

Lower Hunter Particle Characterisation Study Supplementary Report – Quantifying the Coal Particle Component of Airborne Particulate Matter at Stockton

FINAL

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Executive summary

This study quantifies the proportion and mass of **coal particles** in airborne particulate matter (PM) measured at the NSW Office of Environment and Heritage (OEH) Stockton Air Quality Monitoring Station (AQMS) in winter 2015. The aim of the study was to determine an upper limit on the amount of coal particles in the PM, by selecting for analysis sample days when the meteorology was conducive to coal particles being generated and transported to the Stockton AQMS from coal operations on Kooragang Island and adjacent areas at the Port of Newcastle.

The study uses CSIRO's Coal Grain Analysis (CGA) system, which is able to analyse dust samples and provide quantitative detail about **insoluble particles**, specifically coal and non-coal particles as well as their size in a range from about 1–50 micrometres (μm). CGA does not provide any information about soluble particles such as sea salt, because these are dissolved and washed out in the CGA sample preparation procedure. However, the mass of soluble particles in each sample was determined.

Total suspended particle (TSP) samples were collected at the Stockton AQMS daily from 15 June to 17 September 2015 as 24-hour samples. Nine samples were selected for analysis. These were from days most likely to detect coal particles being generated and blown towards the Stockton AQMS. They were days with elevated TSP concentrations and strong north-westerly winds which put the sampling site downwind of the coal operations.

The average **coal particle mass as a proportion of total (soluble + insoluble) particles** is 12% in TSP, 10% in PM_{1-10} and 1.8% in $\text{PM}_{1-2.5}$; the ranges are listed in the table below.

PM fraction	Average and range of coal particle mass as a percentage of total (soluble + insoluble) particles
TSP	12% (3% – 22%)
PM_{1-10}	10% (2% – 24%)
$\text{PM}_{1-2.5}^2$	1.8% (0.5% – 3.3%)

PM_{1-10} refers to particles sized between 1 and 10 micrometres in equivalent aerodynamic diameter.

$\text{PM}_{1-2.5}$ refers to particles sized between 1 and 2.5 micrometres in equivalent aerodynamic diameter.

This proportion of coal particles in TSP is consistent with the 10% coal (range 0–25%) in deposited dust reported in the recent Lower Hunter Dust Deposition Study (AECOM 2016).

This study's result that 10% of the PM_{1-10} are coal particles is consistent with the finding of the Lower Hunter Particle Characterisation Study (LHPCS) that on average 10% of the $\text{PM}_{2.5-10}$ was light-absorbing carbon and that most of this was probably coal particles (Hibberd et al. 2016).

In contrast, the results from this study for coal particles in PM_{1-2.5} suggest that the LHPCS upper limit of 4% of coal particles in PM_{2.5} based on carbon in the soil factor is probably a significant over-estimate. The results from this CGA study suggest an upper limit closer to 0.5% of coal in PM_{2.5}.

Possible sources of coal particles include direct emissions from the coal operations, and resuspension of previously deposited coal particles in the ambient environment around Stockton.

The analysed filters have an average 24-hour TSP concentration of 64µg m⁻³. The average coal particle concentrations in the various PM size fractions are as follows:

PM fraction	Average (and range) of coal particle concentrations
TSP	7.7µg m ⁻³ (1.9–16.4)
PM _{>10}	5.1µg m ⁻³ (1.2–11)
PM _{2.5-10}	2.5µg m ⁻³ (0.6–5.3)
PM _{1-2.5}	0.09µg m ⁻³ (0.02–0.17)

The proportion of coal particle mass in the **insoluble particles** in the samples, as well as the proportion of dark particles (a mixture of soot, sand, clays, organic material, rubber and unidentified particles) and bright particles (a mixture of fly ash, some plastics, paint and unidentified particles) were as follows¹:

- For TSP, the insoluble particles consist on average of 25% coal particles, 51% dark particles and 24% bright particles.
- In the PM_{2.5-10} size fraction, the insoluble particles consist on average of 63% coal particles, 28% dark particles and 9% bright particles.
- In the PM_{1-2.5} size fraction², the insoluble particles on average consist of 83% coal particles, 12% dark particles and 5% bright particles.

¹ The analysis of the CGA results used the characteristics of size-selective inlets for sampling devices specified by the US EPA for compliance with the Federal Reference Method.

² It is important to note that the PM_{1-2.5} size fraction typically only makes up 30% of the total PM_{2.5} in urban samples.

1 Introduction

1.1 Objective

The objective of this study is to quantify the amount of coal particles in the particulate matter (PM) measured at the Office of Environment and Heritage (OEH) Stockton Air Quality Monitoring Station (AQMS) on selected winter days in 2015. In order to determine an upper limit on the amount of coal particles in the PM, days were selected for analysis when the meteorology was conducive to coal particles being generated and transported to the Stockton AQMS from coal operations on Kooragang Island and adjacent areas at the Port of Newcastle.

1.2 Background

The context for this project is the Lower Hunter Particle Characterisation Study (LHPCS; Hibberd et al. 2016), which was based on sampling during the period March 2014 to February 2015. The LHPCS aims were to determine the composition of PM_{2.5} and PM_{2.5-10} air particles, and to identify major sources contributing to PM_{2.5} and PM_{2.5-10} concentrations in the region to inform the NSW Environment Protection Authority's control programs. The community has a strong interest in knowing how much of the particulate pollution in the Newcastle region is coal particles. A limitation of the LHPCS is that it cannot specifically identify coal particles in samples; it only provides the concentration of elemental (or light-absorbing) carbon.

This project uses CSIRO's Coal Grain Analysis (CGA) system, which is able to analyse PM samples and provide quantitative detail on the coal and non-coal particles as well as their size in a range from about 1–50µm. It uses high resolution imaging techniques with reflected light to provide quantitative information on the size and type (e.g. coal, non-coal) of each individual particle.

The Stockton AQMS was selected as the PM sample collection site for this study for the following reasons:

- Stockton was one of the LHPCS sites and the detailed understanding from that study about local and regional PM is available to assist in interpreting the CGA results.
- Stockton is well located for a winter study, being downwind from the coal operations on Kooragang Island and adjacent areas at the Port of Newcastle for much of the winter months.
- Stockton has a range of continuous air quality and meteorological monitoring instruments, which are valuable in interpreting the CGA results.

1.3 Scope of work

The agreed scope of work for the project is included in Appendix B.

2 Method

2.1 Overview of the method

High volume samplers were used to collect 24-hour TSP (total suspended particle) samples at Stockton from mid-June to mid-September 2015. In the laboratory, the filters were weighed and samples prepared for analysis using the Coal Grain Analysis (CGA) technique both to measure the size of the particles (between 1 and 50 μm in diameter) and identify coal particles from non-coal particles using reflectance fingerprints. As the focus of this study was on identifying coal particles, separate measurements of sand particles (often part of analysis of windblown dust) were not undertaken.

Preparation involved washing the particles from the filters, with the insoluble particles collected, dried, set in resin, and a surface of the resin block polished to expose the particles for the CGA technique. The technique provides two-dimensional size details on an average of 6000 particles in each sample, from which the mass of each particle and the size distribution can be determined.

These data provide the proportion of coal particles compared to other insoluble particles in the sample. These can be related to overall PM concentrations in various size fractions using the measurements of mass of particles on the original TSP filter, the mass of insoluble particles in the resin block, and ambient monitoring data on PM_{2.5} and PM₁₀.

2.2 Sample collection

Size fractions. Because the analytical technique for this study (CGA) determines the size of the particles as well as their type, TSP were collected to be able to quantify the coal particles in all size fractions from about 1–50 μm .

Sampler. TSP high volume samplers were used in accordance with AS/NZS 3580.9.3.2003 *Determination of suspended particulate matter – Total suspended particulate matter (TSP) – High volume sampler gravimetric method* (Standards Australia International 2003a).

Filter material. Emfab filters (EMFAB TX40HI20-WW, borosilicate glass microfibers reinforced with woven glass cloth and bonded with PTFE) were used as the filter material.

Gravimetric mass. Gravimetric mass determinations on the Emfab filters were obtained from pre-exposure and post-exposure weighing in accordance with AS/NZS 3580.9.3.2003 *Determination of suspended particulate matter – Total suspended particulate matter (TSP) – High volume sampler gravimetric method* (Standards Australia International 2003a).

Sampling duration. The collection period for each filter was 24 hours from midnight to midnight. The air sampling volume was determined from the requirements of CGA for at least 20mg (preferably 40–50mg) of sample. The volume flow of the high volume sampler used is 78m³ hr⁻¹, so that a 24-hour average PM concentration of 12 $\mu\text{g m}^{-3}$ is required to collect 20mg, or 25–30 $\mu\text{g m}^{-3}$ to collect 40–50mg of PM. Based on results from the ongoing PM₁₀ measurements at Stockton, it was expected that sufficient material would be collected in the 24-hour sampling periods.

Sampling period. Samples were collected daily for three months from mid-June to mid-September 2015 (95 samples). The project used four high volume samplers, each programmed to collect on a one-in-four day cycle. The winter period was selected because of the favourable wind direction for sampling particles from the coal operations on Kooragang Island.

2.3 Sample selection

The project budgeted for analysis of a limited number (9) of the 95 filters collected. These were selected on the basis of conditions expected to be conducive to coal particles being generated and transported to the Stockton AQMS from coal operations on Kooragang Island and adjacent areas at the Port of Newcastle, namely:

- elevated PM concentrations recorded at Stockton
- strong north-westerly winds, dry conditions (no rain).

2.4 Coal Grain Analysis

Coal Grain Analysis (CGA) is an optical reflected light imaging and analysis system which mosaics together calibrated contiguous high resolution colour images, collected with an air objective, to enable detailed information to be obtained on individual dust particles.

The mosaicked images are collected using a Zeiss Axio Imager microscope (Figure 1) which has a very precise automated stage and auto focus capability and is equipped with a 14 bit colour camera. When a 50x magnification objective is used each image covers an area of approximately $180\mu\text{m} \times 130\mu\text{m}$ and each pixel is approximately $0.12\mu\text{m}$ in size. This enables measurement of the size of individual particles which are greater than approximately $1\mu\text{m}$ in diameter. A sufficient number of images are collected to generally provide detail on 2000 to 10,000 dust particles in the sample.

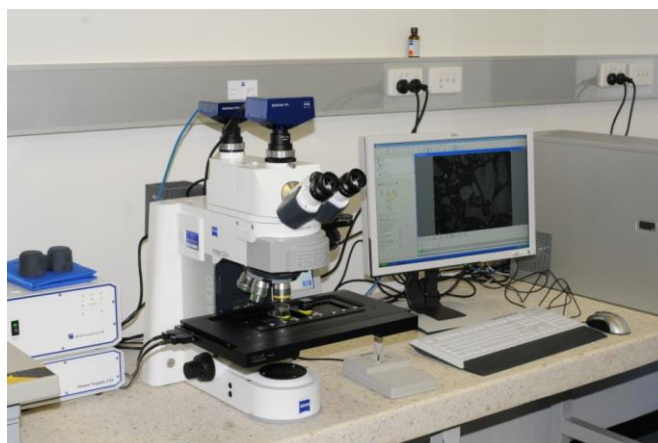


Figure 1. Zeiss imaging system

The image processing software first segments the mosaicked image to enable size information (area, particle length and width) and a reflectance fingerprint to be obtained for each individual particle in the image. This reflectance fingerprint is used to discriminate the coal from non-coal particles. More details on this method are described in Warren et al. (2015) and presented in Section 2.4.1.

2.4.1 Basis of the CGA technique

The CGA technique is based on petrographic principles applied to photomicrographs and the associated reflectance fingerprints of individual particles. It was originally developed to assist in the analysis of coal samples in coal processing, as discussed for example by O'Brien et al. (2007, 2011).

More recently the technique has been extended for the analysis of coal particles in urban dust samples. This builds on the approach used by Diessel (1999) to provide quantitative detail of coal and non-coal particles in urban dust samples. To undertake this work required an understanding of the types of particles that could be found in urban dust samples; therefore CSIRO collected, prepared and imaged a suite of approximately 30 different types of particulates which could be present in urban dust samples. A subset of the images collected for these particulates is shown in Figure 2. This demonstrates the differences in appearance of the various particles, which aids in their identification in urban dust samples.

It is worth noting that the CGA technique has been used for a wider range of coal ranks³ than those shown in Figure 2, and that it is able to identify coal particles composed of mixed macerals⁴ such as that shown in the bottom right-hand corner of Figure 2.

³ Coal rank is a measure of the proportion of carbon that it contains.

⁴ A maceral is a component, organic in origin, of coal. The term maceral in reference to coal is analogous to the use of the term mineral in reference to igneous or metamorphic rocks. Examples of macerals are inertinite, vitrinite and liptinite.

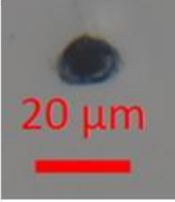
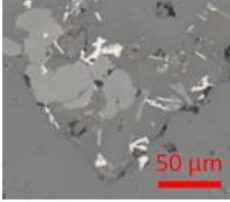
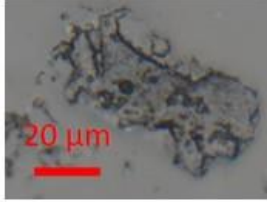
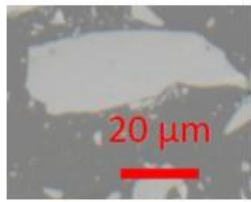
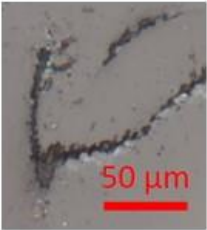
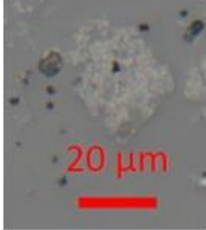
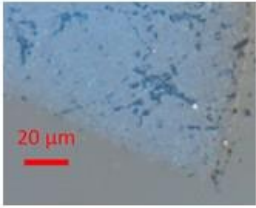
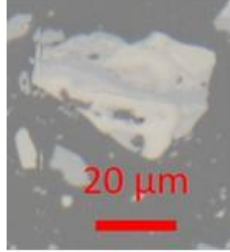
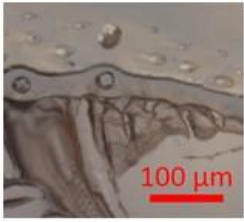
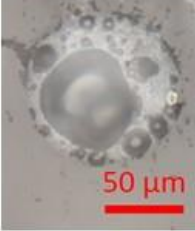
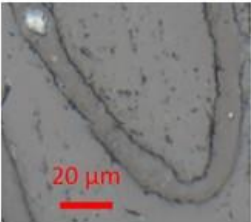
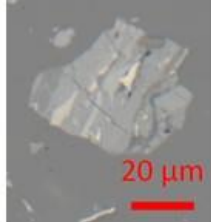
Organic Particles	In-organic Particles		Coal Particles (R_{vr} is a measure of coal rank)
Eucalypt pollen spore 	Basalt 	Rubber 	R_{vr} 1.45 
Moss 	Diesel soot 	Paint 	R_{vr} 1.11 
Insects 	Flyash 	Plastic (bag) 	R_{vr} 0.75 

Figure 2. Photomicrographs for different types of reference urban dust materials

The red, green and blue reflectance fingerprints obtained for these dust particulates are shown in Figure 3. The x-axis of the reflectance fingerprint provides detail of the percent reflectance (measured in air) from 0–15%. Probability density along the y-axis provides detail on the strength of intensity for these measurements.

The reference set currently consists of:

- samples for six coals of different rank and type that cover the rank range of coals transported along the NSW and QLD rail corridors to the ports for export
- samples of different combustion products (i.e. diesel soot, fly ash, slag)
- samples of different inorganic compounds (i.e. sand, dirt, rust, sand, metal grindings)
- samples of the different types of organic matter (i.e. separate samples of different plants and insect components and paper products) which have previously been observed in urban dust samples

- samples of different plastic materials and paints (i.e. plastic bag fragments, hard plastic fragments, different coloured paints).

It is anticipated that this reference set will be continually expanded for future CGA studies.

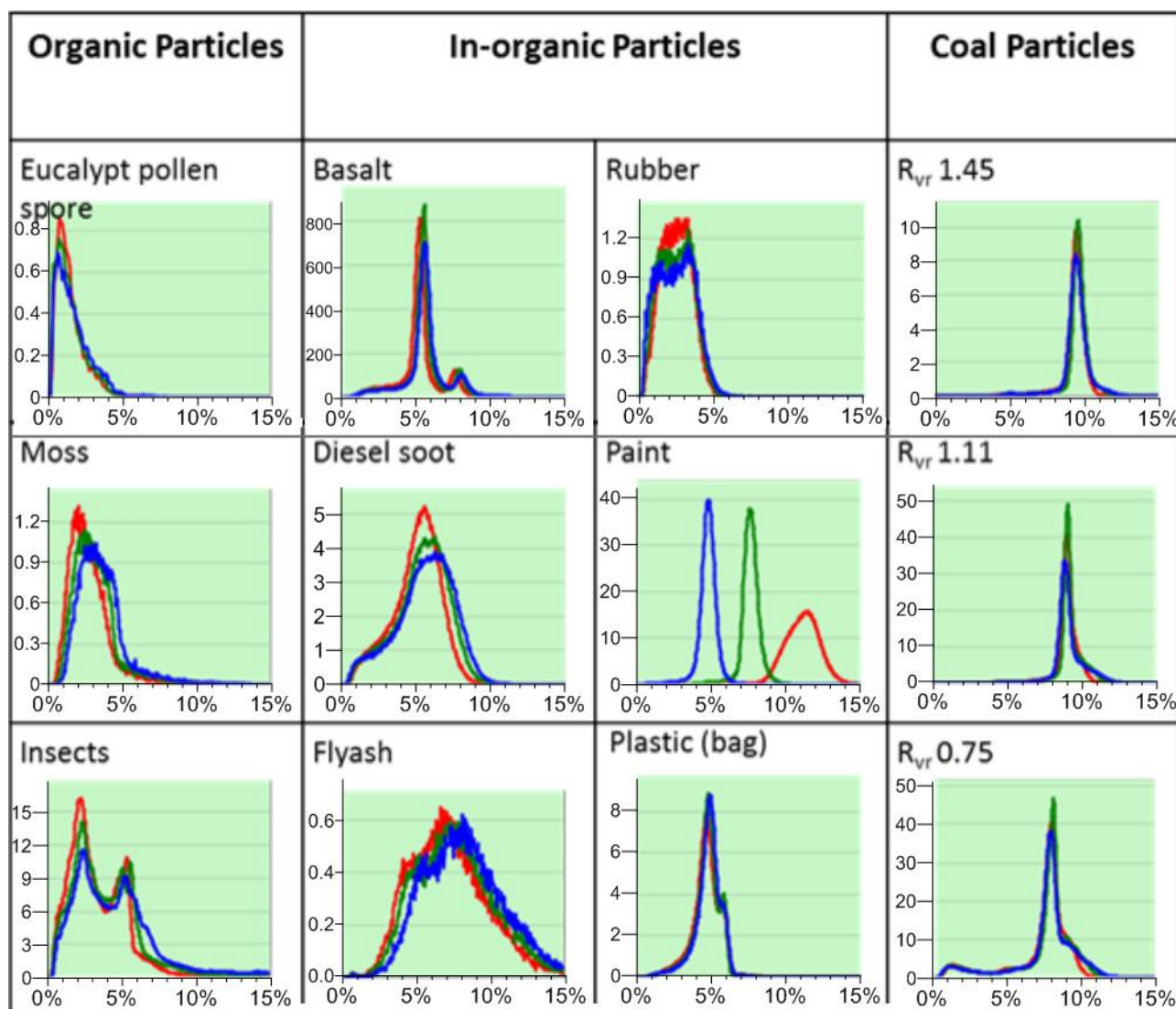


Figure 3. Reflectance fingerprints for different types of urban dust materials. The x-axis represents the reflectance in air from 0 to 15% for each particle and the y-axis the estimated probability density for the RGB measurements

Additional analysis of these reference samples and of an urban dust sample collected from the Newcastle region was undertaken using the infrared beam line of the Australian Synchrotron to verify that particles as small as $10\mu\text{m}$ that had different appearances and reflectance fingerprints were compositionally different (Krahenbuhl et al. 2015). The study focused on the carbon-based particles such as rubber, organic matter, and diesel soot as well as coal, which are difficult to identify and classify on a particle-by-particle basis using other techniques.

The CGA system provides a reflectance ‘fingerprint’ for each individual dust particle and this information is used to categorise the particle as shown in Section 2.4.4. For the analyses of these

samples, a skilled petrographer confirmed or corrected the preliminary characterisation of each particle in the analysis.

In addition to the analyses undertaken on these Stockton samples, the CGA system has been used successfully to analyse dust samples collected at different sampling locations around the coal ports of Hay Point and Dalrymple Bay and the township of Mackay. The coals shipped through these ports spanned a very wide rank range – this provides confidence that this technique was able to accurately identify coal and non-coal particles in the Stockton samples.

2.4.2 Sample preparation

All the samples for CGA were prepared at CSIRO laboratories at the Queensland Centre for Advanced Technologies (QCAT) in Brisbane. The sample preparation included dust extraction, setting in resin and polishing.

The Emfab filters from the TSP high volume sampler were analysed by OEH to determine gravimetric mass before shipping to Brisbane. For CGA they were quartered prior to the extraction step and two opposite quarters of each sample were used for dust extraction. Dust extraction was performed by washing with demineralised water. A two-minute ultrasonic bath step was included for better particle release. The sample eluate was filtered with a Millipore vacuum filtration device using 0.45µm mixed cellulose ester membrane filters (Whatman), which were weighed before use. Samples were dried in an oven with a temperature of 50°C for one hour and set afterwards in polyester resin.

Determination of the mass of insoluble solids collected on the Whatman filters was performed in order to relate the mass of particles identified by CGA to the total mass of particles collected on the TSP filters. Soluble particles such as sea salt and ammonium sulfate are washed out in the extraction process and so were not detected in the CGA technique. The methodology for insoluble mass determination was adapted from the Australian Standards for *Methods for sampling and analysis of ambient air; Method 10.1: determination of particulate matter – Deposited matter – Gravimetric method*, AS/NZS 3580.10.1:2003 (Standards Australia International 2003b). The Whatman filters were equilibrated and weighed at standard laboratory conditions before use and then after collection of the eluate, oven drying, and equilibration of the filters at ambient laboratory conditions. The mass of insoluble particles was doubled to account for only half the Emfab filters being used in the extraction process and the percentage TSP insolubles calculated using the original gravimetric mass determination from OEH.

Samples were prepared using methods adapted from the Australian Standards for *Coal petrography Parts 1–3*, AS2856 (Standards Australia International 1998). To ensure that all the particles, regardless of particle size and density, were quantitatively assessed required a two-step process, whereby the very small amount of dust was mixed with polyester resin and then poured into a hole which had been drilled into a blank block of polyester resin. When cured this block was cut vertically and the cut section remounted into a round mould for polishing. This ensured that the images were collected in a vertical section down the settling plane. A five-step polishing using a Struers Tegramin-25 device was applied to achieve as flat a surface as possible for use in

quantitative microscopic analysis and for imaging purposes. An example of the polished resin block is shown in Figure 4.



Figure 4. Dust sample in polished polyester resin block

2.4.3 Sample imaging

Calibrated photomicrographs of the entire sample surface were collected in reflected white light at 500x magnification with a digital pixel resolution of 0.16 μ m using a Zeiss Axio Image microscope fitted with a Zeiss HrC camera. The mosaics of these images were analysed using CSIRO's imaging analysis techniques. The mosaicked image was first segmented, which enabled size information (area, particle length and width) and a reflectance fingerprint to be obtained for each individual particle in the image. For these samples additional manual effort was required to remove imaging artefacts such as subsurface particles and scratches in the surface of the block. These reflectance fingerprints were then used to classify each particle and a skilled petrographer was used to verify the classification of each particle in the analysis.

The particles were classified as either coal or one of two types of non-coal particles. The non-coal particles were classified as dark material (comprised of a variable mixture of soot, sand, clays, organic material, rubber and unidentified particles) or bright material (comprised of a mixture of fly ash, some plastics, paint, and unidentified particles).

2.4.4 Example of classification of particles using the CGA technique

The process for distinguishing particles is illustrated below using a number of screenshot images from the CGA analysis of one of the samples collected in the Stockton study. Background information about these figures (Figure 5 to Figure 10) is:

- The left-hand side of each figure provides detail of the CGA file storage architecture, and some of the imaging parameters.
- The middle section of each figure contains a small selected part of the overall image which was analysed here.
- The right-hand section of each figure contains the CGA colour reflectance histograms on coloured backgrounds that provide a preliminary indication of the type of particle, which is confirmed or corrected by a skilled petrographer:

- The green shaded section shows the expected reflectance range for the coal particles. This reflectance range can be modified if the sample contains coal particles of lower or higher rank.
- The pink shaded section is used to identify the 'dark material' which has a lower reflectance value than coal.
- The light blue shaded section is used to identify the 'bright material' which has a higher reflectance value than the coal.

The same selected part of the overall image is shown in each figure. The individual dust particles can be distinguished against the darker mounting resin of the particulate block. In the CGA software, when reflectance information (on the right-hand side) is shown for an individual particle, there is a green box around that particle in the image (emphasised here by the large arrow).

Figure 5 shows the selected part of the subset of the image in white light with the right-hand side showing the total red, green, blue reflectance histograms obtained for all particles in the whole sample. The x-axis of this graph shows the reflectance values (measured in air) and the y-axis shows the probability density.

Figure 6 is the same as Figure 5 but with the particles in the image characterised using the following colours: coal particles are coloured green, dark material is coloured red, and bright material is coloured blue.

The next four figures show the identification of specific types of particles. Figure 7 is an organic particle which has been classified as dark material.

Figure 8 and Figure 9 are coal particles. Figure 8 shows a coal particle composed primarily of vitrinite, which is one of the types of organic components of coal. Mixed coal particles would have a histogram which includes detail on the mineral, liptinite, vitrinite and inertinite. When used for coal analysis applications, the CGA software provides detail of the abundance of each of the maceral and mineral constituents in each particle. This dynamic thresholding imaging approach allows these analyses to be accurately undertaken for coal blends.

Figure 9 shows a coal particle composed primarily of inertinite. There are reflectance intensity and colour balance differences between this inertinite particle and the vitrinite particle in Figure 8

Figure 10 shows the reflectance fingerprint for a plastic/paint particle which has been classified as bright material. Note that this particle has a similar brightness but a different reflectance fingerprint than those of the vitrinite and inertinite particles.

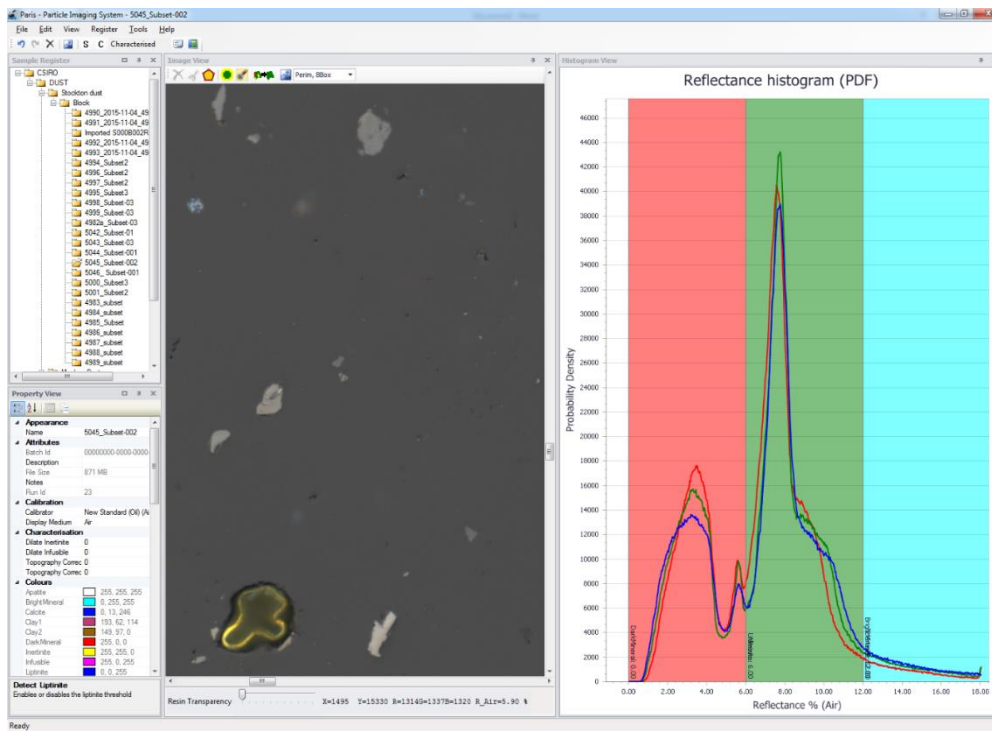


Figure 5. Part of the image of sample 5045 with the histogram for the whole of the 5045 image (not just the part of the image shown). The left-hand side shows the image in white light with the right-hand side showing the total red, green, blue reflectance histograms obtained for all particles in the whole sample. The x-axis of this graph shows the reflectance values (measured in air) and the y-axis shows the probability density

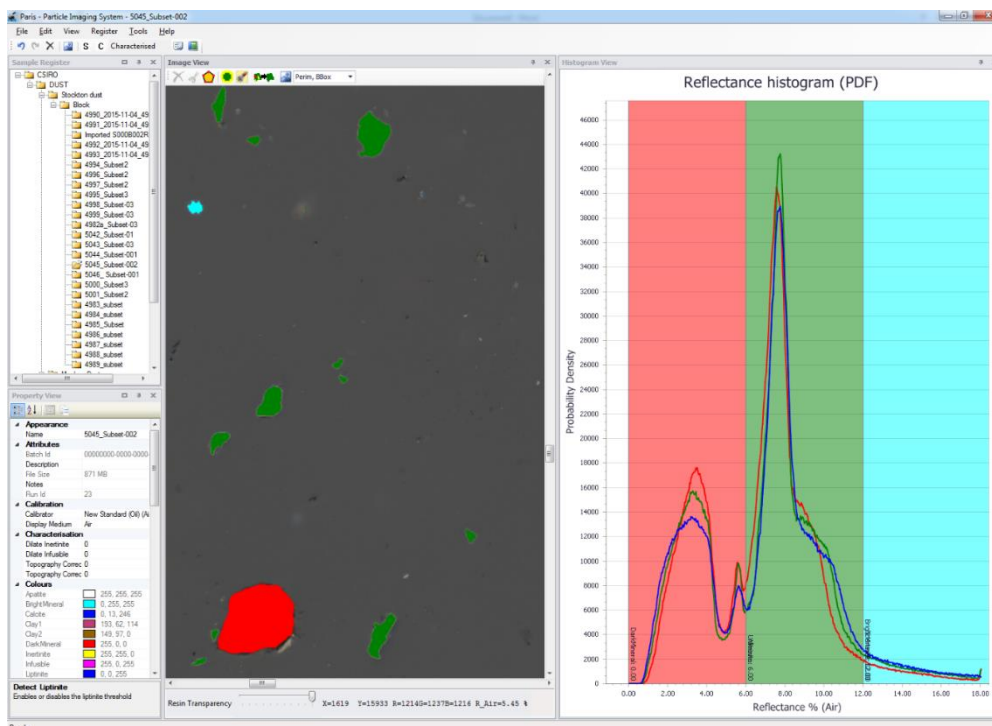


Figure 6. Same as Figure 5 but the particles are characterised using the following colours: coal particles are coloured green, dark material is coloured red, and bright material is coloured blue. The reflectance histogram is the same as for Figure 5, i.e. for the whole sample

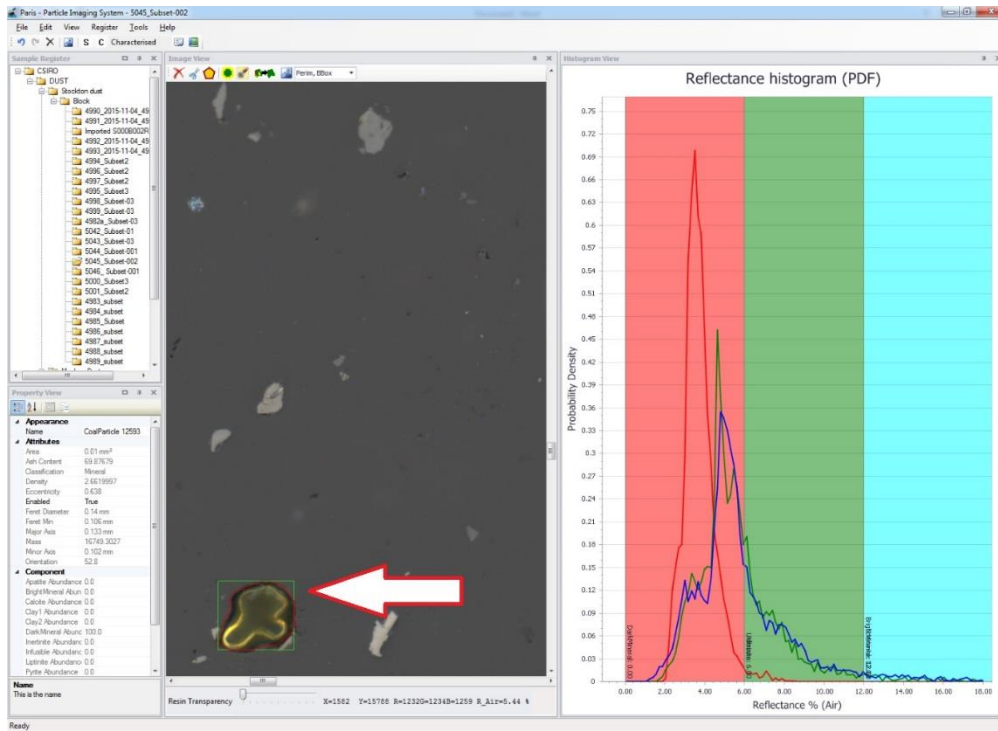


Figure 7. An organic particle with its reflectance histogram – it was classified as dark material

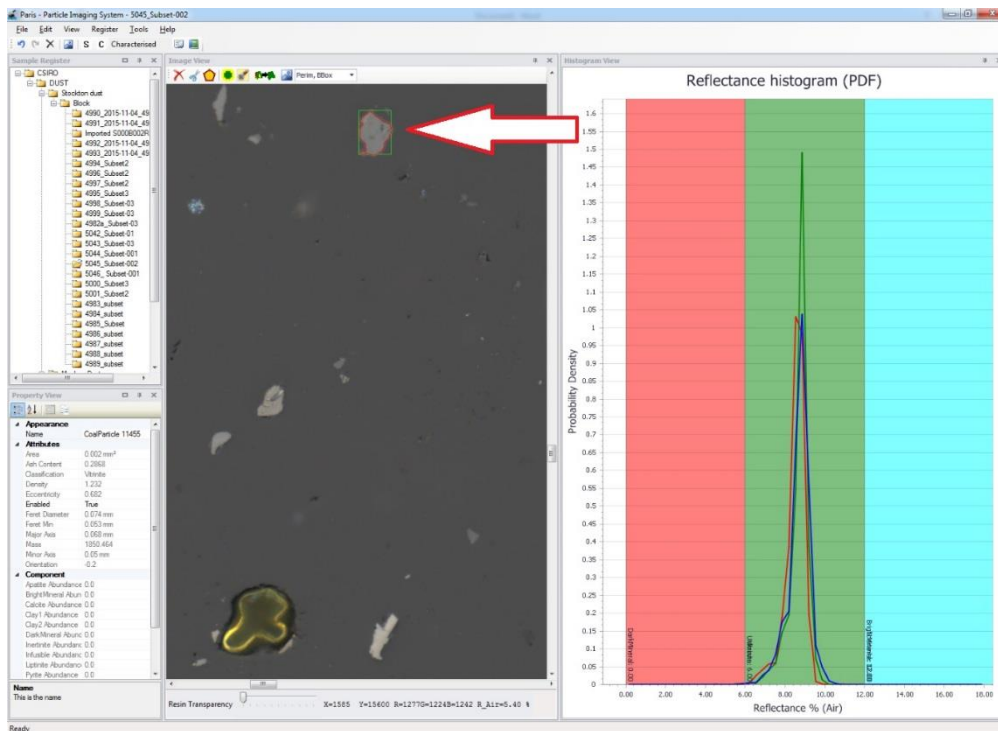


Figure 8. A coal particle comprised primarily of vitrinite. Particles comprised of vitrinite from coals of different ranks have similarly shaped histograms, but at different positions along the x-axis

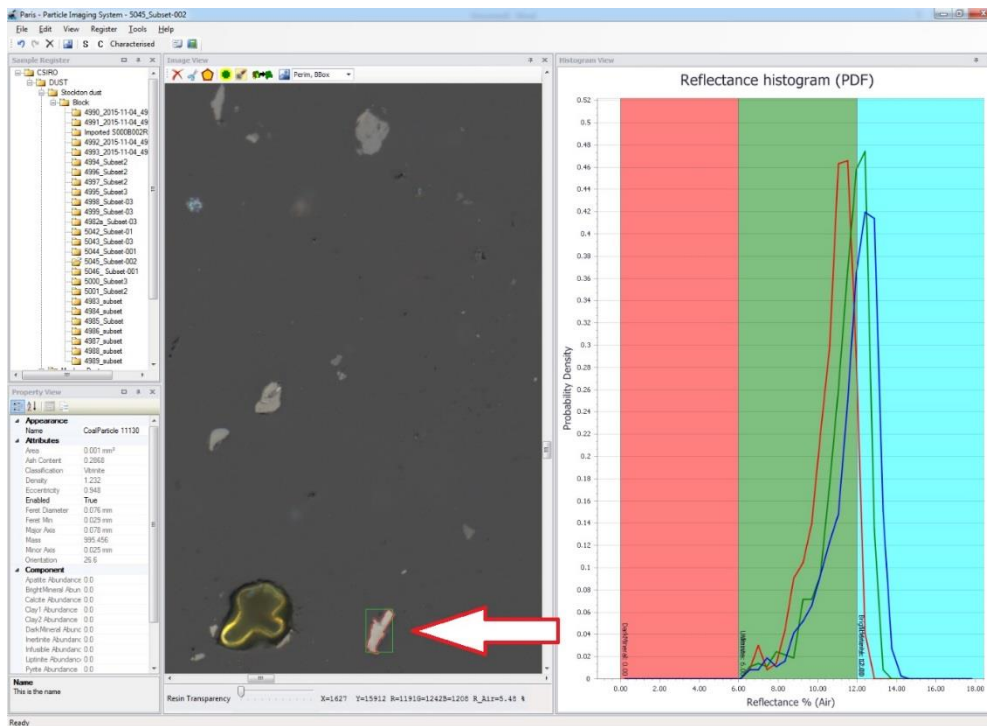


Figure 9. The reflectance fingerprint for an inertinite particle. There are reflectance intensity and colour balance differences between this inertinite particle and the vitrinite particle in Figure 8

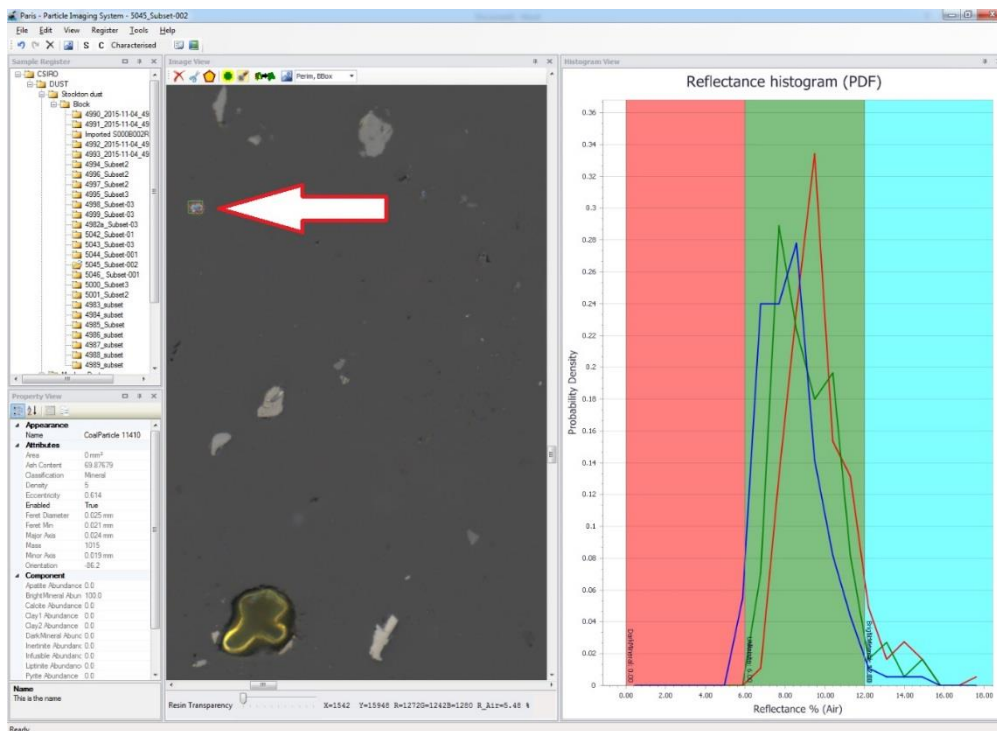


Figure 10. The reflectance fingerprint for a plastic/paint particle which has been classified as bright material. Note that this particle has a similar brightness but different reflectance fingerprint to those of the vitrinite and inertinite particles

2.4.5 CGA results provided in image viewing software

CSIRO has developed image viewing software to allow results for dust analyses to be uploaded to the internet and viewed by interested parties. Links to the mosaicked images for the analysed samples are listed in Table 1.

Table 1. Image viewer links to CGA results reported on an area basis

CSIRO sample number	Collection date	Image viewer link
4990	10/08/2015	https://cloudimaging.csiro.au/Sample/Viewer/cde94154-6701-4e75-aba5-b71e39ab42dd
4991	1/08/2015	https://cloudimaging.csiro.au/Sample/Viewer/ad27d7d5-f9b1-47d7-bf90-036c5687a67e
4992	27/06/2015	https://cloudimaging.csiro.au/Sample/Viewer/7df2ac85-996d-4694-9177-0b679d93fc4a
4993	15/06/2015	https://cloudimaging.csiro.au/Sample/Viewer/744f6abf-ce45-4c3b-ba6f-3c0fb9eff8db
4994	13/09/2015	https://cloudimaging.csiro.au/Sample/Viewer/51260144-c7cf-4958-8c2d-37063f09b455
4995	5/07/2015	https://cloudimaging.csiro.au/Sample/Viewer/617809b2-940b-496b-8abc-527070c2355e
4996	2/08/2015	https://cloudimaging.csiro.au/Sample/Viewer/32d8a0a6-9f56-411b-ab2c-caa51493ccb6
4997	25/06/2015	https://cloudimaging.csiro.au/Sample/Viewer/1f9629a1-6449-493b-9385-f7611835e52d
4998	10/09/2015	https://cloudimaging.csiro.au/Sample/Viewer/af102cc9-87d1-4882-8343-976505d4f7c6

Key features of the image viewing software are:

- A scale bar is shown in the bottom left-hand corner of the image.
- The slider bar on the top left-hand side of the image is used to increase or decrease the image zoom.
- The slider bar at the bottom left-hand side of the image is used to transform the image from raw image to a false coloured classified image and back again.
- Size detail can be obtained for each individual particle in an image by clicking on it.
- The size detail provided for the sample is reported on an area basis.

2.4.6 Estimation of particle mass

CGA provided size detail (particle length, width and area) for each particle in each image. The equivalent diameter of a circle with the measured area was used as the effective diameter for each particle. The particle volume was computed from the effective diameter assuming the

particles were spherical. This approximation is reasonable given the observed shapes of most of the particles.

In petrographic analyses of coal grains, results are usually presented on a volume basis, so this is used for the basic results in Section 3 (Results). However, in air quality studies where particulate standards are specified in terms of mass, it is important to also present the results in mass terms; most of the results in this report are presented on a mass basis.

In order to convert the particle volume to particle mass, a particle density is required. As these densities are not determined by the CGA method, they were estimated from available information as:

- 1400kg m⁻³ for coal (e.g. Williams 1999; Preston & Sanders 1993)
- 2000kg m⁻³ for dark material (mainly soot and soil)
- 2200kg m⁻³ for bright material (mainly fly ash).

The dark material is comprised of soot, sand, clays, organic material, rubber and other particles, and these have densities from about 900–2650kg m⁻³ (CRC 2015), with an average estimated as 2000kg m⁻³. The bright material was mainly fly ash and some plastics and paint. Although the source of the fly ash in the samples is unknown, an indicative density is assumed to be that for commercially available fly ash (supplied, for example, from power station flue gas filtration systems), which is approximately 2200kg m⁻³ (Flyash Australia). There were small contributions from plastics and paint, which have densities of 900–1500kg m⁻³ (CRC 2015). As an indication of typical densities for airborne particulate matter, Hu et al. (2012) reported on winter measurements in Beijing that the effective density of PM_{2.5–10} was 2000kg m⁻³. This is consistent with the values used above, although the composition of PM would be significantly different. The study results were shown to be fairly insensitive to the uncertainties in the densities, as reported in Section 4.4.

The effect of particle density was accounted for in the calculation of the effective aerodynamic diameter of the particle D_p as $D_p = D_{geom} (\rho_p/\rho_0)^{1/2}$, where D_{geom} is the effective geometric diameter of a particle with density ρ_p and ρ_0 is the standard density of 1000kg m⁻³.

Because the CGA results on particle mass concentrations are to be compared with the PM concentrations measured on instruments equipped with size selective inlets and the cut-offs of these inlets are not sharp, it is important to account for the size dependence of the collection efficiency, as shown in Figure 11 (US CFR 1987). These collection efficiencies were used in computing the mass of particles in each size range from the CGA data – PM_{1–2.5}, PM_{2.5–10} and PM_{>10}. GENT stacked filter units were used to sample PM_{2.5–10} particles in the LHPCS. It is seen that the GENT filter cut-off is more gradual than the US EPA Federal Reference Method (FRM), which is the cut-off of size-selective inlets commonly used for regulatory PM₁₀ measurements. When estimating the coal mass concentration in this size fraction reference will therefore be made to both the FRM and GENT filter cut-offs.

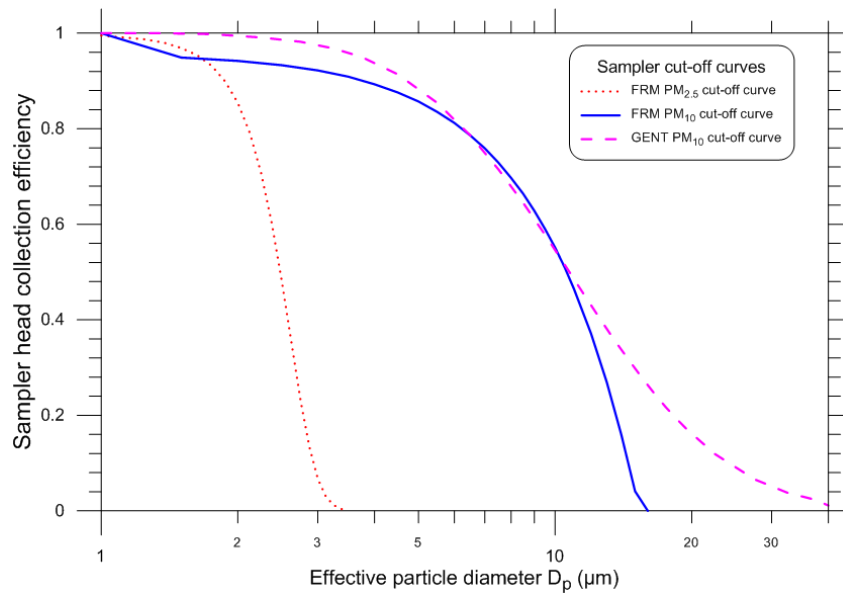


Figure 11. Characteristics of standard sampler inlets with nominal cut-points of $2.5\mu\text{m}$ and $10\mu\text{m}$

3 Results

This section starts with a summary of the concentrations of TSP from the study period and the corresponding PM_{10} and $PM_{2.5}$ concentrations from OEH monitoring equipment as well as the ratios between these parameters (Section 3.1). The selection of filters for full analysis is described in Section 3.2. The basic image analysis results are presented in Section 3.3, showing the identification of coal and non-coal particles, with the particle size distributions given in Section 3.4. Results on coal as a proportion of insoluble particles in various size ranges are presented in Section 3.5, with the results related to total PM_{1-10} and $PM_{1-2.5}$ concentrations (both soluble and insoluble components) in Section 3.6.

3.1 Filter samples

A total of 95 24-hour TSP samples were collected at the Stockton AQMS from 15 June to 17 September 2015 using high volume samplers. The daily TSP concentrations are shown in Figure 12 with the days selected for CGA shown in purple; the selection criteria are described in Section 3.2. The project plan indicated that 24-hour concentrations of $25\text{--}30\mu\text{g m}^{-3}$ would be needed to collect the $40\text{--}50\text{mg}$ of PM required for successful CGA. This was achieved on 75% of the sample days. There were 22 days with TSP concentrations greater than $60\mu\text{g m}^{-3}$ and a total of 36 days with concentrations above $50\mu\text{g m}^{-3}$.

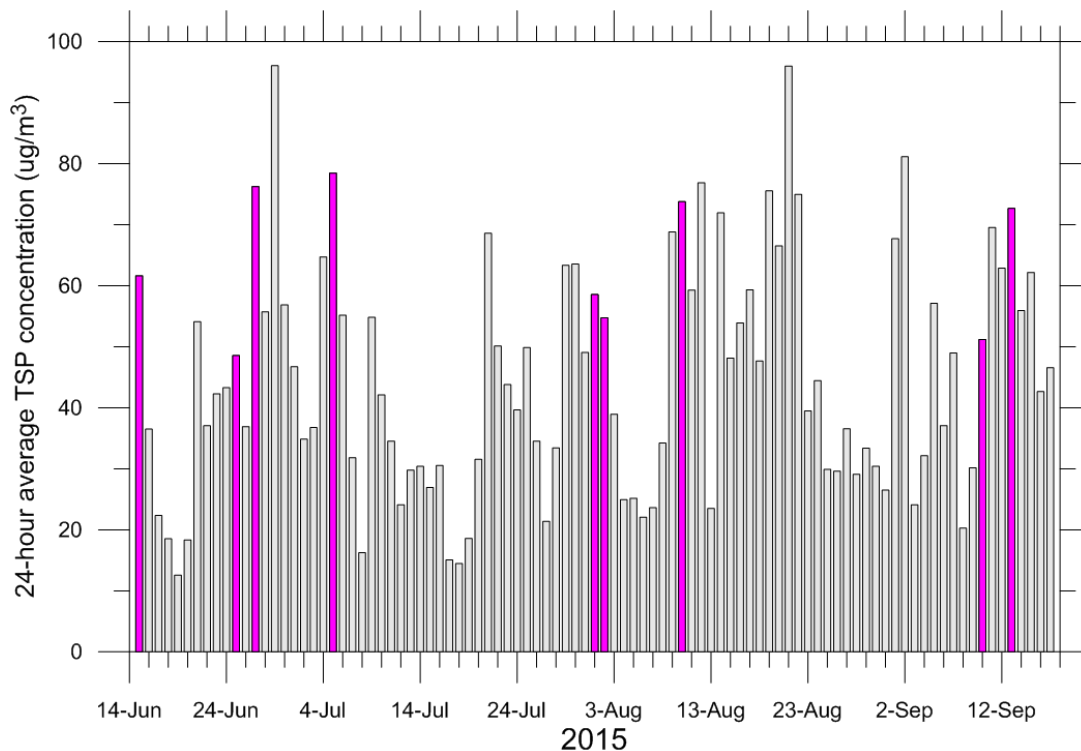


Figure 12. Daily 24-hr average TSP concentrations during the CGA study period.
The purple coloured bars denote filters analysed by CGA

Results on PM₁₀ and PM_{2.5} concentrations for the period are available from the ambient monitoring equipment at the Stockton AQMS. PM₁₀ is measured using a tapered element oscillating microbalance (TEOM) and PM_{2.5} with a beta attenuation monitor (BAM). A scatter plot of the 24-hour average PM₁₀ versus TSP in Figure 13 shows a strong correlation with an r^2 of 0.84 and an average ratio of 0.58.

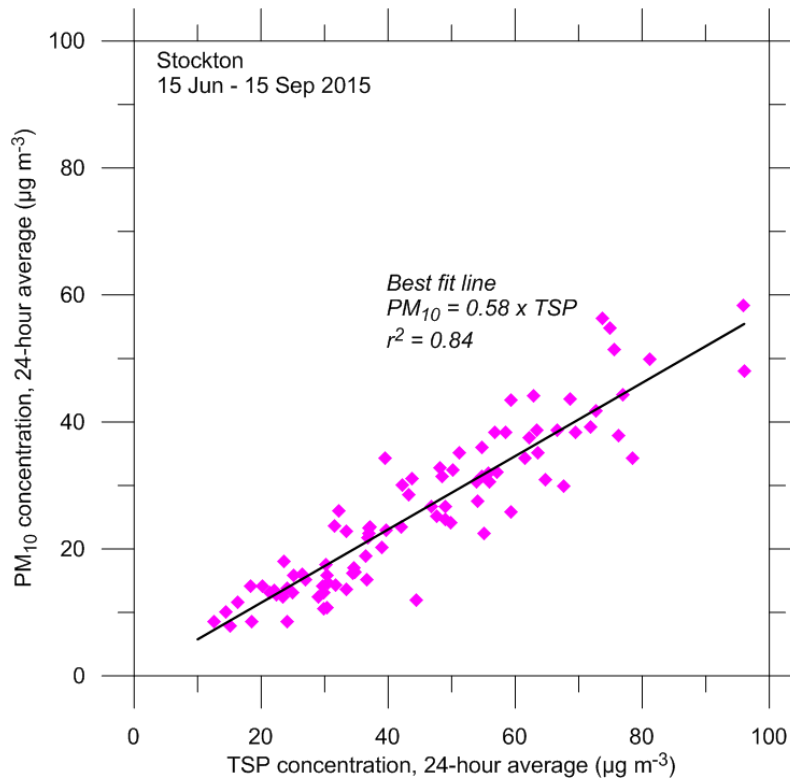


Figure 13. Scatter plot of 24-hour average PM₁₀ versus TSP during the CGA study period

The 24-hour average PM_{2.5}/PM₁₀ ratio was determined using several sets of measurements for 2014 and 2015 (Figure 14). The BAM/TEOM ratio is shown for both years as well as the ratio from the GENT and ASP samplers from the Lower Hunter Particle Characterisation Study for June to September 2014. Because of the greater heating of the inlet for the TEOM than the BAM instruments, there are occasions when the measured PM_{2.5} concentration exceeds the measured PM₁₀ concentration due to greater loss of volatile compounds in the TEOM inlet. The figure shows much more scatter than for the PM₁₀/TSP ratio but with an average of about 0.45 and a downward trend during the study as indicated by the linear fit reducing from 0.57 to 0.35.

In summary, Figure 13 shows that the average PM₁₀/TSP ratio is 0.58 and Figure 14 shows that the average PM_{2.5}/PM₁₀ ratio is 0.45.

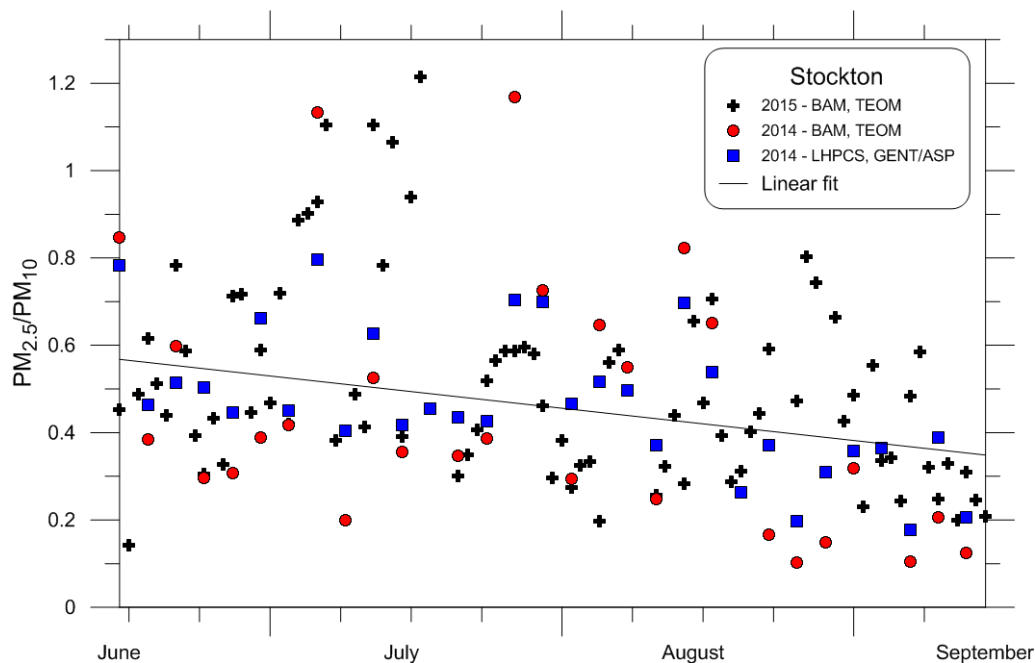


Figure 14. $PM_{2.5}/PM_{10}$ ratio from June to September in 2014 and 2015 determined using various measures

As the minimum size of particles identified by CGA is approximately $1\mu m$, it is important to note in the following that the smallest size fraction reported on is $PM_{1-2.5}$, not $PM_{2.5}$. Keywood et al. (1999) made size-resolved measurements in several Australian cities and consistently found that about 70% of the $PM_{2.5}$ was smaller than $1\mu m$ in diameter, i.e. was in the PM_1 fraction, so that just 30% of the $PM_{2.5}$ was in the $PM_{1-2.5}$ range. This current study did not determine the proportion of $PM_{2.5}$ in the $PM_{1-2.5}$ range, so the above proportion of 30% was used as indicative for Stockton.

3.2 Selection of filters for CGA

Visual inspection of the filters did not reveal any significant differences in the blackness of the filters. They were all brown with slight variations in the shade of brown depending on the filter loading.

3.2.1 Wind and pollution roses

The wind rose for the study period (Figure 15) shows a predominance of north-westerly winds, more precisely around 300° , in line with expectations from the climatology (e.g. www.bom.gov.au/climate/averages/tables/cw_061390.shtml). The wind rose shows the distribution of wind direction experienced at Stockton. The direction of each sector radiating from the centre is the wind direction (the direction the wind is blowing from). Its total length is proportional to the frequency of the wind from that direction, and the proportion of each wind speed range is shown by the coloured sectors.

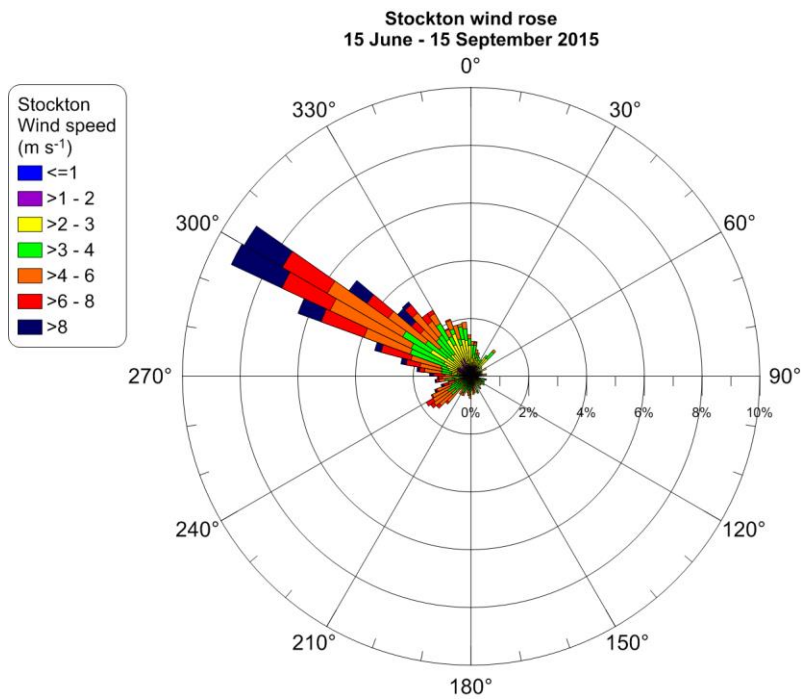


Figure 15. Wind rose for Stockton for three month CGA study period

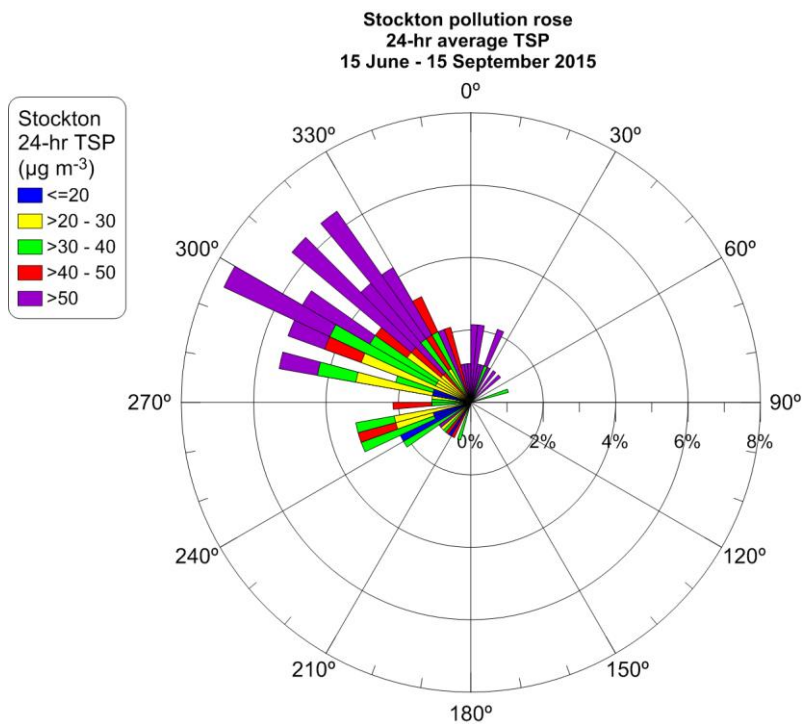


Figure 16. Pollution rose for Stockton for 24-hour average TSP

Replacing the wind speed in the wind rose by the pollution concentration gives a pollution rose. This is shown for the 24-hour TSP concentrations in Figure 16 using 24-hour average wind directions. Comparing this figure with the wind rose (Figure 15) and focusing on the high TSP

concentration days, there are distinct differences. Some of these days occur with a wind direction of 300°, but there is also a group from 310–330° and also some at 0–10° and at 20°, indicating local sources of TSP, as expected for this size fraction which has much higher deposition (settling) velocities than the finer PM_{2.5}.

However, the 24-hour average wind directions smooth out the hourly variability and do not necessarily provide good information about actual wind directions during the day for selecting the samples for CGA. The strong correlation between the 24-hour PM₁₀ and TSP concentrations shown in Figure 13 shows that the PM₁₀/TSP ratio of 24-hour averages is relatively constant during the study period. This justifies the assumption that the 1-hour average PM₁₀ concentrations will generally vary in a similar fashion to the 1-hour TSP concentrations (which weren't measured). That is, when PM₁₀ is high (low), then TSP is also generally high (low), so that the variation in 1-hr PM₁₀ concentrations can be used to identify the wind directions associated with the highest 1-hr TSP concentrations.

Figure 17 and Figure 18 show PM₁₀ pollution roses using 1-hour averages. Figure 17 shows the pollution rose for PM₁₀ concentrations up to 50µg m⁻³ with the main direction corresponding with the dominant wind direction (Figure 15). In contrast, Figure 18, which is the pollution rose for PM₁₀ >50µg m⁻³, shows that most of these events are centred around wind directions of 330° and 40°. The underlying map shows that these correspond to upwind sources of the coal stockpiles (310–345°) and the ocean coastline to the north-east with large expanses of exposed sand (35–50°). It is important to note that the relative length of the sectors from the centre indicates the relative frequency of occurrence from that direction, but the absolute length is not significant, i.e. the location of the end of the sector on the underlying map is not significant.

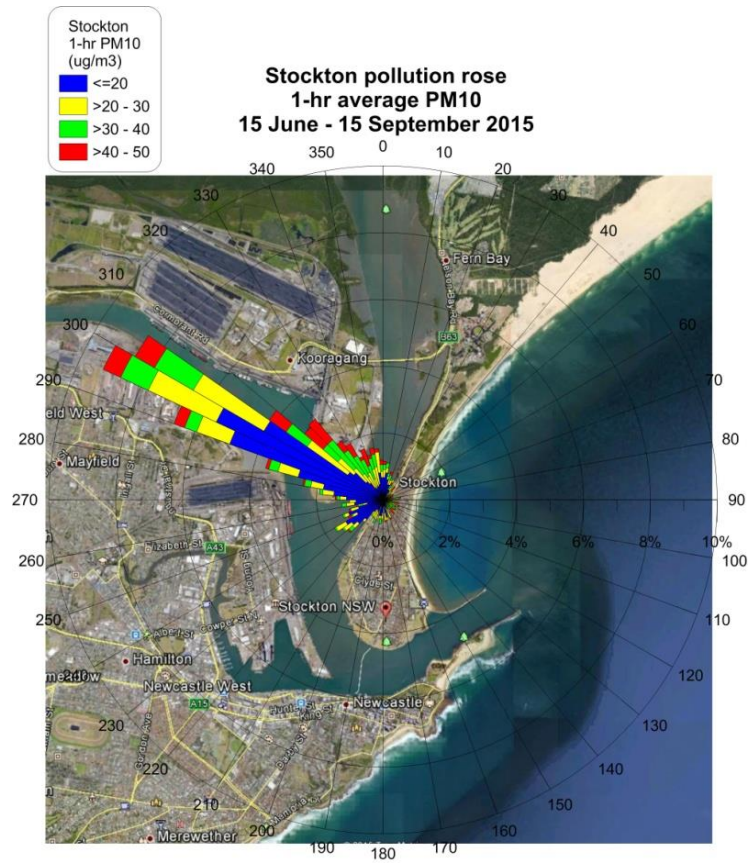


Figure 17. PM_{10} pollution rose for $PM_{10} < 50 \mu g m^{-3}$ centred on Stockton AQMS and overlaid on map of the region

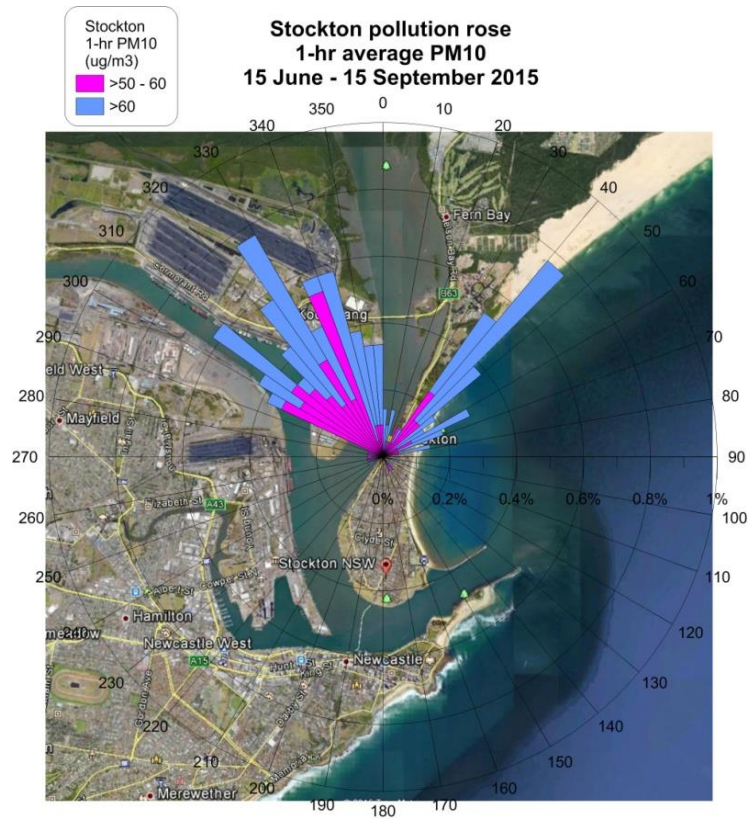


Figure 18. PM_{10} pollution rose for $PM_{10} > 50 \mu g m^{-3}$ centred on Stockton AQMS and overlaid on map of the region

3.2.2 Selection of the filters for analysis

In order to determine an upper limit on the amount of coal particles in PM, filters were selected for analysis when conditions were conducive to coal particles being generated and transported to the Stockton AQMS from coal operations on Kooragang Island and adjacent areas at the Port of Newcastle. The selection criteria were:

- elevated 24-hour average TSP concentrations $>40\mu\text{g m}^{-3}$
- several hours with PM_{10} concentrations $>50\mu\text{g m}^{-3}$ and winds from $295\text{--}360^\circ$.

The days were determined that had the greatest number of hours with high PM_{10} concentrations when the wind direction was from the coal stockpile/operations sector. To account for wind direction variability, the sector was expanded by $\pm 15^\circ$ as shown by the $295\text{--}360^\circ$ sector in Figure 18.

Table 2. Selected filters for CGA analysis. (σ_θ – standard deviation of 24-hr average wind direction)

ID	Date	24-hr average TSP ($\mu\text{g m}^{-3}$)	24-hr average PM_{10} ($\mu\text{g m}^{-3}$)	24-hr $\text{PM}_{2.5}$ ($\mu\text{g m}^{-3}$)	# hours when $295^\circ < \text{WD} < 360^\circ$ & $\text{PM}_{10} > 60\mu\text{g m}^{-3}$	# hours when $295^\circ < \text{WD} < 360^\circ$ & $\text{PM}_{10} > 50\mu\text{g m}^{-3}$	Total # hours in previous 2 columns	24-hr average wind direction ($^\circ$)	σ_θ ($^\circ$)	24-hr average wind speed (m s^{-1})	Rain	Comments
4990	10/08	73.8	56.3	18.1	4	1	5	318	19	4.9	0	
4991	1/08	58.6	38.3	14.6	2	3	5	323	19	4.4	0	
4992	27/06	76.2	37.9	27.0	1	4	5	324	26	2.9	0	day before
4993	15/06	61.6	34.3	15.5	2	3	5	365	56	2.8	0	
4994	13/09	72.7	41.7	12.9	2	2	4	38	77	2.5	0	also 40°
4995	5/07	78.5	34.3	30.9	1	3	4	311	17	4.1	0	
4996	2/08	54.7	36.0	9.9	1	2	3	317	32	4.9	0	
4997	25/06	48.6	31.5	13.6	1	2	3	267	62	2.9	?	
4998	10/09	51.2	35.2	8.7	2	1	3	232	49	3.9	?	
Average		64.0	38.4	16.8						3.7		

Table 2 lists the nine sample days elected for CGA. The table includes the CGA ID number, the sample date, the 24-hour average TSP, PM_{10} and $\text{PM}_{2.5}$ concentrations, the number of hours with high PM_{10} concentrations when the wind direction was in coal stockpile/operations sector, the 24-hour average wind direction and speed, and the standard deviation of wind direction, σ_θ . An additional column indicates whether it was a rain day. As this was based on the Bureau of Meteorology’s daily totals to 9am, there is some uncertainty in these (indicated by a “?”), although most were rain-free and also preceded by rain-free days. The comments column notes when the wind direction was from about 40° for some of the day, i.e. blowing from the ocean coastline to the north-east of the Stockton site, and hence possibly including enhanced levels of wind-blown sand and/or sea salt. The pollution rose in Figure 20 confirms the predominance of NW winds for these samples.

Figure 19 shows the time series of PM₁₀ concentrations and wind direction for the nine days in Table 2. Because of the criteria used to select the days, most of the high PM₁₀ values correspond to north-westerly winds but on 13/09, for example, they also occur in north-easterly winds.

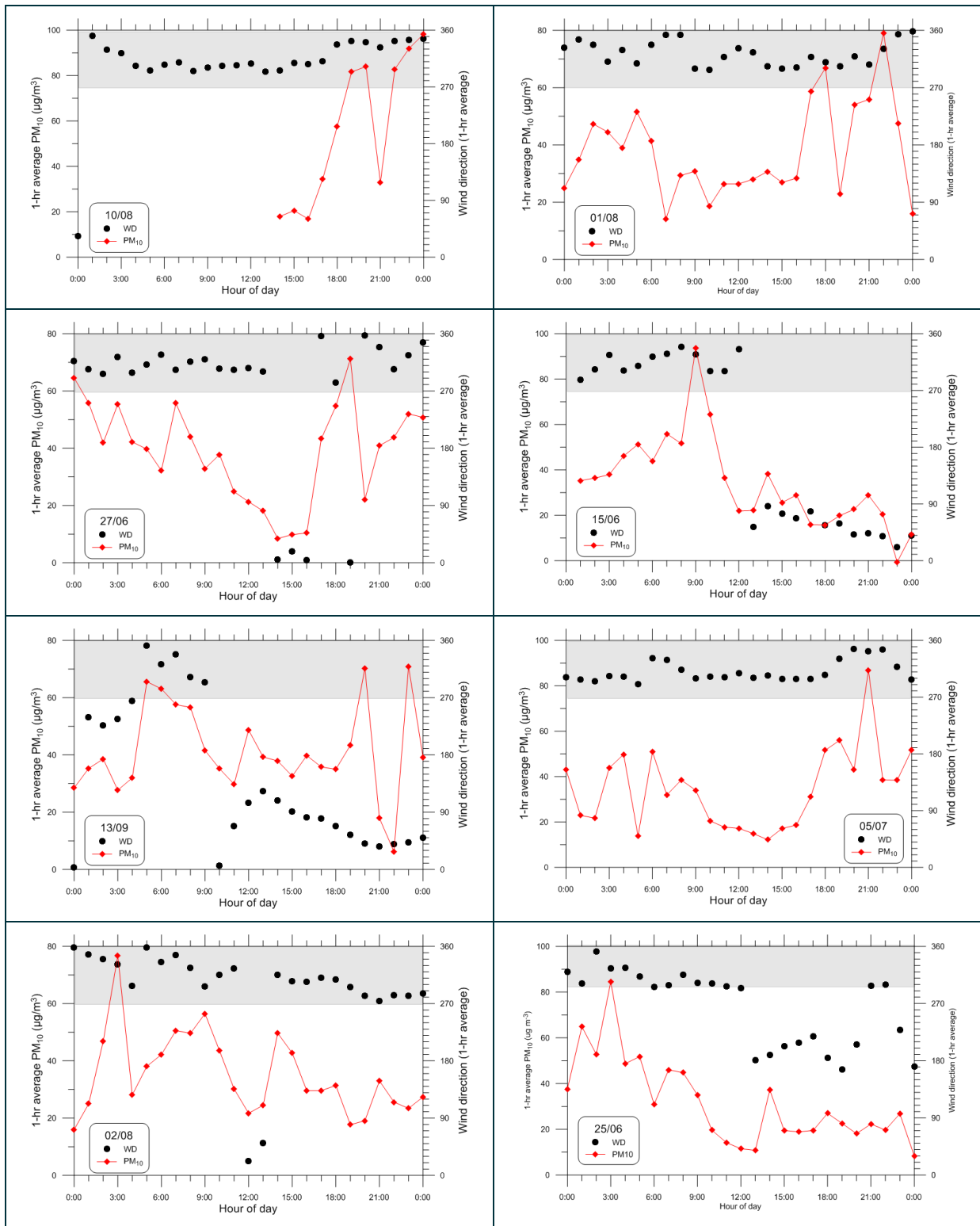


Figure continued over page

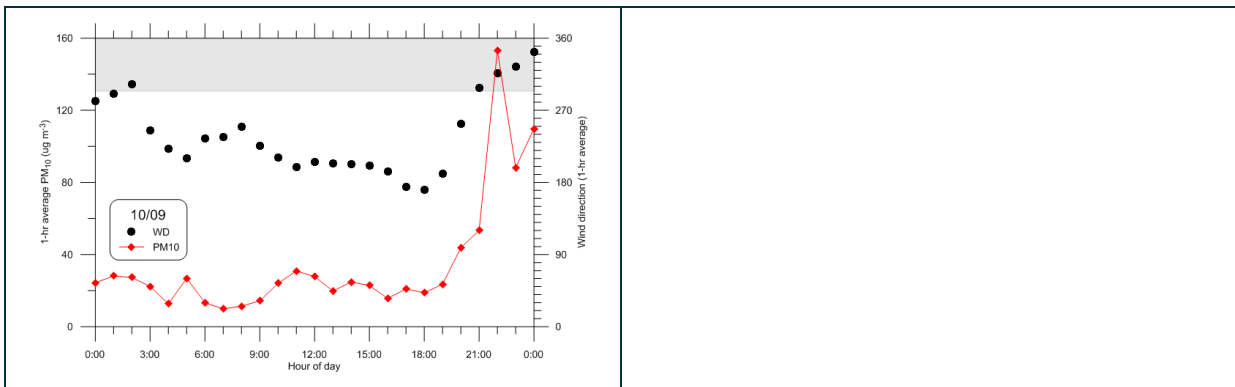


Figure 19. Daily time series of 1-hour average PM₁₀ concentrations and wind direction (WD) on the analysed days in Table 2. The shaded region is the 295–360° wind direction sector

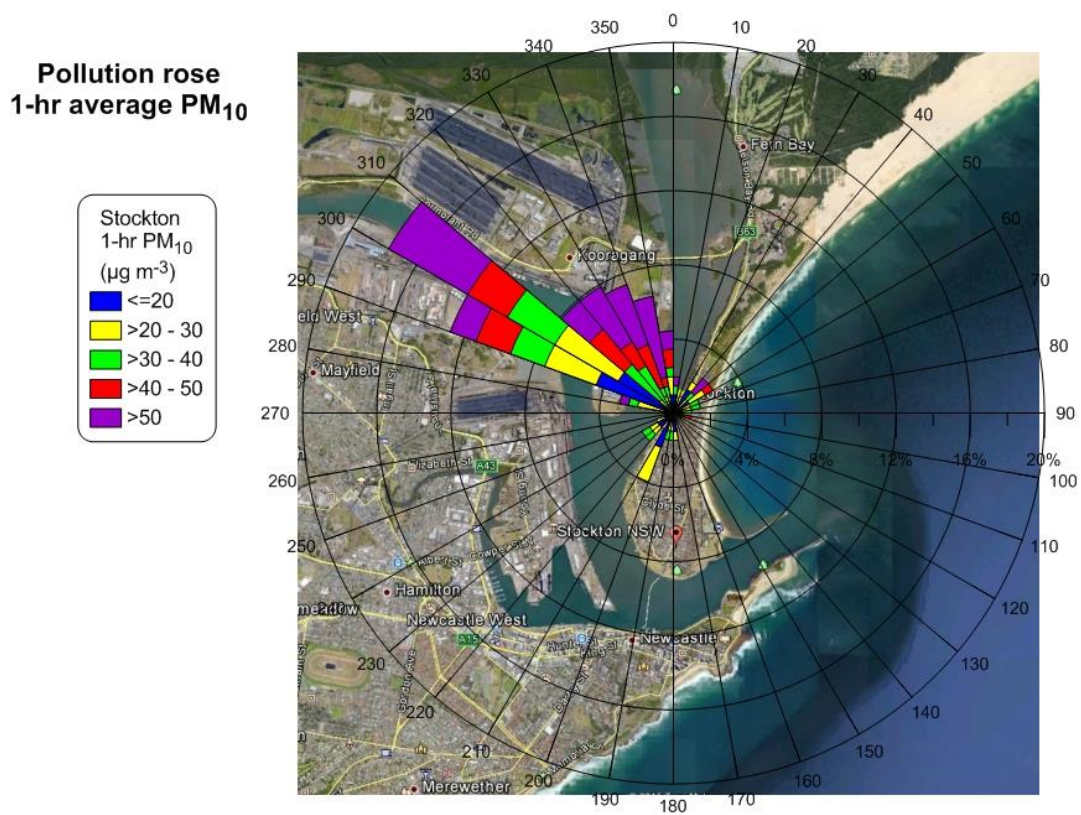


Figure 20. PM₁₀ pollution rose for elevated concentrations for the selected set of filters (predominantly north-westerly winds)

3.3 Image analysis

The CGA method is described in Section 2.4. An example of part of the mosaicked image for one sample (#4992) is shown in Figure 21, the image on the left shows the particles in white light whereas the image on the right is the same area after characterisation with the particles identified as coal shown in green and the non-coal particles classified as dark material (mainly soot and soil) shown in red or bright material (mainly fly ash) shown in blue.

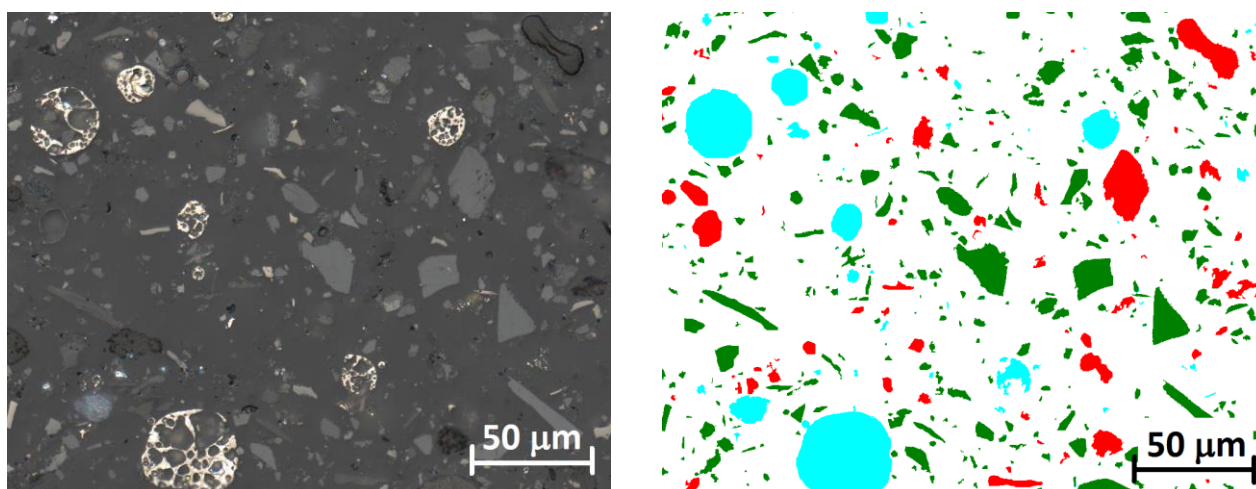


Figure 21. Particles imaged in white light (left) and identified by reflectance fingerprint and given false colours (right) as coal – green, dark material – red, and bright material – blue (Sample #4992)

The CGA technique fully automates the identification of coal particles but classification of non-coal particles also relies to some extent on the technician's experience. It was based on the definitions in the McCrone online atlas (McCrone Atlas of Microscopic Particles 2012). A summary of the types of particles identified is:

- **Coal particles** occurred in the form of fresh angular fragments of vitrinite and inertinite of mostly medium, but also some low and high rank coal in a range of sizes.
- **Fly ash** was present in all samples and consisted of large airborne single and multi-chambered isotropic cenospheres of char. The cavities for some of the larger cenospheres appeared to contain finer particles of ash and other materials and these particles could be classified as plerospheres. Many of the fly ash particles have large diameters ($>10\mu\text{m}$), indicating local sources rather than airborne transport of emissions from Hunter Valley power station stacks.
- **Soil (stone dust)** comprised a mixture of mineral grains, including quartz, clusters of minute clay minerals and some pyrite.
- **Soot** consisted of a wide range of large and small clusters of small, highly reflecting and anisotropic carbon spheres.
- **Organic matter** mostly consisted of large pieces of plant and insect remains. There were also spores and degraded vegetable matter.

- **Rust and Fe-oxides** occurred as flakes, sometimes quite large, of variously hydrated, amorphous to fine-crystalline coagulations.
- **Slag** was present as fragments of fresh and weathered/degraded material.
- **Plastics and paint** consisted of small droplets and flakes of mostly blue, red and white paint.
- **Graphite** was rare in the samples. It occurred in the form of poorly crystallised laths.

The photomicrograph from Figure 21 is shown in Figure 22 with labels showing some of the main types of particles. Appendix A includes these images for a number of the samples.

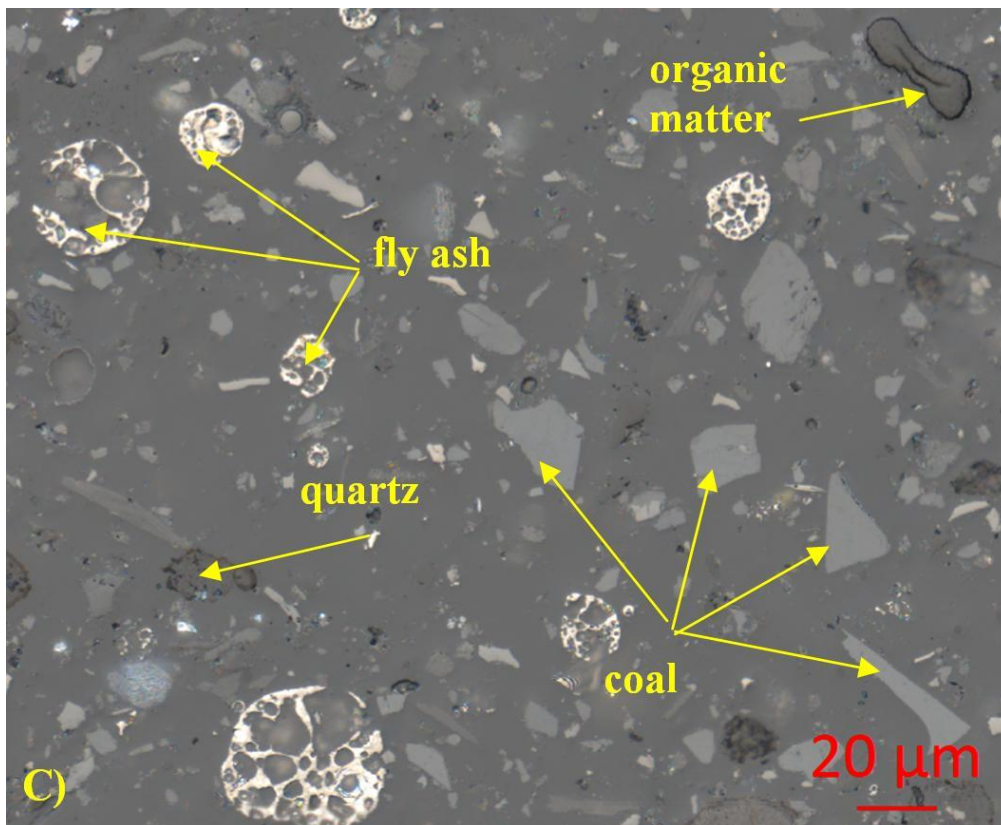


Figure 22. Photomicrograph of some identified types of dust particles in CGA resin sample #4992

3.4 Particle size distributions

Table 3 lists the number of particles of each type identified in each sample. An average of about 6000 particles were identified per sample. The average split was 72% coal particles, 20% dark particles, and 8% bright particles.

Table 3. Number of particles identified by CGA in each sample

Sample #	Date	Number of particles identified by CGA technique			Total
		Coal particles	Dark material (e.g. soot, soil)	Bright material (e.g. fly ash)	
4990	10/08/2015	4,478	772	660	5,910
4991	01/08/2015	6,301	1,354	917	8,572
4992	27/06/2015	6,040	1,522	576	8,138
4993	15/06/2015	4,612	1,379	551	6,542
4994	13/09/2015	2,818	1,124	369	4,311
4995	05/07/2015	4,837	1,453	318	6,608
4996	02/08/2015	4,714	2,210	463	7,387
4997	25/06/2015	2,527	846	350	3,723
4998	10/09/2015	5,127	854	314	6,295
Average		4,606	1,279	502	6,387

The distributions of particle mass for the coal particles identified in each sample are shown in Figure 23. The overall averages have a broad peak from 10–20 μm with a maximum at 15 μm . Most of the samples are well represented by the average distributions, although they have more scatter because of the relatively larger variability associated with the smaller number of particles in each individual sample. Two samples (4991 and 4992) have a slightly stronger peak at about 20–23 μm and 4998 has a trough in this region.

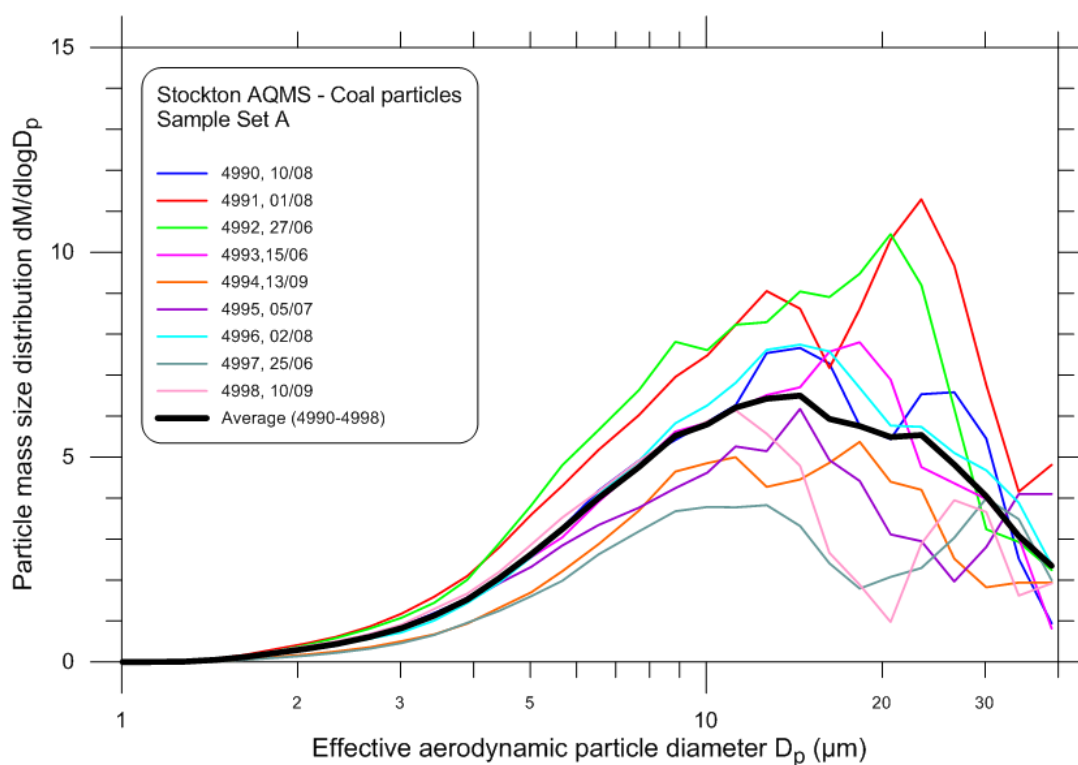


Figure 23. Coal particle mass distributions for analysed samples (4990–4998)

With the peak in the distribution of coal particles just above a standard cut-point of $10\mu\text{m}$, it is important to show how the distribution would be split by instruments with size selective inlets with nominal cut-points of $2.5\mu\text{m}$ and $10\mu\text{m}$ (Figure 24). The inlet collection efficiency curves shown by the dashed red lines are the US EPA FRM curves (US CFR 1987). About a third of the coal mass is in the $\text{PM}_{2.5-10}$ fraction with most of the rest in the $\text{PM}_{>10}$ fraction, and only a very small amount in the $\text{PM}_{1-2.5}$ fraction.

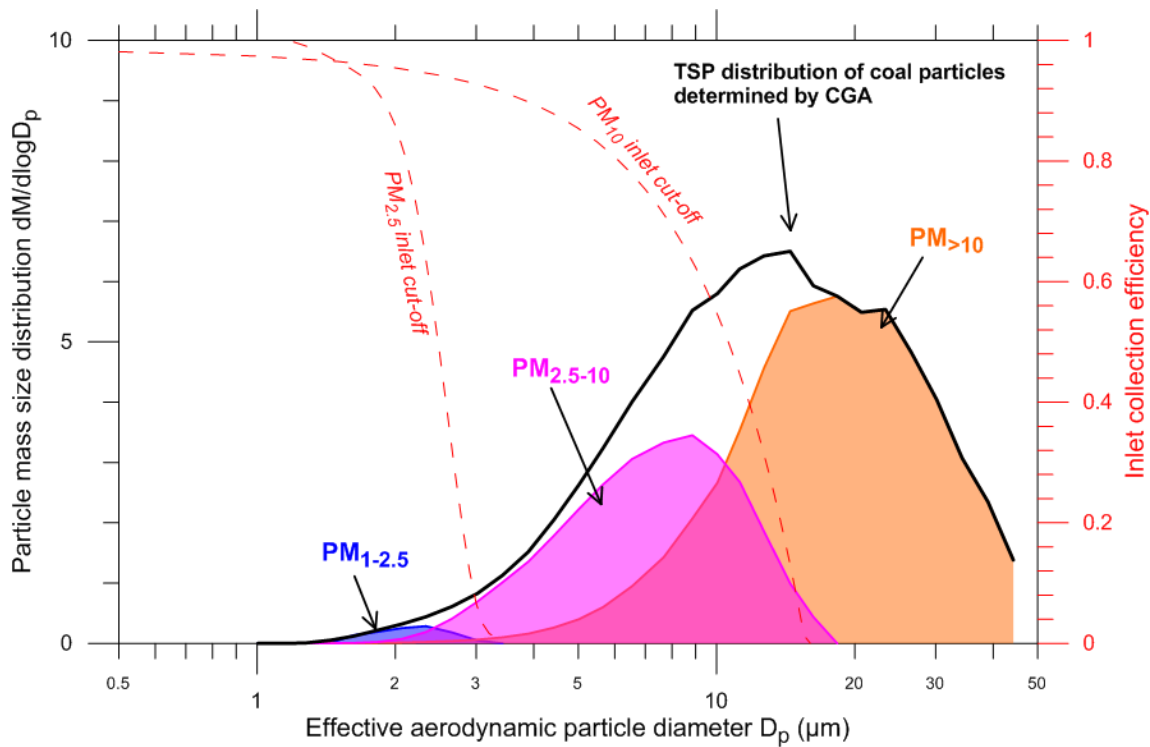


Figure 24. Split of the average coal particle mass distribution into the $\text{PM}_{1-2.5}$, $\text{PM}_{2.5-10}$ and $\text{PM}_{>10}$ size fractions

The mass distributions of the two other groups of particles identified in the CGA are compared with the coal distribution in Figure 25. The peaks in the non-coal particle distributions are at $35\text{--}40\mu\text{m}$ for both dark and bright material.

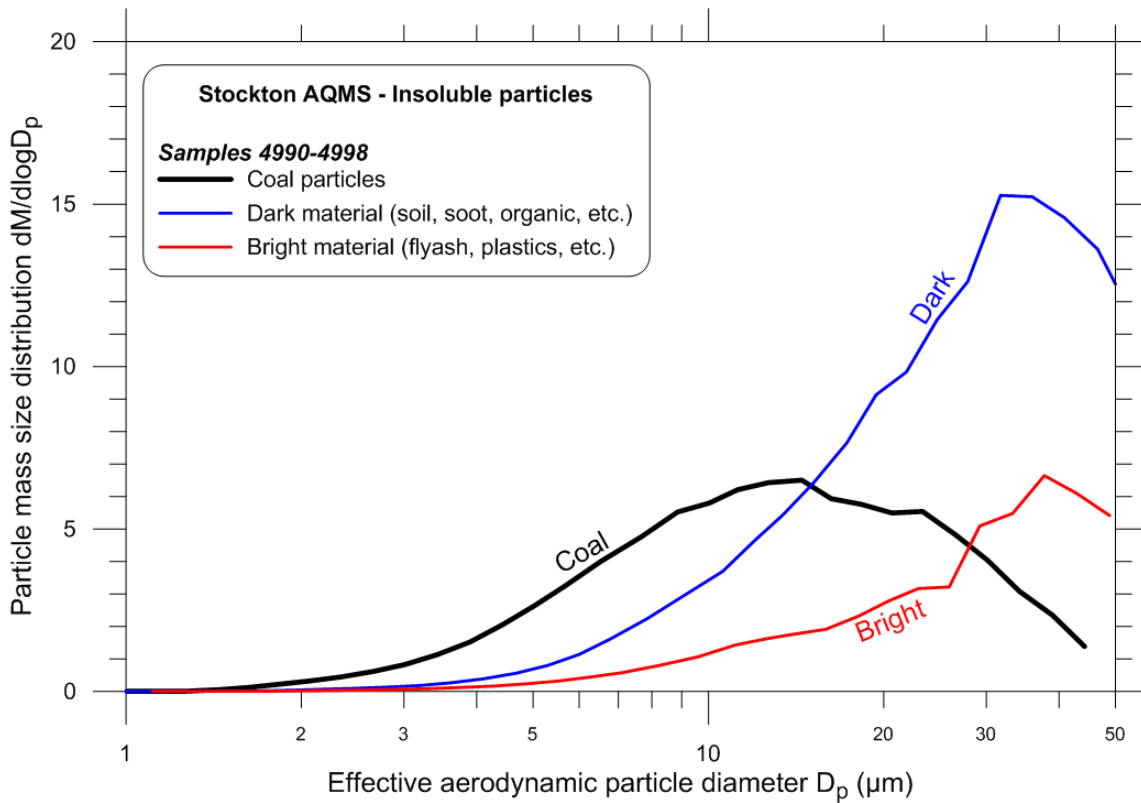


Figure 25. Particle mass distributions for the separate types of particles identified by CGA – coal, dark material and bright material

3.5 Proportion of coal particles and other insoluble particles

The results are first shown on a volume basis, which is the method commonly used in microscopic petrographic analysis of particles. The $\text{PM}_{2.5}$ and PM_{10} collection efficiencies shown in Figure 24 were used to sum the volume of each type of particle in each size range from the CGA data – $\text{PM}_{2.5}$, $\text{PM}_{2.5-10}$, and $\text{PM}_{>10}$ (using the FRM cut-offs). Table 4 lists the proportion of coal particles, dark material, and bright material in the various size fractions. The first line in the table lists results for the whole sample (TSP), followed by results for the specified PM fractions. Coal particles make up 33% of all insoluble particles (by volume); slightly more than half in the $\text{PM}_{>10}$ fraction, slightly less than half in the $\text{PM}_{2.5-10}$ fraction, and a fiftieth in the smallest $\text{PM}_{1-2.5}$ fraction.

Table 4. CGA results (by volume) of average and range of percentage of total insolubles for each type of insoluble particle in each size range (samples 4990–4998)

Size fraction	Results by volume as percentage of insolubles			
	Coal particles	Dark material e.g. soot, soil	Bright material e.g. fly ash	Total
TSP	33% (22%–42%)	47% (29%–69%)	20% (8%–42%)	100%
PM_{>10µm}	19% (13%–25%)	41% (22%–64%)	18% (7%–40%)	78% (75%–84%)
PM_{2.5–10µm}	13.1% (8.8%–16.8%)	6.2% (4.0%–9.5%)	2.0% (1.2%–3.6%)	21.3% (16%–24%)
PM_{1–2.5µm}	0.69% (0.37%–0.98%)	0.14% (0.09%–0.25%)	0.06% (0.03%–0.09%)	0.89% (0.49%–1.27%)

As described in Section 2.4.6, the mass of each particle was determined assuming a density for coal particles of 1400kg m⁻³, for dark material (mainly soot and soil) of 2000kg m⁻³, and for bright material (mainly fly ash) of 2200kg m⁻³. The particles identified by CGA do not include the mass of soluble particles, which are washed out in the CGA preparation procedures (Section 2.4.2). In a similar way as for Table 4, but in this case by mass, the percentage of the total mass in each bin (size and particle type) was calculated, as shown in Table 5.

Table 5. CGA results (by mass) of average and range of percentage of total insoluble mass for each type of insoluble particle in each size range (samples 4990–4998)

Size fraction	Results by mass as percentage of insolubles			
	Coal particles	Dark material e.g. soot, soil	Bright material e.g. fly ash	Total
TSP	25% (16%–33%)	51% (30%–74%)	24% (9%–48%)	100%
PM_{>10µm}	16% (11%–22%)	47% (26%–71%)	23% (9%–47%)	87% (84%–91%)
PM_{2.5–10µm}	8.4% (5.4%–10.9%)	3.6% (2.1%–5.7%)	1.2% (0.7%–2.4%)	13% (9%–15%)
PM_{1–2.5µm}	0.30% (0.15%–0.43%)	0.04% (0.03%–0.07%)	0.02% (0.01%–0.02%)	0.4% (0.2%–0.5%)

Table 5 shows that coal particles make up 25% of the total mass of insoluble particles; a third of this (8.4%) is in the PM_{2.5–10} fraction, just 0.3% in the PM_{1–2.5} fraction, and the other two thirds as PM_{>10}. The data in Table 5 are shown graphically in Figure 26, but in this case presented as percentages of the mass of insolubles in each size fraction, not the total insoluble mass. In

addition to this being more relevant for understanding the proportion of coal particles in air quality measures such as PM₁₀, the results show more sample-to-sample consistency. For example, the ratio of coal to total insolubles in the PM_{2.5-10} fraction averages 0.63 with a range of just 0.55 to 0.71. Note that data for the smallest size fraction (PM_{1-2.5}) need to be interpreted carefully because the limit of 1µm for the CGA technique means that smaller particles are not detected, so that only about 30% of the total PM_{2.5} is included in the analysis.

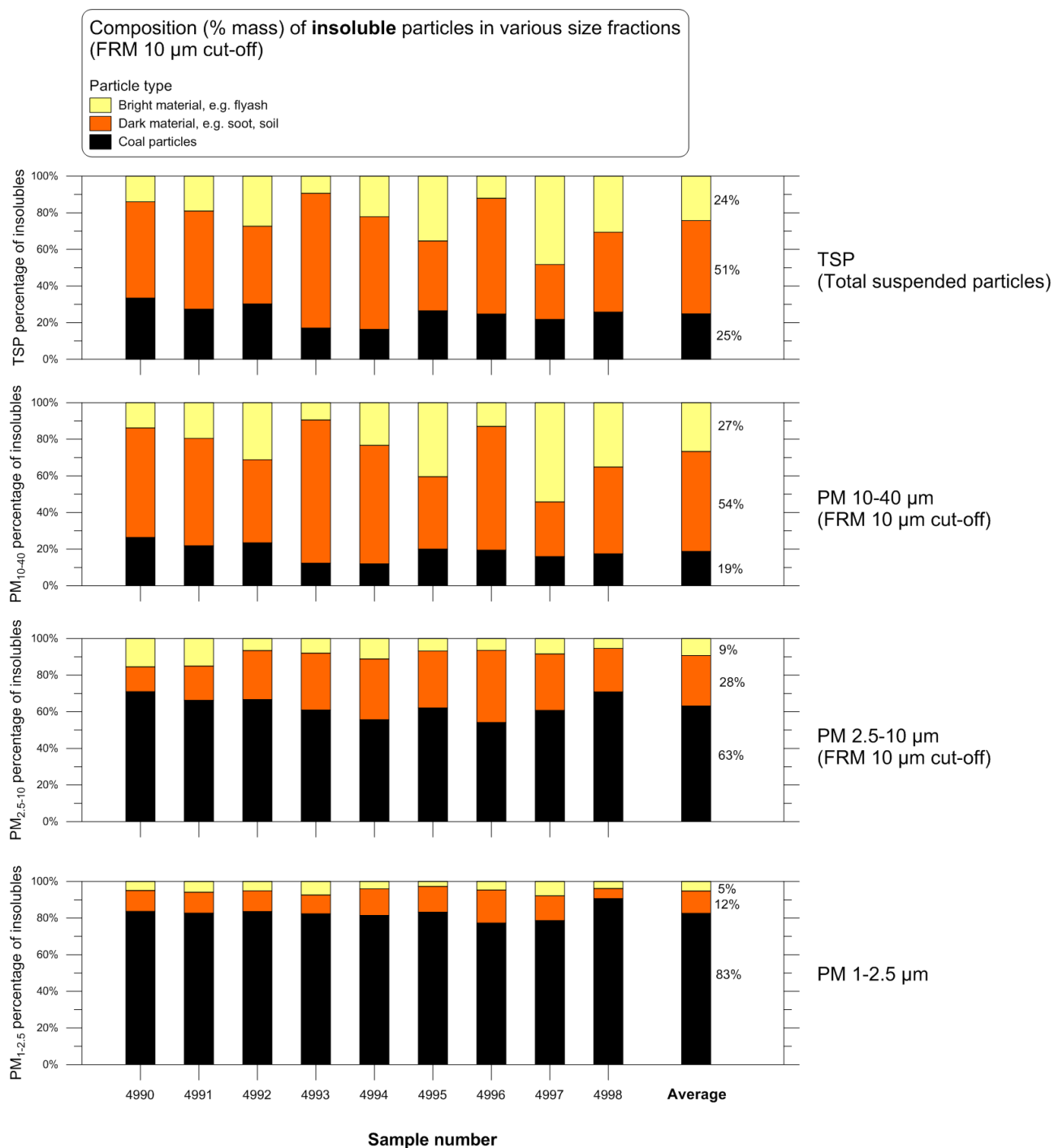


Figure 26. Percentage of coal and other insoluble particle types identified by CGA in each of the samples and each of the size fractions. (Note that the PM_{1-2.5} size fraction typically only makes up 30% of the total PM_{2.5} in urban samples.)

With the FRM cut-offs:

- In the PM₁₀₋₄₀ size fraction the insoluble particles consist on average of 19% coal particles, 54% dark material and 27% bright material.
- In the PM_{2.5-10} size fraction the insoluble particles consist on average of 63% coal particles, 28% dark material and 9% bright material.
- In the PM_{1-2.5} size fraction (note, not PM_{2.5}) the insoluble particles consist on average of 83% coal particles, 12% dark material and 5% bright material (mainly fly ash).

In the Lower Hunter Particle Characterisation Study (Hibberd et al. 2016), the PM_{2.5-10} fraction was measured with a GENT sampler, which as shown in Figure 11 has different size selection characteristics, broader than the standard PM₁₀ size selective inlet. The results described above were reanalysed using this characteristic. The overall results were very similar to Figure 26 with the only significant differences being for the PM_{2.5-10} fraction that the proportion of coal decreases from 63% (FRM) to 55% (GENT). The proportions are listed in Table 6. With the GENT cut-offs:

- In the PM_{2.5-10} size fraction the insoluble particles consist on average of 55% (GENT) coal particles, 34% (GENT) dark material and 11% (GENT) bright material.

Table 6. Percentage (by mass) of each particle type in PM_{2.5-10} insolubles using GENT cut-off

Sample #	Coal particles [%]	Dark material (e.g. soot, soil) [%]	Bright material (e.g. fly ash) [%]
Set A 4990	63	22	15
4991	59	27	14
4992	59	33	8
4993	53	38	9
4994	43	41	16
4995	56	34	10
4996	48	45	7
4997	52	34	14
4998	63	29	8
Average	55 ± 7	34 ± 6	11 ± 3

3.6 Concentration of coal particles and other insoluble particles

The above results show the proportion of each type of insoluble particle. In order to determine the corresponding ambient concentrations in $\mu\text{g m}^{-3}$, the percentage of insoluble particles on the TSP Emfab filters was determined as described in Section 2.4.2. The results are listed in Table 7.

The 100% in Table 5 represents the 24-hour average TSP multiplied by the insoluble fraction in Table 7. The resulting ambient concentrations for each particle type in each size fraction are

shown in Figure 27 for the results using the FRM cut-off. Note that the scales on the vertical axes are different for each size fraction as there is correspondingly less material in the smaller size fractions.

Table 7. Fraction of insoluble material in the analysed samples by % mass

Sample	Date	Insoluble (mass %)	24-hour TSP concentration ($\mu\text{g m}^{-3}$)
4990	10/08/2015	66%	73.8
4991	1/08/2015	65%	58.6
4992	27/06/2015	42%	76.2
4993	15/06/2015	18%	61.6
4994	13/09/2015	20%	72.7
4995	05/07/2015	41%	78.5
4996	02/08/2015	64%	54.7
4997	25/06/2015	37%	48.6
4998	10/09/2015	34%	51.2
Average		43%	64$\mu\text{g m}^{-3}$

The average concentrations of coal particles shown in Figure 27 are listed in Table 8 using the FRM cut-off. In summary, although the proportion of coal particles in the insolubles increases as the particle size decreases (Figure 26), the total mass of coal particles decreases (Table 8) because there is much less mass in the smaller size fractions.

Table 8. Average (and range) of coal particle concentrations

PM fraction	Average (and range) of coal particle concentrations
TSP	7.7 $\mu\text{g m}^{-3}$ (1.9–16.4)
PM _{>10}	5.1 $\mu\text{g m}^{-3}$ (1.2–11)
PM _{2.5–10}	2.5 $\mu\text{g m}^{-3}$ (0.6–5.3)
PM _{1–2.5}	0.09 $\mu\text{g m}^{-3}$ (0.02–0.17)

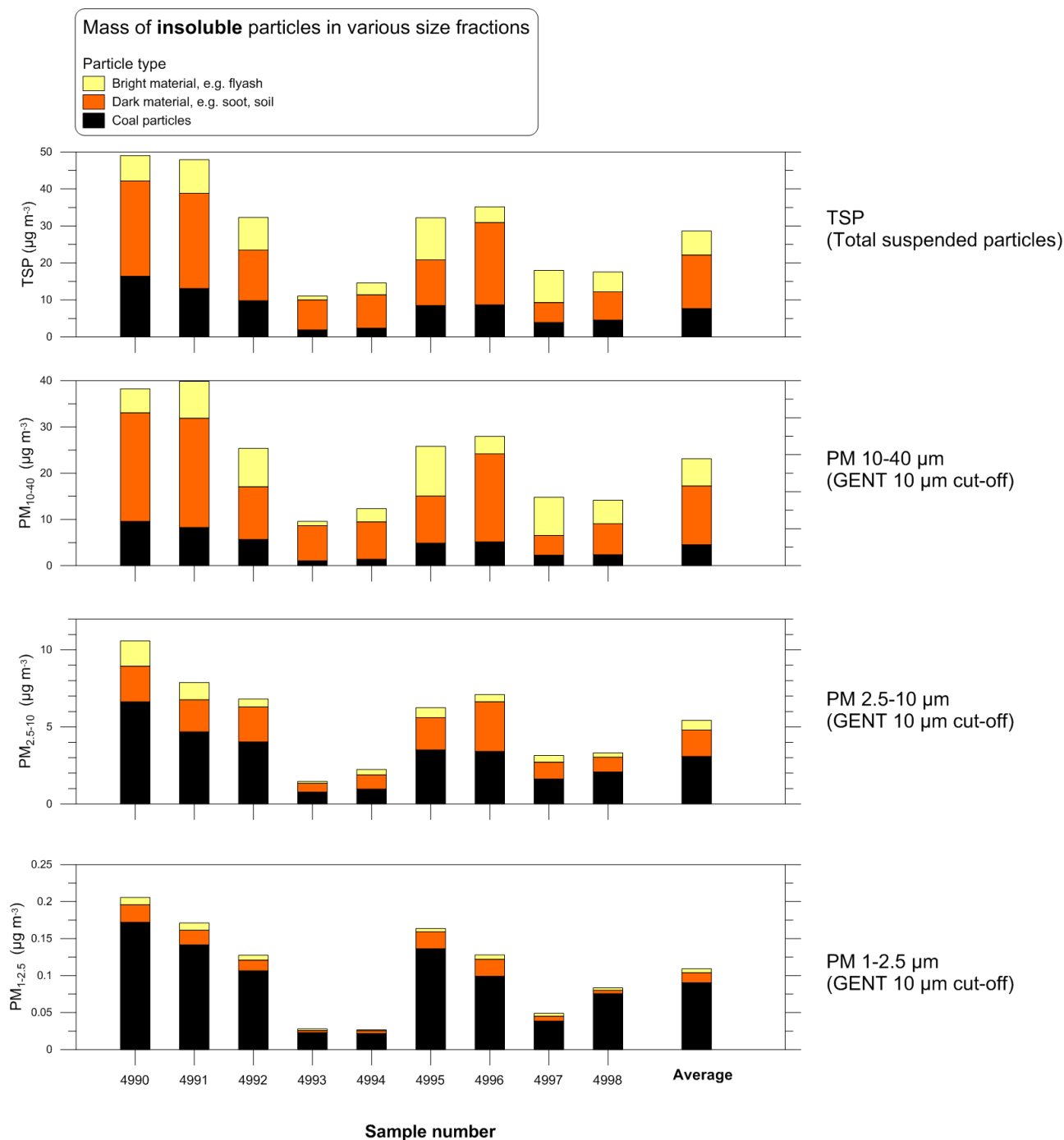


Figure 27. Mass of coal and other particle types identified by CGA in each of the samples and each of the size fractions. (Note that the PM_{1-2.5} size fraction typically only makes up 30% of the total PM_{2.5} in urban samples.)

3.7 Concentration of soluble and insoluble particle types

The fraction of insoluble particles listed in Table 7 is for each TSP sample and can be used to compute the fraction of both solubles and insolubles in TSP, as shown in the top panel of Figure 28. However, the insoluble fractions in Table 7 cannot be assumed to apply for each individual size range, i.e. the proportion of insoluble particles in the PM_{2.5-10} fraction is not necessarily the same as in total TSP or the PM₁₀₋₄₀ fraction. Furthermore, although ambient PM₁₀ and PM_{2.5} measurements are available for the CGA study period, the differences in the measurement

technologies between the TSP high volume sampler, the PM₁₀ TEOM instrument and the PM_{2.5} BAM instrument mean that there are very large uncertainties when computing differences between the concentrations, e.g. PM₁₀₋₄₀ or PM_{2.5-10} size fractions.

In spite of these uncertainties, Figure 28 does include an estimate of the soluble component for PM₁₋₁₀ and PM_{1-2.5}. As discussed in Section 3.1, the PM_{1-2.5} size fraction typically only makes up 30% of the total PM_{2.5}, so we can use this assumption to estimate PM₁₋₁₀ and PM_{1-2.5} from the measured PM₁₀ and PM_{2.5} concentrations. The estimate for the soluble component (light green in Figure 28) was then computed as the difference between these values and the concentration of insolubles shown in Figure 27. Note that there is considerable uncertainty in these estimates, mainly because of the differences in measurement technology between the TEOM and BAM instruments.

The results from Figure 28 are summarised in Table 9. A key result from this analysis is that although coal particles are on average about 50% of the insolubles in PM_{2.5-10}, they are on average 10% of total (soluble + insoluble) PM₁₋₁₀.

Table 9. Average percentage (and range) of coal particles as a proportion of the mass of total (soluble + insoluble) particles

PM fraction	Coal particle percentage (by mass) of total (soluble + insoluble) particles
TSP	12% (3%–22%)
PM₁₋₁₀	10% (2%–24%)
PM_{1-2.5}	1.8% (0.5%–3.3%)

The proportion of coal particles in TSP listed in Table 9 is consistent with results reported in the recent Lower Hunter Dust Deposition Study (AECOM 2016) of coal forming on average 10% of total deposited dust with a range of 0% to 25%. Similar results were referenced by Environ (2012) based on the analysis of dust deposition gauges collected at residences in Stockton, Fern Bay (3km north of Stockton AQMS), and Fullerton Cove (4km further north). In their assessment of baseline air quality in the region, they reported that the contribution of coal dust to annual dust deposition based on available sampling results for the 2005–2010 period was in the range 5% to 16%. Environ (2012) also noted that the sampling showed greater contributions from coal in deposited dust in proximity to the port especially in Mayfield East and Kooragang.

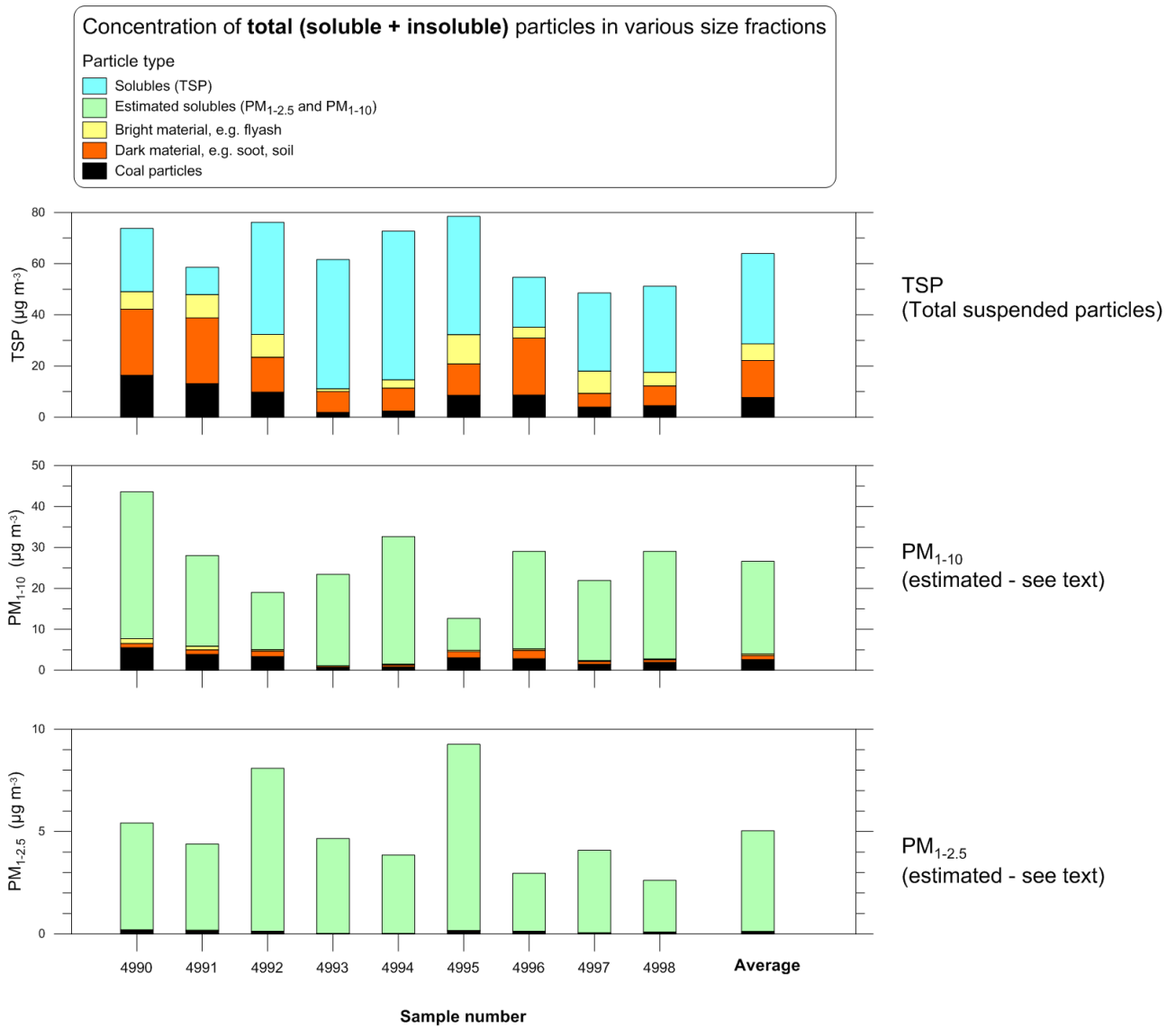


Figure 28. Concentration of solubles (estimated for PM₁₋₁₀ and PM_{1-2.5}) and the three types of insolubles in all samples. (Note that the PM_{1-2.5} size fraction typically only makes up 30% of the total PM_{2.5} in urban samples.)

4 Discussion

4.1 Relating CGA results to the Lower Hunter Particle Characterisation Study

4.1.1 PM_{2.5-10}

The most significant results from this CGA study for PM_{2.5-10} are:

- (i) in all samples approximately half the mass of insoluble PM_{2.5-10} particles is coal particles, and
- (ii) coal particles make up on average 10% (range 2–24%) of the total mass of all PM_{2.5-10} particles when winds are from the north-west.

Both of these CGA results are consistent with the results from the LHPCS (Hibberd et al. 2016), as discussed below.

(i) CGA result: In all samples approximately half the insoluble PM_{2.5-10} particles are coal particles.

The LHPCS analysed both the soluble and insoluble components. It could not specifically identify coal particles but concluded that in the PM_{2.5-10} fraction they would be measured as light-absorbing carbon. The components of PM_{2.5-10} determined in the LHPCS using the GENT sampler are shown in Figure 29 – the main insoluble components are soil and light-absorbing carbon.

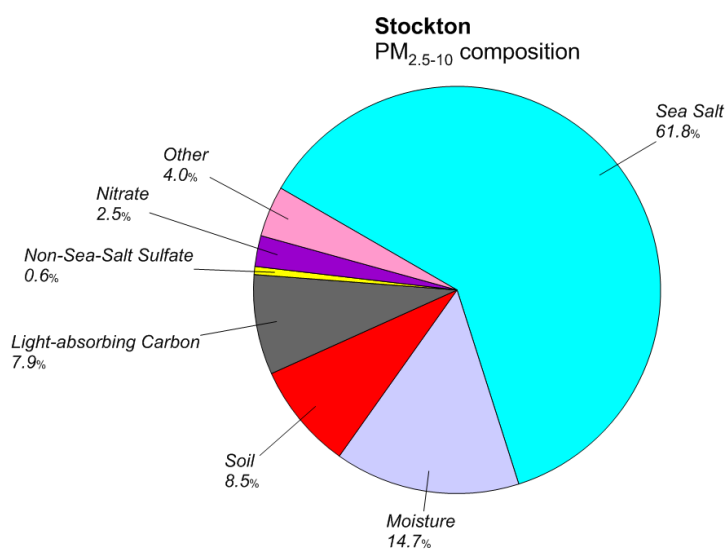


Figure 29. Main components and annual average composition of PM_{2.5-10} at Stockton based on chemical speciation in the LHPCS (Hibberd et al. 2016)

The LHPCS value for the proportion of coal in the insoluble particles is estimated as the ratio of the light-absorbing carbon to the total insolubles (assumed here to be light-absorbing carbon + soil), which is shown in Figure 30 for each day during the LHPCS. The ratio is anomalously low from mid-June to mid-July, but the average during the rest of winter until 15 September is $58 \pm 22\%$, and for

the whole year the average is $51 \pm 24\%$. We can compare this with the CGA result for $PM_{2.5-10}$ (calculated using the GENT cut-off function because the GENT instrument was used for the LHPCS measurements) that overall 55% (range 43–63%) of the mass of insoluble particles was coal. This close agreement provides strong evidence that all or most of the light-absorbing carbon identified in the LHPCS analysis of $PM_{2.5-10}$ was coal particles.

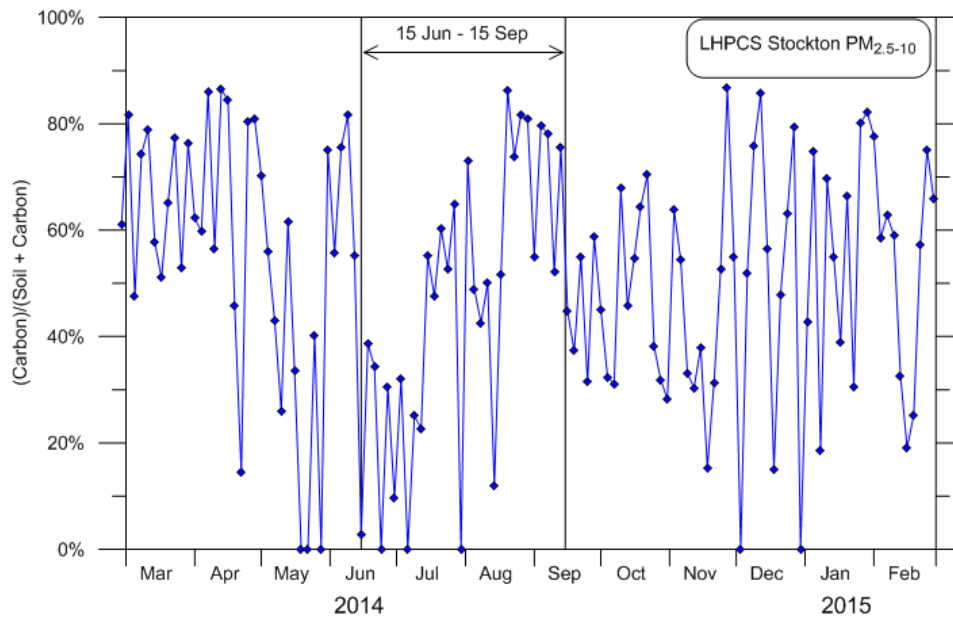


Figure 30. Ratio of light-absorbing carbon to total insolubles in $PM_{2.5-10}$ during the Lower Hunter Particle Characterisation Study

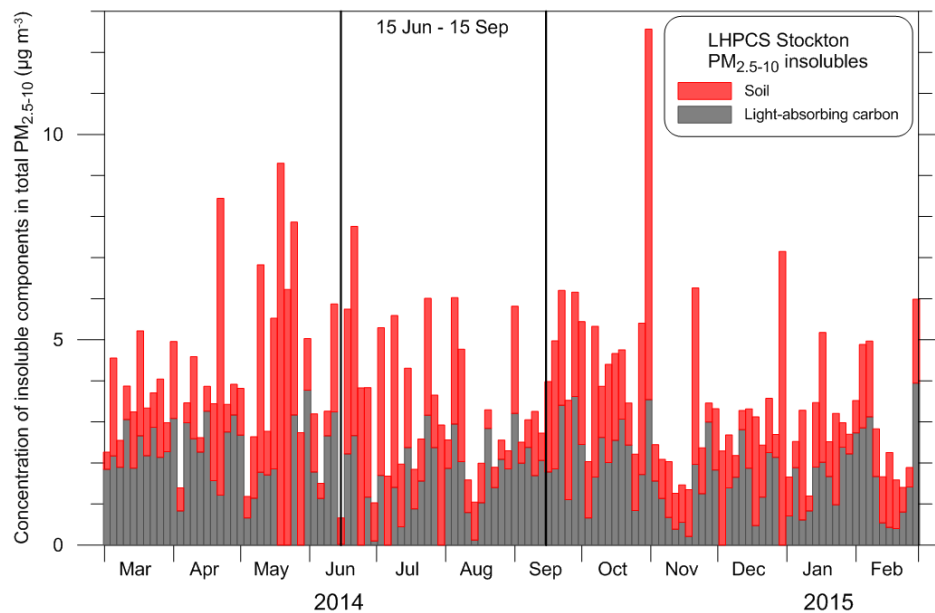


Figure 31. Measured soil and light-absorbing carbon components of $PM_{2.5-10}$ during the Lower Hunter Particle Characterisation Study

Figure 31 shows the variation in the contributions of these two insoluble components during the LHPCS as absolute concentrations. As noted in the LHPCS report, there is no significant seasonal trend in either component but there is greater variability in the soil component. The LHPCS range of total insolubles during winter was $0.7\text{--}7.8\mu\text{g m}^{-3}$ with an average of $3.4\mu\text{g m}^{-3}$. These are generally consistent with the CGA range of values for $\text{PM}_{2.5-10}$ of $0.6\text{--}5.3\mu\text{g m}^{-3}$ with an average of $2.5\mu\text{g m}^{-3}$ (see Table 8).

(ii) CGA result: Coal particles make up on average 10% (range 2–24%) of the total mass of all $\text{PM}_{2.5-10}$ particles when winds are from the north-west.

Figure 32 shows the proportion of total $\text{PM}_{2.5-10}$ that was light-absorbing carbon during the LHPCS. The annual average is 10% (range 0–28%). During the period 15 June – 15 September the average is 13% (range 0–28%).

Because the CGA data were collected in the winter after the LHPCS, direct comparison is difficult; however, the CGA results showing that coal is on average 10% (range 2–24%) of the $\text{PM}_{2.5-10}$ mass are similar to the LHPCS results, which is consistent with the conclusion in the LHPCS that most if not all of the annual average 10% light-absorbing carbon is likely to be coal particles.

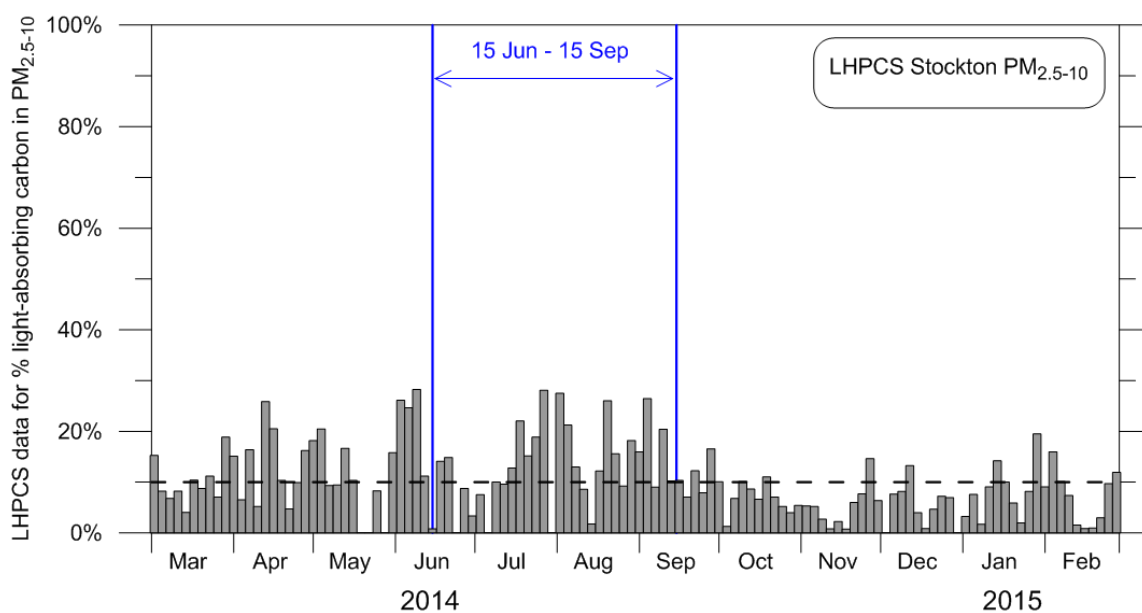


Figure 32. Measured percentage of light-absorbing carbon in total $\text{PM}_{2.5-10}$ during the Lower Hunter Particle Characterisation Study

4.1.2 $\text{PM}_{1-2.5}$

The LHPCS did not identify a specific coal factor but concluded that any coal particles present in $\text{PM}_{2.5}$ would be most likely to be in the soil factor with an upper limit on the contribution of coal particles being 4% of total annual average $\text{PM}_{2.5}$. Of the carbon in $\text{PM}_{2.5}$, the fine soot due to

combustion is generally much smaller than $1\mu\text{m}$ (i.e. in the PM_1 fraction), whereas coal particles generated by mechanical abrasion are generally considered to be larger than $1\mu\text{m}$.

The results in Table 9 list the proportion of coal particles in the $\text{PM}_{1-2.5}$ mass fraction as an average of 1.8% (range 0.5–3.3%). As discussed at the end of Section 3.1, total $\text{PM}_{1-2.5}$ has been estimated to be 30% of total $\text{PM}_{2.5}$. If all coal particles are assumed to be larger than PM_1 , then the CGA results would indicate that the proportion of coal in $\text{PM}_{2.5}$ is about 0.3 times the values in Table 9, i.e. an average of about 0.5% (range 0.15–1.0%).

On the other hand, a reasonable upper limit for the proportion of coal in $\text{PM}_{2.5}$ can be obtained by assuming that the proportion of coal in the PM_1 fraction is the same as in the $\text{PM}_{1-2.5}$ fraction. This produces the result that coal is an average 1.8% (range 0.5–3.3%) of $\text{PM}_{2.5}$.

Both these estimates are smaller than the maximum of 4% identified in the LHPCS as possibly coal particles. The results from this CGA study suggest an upper limit closer to 0.5% of coal in $\text{PM}_{2.5}$.

4.2 Possible sources of coal particles

The primary sources of coal particles in the region are generally considered to be the coal export facilities including the coal train movements (e.g. NSW Chief Scientist & Engineer 2015). The results from this study show that in north-westerly winds, the coal concentrations in TSP averaged $7.7\mu\text{g m}^{-3}$ (range $1.9\text{--}16.4\mu\text{g m}^{-3}$). These results are consistent with the coal export facilities, which are located to the west and north-west of Stockton, being sources of the observed coal particles.

Another possible source is resuspension of previously deposited coal particles in the ambient environment around Stockton.

4.3 Fly ash composition

Fly ash is identified by CGA as a significant component of the samples analysed. It is generated in the high temperature combustion of fossil fuels such as coal and heavy oil. Fly ash particles have a wide range of sizes and structures. The fine particles (e.g. $\text{PM}_{2.5}$) emitted from power station stacks are generally smooth cenospheres, i.e. hollow alumina-silicate spheres. The fly ash particles identified in the CGA photomicrographs (e.g. Figure 22) include larger and more complex structures, which have been reported on by Goodarzi and Sanei (2009) with some examples shown in Figure 33. These are trapped in electrostatic precipitators and baghouses of the power stations. They are sold commercially for a range of applications including in concrete products.

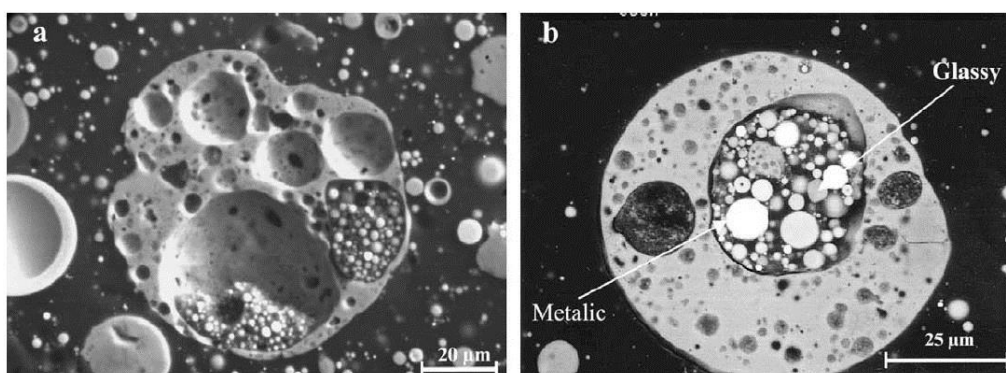


Figure 33. Examples of fly ash particles from a coal-fired power station: (a) fly ash particles with multi-cavities containing microspheres; (b) thick wall plerosphere in fly ash containing metallic and glassy spherical particles (Goodarzi & Sanei 2009)

The source of the fly ash in the CGA samples is not known, but possible sources include the concrete batching plant on Kooragang Island or nearby industrial furnaces. Its chemical composition depends on the fuel source and characteristics of the combustion. Here we use data for fly ash from the Eraring and Bayswater power stations (Flyash Australia website) to compute the elemental ratios listed in Table 10. They are compared to the ratios in the PM_{2.5-10} soil factor obtained from PMF (positive matrix factorisation) analysis undertaken for the LHPCS (Hibberd et al. 2016), and to typical Australian dust.

Given that the ratios for the PM_{2.5-10} soil factor match those for fly ash much better than those for typical Australian dust, it appears that fly ash was probably a major contributor to the PM_{2.5-10} soil factor at Stockton.

This indicates that the calculation in Figure 30 and Figure 31 of the insolubles from LHPCS data includes the fly ash within the soil component.

Table 10. Comparison of fly ash composition (Flyash Australia) with PM_{2.5-10} soil factor at Stockton (LHPCS) and with some typical Australian dust (Radhi et al. 2010)

Species ratio	Fly ash (Eraring, Bayswater)	Stockton LHPCS PM _{2.5-10} soil factor	Australian dust
Al/Ti	20–23	25	11.5–15.1
Al/Si	0.29–0.45	0.38	0.27–0.29
Ti/Si	0.020	0.015	0.018–0.026
Fe/Si	0.09–0.20	0.14	0.22–0.23
Ca/Si	0.05–0.15	0.07	–

4.4 Uncertainties

There is a range of uncertainties in this study including:

- uncertainties in determining the volume, mass and aerodynamic diameter of the particles identified by CGA
- uncertainty in comparing CGA results for PM₁₀ and PM_{2.5} with results from the standard ambient monitoring equipment (TEOM/BAM) at Stockton because of differences in the sampling technology
- uncertainty in the soluble/insoluble ratio for size fractions such as PM₁₋₁₀ and PM_{1-2.5}
- uncertainties due to incorrect classification of particles
- insufficient sampling as it only occurred for a few months of the year, so is not representative of conditions during the whole year.

Some of these have been discussed in the text in Sections 2 and 3, so we discuss only two of them in more detail below.

4.4.1 Uncertainties in determining the volume, mass and aerodynamic diameter of the particles identified by CGA

The CGA measures the area of each particle on the surface of the resin in which it is embedded. The equivalent diameter of a circle with the measured area was used as the effective diameter for each particle and the particle volume was computed from the effective diameter assuming the particles were spherical. As shown for example in Figure 22, many of the particles do not have a regular shape, so there is some uncertainty arising from this assumption, but it is difficult to quantify and this has not been done here.

Table 11. Sensitivity of analysis to assumptions about particle density

Coal particle density [kg m ⁻³]	Dark particle density [kg m ⁻³]	Bright particle density [kg m ⁻³]	Calculated percentage (by mass) of coal particles in PM _{2.5-10}
1,400	2,000	2,200	63.2%
1,400	3,500	2,200	64.1%
1,400	2,000	3,500	63.3%
1,400	3,500	3,500	64.3%
1,400	1,000	2,200	64.1%
1,400	1,000	1,000	64.6%

The calculation of mass requires an estimate of particle density. In this report, it has been assumed that the density of coal particles is 1400kg m⁻³, that of the dark material (mainly soot and soil) is 2000kg m⁻³, and of the bright material (mainly fly ash) is 2200kg m⁻³. Table 11 shows the results of the sensitivity analysis using a range of densities (as listed) on the proportion of coal in

the PM_{2.5-10} fraction, which is shown in the right-hand column. There is less than 2% variation in this figure, so it is concluded that the main result from this study about PM_{2.5-10} is not sensitive to the assumptions about particle density.

The above sensitivity test for density also included its effect in the calculation of the effective aerodynamic diameter of the particle as described in Section 2.4.5. However, for irregularly shaped particles a shape factor should be included to represent the difference in drag between the irregularly shaped particle and the assumed spherical shape. Given the insensitivity of the main result to changes in particle density, it is estimated that the effect of neglecting a shape factor is not significant for PM₁₀.

There is some uncertainty in the mass estimates for the largest particles identified by CGA in this study (diameter >30µm) because some of them have aspect ratios significantly larger than one. However, they would need to be checked individually to make better mass estimates and this has not been done for this study. Any errors would not affect the main conclusions from this study about the composition of PM_{2.5-10}.

4.4.2 Uncertainties due to incorrect classification of particles

Overall there is a high level of confidence in the identification of coal particles in the samples. The CGA has been used successfully to analyse dust samples around coal ports at Hay Point and Dalrymple Bay and in the township of Mackay. Classification of particles in the CGA technique uses reflectance histograms, which have been validated using several techniques including measurement with the infrared beam line of the Australian Synchrotron. In this study, these automated results were confirmed or corrected by a skilled petrographer. Additional validation, particularly of the non-coal particles, could be undertaken using confirmatory mineral mapping and chemistry at the micro level using techniques such as Fourier Transform Infrared (FTIR) Microscopy and Imaging Systems, QEMSCAN (SEM/EDS)⁵ or automated electron probe micro-analysis (EPMA), e.g. Johnson et al. 2015.

⁵ Quantitative Evaluation of Minerals by SCANNing electron microscopy (QEMSCAN) using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS).

5 Conclusion

This study has quantified the proportion and mass of coal particles in particulate matter (PM) measured at the OEH Stockton Air Quality Monitoring Station (AQMS) on selected winter days in 2015.

The study uses CSIRO's Coal Grain Analysis (CGA) system, which is able to analyse dust samples and provide quantitative detail about insoluble particles, specifically coal and non-coal particles, as well as their size in a range from about 1–50µm. CGA does not provide any information about soluble particles such as sea salt, because these are dissolved and washed out in the CGA sample preparation procedure.

Total suspended particle (TSP) samples were collected at the Stockton AQMS daily from 15 June to 17 September 2015 as 24-hour samples. Stockton was selected because (i) it is downwind from the coal operations on Kooragang Island and the adjacent areas of the Port of Newcastle for much of the winter months, (ii) it was a study site for the Lower Hunter Particle Characterisation Study (LHPCS), and (iii) it has a range of continuous air quality and meteorological monitoring instruments to provide information for interpreting the coal particle results.

The samples selected for analysis were from days with north-westerly winds, i.e. the Stockton sampling site was downwind of the coal operations. A total of nine samples was analysed.

The average **coal particle mass as a proportion of total (soluble + insoluble)** particles is 12% in TSP, 10% in PM_{1–10} and 1.8% in PM_{1–2.5}; the ranges are listed in the table below.

PM fraction	Average and range of coal particle mass as a percentage of total (soluble + insoluble) particles
TSP	12% (3%–22%)
PM _{1–10}	10% (2%–24%)
PM _{1–2.5} ⁶	1.8% (0.5%–3.3%)

This proportion of coal particles in TSP is consistent with the 10% coal (range 0–25%) in deposited dust reported in the recent Lower Hunter Dust Deposition Study (AECOM 2016). It is also consistent with analysis of dust deposition gauges collected at residences in Stockton, Fern Bay (3km north of Stockton AQMS), and Fullerton Cove (4km further north) as reported within the baseline air quality section of the air quality impact assessment for the fourth coal terminal project

⁶ It is important to note that the PM_{1–2.5} size fraction typically only makes up 30% of the total PM_{2.5} in urban samples.

by Environ (2012). They reported that the contribution of coal dust to annual dust deposition based on sample analysis available for the 2005–2010 period was in the range 5% to 16%.

The analysed filters have an average 24-hour TSP concentration of $64\mu\text{g m}^{-3}$. The average coal particle concentrations in the various PM size fractions are as follows:

PM fraction	Average (and range) of coal particle concentrations
TSP	$7.7\mu\text{g m}^{-3}$ (1.9–16.4)
PM _{>10}	$5.1\mu\text{g m}^{-3}$ (1.2–11)
PM _{2.5–10}	$2.5\mu\text{g m}^{-3}$ (0.6–5.3)
PM _{1–2.5}	$0.09\mu\text{g m}^{-3}$ (0.02–0.17)

The proportion of **coal particle mass in the insoluble particles** in the samples, as well as the proportion of dark particles (a mixture of soot, sand, clays, organic material, rubber and unidentified particles) and bright particles (a mixture of fly ash, some plastics, paint and unidentified particles) were determined to be as follows (using standard FRM cut-points):

- For TSP, the insoluble particles consist on average of 25% coal particles, 51% dark particles and 24% bright particles.
- In the PM_{2.5–10} size fraction, the insoluble particles consist on average of 63% coal particles, 28% dark particles and 9% bright particles.
- In the PM_{1–2.5} size fraction, the insoluble particles on average consist of 83% coal particles, 12% dark particles and 5% bright particles.

As discussed in Section 3.5 with the cut-points relevant for the GENT sampler:

- In the PM_{2.5–10} size fraction the insoluble particles consist on average of 55% coal particles, 34% dark material and 11% bright material.

This is relevant here because the GENT sampler was used in the LHPCS for the PM_{2.5–10} sampling. The proportion of coal particles in the insoluble part of the PM_{2.5–10} fraction obtained from CGA ($55\% \pm 7\%$) agreed very closely with results from the LHPCS for the annual average of the proportion of light-absorbing carbon in the insoluble components of the PM_{2.5–10} fraction ($51 \pm 24\%$). This provides strong evidence that all or most of the light-absorbing carbon identified in the LHPCS analysis of PM_{2.5–10} consisted of coal particles.

The results from this study for coal particles in PM_{1–2.5} suggest that the LHPCS upper limit of 4% of coal particles in PM_{2.5} based on carbon in the soil factor is probably an over-estimate. The results from this CGA study suggest an upper limit closer to 0.5%.

The ratios of elemental Al, Si, Ti, Fe and Ca in for the PM_{2.5–10} soil factor reported in the LHPCS match those for fly ash much better than those for typical Australian dust. Thus it is concluded that fly ash was probably a major contributor to the PM_{2.5–10} soil factor in the LHPCS.

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Appendix A. Selected CGA images and results

Sample 4990 from 10/08/2015

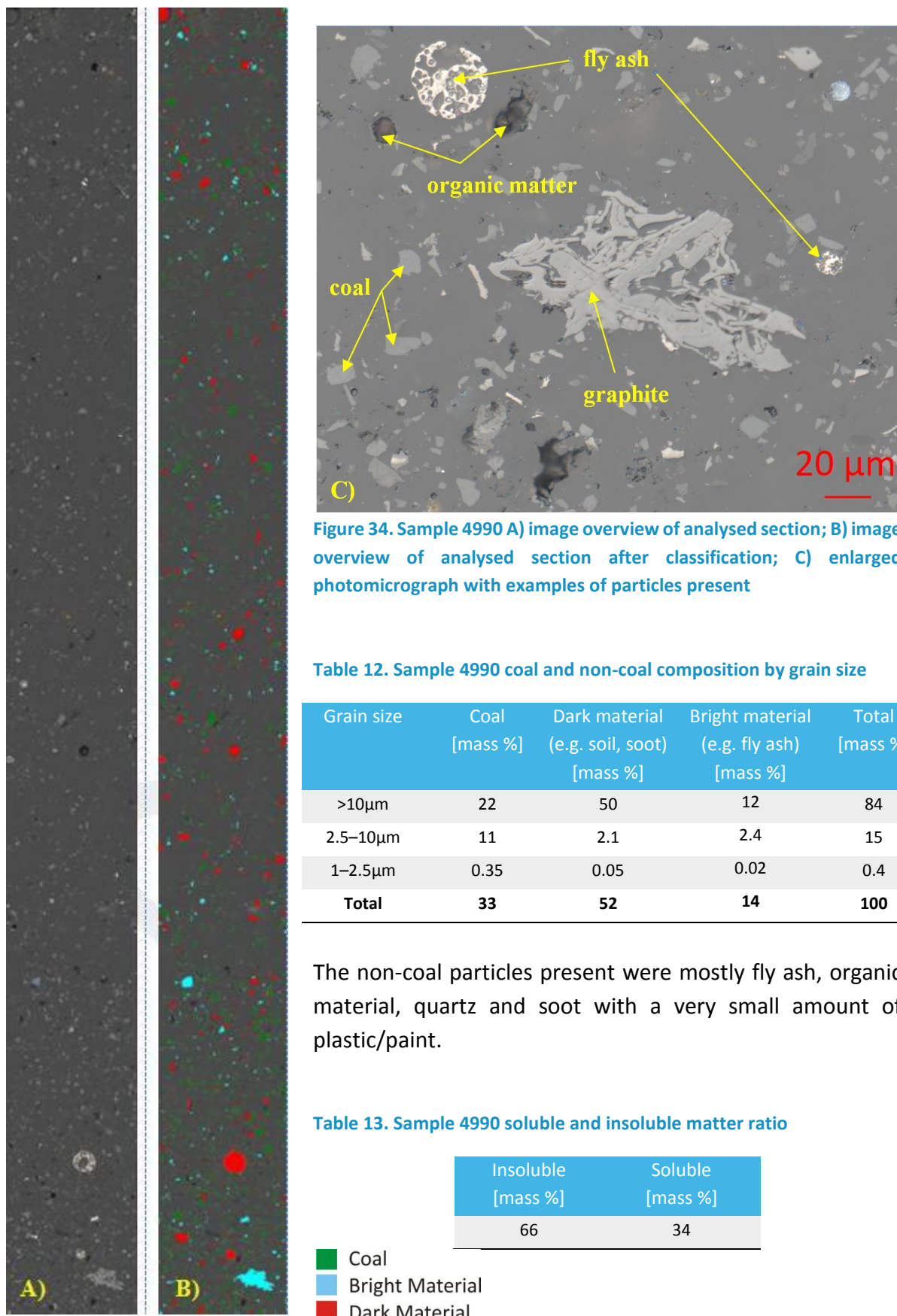


Figure 34. Sample 4990 A) image overview of analysed section; B) image overview of analysed section after classification; C) enlarged photomicrograph with examples of particles present

Table 12. Sample 4990 coal and non-coal composition by grain size

Grain size	Coal [mass %]	Dark material (e.g. soil, soot) [mass %]	Bright material (e.g. fly ash) [mass %]	Total [mass %]
>10µm	22	50	12	84
2.5–10µm	11	2.1	2.4	15
1–2.5µm	0.35	0.05	0.02	0.4
Total	33	52	14	100

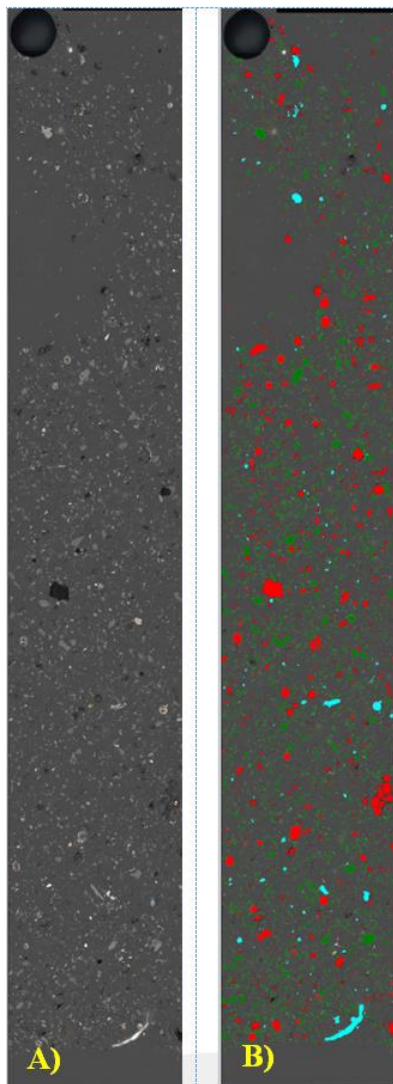
The non-coal particles present were mostly fly ash, organic material, quartz and soot with a very small amount of plastic/paint.

Table 13. Sample 4990 soluble and insoluble matter ratio

Insoluble [mass %]	Soluble [mass %]
66	34

- Coal
- Bright Material
- Dark Material

Sample 4991 from 01/08/2015



- Coal
- Bright Material
- Dark Material

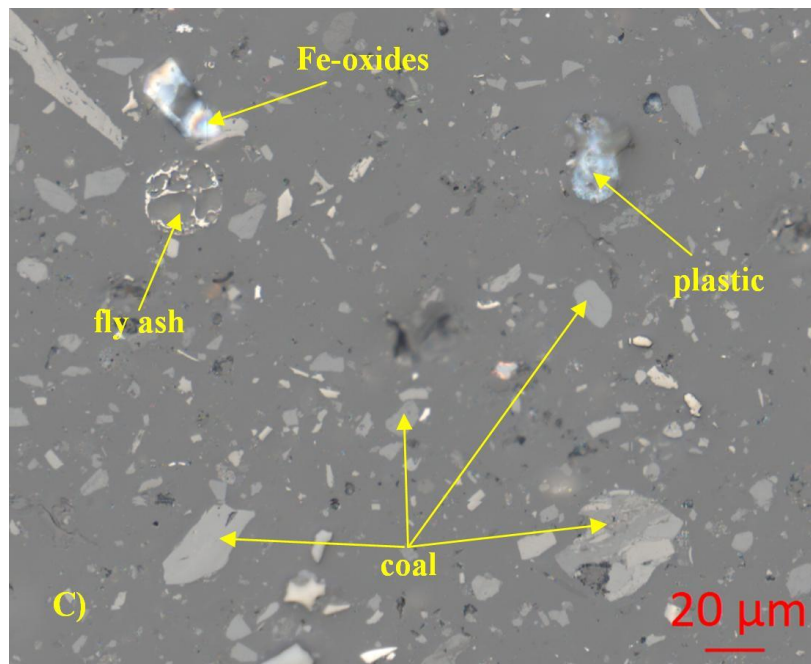


Figure 35. Sample 4991 A) image overview of analysed section; B) image overview of analysed section after classification; C) enlarged photomicrograph with examples of particles present

Table 14. Sample 4991 coal and non-coal composition by grain size

Grain size	Coal [mass %]	Dark material (e.g. soil, soot) [mass %]	Bright material (e.g. fly ash) [mass %]	Total [mass %]
>10 μ m	19	51	17	88
2.5–10 μ m	8	2.2	1.8	12
1–2.5 μ m	0.30	0.04	0.02	0.4
Total	27	53	19	100

The non-coal particles were mostly soot, organic material, fly ash and quartz with a very small amount of plastic/paint.

Table 15. Sample 4991 soluble and insoluble matter ratio

Insoluble [mass %]	Soluble [mass %]
65	35

Sample 4992 from 27/06/2015

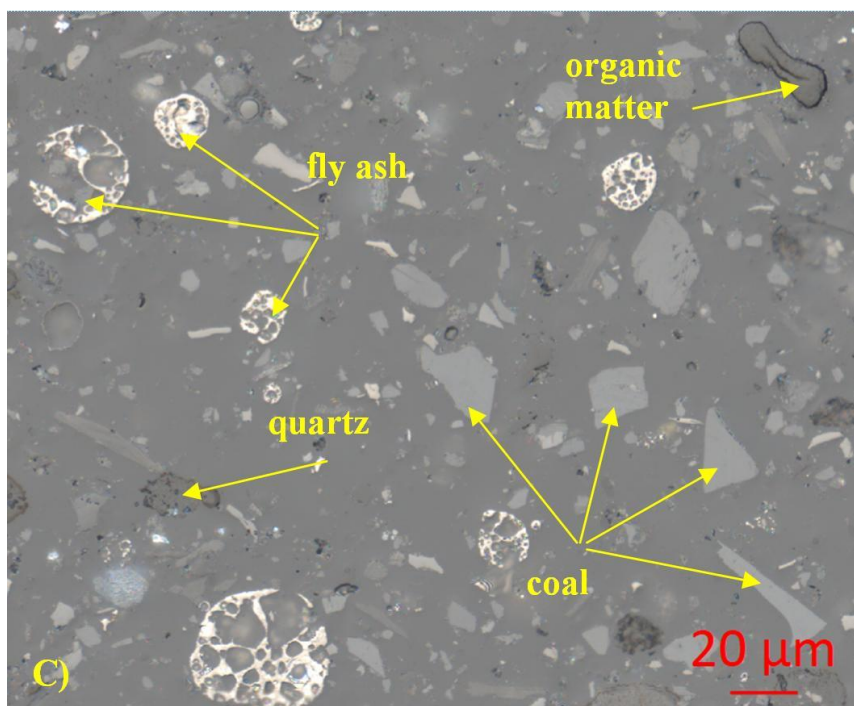
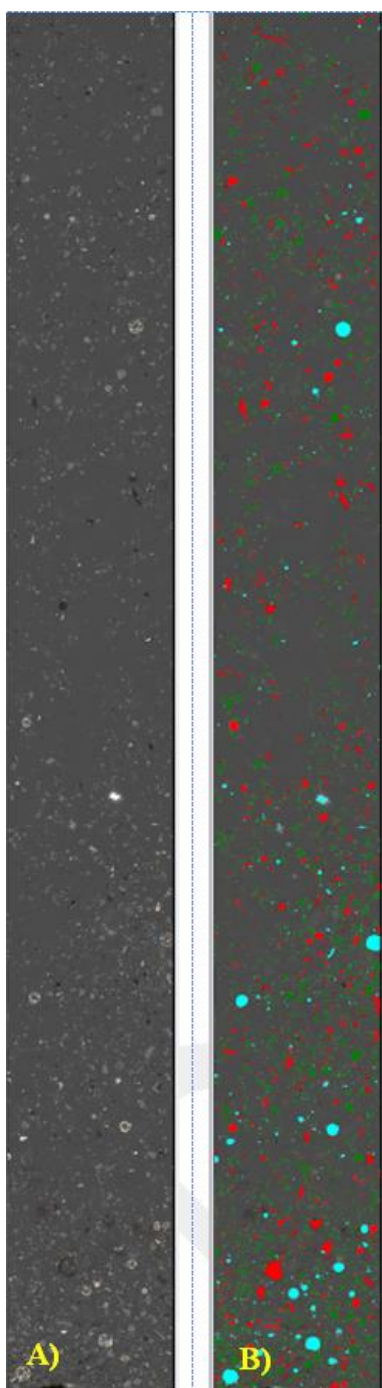


Figure 36. Sample 4992 A) image overview of analysed section; B) image overview of analysed section after classification; C) enlarged photomicrograph with examples of particles present

Table 16. Sample 4992 coal and non-coal composition by grain size

Grain size	Coal [mass %]	Dark material (e.g. soil, soot) [mass %]	Bright material (e.g. fly ash) [mass %]	Total [mass %]
>10μm	20	38	26	84
2.5–10μm	10	4.1	1.0	15
1–2.5μm	0.33	0.04	0.02	0.4
Total	30	42	27	100

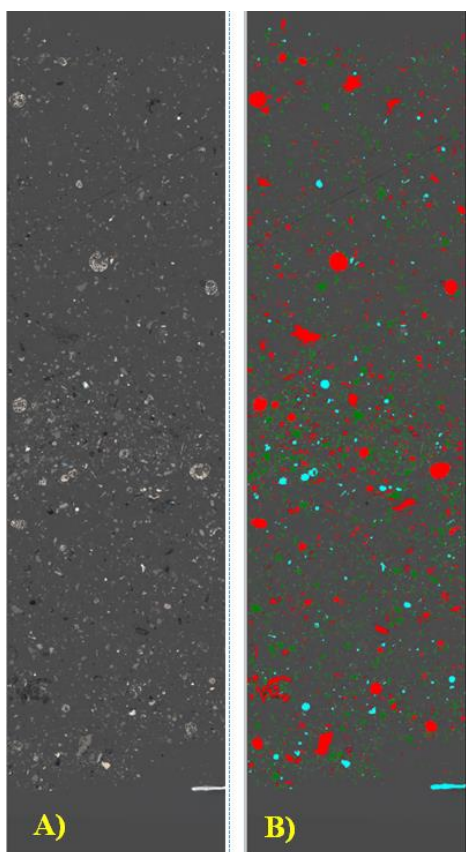
Wide rank range for coal particles. A lot of fly ash, organic material and quartz. Small rust iron particles. Minimal amounts of soot.

- Coal
- Bright Material
- Dark Material

Table 17. Sample 4992 soluble and insoluble matter ratio

Insoluble [mass%]	Soluble [mass%]
42	58

Sample 4993 from 15/06/2015



- Coal
- Bright Material
- Dark Material

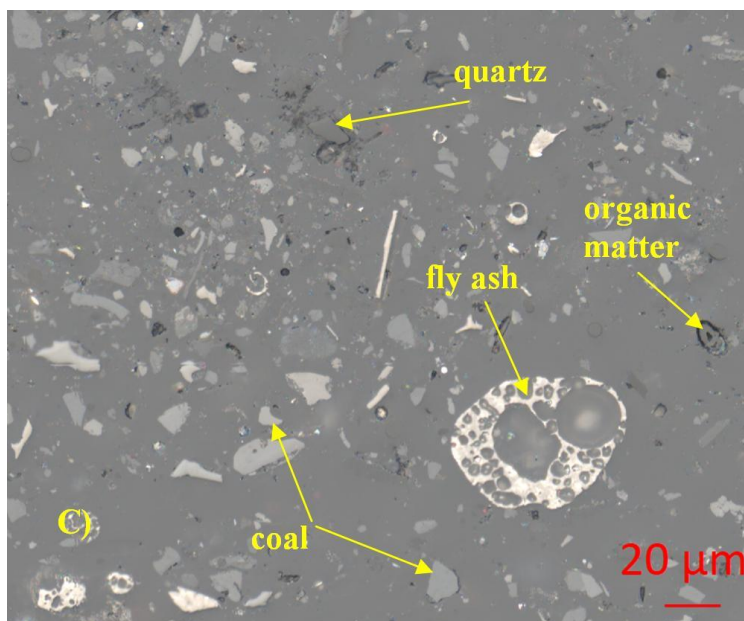


Figure 37. Sample 4993 A) image overview of analysed section; B) image overview of analysed section after classification; C) enlarged photomicrograph with examples of particles present

Table 18. Sample 4993 coal and non-coal composition by grain size

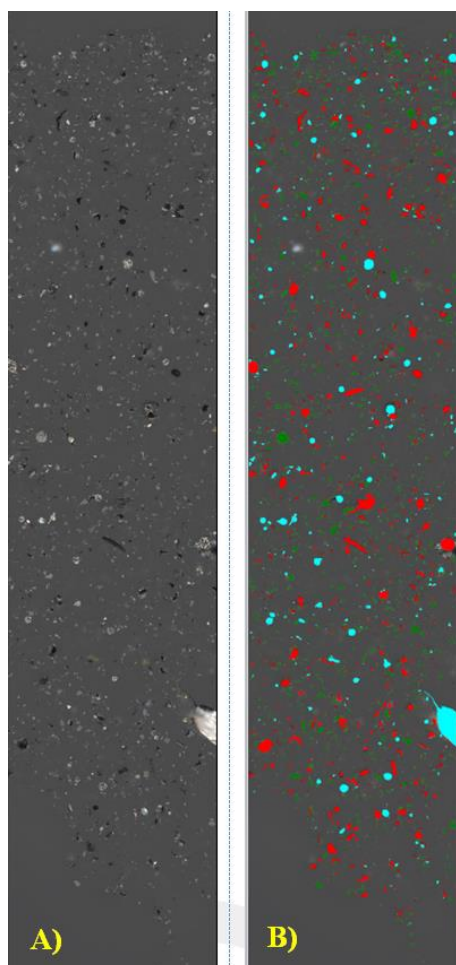
Grain size	Coal [mass %]	Dark material (e.g. soil, soot) [mass %]	Bright material (e.g. fly ash) [mass %]	Total [mass %]
>10μm	11	71	9	91
2.5–10μm	6	2.9	0.7	9
1–2.5μm	0.21	0.03	0.02	0.3
Total	17	74	10	100

The non-coal particles were mostly organic material, including some large particles of organic origin; there was a lot of fly ash, soot and quartz present. Minimal amounts of paint, plastic and iron.

Table 19. Sample 4993 soluble and insoluble matter ratio

Insoluble [mass%]	Soluble [mass%]
18	82

Sample 4994 from 13/09/2015



- Coal
- Bright Material
- Dark Material

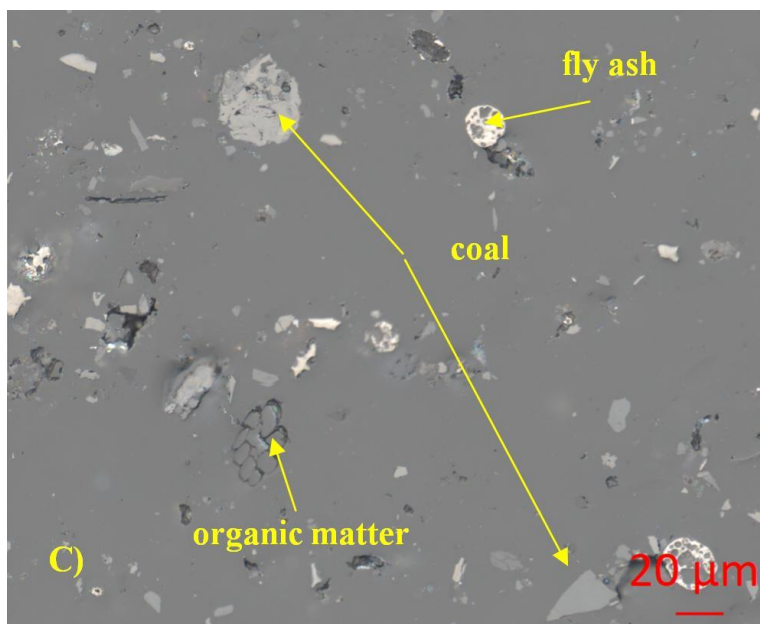


Figure 38. Sample 4994 A) image overview of analysed section; B) image overview of analysed section after classification; C) enlarged photomicrograph with examples of particles present

Table 20. Sample 4994 coal and non-coal composition by grain size

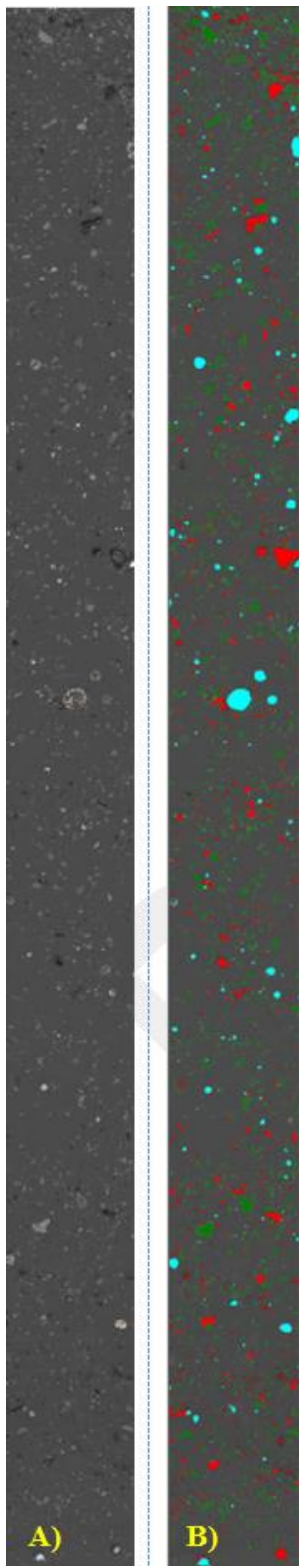
Grain size	Coal [mass %]	Dark material (e.g. soil, soot) [mass %]	Bright material (e.g. fly ash) [mass %]	Total [mass %]
>10 μ m	11	58	21	90
2.5–10 μ m	5.4	3.2	1.1	10
1–2.5 μ m	0.15	0.03	0.01	0.2
Total	17	61	22	100

The non-coal particles were mostly fly ash, organic material including some large particles of organic origin, stone dust and soot, with a very small amount of plastic/paint.

Table 21. Sample 4994 soluble and insoluble matter ratio

Insoluble [mass %]	Soluble [mass %]
20	80

Sample 4995 from 05/07/2015



- Coal
- Bright Material
- Dark Material

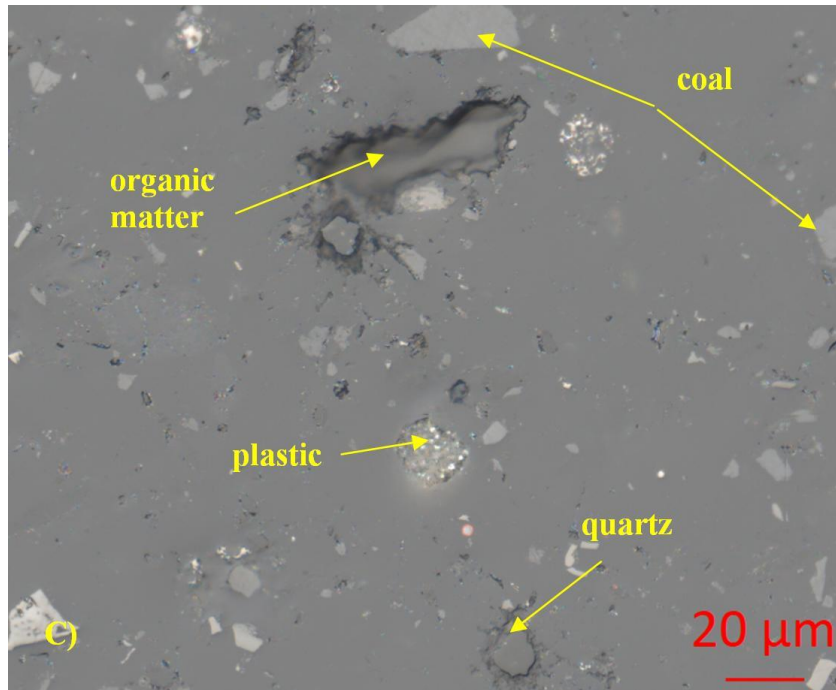


Figure 39. Sample 4995 A) image overview of analysed section; B) image overview of analysed section after classification; C) enlarged photomicrograph with examples of particles present

Table 22. Sample 4995 coal and non-coal composition by grain size

Grain size	Coal [mass %]	Dark material (e.g. soil, soot) [mass %]	Bright material (e.g. fly ash) [mass %]	Total [mass %]
>10 μ m	17	34	34	85
2.5–10 μ m	9.1	4.6	1.0	15
1–2.5 μ m	0.42	0.07	0.01	0.5
Total	27	39	35	100

The non-coal particles were mostly organic material, including some large particles of organic origin. There was a lot of fly ash, soot and sandstone present. Minimal amounts of paint, plastic and iron.

NOTE: Insoluble matter is 42% of total mass.

Sample 4996 from 02/08/2015

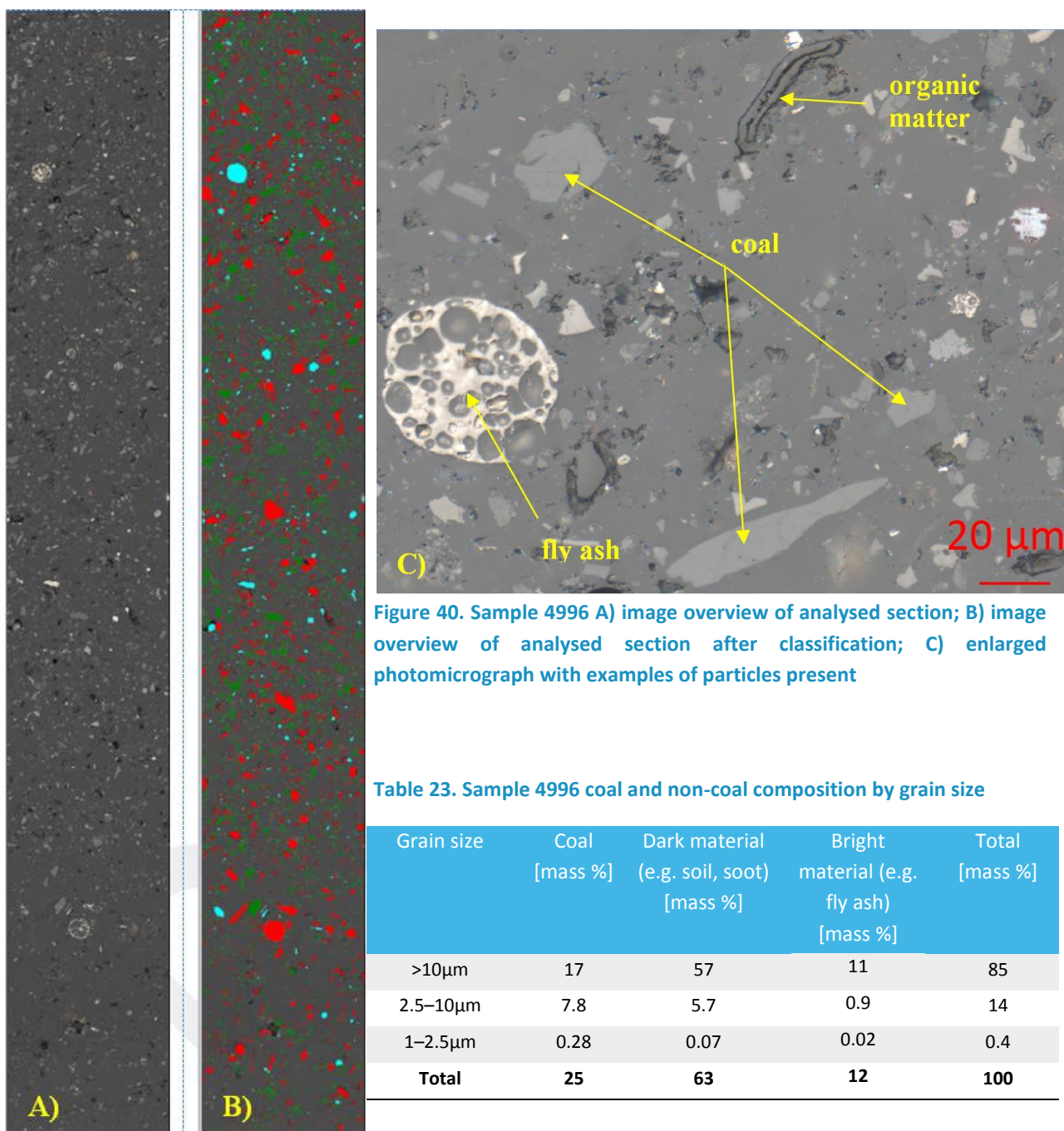


Figure 40. Sample 4996 A) image overview of analysed section; B) image overview of analysed section after classification; C) enlarged photomicrograph with examples of particles present

Table 23. Sample 4996 coal and non-coal composition by grain size

Grain size	Coal [mass %]	Dark material (e.g. soil, soot) [mass %]	Bright material (e.g. fly ash) [mass %]	Total [mass %]
>10µm	17	57	11	85
2.5–10µm	7.8	5.7	0.9	14
1–2.5µm	0.28	0.07	0.02	0.4
Total	25	63	12	100

- Coal
- Bright Material
- Dark Material

A lot of sandstone, quartz and organic material present in this sample. Levels of the fly ash were lower in comparison with previous samples (4990–4995), however some large fly ash particles were still present.

NOTE: Insoluble matter is 64% of total mass.

Appendix B. Agreed scope of work

Quantifying the coal dust component of PM at Stockton

26 June 2015

1. Objective: To quantify the coal dust component of (fine) PM_{2.5}, (coarse) PM_{2.5-10} and (larger) PM_{>10} particles measured at the OEH Stockton Air Quality Monitoring Station on winter days conducive to coal dust being generated and transported to the station from coal operations on Kooragang Island.

2. Background: The context for this project is the Lower Hunter Particle Characterisation Study (LHPCS), which will deliver its final report in February 2016. The LHPCS aims are to determine the composition of PM_{2.5} and PM₁₀ air particles, and to identify major sources contributing to PM_{2.5} and PM₁₀ concentrations in the region to inform EPA's control programs. The community has a strong interest in knowing how much coal dust is in the particulate pollution in the Newcastle region. A limitation of the LHPCS is that it cannot definitively identify coal dust in samples; it only provides the concentration of elemental carbon.

This project will use CSIRO's Coal Grain Analysis (CGA) system from the Energy Flagship in Brisbane, which is able to analyse dust samples and provide quantitative detail on the coal and non-coal dust particles in the respirable and non-respirable size fractions. It uses high resolution imaging techniques with reflected light to provide quantitative information on the size and composition of each individual particle.

The Stockton Air Quality Monitoring Station has been selected as the PM sample collection site for several reasons:

- Stockton is one of the LHPCS sites and the detailed understanding from that study about local and regional PM will greatly assist in interpreting the coal dust results.
- Stockton is well located for a winter study, being downwind from the coal operations on Kooragang Island for much of the winter months (see figure below).
- Stockton has a range of continuous air quality and meteorological monitoring instruments, which will be valuable in interpreting the coal dust results.

3. Method

3.1 Sample collection

- a) Samplers – TSP high volume samplers will be used, in accordance with AS/NZS 3580.9.3.2003 *Determination of suspended particulate matter – Total suspended particulate matter (TSP) – High volume sampler gravimetric method*. The CGA analysis

technique determines the size of the particles as well as whether or not they are coal, so it is best to collect TSP to quantify the coal dust in all size fractions.

- b) Filter material – Emfab filters (EMFAB TX40HI20-WW, borosilicate glass microfibers reinforced with woven glass cloth and bonded with PTFE) will be used as the filter material to enable gravimetric mass determinations in accordance with AS/NZS 3580.9.3.2003 *Determination of suspended particulate matter – Total suspended particulate matter (TSP) – High volume sampler gravimetric method.*
- c) Sampling duration – Collect 24-hour samples, midnight to midnight. The CGA technique requires at least 20mg (preferably 40–50mg) of sample. The volume flow of a HiVol sampler is 78m³/hr, so that a 24-hour average PM concentration of 12µg m⁻³ is required to collect 20mg, or 25–30µg m⁻³ to collect 40–50mg of PM.
- d) Sampling period – Daily for three months from mid-June to mid-September (~90 samples). The project will use four HiVol samplers, each programmed to collect on a one-in-four day cycle. The winter period is selected because of the favourable wind direction for sampling particles from the coal operations on Kooragang Island.

3.2 Sample analysis

Approximately 20 filters will be analysed using the CGA technique. The criteria for selecting these samples will include:

- meteorology – NW quadrant airflow prevails, strong winds, dry conditions (no rain)
- elevated PM concentrations recorded at Stockton
- visual inspection of filters for blackness (possible coal dust particles).

4. Procedures:

OEH will:

- install the samplers
- prepare and pre-weight the filters, load and collect exposed filters
- weigh the filters post-exposure for gravimetric analysis
- dispatch the filters to CSIRO Aspendale.

CSIRO Aspendale will:

- select the filters for CGA analysis and dispatch to CSIRO Energy Flagship (Graham O'Brien, Pullenvale)
- prepare a brief report on the results, and if possible include the results in the final LHPCS report.

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