showed negative concentrations). The figure also shows data quality issues at Stockton in the first half of April with significantly lower values than at the other two sites.

The average $PM_{2.5}$ concentrations for the 2½ months from mid-March (period with data from all sites) were 7.1 µg m^{-3} at Newcastle, 6.8 µg m^{-3} at Beresfield, and 7.8 µg m^{-3} at Stockton.

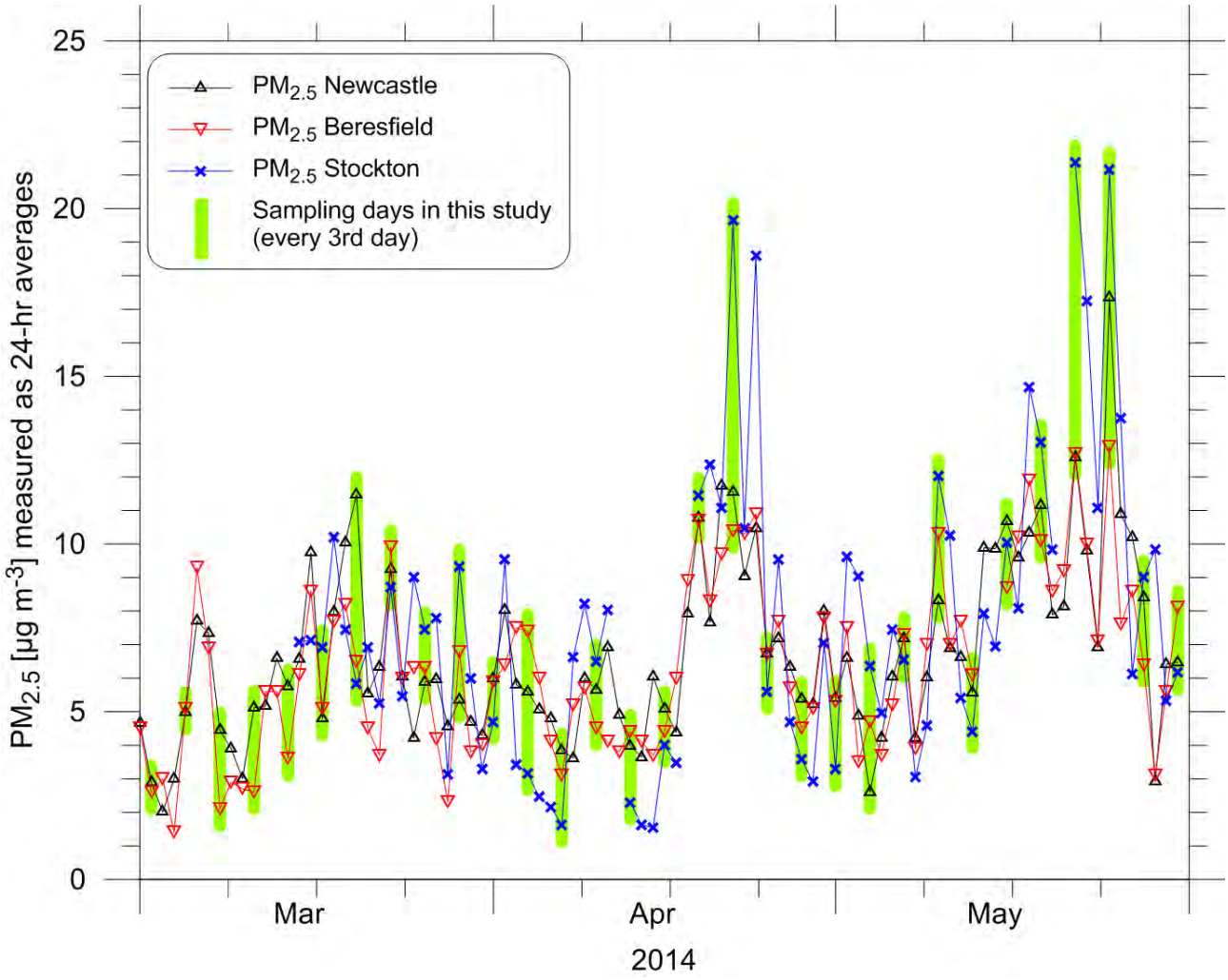

Figure 11 Time series of 24-hour average $PM_{2.5}$ concentrations measured at the Newcastle, Beresfield and Stockton sites using the standard BAM and TEOM equipment. The green bars show the days when sampling for the current study was carried out.

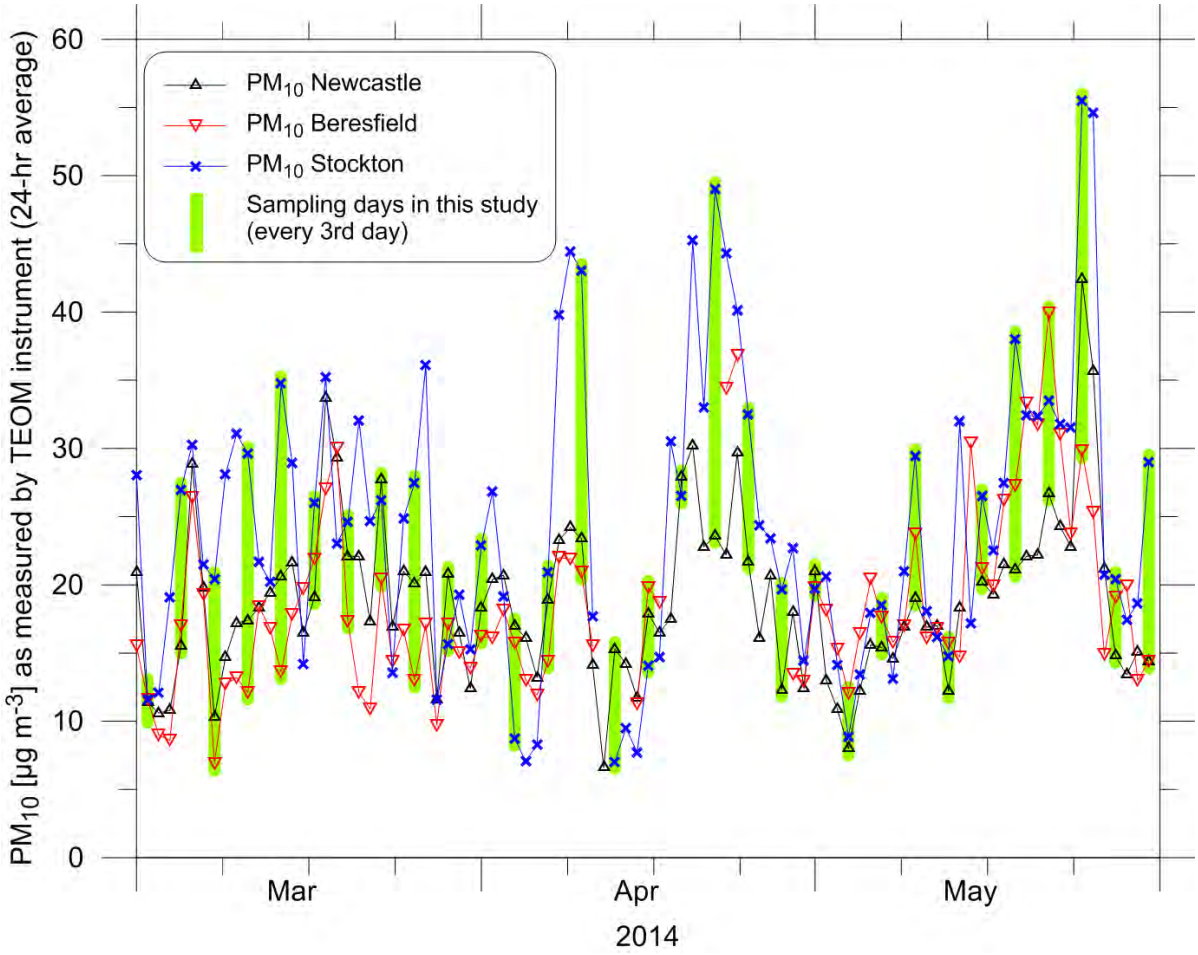

Figure 12 Time series of 24-hour average PM_{10} concentrations measured at the Newcastle, Beresfield and Stockton sites using the standard TEOM equipment. The green bars show the days when sampling for the current study was carried out.

Figure 12 shows the equivalent results for PM_{10} concentrations. As above, the green bars highlight the days when 1-in-3-day sampling was carried out for the current study, and show that these are representative of the full period, including days with both high and low concentrations.

The average PM_{10} concentrations for March –May were 18.9 µg m^{-3} at Newcastle, 18.6 µg m^{-3} at Beresfield, and 24.4 µg m^{-3} at Stockton. On most days the PM_{10} concentration at Stockton was higher than at the other two sites.

3.4 Conclusion

The sampling conducted during the March to May 2014 period was successfully undertaken and will support chemical analysis and source apportionment for the Autumn season. This is concluded based on the findings of the initial audit undertaken following commissioning of the sampling program, the overall sample collection rate of 98% achieved, and sampling days coinciding with low, high and average ambient particle concentration measurements.

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