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Comparison of Methods for Organic and Elemental Carbon PM_{10} Concentrations at Marylebone Road for the Period 07/09/06 to 31/12/06

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Executive Summary

This Report was prepared by NPL as part of the 2005-2007 UK Airborne Particulate Concentrations and Numbers Monitoring contract with the Department for the Environment, Food and Rural Affairs.

The report summarises the results of parallel measurements of the organic and elemental (OC/EC) carbon content of PM_{10} suspended particulate matter at Marylebone Road during the period 07/09/06 to 31/12/06. Measurements were made manually using a Partisol sampler with a Sunset Laboratory Carbon Aerosol Analysis Instrument at NPL and with the automatic Thermo Electron Corporation Series 5400 Ambient Carbon Particulate Monitor.

The aim of the intercomparison was to see if the automatic (Thermo) instrument gave similar values to the manual (Sunset) instrument, which follows a method similar to the US reference method. There is no European reference method for these measurements. A US EPA study in December 05 showed that the automatic method gave poor agreement with the manual reference method for elemental carbon.

The study will inform the interpretation of results from the Network, which currently includes four Thermo instruments, and also a strategy for monitoring OC/EC by the Network in the future.

The results of the intercomparison showed that that the manual method reported organic carbon concentrations similar to the automatic method, while it reported elemental carbon concentrations between three and four times the value of the automatic method. When adding the organic and elemental concentrations to form a measure of total carbon, the manual method reported approximately two times the concentration of the automatic method. The measurements produced by the manual method are in line with previous measurements reported by the Air Quality Expert Group in the UK.

Further work is to be carried out at an urban background site to show whether these results are applicable to other site designations.

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Contents

Executive Summary 1

1.0 Introduction 3

2.0 Measurement Methods 3
  2.1 Manual OC/EC Analysis 3
  2.2 Automatic OC/EC Analysis 5

3.0 Results 6

4.0 Conclusions 9

5.0 Further Work 10

6.0 Acknowledgements 10

7.0 References 11

1.0 Introduction

Organic and elemental carbon forms a major component of suspended particulate matter, forming around 40% of average roadside PM_{10} in the UK, according to AQEG (2005)[1] based on the work of Harrison et al (2003)[2].

Currently the hourly organic and elemental carbon content of suspended particulate matter is measured automatically at four sites in the UK. This work is undertaken by the Airborne Particle Concentration and Numbers Network, which is funded by the Department of Environment, Food and Rural Affairs (Defra). The instrument used is proving to be unreliable and recent studies performed by the US EPA[3] have shown that its results do not agree well with reference methods (NIOSH 5040).

Organic and elemental carbon measurements produced by the network are of low data quality and NPL have not been able to ratify the data produced since taking over operation of the network in 2005.

The aim of the intercomparison was to see if the automatic (Thermo) instrument gave similar values to the manual (Sunset) instrument, which follows a method similar to the US reference method (NIOSH 5040).

An intercomparison between the two measurement methods was performed at Marylebone Road over the period 07/09/06 to 31/12/06 to determine how the automatic instrument compared with the manual reference instrument at a highly trafficked London roadside site.

2.0 Measurement Methods

Measurements were made by two different methods. The first was by sampling the air onto quartz filters using a Partisol 2025 sampler fitted with a PM_{10} head, followed by the manual analysis of the collected carbon using a Sunset Laboratory Carbon Aerosol Analysis Lab Instrument at NPL. The second was by using the automatic Thermo Electron Corporation Series 5400 Ambient Carbon Particulate Monitor that is already installed at the site and run by NPL and ERG under the Airborne Particle Concentration and Numbers Network.

2.1 Manual OC/EC Analysis

Daily samples were collected onto Pallflex Tissuequartz 2500QAT-UP 47mm filters using a Partisol 2025 sampler fitted with a PM_{10} head. The filters are binder free pure quartz filters that have been heat-treated by the manufacturer to remove trace organics. This is checked by routine blank measurements. Therefore, NPL did not pre-bake the filters before they were sampled. After sampling, the filters were returned to NPL and kept in a fridge before analysis. 1.5 cm^2 punches are then taken from the sampled filter and analysed on the Sunset Laboratory Carbon Aerosol

Analysis Lab Instrument. As with all OC/EC measurement procedures the analysis is method defined. The following description of the analysis method is taken from Sunset Laboratory literature:

Part A

In a completely oxygen-free helium atmosphere, the sample is heated in four increasing temperature steps to remove all 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. As much as 30% of the organics may be pyrolitically converted to elemental carbon. This pyrolitic conversion is continuously monitored by measuring the transmission of a laser through the filter. 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. The methane is then detected by a flame ionisation detector (FID).

Part B

After the sample oven is cooled to 525°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 850°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 transmission 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	60
475	60
615	60
870	90

Part B

Temperature, ^{o}C	Duration, seconds
550	45
625	45
700	45
775	45
850	45
870	120

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

2.2 Automatic OC/EC Analysis

After sampling ambient air through a PM_{10} inlet, the Thermo Electron Corporation Series 5400 Ambient Carbon Particulate Monitor collects particulate matter on an internal impactor with a 50% cut off point of 100nm, i.e. only particles larger than around 100nm in aerodynamic diameter are collected and measured. After sampling, the impactor is heated to two temperatures (~325^{o}C and ~750^{o}C) to get a measurement of organic and total carbon content through the amount of carbon dioxide generated. Elemental carbon is calculated by subtraction of the organic carbon content from the total carbon content. . The analysis in this system is performed in ambient air, in a closed loop system using an infrared detection system to measure the amount of CO_2 generated. There is no correction for the pyrolysis of organics during the first heating phase. For this intercomparison, daily mean concentrations were calculated from the hourly measured values.

The data for the automatic instrument has been passed through NPL’s QA/QC procedures for the network and has been scaled using the on site regular calibrations. Due to the poor quality of the data, it has only been validated and not ratified.

3.0 Results

Measurements of PM_{10} organic and elemental carbon suspended in ambient air at Marylebone Road were measured over the period 07/09/06 to 31/12/06. The time series of these concentrations can be seen in Figures 1a and 1b below:

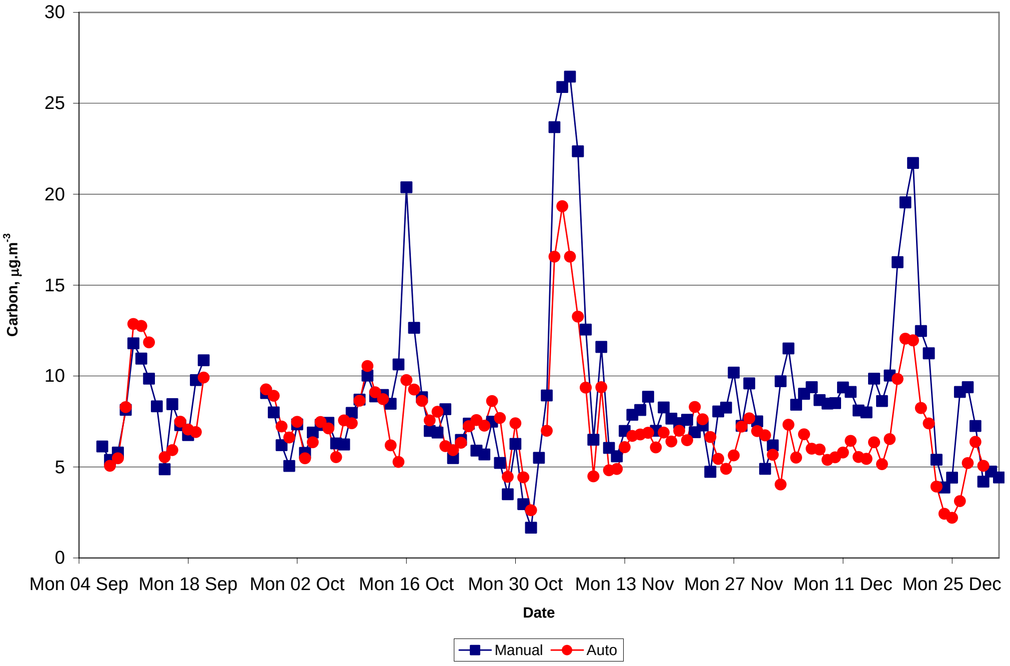

Figure 1a **Time series of organic carbon measurements at Marylebone Road.**

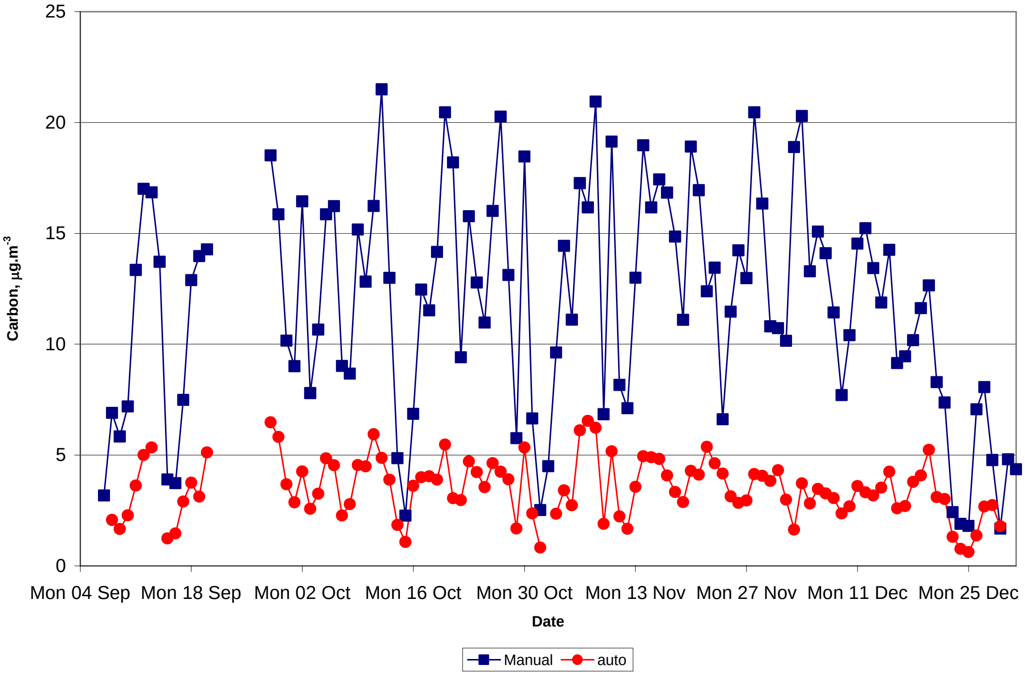

Figure 1b **Time series of elemental carbon measurements at Marylebone Road.**

It can be seen that while the organic carbon measurements agree quite well, there is a large difference between the amounts of elemental carbon reported by each method. The ratios are shown in Figure 2 below. The differences are such that there is more elemental carbon than organic carbon reported at the site by the manual method, while for the automatic method this situation is reversed.

The most likely cause of this is that a large proportion of the elemental carbon is in the form of particulates with aerodynamic diameter less than 100nm, and hence is not collected by the automatic instrument.

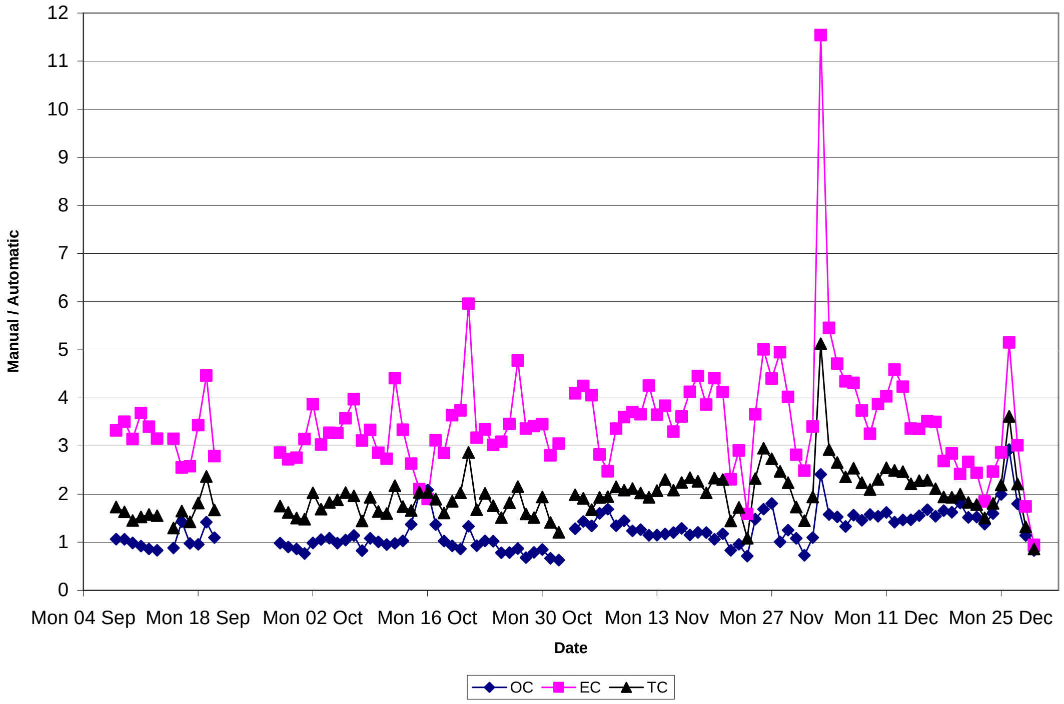

Figure 2 Ratio of Manual to Automatic Analysis Results for OC/EC

There is a step change in ratio for the organic carbon results, which coincides with the six monthly service visit on 2nd November. The automatic data has been scaled using the routine calibrations performed on site, but this has not removed the effect. There was no obvious change at the site for the manual method over this period.

The anomalously high elemental carbon ratio on 3rd December appears to be the result of a particularly low result on the automatic instrument on a day when elemental carbon formed an unusually high proportion on the PM_{10} concentration (Figure 3).

During the measurement period a PM_{10} TEOM (in standard 50°C mode) was also run at Marylebone Road. Figure 3 shows the percentage of particulate mass collected by the TEOM that is attributable to the carbon, as measured by the manual method. The gap in the data around the 13th November is due to the lack of TEOM data for this period.

These results show that according to the manual method, organic carbon forms around 10 – 30% of the TEOM PM_{10} mass, with a mean of 16%, while the elemental carbon falls within a similar range with a mean of 22%. The mean total carbon is 39% of the TEOM mass, which is very similar to the AQEG figures for roadside PM_{10} given in the Introduction. This provides good evidence that the manual results are in line with consensus values, in contrast to the automatic instrument, which gives a corresponding figure of 20% for mean total carbon.

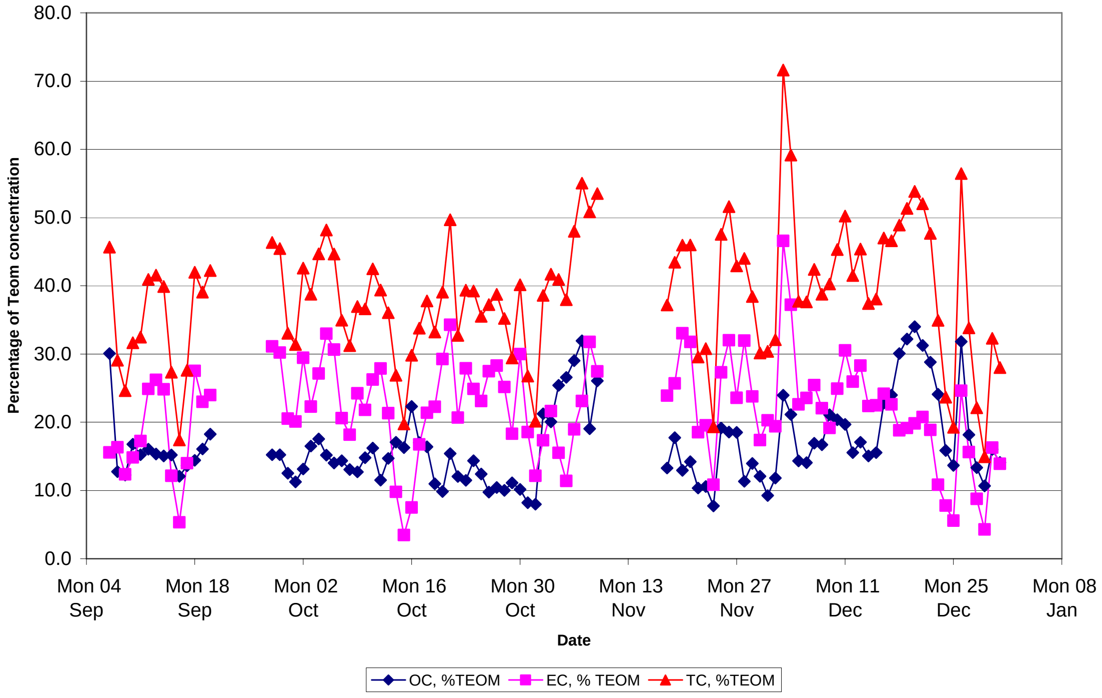

Figure 3 **Percentage of Particulate Mass Collected by the TEOM that is Attributable to Carbon, as Measured by the Manual Method**

Figure 4 shows the mean organic and elemental concentrations measured on individual days of the week by the manual method. It can be seen that there is a substantial drop in elemental carbon concentrations over the weekend, as expected from the drop in heavy goods vehicles.

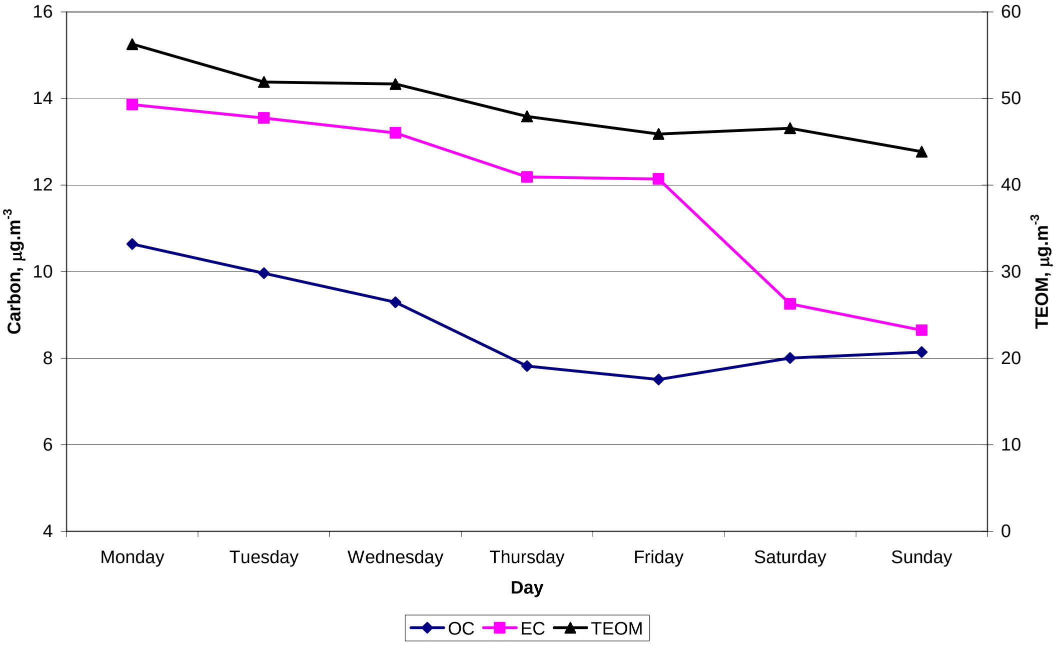

Figure 4 **Mean Organic And Elemental Concentrations Measured On Each Day Of The Week As Measured By The Manual Method**

4.0 Conclusions

Organic and elemental carbon concentrations were successfully measured by both the manual and automatic methods at Marylebone Road for the period 07/09/06 to 31/12/06. It can be seen that the manual method reports organic carbon concentrations similar to the automatic method, while it reports elemental carbon concentrations between three and four times the size of the automatic method. When adding the organic and elemental concentrations to form a total carbon concentration, the manual method reports approximately two times the concentration of the automatic method.

Using the results from the manual method, elemental carbon makes up between 4% and 47% of the particulate concentration measured by a PM_{10} TEOM with a mean of 16%, while organic carbon makes up between 8% and 34% with a mean of 22%. Total carbon makes up between 15% and 72% of the particulate concentration measured by a PM_{10} TEOM with a mean of 39%. These figures agree well with the data published by AQEG. Although the manual system will only produce daily rather than hourly data, the resulting data is much closer to the *de facto* reference data, and to the results accepted by the scientific community.

5.0 Further Work

Quartz filters have been requested from Bureau Veritas from the gravimetric sampler installed at the North Kensington AURN and Airborne Particle Concentration and Numbers Network site, so that they can be analysed for organic and elemental carbon content. The gravimetric sampler is colocated with the automatic Thermo Electron Series 5400 Ambient Carbon Particulate Monitor and will allow comparison of methods at a London urban background site.

Results from this intercomparison should be available by the end of March 06.

6.0 Acknowledgements

This work was co funded by Defra using facilities at NPL supported by DTI through the Valid Analytical Measurement Programme.

7.0 References

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