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Upper Hunter Valley Particle Characterization Study

3rd Progress Report

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Prepared for
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CSIRO Marine & Atmospheric Research

Contents

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We acknowledge the contributions of the CSIRO project team: Kate Boast, Paul Selleck, Fabienne Reisen and Mahendra Buhjel for the analyses.

1 Aim of Study

The objective of the Upper Hunter Valley Particle Characterization Study is to determine the major components and sources of particulate matter (as PM2.5 – particles with a diameter of less than 2.5 micrometres) in the two main population centres in the Upper Hunter Valley, namely Singleton and Muswellbrook.

This 3rd Progress Report presents an update on the project and some quality checks of the data.

2 Project description

This project will determine the major components and sources of PM2.5 in the two main population centres in the Upper Hunter. This will be achieved by collecting PM2.5 samples in Muswellbrook and Singleton. Because the sources of PM2.5 and their relative contributions vary from season to season, samples will be collected over one full calendar year (January 2012 to December 2012). Two different types of samplers will be used to collect 24-hour samples every third day. Two samplers are required since different chemical analyses require different filter media. One sampler will collect particles on quartz fibre filters for the analysis of organic carbon, elemental carbon, soluble ions, anhydrous sugars, and pH, while the second sampler will collect particles on stretched Teflon filters for the analysis of elemental composition, and gravimetric mass. A range of analysis techniques will be employed to determine the concentrations in these species. The full chemical composition of all the samples from each site will be analysed using Positive Matrix Factorisation to determine the sources of PM (particulate matter) at the sites and the contribution each source makes to the particulate loading. This analysis will enable the study to provide:

- a description of the contributors to fine particles in the Upper Hunter
- an estimate of which sources are important and their relative contribution to fine particles in the Upper Hunter
- an indication of any weekly and seasonal changes in PM2.5 particles in the Upper Hunter.

2.1 Sampling strategy

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

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

Field blank samples are collected every 30 days.

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

3 Project status

The sampling and shipping for analysis is progressing according to plan. Table 1 lists the status at the end of December of the sample collection and analysis. A teleconference between study participants (OEH, DoH, ANSTO, CSIRO) was held on 22 November to check on progress and plan for the wind-up of the sampling program in January. The key OEH contact Chris Eiser retired in November and was replaced by Matt Riley. There were no significant issues. The study was progressing well and sampling has now been completed.

Table 1 Status of sample collection and analysis

#	SAMPLE DATE	COLLECTED & SHIPPED	CSIRO ANALYSIS	ANSTO ANALYSIS	#	SAMPLE DATE	COLLECTED & SHIPPED	CSIRO ANALYSIS	ANSTO ANALYSIS
1	04/01/2012	✓	✓	✓	28	25/03/2012	✓	✓	✓
2	07/01/2012	✓	✓	✓	29	28/03/2012	✓	✓	✓
3	10/01/2012	✓	✓	✓	30	31/03/2012	✓	✓	✓
4	13/01/2012	✓	✓	✓	31	03/04/2012	✓	✓	✓
5	16/01/2012	✓	✓	✓	32	06/04/2012	✓	✓	✓
6	19/01/2012	✓	✓	✓	33	09/04/2012	✓	✓	✓
7	22/01/2012	✓	✓	✓	34	12/04/2012	✓	✓	✓
8	25/01/2012	✓	✓	✓	35	15/04/2012	✓	✓	✓
9	28/01/2012	✓	✓	✓	36	18/04/2012	✓	✓	✓
10	31/01/2012	✓	✓	✓	37	21/04/2012	✓	✓	✓
11	03/02/2012	✓	✓	✓	38	24/04/2012	✓	✓	✓
12	06/02/2012	✓	✓	✓	39	27/04/2012	✓	✓	✓
13	09/02/2012	✓	✓	✓	40	30/04/2012	✓	✓	✓
14	12/02/2012	✓	✓	✓	41	03/05/2012	✓	✓	✓
15	15/02/2012	✓	✓	✓	42	06/05/2012	✓	✓	✓
16	18/02/2012	✓	✓	✓	43	09/05/2012	✓	✓	✓
17	21/02/2012	✓	✓	✓	44	12/05/2012	✓	✓	✓
18	24/02/2012	✓	✓	✓	45	15/05/2012	✓	✓	✓
19	27/02/2012	✓	✓	✓	46	18/05/2012	✓	✓	✓
20	01/03/2012	✓	✓	✓	47	21/05/2012	✓	✓	✓
21	04/03/2012	✓	✓	✓	48	24/05/2012	✓	✓	✓
22	07/03/2012	✓	✓	✓	49	27/05/2012	✓	✓	✓
23	10/03/2012	✓	✓	✓	50	24/05/2012	✓	✓	✓
24	13/03/2012	✓	✓	✓	51	27/05/2012	✓	✓	✓
25	16/03/2012	✓	✓	✓	52	30/05/2012	✓	✓	✓
26	19/03/2012	✓	✓	✓	53	02/06/2012	✓	✓	✓
27	22/03/2012	✓	✓	✓	54	05/06/2012	✓	✓	✓

#	SAMPLE DATE	COLLECTED & SHIPPED	CSIRO ANALYSIS	ANSTO ANALYSIS	#	SAMPLE DATE	COLLECTED & SHIPPED	CSIRO ANALYSIS	ANSTO ANALYSIS
55	08/06/2012	✓	✓	✓	91	24/09/2012	✓		✓
56	11/06/2012	✓	✓	✓	92	27/09/2012	✓		✓
57	14/06/2012	✓	✓	✓	93	30/09/2012	✓		✓
58	17/06/2012	✓	✓	✓	94	03/10/2012	✓		✓
59	20/06/2012	✓	✓	✓	95	06/10/2012	✓		✓
60	23/06/2012	✓	✓	✓	96	09/10/2012	✓		✓
61	26/06/2012	✓	✓	✓	97	12/10/2012	✓		✓
62	29/06/2012	✓	✓	✓	98	15/10/2012	✓		✓
63	02/07/2012	✓	✓	✓	99	18/10/2012	✓		✓
64	05/07/2012	✓	✓	✓	100	21/10/2012	✓		✓
65	08/07/2012	✓	✓	✓	101	24/10/2012	✓		✓
66	11/07/2012	✓	✓	✓	102	27/10/2012	✓		✓
67	14/07/2012	✓	✓	✓	103	30/10/2012	✓		✓
68	17/07/2012	✓	✓	✓	104	02/11/2012	✓		
69	20/07/2012	✓	✓	✓	105	05/11/2012	✓		
70	23/07/2012	✓	✓	✓	106	08/11/2012	✓		
71	26/07/2012	✓	✓	✓	107	11/11/2012	✓		
72	29/07/2012	✓	✓	✓	108	14/11/2012	✓		
73	01/08/2012	✓	✓	✓	109	17/11/2012	✓		
74	04/08/2012	✓		✓	110	20/11/2012	✓		
75	07/08/2012	✓		✓	111	23/11/2012	✓		
76	10/08/2012	✓		✓	112	26/11/2012	✓		
77	13/08/2012	✓		✓	113	29/11/2012	✓		
78	16/08/2012	✓		✓	114	02/12/2012	✓		
79	19/08/2012	✓		✓	115	05/12/2012	✓		
80	22/08/2012	✓		✓	116	08/12/2012	✓		
81	25/08/2012	✓		✓	117	11/12/2012	✓		
82	28/08/2012	✓		✓	118	14/12/2012	✓		
83	31/08/2012	✓		✓	119	17/12/2012	✓		
84	03/09/2012	✓		✓	120	20/12/2012	✓		
85	06/09/2012	✓		✓	121	23/12/2012	✓		
86	09/09/2012	✓		✓	122	26/12/2012	✓		
87	12/09/2012	✓		✓	123	29/12/2012	✓		
88	15/09/2012	✓		✓	124	01/01/2013	✓		
89	18/09/2012	✓		✓	125	04/01/2013	✓		
90	21/09/2012	✓		✓					

4 Preliminary QA/QC of results

4.1 PM2.5 measurements

Figure 1 shows the time series of 24-hour average PM2.5 concentrations measured at Singleton by the OEH Beta Attenuation Mass (BAM) monitor for 2012. The red symbols highlight the days when 1-in-3-day sampling was carried out by CSIRO and ANSTO for the current study. It shows that these are representative of the full period, including days with both high and low PM2.5 concentrations. The equivalent time series for Muswellbrook is given in Figure 2.

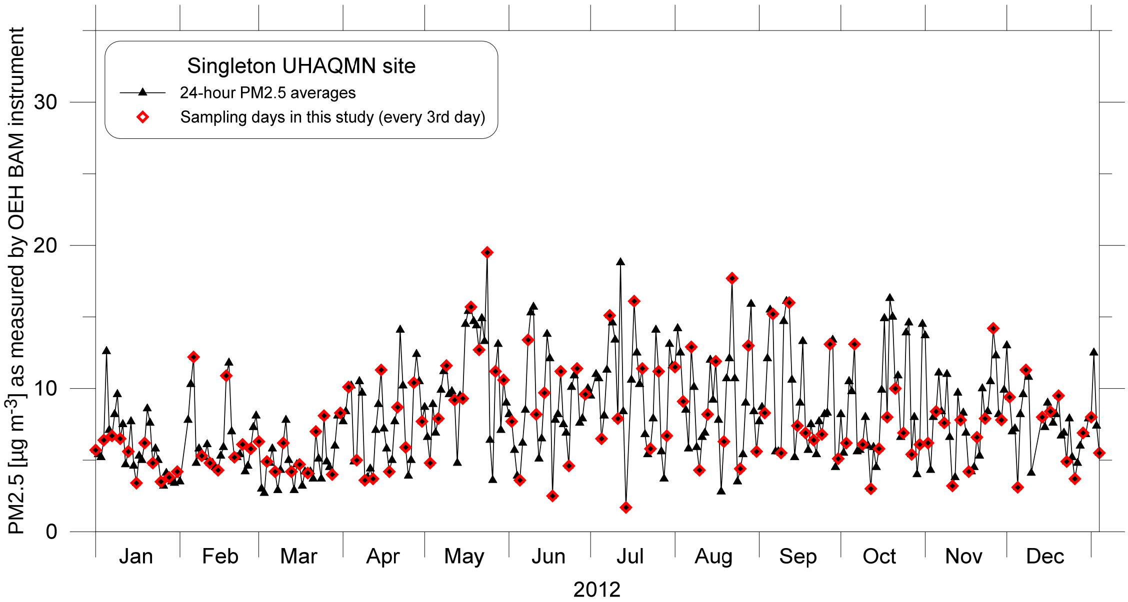

Figure 1 Time series of 24-hour average PM2.5 concentrations measured by the OEH BAM (Beta Attenuation Mass) monitor at Singleton. The red symbols show the days when sampling for the current study was carried out.

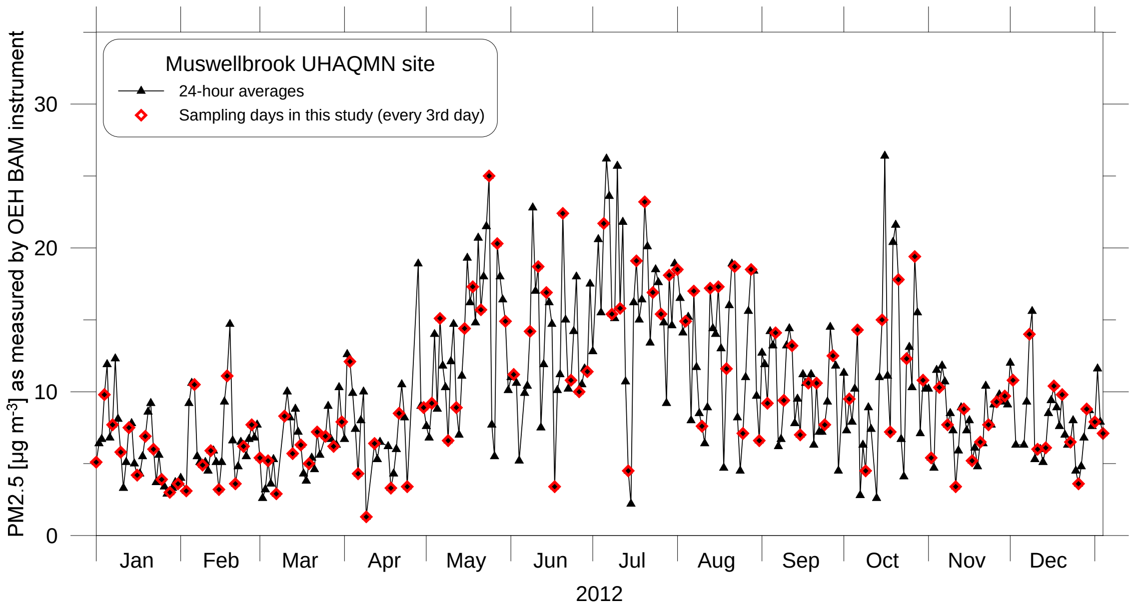

Figure 2 Time series as in previous figure but for Muswellbrook.

By plotting the time series as running averages in Figure 3, it is easier to compare the PM2.5 levels at the two sites (higher winter PM2.5 in Muswellbrook) and to identify two main periods in the data – higher levels in winter/spring and lower levels in summer/autumn. These periods are being used as an initial criterion for splitting the data for analysis.

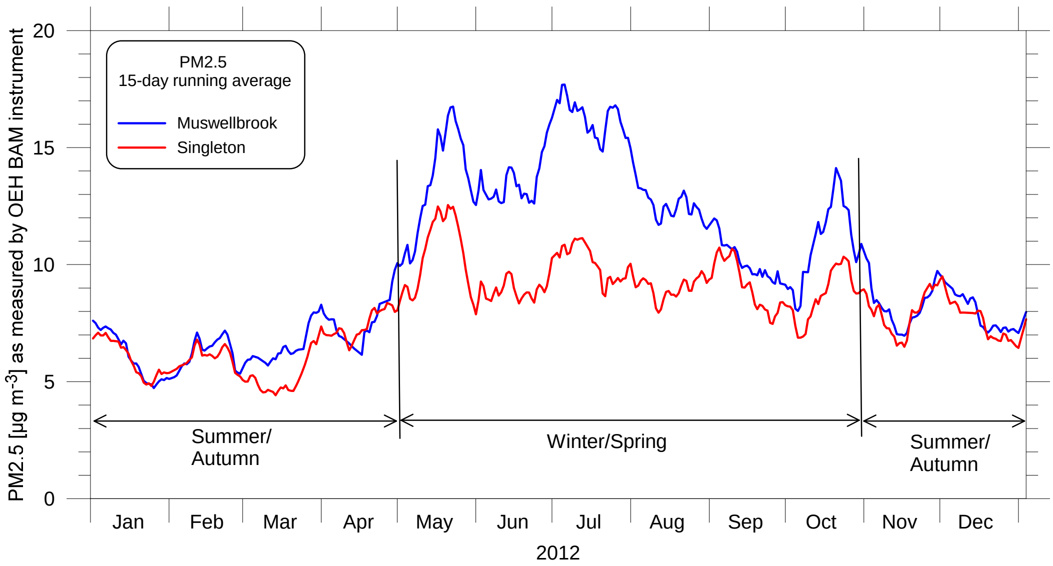

Figure 3 Identification of the Winter/Spring period with generally elevated PM2.5 levels and the Summer/Autumn period with lower PM2.5 levels.

Comparison in Figure 4 between the OEH PM2.5 results and the gravimetric mass determination of PM2.5 from the ANSTO sampler shows that apart from a few outliers (requiring further checking), the gravimetric mass is on average close to but about 10% lower than the BAM measurement – probably due to slight differences in the measurement techniques – but the agreement is considered to be good.

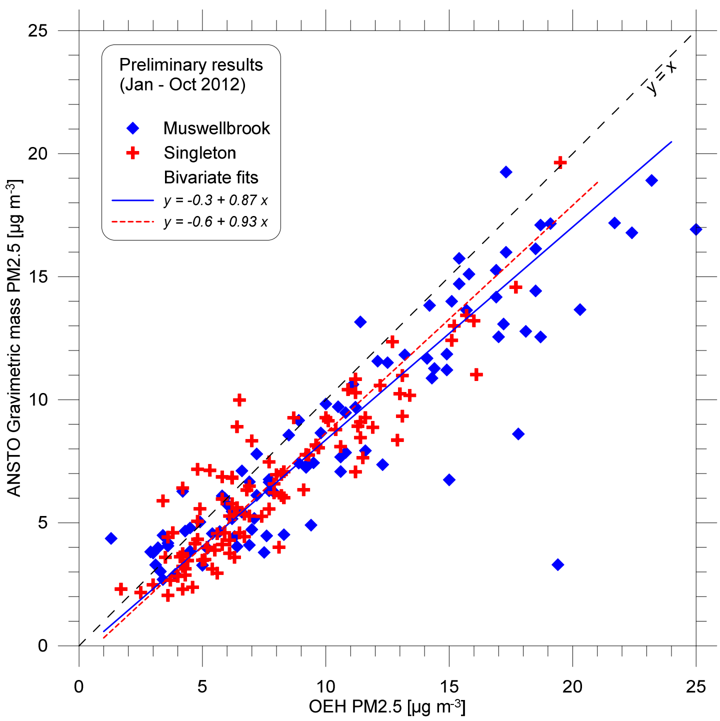

Figure 4 Comparison of PM2.5 measured on ANSTO filters and by OEH BAM instrument.

4.2 Elemental carbon, Organic carbon, Black carbon

The relationship between OC and EC in the PM2.5 samples (collected in the CSIRO high-volume samplers) is shown in the scatter plot in Figure 5 for the summer and winter periods. In summer, there is little difference between the sites. On most days the ratio lies between 1.5 and 3.0 with an average of 2.1, but there are some days outside this range when the EC is below 0.5 µg m^{-3}. In contrast, in winter the OC/EC ratios are significantly different at the two sites and the bivariate fits both show an offset of the intercept on the OC axis of about 0.5 µg m^{-3}. The ratios at Muswellbrook are higher than in summer whereas at Singleton they are lower. Further analysis is underway.

The average ratio of 2 in Figure 5 agrees with average value s in the literature summarised by Na et al (2004) for sites with average PM2.5 concentrations below 15 µg m^{-3}. Keywood et al. (2007) measured OC/EC ratios in PM10 in suburban Melbourne between 1.6 and 14.8 and reported a winter average of 4 and a summer average of 6.

The lower bound of about 1.5 in Figure 5 is consistent with PM2.5 emissions from most sources (such as vehicles, biomass burning, coal combustion, natural gas combustion, paved road dust) having OC/EC ratios greater than 1, some much larger.

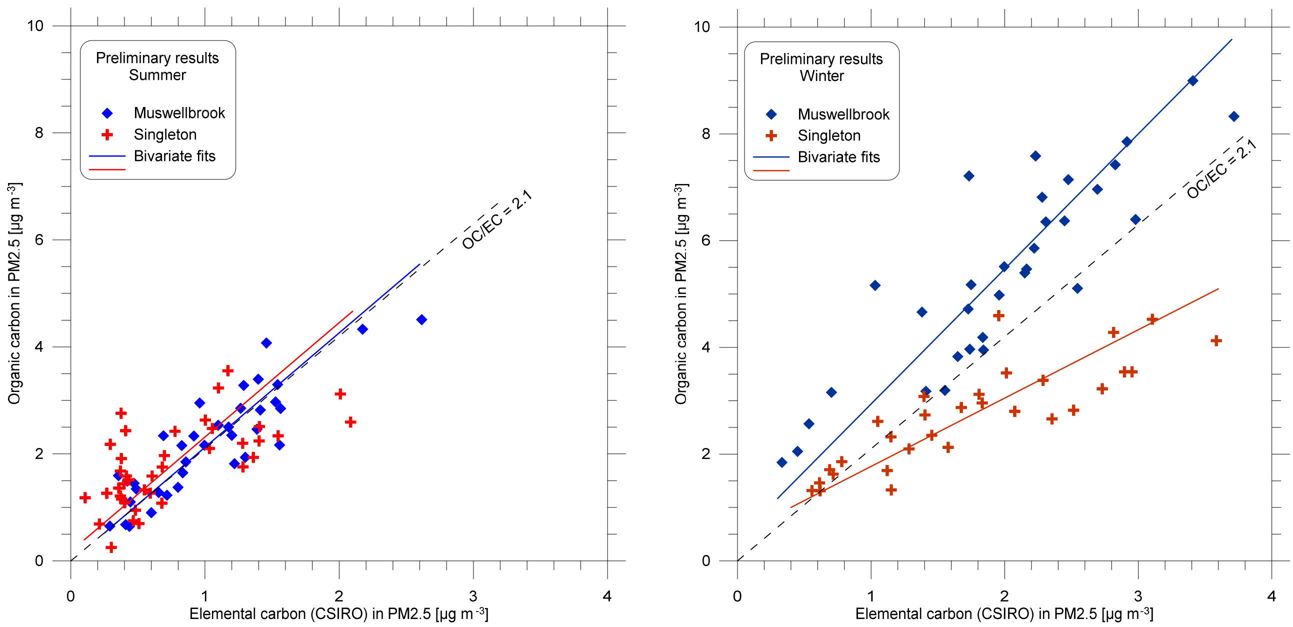

Figure 5 Preliminary results for OC (organic carbon) versus EC (elemental carbon) concentrations in high volume PM2.5 samples for the summer and winter periods

Figure 6 shows a comparison elemental carbon (EC) and black carbon (BC) measurements, which are often taken to be equivalent. The elemental carbon concentrations were measured by CSIRO using the Thermal-Optical Carbon Analyzer and the black carbon measurements were made by ANSTO using the Laser Integrated Plate Method (both techniques described in the 2nd Progress Report). There is seen to be a good correlation between the techniques apart from one outlier (requiring further checking), although at low concentrations, the BC value tends to be slightly greater than EC whereas at higher concentrations the EC value is slightly greater than the BC measurement.

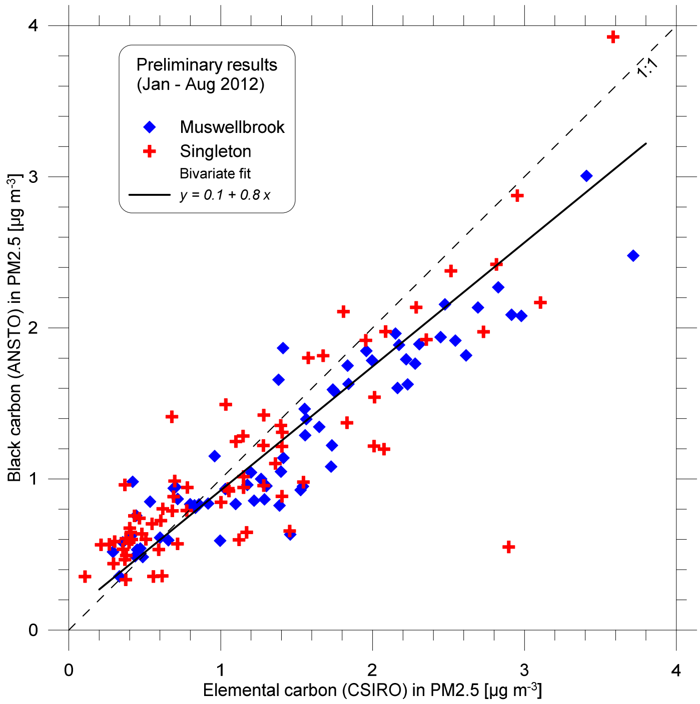

Figure 6 Scatter plot of BC (black carbon) measurements by ANSTO versus EC (elemental carbon) measurements by CSIRO

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

SITE	DATE	OC BLANK [µg m^{-3}]	EC BLANK [µg m^{-3}]
Muswellbrook	14/01/2012	0.12	0.00
"	21/02/2012	0.10	0.00
"	14/03/2012	0.13	0.00
"	26/04/2012	0.13	0.00
"	21/05/2012	0.07	0.00
"	20/06/2012	0.17	0.00
"	26/07/2012	0.09	0.00
Singleton	11/01/2012	0.10	0.00
"	21/02/2012	0.12	0.00
"	02/04/2012	0.05	0.00
"	28/04/2012	0.26	0.00
"	21/05/2012	0.07	0.00
"	17/06/2012	0.10	0.00
"	26/07/2012	0.13	0.00
Average blank		0.12 ± 0.05	0.00

The sampling includes field blanks, which are filters that are installed in the sampler and then immediately removed, without any air having been drawn through the filter. This checks the whole filter handling and analyses procedures for possible contamination or artefacts. The blank values are subtracted from the measurements of the actual samples. Table 2 lists the field blank values for OC and EC from the samples analysed to date. It shows that average blank value for EC is less than 0.005 µg m^{-3} and for OC equal to 0.12 µg m^{-3}, both of which are very small compared to the observations in Figure 5. Based on the uncertainty in the blanks and the number of blanks, the limit of detection for OC in this study is calculated to be 0.09 µg m^{-3}.

4.3 Ion balance

The quality check of the ion chromatography measurements is shown by the balance between the measured anions and cations in Figure 7. In most cases they are balanced to within 5 µeq/L over more than an order of magnitude of concentrations.

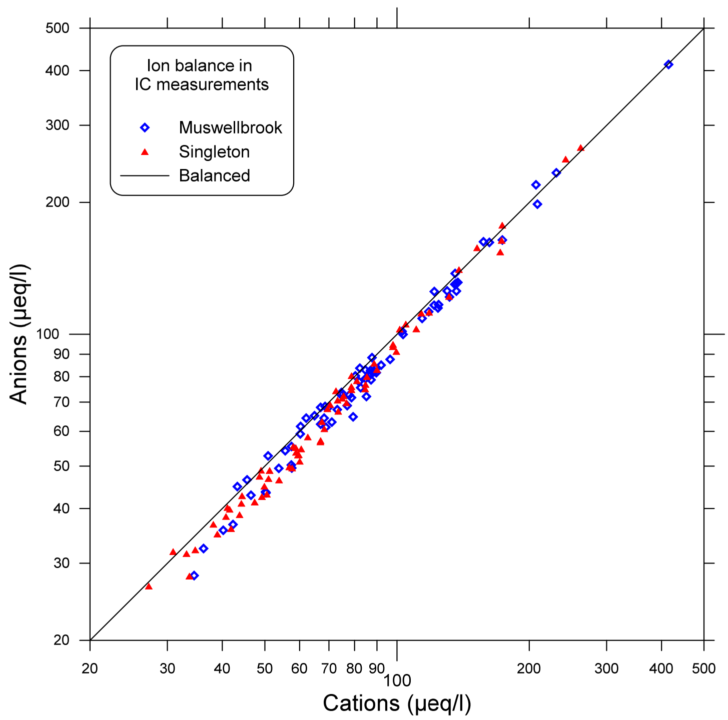

Figure 7 Ion balance for the ion chromatography measurements on the CSIRO high volume samples

5 Project completion

The next step in the study is to complete the analysis of the samples. The results from each site will then be analysed using Positive Matrix Factorisation to determine the sources of PM2.5 at the sites and the contribution each source makes to the particulate loading. This analysis will enable us to report on:

- Which sources are the most important and what are their relative contributions to the PM2.5 burden in the Upper Hunter?
- How does the composition of PM2.5 change weekly and seasonally in the Upper Hunter?

- Are these results consistent with the current emissions inventory for the region?

A draft final report will be submitted in May 2013. Following review by OEH and DoH, the final report will be submitted in June 2013.

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