Marylebone Road Aethalometer Trial Report

Prepared for Department for Environment, Food and Rural Affairs (DEFRA), the Scottish Executive, the Welsh Assembly Government and the DoE in Northern Ireland

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SUMMARY

The traditional British Smoke Stain method has a number of limitations. In common with many manually operated instruments, it is labour intensive, prone to human error and cannot provide measurements in real time. The equipment design makes is susceptible to measurement uncertainties induced by non-uniform inlet design across the network, sample flow errors and leaks. It was therefore desirable to compare commercially available automatic instruments that measure black smoke and the similar metrics with the traditional British Smoke Stain method to identify a suitable replacement for the UK Black Smoke Network.

To this end, seven instruments that measured either black smoke, black carbon or elemental carbon, were operated at Marylebone Road during 2006. These were the traditional 8-port sampler (used to collect samples for subsequent reflectometry analysis), the ETL SX200, the MAAP 5012, the R&P Aethalometer 8100, Magee Aethalometer AE-21, R&P Automatic Carbon Monitor 5400 and a Partisol 2025 (used to collect samples for analysis by the Sunset Laboratories Carbon Aerosol Analysis Lab Instrument). The comparability to the existing black smoke measurement and the agreement to measurements of elemental carbon were the key factors assessed. The ease of operation and the ability to integrate the instruments into a monitoring network that uses remote data download and fault diagnosis to maintain high data capture rates were also considered.

The measurements of black smoke made using the SX200 automatic black smoke monitor, agreed well with the established black smoke measurements. This instrument is therefore recommended if continuity with the established network is the highest priority. This instrument was also deemed suitable to integrate into a remote monitoring network. However, measurements of black smoke far exceeded measurements of PM_{10} at this site.

The high quality measurements of elemental carbon undertaken by NPL using the Sunset Laboratories instrument provided a reference against which the other instruments could be measured. The Magee AE-21 provided the closest agreement to the elemental carbon measurement over a long time period, the next generation of Magee aethalometer would also appear to integrate well into a remote monitoring network.

The measurements from all of the automatic instruments were strongly correlated and potential therefore exists to establish factors to relate the aethalometer measurements of black carbon to black smoke and vice versa.

1 INTRODUCTION

Following the decision by DEFRA to re-instate the black smoke network, a review of available continuous and semi continuous instruments for the measurement of black smoke and black carbon was undertaken at Marylebone Road. The aim of this study was to determine whether alternatives to the traditional 8-port sampler method could be used to measure black smoke as the 8-port sampler method is it is labour intensive, prone to human error and cannot provide measurements in real time. The equipment design makes is susceptible to measurement uncertainties induced by non-uniform inlet design across the network, sample flow errors and leaks.

Rupprecht & Patashnick, Thermo Fisher Scientific and Magee Scientific all supplied instruments specifically for this study, whilst other instruments were already in use at the site. Additionally, filters collected during the trial period have been analysed using the Sunset Laboratories Carbon Aerosol Analysis Lab Instrument by NPL, which provided a mass concentration of elemental carbon in PM_{10}. Some instruments were offered for comparison after the trial had begun; it was therefore not possible to compare each instrument for the entire trial period.

Comparability of all measurements those made using the 8-port sampler and to accurate measurements of elemental carbon (using the Sunset Laboratories instrument) were considered. The practicality of integrating these continuous instruments into the network was also evaluated.

Because the instruments used had fundamentally different methodologies there was some discrepancy over the parameter being measured; different instruments give different names to the black sooty material collected and for the purposed of this report we will consider black smoke, black carbon and elemental carbon as the parameters being measured. Three methodologies were utilised: reflectometry, absorbency or attenuation at specific wavelengths and detection of thermal decomposition products. More detail of the different methodologies is given in section 2.2.

There is no generally accepted definition for the elemental carbon or black carbon component of airborne particulate matter (PM). Methods are based either on the determination of carbon content, in which case there is an operational definition of the “elemental” and “organic” parts, or on the light-absorption properties of the PM, in which case there can be interferences from non-carbonaceous PM.

There has been considerable interest in these methods in recent years, in part because of the effect of airborne carbonaceous particles on the climate. Two recent studies in this area are Schmid *et al* (2005) and Hitzenberger *et al* (2006).

2 METHODS

This section outlines the monitoring location, the methods used, and the treatment of data. It also provides a summary of the data analysis techniques used.

2.1 Monitoring Location - Marylebone Road

Marylebone Road is a kerbside monitoring site in central London shown in Figure 1 (grid reference 528120 182000) and is affiliated to the AURN. Marylebone Road is a major route in and out of Central London, running north-east to south-west and carries approximately 90,000 vehicles per day. The tall buildings on either side form a broad street canyon and 40m across. The monitoring cabin is located 1m from the kerb on the southern side of the road.

Figure 1: Marylebone Road site picture and location

Due to space limitations it was not possible to site all the equipment exactly equidistant from the kerb. Although disparities were kept to a minimum, the dominating effect of emissions from the road can impact on measurements over a short distance, these should therefore be considered when examining the measurements. The exact distances are shown in Table 1.

Instrument	Distance from Kerb (m)
8-port sampler	1.50
ETL SX200	2.23
MAAP 5012	2.23
R&P Aethalometer 8100	1.78
Magee Aethalometer AE-21	2.97
R&P Automatic Carbon Monitor 5400	2.23
Partisol 2025 (used to collect samples for analysis by Sunset)	2.97

Table 1: Sample inlet distances from the kerb

The layout of the instruments is shown in the following diagram. With the exception of the Partisol 2025 that was used to collect samples for analysis by the Sunset Laboratory analyser and the Magee Aethalometer, all instrument were installed as close to the roadside edge of the cabin as possible. Note that the MAAP and SX200 were installed at the same location but at different times. The R&P 8100 was sampling from the auxiliary flow on the PM_{10} TEOM and so also appears in the same location on the diagram.

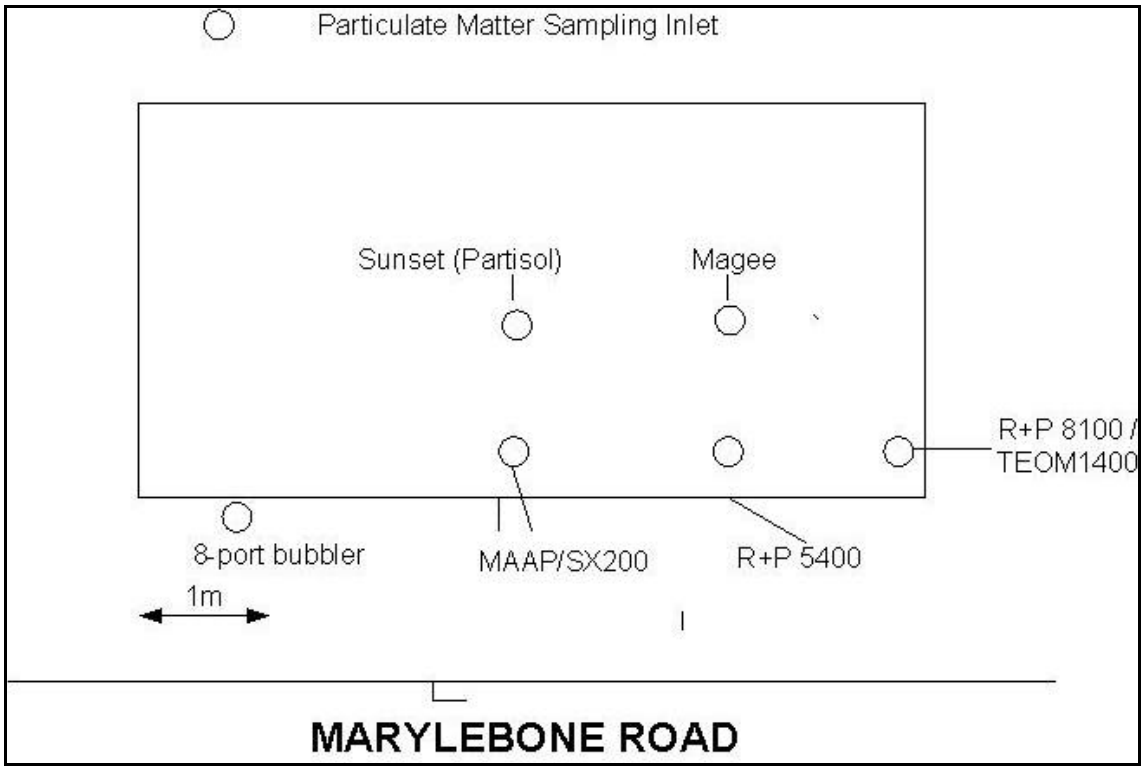

Figure 2: Marylebone Road site plan

2.2 Monitoring Methods

Measurements of black smoke were made using an 8-port sampler and the ETL SX200. Black carbon measurements were made using the R&P and Magee aethalometers. Elemental carbon measurements were made using the R&P 5400 and by the Sunset Laboratories instrument on quartz fibre filters.

Basis	Technique	Variation	Example	Comment
Amount of carbon atoms (filter based samples)	Thermal (oxidation to CO_2)	Temperature protocol	R & P 5400 (automatic)	Collection by impaction (small particles are excluded)
	Thermo-optical (oxidation to CO_2 with pyrolysis correction)	Temperature protocol e.g. NIOSH and IMPROVE	Sunset Labs (manual or automatic)	
	X-ray photoelectron spectroscopy			Quantitative, with binding information, but limited to surface layers
Light absorption	Filter reflectance	White light	Black Smoke (manual) ETL SX200 (automatic)	Black Smoke "Index" (in µg/m^3) is by convention much higher than black carbon concentration.
	Filter transmittance (aethalometry)	Single wavelength	Magee AE16 / Thermo 8100 (880 nm)	The aethalometer optical data is processed to give results much closer to the true black carbon concentration
		Multi-wavelength	Magee AE21 (880nm and 370 nm) Magee AE31 (7 wavelengths 350 – 950 nm	
	Filter multi-angle		Thermo 5012 MAAP	
	Photoacoustic spectrometry			Aerosol i.e. not filter based. Can be calibrated directly with gas.

Table 2: Selective summary of elemental and black carbon techniques

2.2.1 British Smoke Stain (8-port sampler)

Sample stains are collected over 24 hours using the 8 port sampler apparatus, which switches ports daily to expose a fresh filter. These filters are removed and the staining measured by reflectometer and calibrated against a calibration curve for the photometer. This has been the standard method for assessing black smoke in the UK since the 1960's.

2.2.2 ETL SX200

The SX200 sampler uses reflectometry to measure the light absorbance of collected particulate matter from a known source as described by EC directive 80/779/EEC. This directive is the basis for the traditional 8-port sampler method although the SX200 operated continuously. Samples are collected to a Whatman grade 1 filter paper spool and the length of time between each collection and measurement of reflectance can be changed, to some extent, by the operator. In the case of this comparison, 8 hours was selected as a suitable averaging period as

this was the lowest permitted time interval. The SX200 analyser is widely used in the Dutch Air Quality Network and has been compared to the Black Smoke measurements from the UK Smoke and SO_2 network site at Halifax in the UK (Loader, 2005). The instrument reported measurements as OECD black smoke measurements, the reflectometry measurements were used to recalculate the British Smoke Stain concentration according to the standard calibration curves (Loader, 1999).

2.2.3 R&P 8100 Aethalometer

Based on the same operating principles of the Magee Aethalometer; the R&P 8100 measures light attenuation through a sample of particulate collected on a quartz filter paper. Unlike the Magee, the 8100 requires an external logger or can be logged on an existing TEOM 1400 or FDMS 8500 control unit (where spare logging capacity is available).

2.2.4 Magee Aethalometer AE-21

The Magee AE-21 measures light absorbing carbon particles collected on a quartz filter paper by measurement of the light attenuation when a known frequency of light is passed through the filter and sample. Additionally the AE-21 offers measurement in the near UV, which can highlight the presence of highly UV absorbing compounds such as aromatic organic species, these are discussed briefly in section 4.3. Analysis is continuous and measurement can be set between 1-5 minutes. In this comparison, the time base was set to the maximum of 5 minutes. The AE-21 is equipped with an internal 3.5 inch floppy disc drive or memory card for data logging and transfer.

The measurements from the Magee AE-21 were processed by the manufacturers in the US using an algorithm that will be installed in the next generation of aethalometers available on the UK market (Hansen, 2006). This gave us the opportunity to assess the impact of this algorithm rather than conduct a second trial when new instrumentation is available; the impact on measurements is discussed in section 4.3.

2.2.5 Multi Angle Adsorption Photometer

The MAAP 5012 / CARUSSO instrument provides a hybrid approach combining reflectometry at given angles with light attenuation measurements to give a measurement of “black carbon” Samples are collected on a filter tape and the measurements provide continuous black carbon concentrations in ambient air. Data is stored on internal memory. In this study, sampling was carried out at 5 min intervals.

2.2.6 R&P 5400 Continuous Carbon Analyser

The R&P 5400 Carbon analyser is a thermal decomposition method of analysing carbon and gives a measurement of both “organic” and “elemental” carbon. After collecting particulate sample (particles larger than around 100nm) for a given period, the instrument carries out a two stage heating cycle at ~325 and ~750 degrees C, which converts carbon particulate to CO_2. This CO_2 is measured by infrared detection and the concentration of carbon calculated. By heating in stages it is possible to attribute carbon broken down at the lower temperature to “organic” carbon materials and those that require higher temperatures to “elemental” carbon. A number of these instruments have been in operation under Defra’s particulate number and concentrations project for several years. This is not considered as a suitable replacement for the 8-port sampler but is included in some analysis for information purposes.

2.2.7 Sunset Laboratories Carbon Aerosol Analysis Lab Instrument

Samples were collected on 47mm quartz fibre filters using an R&P Partisol 2025 instrument fitted with a PM_{10} head. Filters were sent to NPL for analysis by the Sunset Laboratories instrument. Full details of the methodology can be found in NPL report DQL-AS 035.

The Partisol 2025 is a sampler system that drew air through a PM_{10} size selective inlet air through a 1 m^3 h^{-1}. This total flow was passed through a 47 mm quartz fibre filter at a volumetric

flow rate of 1 m^3 h^{-1} for 24 hours between midnight and midnight each day. The filters, pre and post exposure, were kept in two canisters, to the left and right of the sampling filter respectively. At midnight sampling was stopped briefly while the filter being exposed was pneumatically shuttled to the top of the canister containing exposed filters. At the same time an unexposed filter was pneumatically shifted into the sampling position and sampling was restarted. To minimise the loss of volatile material from the exposed filters air was drawn through the equipment housing in an attempt to maintain the storage temperature within 5ºC of ambient temperature, as specified by the US EPA.

2.3 Data Averaging

The instruments described in section 2.2 reported mean concentrations with different averaging periods. As both the 8-port sampler and the Sunset manual method provide daily mean concentrations; higher time resolved measurements were averaged to daily mean concentrations using a 75% data capture threshold. Therefore, valid daily means were calculated where a minimum of 18 valid hourly means were present. Hourly means were calculated where a minimum of three valid 15-minute means or nine valid 5-minute means were present. In the case of the SX200, which reported 8-hour mean concentrations, all three valid 8-hour means were required to produce a valid daily mean concentration.

3 OPERATIONAL CONSIDERATIONS

The limitations of the 8-port sampler are well known. The filters need to be exchanged on a weekly basis and then returned to the laboratory for analysis; the method is therefore labour intensive and there is a delay in reporting measurements. The absence of any logging and remote access to measurements and diagnostics means that breakdowns between LSO visits cannot be identified and there is limited information for subsequent measurement ratification. Each of the 'candidate' instruments used in the trial was therefore assessed for ease of use and how readily they could be integrated into existing site operations and data collection.

Instruments such as the R&P 8100, SX200, Magee AE-21 and MAAP 5012, which sample onto a filter tape will often fail the leak test currently employed during the AURN QA/QC audits. The negative pressure on the system overwhelms the seal between the tape and the sample system that would not leak under ambient pressure. This issue needs to be addressed when designing the QA/QC procedures.

Instrument	Manual filter change / analysis	Onboard logging	Remote data retrieval
8 port Sampler	Y	N	N
R&P 8100	N	N(1)	N (1)
SX200	N	Y	Y
Magee AE-21	N	Y	Y
MAAP 5012	N	Y	Y

(1) Via TEOM or FDMS other data logger

Table 3: Summary of operational considerations

3.1 R&P 8100

The R&P 8100 uses a filter tape to collect the sample, this advances on a periodic basis; in this trial the tape lasted approximately 10 months. The unit can be integrated into a TEOM or FDMS, which then supplies the sample, logging and remote communication facility. There are no diagnostics available from the 8100, however, operational parameters such as flow are available from the TEOM or FDMS instrument. Proprietary software is available for the TEOM and FDMS and measurements from both instruments are collected routinely using a variety of in-house software in many institutions in the UK. The R&P 8100 cannot be operated without a TEOM or FDMS unit unless an additional pump, sample inlet and logger are installed. The instrument operated without any problems during the trial.

3.2 SX200

The SX200 uses a filter tape to collect the sample, this advances on a predefined basis (in this case every 8 hours); in this trial the tape lasted approximately two months. This system has an integrated logging facility which records the sample flow, the date and time when each measurement is made, instrument status, the reflectance measurement and also calculates the black smoke concentration according to a programmable algorithm. This information can be downloaded easily using the proprietary software; it is also possible to adapt in-house software to download measurements. The instrument operated without any problems during the trial.

3.3 Magee AE-21

The Magee AE-21 uses a filter tape to collect the sample, this advances based on filter loading and can be configured to two levels of tape saving mode. During the two months that the instrument operated the tape did not require replacing. The instrument used in this trial recorded measurements (date and time, attenuation, black carbon concentration, UV concentration) and diagnostic information (sensor and reference beam zero and output) onto a flash memory card which was downloaded onto a laptop periodically. The outputs could also have been logged using a separate logger to enable remote data download and fault diagnosis. The next

generation of Magee aethalometers are IP-enabled to overcome this limitation. It should be possible to adapt in-house software to download measurements and provide a remote diagnosis facility.

3.4 MAAP 5012

The MAAP 5012 uses a filter tape to collect the sample, this advances on a predefined basis; during the two months that the instrument operated the tape did not require replacing. The MAAP 5012 stored measurements as 5 minute averages, these were downloaded via a laptop during each site visit, however, this could have been done remotely. The download facility was cumbersome, requiring the whole memory to be downloaded on each occasion; this would not integrate well into an automatic data collection system.

4 RESULTS AND DISCUSSION

The availability for all the instruments included in this study is detailed in Table 2. The 8-port sampler, the R&P 8100 and the R&P 5400 were operating for much of 2006, while the remaining instruments only operated for periods of 1 to 3 months. Limitations on space within the Marylebone Road cabin and the instrument availability meant that there is no period when all the instruments operated at the same time. The daily mean concentrations from all the instruments are shown in Figure 3 to Figure 10; periods within the dotted lines are those examined in section 4.1.

Instrument	Start Date	End Date
8 port Sampler	01/01/2006	31/12/2006
R&P 8100	18/02/2006	06/12/2006
SX200	03/10/2006	26/11/2006
Magee AE-21	06/10/2006	14/12/2006
MAAP 5012	15/07/2006	20/09/2006
R&P 5400	10/05/2006	31/12/2006
Sunset EC/OC	07/09/2006	19/12/2006

Table 4: Availability of measurements

4.1 Analysis of Mean Concentrations

Comparing the mean concentration from each instrument together demonstrates the impact of the different metrics used (black smoke, black smoke and elemental carbon). The issue of which instruments agree best with the traditional 8-port sampler and Sunset EC measurement is examined in greater detail in section 4.2.

Unfortunately, the lack of a period when all the instruments are monitoring concurrently necessitates examining the means of all the instruments for two restricted periods (7th to 20th September and 12th October to 26th November). These periods were chosen as the elemental carbon measurements from the Sunset instrument were available in both periods; therefore providing a reference for the black carbon measurements. The means for each of the instruments when daily means were available from all operational instruments during the specified time periods are shown in Table 5.

Instrument	**Period 1** 9th to 17th September (μg m^{-3})	**Period 2** 12th October to 26th November (μg m^{-3})
n	6	32
8 port Sampler Black Smoke	39.1	64.4
R&P 8100 Black Carbon	10.7	18.1
SX200 Black Smoke	-	76.1
Magee AE-21 Black Carbon	-	13.9 (12.1)*
Magee AE-21 (UV)	-	12.2 (10.0)*
MAAP 5012 Black Carbon	7.5	-
R&P 5400 Elemental Carbon	2.2	3.7
Sunset Elemental Carbon	6.9	13.2

Table 5: Mean concentrations from each instrument during two periods (9th to 17th September and 12th October to 26th November) when daily means from all operational instruments are present

***Concentration in parentheses represents unprocessed Magee AE-21 measurements, additional analysis of this processing and the relationship between the black carbon and UV black carbon measurements is provided in section 4.3.**

4.1.1 Period 1 - 9th to 17th September (µg m^{-3})

Only six daily means were available during the first period as the Sunset analysis began as the MAAP monitoring finished; this period should therefore only be treated as indicative of the relationship between the different instruments. Additionally, the concentrations measured during this 8 day period when compared with the second period indicate that ambient concentrations of black smoke and elemental carbon were low. Nevertheless, during Period 1, the MAAP measurement of black carbon appeared to agree well with the Sunset measurement of elemental carbon (means of 7.5 µg m^{-3} and 6.9 µg m^{-3} respectively). Relationships between other instruments are drawn out in the discussion of the more extensive second period.

4.1.2 Period 2 - 12th October to 26th November (mg m^{-3})

The second period provided an adequate number of daily means (32) with which to compare the different instruments. Unfortunately the equipment supplier removed the MAAP on 18th September and it therefore cannot be included in this comparison.

The mean concentrations during this period can be divided into three groups:

a) *Instruments measuring black smoke.* It is clear from the means during this period that the SX200 agrees best with the 8-port sampler (76.1µg m^{-3} and 64.4 µg m^{-3} respectively).

b) *The instruments measuring black carbon using an aethalometer (R&P 8100 and Magee AE-21) and the Sunset Laboratories instrument measurement of elemental carbon.* The Magee AE-21 mean (13.9 µg m^{-3}) was closest to the Sunset mean (13.2 µg m^{-3}), while the R&P 8100 mean was higher (18.1 µg m^{-3}). This may, in part, be due to the R&P 8100 inlet being 1.21 m closer to the kerb than both the Magee and the Sunset instruments although a discrepancy due to sampling location of this magnitude would be unexpected on the basis of previous studies at this site (Green, 2004).

c) *The R&P 5400 measurement of elemental carbon.* It is clear that the measurement of elemental carbon by R&P 5400 is too low, this has been observed in a previous study at Marylebone Road.

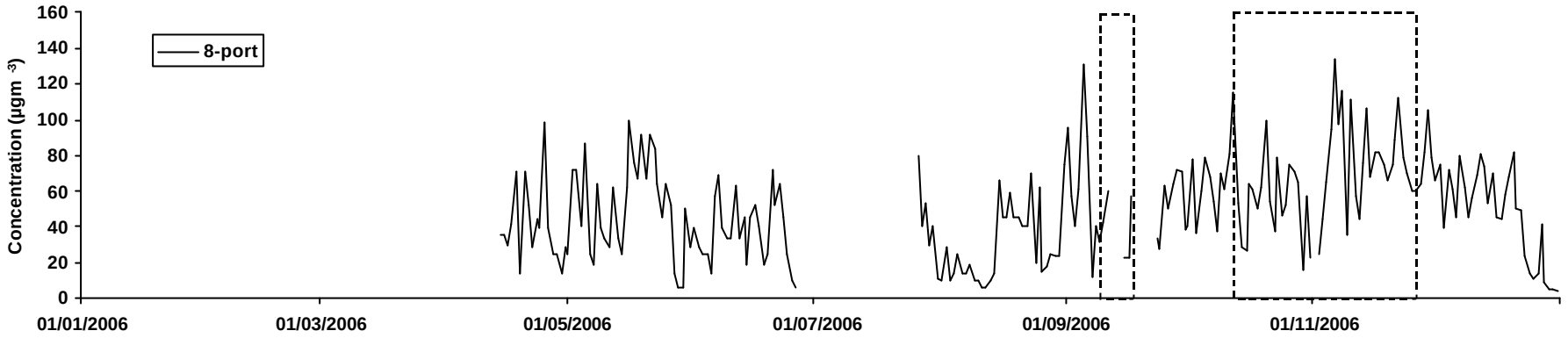

Figure 3: Daily mean concentrations for the 8-port sampler. Periods within the dotted lines are those examined in section 4.1.

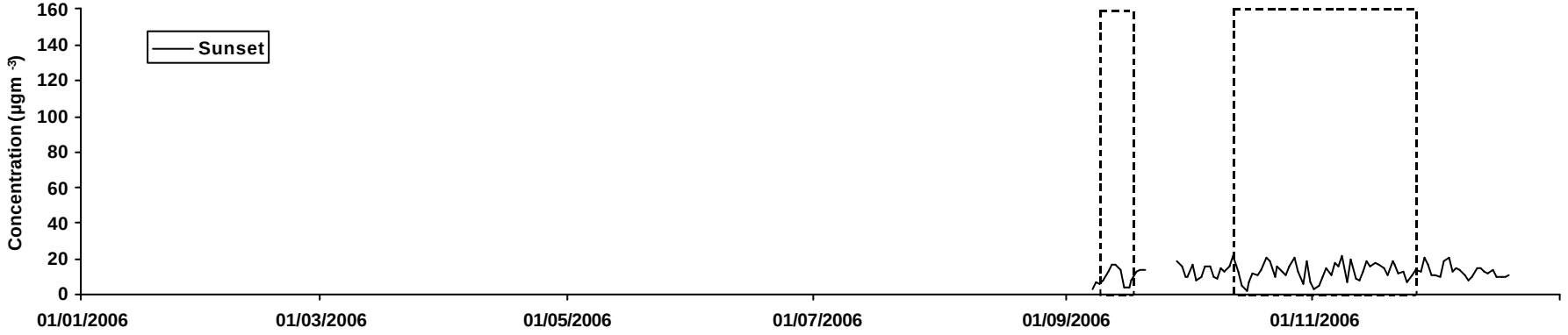

Figure 4: Daily mean concentrations for the Sunset manual method. Periods within the dotted lines are those examined in section 4.1.

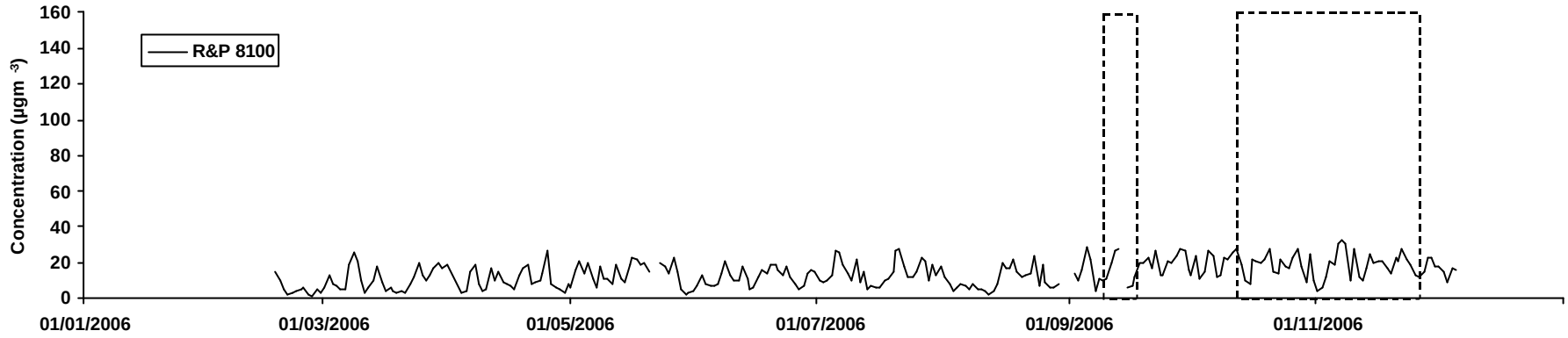

Figure 5: Daily mean concentrations for the R&P 8100. Periods within the dotted lines are those examined in section 4.1

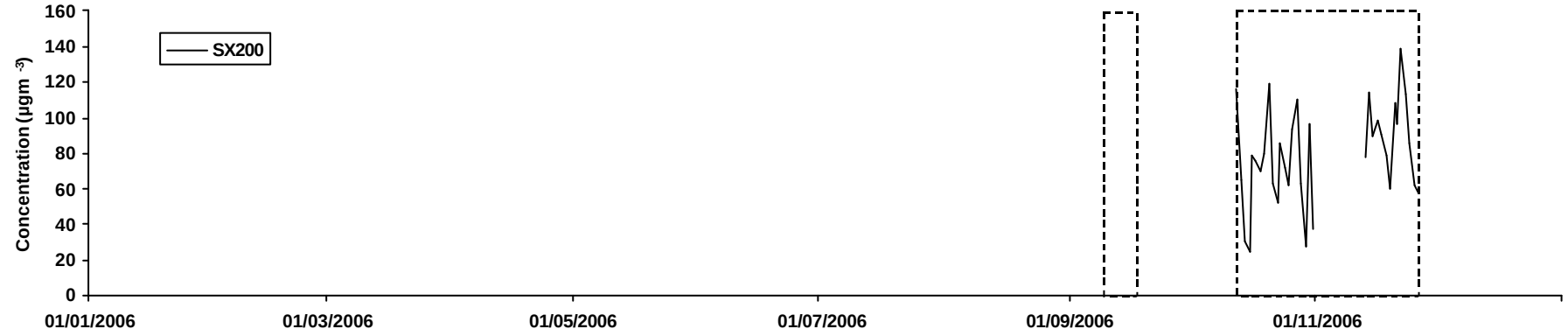

Figure 6: Daily mean concentrations for the SX200. Periods within the dotted lines are those examined in section 4.1.

Figure 7: Daily mean concentrations for the Magee AE-21 Black Carbon. Periods within the dotted lines are those examined in section 4.1.

Figure 8: Daily mean concentrations for the Magee AE-21 UV. Periods within the dotted lines are those examined in section 4.1.

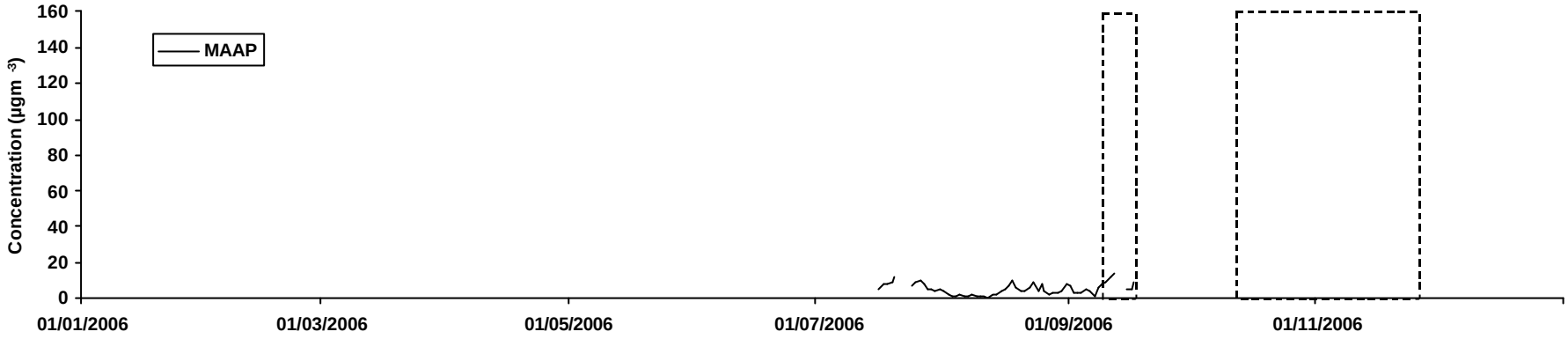

Figure 9: Daily mean concentrations for the MAAP. Periods within the dotted lines are those examined in section 4.1.

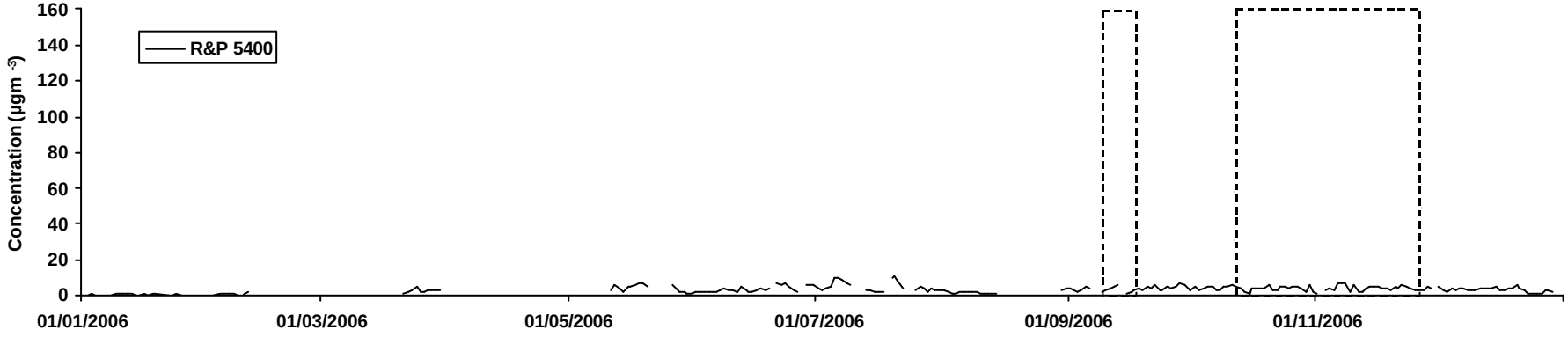

Figure 10: Daily mean concentrations for the R&P 5400. Periods within the dotted lines are those examined in section 4.1.

4.2 Regression Analysis

The results from the 'candidate' instruments are considered alongside the existing 8-port sampler (to show continuity with the existing methods) and the Sunset manual method (to demonstrate the ability to measure elemental carbon). Two sets of orthogonal regression analysis were therefore undertaken using the method described in the EC Working Group document - Demonstration of Equivalence of Ambient Air Monitoring Methods (EC, 2005). This analysis established the relationship between each 'candidate' instrument and the existing 8-port sampler and the Sunset manual method. The results of this analysis are summarised in Table 6 and Table 7, each correlation is shown in the APPENDIX.

4.2.1 8-port sampler regression analysis

	Slope	Intercept	r^2	8 Port mean (µg m^{-3})	Candidate mean (µg m^{-3})	n
ETL SX200	1.23 (+/-0.09)	-2.30 (+/-5.95)	0.82	64.2	76.5	36
R&P 8100	0.22 (+/-0.01)	3.66 (+/-0.58)	0.69	49.6	14.4	193
Magee AE-21 Processed	0.17 (+/-0.01)	2.38 (+/-0.86)	0.75	66.7	13.6	64
Magee AE-21 unprocessed	0.14 (+/-0.01)	2.72 (+/-0.73)	0.75	66.7	12.1	64
MAAP	0.06 (+/-0.01)	1.93 (+/-0.54)	0.35	37.6	4.2	51
R&P 5400	0.04 (+/-0.00)	1.37 (+/-0.16)	0.54	51.9	3.3	171
Sunset	0.15 (+/-0.01)	3.22 (+/-0.93)	0.56	63	12.5 (+/-1.28)	90

Table 6: Summary of the orthogonal regression analysis between the 8port sampler and the 'candidate' instruments at Marylebone Road

As discussed the 8-port sampler method is currently used on the UK Black Smoke network. It would therefore be advantageous for a replacement automatic instrument to demonstrate continuity with this method.

ETL SX200

The ETL SX200 shows a good agreement with the 8-port sampler. The means for the period are 64.2 µg m^{-3} and 76.5 µg m^{-3} for the 8-port sampler and the SX200 respectively; a difference of 19%. The orthogonal regression analysis yielded a slope of 1.23 and an intercept of -2.3 µg m^{-3} with an r^2 of 0.82.

The instruments did not agree as well during the Marylebone Road study as they have done in the previous collocation studies. The previous comparison between the 8-port sampler and the SX200 in the UK (Halifax) (Loader, 2005) and in the Netherlands (Hijink, 2002) also showed a good agreement between these instruments. The means during the Halifax study were 14.5 µg m^{-3} and 13.2 µg m^{-3} respectively, a difference of 10 %; a 5 % difference was identified in the Dutch study.

Although the concentrations measured at Marylebone Road are over four times those measured during in the Halifax study, the reflectance measurements used to calculate the mass concentration were of a similar magnitude (70-100 in Halifax, 67-99 at Marylebone Road). This is due to the increased time resolution at Marylebone Road (8 hours) when compared to the Halifax Study (24 hours). The larger difference between the instruments at Marylebone Road was therefore likely to be caused by losses in the sample tubing as the 8-port sample tubing is narrower, longer and more convoluted that the SX200 sample tubing and is also prone to leaks.

Despite these differences, this study, together with the previous studies demonstrates that the SX200 is a good replacement for the 8-sampler.

R&P 8100

The R&P 8100 operated alongside the 8-port sampler for much of 2006; the lower mean concentrations reflect the sampling period which incorporated the lower concentrations measured during the summer months. The black carbon concentrations reported by the aethalometer are approximately 30 % of the black smoke measurements made using the 8-port sampler. The agreement between the two metrics is reasonably good, resulting in an r^2 of 0.69. The slope of the regression was small (0.22) and the intercept was significant at 3.66 µg m^{-3}.

Magee AE-21

This Magee AE-21 showed a similar relationship to that demonstrated by the R&P 8100; this is unsurprising given the similarity in the methods for measuring black carbon. The agreement between the 8-port sampler and the Magee was better than between the 8-port sampler and the R&P 8100; the r^2 was 0.75. However, the slopes of the regression equation were again significantly below 1, the intercept was also significant. The processing described in section 4.5 had little effect on the agreement but increased the slope and reduced the intercept.

MAAP

The MAAP showed the worst agreement with the 8-port sampler, recording a mean concentration 11 % of the 8-port sampler. The r^2 was only 0.35, the slope small and the intercept significant at 1.93 µg m^{-3}.

R&P 5400

The R&P 5400 operated alongside the 8-port sampler for much of 2006, however, the elemental carbon concentration recorded by the R&P 5400 was only a 6% of the black smoke concentration measured by the 8-port sampler. The agreement between the two metrics was not as good as that recorded by the aethalometers, an r^2 of only 0.54.

Sunset Laboratories

The analysis of filters for elemental carbon using the Sunset Laboratories instrument resulted in a mean concentration 20 % of the black smoke measurement made using the 8-port sampler. The agreement between the two metrics was not as good as that recorded by the aethalometers, an r^2 of only 0.56.

4.2.2 Sunset regression analysis

	Slope	Intercept	r^2	Sunset mean (µg m^{-3})	Candidate mean (µg m^{-3})	n
8-port sampler	6.76 (+/-0.36)	-21.79 (+/-4.86)	0.56	12.5 (+/-1.28)	63	90
ETL SX200	7.37 (+/-0.62)	-19.58 (+/-8.69)	0.61	13.3 (+/-1.33)	76.5	36
R&P 8100	1.46 (+/-0.09)	-0.64 (+/-1.22)	0.65	12.7 (+/-1.3)	17.9	82
Magee AE-21 processed	1.00 (+/-0.08)	0.44 (+/-1.14)	0.59	13.3 (+/-1.36)	13.6	64
Magee AE-21 unprocessed	0.79 (+/-0.07)	1.56 (+/-0.93)	0.61	13.3 (+/-1.36)	12.1	64
MAAP	0.88 (+/-0.11)	0.63 (+/-0.95)	0.89	7.6 (+/-0.78)	7.3	9
R&P 5400	0.22 (+/-0.02)	0.88 (+/-0.26)	0.58	12.8 (+/-1.31)	3.7	92

Table 7: Summary of the orthogonal regression analysis between the Sunset manual method and the 'candidate' instruments at Marylebone Road

As discussed, the Sunset Laboratories instrument can be viewed as the reference method for elemental carbon. Comparisons with this instrument therefore assess the candidate instrument's ability to measure elemental carbon.

8-port Sampler

As discussed in Section 4.2.1, the agreement between the black smoke measurement and elemental carbon is not as good as between the other instruments; the r^2 of the regression was 0.56.

SX200

The black smoke concentration recorded by the SX200 shows a slightly better relationship with the elemental carbon concentration measured using the Sunset Laboratories instrument than the 8-port sampler. The r^2 is a little higher at 0.61.

R&P 8100

The R&P 8100 showed a good agreement with the Sunset instrument (r^2 = 0.65), however, the mean concentration was 40% higher than the Sunset instrument. The slope was 1.46 but the intercept was insignificant.

Magee AE-21

The processed Magee AE-21 also showed a good agreement (r^2 = 0.59) with a slope of exactly 1 and an insignificant intercept. The mean concentration for the Magee AE-21 was 13.6 µg m^{-3}, within the estimated uncertainty (95 % CL) for the Sunset instrument. This instrument appears to be the best 'candidate' instrument for measuring elemental carbon concentrations.

The processing undertaken on the Magee AE-21 measurements reduced the r^2 value marginally but increased the mean to within the uncertainty of the Sunset instrument. It also reduced the intercept to an insignificant level and improved the slope to a value of 1.00 (±0.08). The processing clearly has a beneficial effect on the Magee measurements.

MAAP

The MAAP comparison with the Sunset instrument was limited to nine daily mean concentrations as their operational dates only briefly overlapped. During this time the instruments showed the highest level of agreement of all candidate instruments (r^2 = 0.89). Unfortunately, this period was characterised by low ambient elemental carbon concentrations and the response over the full range of ambient concentrations could therefore not be assessed. A further study between these two instruments would be informative, as conclusions cannot be drawn from this limited data set.

R&P 5400

The R&P 5400 is designed to measure elemental carbon, however, this instrument only measured a concentration of 3.7 µg m-3 compared to the 12.8 µg m-3 measured by the Sunset instrument. Butterfield et al (2007) attributed this to the loss of particulate matter of less than 100 nm in diameter from the impaction plate of the R&P instrument.

4.3 Correlation between Automatic Instruments

It is clear from sections 4.2.1 and 4.2.2 that the agreement between the manual methods and the automatic instruments was susceptible to the uncertainties associated with the manual methods. In principle black smoke and black carbon are determined by the absorption of the sampled particulate matter, and the difference in results is due to how the raw optical measurements are processed. Table 8 shows the correlation coefficients (r^2) between the automatic instruments for both Period 1 (7th to 20th September) and Period 2 (12th October to 26th November 2006) independently. This demonstrates that the correlation coefficients between these automatic instruments was much higher (0.93 - 1.00) than those between the automatic and the manual methods (0.54 – 0.82 for the 8-port sampler and 0.58 – 0.89 for the Sunset Laboratories instrument). This supports the argument that there are instrinsic uncertainties associated with the manual methods. Furthermore, the excellent correlations between the automatic instruments indicate that elental carbon concentrations can be inferred from black smoke measurements and vice versa.

	R&P 5400	R&P 8100	Magee AE-21	Magee AE-21UV	SX200	MAAP
R&P 5400	#	0.98	-	-	-	0.96
R&P 8100	0.93	#	-	-	-	0.98
Magee AE-21	0.95	0.98	#	-	-	-
Magee AE-21UV	0.95	0.98	1.00	#	-	-
ETL SX200	0.93	0.94	0.97	0.97	#	-
MAAP	-	-	-	-	-	#

Table 8: Correlation coefficient (r^2) matrix between automatic instruments. Period 1 (7th to 20th September) right of the # and Period 2 (12th October to 26th November 2006) left of the #.

4.4 Measurements of UV Absorbing Compounds by the Magee AE-21

The Magee AE-21 also provides a second light source in the UV region (370 nm), which provides a qualitative measurement of the carbon species that absorb light in this wavelength; such as PAHs. This can be used to detect the impact of sources such as wood burning on the PAH concentration which would be overlooked by the 880 nm light source. When the black carbon and UV equivalent black carbon measurements from the Marylebone Road site are compared in Figure 11 and Figure 12, it is clear that there is little impact from PAHs above that associated with the nearby road. Nevertheless, this measurement may prove useful in the long term to assess changes in carbon emissions, especially those related to biofuels.

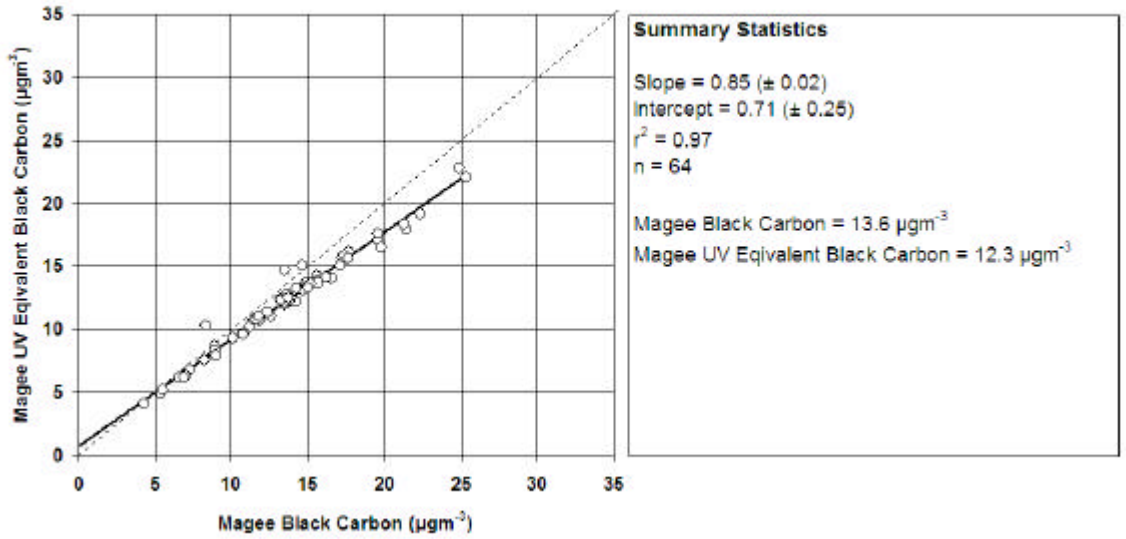

Figure 11: Orthogonal regression between the Magee AE-21 black carbon measurements and the UV equivalent black carbon measurements

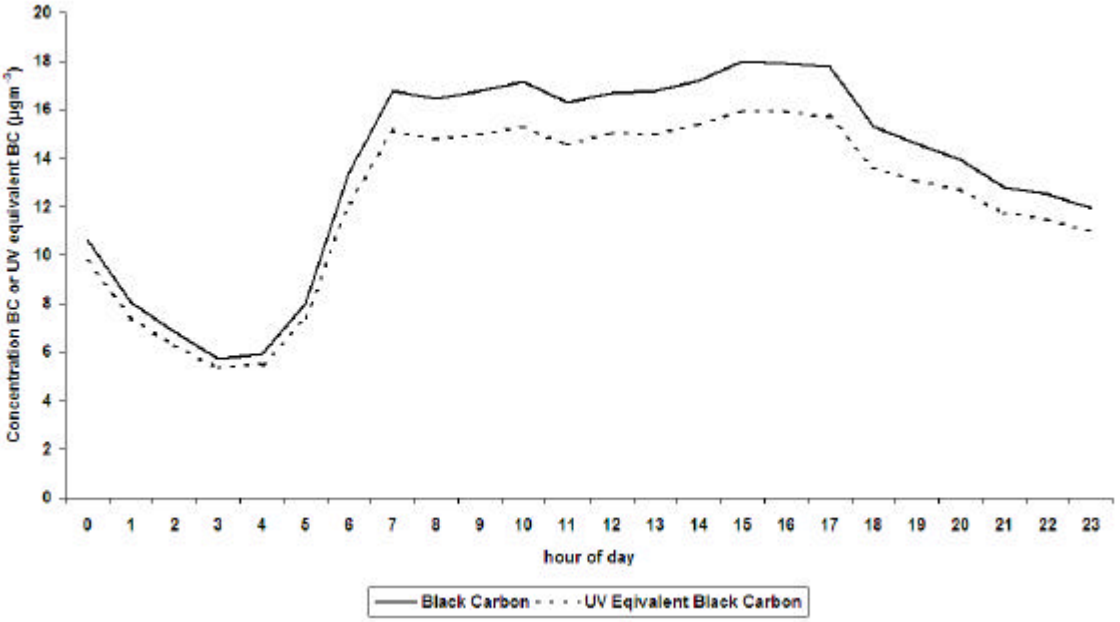

Figure 12: Diurnal variation in the Magee AE-21 black carbon measurements and the UV equivalent black carbon measurements

4.5 Magee AE-21 Processing

The measurements from the Magee AE-21 were processed by the manufacturer in the US using an algorithm that will be installed in the next generation of aethalometers available on the UK market (Hansen, 2006). This algorithm compensates the instrument response for gradually increasing optical loading as the collected sample becomes darker. This compensation is site and season specific, and depends strongly on the nature and 'freshness' of the aerosol. The algorithm is also auto-adaptive. Examining both the measurement processed using the algorithm and unprocessed measurements gave us the opportunity to assess the impact of this algorithm rather than conduct a second trial when new instrumentation is available; the impact on measurements is shown in Figure 13.

The best indication of whether the processing improved the measurement of black carbon was gained by comparing the both processed and unprocessed measurements against the measurements of elemental carbon made using the Sunset Laboratories instrument. As discussed in section 4.2.2, the processing marginally reduced the r^2 value but increased the mean to within the relative uncertainty of the Sunset instrument. It also reduced the intercept to an insignificant level and improved the slope to a value of 1.00 (±0.08). Overall this clearly has a beneficial effect on the Magee measurements.

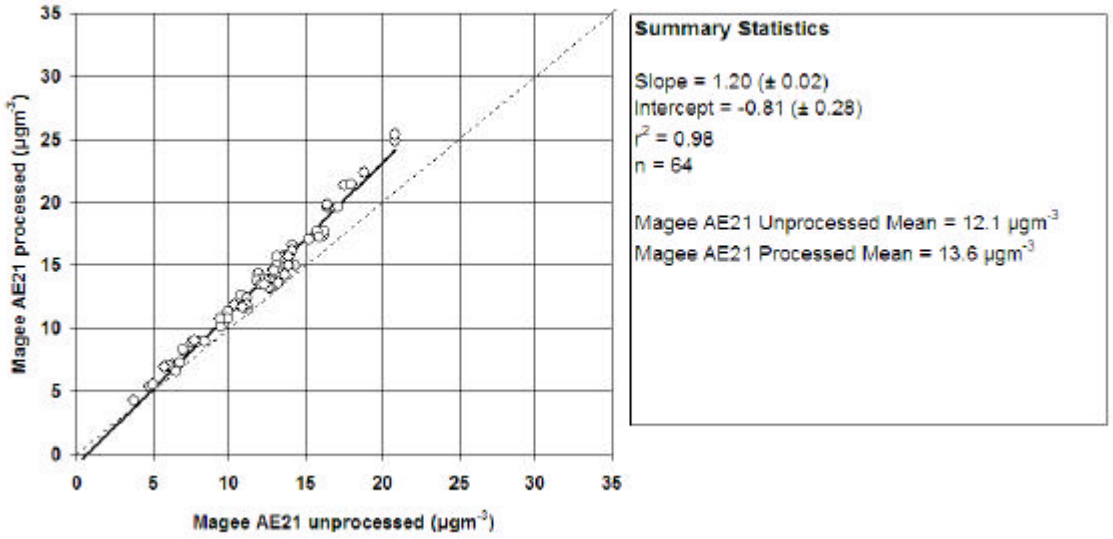

Figure 13: Orthogonal regression between the unprocessed and processed Magee AE-21 measurements

5 CONCLUSIONS

Seven instruments which measured either black smoke, black carbon or elemental carbon were operated successfully at Marylebone Road during 2006. The local traffic, and diesel vehicles in particular, heavily influence all three metrics. All measurements were therefore unsurprisingly strongly correlated. This trial was designed to inform the choice of instrument for the UK Black Smoke Network and determine which were:

a) Comparable to the existing black smoke measurement

b) The best measurement of elemental carbon

Predictably the ETL SX200, as the only other instrument to use reflectometry, showed the greatest agreement with the established black smoke measurement. This has also been established in previous studies (Hijink, 2002; Loader, 2005). ***Therefore, if continuity with the established network is of the highest priority then the ETL SX200 is the preferred instrument for the UK Black Smoke Network.***

The concentration of black smoke measured by the 8-port sampler and the ETL SX200 during the trial was 64.2 µg m^{-3} and 76.5 µg m^{-3} respectively, compared to the mass concentration of PM_{10} of 45 µg m^{-3}. This discrepancy clearly demonstrates the limitations of the black smoke methodology; especially in locations such as these. The black smoke measurements could therefore never be used in any type of mass closure analysis in this format. Nevertheless, as the relationships between the SX200 black smoke measurements and the elemental carbon measurements are strongly correlated (r^2 = 0.61) there is potential to establish factors to relate the two. However, further collocations or analysis may need to be undertaken at a range of site types to provide a robust set of conversion factors.

All three of the aethalometer-type measurements (R&P 8100, Magee AE-21 and the MAAP 5012) showed a strong correlation with the Sunset measurements of elemental carbon (0.65, 0.59 and 0.89 respectively). The Magee AE-21 showed the most consistent agreement in terms of mean concentrations over a long time period (13.6 µg m^{-3} vs. 13.3 µg m^{-3} for the Sunset). The MAAP 5012 showed an encouraging agreement with the elemental carbon measurements, unfortunately, the period of overlap between the two measurement methods was limited to nine days. Further evidence is therefore needed before firm conclusions can be drawn regarding the performance of this instrument. ***On balance, the Magee AE-21 provides the best measurement of elemental carbon when compared to the Sunset instrument.***

From an operational point of view both the ETL SX200 and the Magee AE-21 could be operated in an automatic network. Data logging and remote data retrieval methodologies are consistent with those already in place.

As discussed, the measurements from all the automatic instruments are strongly correlated and potential exists to establish factors to relate the aethalometer measurements of black carbon to black smoke and vice versa. Furthermore, there is a closer relationship between these automatic instruments than between the automatic and manual methods, presumably due to inherent uncertainties in the manual methods.

6 REFERENCES

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Schmid, O., P. Artaxo, W. P. Arnott, D. Chand, L. V. Gatti, G. P. Frank, A. Hoffer, M. Schnaiter and M. O. Andreae (2005). "Spectral light absorption by ambient aerosols influenced by biomass burning in the Amazon Basin - 1. Comparison and field calibration of absorption measurement techniques." Atmospheric Chemistry and Physics Discussion **5**: 9355-9404.

7 APPENDIX

7.1 Measuring Black Smoke Index with an Aethalometer

Aethalometers give a measurement of "Black Carbon" based on the transmission of light through a filter sample, while Black Smoke Index is based on the reflection of light from a filter sample. However, as the Black Smoke standard (ISO 9835:1993) points out, the reflectance measurement effectively assumes that the filter, and whatever is behind the filter, together act as a mirror, and the reflectance is in essence a measure of light absorbed by two passes through the sample.

Although aethalometers in general operate at a single wavelength, and Black Smoke measurements use a broad band light source, the two types of measurement are in principle both based on the absorption of light as it passes through the sample, and should be closely related. This note explores the expected relationship using a simplified model, and compares this with some real data.

In both cases the basic equation is:

$$I = I_0 \exp(-al)$$

where *I* is the intensity of transmitted light

I_0 is the intensity of the incident light

a is the absorption coefficient of the sampled air, in units of m^{-1} (for each metre of air "passed through", light intensity is reduced by a factor e^{-a})

l is the thickness of absorbing material, in units of m

The thickness of absorbing material is taken to be the "thickness" of air sampled through the filter, ie

$$l = V/A$$

where V is the volume of air sampled (in m^3)

A is the exposed filter area (in m^2).

V and A of course depend on the instruments being used.

7.1.1 Aethalometer version of "black carbon" concentration, C_A

For an aethalometer, and absorption coefficient is calculated simply from the equations above:

$$a = \frac{A}{V} \ln\left(\frac{I_0}{I}\right)$$

This is converted to a Black Carbon concentration C_A, as a first approximation, using the specific attenuation a_{atn}, which is dependent on the wavelength of the light used, so that:

C_A [µg/m^3] = 10^6 . a [m^{-1}]/ a_{atn} [m^2/g]

Where a_{atn} = 14,625/? (with ? in nm) (taken from Magee literature)

For a wavelength of 880 nm (as for the data to be used below),

$$C_A\ [\mu g/m^3] = 60{,}170.\ a \qquad (A.1)$$

Commercial aethalometers then make various further corrections for multiple scattering etc that are not considered here.

7.1.2 Black Smoke version of "black carbon" concentration, C_B

For a reflectometer, following ISO 9835, a working absorption coefficient a' is given by:

$$a' = \frac{A}{2V}\ln\left(\frac{R_0}{R}\right)$$

where R is the intensity of the light reflected from a sampled filter (effectively transmitted through the particulate sample twice)

R_0 is the intensity of the light reflected from a clean filter.

Again following ISO 9835, there is a convention for converting this to a Black Smoke Index result (OECD method). The working absorption coefficient (in m^{-1}) is converted to a Black Smoke Index (in $\mu g/m^3$) using a standard table, eg Table A.1 in ISO 9835, which is acknowledged to give results very different from those for black carbon expressed in $\mu g/m^3$.

Table A.1 in ISO 9835 is not given in analytical form, but in the range of interest (concentrations up to 200 $\mu g/m^3$) it is very well approximated ($R^2 = 0.9999$) by the quadratic curve:

$$C_B\ [\mu g/m^3] = 3.462.x\ 10^9\ a'^2 + 4.438 \times 10^5.\ a'$$

Where a' is the working absorption coefficient.

ISO 9835 states in Annex A that the true absorption coefficient approximates to the working absorption coefficient multiplied by a factor of 2, supposedly to account for the white light source and the penetration of particles into the filter paper.

This gives the relationship between C_B and the "true" absorption coefficient as:

$$C_B\ [\mu g/m^3] = 8.655 \times 10^8.\ a^2 + 2.219 \times 10^5.\ a \qquad (A.2)$$

7.1.3 Simplistic relationship between the two measurements

From (1) and (2) above, we would expect a relationship between the two measurements, on purely theoretical grounds, of

$$C_B = 0.239.C_A^{\ 2} + 3.69.\ C_A \qquad (A.3)$$

Where C_B is the Black Smoke Index and C_A is the aethalometer Black Carbon concentration.

7.1.4 Observed relationship during Marylebone Road trial

Aethalometer Black Carbon results from the Magee AE21 can be plotted against the ETL SX200 automated Black Smoke Index results from this trial.

This is done on Figure A.1, together with the theoretical relationship derived above (with no arbitrary fitting parameters). The AE21 data is both processed and unprocessed, as the further processing provided by Magee, while improving the quality of the results as a measure of black carbon, is expected to create differences from the SX200 data, which does not have similar processing. The SX200 data is the OECD version, to match the modelling used.

(The British Smoke Stain convention for Black Smoke gives results that are the OECD version multiplied by a factor of 0.8667.)

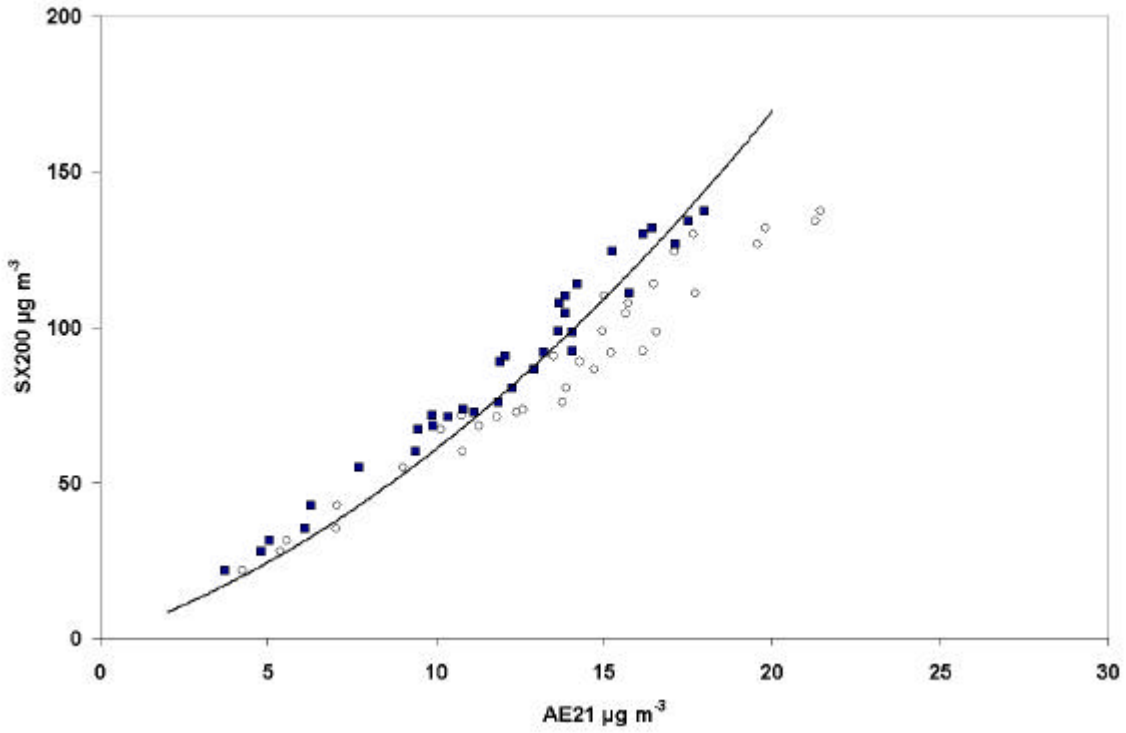

Figure 14: Unprocessed aethalometer data (dark blue diamonds) and processed aethalometer data (red triangles) plotted against the SX200 data, together with the derived theoretical relationship between aethalometer and black smoke measurements (black line).

These results provide good evidence for the hypothesis that the two instruments are in essence measuring the same physical property and presenting the answer in different ways, rather than that there is a site-dependent correlation between the two measurements.

7.1.5 Using Aethalometers to measure Black Smoke

Equation (A.3) can be used to convert the AE21 (unprocessed) aethalometry measurements directly to Black Smoke measurements (following the simplistic model used). Such "converted" results are plotted against the SX200 results in Figure 15.

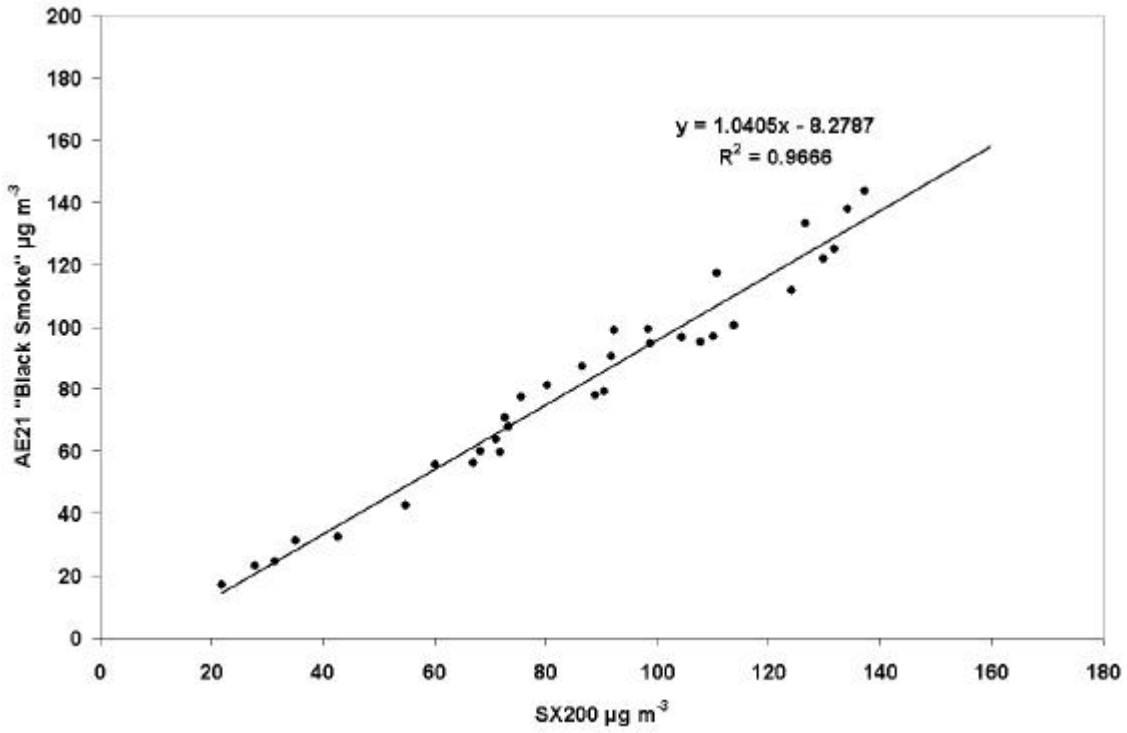

Figure 15: Aethalometry results directly converted to Black Smoke Index from Equation (A.3), compared with SX200 results.

These results give a very encouraging slope and correlation coefficient, from a very simple model. Differences between the two data sets could arise from deviations from ideal flow rate (and leaks) in the two instruments, as well as from deficiencies in the model. They suggest that aethalometers can be used to provide Black Smoke Index results "equivalent" to those from automated Black Smoke instruments such as the SX200, while providing far greater time resolution of results, and additional information when more than one wavelength is used.

It should be possible to improve the model (and the conversion equation) using further information about internal processing of the data in the two instruments.

7.2 8-port Sampler Regressions

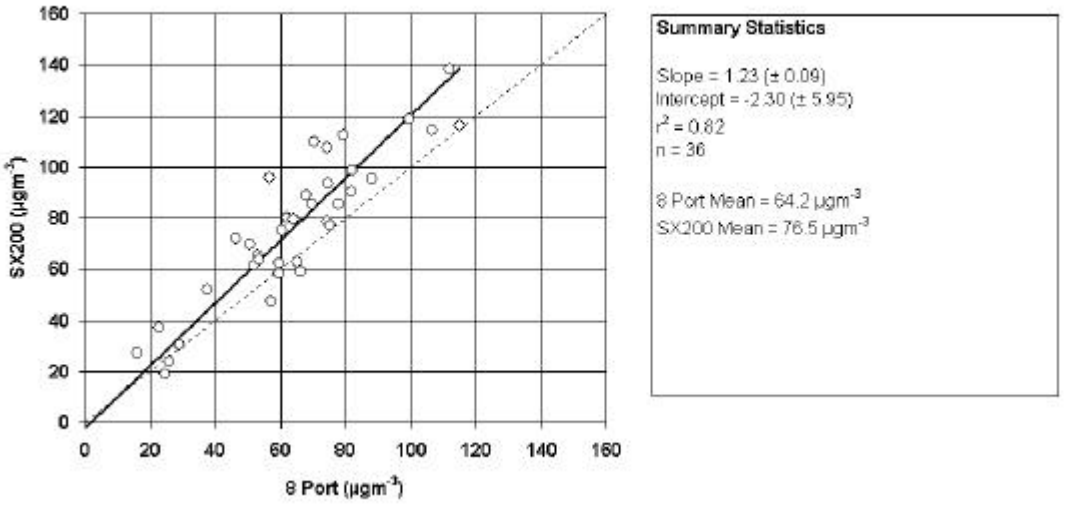

Figure 16: Orthogonal regression between the 8 Port Sampler and the ETL SX200

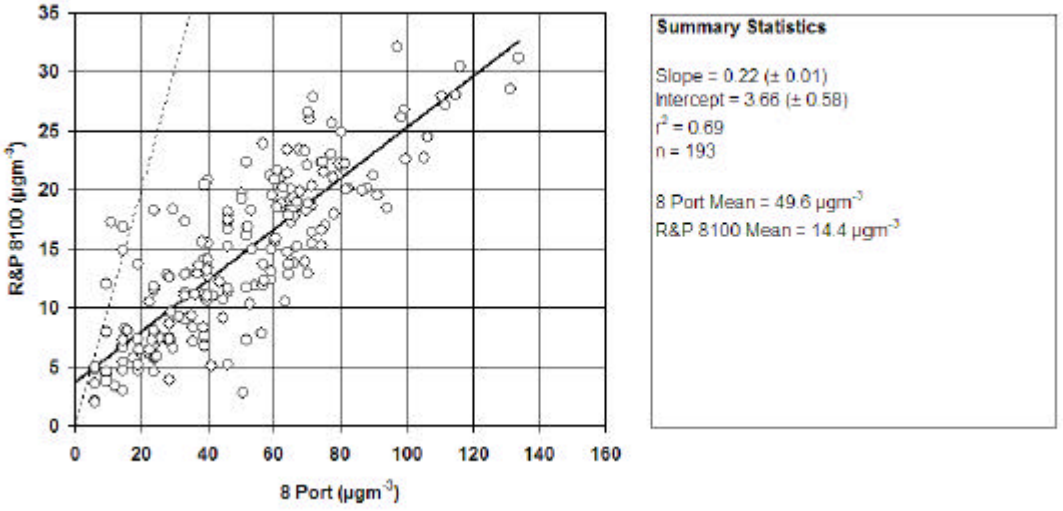

Figure 17: Orthogonal regression between the 8 Port Sampler and the R&P 8100

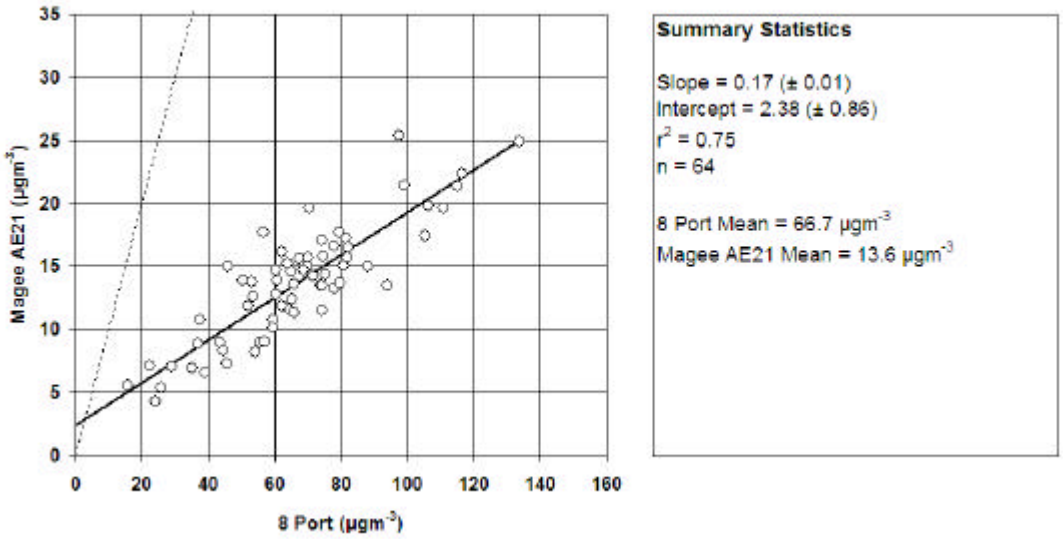

Figure 18: Orthogonal regression between the 8 Port Sampler and the processed Magee AE-21

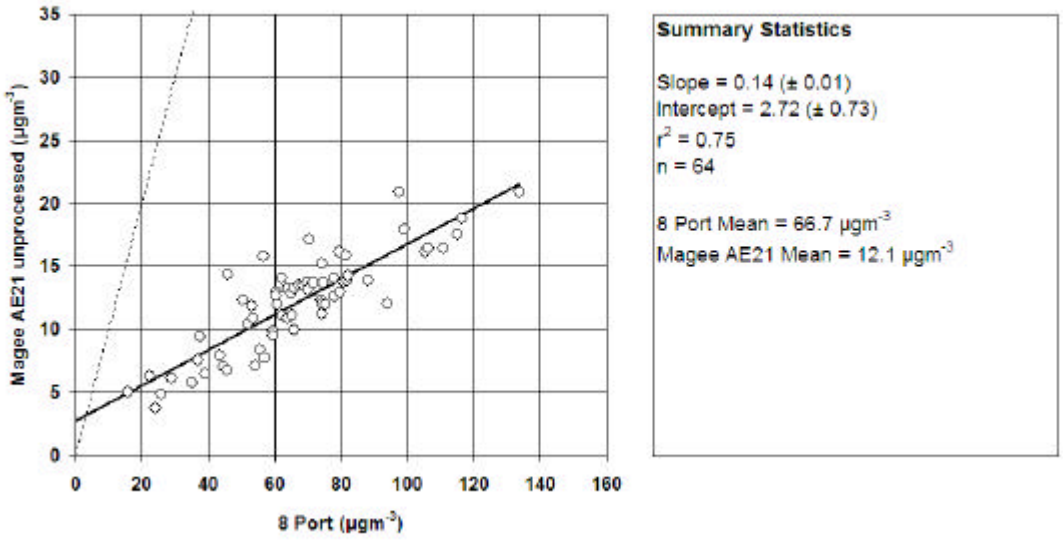

Figure 19: Orthogonal regression between the 8 Port Sampler and the unprocessed Magee AE-21

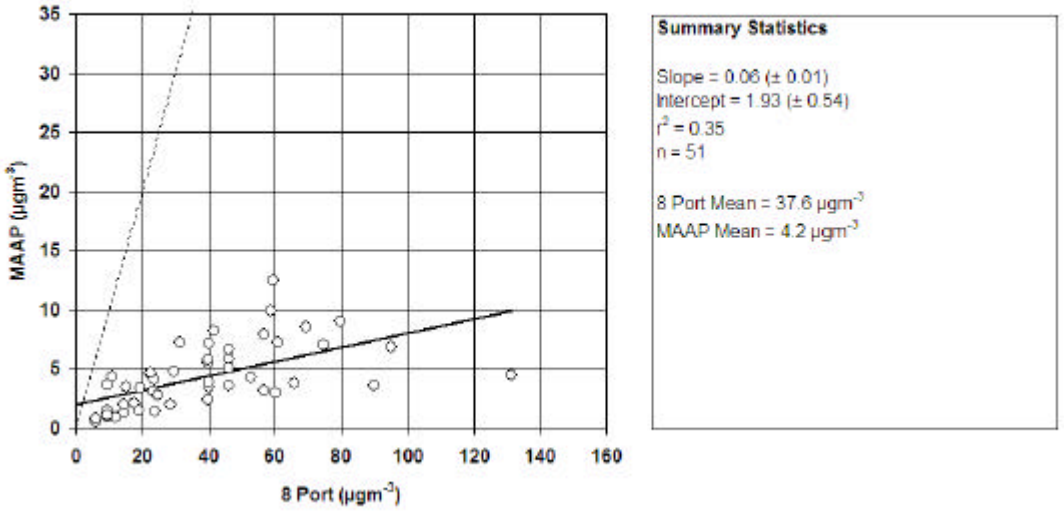

Figure 20: Orthogonal regression between the 8 Port Sampler and the MAAP

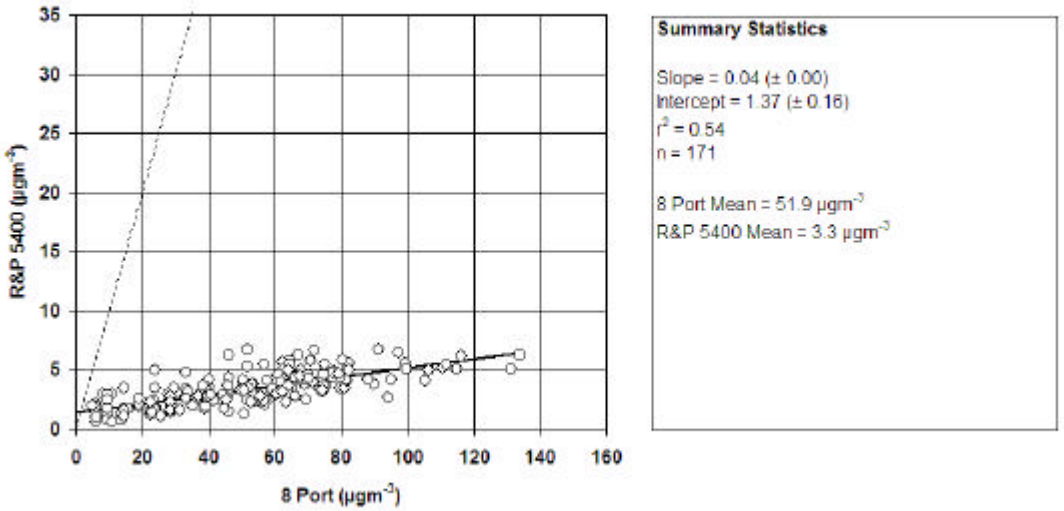

Figure 21: Orthogonal regression between the 8 Port Sampler and the R&P 5400

7.3 Sunset Analyser Regressions

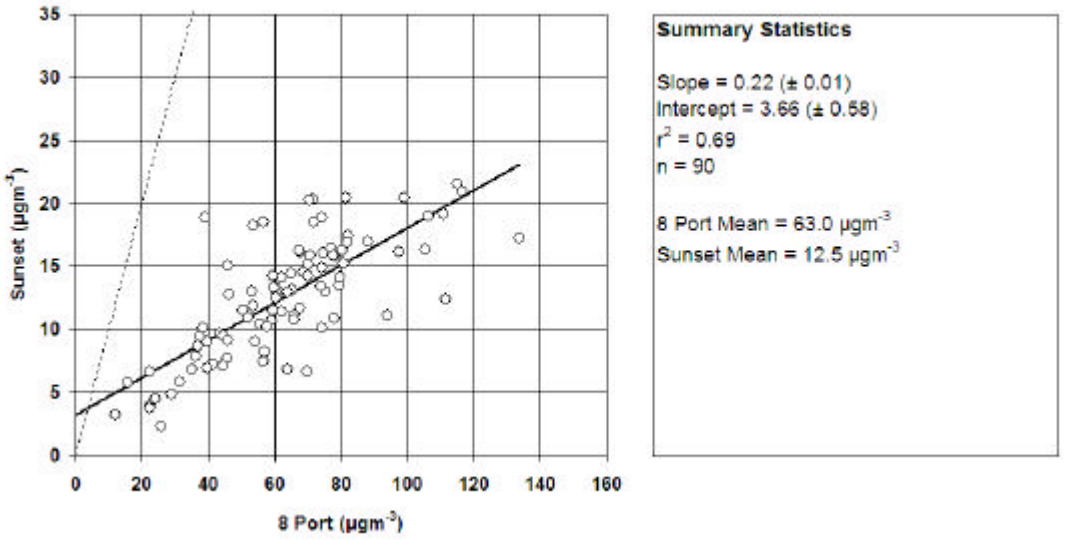

Figure 22: Orthogonal regression between the 8 Port Sampler and the Sunset manual method

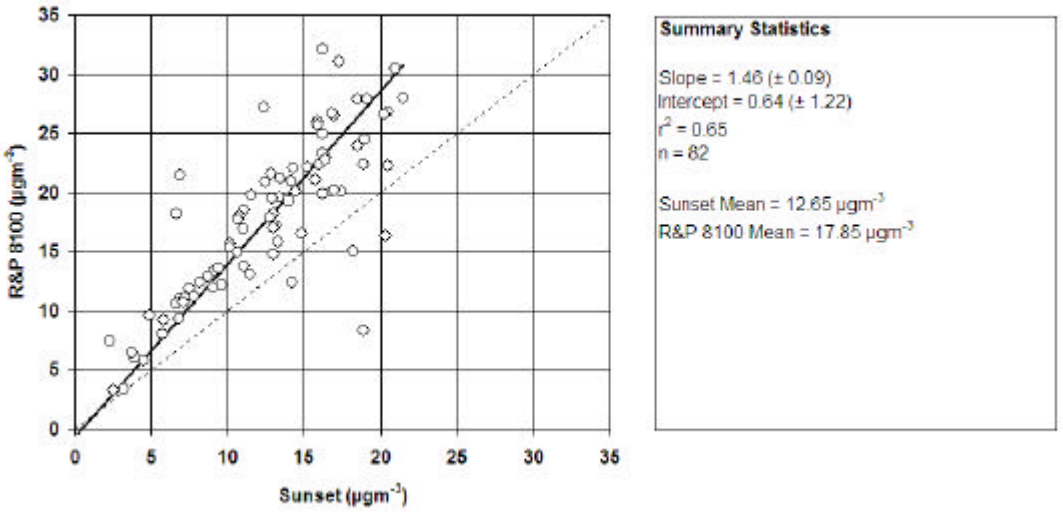

Figure 23: Orthogonal regression between the Sunset manual method and the R&P 8100

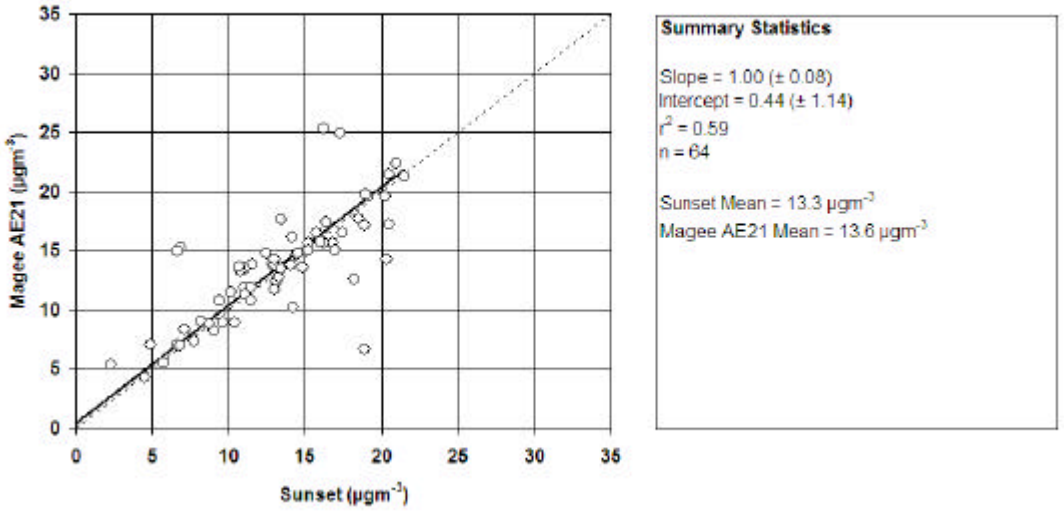

Figure 24: Orthogonal regression between the Sunset manual method and the processed Magee AE-21

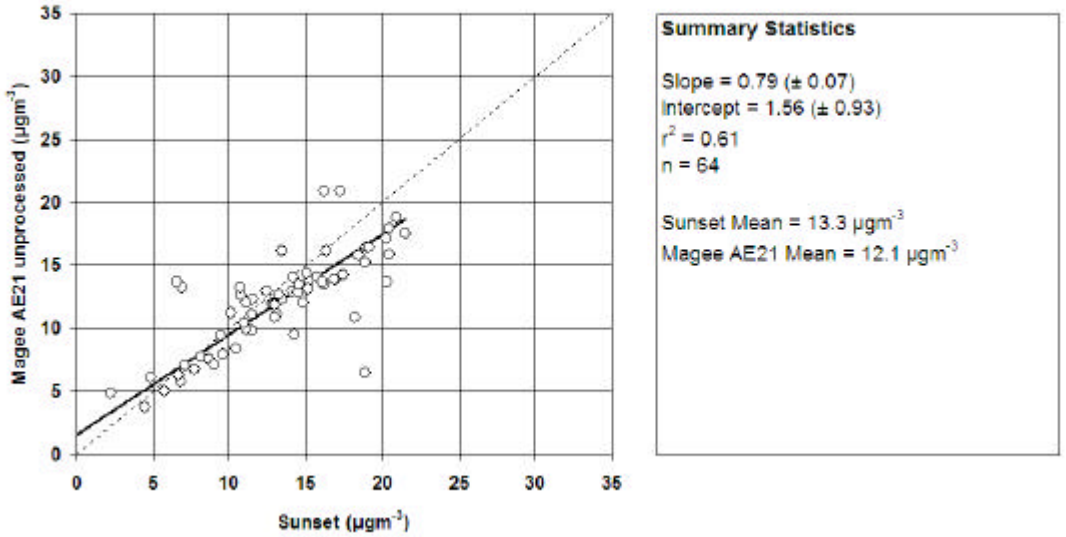

Figure 25: Orthogonal regression between the Sunset manual method and the unprocessed Magee AE-21

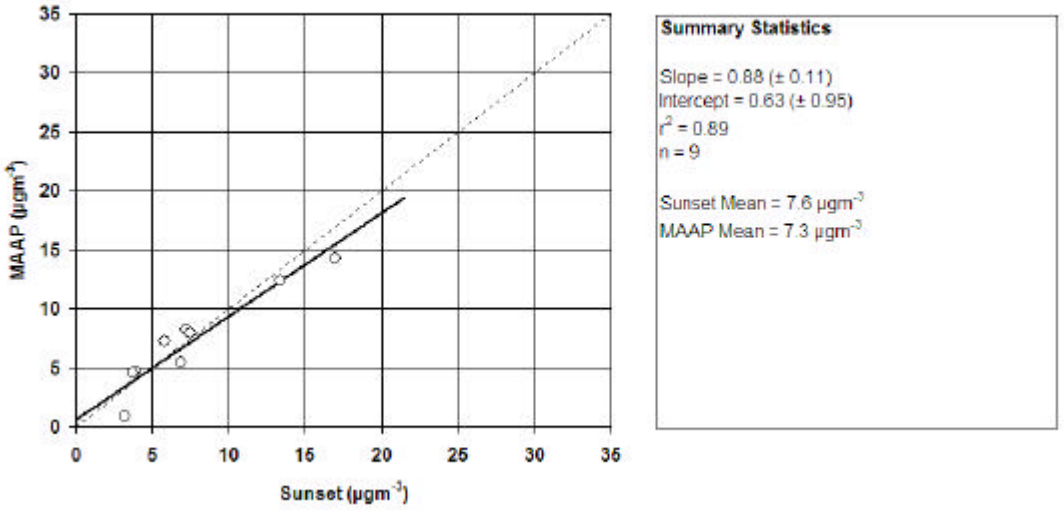

Figure 26: Orthogonal regression between the Sunset manual method and the MAAP

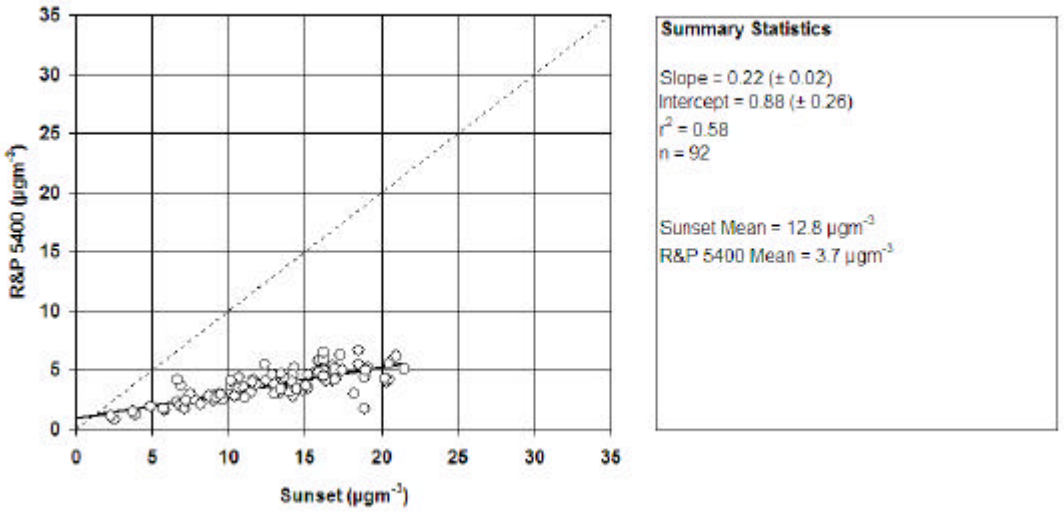

Figure 27: Orthogonal regression between the Sunset manual method and the R&P 5400

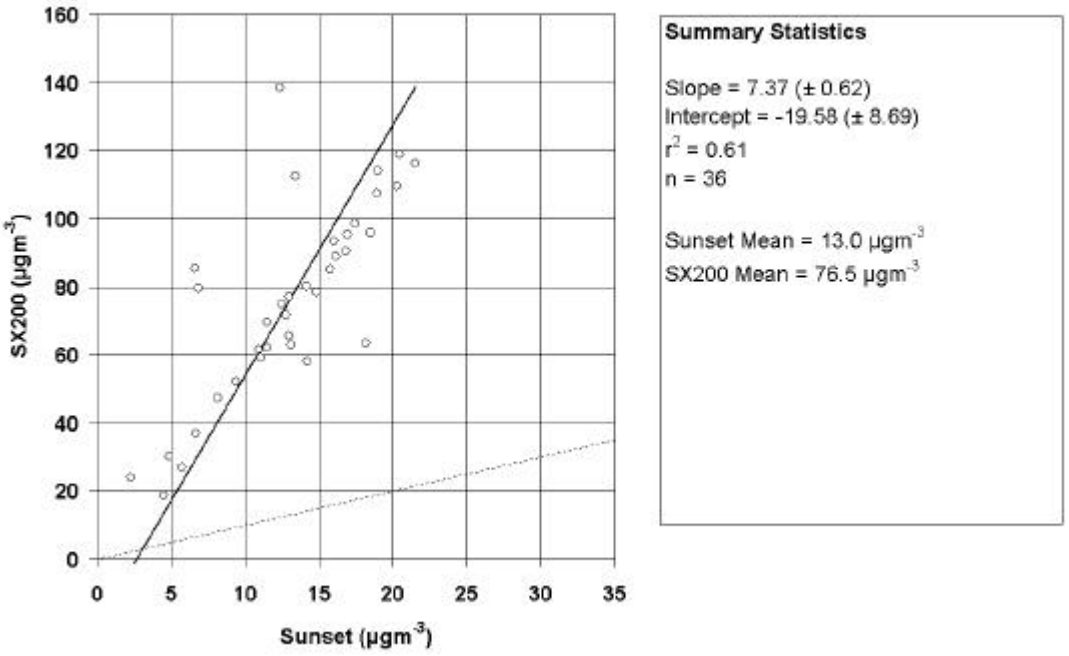

Figure 28: Orthogonal regression between the Sunset manual method and the ETL SX200

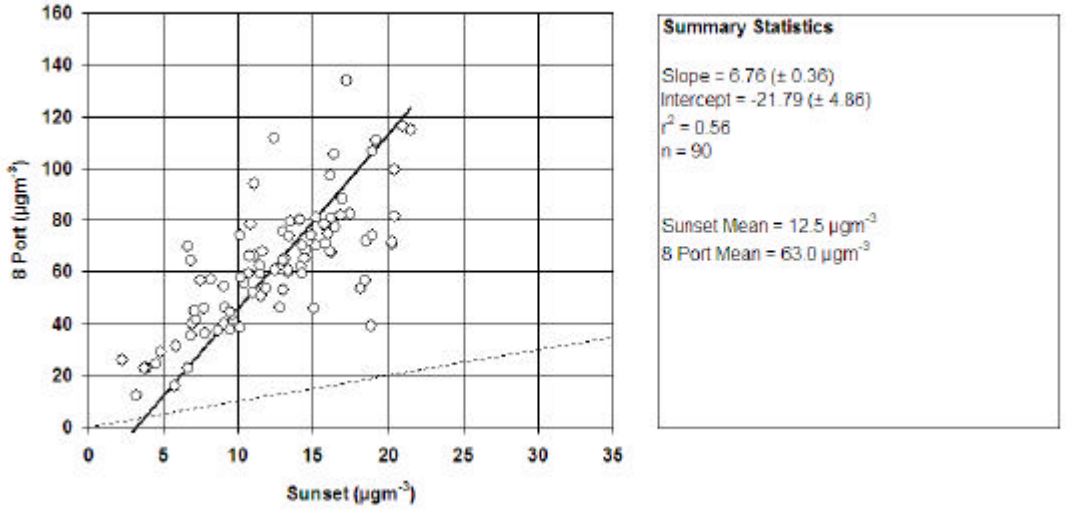

Figure 29: Orthogonal regression between the Sunset manual method and the 8 Port Sampler