NPL
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Report

NPL REPORT AS 21

Report On Organic Carbon / Elemental Carbon (OC/EC) and Anion Analysis Of Filter PM Samples From Auchencorth Moss

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NOT RESTRICTED

March 2008

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ISSN 1754-2928

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Executive Summary

Organic and elemental carbon (OC/EC), and chloride, nitrate and sulphate anion measurements were made on existing $PM_{2.5}$ samples on quartz filters from Auchencorth Moss. The samples were taken for measurements of total gravimetric $PM_{2.5}$, with no special measures such as pre-baking to reduce blank levels of organic carbon on the filters.

A provisional study[1] has shown that blank levels of OC on the quartz filters made OC measurements unreliable.

109 filters were analysed covering the period 02/06/06 to 30/01/2007.

Introduction

The aim of contract H/Q207 is to make OC/EC and anion measurements using existing PM samples on quartz filters from Auchencorth Moss. The samples were taken for measurements of total gravimetric PM, with no special measures such as pre-baking to reduce blank levels of carbon on the filters. Bureau Veritas supplied the gravimetric $PM_{2.5}$ data from these filters. It should be noted that there are strong indications that the $PM_{2.5}$ values may be too high because of problems with the BV filter weighing procedure, and this is currently being investigated elsewhere.

As a preliminary assessment of the scale of the blank levels of OC/EC on the resulting data, 33 blank filters were analysed. 25 sampled filters were also analysed to give an idea of real concentrations. The results from this preliminary assessment are published in NPL Report DQL AS (RES) 011[1], and it concluded that the level of organic carbon in travel blank filters was too variable to allow reliable blank corrections to be used. The average blank level of organic carbon was found to be 47.0 µg with a standard deviation of 28.8 µg, while the average blank level of elemental carbon was found to be 0.0 µg.

Following the preliminary assessment, it was decided to measure EC and anions on a targeted subset of filters when there was both valid PM data and aethalometer data available from Auchencorth Moss. Only $PM_{2.5}$ sampled filters were analysed for this report. The results from the aethalometer are not given in this report.

The analytical methods for OC/EC and anions are summarised in Annex 1 and Annex 2 respectively.

Results

All of the results for the OC/EC and anion measurements are not blank corrected and are expressed as µg on the whole filter and therefore are not ambient air concentrations. Blank values for the anions are given in the relevant section below.

Organic and Elemental Carbon Data

The amount of organic (OC) and elemental carbon (EC) measured on each whole sampled filter is given in Table 1 below:

Start Date	OC (µg)	EC (µg)	$PM_{2.5}$ Mass (µg)
02/06/2006	25.0	0.0	422
03/06/2006	21.2	0.0	386
05/06/2006	62.2	5.1	584
06/06/2006	37.3	0.0	509
07/06/2006	66.6	4.0	619
08/06/2006	50.2	5.4	531
09/06/2006	43.0	0.0	796
10/06/2006	77.9	2.5	781
11/06/2006	70.6	9.6	594
12/06/2006	42.9	0.0	367
13/06/2006	103	9.8	451
14/06/2006	45.4	3.6	433
15/06/2006	47.3	3.1	480
16/06/2006	56.8	2.1	447
17/06/2006	33.4	0.0	471
18/06/2006	22.5	0.0	375
19/06/2006	23.2	0.0	295
20/06/2006	33.4	0.0	314
21/06/2006	26.2	0.0	357
22/06/2006	24.9	0.0	335
23/06/2006	38.9	1.0	330
24/06/2006	33.7	0.0	352
25/06/2006	25.6	0.0	340
26/06/2006	49.7	2.1	237
27/06/2006	39.0	2.5	248
28/06/2006	30.3	0.0	346
29/06/2006	34.2	0.0	286
30/06/2006	27.9	0.0	236
08/07/2006	30.6	0.0	227
09/07/2006	28.9	0.0	191
10/07/2006	31.3	0.0	391
11/07/2006	34.6	0.0	396
20/07/2006	26.5	0.0	574
25/07/2006	46.5	0.0	496
25/08/2006	47.7	0.0	265
26/08/2006	36.5	1.7	268
27/08/2006	35.8	0.0	229
28/08/2006	32.5	0.0	224
29/08/2006	45.8	0.0	216
30/08/2006	31.7	0.0	201
06/09/2006	27.1	0.0	241
07/09/2006	30.8	0.0	226
08/09/2006	50.1	3.3	263
09/09/2006	69.9	9.2	358

Start Date	OC (μg)	EC (μg)	$PM_{2.5}$ Mass (μg)
10/09/2006	58.0	5.2	489
11/09/2006	57.1	5.4	453
12/09/2006	59.3	1.2	234
13/09/2006	42.0	1.6	369
14/09/2006	58.5	9.9	243
15/09/2006	44.5	0.0	226
16/09/2006	55.6	9.0	468
12/10/2006	28.0	0.0	225
13/10/2006	36.1	2.7	297
14/10/2006	59.7	7.9	536
15/10/2006	61.8	9.4	554
16/10/2006	75.7	12	684
20/10/2006	105	10	194
21/10/2006	53.5	0.0	146
22/10/2006	42.8	0.0	148
23/10/2006	41.9	1.2	136
24/10/2006	82.0	0.0	124
25/10/2006	31.7	0.0	187
26/10/2006	154	0.7	124
31/10/2006	27.9	0.0	167
02/11/2006	49.7	9.3	218
25/11/2006	30.8	0.5	123
26/11/2006	38.2	0.0	141
27/11/2006	40.1	0.0	174
28/11/2006	21.0	0.0	159
29/11/2006	38.0	0.0	265
30/11/2006	58.4	0.0	262
16/12/2006	64.3	0.0	111
17/12/2006	72.7	2.7	111
18/12/2006	73.8	8.3	202
19/12/2006	55.7	4.6	295
20/12/2006	42.9	4.4	279
21/12/2006	51.4	2.4	274
22/12/2006	130	1.2	201
23/12/2006	51.5	1.8	277
24/12/2006	86.6	16	303
25/12/2006	67.7	7.0	210
26/12/2006	39.6	0.3	190
27/12/2006	51.8	4.0	300
29/12/2006	31.4	0.0	287
30/12/2006	25.3	0.0	128
04/01/2007	95.4	7.5	
06/01/2007	59.8	17	104
07/01/2007	36.1	0.0	73
08/01/2007	36.7	0.0	109

Start Date	OC (µg)	EC (µg)	$PM_{2.5}$ Mass (µg)
09/01/2007	82.0	0.0	143
10/01/2007	61.4	0.0	150
11/01/2007	50.0	2.2	291
12/01/2007	41.2	0.0	339
13/01/2007	34.5	0.0	171
14/01/2007	91.1	0.0	220
15/01/2007	30.0	0.0	223
16/01/2007	34.8	2.8	248
17/01/2007	28.6	0.0	185
18/01/2007	32.4	2.0	177
19/01/2007	71.2	0.0	188
20/01/2007	23.0	0.0	371
21/01/2007	52.2	0.7	132
22/01/2007	39.2	0.0	175
23/01/2007	33.3	0.0	198
24/01/2007	42.4	2.9	103
25/01/2007	37.0	1.3	349
26/01/2007	27.7	1.3	317
29/01/2007	25.6	0.0	358
30/01/2007	39.5	0.0	350

Table 1. Mass of organic carbon, elemental carbon and $PM_{2.5}$

The analysis uncertainty on the EC results is ±20.9% above 0.5µg and ±0.1µg below 0.5µg, expressed with a level of uncertainty of 95%. As described above in the preliminary report[1], the uncertainty of the OC results is large because of the high and variable blank values.

Chloride, Nitrate And Sulphate Anion Data

Measurements of typical sample blanks gave average concentrations of 4.3µg, 4.5µg and 3.3 µg for chloride, nitrate and sulphate, respectively.

The amount of chloride, nitrate and sulphate anions measured on each whole sampled filter is given in Table 2 below:

Start Date	Chloride (µg)	Nitrate (µg)	Sulphate (µg)	$PM_{2.5}$ Mass (µg)
02/06/2006	10.0	7.24	5.38	422
03/06/2006	6.98	14.2	7.00	386
05/06/2006	0.97	223	35.0	584
06/06/2006	0.88	4.63	3.61	509
07/06/2006	3.69	1.77	6.69	619
08/06/2006	0.81	213	0.82	531
09/06/2006	0.88	5.23	0.86	796
10/06/2006	0.92	4.97	0.58	781
11/06/2006	0.94	222	0.59	594
12/06/2006	0.93	4.90	2.38	367
13/06/2006	0.92	4.74	1.18	451
14/06/2006	25.0	42.6	149	433
15/06/2006				480
16/06/2006	15.0	79.1	87.4	447
17/06/2006	30.1	29.6	82.6	471
18/06/2006	37.4	32.1	163	375
19/06/2006	10.7	19.3	52.4	295
20/06/2006	13.3	29.3	85.4	314
21/06/2006	17.3	12.4	50.4	357
22/06/2006	11.7	58.0	52.4	335
23/06/2006	12.8	67.3	39.7	330
24/06/2006	11.3	14.2	28.8	352
25/06/2006	22.8	13.3	37.3	340
26/06/2006	12.4	18.4	62.2	237
27/06/2006	10.7	20.0	57.7	248
28/06/2006	12.8	26.8	76.8	346
29/06/2006	9.80	11.4	29.9	286
30/06/2006	15.7	19.0	120	236
08/07/2006	8.07	13.1	32.2	227
09/07/2006	16.6	50.7	57.9	191
10/07/2006	12.8	62.5	56.8	391
11/07/2006	10.2	52.0	46.5	396
20/07/2006	16.2	5.88	9.04	574
25/07/2006	17.2	7.82	7.71	496
25/08/2006	8.50	29.6	10.3	265
26/08/2006	7.40	20.6	105	268
27/08/2006	11.2	22.5	17.4	229
28/08/2006	8.98	14.0	9.95	224

Start Date	Chloride (μg)	Nitrate (μg)	Sulphate (μg)	PM$_{2.5}$ Mass (μg)
29/08/2006	16.2	33.9	12.9	216
30/08/2006	10.4	25.3	12.7	201
06/09/2006	12.1	51.6	15.3	241
07/09/2006	8.46	59.9	71.9	226
08/09/2006	7.54	22.1	43.5	263
09/09/2006	16.1	40.6	12.7	358
10/09/2006	8.31	31.2	85.8	489
11/09/2006	7.80	14.0	43.7	453
12/09/2006	6.79	13.7	36.0	234
13/09/2006	7.04	28.1	21.0	369
14/09/2006	7.16	22.7	12.8	243
15/09/2006	7.42	50.7	8.03	226
16/09/2006	8.95	39.4	52.2	468
12/10/2006	11.1	11.5	49.7	225
13/10/2006	13.9	35.3	183	297
14/10/2006	15.8	43.5	191	536
15/10/2006	22.5	56.0	134	554
16/10/2006	15.9	80.5	299	684
20/10/2006	13.1	8.47	19.4	194
21/10/2006	12.1	6.74	20.4	146
22/10/2006	8.90	20.3	38.9	148
23/10/2006	16.2	29.4	34.1	136
24/10/2006	12.6	6.31	27.5	124
25/10/2006	7.87	18.1	53.9	187
26/10/2006	19.2	3.61	49.0	124
31/10/2006	9.13	20.0	14.6	167
02/11/2006	20.2	75.2	249	218
25/11/2006	8.55	44.4	96.9	123
26/11/2006	14.0	28.5	12.6	141
27/11/2006	9.33	12.3	43.7	174
28/11/2006	7.56	20.8	28.3	159
29/11/2006	17. 7	109	167	265
30/11/2006	10.3	48.5	73.0	262
16/12/2006	47.0	132	135	111
17/12/2006	13.4	55.9	47.0	111
18/12/2006				202
19/12/2006	10.4	13.7	85.5	295
20/12/2006	5.52	20.5	11.2	279
21/12/2006	13.5	23.7	89.9	274
22/12/2006	3.04	6.40	11.4	201
23/12/2006	13.8	11.0	3.03	277
24/12/2006	5.46	2.68	14.6	303
25/12/2006	6.20	10.2	4.22	210
26/12/2006	16.4	54.0	7.92	190
27/12/2006	12.8	83.3	75.7	300

Start Date	Chloride (µg)	Nitrate (µg)	Sulphate (µg)	$PM_{2.5}$ Mass (µg)
29/12/2006	9.54	29.6	54.0	287
30/12/2006	13.6	5.99	20.2	128
04/01/2007	14.1	6.37	21.3	
06/01/2007	15.7	6.22	20.7	104
07/01/2007	18.0	7.27	21.2	73
08/01/2007	10.9	5.78	22.3	109
09/01/2007	13.0	8.54	22.1	143
10/01/2007	5.78	36.6	51.2	150
11/01/2007	3.84	0.57	6.44	291
12/01/2007	16.9	6.75	14.5	339
13/01/2007	15.0	66.7	9.32	171
14/01/2007	0.75	44.6	19.8	220
15/01/2007	7.47	23.0	8.58	223
16/01/2007	27.9	26.6	20.9	248
17/01/2007	11.3	30.4	11.9	185
18/01/2007	73.3	49.0	23.4	177
19/01/2007	20.4	7.95	12.8	188
20/01/2007	18.1	25.6	11.4	371
21/01/2007	15.9	8.61	17.5	132
22/01/2007	37.2	30.1	12.4	175
23/01/2007	7.66	53.5	6.90	198
24/01/2007	21.9	4.85	9.15	103
25/01/2007	10.7	218	47.2	349
26/01/2007	0.84	213	31.1	317
29/01/2007	0.91	5.01	0.88	358
30/01/2007	10.8	33.9	20.4	350

Note: Filters exposed on 15/06/06 and 18/12/06 were not analysed by ion chromatography as the filters were misplaced after analysis for OC/EC.

Table 2. Mass of anions and PM

The analysis uncertainty on the anion results is ±14.0%, expressed with a level of uncertainty of 95%. This uncertainty assumes a 5% standard uncertainty in the extraction efficiency of the anions from the filter, and does not take account of errors due to blank corrections.

Time Series – All Data

Figure 1 is a time series plot of the elemental carbon sampled amount plotted along with the collected $PM_{2.5}$ mass. Figure 2 is a similar plot for the anion measurements.

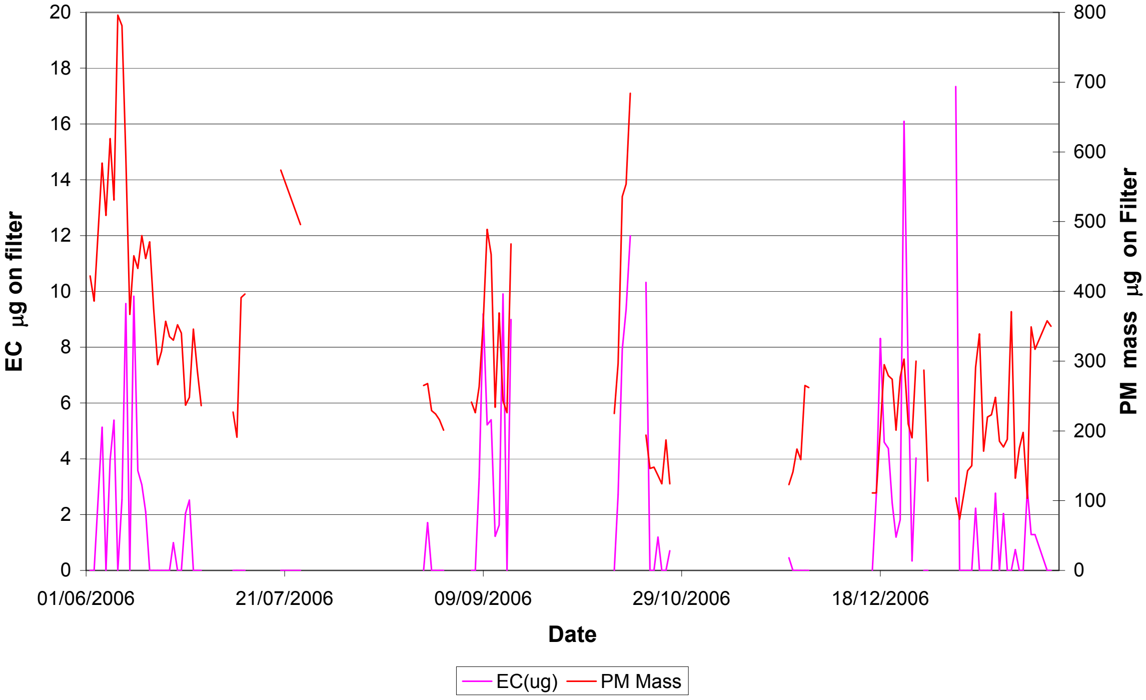

Figure 1 **Elemental Carbon and $PM_{2.5}$ Mass collected on a filter**

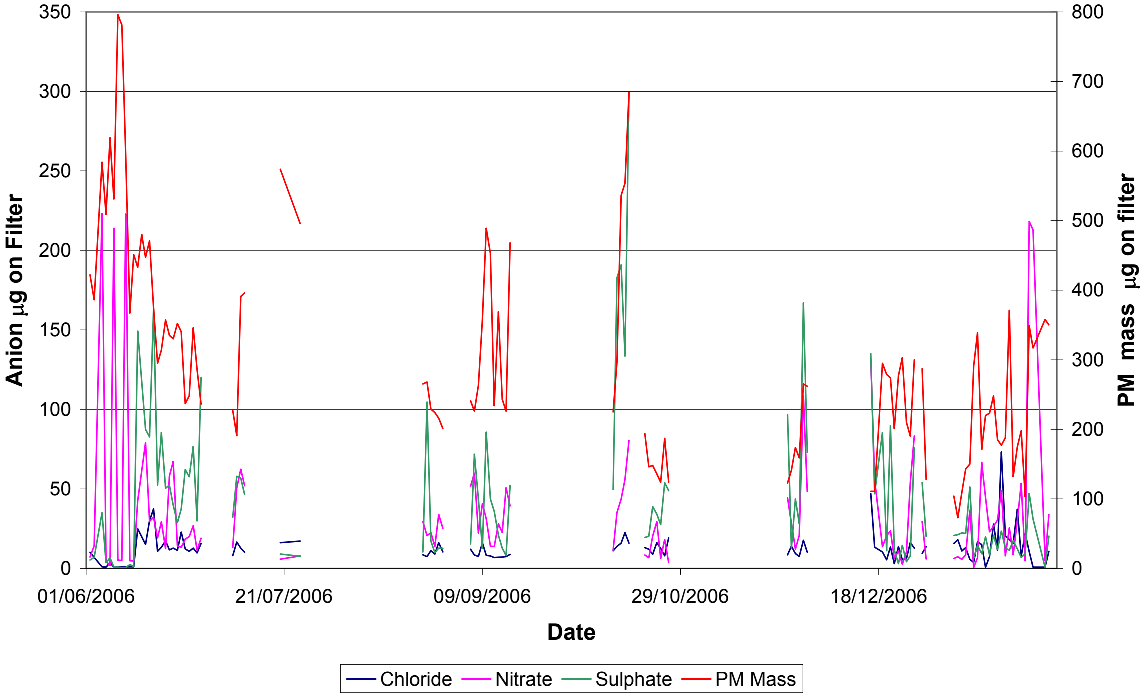

Figure 2 **Anions and $PM_{2.5}$ Mass collected on a filter**

References

1 NPL REPORT DQL AS RES 011, Interim Report On Organic Carbon / Elemental Carbon (OC/EC) Analysis Of Filter PM Samples From Auchencorth Moss, D Muhunthan, R Yardley and D Butterfield, Feb 2008

Annex 1 OC/EC Analysis Method

1.5 cm^2 punches are taken from filters and analysed on the Sunset Laboratory Carbon Aerosol Analysis Lab Instrument. As with all OC/EC measurements, the analysis is method defined. The following description is a summary of the analysis method taken from Sunset Laboratory literature:

Part A

In an oxygen-free helium atmosphere, the sample is heated in four increasing temperature steps to remove organic carbon on the filter. The transition from the third temperature to the fourth (from ~500°C to ~700°C) will quickly decompose inorganic carbonates, producing a sharp, characteristic peak. During this first phase there are usually some organic compounds that are pyrolitically converted to elemental carbon. This can apply to as much as 30% of the organic carbon. Measuring the transmission or reflectance of a laser beam through or from the filter provides a means to monitor this pyrolitic conversion. As the organic compounds are vaporized, they are immediately oxidized to carbon dioxide in an oxidizer oven, which follows the sample oven. The flow of helium, containing the carbon dioxide, then goes to a methanator oven where the CO_2 is reduced to methane. A flame ionisation detector (FID) is then used to detect the methane.

Part B

After the sample oven is cooled to 550°C, the pure helium eluent is switched to a 2% oxygen/helium mixture in the sample oven. Then the sample oven temperature is stepped up to 870°C. During this phase, both the original elemental carbon and that produced by the pyrolysis of organics during the first phase (Part A) are oxidized to carbon dioxide due to the presence of oxygen in the eluent. The carbon dioxide, as in Part A, is then converted to methane and detected by the FID. As previously stated, the darkness of the filter is continuously monitored throughout all stages of the analysis.

Part C

After all carbon has been oxidized from the sample, a known volume and concentration of methane is injected into the sample oven. Thus, each sample is calibrated to a known quantity of carbon. This also provides a means of checking the operation of the instrument. Based on the FID response and laser data, the quantities of organic and elemental carbon are calculated for the sample.

The temperature ramp that defines the method used is outlined below:

Part A

Temperature, ^{o}C	Duration, seconds
310	70
475	60
615	60
870	105

Part B

Temperature, ^{o}C	Duration, seconds
550	60
625	60
700	60
775	60
890	110

Putting known amounts of sucrose on a filter and then analysing these using the method outlined above calibrate the response to particulate carbon of the entire Sunset instrument. Machine blanks are routinely measured to assess and correct for, if required, trace carbon contamination from the machine.

Annex 2 Ion Chromatography Analysis Method

The analysis was performed on one half of the sampled filter as the other half had been used for OC/EC analysis. The method measures the concentration of non-volatile, chemically stable, water-soluble nitrate, sulphate and chloride ions in the $PM_{2.5}$ fraction of airborne particulates. It does not measure the concentrations of specific compounds such as ammonium nitrate or sodium nitrate.

Due to the method of sample collection, particle-laden filters can be exposed to ambient temperatures and gases for up to two weeks. During this time, it is possible that some volatile species (such as ammonium nitrate) are removed from the filter, particularly during the summer months. It is also possible that some species are involved in chemical reactions with ambient gases, during or after sampling.

Sampled filters are extracted by sonication in a known mass of aqueous 11mM Na_2CO_3/ 2mM $NaHCO_3$. The extracted solution is analysed by ion chromatography.

The sample first passes through a guard column, to remove non-volatile residues. It then enters an anion exchange column that separates the anions according to their steric bulk and charge. The chloride ion emerges first, followed by the larger nitrate and then sulphate ions.

The sample then enters a self-regenerating suppressor, in order to reduce the background conductivity by removing the eluent anions (from sodium carbonate and sodium hydrogen carbonate). These basic anions attract hydrogen cations from the column and then dissociate to form water and carbon dioxide. The holes left by the H^+ ions are filled by Na^+ from the eluent.

Finally, a conductivity cell detects the anions, and a chromatograph is generated (see example in Figure 3). For each sample, the area under each peak is related to peak areas from a set of analysed calibration standards. These are prepared gravimetrically from reagent grade sodium salts, diluted into the same matrix as the samples.

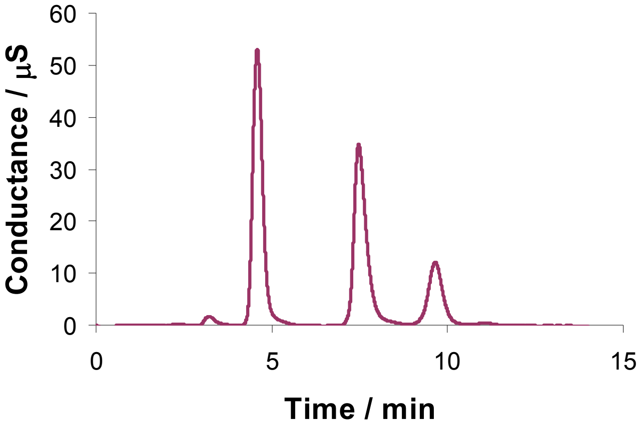

Figure 3. Typical Ion Chromatograph