PM_{10} in New Zealand's urban air: a comparison of monitoring methods

NIWA Client Report: CHC2007-059
June 2007

NIWA Project: PCCA075

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Foundation for Science, Technology and Research

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IWA Client Report: CHC2007-0
May 2007
NIWA Project:

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Reviewed by: Approved for release by:

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Acknowledgements

The Authors of this report acknowledge that without the generous support of numerous collaborators this project could not have been undertaken. The Authors would like to specifically acknowledge:

Auckland Regional Council, Environment Canterbury, Nelson City Council, the Ministry for the Environment and Greater Wellington Regional Council for allowing the use of their valuable PM_{10} monitoring data.

The air quality technicians of Auckland Regional Council, Environment Canterbury, Nelson City Council, Greater Wellington Regional Council and NIWA for their know-how, can-do and dedication.

The air quality scientists of Auckland Regional Council, Environment Canterbury, Nelson City Council, the Ministry for the Environment for their expertise and significant staff time that was invested in writing the report.

Environment Canterbury for the Cover Photograph.

The analysis and write up of this report was completed with funding from:

- The Ministry for the Environment
- The New Zealand Foundation for Research, Science and Technology, under contract C01X0405.

The PM_{10} monitoring data undertaken by NIWA was funded by the New Zealand Foundation for Research, Science and Technology, under contract C01X0405.

Executive Summary

There are a number of methods which comply with the requirements for monitoring PM_{10} under New Zealand's Air Quality National Environmental Standards. The methods that comply include gravimetric (filter based) and equivalent methods such as the Tapered Element Oscillating Microbalance (TEOM) and Beta Attenuation Monitor (BAM). This project aims to provide Environmental Regulators in New Zealand with information which will to enable them to answer the following questions:

- *Are continuous methods of monitoring PM_{10} equivalent to the results achieved using a gravimetric approach?*
- *Does the performance of continuous PM_{10} monitors vary with location, season or meteorology?*
- *What methods can be used to adjust continuous PM_{10} data sets to a gravimetric equivalent?*

To answer these questions, the study pooled a nationwide data set of co-located gravimetric and continuous PM_{10} measurements. The data was collected from six environmental agencies within New Zealand from a total of 13 sites, located between Auckland and South Canterbury. The data set contained over 3000 points. Comparisons between the gravimetric and continuous PM_{10} data were undertaken using quantitative methods. Statistical tests were used to test the significance of any differences observed.

It is outside the scope of this project to recommend the use of one particular PM_{10} monitoring method over another. However, it is anticipated that this report will provide Regional Council Staff with a sound foundation to debate and make informed decisions on the "equivalence" of the PM_{10} data they are collecting.

Overall performance of the instruments

Compared to Gravimetric results the:

- TEOM-FDMS showed no obvious trend toward under- or over-measurement
- TEOM(40) under-measures by about 20% and 24% at 50 and 100 μgm^{-3} respectively
- BAM under-measures by about 7% and 9% at 50 and 100 μgm^{-3} respectively

The TEOM and BAM are USEPA equivalent-designated methods and are both defined as suitable for monitoring PM_{10} under the NES. However the analysis undertaken in this study suggests the measurements produced by the TEOM(40) and BAM are not equivalent in a quantitative sense to measurements obtained using gravimetric methods. The TEOM-FDMS data is much closer to being quantitatively equivalent to measurements obtained using gravimetric methods than either the TEOM(40) or the BAM.

Effect of season on performance

The data set from each of the instruments was divided in to 4 seasons, summer (December to February), autumn (March to May) winter (June to August) and spring (September to November). The data set used in this study shows that performance of the continuous instruments does vary with season. The analysis showed the winter BAM and TEOM-FDMS data were closer to gravimetric measurements than any of the other three seasons. In contrast to this result the disparity between the TEOM(40) and gravimetric data was largest during winter.

Effect of meteorological factors

The data set from each of the instruments was analysed to investigate the effect of the meteorological factors; temperature, wind speed and relative humidity. The data set used in this study showed that there were significant but fairly weak relationships between the performance of the TEOM(40) and both ambient temperature and windspeed. A weak relationship was also observed with temperature and the BAM data set. Temperature did not appear to have a significant effect on the performance of the TEOM-FDMS. The performance of the continuous instruments did not appear to vary significantly with wind speed or relative humidity.

Effect of Location on Performance

Data were collected from four TEOM-FDMS, four TEOM(40) and eight BAM sites. The data set used in this study shows that performance of continuous instruments can vary with location. The main geographical differences likely to impact on the performance of the samplers are variations in sources of PM_{10} and meteorological parameters such as temperature and relative humidity. The main location differences observed were for the BAMs and were between South Island locations (Christchurch and Nelson), which tended to underestimate and Auckland, which tended to overestimate relative to the Gravimetric method. The extent to which the variations in response occurred as a result of meteorological variations as opposed to source variations is uncertain.

Effect of site type on performance

The full data set from each of the instruments was divided in to different site types: traffic, industrial and residential. Performance of the TEOM-FDMS was considered at two traffic and two residential sites. Site type may be a factor in determining the performance but no firm conclusions could be drawn. All TEOM(40) sites were classified as Residential Neighbourhood. Thus no analysis of differences by site type was possible. Performance of the BAM was considered at two traffic and six residential sites and two industrial sites. It was uncertain from the relationships whether site type plays some role in determining performance.

In attempting to identify the effect of location or site type confounding factors such as instrument operation were not accounted for beyond an assumption that instruments were operated according to best practice. Therefore further work and perhaps a more extensive data set would be needed to draw a firm conclusion about the variation of continuous PM_{10} monitors with geographic location and site type in New Zealand.

Adjustment factors

The analysis undertaken in this study suggests the measurements produced by the TEOM(40) and BAM are not quantitatively equivalent to measurements obtained using gravimetric methods. Therefore if a gravimetric equivalent measurement is required from TEOM or BAM data, then it is necessary to apply an adjustment factor.

Regression Trees and Multi Linear Regression (MLR) models can be used to determine adjustment factors. Both models improve the relationship between TEOM(40) and gravimetric data and significantly reduce both under-measurement and the number of exceedances missed in un-adjusted TEOM(40) data. MLR provides a better improvement than regression trees.

The two models used to calculate adjustment factors for TEOM(40) data can equally well be applied to BAM data. The adjustment factors would be different from those used for TEOM(40) data. However the outcome would be the same – an ability to convert a BAM data set to a gravimetric equivalent data set.

Adjustment factors are derived from the relationship between co-located continuous and gravimetric data and therefore may differ from season to season and from site to site. Ideally each monitoring site would have its unique adjustment factor. However robust adjustment factors require a significant amount of data (at least one year) and in a practical sense this amount of data will not be available for many sites. A first pass estimation of a gravimetric equivalent data set could be obtained by using an adjustment factor derived from a similar site or from a large and representative data set.

(Continued….)

Recommendations for future work

There is potential to enhance and/or extend the outcomes derived from this project. It is recommended that the research team and MfE evaluate the benefits of:

- Expanding the co-location data set and repeating the analysis
- Exploring why variations in instrument performance occur season to season and site to site
- Investigating the measurement of PM_{10} on a temporal scale finer than 24-hours
- Holding a workshop on PM_{10} Monitoring with the aim of facilitating the collection of good quality data in a nationally consistent manner
- Enhancing existing and formulating new guidance on practical and operational issues associated with monitoring PM_{10} in New Zealand

1. Background

Air pollution is a significant environmental issue in New Zealand. To keep the air clean and safe and to improve the quality of the air breathed by New Zealanders, the Ministry for the Environment promulgated the ambient air quality National Environmental Standards (NES). The NES came into effect on the 1st September 2005 and contain five standards for ambient (outdoor) air quality. The air pollutants addressed in the NES include particles (PM_{10}), sulphur dioxide, carbon monoxide, nitrogen dioxide and ozone. Details on the NES can be found at http://www.mfe.govt.nz/laws/standards/index.html#air.

Due mainly to the widespread use of solid fuel domestic heating during winter, the NES for PM_{10} is exceeded frequently at a large number of locations in New Zealand and is therefore one of the most significant air quality issues facing environmental regulators. The NES for PM_{10} is set at 50 μgm^{-3} for a 24-hour period (midnight to midnight) and requires monitoring of PM_{10} in airsheds where the standard is likely, or known, to be breached.

Detailed technical descriptions of methods available to monitor PM_{10} are provided by Chow (1995), McMurray (2000) and Baron and Willeke (2005). Only a small subset of the methods described in the literature comply with the requirements for monitoring PM_{10} under the NES. Internationally there is a large volume of scientific literature which shows that the various methods of monitoring PM_{10} produce different results when compared to each other. Two of the larger programmes addressing this issue are European Union's INTERCOMP2000 (Histzenberger *et. al.* 2004) and the USEPA's Particulate Matter Supersites Study (http://www.epa.gov/nerl/research/2005/g1-3.html). This international literature poses a number of important questions for Environmental Regulators in New Zealand. These include:

- *Are continuous methods of monitoring PM_{10} equivalent to the results achieved using a gravimetric approach?*

- *Does the performance of continuous PM_{10} monitors vary with location, season or meteorology?*

- *What methods can be used to adjust continuous PM_{10} data sets to a gravimetric equivalent?*

This project aims to provide Environmental Regulators in New Zealand with information which will enable them to answer these questions with confidence. Specifically, the key question is *"Are continuous methods of monitoring PM_{10} truly* *equivalent to the results achieved using a gravimetric approach?"* To achieve this aim, the study pooled a nationwide data set of collocated gravimetric and continuous PM_{10} measurements made in New Zealand over the last 5 years. An in-depth analysis and comparison of the data was undertaken and the results are presented in this report.

1.1. The Issue – Monitoring PM_{10} under the NES

Monitoring methods suitable for the purposes of assessing compliance with the standards are listed in Schedule 2 of the *Resource Management (National Environmental Standards Relating to Certain Air Pollutants, Dioxins and Other Toxics) Regulations 2004* (the regulations) http://www.mfe.govt.nz/laws/standards/air-quality-standards.html. Schedule 2 requires that PM_{10} (particulate matter of 10µm in diameter or less) is monitored in accordance with the AS/NZS 3580.9.6:2003 standard or the United States Code of Federal Regulations Title 40, Part 50 Appendix J (US CFR 40, Part 50, Appendix J). Both of these methods are gravimetric, i.e. direct mass measurement. There are other methods designated by the US EPA (in 40 CFR, Part 53) as equivalent to the gravimetric method – see http://epa.gov/ttn/amtic/files/ambient/criteria/ref0506.pdf for the full list. Consequently there are a number of methods available to monitor the air quality standard for PM_{10} in New Zealand.

The measurement of particulate matter, unlike other air contaminants, has been defined based on a number of methods (each with its own limitations). As a result there can be some variation in the mass concentrations of PM_{10} obtained from different monitoring methods. The variation is principally caused by two factors:

- Differing composition of the particulate being monitored from site to site
- Contrasting technologies used to measure particulate

The main issue with respect to these two factors is the measurement of particulate at different temperatures. A number of US EPA equivalent-designated methods use a heated inlet manifold and sample chamber to exclude the measurement of water vapour. In addition to removing moisture the increased temperature can result in volatilisation of a portion of the PM_{10} aerosol. This often causes an under-estimation of PM_{10} mass concentration compared to the gravimetric method (such as the Hi-Vol or Partisol), which aim to measure particulate based on ambient temperatures.

Guidance in the Ministry for the Environment's *Good Practice Guide for Monitoring and Data Management (MfE 2000)* recommends that US EPA equivalent-designated methods are co-located with the gravimetric method to determine an adjustment factor. These factors are thought to be site specific since the volatile component of PM_{10} varies from location to location, depending on the composition of the emissions. It should be pointed out that gravimetric methods themselves are also potentially subject to some volatile loss during sampling and prior to weighing.

Other problems may also occur through the use of non-direct measurements of mass. For example, the relationship between beta attenuation and mass may vary depending on the composition of the particulate.

The majority of PM_{10} monitoring for the NES uses equivalent-designated methods rather than direct mass measurement of material collected on filters. The equivalent methods offer two advantages over gravimetric methods; they provide measurements every day as required in the regulations (daily monitoring is generally not practicable with a single gravimetric sampler) and they avoid the resource intensive gravimetric analysis. The Updated Users Guide to Resource Management *(*National Environmental Standards Relating to Certain Air Pollutants, Dioxins and Other Toxics) Regulations 2004 (MfE 2005) states that for TEOMs it is important to determine a site specific adjustment factor, or use a Filter Dynamics Measurement System (FDMS) to ensure that the ambient air quality standard is not being under-estimated when using equivalent methods. Some indication of the degree of volatile loss of a particular method is particularly important when trying to compare data from different instruments and different locations or when the monitoring method at a site is changed. Other equivalent methods, such as the BAM may be subject to volatile loss and this issue should be considered when interpreting the PM_{10} data.

A number of independent co-location studies to investigate differing instrument responses have already been carried out around New Zealand. The purpose of this project is to combine the results of a number of these studies to further the understanding of mass measurement from different PM_{10} monitoring methods in the New Zealand context.

1.2. The Team

This project is a collaborative effort between the FRST programme 'Protecting New Zealand's Clean Air', the Ministry for the Environment and Environet Ltd, Auckland Regional Council, Environment Canterbury, Greater Wellington Regional Council, Nelson City Council and NIWA.

1.3. The Process

A number of co-location datasets were made available from independent studies carried out by team members. These data sets provided good representation across New Zealand.

The next step was to identify the priority objectives which would be explored within the available timeframe. The desired objectives of each team member were identified. These objectives were compiled and ranked according to the level of importance given by each team member. The priority objectives were selected from this ranking.

The priority objectives for this project were then broken down into individual tasks and a task schedule developed. The final list of aims and objectives are outlined in Section 2 of this report

This process raised other objectives that are beyond the scope of the current project. Many of these issues are important and were noted by the team for future work.

2. Aims and objectives of the study

The difference in mass concentrations from co-located gravimetric and equivalent PM_{10} monitoring has long been a concern for air quality professionals. Though individual co-location studies have been conducted at a number of locations to determine site specific data, there has been little research in New Zealand that compares these studies. By comparing data from a range of New Zealand environments and seasons a greater understanding of the differences between instruments can be obtained.

The aims and objectives of this study are set out under the following three category headings:

Objectives Group 1: Undertaking a Robust Nationwide Study

- set up a framework which will ensure that the different co-location data sets are analysed in a consistent and robust method;
- enable people to have faith in the inter-comparison study;
- ensure that the collocated data sets collected by the various Regional Councils gain maximum exposure and provide as much value as possible.

Objective Group 2: Comparison of Gravimetric and Continuous PM_{10} Monitoring Methods

- compare equivalent (TEOM and BAM) PM_{10} monitoring methods against the gravimetric method (Hi-Vol and Partisol);
- promote confidence in the "equivalence" of PM_{10} data collected by various methods;
- understand how and perhaps why comparisons differ with season, site and meteorology.

Objective Group 3: Gravimetric/Equivalent Method Adjustment Factors

- assess the need for adjustment factors for the different monitoring methods considered;
- suggest methods by which adjustment factors can be arrived at;

- establish whether adjustment factors differ with season, region, year and site type.

It is outside the scope of this project to recommend the use of one particular PM_{10} monitoring method over another. However, it is anticipated that this report will provide Regional Council Staff with a sound foundation to debate and make informed decisions on the "equivalence" of the PM_{10} data they are collecting.

It is also outside the scope of this project to recommend specific adjustment factors be applied to TEOM or BAM data. However, given the reporting requirements of the NES it may be appropriate for the air quality community to consider a nationally consistent approach for the use of adjustment factors for different monitoring methods.

3. Methods for monitoring PM_{10}

3.1. Gravimetric

There are a number of instruments that are used to draw air through a pre-weighed filter, which after exposure, is then weighed again to determine the amount of particulate captured on the filter - a process know as gravimetric analysis. A detailed description of the instruments and processes used for gravimetric analysis is provided by Chow (1995). Gravimetric methods, such as the high volume sampler (Hi-Vol), draw ambient air at a constant flow rate of $68m^3/hr$ (via a size separating inlet) onto a pre-weighed glass-fibre filter. Hi-Vols are a commonly used gravimetric method in New Zealand. The filter is exposed for a 24 hour period and then re-weighed. The total volume of air sampled is determined from the flow rate and the sampling time. The mass concentration is calculated as the mass of the sample collected divided by the volume of air sampled.

Hi-Vols either have a mass flow controller or volumetric flow control to maintain a constant flow rate as the filter becomes loaded with particulate matter during sampling. Care must be taken to use appropriate filters that will not become overburdened during the sampling period. It is also important to use the appropriate (PM_{10}) size selective inlet.

Monitoring of the PM_{10} standard, for the purposes of the regulations, requires 24-hour average concentrations to be monitored every day from midnight to midnight. Given these requirements a single Hi-Vol sampler at a site is not suitable for NES monitoring because manual midnight filter changes are impractical. The ‘one day in three’ or ‘one day in two’ regimes usually adopted for Hi-Vol monitoring, allowing filters to be changed during the day, do not meet the requirements of the NES.

Other gravimetric methods such as the Partisol operate on the same mass measurement principle but use a flow rate of 16.7 litres/minute. Partisols are available in a number of configurations including hub and satellite systems and sequential samplers. Hub and satellite systems, incorporate two or more intakes each fitted with its own size selective intake and filter cassette. Flow can be switched daily to a new intake (and hence filter) to allow daily sampling. The filter cassette system uses 1 intake but has a filter cassette capable of loading up to 16 filters which are changed automatically at a pre-determined time, i.e. midnight. This system can be left unattended and its progress can be monitored remotely by telemetry. Such systems can therefore be set up to meet NES monitoring requirements.

Gravimetric methods require careful pre- and post-conditioning of the filter and accurate weighing to the milligram precision for Hi-Vols and the microgram precision for Partisols. Filters absorb moisture from the atmosphere, and the weight will therefore vary in accordance with the surrounding humidity. Particulate matter collected on the filters will also behave in a similar way. The filters must therefore be carefully conditioned and weighed under constant temperature and humidity before and after sampling. Detailed procedures for filter handling, conditioning and weighing are given in the monitoring method specifications, ie AS/NZS 3580.9.6;2003 or US CFR 40, Part 50, Appendix J.

Other factors that can affect the measurements are the method used for size selection , variations in air temperature during the exposure period and the filter substrate. Size selection is usually either through cyclone or impactor heads (although other methods also exist) and the design of these can affect the efficiency of separation of the PM_{10} particles from the larger particles. Impactor heads generally have a sharper cut point than cyclone heads (i.e. more efficient at removing larger particles), although size selection for most methods used in New Zealand is by cyclone. Loss of particulate can occur during the exposure period as a result of changes in ambient temperature. For example, ammonium nitrate collected on the filter during the nighttime or morning may volatilise as temperatures increase around midday. The impact of fluctuations in temperature during the exposure period will vary with particulate composition. The collection efficiency can vary between different filter substrates, and some filters (glass fibre) can have sulphate or nitrate formation on the surface of the filter, although in general moisture and static effects are more significant than these variations (Baron and Willeke 2001). Filters used in gravimetric analysis in New Zealand are typically glass fibre (Hi-vols), Teflon Coated Glass Fibre (Partisol) or Teflon (Partisol). To be comparable, results should also be corrected to the same temperature (as this affects the volume calculation), and for New Zealand this should be zero degrees Celsius.

Results obtained using the different gravimetric methods described above can vary depending on environmental factors persisting at the time of monitoring and the analytical methods followed. A limited comparison of different gravimetric methods is made in Appendix 4. One set of data shows a very good relationship between methods but the other illustrates the differences that can occur. In this study differences between gravimetric methods have not been accounted for. All data collected using different gravimetric methods is treated as equivalent.

Other gravimetric methods such as the mini-vol (5 litres/min) and micro-vol (3 litres/min) do not comply with US 40 CFR Part 50, Appendix J and are therefore unsuitable for NES monitoring. These methods are not as precise nor as accurate as NES compliant methods. However, they may be suitable for screening monitoring programmes.

3.2. Tapered Element Oscillating Microbalance – TEOM

The tapered element oscillating microbalance (TEOM), a proprietary system, provides continuous monitoring of PM_{10} or $PM_{2.5}$. A detailed description of the principals of operation of the instrument is provided by Patashnick and Rupprecht (1991). Very briefly the TEOM draws air through the analyser at a rate of 16.7 litres per minute to ensure an accurate cut point for the size separating inlet with a 3 litres per minute flow passing through the filter. The oscillating microbalance detects mass changes on an exchangeable filter by measuring frequency changes of the tapered element upon which the filter resides. This provides a mass measurement and, in conjunction with measured flow rate (using a mass flow controller), concentration can be calculated at a frequency down to ten minute averages.

The system allows for continuous unattended monitoring over extended periods of time. It is classified as an equivalent method for PM_{10} monitoring when operated in accordance with 40 CFR Part 53, Appendix J and is suitable for national environmental standards.

Comparative studies of the TEOM against gravimetric methods have shown that the heated inlet, designed to remove unwanted water vapour from the sample, inadvertently causes the loss of volatile particulates (such as ammonium nitrate) both in the sample train and from the filter itself. The loss of volatile material during sampling by the TEOM is described in detail by Hering *et. al.* (2004). There is a large volume of literature exploring the effects of lost volatiles on the measurement of mass concentration. Three recent examples are provided by Kingham *et. al*. (2006), Schwab *et. al.* (2006) and Charron (2004). The extent of volatile loss, relative to a gravimetric method will depend on the composition of the particulate, in particular the proportion of particulate that is volatile at the sample air temperature. The relative humidity and ambient temperate at the time of sample collection are also factors that determine the extent of volatile loss. Volatile loss is expected to be greater in cooler climates because of the greater differential between ambient and inlet temperatures. The effect of inlet temperature on the measurement of PM_{10} concentrations is explored by Mignacca and Stubbs (1999). Volatile loss and hence under-measurement of PM_{10} can be reduced by operating the sampler at temperatures lower than 50^{o}C. The Good Practice Guide for Monitoring and Data Management (MfE 2000) recommends using an inlet temperature of 40^{o}C.

Volatile loss can cause quite large differences between concentrations measured by TEOMs and gravimetric methods. To account for this loss a site specific adjustment factor can be established by co-locating the two methods. The difference between TEOM and gravimetric methods has been shown to vary with season and location (Green, Fuller and Barrett, 2001 and Muir, 2000). The variation of correction factors with season and location are considered in this study's analysis. Greater differences are likely to occur where wood smoke comprises a large portion of the PM_{10}. Wood smoke contains a significant fraction of low molecular weight volatile organic compounds that are volatilised by the TEOM's heating system.

The manufacturers recommend a minor adjustment to the mass concentration, which is integrated into the TEOM software to account for empirical differences between the TEOM and gravimetric methods. The adjustments ($y = 1.03x + 3$) are insignificant relative to differences related to the heating of the sample line detailed in this report.

TEOMs can be fitted with the Series 8500 Filter Dynamics Measurement System (FDMS) which accounts for the volatile component of PM_{10}. In simple terms, the FDMS alternates between sampling volatile-laden and volatile-purged air. Any decrease in filter mass as a result of being purged of volatile is added back to the un-purged mass in order to take account of the volatilised component. This minimises the under-measurement of PM_{10} due to losses of the volatile component. A more complete description of the TEOM-FDMS is provided by Jaques et. al. (2004). It should be noted that US EPA approval for equivalency applies only to the TEOM, and does not cover TEOM-FDMS. However, the California Air Resources Board (CARB) selected TEOM-FDMS as a California Approved Sampler (CAS) in June 2003**.** While the TEOM-FDMS does not currently have the status of a USEPA equivalent method, the use of TEOM-FDMS for monitoring compliance with New Zealand's NES PM_{10} standard is recommended within the updated NES user's guide.

For the purposes of this study TEOMs operated with inlet temperatures of 40 and 50^{o}C are denoted as TEOM(40) and TEOM(50) respectively.

3.3. Beta Attenuation Monitor – BAM

The Beta Attenuation Monitor (BAM) is another continuous monitoring method. A detailed description of the principals of operation of the instrument is provided by Husar (1974) and Chueinta and Hopke (2001). The BAM operates by passing air through a continuous glass or PTFE tape at 16.7 litres per minute via a size separating inlet. Beta particles are passed through the material deposited on the tape, and the attenuation (or reduction) of ionising radiation as it passes through provides a measure of the mass.

This method allows for unattended operation over extended periods of time, and has a time resolution of about 0.5 to 2 hours. The response of the instrument depends on the beta absorption coefficient of the particulate, and this can vary with chemical composition. BAMs may be less prone to volatile loss than TEOMs.

Some (but not all) beta attenuation methods have been classified as equivalent methods for PM_{10} monitoring when operated in accordance with 40 CFR Part 50, Appendix J. Examples of these used in New Zealand include the FH62 C14 continuous PM_{10} monitor and the MetOne 1020 BAM.

3.3.1. Differences between BAM Manufacturers

The FH62 and MetOne BAM have different operational approaches. The MetOne BAM is described as a 'step-wise' instrument. For hourly measurements this entails movement of the filter tape to carry out a zeroing measurement across a clean section of tape for 5 minutes. The section is then mechanically moved under the sample inlet and particles in the sample air are deposited on the filter tape for 50 minutes. At the end of the period the sample tape is returned to the original position and re-measured. The difference in beta attenuation between the two readings is then used (in conjunction with the flow rate) to calculate the mass concentration.

The FH62 is described as a 'continuous' instrument in terms of its operation. The sample material is continually accumulated on the filter tape, unlike the step-wise measurement approach described above. The filter tape stays in position for a pre-determined period (often 24 or 48 hours) or until the tape reaches its full loading capacity. The zeroing cycle can be set up to occur once a day at midnight.

3.4. Operational Issues of continuous monitoring methods

Like the TEOM, most BAMs heat the inlet air in order to control the effect of moisture on particulate measurement. The effect of relative humidity on BAM measurements is discussed by Tsai, Chang and Huang (2006). Met One BAMs and FH62s maintain the sample air in the measurement chamber at a constant temperature. This temperature can be set by the operator (the temperature is set to keep the relative humidity below a certain threshold). Very recent versions of the FH62 have the option of an Intelligent Moisture Reduction (IMR) system. This uses a "*smart heater*" to modulate the sample temperature, ensuring the sample flow has a relative humidity of less than 60%.

Because BAM inlets are heated some loss of volatile matter from the particulate may occur, both from the incoming particle surfaces and from the particles trapped on the filter for a time. To date it is unclear how much (if any) volatile loss affects PM_{10} concentrations measured with BAMs in New Zealand.

The TEOM, FH62 and MetOne BAM have US EPA equivalency based on a time resolution of 24 hours. However, all of these instruments are capable of providing finer time resolution data. The TEOM provides near real-time resolution with 10 minute averages (the TEOM-FDMS outputs a running hour average every 10 minutes). BAMs can be set up to provide finer time resolutions (such as 10 or 30 minute averages) but this can result in less accurate readings due to the proportionally greater background 'noise' in the instrument response over the shorter time period. For this reason time resolutions of less than 24 hours are inherently less accurate.

4. Data and methods

4.1. The data sets

A list of the co-location PM_{10} measurement data available in New Zealand was compiled. The Team agreed on a set of criteria and the list of studies to be included was reduced to those that met the following criteria:

i) data from both a gravimetric method and an equivalent method available

ii) data was of good quality, and had been quality assured

The owners of the target data were approached and permission to use requested. The data that were used in the study are detailed in Table 4.1. A detailed summary of the data is provided in Appendix 1: Data Tables and Appendix 2: Data Set Scatter Plots.

4.2. Data quality

The data supplied have been subjected to and passed its owners quality assurance procedures. For the purposes of this study the data were accepted at face value and were not subjected to an independent quality assurance check.

However as with any data set there is a possibility that some undetected problem with the instrumentation or laboratory procedures has occurred. The rigour of weighing practices and issues surrounding the impact of laboratory conditioning practices are two areas of uncertainty with results obtained using the gravimetric method.

There are differences in quality assurance protocols employed by the owners of the data used in the study, such as gravimetric analysis and data quality assurance procedures. The extent to which these differences impact on the relationships observed is uncertain. It is possible (but unlikely) that variations in the relationship between methods may occur in some instances because of data quality issues. All due care has been taken with the data set used for this study and within practical restrictions it is the best available.

4.3. Description of analysis undertaken

The method for evaluating the relationship between two different sets of PM_{10} results was Reduced Major Axis (RMA). This differs from the Least Squares Regression (often referred to as standard linear regression) method used in MS Excel.

Table 4.1: Description of data used in the study.

Data source	Monitoring locations	Dates	Instruments used	Number of data
Auckland Regional Council	**Takapuna**	**Nov 96 to Aug 99**	**TEOM(50) and Hi-Vol**	**142**
		Feb 04 to Dec 05	**BAM and Partisol**	**216**
	Penrose	**May 03 to Dec 05**	**BAM and Hi-Vol**	**304**
		Jan 01 to Dec 02	**TEOM(50) and Hi-vol**	**55**
		Oct 01 to Dec 02	**TEOM(50) and Partisol**	**111**
	Mount Eden-Mount Eden Road	**Jul 02 to Dec 02**	**TEOM(50) and Partisol**	**50**
		Jan 03 to Dec 05	**BAM and Partisol**	**318**
	Kowhai School, Mount Eden	**Apr 04 to Dec 05**	**BAM and Partisol**	**197**
Environment Canterbury	**Coles Place, Christchurch**	**Jul 01 to Dec 04**	**TEOM(40) and Hi-Vol**	**808**
		Jun 03 to Dec 04	**TEOM-FDMS and Hi-Vol**	**384**
	Timaru	**Jul 05 to Dec 05**	**TEOM(40) and Hi-Vol**	**39**
		Jul 05 to Dec 05	**TEOM-FDMS and Hi-Vol**	**39**
Ministry for the Environment	**Packe Street, Christchurch**	**Jul 96 to Aug 96**	**TEOM(50), BAM and Hi-Vol**	**30**
	Burnside, Christchurch	**Apr 05 to Aug 05**	**TEOM(40) and Hi-Vol**	**41**
		Mar 05 to Aug 05	**BAM and Hi-Vol**	**47**
Nelson City Council	**St Vincent Street**	**Feb 06 to Apr 06**	**BAM and Partisol**	**57**
	Vivian Place	**Jul 05 to Mar 06**	**BAM and Partisol**	**144**
NIWA	**Khyber Pass, Auckland**	**Jul 04 and Mar 05**	**TEOM-FDMS and Dichotomous-Partisol**	**26**
	Richardson Road (SH20) Auckland	**Oct 05 to Nov 05**	**TEOM-FDMS and Partisol**	**29**
Greater Wellington Regional Council	**Wairarapa College-Masterton**	**Apr 03 to Dec 04**	**TEOM(40) and Hi-Vol**	**149**

Further specific detail on datasets if available in Appendix 1.

The least squares method of analysis was considered less appropriate because it estimates the relationship between the two variables based on the assumption that there is no error or uncertainty in the independent variable, in this case the gravimetric sampling method. Also the least squares method assumes one variable depends on the other which is not true for these datasets. RMA assumes that there is error or uncertainty in both PM_{10} datasets. Based on the work and recommendations of Ayres (2001) RMA is used in this study. Both methods were illustrated graphically to allow for a comparison of the differences in results between the two methods.

The Kruskal-Walllis test was used to assess significant differences in the relationships across different seasons and locations. This function compares the mean ranks of the data, and returns the p-value for the null hypothesis that all samples are drawn from the same population. If the p-value is sufficiently low then it can be concluded that the groups are ‘significantly’ different. Note that the Kruskal-Wallis test is a nonparametric version of the classical one-way ANOVA. It differs in that it works with ranks instead of actual values and therefore makes no assumptions about the distribution of the data.

Initially the Kruskal Wallis tests were performed on two datasets:

1. The ratio of one method to the other for each data point (e.g., TEOM/ gravimetric)

2. The residual or absolute difference between each data point (e.g., TEOM – gravimetric)

While results were generally similar, the residual (absolute difference) method was preferred as the concentration dependent aspect meant it provided a better indication of the significant impacts. In contrast, the ratio method suggested some minor variations were more meaningful than other major ones because they did not allow for differences in the magnitude of concentration. For example, using the ratio method a slight overestimation of the TEOM relative to the gravimetric during the summer months appeared to be a more significant impact than the underestimate of concentrations during the winter months.

The correlation between meteorological variables and measurement residuals was checked for linear relationships. Any linear relationships that were significant ($p<0.01$) and explained at least 10% of the variance ($R^2>0.1$) are shown on the scatterplots.

5. Comparison of monitoring methods

5.1. All sites

This section compares data collected at all the sites at which the TEOM-FMDS, TEOM(40) and BAM instruments were operated. Scatterplots are available for each site individually in Appendix 2.

5.1.1. Gravimetric vs TEOM-FDMS

Figure 5.1 shows the correlation plot for 24-hour average TEOM-FDMS and gravimetric measurements collected at: Christchurch (Coles Place) Timaru and Auckland (Khyber Pass and Richardson Rd, (SH20)).

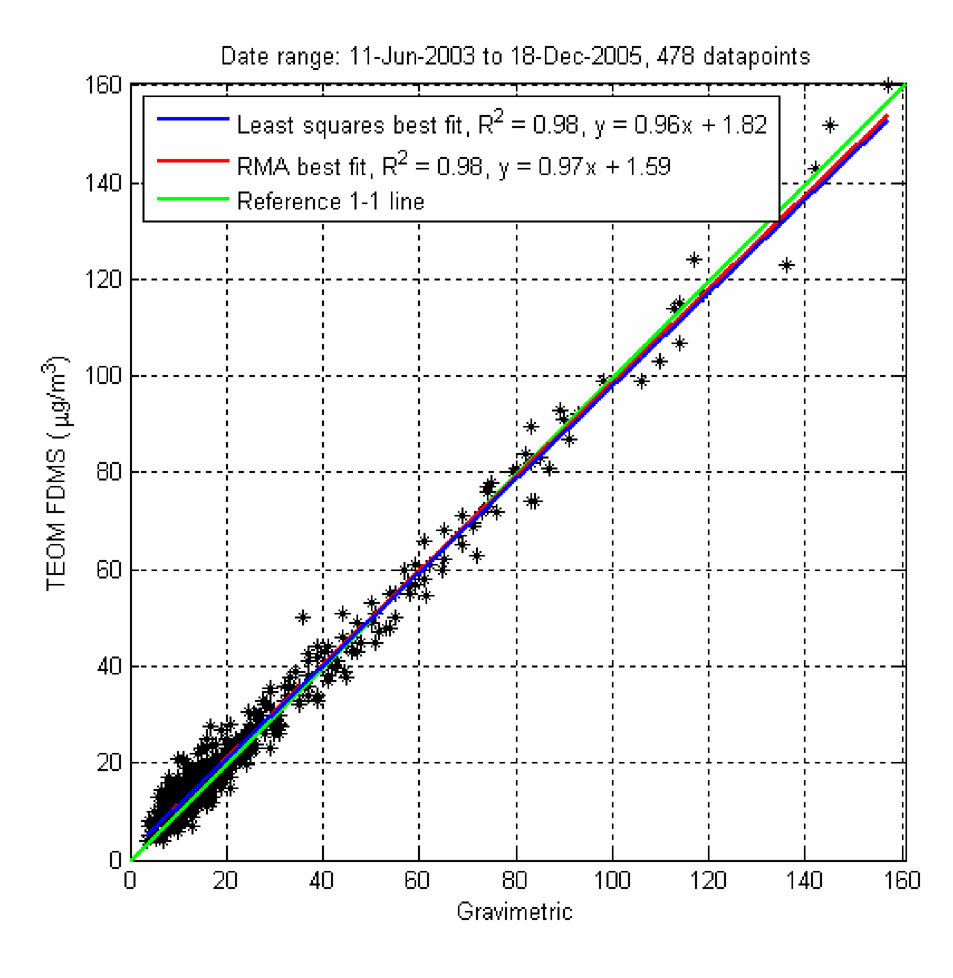

Figure 5.1: Correlation plot for 24-hour average TEOM-FDMS versus gravimetric measurements – all data

Figure 5.1 shows a very good fit (R^2=0.98) between the gravimetric and TEOM-FDMS measurements. There is no obvious trend in under or over measurements. Both the blue-Least squares best fit line and red-RMA best fit line are very close to the green 1-1 line.

5.1.2. Gravimetric vs TEOM(40)

Figure 5.2 shows the correlation plot for 24-hour average TEOM(40) and gravimetric measurements collected at: Christchurch (Packe Street, Coles Place and Burnside), Timaru, and Masterton.

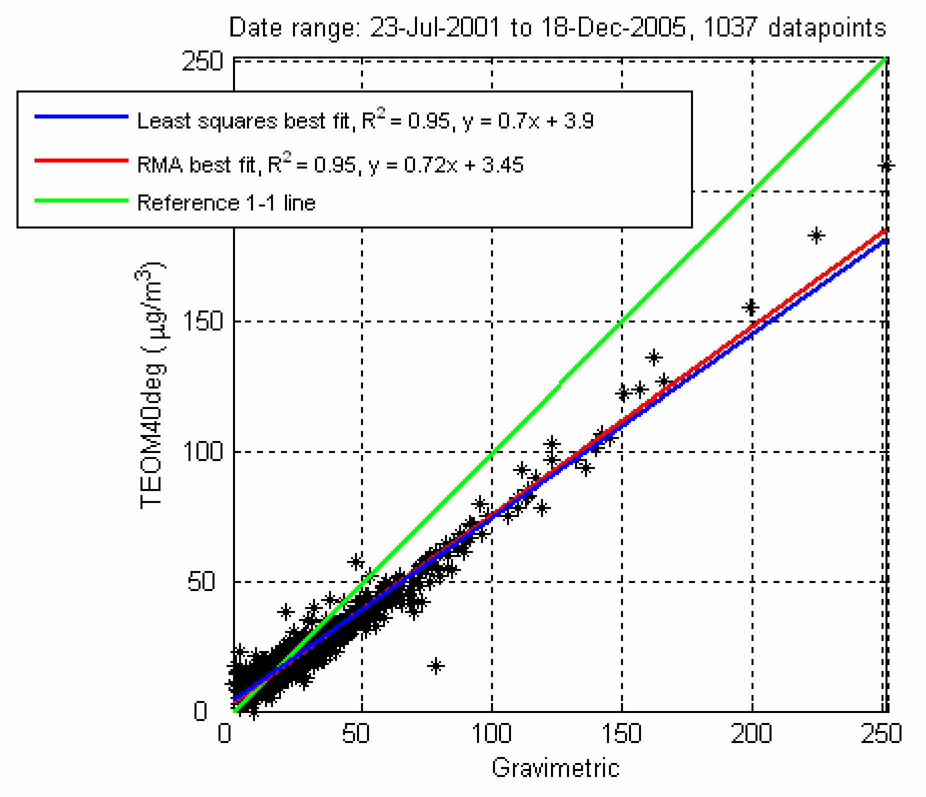

Figure 5.2: Correlation plot for 24-hour average TEOM(40) versus gravimetric measurements – all data

Figure 5.2 shows a good fit (R^2=0.95) between the gravimetric and TEOM measurements. Figure 5.2 shows that the TEOM (40) measures less than the gravimetric method (for concentrations above about 20 µgm^{-3}) and this effect increases with PM_{10} concentration. For concentrations about 50 µgm^{-3} the difference is about 21% and for high (~100 µgm^{-3}) concentrations it is around 25%. The underestimation is demonstrated by the red (RMA) and blue (least squares) lines being below the green 1:1 reference line at concentrations above 20 µgm^{-3}. At low concentrations (less than ~20 μgm^{-3}) the trend is reversed and the TEOM(40) tends to measure higher than the gravimetric method.

It is interesting to contrast this result against that found when comparing the TEOM operated with an inlet temperature of 50°C (TEOM50). Unsurprisingly the disparity between TEOM(50) and gravimetric data is greater than that observed between TEOM(40) and gravimetric data. A comparison between 24-hour average TEOM(50) and gravimetric measurements collected in Auckland (Takapuna, Penrose, Mount Eden) is contained in Appendix A3.1.

5.1.3. Gravimetric vs BAM

Figure 5.3 shows the correlation plot for 24-hour average BAM and gravimetric measurements collected at: Auckland (Takapuna, Penrose, Mount Eden, Kowhai School), Christchurch (Packe Street) and Nelson (St Vincent Street and Vivian Place).

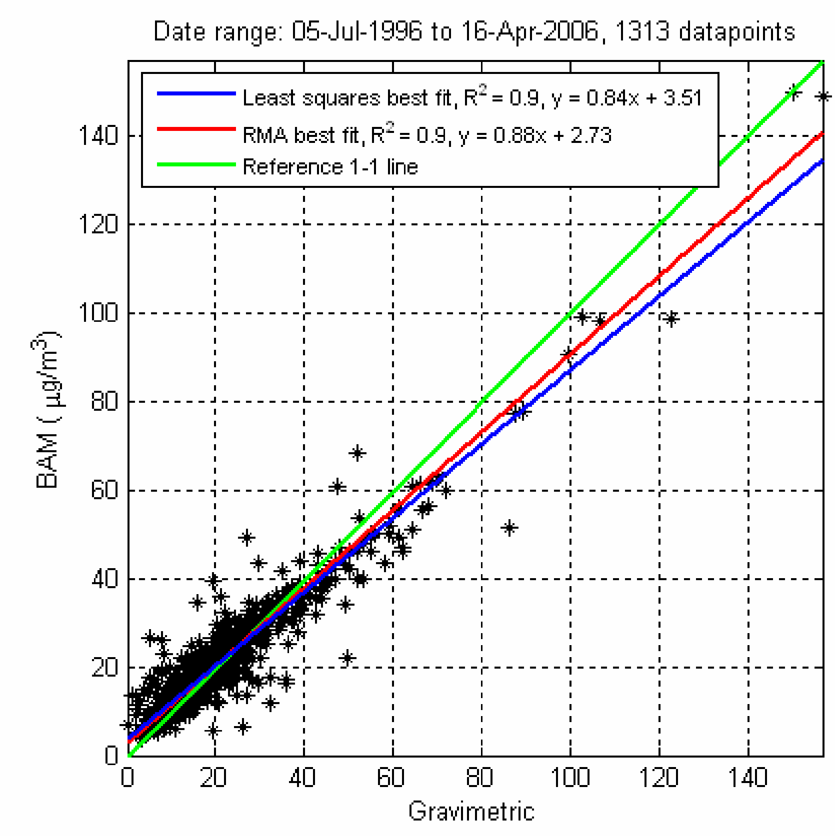

Figure 5.3: Correlation plot for 24-hour average BAM versus gravimetric measurements – all data

Figure 5.3 shows a good fit (R^2=0.90) between the gravimetric and BAM measurements. Figure 5.3 shows that the BAM typically measures around 7% less than the gravimetric method at 50 μg m^{-3} and 9% less than the gravimetric method at

100 μgm^{-3}. The underestimation is demonstrated by the red (RMA) and blue (least squares) lines being below the green 1:1 reference line at concentrations around 25 μg m^{-3}. At low concentrations (less than around 25 μgm^{-3}) the trend is reversed and the BAM tends to measure slightly higher than the gravimetric method.

5.2. Effect of season

This section explores the effect of season on the comparison of TEOM-FMDS, TEOM(40) and BAM with gravimetric measurements. Data is included from all sites at which the instruments were operated. Seasons are defined as Autumn March to May, Winter June to August, Spring September to November and Summer from December to February.

5.2.1. Gravimetric vs TEOM-FDMS

Figure 5.4 shows the residual (TEOM-FDMS minus Gravimetric) between 24-hour average TEOM-FDMS and Gravimetric measurements broken down by season. Measurements were collected at Christchurch (Coles Place), Timaru and Auckland (Khyber Pass and Richardson Rd, (SH20)).

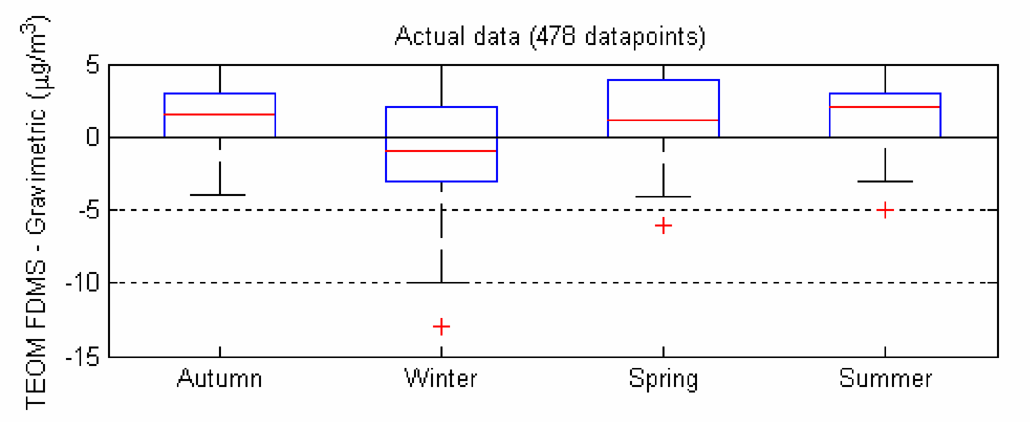

Figure 5.4: Residuals of 24-hour average TEOM-FDMS minus gravimetric measurements by season

A residual of zero means that there was no difference between the TEOM-FDMS and Gravimetric measurement. A positive residual results when the TEOM-FDMS is greater than the gravimetric measurement. A negative residual results when the TEOM-FDMS is less than the gravimetric measurement.

The bottom and top of each blue box mark the 25th and 75th percentile values respectively. The median value (50th percentile) is marked by the red line within the box. The whiskers extend to 1.5 times the inter-quartile range (1.5 x the difference between the 75th and 25th percentile values). Any data outside that range is marked with a red star.

Figure 5.4 shows that a seasonal difference is observed. TEOM-FDMS operates closest to gravimetric in winter, with a marginal tendency to slightly under-measure. In the other seasons there is a reasonably strong trends toward slight over measurements by the TEOM-FDMS.

The seasonal variations observed in Figure 5.4 were analysed with Kruskal-Wallis (K-W) test for significant difference at a 99% confidence level. The detailed results of this test are contained in Appendix 7.1 In summary the K-W test showed that the difference in performance of the TEOM-FDMS during winter compared to that observed in spring, summer and autumn was statistically significant. Differences in the performance of the TEOM-FDMS during these three warmer seasons was not statistically significant at the 99% confidence level.

5.2.2. Gravimetric vs TEOM(40)

Figure 5.5 shows the residual (TEOM(40) minus Gravimetric) between 24-hour average TEOM(40) and Gravimetric measurements broken down by season. Measurements were collected at: Christchurch (Packe Street, Coles Place, and Burnside), Timaru, and Masterton.

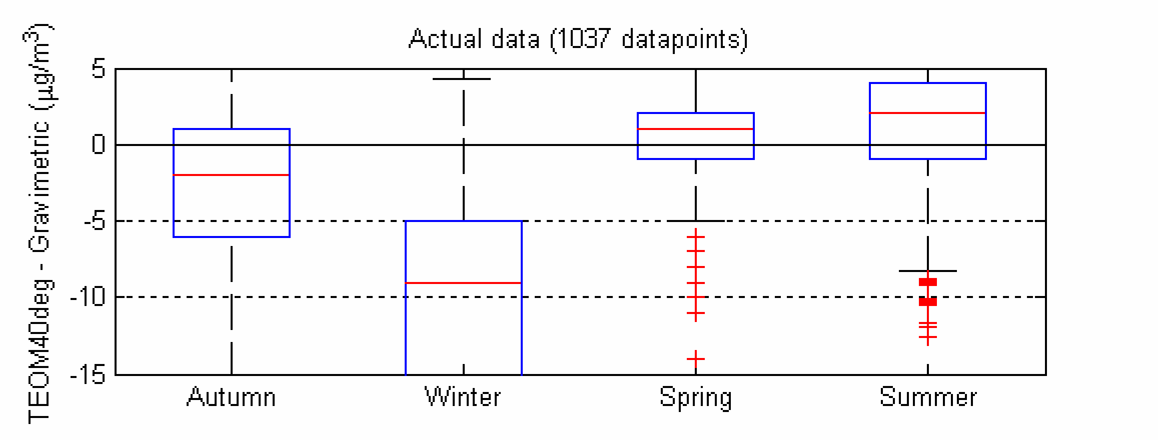

Figure 5.5: Residuals of 24-hour average TEOM(40) to gravimetric measurements by season

Figure 5.5 shows that a seasonal difference is observed. TEOM(40) operates closest to gravimetric in Spring. TEOM(40) has a strong tendency toward under measurement during winter. These effects are also observed in the autumn and spring data but to a lesser extent.

The seasonal variations observed in Figure 5.5 were analysed with Kruskal-Wallis (K-W) test for significant difference at a 99% confidence level. The detailed results of this test are contained in Appendix 7.1 In summary the K-W test showed that there is no significant difference in the TEOM(40) performance during spring and summer but that the differences between winter and autumn and the spring-summer time were significantly different at the 99% confidence level

A comparison of the residual (TEOM(50) minus Gravimetric) between 24-hour average TEOM(50) and Gravimetric measurements broken down by season is contained in Appendix A3.2. Figure A3.3 showed that the difference in performance of the TEOM50 in winter compared to spring and summer was statistically significant.

5.2.3. Gravimetric vs BAM

Figure 5.6 shows the residual (BAM minus Gravimetric) between 24-hour average BAM and gravimetric measurements broken down by season. Measurements were collected at: Auckland (Takapuna, Penrose, Mount Eden and Kowhai School), Christchurch (Packe Street) and Nelson (St Vincent Street and Vivian Place).

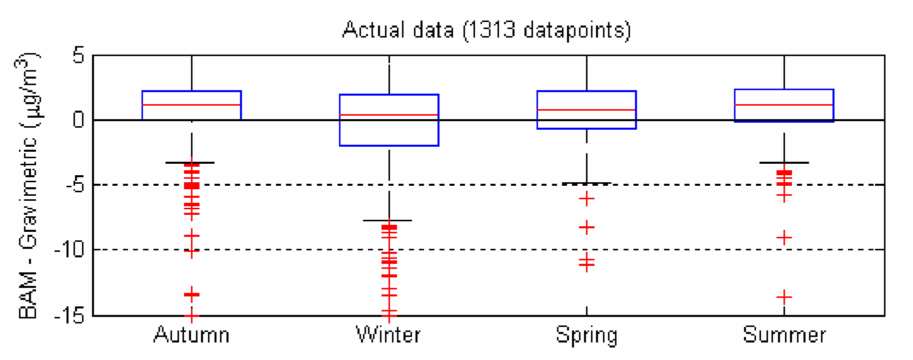

Figure 5.6: Residuals of 24-hour average BAM to gravimetric measurements by season.

Figure 5.6 shows that that the BAM tends toward over measurement relative to gravimetric in all seasons. During winter the trend to over measure is less pronounced.

The trend toward over measurement shown in Figure 5.6 may at first glance appear to be inconsistent with Figure 5.3, which shows the BAM with a tendency toward under-measurement, especially at higher concentrations. Across the whole dataset the BAM overestimates because a large proportion of the PM_{10} concentrations are less than 23 μgm^{-3} (the threshold below which the BAM typically over-estimates relative to the gravimetric method). The average residuals are closest to gravimetric during the winter months because higher concentrations, and hence BAM under prediction, occur during the winter months and offset some of the overestimation occurring at the lower concentrations.

The seasonal variations observed in Figure 5.6 were analysed with Kruskal-Wallis (K-W) test for significant difference at a 99% confidence level. The detailed results of this test are contained in Appendix 7.1 In summary the K-W test showed that the difference in the winter performance of the BAM compared to autumn and summer is statistically significant. There is no significant difference between the performance of the BAM during autumn, spring and summer.

5.3. Effect of Meteorological Factors

This section explores the effect of the meteorological factors, (temperature, wind speed and relative humidity) on the comparison of TEOM-FMDS, TEOM(40) and BAM with gravimetric measurements. Data collected at all the sites where the instruments were operated are included in the analysis.

5.3.1. Gravimetric vs TEOM-FDMS

Figure 5.7 shows the variation of residuals (TEOM-FDMS minus Gravimetric 24-hour averages) for the three meteorological variables; temperature, wind speed and relative humidity. Any statistically significant relationship between the residual and a particular meteorological variable is signalled by a black line on that chart.

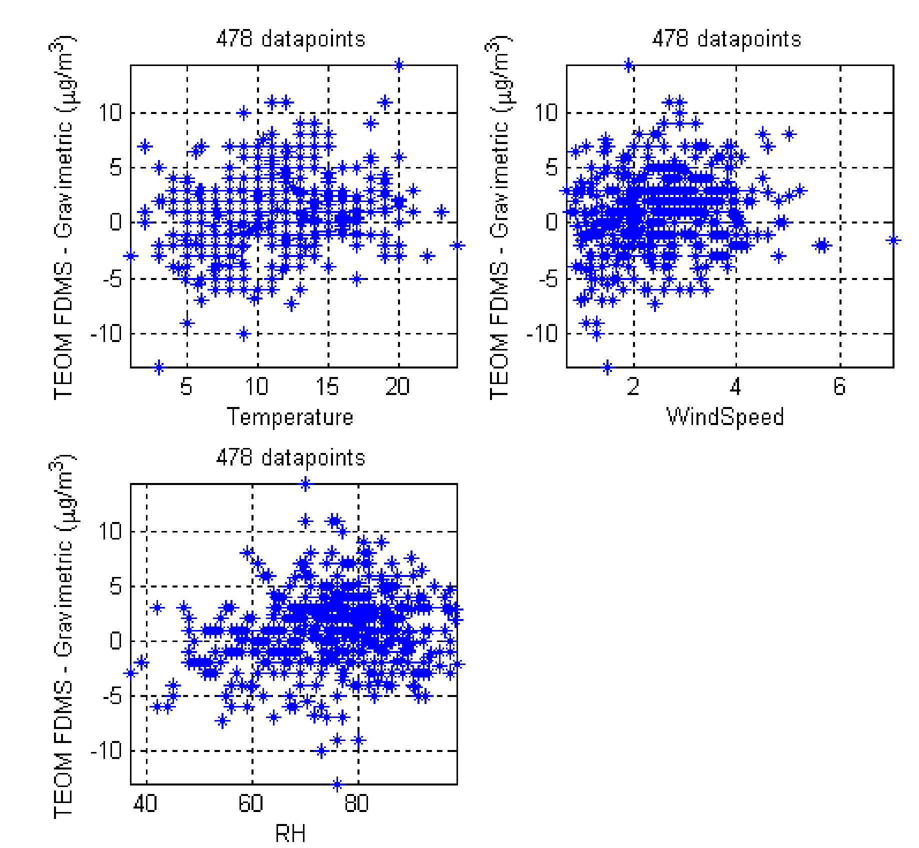

Figure 5.7: Variation of the residuals of 24-hour average TEOM-FDMS and gravimetric measurements with temperature, wind speed and relative humidity.

Figure 5.7 shows that no statistically significant relationships exist between the TEOM-FDMS and gravimetric residual and any of the three meteorological variables tested.

5.3.2. Gravimetric vs TEOM(40)

Figure 5.8 shows the variation of residuals (TEOM(40) minus Gravimetric) for the three meteorological variables; temperature, wind speed and relative humidity.

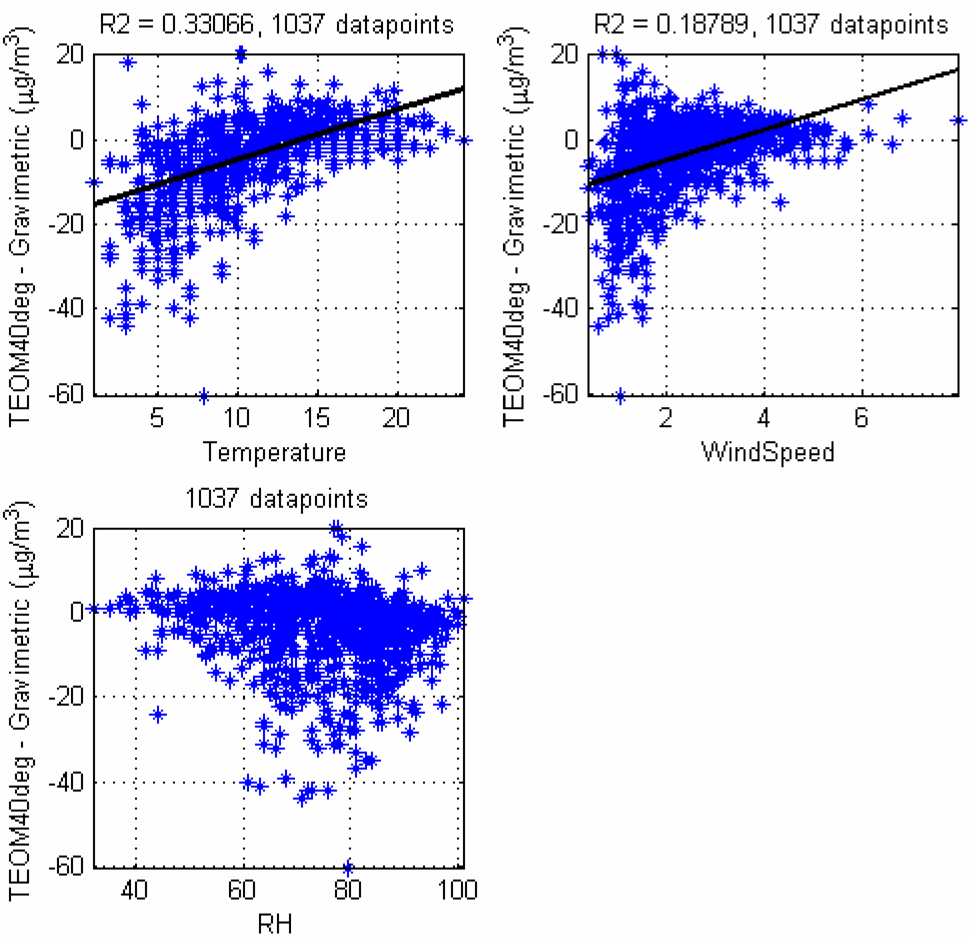

Figure 5.8: Variation of the residuals of 24-hour average TEOM(40) and gravimetric measurements with temperature, wind speed and relative humidity.

Figure 5.8 shows that a statistically significant but not strongly linear relationship exists between the TEOM(40) and gravimetric residual for temperature and windspeed. The temperature figure shows that at low temperatures (less than 10°C) the TEOM(40) tends to under measure, while at higher temperatures (above 15 °C) it tends to over-measure. Figure 5.12 shows that no statistically significant relationships exist between the TEOM(40) and gravimetric residual for relative humidity.

A comparison of the residual (TEOM(50) minus Gravimetric) between 24-hour average TEOM(50) and Gravimetric measurements broken down by the three meteorological variables; temperature, wind speed and relative humidity is contained in Appendix A3.4.

5.3.3. Gravimetric vs BAM

Figure 5.9 shows the variation of residual (BAM minus Gravimetric) for the three meteorological variables; temperature, wind speed and relative humidity.

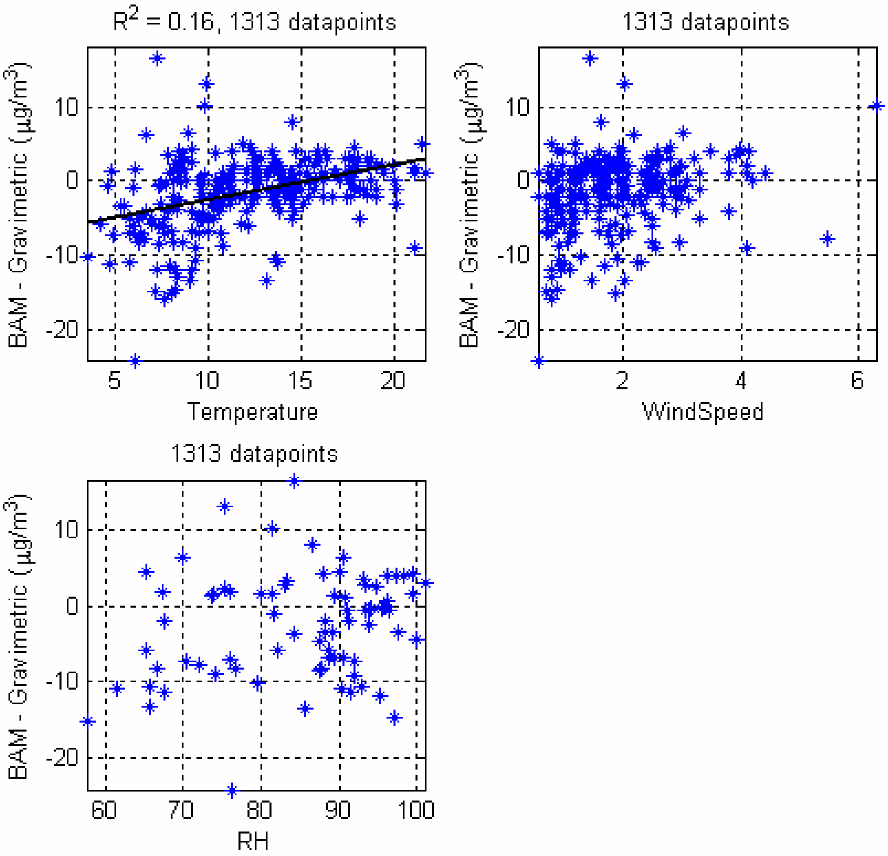

Figure 5.9: Variation of the residuals of 24-hour average BAM and gravimetric measurements with temperature, wind speed and relative humidity.

Figure 5.9 shows that a statically significant but not strong relationship exists between the BAM and gravimetric residual for temperature. The temperature figure shows that at low temperatures (less than 15°C) the BAM tends to under measure, while at higher temperatures (above 20°C) it tends to over-measure. Figure 5.13 shows that no statically significant relationships exist between the BAM and gravimetric residual for either of the other two meteorological variables tested.

5.4. Effect of location

This section explores the effect of location on the comparison of TEOM-FMDS, TEOM(40) and BAM with gravimetric measurements. All data collected by each of the instruments is included in the analysis.

5.4.1. Gravimetric vs TEOM-FDMS

Figure 5.10 shows the residual (TEOM-FDMS minus Gravimetric) between 24-hour average TEOM-FDMS and gravimetric measurements broken down by location.

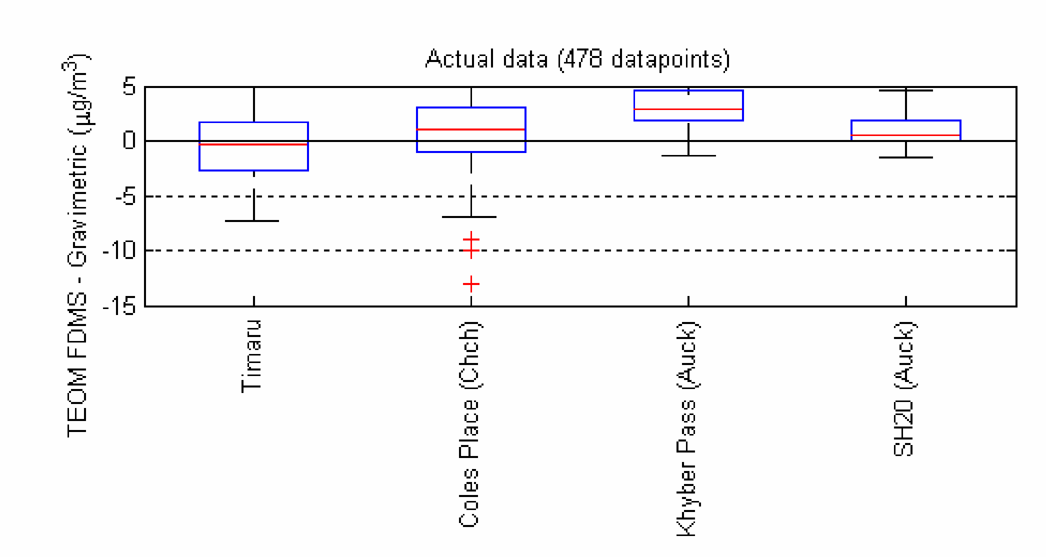

Figure 5.10: Residuals of 24-hour average TEOM-FDMS to gravimetric measurements by location

Figure 5.10 shows that there are differences in performance from location to location. The Khyber Pass instrument appears to have a tendency to over-measure compared to gravimetric measurements. SH20 (Auckland) and Coles Place (Christchurch) also shows tendencies to over measure but to a lesser extent. The Timaru location produces results which on average are very close to the gravimetric results.

The location to location variations observed in Figure 5.10 were analysed with Kruskal-Wallis (K-W) test for significant difference at a 99% confidence level. The detailed results of this test are contained in Appendix 7.2 In summary the K-W test showed that the difference in performance of the TEOM-FDMS at Khyber Pass was significant when compared to the instruments at the other three 3 locations. There was no significant difference in the performance of the instruments at SH20, Timaru or Coles Place.

5.4.2. Gravimetric vs TEOM(40)

Figure 5.11 shows the residual (TEOM(40) minus Gravimetric) between 24-hour average TEOM(40) and Gravimetric measurements broken down by location.

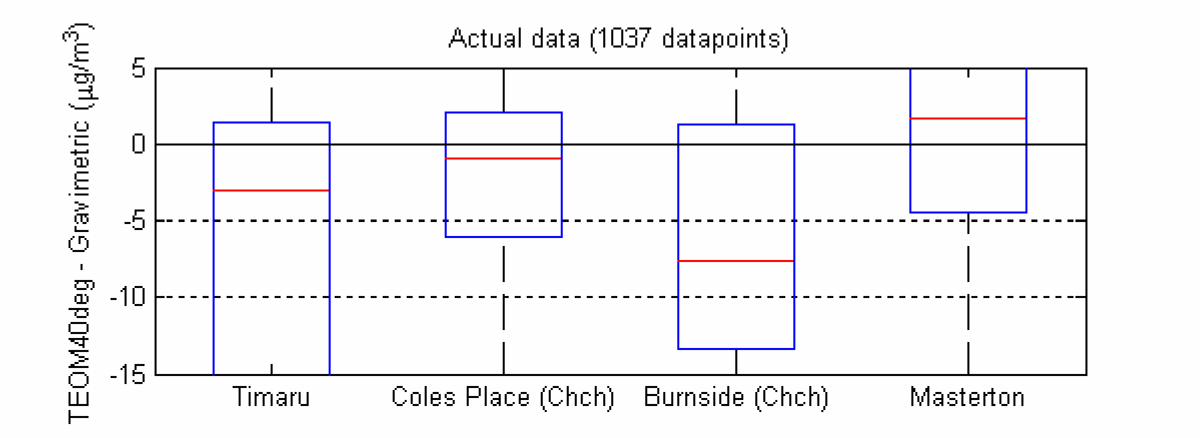

Figure 5.11: Residuals of 24-hour average TEOM(40) to gravimetric measurements by location

Figure 5.11 shows that a difference in performance of the TEOM(40) is observed from location to location. TEOM(40) operates closest to gravimetric at Coles Place and Masterton, with a tendency towards under and over-measurement respectively. TEOM(40) tends strongly toward under measurement at Burnside and Timaru.

The three South Island locations are in contrast to Masterton, where the instrument tends toward over measurement. The relationship between the TEOM and gravimetric method at this location was not as strong ($R^2 = 0.71$) as the other sites. However no explanation has been found to account for these differences.

Another point to note about Masterton is that although Figure 5.11 shows an average over-measurement, a scatterplot of the same data (Figure A2.5) shows clear under-measurement for values above about 15 μgm^{-3}. This apparent inconsistency occurs because the data density is very skewed and most of the data is at low concentrations (below about 15 μgm^{-3}) where the TEOM is over-measuring.

The location to location variations observed in Figure 5.11 were analysed with Kruskal-Wallis (K-W) test for significant difference at a 99% confidence level. The detailed results of this test are contained in Appendix 7.2 In summary the K-W test showed with the exception of the Masterton, the differences in performance of the TEOM(40)s were not statistically significant.

A comparison of the residual (TEOM(50) minus Gravimetric) between 24-hour average TEOM(50) and Gravimetric measurements broken down by location is contained in Appendix A3.3.

5.4.3. Gravimetric vs BAM

Figure 5.12 shows the residual (BAM minus Gravimetric) between 24-hour average BAM and gravimetric measurements broken down by location. It is important to note that with the exception of the Christchurch-Packe Street site, the BAMs were operated with an inlet temperature of 40°C. The Christchurch-Packe Street site inlet tubing was not heated. The length of inlet tubing used at the Auckland, Nelson and Christchurch locations was 3m, 1m and 3.5m respectively. With the exception of the Christchurch-Packe Street site, the set-ups are similar, the only variable being inlet tube length. It is unclear how varying tube lengths will affect the rate of volatile loss from the particulate being measured.

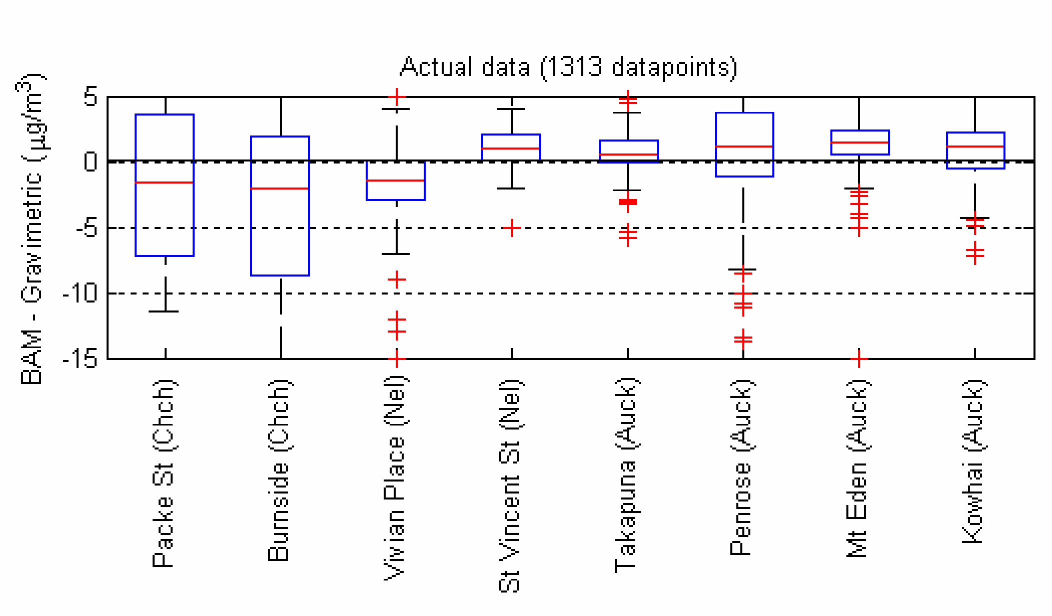

Figure 5.12: Residuals of 24-hour average BAM to gravimetric measurements by location

Figure 5.12 shows that there are location based differences between the BAM and the gravimetric monitoring method. At the Christchurch locations a tendency to under-measure is observed. The Auckland locations, in contrast to Christchurch, show a tendency to over-measure. Nelson has one location that tends toward under-measurement and one that tends toward over-measurement. The under and over-measurement observed at the Nelson locations is not as strong as that seen respectively at the Christchurch and Auckland locations.

The location to location variations observed in Figure 5.12 were analysed with Kruskal-Wallis (K-W) test for significant difference at a 99% confidence level. The detailed results of this test are displayed in Figure 5.13.

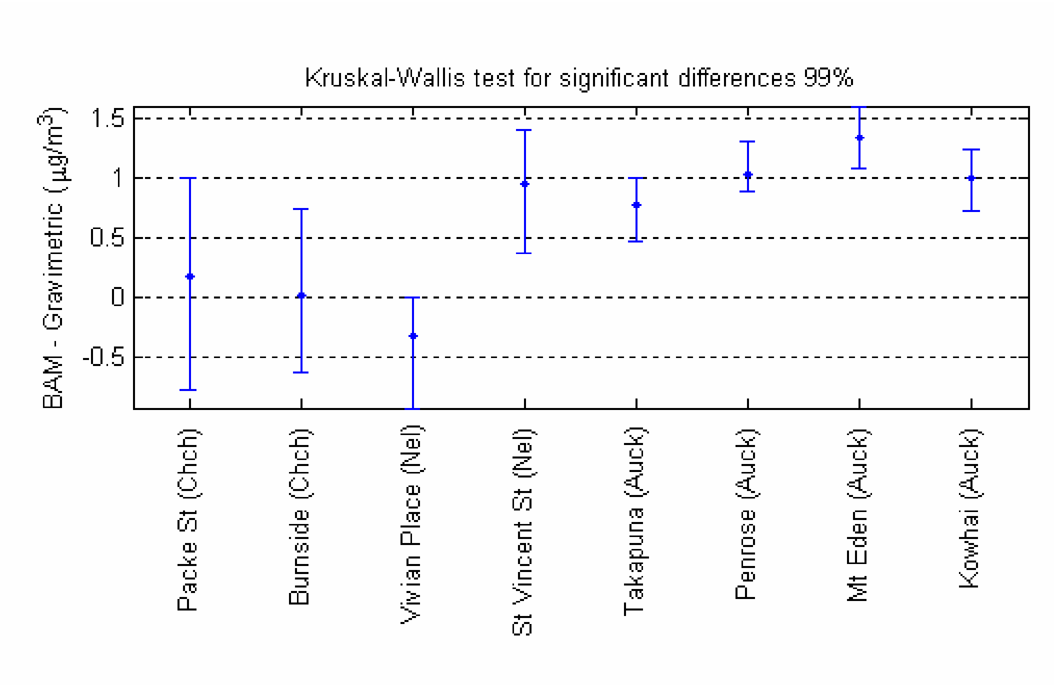

Figure 5.13: Kruskal-Wallis test for significant difference by location at the 99% confidence level of 24-hour average BAM to gravimetric residuals

Figure 5.13 shows that the under-measurement observed at the Christchurch (Burnside) and Nelson (Vivian Place) and the over-measurement observed at the two Auckland locations - Penrose and Mount Eden are statistically significant. The difference in performance of instruments at the other sites is not significant compared to the groups of instruments which have stronger tendencies to under- or over-measure.

5.5. Effect of site type

This section explores the effect of monitoring site type on the comparison of TEOM-FDMS, TEOM(40) and BAM with gravimetric measurements. All data collected by each of the instruments are included in the analysis.

Four site types have been defined by the Ministry for the Environment (1999); traffic, industrial, residential and special sites. Detailed descriptions of site types are provided in Appendix A5. Site type could impact on the relationships between measurement methods because of the varying chemistry associated with different sources of PM_{10}. For example, a site impacted on largely by home heating will have a large proportion of low molecular weight organics that can volatilise at higher sample temperatures. Similarly, variations in beta attenuation may occur with varying particulate composition.

5.5.1. Gravimetric vs TEOM-FDMS

Of the four sites included in the Gravimetric versus TEOM-FDMS analysis, two (Coles Place and Timaru) were classified as Residential Neighbourhood and two (Khyber Pass and SH20) as Traffic Peak. Figure 5.10 shows the Khyber Pass relationship is significantly different from both Residential Neighbourhood sites but is not significantly different to SH20. Results for SH20 were not significantly different to either Coles Place or Timaru.

While it is possible that the differences observed in these relationships are related to site types, it should be noted that both Traffic Peak sites are located in Auckland whereas the Residential Neighbourhood sites are located in Canterbury. It is possible that differences in climate, rather than site characteristics contribute to the differences observed. For example, warmer temperatures in Auckland could result in a greater amount of volatile loss on the exposed gravimetric filters.

Based on the data used in this analysis, there are indications that site type may be a factor in determining the relationship between the TEOM-FDMS and Gravimetric measurement methods, but it is not possible to draw any definitive conclusions, particularly given the limited number of sites considered in the analysis.

5.5.2. Gravimetric vs TEOM(40)

All three TEOM(40) versus Gravimetric sites were classified as Residential Neighbourhood. Thus no analysis of differences by site type was possible.

5.5.3. Gravimetric vs BAM

Five of the eight sites included in the Gravimetric versus BAM analyses were classified as Residential Neighbourhood under the MfE (1999) site classifications. These were St Vincent Street in Nelson, Packe Street and Burnside in Christchurch and Mt Eden and Kowhai in Auckland. Figure 5.9 shows that significant differences in the relationship between the Gravimetric method and the BAM were observed between Packe Street and Mt Eden.

One site - Takapuna – was classified as a Residential Dense site. This site was more similar in results to the residential neighbourhood Packe Street site than any of the other Auckland sites. The relationship between the BAM and gravimetric method at Takapuna was significantly different to the Mt Eden site.

Two "Industrial Dense" sites were included in the analysis. These were the Vivian Place site in Nelson and the Penrose site in Auckland. The two sites were not similar in the relationship between the BAM and the Gravimetric method. The relationship observed at the Vivian Place site was significantly different from all sites except Packe Street. The Penrose site was not significantly different from any site except Vivian Place.

Overall, site type does not appear to be a major factor in determining the relationship between the BAM and Gravimetric measurement methods. However, the analysis does show some similarities between sites predominantly surrounded by a particular source type. In particular, similarities between Takapuna (the residential dense site in Auckland) and Packe Street may occur because both are largely impacted on by PM_{10} from wood burning. Similarly, the main source of PM_{10} at the Vivian Place site is industrial wood burning and this site showed a relationship not dissimilar to Packe Street.

6. Adjustment factors

Previous sections of this report show that the difference between TEOM(40) and gravimetric results are larger than the equivalent comparisons between TEOM-FDMS and BAM instruments. The data set considered shows that TEOM(40) under-measures PM_{10} compared to gravimetric methods.

The Updated NES Users Guide states that for TEOMs it is important to determine a site specific adjustment factor, to ensure the volatile fraction of the particulate is accounted for – (unless the instrument is fitted with FDMS). It is outside the scope of this report to define what adjustment factor/s should be applied to TEOM data. However, to facilitate informed debate on the topic of adjustment factors, this section will use the TEOM(40) data set to illustrate:

- two methods by which adjustments can be calculated
- the effect on TEOM(40) data of applying adjustment factors

Two types of adjustment were considered: multi-linear regression models and regression tree models. These methods produce fundamentally different adjustment factors. Each method has its advantages and disadvantages, which are described in Section 6.4.

This study also showed that BAMs tend to under-measure PM_{10} compared to gravimetric method. The two models used in this section to calculate adjustment factors for TEOM(40) data can equally well be applied to BAM data. The adjustment factors would be different from those used for TEOM(40) data. However the outcome would be the same – an ability to convert a BAM data set to a gravimetric equivalent data set.

6.1. Regression Tree Model

In the first step of the regression tree model analysis, the regression tree identifies which variables cause the most variation in the residuals (difference between the TEOM(40) and gravimetric data). The tree model clusters the data into groups which have similar “predictor variables”. In this example the predictor variables include season, temperature, and TEOM(40) data (e.g. TEOM(40) data greater than 50 μgm^{-3} or data recorded in winter). The tree then defines an adjustment to be applied to each point within a particular group of data. The adjustment factor is defined to minimise the difference between the TEOM(40) and gravimetric data (i.e. make the residual zero). The distribution of adjustment factors within each group is used to define the single and most useful adjustment factor for that particular group. Therefore the tree produces a stepwise, rather than continuous, adjustment factor. A more detailed description about tree models is contained in Appendix 6. A full technical description of the method can be found in De'ath et al, 2000.

Figure 6.1 shows a regression tree used to predict the adjustment required (TEOM(40)-gravimetric) using TEOM(40) data and season as the predictor variables. Detail on the regression tree method is provided in Appendix 6.

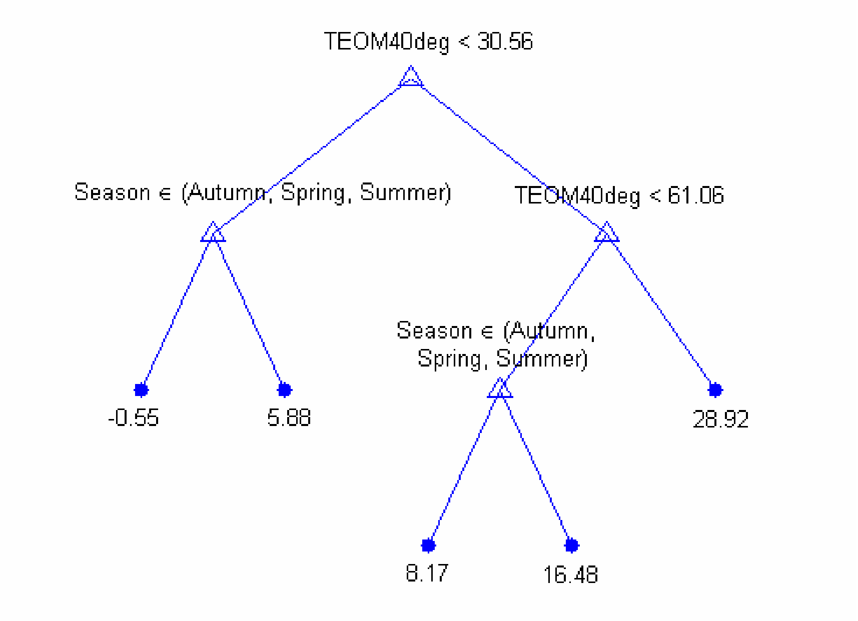

Figure 6.1: Regression Tree to predict the adjustment required (to the TEOM(40) data) using TEOM(40) data and season as predictor variables.

Figure 6.2 shows the distribution of adjustment factors within each of the groups (nodes) contained in the regression tree displayed in Figure 6.1.

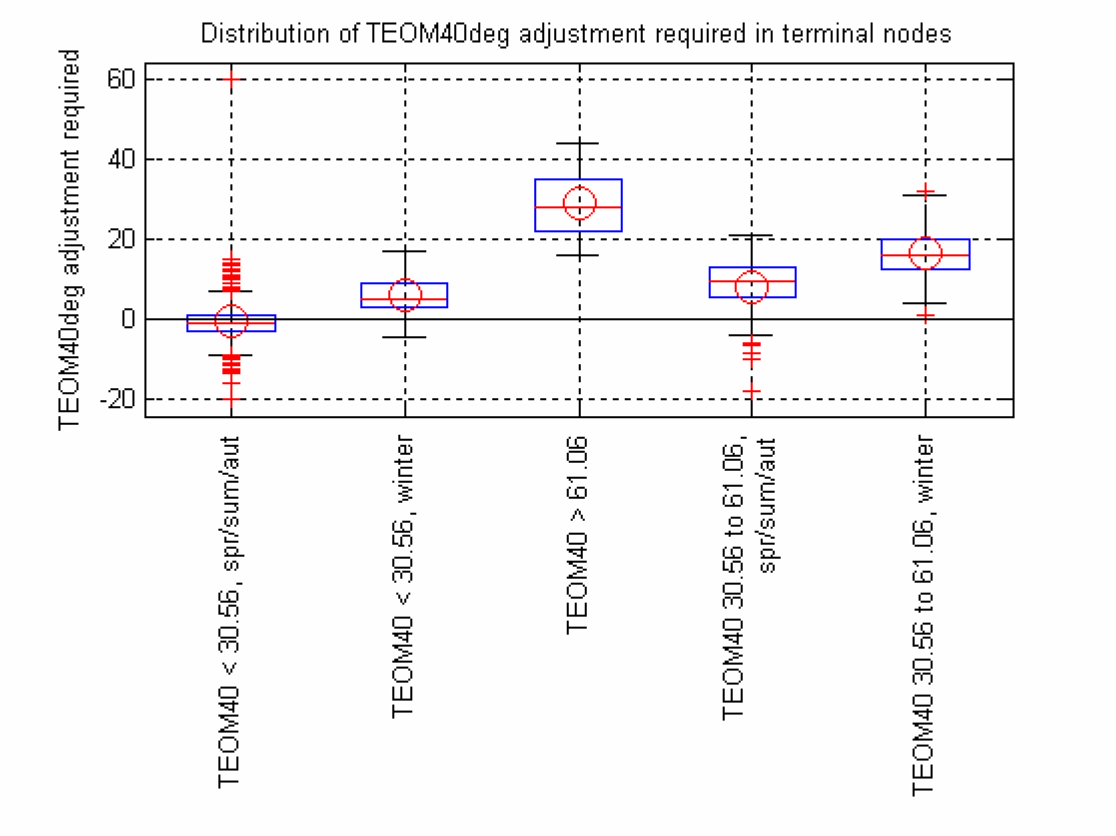

Figure 6.2: Definition of adjustment values for each group defined by regression tree.

Figure 6.2 shows that the regression tree used 5 groups (nodes). Four groups needed a positive adjustment factor (TEOM(40) data lower than gravimetric) the other group needed a small negative adjustment (TEOM(40) data slightly higher than gravimetric). Visible differences in the adjustment required in each node are observed in Figure 6.2. This indicates the tree has done a reasonable job of categorising the data into classes for adjustment.

Figure 6.1 and Figure 6.2 shows that the using a regression tree with TEOM(40) data and season as predictors the adjustment factors for TEOM(40) data will be:

- TEOM(40) data greater than 61.1 add 28
- TEOM(40) data between 30.6 and 61.1 and season is winter add 16.5
- TEOM(40) data between 30.6 and 61.1 and season is not winter add 8.2
- TEOM(40) data less than 30.6 and season is winter add 5.9
- TEOM(40) data less than 30.6 and season is not winter subtract 0.6

Figure 6.3 shows a correlation plot for 24-hour average regression tree adjusted TEOM(40) versus gravimetric measurements.

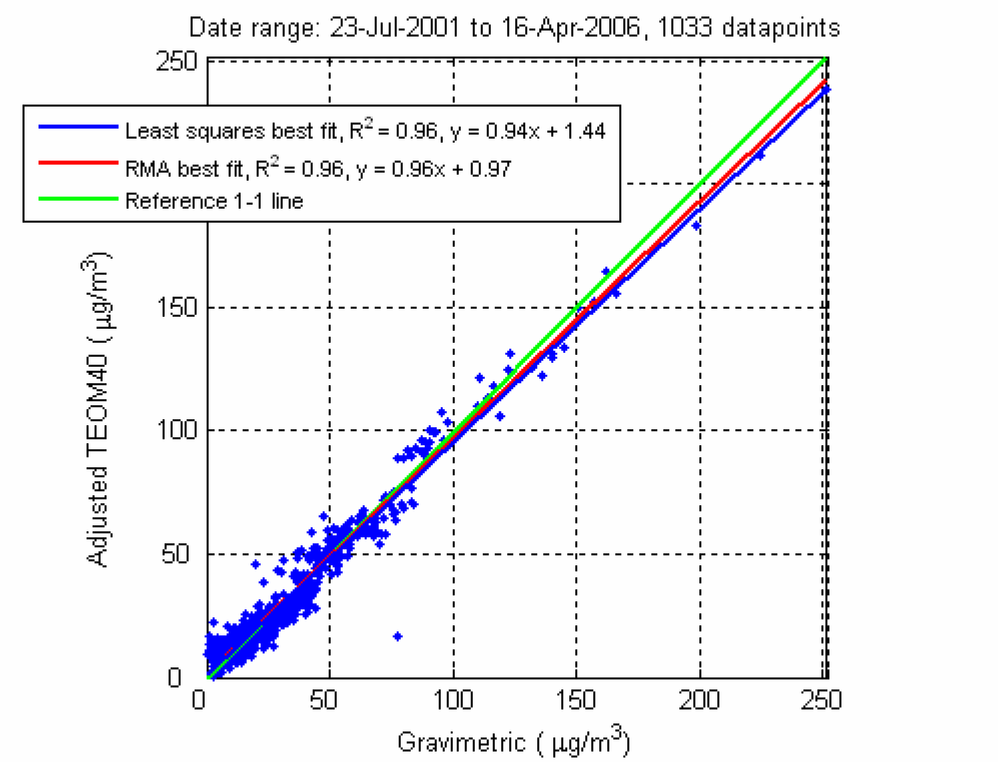

Figure 6.3: Correlation plot for 24-hour average regression tree adjusted TEOM(40) versus gravimetric measurements.

A comparison between Figure 5.2 (unadjusted TEOM(40)) and Figure 6.2 (regression tree adjusted TEOM(40)) shows that the R^2 for the adjusted data set is slightly improved to 0.96 from the unadjusted 0.95. More interestingly, adjusting the data has lowered the TEOM(40) under-measurement from 21% to only 2% at 50 μgm^{-3} and from 25% to 3% at 100 μgm^{-3} (using the reduced major axis line).

A regression tree analysis to define adjustment factors for TEOM(50) is contained in Appendix A3.5.

6.2. Multi-Linear Regression Model

Multi-Linear Regression (MLR) aims to transform the continuum of TEOM(40) data to match the corresponding gravimetric values. MLR produces an adjustment equation that is applied to all data points in the dataset.

The calibration equation was obtained by fitting a MLR model using TEOM40 and ambient temperature to predict the gravimetric measurement. The equation is:

$$\text{Adjusted TEOM(40)} = 1.29 * \text{TEOM(40)} - 0.65 * \text{Temperature} + 4.57$$

The Figure 6.4 shows a correlation plot for 24-hour average MLR adjusted TEOM(40) versus gravimetric measurements.

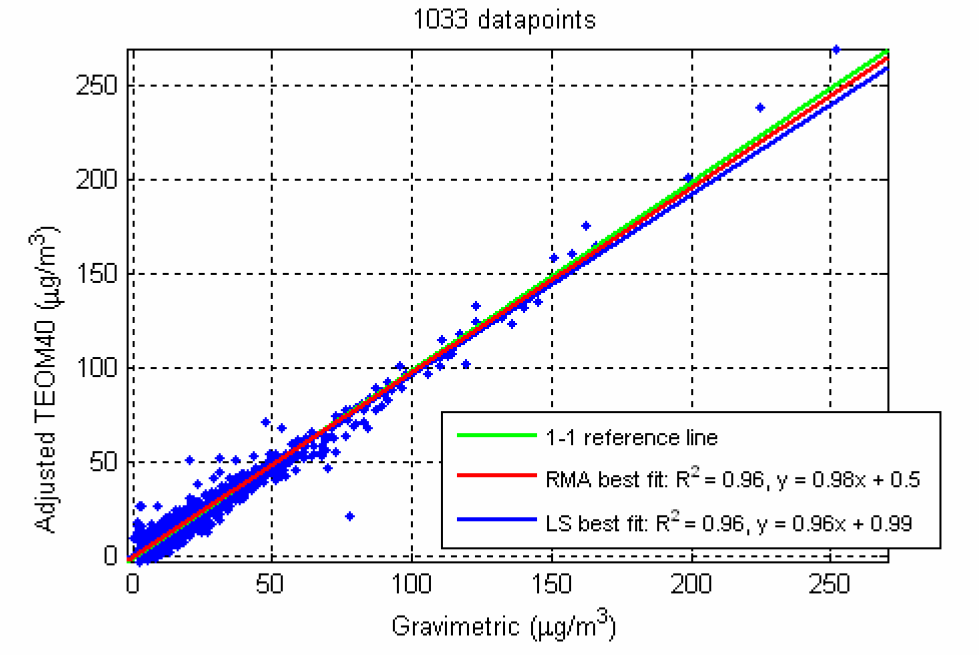

Figure 6.4: Correlation plot for 24-hour average MRL adjusted TEOM(40) versus gravimetric measurements.

A comparison between Figure 5.2 (unadjusted TEOM(40)) and Figure 6.4 (MLR adjusted TEOM(40)) shows that the R^2 for the adjusted data set is slightly improved to 0.96 from the unadjusted 0.95. Adjusting the data lowered the TEOM(40) under-measurement from 21% to only 1% (using the reduced major axis line) at 50 µgm^{-3} and from 25% to 2% at 100 µgm^{-3}.

6.3. Comparison of Methods Used to Define Adjustment Factors

The regression tree and MLR analysis described in Sections 6.1 and 6.2 are just one example of how these methods could be applied to the TEOM(40) data set. It is possible to use the same methods but employ different or more predictor variables. Generally the more variables employed the more complex and resource intensive the analysis becomes. There is a trade off between the quality of results achieved and the complexity of the model used. To illustrate this issue, a comparison of the performance of five adjustment models was undertaken.

The models tested were:

- MLR using TEOM40
- MLR using TEOM and temperature

- MLR using TEOM, temperature and winter season
- Tree using Teom
- Tree using Teom and season

These models will be compared using three statistics:

- Correlation with gravimetric data (R^2).
- Sum of squared residuals from gravimetric data (this is a general measure of how far out the TEOM40 values are from the gravimetric so it does measure under/over estimation).
- Number of exceedances (readings > 50 $\mu g/m^3$) compared to gravimetric data

Table 6.1 shows these three statistics for the five adjustment models.

Table 6.1: Statistics for models to adjust TEOM(40) data.

Model name	**R^2**	**Sum of squared residuals***	**Number of exceedances**
Unadjusted TEOM40	0.95	91,628	63
MLR using TEOM40	0.95	35,436	105
MLR using TEOM and temperature	0.96	28,875	113
MLR using TEOM, temperature and winter season	0.96	25,729	111
Tree using TEOM	0.95	33,627	122
Tree using TEOM and season	0.96	28,311	121

*Residual = Gravimetric – Adjusted TEOM(40)

**Exceedance = measurements > 50 compared to 116 for the gravimetric data)

Note that the R^2 statistic ignores under/over estimation and measures only the ‘tightness’ of the data around the best fit line. There was very little variation in the R^2 statistic between the unadjusted TEOM40 data and the models (**Error! Reference source not found.**). For both these reasons, R^2 is not a useful way to compare the adjustment models in this case.

Figure 6.5 graphs the effectiveness of the five models in terms of the sum of squared residuals. The residual is the just the subtracted difference between each gravimetric reading and the corresponding TEOM40 reading. We applied the Kruskal-Wallis test to establish whether there was any significant difference between the distribution of squared residuals between the models. Figure 6.6 compares the performance of the 5 adjustment models using the Kruskal-Wallis test for significant difference at the 99% confidence level.

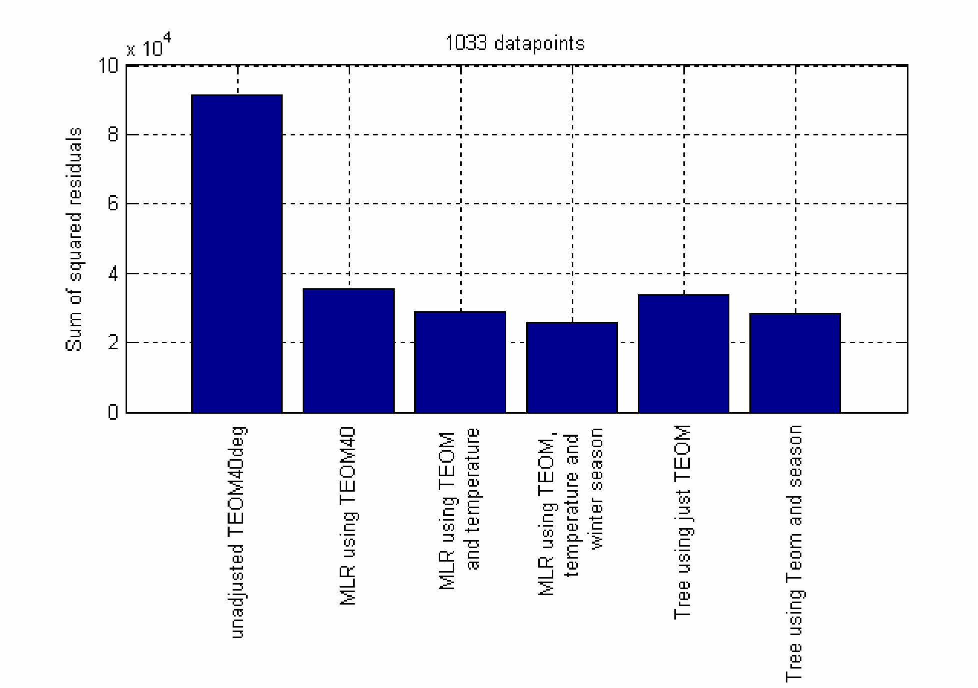

Figure 6.5: Comparison of sum of squared residuals for five different models used to define the adjustment factors for TEOM(40) measurements

Figure 6.6 shows that four of the options are significantly better (at 99% level) than no adjustment (the squared residuals are lower). One of the options (MLR with TEOM) is not statistically different from no adjustment. There is no significant difference between the distribution of squared residuals for the other four models.

The third way of assessing the performance of each of the adjustment factors is to consider how the number of exceedances of the NES PM_{10} concentration (50 μgm^{-3}) changes once the adjustment factor is applied. Figure 6.7 shows the number of concentrations above 50 μgm^{-3} under each adjustment option. The MLR options underestimate the number of exceedances relative to the gravimetric data and the tree methods overestimate this statistic. However, all the adjustment options are much better than the unadjusted TEOM40 data, which underestimates the number of exceedances by about 50%. There is not much difference in performance between the five adjustment options but the model that performs closest to the gravimetric data is the MLR using TEOM40 and temperature. This model underestimates exceedances by only 3% compared with the Tree using TEOM and season, which underestimates by 4%.

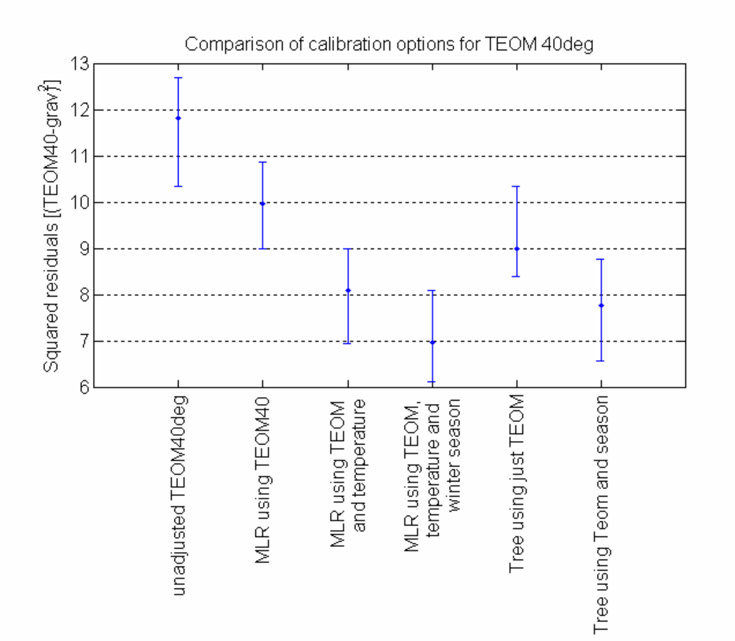

Figure 6.6: Comparison of the performance of 6 adjustment models using the Kruskal-Wallis test for significant difference at the 99% confidence level.

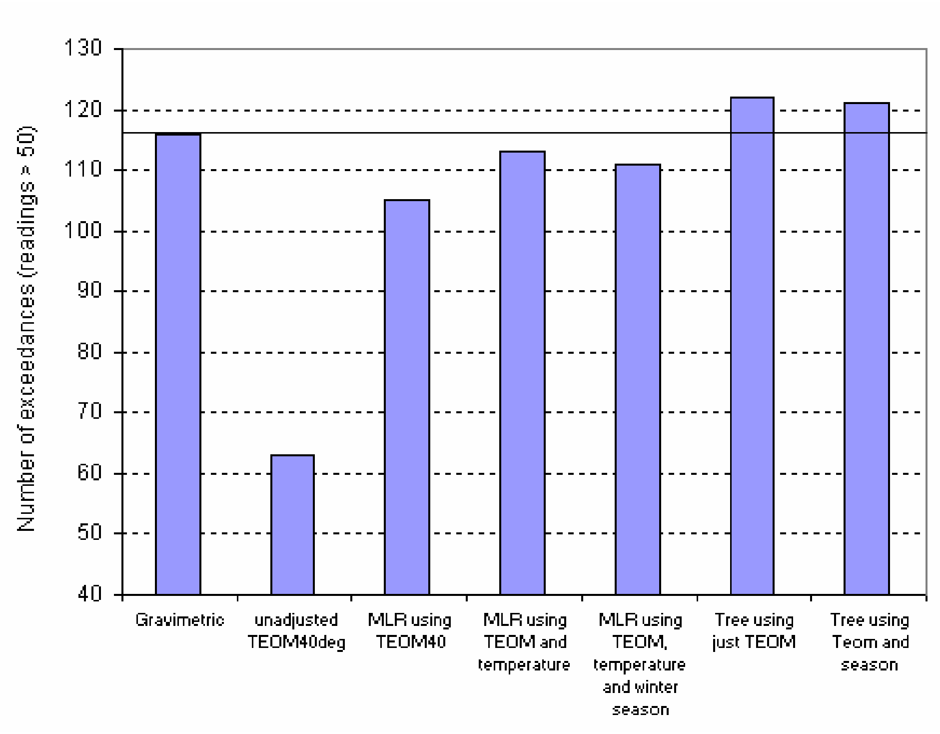

Figure 6.7: Comparison of the number of exceedances for five different models used to define the adjustment factors for TEOM(40) measurements

The best compromise between effectiveness of calibration and simplicity of model in this case is probably given by the MRL model using TEOM data and temperature (see Section 6.1). However in some circumstances a tree may prove to be more useful.

6.4. Improving adjustment factors

Figure 6.8 shows how the residuals (TEOM40 minus gravimetric) vary with PM_{10} concentration as measured by gravimetric methods

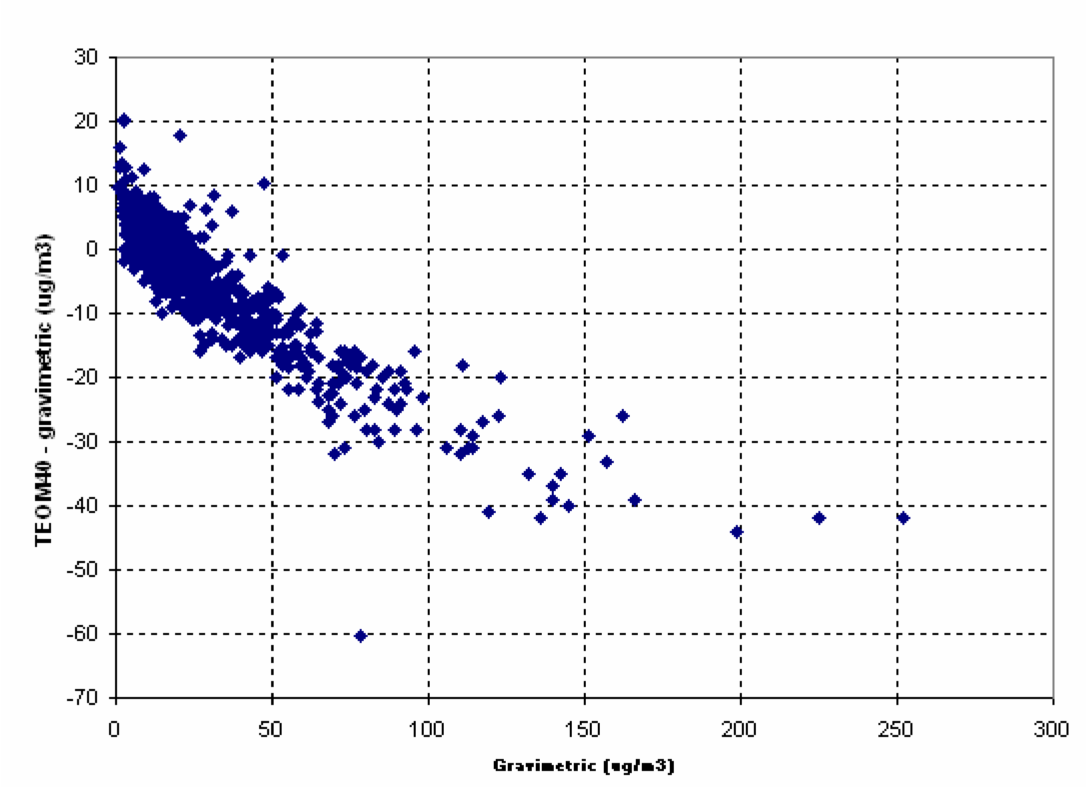

Figure 6.8: Difference between TEOM(40) and gravimetric measurements verses PM_{10} gravimetric values

Figure 6.8 shows that the residuals (Gravimetric –TEOM(40)) increase with PM_{10} concentration. The size of the difference between the two measurement methods is determined by environmental factors such as season, meteorology and location. These factors are explored in further detail in Sections 7.2-7.4. The set of factors influencing the magnitude of the residual tends to be different for high PM_{10} values compared to low PM_{10} values. This suggests that more refined and perhaps accurate adjustment factors could be defined if separate adjustment models are run for higher (above say 40 μgm^{-3}) and lower TEOM(40) data. The same models described in Sections 6.1 to 6.3 could be used for this purpose.

6.5. Choosing an adjustment method

There are a number of issues which will need to be considered before any particular model is chosen to adjust a particular data set.

One issue to consider is the resources and expertise required to undertake the two types of analysis detailed in sections 6.1 and 6.2. Linear regression calibration (using one predictor variable) can be calculated in excel. For multi-linear regression and regression trees, a suitable statistics package would be required (the models in this paper were fit using MATLAB). In addition to the specialist software, undertaking multi-linear regression and regression trees requires some statistical expertise.

Another main factor influencing the choice of method for adjusting the TEOM dataset for gravimetric equivalency is the purpose for which the adjusted data will be used. Two likely purposes for using adjusted TEOM data are to:

(a) evaluate maximum concentrations for determining the starting point for straight line paths under the NES

(b) determine the number of exceedances of the NES of 50 µg m^{-3} per year

For objective (a), an adjustment method that achieves a good fit (smaller residuals) at higher concentrations is preferable. Sections 6.1 and 6.2 indicate that the MLR calibration option does a better job of correcting the under-reading of the TEOM(40) data at high concentrations. The MLR adjusted TEOM(40) data underestimates the gravimetric method by only 1 and 2% (at 50 and 100 µgm-3 respectively) compared to 3 and 4% at the same values for the tree calibration option.

For objective (b), the preferred adjustment method will achieve a similar number of exceedances to that measured by the Gravimetric method. Figure 6.7 shows that the model that achieves this best is the MLR model using TEOM data and temperature (underestimates exceedances by 3%).

7. Summary of results

This section presents a summary of the key findings. The data and methods described above are focused on 24-hour average PM_{10} data. No attempt has been made to compare the measurement of annual average concentrations by different methods. The findings and conclusions below should not be applied to annual average concentrations, but could be applied to the 24 hour averages that can be combined to give an annual average.

7.1. Overall performance of the instruments

Compared to Gravimetric results the:

- TEOM-FDMS data had a very good correlation (R^2=0.98) and showed no obvious trend in under or over measurements
- TEOM(40) data had a good correlation (R^2=0.95) and typically measures around 21 and 25% less than the gravimetric method at 50 and 100 μgm^{-3} respectively. At low concentrations (<15 μgm^{-3}) the TEOM(40) tended to measure higher than the gravimetric method.
- BAM data had a good correlation (R^2=0.90) and typically measures around 6 and 9% less than the gravimetric method at 50 and 100 μgm^{-3} respectively. At low concentrations (<25 μgm^{-3}) the BAM tended to measure higher than the gravimetric method.

7.2. Effect of aeason on performance

The full data set from each of the instruments was divided into 4 seasons, summer (December to February), autumn (March to May) winter (June to August) and spring (September to November). The seasonal data sets showed the:

- TEOM-FDMS data was closest to the gravimetric results in winter and a slight tendency toward under-measurement was observed. In the other seasons there is a trend toward slight over measurements. The difference between the winter performance and the other 3 seasons of the years was statistically significant at the 99% confidence level. There is no significant difference between the performance of the TEOM-FDMS during autumn, spring and summer.

- TEOM(40) data was closest to the gravimetric results in autumn and spring. A tendency to under-measurement was observed in autumn and more strongly in winter. In spring and summer there was a trend toward slight over measurement. The performance of the TEOM(40) was similar during spring and summer but there was a significant difference between the remaining three times of year: winter, autumn and spring-summer at the 99% confidence level.

- Although the BAM underestimated relative to Gravimetric at higher concentrations, across all concentrations ranges the BAM tended toward over measurement relative to gravimetric in all seasons. During winter the trend to over measure is the least of the four seasons because of the modifying effect of the higher concentrations. The difference between the winter performance and the other 3 seasons of the years was statistically significant at the 99% confidence level. There is no significant difference between the performance of the BAM during autumn, spring and summer.

7.3. Effect of meteorological factors

The full data set from each of the instruments was analysed to investigate the effect of the meteorological factors; temperature, wind speed and relative humidity.

- The TEOM-FDMS performance showed no statistically significant relationships with any of the three meteorological variables tested.

- The TEOM(40) performance showed a statically significant but not strong relationship with temperature and windspeed. At lower temperatures, the TEOM(40) tends to under-measure, while at higher temperatures it tends to over-measure. This is likely to reflect the occurrence of high concentrations of PM_{10} during the winter when temperatures are colder. No statistically significant relationships were observed with relative humidity.

- The BAM performance showed a statistically significant but not strong relationship with temperature. At lower temperatures, the BAM tends to under measure, while at higher temperatures it tends to over-measure. As with the TEOM, this is likely to reflect the relationship between cold temperatures and higher PM_{10} concentrations. No statistically significant relationships were observed with either of the other two meteorological variables tested.

7.4. Effect of location on performance

The full data set from each of the instruments was divided in to geographic locations.

- The TEOM-FDMS performance was considered at 4 locations, two in Auckland and two in Christchurch. Statistical differences were observed between one Auckland site and the other three sites.
- The TEOM(40) performance was considered at 4 locations, two in Christchurch, one in both Timaru and Masterton. The three South Island instruments tended toward under-measurement in contrast to Masterton's over-measurement. With the exception of Masterton the differences in performance of the TEOM(40) instruments were not statically significant.
- The BAM performance was considered at 8 locations, four in Auckland and two each in Nelson and Christchurch. At the Christchurch locations a tendency to under-measure was observed. The Auckland locations, in contrast show a tendency to over-measure. Christchurch experiences much higher PM_{10} concentrations than Auckland. The difference between Christchurch and Auckland in BAM response may therefore reflect the differences in concentration ranges, described previously, rather than location dependent differences in instrument response occurring as result of differences in factors such as the impact of chemistry or meteorology. Nelson had one location that tended toward under-measurement and one that tended toward over-measurement. The maximum concentrations measured at the site that over measured was 23 $\mu g\ m^{-3}$ compared with 60 $\mu g\ m^{-3}$ at the under-measurement site. As with the Auckland and Christchurch scenarios, it is possible that these were differences in concentrations rather than location dependent differences in instrument response.

7.5. Effect of site type on performance

The full data set from each of the instruments was divided in to different site types: traffic, industrial and residential.

- The TEOM-FDMS performance was considered at two traffic and two residential sites. This analysis indicated that site type may be a factor in determining the relationship between the TEOM-FDMS and Gravimetric measurement methods, but it is not possible to draw any definitive conclusions.

- All three TEOM(40) sites were classified as Residential Neighbourhood. Thus no analysis of differences by site type was possible.

- The BAM performance was considered at two traffic, six residential sites and two industrial sites. This analysis indicated that site type does not appear to be a major factor in determining the relationship between the BAM and Gravimetric measurement methods.

7.6. Adjustment factors

The Updated NES Users Guide states that for TEOMs it is important to determine a site specific adjustment factor to ensure the volatile fraction is not lost (unless the instrument is fitted with FDMS). It is outside the scope of this report to define what adjustment factor/s should be applied to TEOM or other continuous PM_{10} data. However, to facilitate informed debate on the topic of adjustment factors, two methods, Regression Tree and Multi Linear Regression, were used to illustrate how adjustment factors could be calculated: A comparison between the unadjusted TEOM(40) data and the:

- Multi Linear Regression adjusted TEOM(40) data shows that the R^2 for the adjusted data set is slightly improved to 0.96 from the unadjusted 0.95. Adjusting the data lowered the TEOM(40) under-measurement from 21-25% to 1-2% at 50-100 μgm^{-3}.

- Regression tree adjusted TEOM(40) data shows that the R^2 for the adjusted data set is slightly improved to 0.96 from the unadjusted 0.95. Adjusting the data lowered the TEOM(40) under-measurement from 21-25% to 2-3% at 50-100 μgm^{-3}.

The unadjusted TEOM(40) data missed 47% of NES exceedances (>50 μgm^{-3}) measured using gravimetric methods. The MLR adjusted TEOM(40) data over predicted the number of NES exceedances by about 3%. The regression tree adjusted TEOM(40) data reduced the number of exceedances missed to about 4%.

The two models used to calculate adjustment factors for TEOM(40) data can equally well be applied to BAM data. The adjustment factors would be different from those used for TEOM(40) data. However the outcome would be the same – an ability to convert a BAM data set to a gravimetric equivalent data set.

8. Achievement of study objectives

There are a number of methods which comply with the requirements for monitoring PM_{10} under New Zealand's Air Quality National Environmental Standards. The methods that comply include gravimetric (filter based) and equivalent methods such as the Tapered Element Oscillating Microbalance (TEOM) and a number of Beta Attenuation Monitors (BAMs). The difference in mass concentrations from co-located gravimetric and equivalent PM_{10} monitoring has long been a concern for air quality professionals. This project aimed to provide Environmental Regulators in New Zealand with information which will to enable them to answer the following questions:

- *Are continuous methods of monitoring PM_{10} equivalent to the results achieved using a gravimetric approach?*
- *Does the performance of continuous PM_{10} monitors vary with location, season or meteorology?*
- *What methods can be used to adjust continuous PM_{10} data sets to a gravimetric equivalent?*

The objectives set, and outcomes achieved from this study, fell into three categories.

Objectives Group 1: Undertaking a Robust Nationwide Study

- set up a framework which will ensure that the different co-location data sets are analysed in a consistent and robust method
- enable people to have faith in the inter-comparison study
- ensure that the collocated data sets collected by the various Regional Councils gain maximum exposure and provide as much value as possible

Outcomes:

A data set of collocated gravimetric and continuous PM_{10} measurements were pooled from six environmental agencies within New Zealand. These data was collected from a total of 13 sites, located between Auckland and South Canterbury and contained over 3000 data points. Comparisons between the gravimetric and continuous PM_{10} data were undertaken using quantitative methods. Statistical tests were used to test the significance of any differences observed.

Objective Group 2: Comparison of Gravimetric and Continuous PM_{10} Monitoring Methods

- compare equivalent (TEOM and BAM) PM_{10} monitoring methods against the gravimetric method (Hi-Vol and Partisol)

- promote confidence in the "equivalence" of PM_{10} data collected by various methods

- understand how and perhaps why comparisons differ with season, site and meteorology

Outcomes:

Differences were observed between the measurements made by gravimetric and continuous methods. At concentrations above about 25 μgm^{-3} (BAM), and 20 $\mu g\ m^{-3}$ (TEOM(40) measurements tend to be lower than gravimetric measurements. Under-measurement by the TEOM(40) tends to be greater than that by the BAM. At concentrations below about 15 μgm^{-3} for TEOM, and 20 μgm^{-3} for BAM, measurements both tend to be slightly higher than gravimetric measurements. Differences were observed between individual TEOM-FDMS and gravimetric measurements, however no general trend toward under- or over-measurement was evident.

The TEOM and BAMs used in the study are USEPA equivalent-designated methods and are both defined as suitable for monitoring PM_{10} under the NES. However the analysis undertaken in this study suggests the measurements produced by the TEOM(40) and BAM are not equivalent in a quantitative sense to measurements obtained using gravimetric methods. The TEOM-FDMS data is much closer to being quantitatively equivalent to measurements obtained using gravimetric methods than either the TEOM(40) or the BAM. However this conclusion should be treated with some caution as the data set was approximately one third the size and over a shorter time period of that available for the TEOM(40) and BAM instruments.

The data set used in this study shows that performance of the equivalent methods varies with season. The analysis showed the winter BAM and TEOM-FDMS data were closer to gravimetric measurements than any of the other three seasons. However, closer inspection indicates that the improved BAM response during winter occurs because the overall over-estimation of this method is offset by an underestimation at times when PM_{10} concentrations are elevated. The underestimation between the TEOM(40) and gravimetric data was largest during winter.

Data were collected from four TEOM-FDMS, four TEOM(40) and eight BAM sites. The data set used in this study shows that performance of equivalent methods may vary with location. The performance of the TEOM-FDMS at three sites was clustered together, while the performance of the fourth instrument over-measured significantly compared to the other three. No reason for this disparity was identified. An identical situation was observed with the TEOM(40). Two of BAM sites were identified as significantly under-measuring as compared to another group of two which over-measured. The performance of the instruments at the remaining four sites was not significantly different from the two "*extreme*" groups. The data indicates there may be a location related trend in the performance of the instruments. However, some differences between locations may also occur as a result of differences in the range of concentrations measured. The under-measurement sites tended to occur more frequently in the South Island and the over-measurement sites were predominantly Auckland locations. The data suggests that there may be a potential link between geographic location and instrument performance. This may be related to location differences in sources or differences in other factors such as meteorological conditions.

The full data set from each of the instruments was divided in to different site types: traffic, industrial and residential. Performance of the TEOM-FDMS was considered at two traffic and two residential sites. Site type may be a factor in determining the performance but no firm conclusions could be drawn. All TEOM(40) sites were classified as Residential Neighbourhood. Thus no analysis of differences by site type was possible. Performance of the BAM was considered at two traffic and six residential sites and two industrial sites. It is uncertain whether site type is a major factor in determining performance.

In attempting to identify the effect of location or site type confounding factors such as instrument operation were not accounted for. Therefore further work and perhaps a more extensive data set would be needed to draw a firm conclusion about the variation of continuous PM_{10} monitors with geographic location and site type in New Zealand.

The data set used in this study showed that there was a significant but weak relationship between the performance of the TEOM(40) and ambient temperature. A similar relationship was observed with the BAM data set. These are likely to reflect the relationship between temperature and elevated PM_{10} concentrations, with higher PM_{10} (and greater differences with both methods) occurring during the winter when temperatures are colder. Temperature did not appear to have a significant effect on the performance of the TEOM-FDMS. The performance of the continuous instruments did not appear to vary significantly with wind speed or relative humidity.

Objective Group 3: Gravimetric/Equivalent Method Adjustment Factors

- assess the need for adjustment factors for the different monitoring methods considered

- suggest methods by which adjustment factors can be arrived at

- establish whether adjustment factors differ with season, region, year and site type

Outcomes:

The analysis undertaken in this study suggests the measurements produced by the TEOM(40) and BAM are not quantitatively equivalent to measurements obtained using gravimetric methods. Both the TEOM(40) and the BAM tend to under-measure the amount of PM_{10} when concentrations are above about 15 μgm^{-3} and 25 $\mu g\ m^{-3}$ respectively i.e. concentrations around and above the standard (50 μgm^{-3}) can be under-measured by TEOM(40) and BAMs. While the TEOM and BAM methods are both defined as suitable for monitoring PM_{10} under the NES, if for any reason (such as national consistency and regional intercomparisons), air quality managers require a gravimetric equivalent measurement from TEOM or BAM data, then it may be necessary to apply an adjustment factor.

A tendency to over- or under-measure was not observed in the full TEOM-FDMS data set. Therefore applying an adjustment factor is unlikely to provide significant benefit. However, the TEOM-FDMS's performance does show some seasonal variation and some benefit may be gained if a season specific adjustment factor can be determined and applied.

Regression Trees and Multi Linear Regression (MLR) models were used to illustrate two methods by which adjustment factors can be calculated. There are other methods by which adjustment factors can be determined. Regression Trees and MLR were used in this study because they can be referenced in scientific literature, and while requiring some statistical expertise, can be undertaken without extensive resourcing.

A comparison between non-adjusted and adjusted TEOM(40) data shows that using a regression tree or MLR model slightly improves the relationship (R^2) between TEOM(40) and gravimetric data. Both adjustment methods significantly reduce under-measurement and the number of exceedances missed in un-adjusted TEOM(40) data. MLR provides a slightly larger improvement than regression trees and is easier to fit, so is our preferred model in this case.

Adjustment factors are derived from the relationship between collocated continuous and gravimetric data and therefore may differ from season to season and from site to site. This study has shown the TEOM(40) performance differed significantly from season to season, and there may have also been a site to site difference. For these reasons it would be ideal to have a seasonal and site specific adjustment factor. However robust adjustment factors require a significant amount of data and in a practical sense this amount of data will not be available for most sites. In this case, as a first pass estimation of a gravimetric equivalent data set could be obtained by using an adjustment factor derived from a similar site or from large and representative data set.

9. Recommendations for further work

There is potential to enhance and/or extend the outcomes derived from this project. A number of recommendations are made to with a view to realise this potential. The recommendations fall into two categories: further research and practical implications.

9.1. Further Research

It is recommended that the research team evaluate the benefits of:

- Expanding the collocation data set and repeating the analysis using;
    - More data – especially TEOM-FDMS;
    - Increased number of sites;
    - Longer record.
- Exploring in more detail why variations in instrument performance occur at different times of the year and site to site.
- Investigating the measurement of PM_{10} on a finer temporal scale than 24-hours
    - Differences in 1-hour concentrations measured by different methods;
    - Causes and effects of negative PM_{10} values;
    - Stability and reliability of 1-hour (or shorter) average concentrations.

9.2. Practical implications

The collation, analysis and reporting of the data set used in this study has raised a number of practical issues associated with the collection, management and interpretation of PM_{10} data. At the time of writing this report, the Ministry for the Environment are in the process of updating their Good Practice Guide (GPG) for Air Quality Monitoring and Data Management. There maybe an opportunity to dove-tail and perhaps integrate some of the issues raised in this report with the updated GPG. It is therefore recommended that MfE evaluate the benefits of:

- Holding a workshop on PM_{10} monitoring with the aim of facilitating the collection of good quality data in a nationally consistent manner. Matters to address could include:
    - Equipment purchase, siting, installation, operation and maintenance;

    - Data quality assurance procedures;
    - Data reporting and interpretation of data collected by different methods;
    - The formulation and use of adjustment factors for data collected by continuous monitoring methods.

- Formulating and providing guidance on:
    - Pros and cons of the different monitoring methods - including the impact of the volatilisation;
    - The causes of variation between methods;
    - “Error bars” for each method;
    - Operational aspects of Hi-Vol sampling including RH and temperature conditioning of laboratory, timing of flow calibrations and the impact of changes in set point;
    - The application of adjustment factors for equivalent methods.

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Appendix 1: Data Tables

Summary tables were prepared for each data set. RMA results are shown in the following data tables based on season, concentration (high > 20 µg m^{-3} , low < 20 µg m^{-3}) and season and concentration. R^2 values are only shown if at least 6 datapoints were used.

Khyber Pass	RMA			
TEOM-FDMS vs Partisol	Slope	Intercept	R^2	No. of data points
All	1.18	-1.0	0.90	26
All high	1.17	-0.4	0.85	21
All low	1.04	-0.2		5
Winter	1.13	-0.7	0.98	14
Winter high	1.06	1.7	0.97	10
Winter low	1.01	-0.1		4
Summer	1.36	-4.1	0.81	12
Summer high	1.36	-4.1	0.79	11
Summer low				

SH 20	RMA			
TEOM-FDMS vs Partisol	Slope	Intercept	R^2	No. of data points
All	0.88	2.4	0.87	29
All high	12.74	-280.0		2
All low	0.89	2.4	0.73	26
Summer	0.88	2.4	0.87	29
Summer high	12.74	-280.0		2
Summer low	0.89	2.4	0.73	26

Coles Place	RMA			
TEOM Hi-Vol	Slope	Intercept	R^2	No. of data points
All	0.73	2.9	0.97	808
All high	0.75	1.8	0.97	239
All low	0.76	2.8	0.48	569
Winter	0.76	0.4	0.98	431
Winter high	0.77	-0.7	0.97	201
Winter low	0.70	1.6	0.57	230
Summer	0.99	1.6	0.79	377
Summer high	0.99	1.6	0.79	377
Summer low				

Coles Place	RMA			
TEOM-FDMS Hi-Vol	Slope	Intercept	R^2	No. of data points
All	0.99	1.1	0.98	384
All high	0.97	1.8	0.98	150
All low	1.08	0.2	0.54	234
Winter	0.99	0.0	0.99	216
Winter high	0.99	0.0	0.99	129
Winter low	0.99	0.0	0.59	87
Summer	1.18	0.3	0.66	168
Summer high	1.18	0.3	0.66	168
Summer low				

Packe Street	RMA			
BAM - Hi-Vol	Slope	Intercept	R^2	No. of datapoints
All	0.94	1.4	0.98	30
All high	0.93	2.8	0.97	16
All low	0.35	11.0	0.29	14
Winter	0.94	1.4	0.98	30
Winter high	0.93	2.8	0.97	16
Winter low	0.35	11.0	0.29	14

Burnside	RMA			
BAM vs Hi-Vol	Slope	Intercept	R^2	No. of data points
All	0.82	2.7	0.94	47
All high	0.81	2.7	0.92	25
All low	0.80	3.1	0.30	22
Winter	0.81	2.8	0.94	42
Winter high	0.81	2.8	0.92	24
Winter low	0.75	3.9	0.10	18
Summer	0.91	1.6		5
Summer high				
Summer low	1.12	0.3		4

Burnside	RMA			
TEOM vs Hi-Vol	Slope	Intercept	R^2	No. of data points
All	0.77	1.9	0.92	41
All high	0.75	2.7	0.89	25
All low	0.84	1.1	0.03	16
Winter	0.76	2.3	0.92	41
Winter high	0.75	2.7	0.89	25
Winter low	0.78	2.0	0.03	16

Takapuna	RMA			
TEOM - High-vol	Slope	Intercept	R2	No. of data points
All	0.92	2.1	0.60	142
All high	0.56	11.5	0.47	43
All low	0.98	0.9	0.35	99
Winter	0.86	2.9	0.70	91
Winter high	0.60	8.8	0.62	26
Winter low	1.01	0.4	0.11	39
Summer	1.12	0.1	0.35	78
Summer high	0.84	8.5	0.23	17
Summer low	1.04	0.3	0.93	61

Takapuna	RMA			
BAM - Partisol	Slope	Intercept	R^2	No. of data points
All	0.91	2.3	0.79	216
All high	0.62	10.7	0.66	68
All low	0.97	1.0	0.67	148
Winter	0.82	4.2	0.78	115
Winter high	0.56	12.0	0.76	52
Winter low	0.92	2.0	0.47	63
Summer	1.07	-0.4	0.84	101
Summer high	1.21	-2.8	0.38	16
Summer low	1.03	0.1	0.99	85

Penrose	RMA			
TEOM - Hi-Vol	Slope	Intercept	R^2	No. of data points
All	1.00	1.8	0.08	55
All high	0.54	17.2	0.52	30
All low	0.65	1.4	0.16	25
Winter	1.03	1.7	0.20	44
Winter high	0.55	16.9	0.54	24
Winter low	0.75	0.8	0.16	20
Summer	0.88	2.3	0.14	11
Summer high	0.45	19.2	0.19	6
Summer low	0.45	1.7		5

Penrose	RMA			
BAM - Hi-Vol	Slope	Intercept	R^2	No. of data points
All	0.97	1.8	0.67	304
All high	0.73	8.1	0.52	90
All low	0.95	1.8	0.39	214
Winter	0.98	1.5	0.73	154
Winter high	0.73	8.3	0.63	59
Winter low	0.99	1.2	0.37	95
Summer	0.93	2.5	0.50	150
Summer high	0.74	7.8	0.14	31
Summer low	1.04	0.7	0.91	119

Penrose	RMA			
TEOM- Partisol	Slope	Intercept	R^2	No. of data points
All	0.95	1.1	0.92	111
All high	0.72	6.7	0.81	51
All low	1.02	0.4	0.80	60
Winter	0.83	3.2	0.91	60
Winter high	0.68	7.7	0.83	34
Winter low	0.86	2.1	0.86	26
Summer	1.03	0.5	0.92	51
Summer high	1.06	-1.0	0.78	17
Summer low	1.08	0.2	0.99	34

Mt Eden TEOM - Partisol	RMA Slope	Intercept	R^2	No. of data points
All	1.03	0.4	0.63	50
All high	0.66	8.9		5
All low	1.02	0.5	0.58	45
Winter	1.07	0.1	0.80	22
Winter high	0.30	17.8		3
Winter low	1.07	0.0	0.80	19
Summer	0.98	0.7	0.56	28
Summer high	0.21	16.3		2
Summer low	0.97	0.7	0.91	26

Mt Eden BAM- Partisol	RMA Slope	Intercept	R^2	No. of data points
All	1.03	0.8	0.73	318
All high	0.60	10.3	0.18	37
All low	1.06	0.6	0.67	281
Winter	1.07	0.4	0.80	166
Winter high	0.99	2.2	0.56	26
Winter low	1.06	0.5	0.65	140
Summer	0.98	1.3	0.63	152
Summer high	0.39	13.7	0.09	11
Summer low	1.09	0.3	0.96	141

Kowhai BAM- Partisol	RMA Slope	Intercept	R2	No. of data points
All	1.10	-0.7	0.73	197
All high	1.34	-5.8	0.47	44
All low	0.87	2.1	0.53	153
Winter	1.16	-1.7	0.72	109
Winter high	1.48	-9.4	0.44	32
Winter low	0.89	1.9	0.41	77
Summer	0.97	1.0	0.72	88
Summer high	0.73	8.0	0.58	12
Summer low	0.85	2.3	0.60	76

Masterton TEOM vs High-vol	RMA Slope	Intercept	R2	No. of datapoints
All	0.64	6.2	0.71	148
All high	0.59	10.0	0.61	38
All low	0.42	7.7	0.23	110
Winter	0.70	5.1	0.06	96
Winter high	0.56	17.6	0.02	37
Winter low	0.23	8.3	0.03	59
Summer	1.35	5.5	0.00	52
Summer high	0.84	19.5		3
Summer low	1.05	6.4	0.00	49

St Vincent St	RMA			
BAM - Partisol	Slope	Intercept	R^2	No. of data points
All	1.03	0.4	0.81	57
All high				
All low	1.03	0.4	0.79	56
Winter	1.03	0.3	0.85	14
Winter high				
Winter low	1.06	0.0	0.99	14
Summer	1.02	0.4	0.81	43
Summer high				
Summer low	1.04	0.3	0.97	42

Vivian Place	RMA			
BAM - Partisol	Slope	Intercept	R^2	No. of data points
All	0.88	1.7	0.93	144
All high	0.78	5.6	0.90	100
All low	0.95	0.0	0.72	44
Winter	0.89	1.1	0.94	88
Winter high	0.80	4.3	0.92	76
Winter low	0.90	0.0	0.99	12
Summer	0.91	1.8	0.89	56
Summer high	0.72	8.6	0.83	24
Summer low	0.98	0.0	0.98	32

Timaru	RMA			
TEOM vs Hi-Vol	Slope	Intercept	R^2	No. of data points
All	0.65	5.0	0.96	39
All high	0.64	5.1	0.89	18
All low	0.80	3.3	0.49	21
Winter	0.66	3.8	0.95	26
Winter high	0.64	5.1	0.89	18
Winter low	0.83	0.6	0.58	8
Summer	1.30	0.2	0.38	13
Summer high				
Summer low	1.30	0.2	0.38	13

Timaru	RMA			
TEOM-FDMS vs Hi-Vol	Slope	Intercept	R^2	No. of data points
All	1.01	-0.5	0.98	39
All high	1.10	-6.4	0.96	18
All low	0.96	0.6	0.72	21
Winter	1.04	-2.8	0.98	26
Winter high	1.10	-6.4	0.96	18
Winter low	1.13	-3.4	0.61	8
Summer	1.16	-0.8	0.38	13
Summer high				
Summer low	1.16	-0.8	0.38	13

Timaru Hi-Vol vs Hi-Vol*	RMA Slope	Intercept	R^2	No. of data points
All	1.02	2.0	1.00	40
All high	1.01	2.5	1.00	20
All low	1.11	1.2	0.86	20
Winter	1.01	2.5	1.00	26
Winter high	1.01	2.5	1.00	20
Winter low	1.16	0.9	0.77	6
Summer	0.96	2.1	0.73	14
Summer high				
Summer low	0.96	2.1	0.73	14

* These results are from one gravimetric high volume sampler but with filters analysed in two separate laboratories (one with climate control and one without).

Appendix 2: Data Set Scatter Plots

A2.1 Gravimetric vs TEOM-FDMS

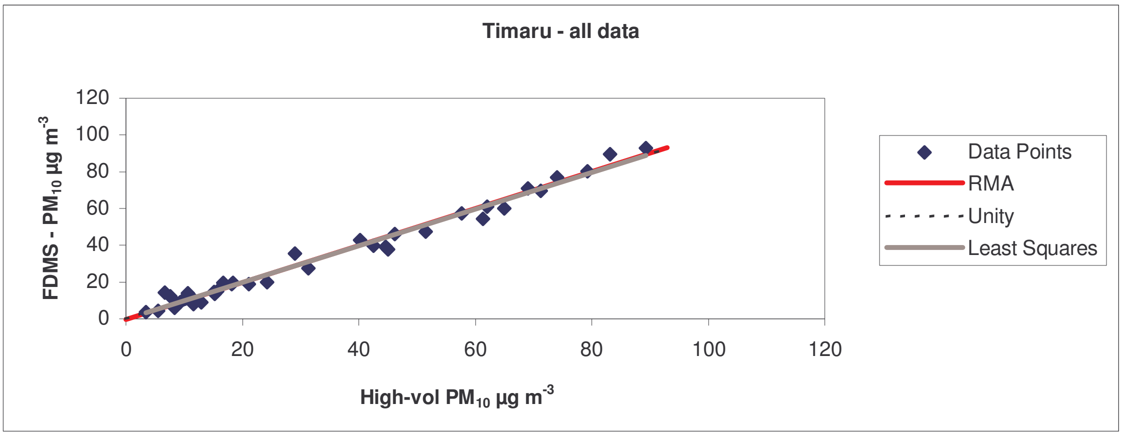


Figure A2.1: Correlation plot for 24-hour average TEOM-FDMS versus gravimetric measurements – Timaru

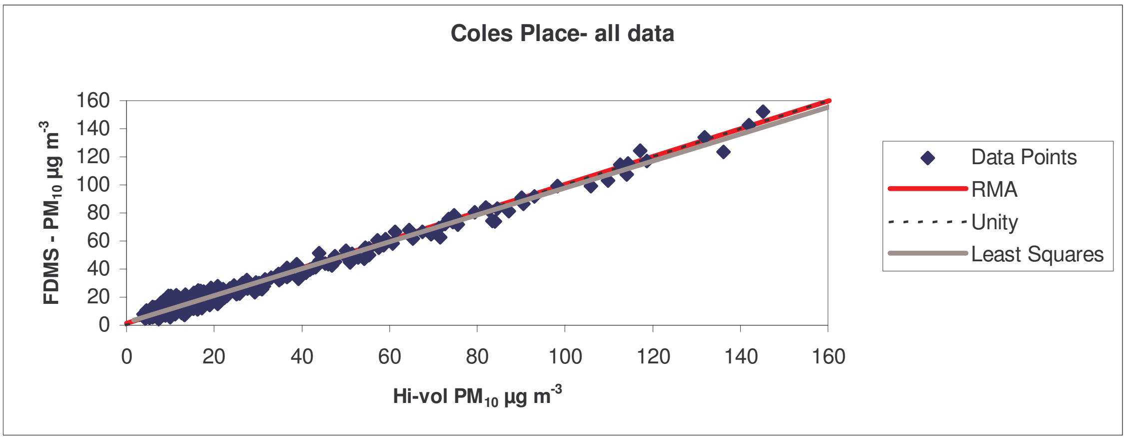


Figure A2.2: Correlation plot for 24-hour average TEOM-FDMS versus gravimetric measurements – Coles Place, Christchurch

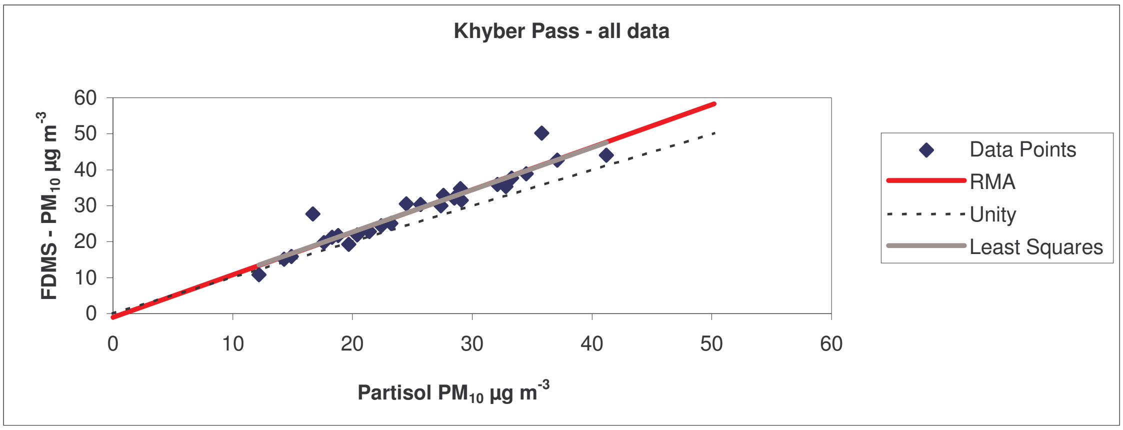


Figure A2.3: Correlation plot for 24-hour average TEOM-FDMS versus Partisol gravimetric measurements – Khyber Pass, Auckland

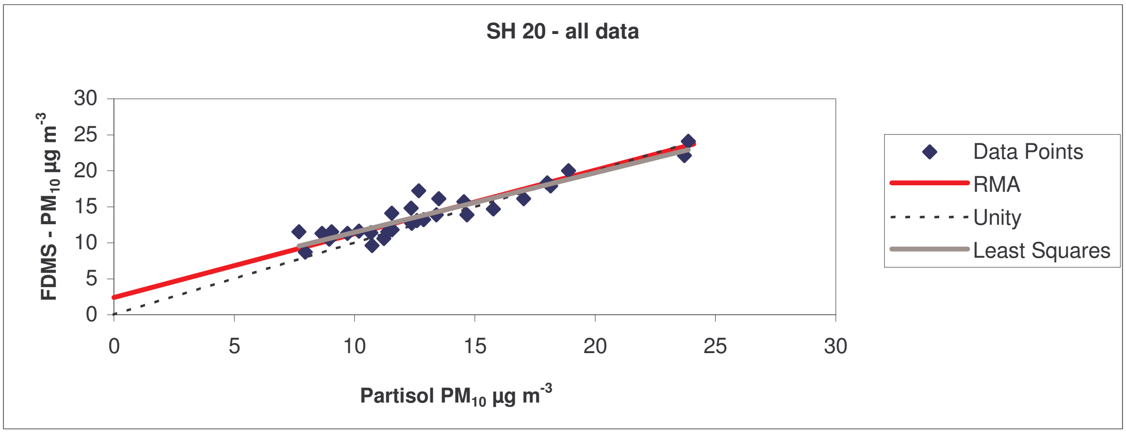


Figure A2.4: Correlation plot for 24-hour average TEOM-FDMS versus gravimetric measurements – SH20 Auckland

A2.2 Gravimetric vs TEOM(40)

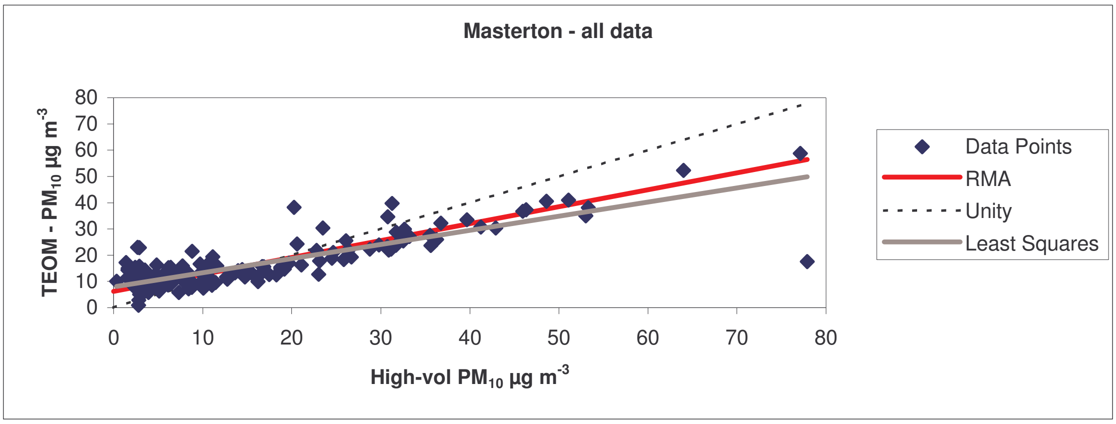


Figure A2.5: Correlation plot for 24-hour average TEOM(40) versus gravimetric measurements – Masterton

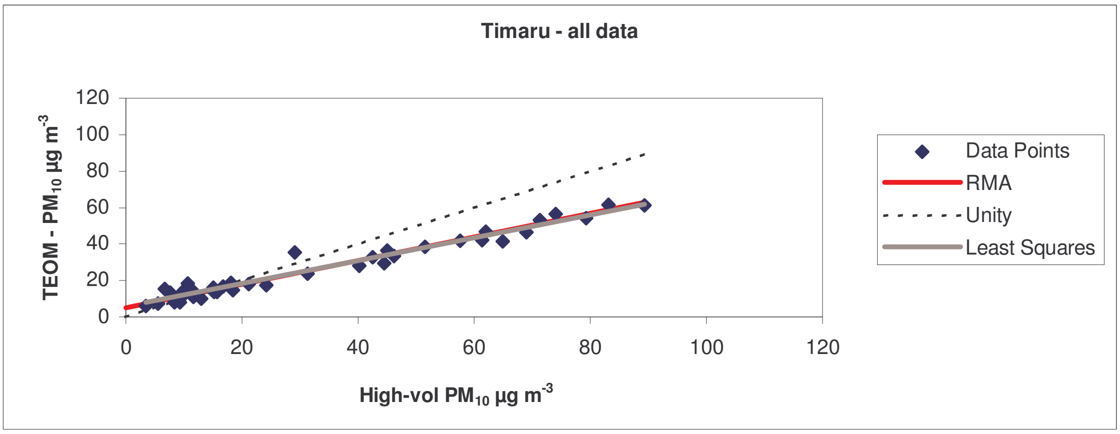


Figure 2.6: Correlation plot for 24-hour average TEOM(40) versus gravimetric measurements – Timaru

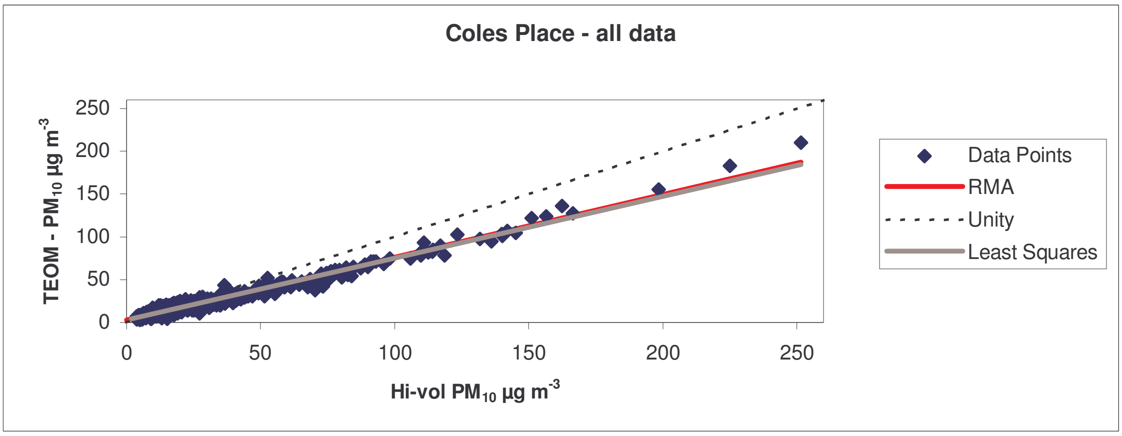


Figure A2.7: Correlation plot for 24-hour average TEOM(40) versus gravimetric measurements – Coles Place, Christchurch

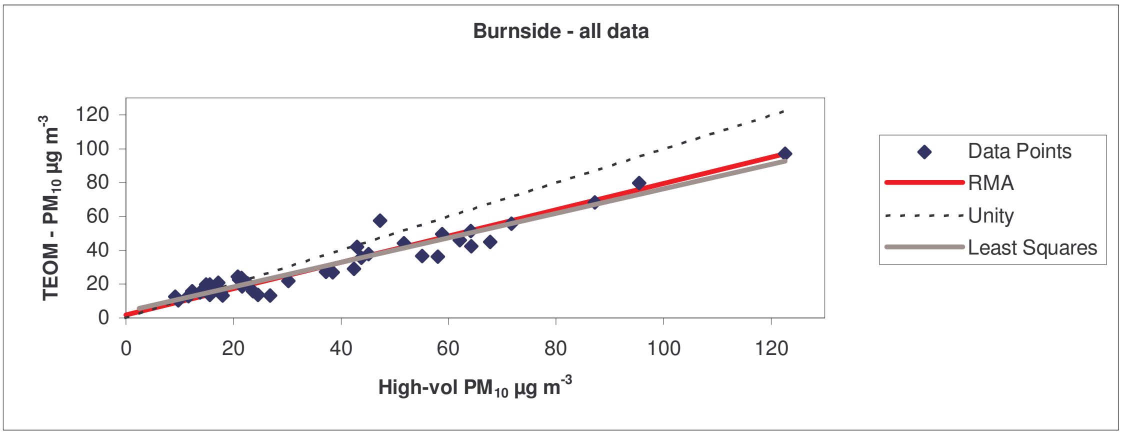


Figure A2.8: Correlation plot for 24-hour average TEOM(40) versus gravimetric measurements – Burnside, Christchurch

A2.3 Gravimetric vs BAM

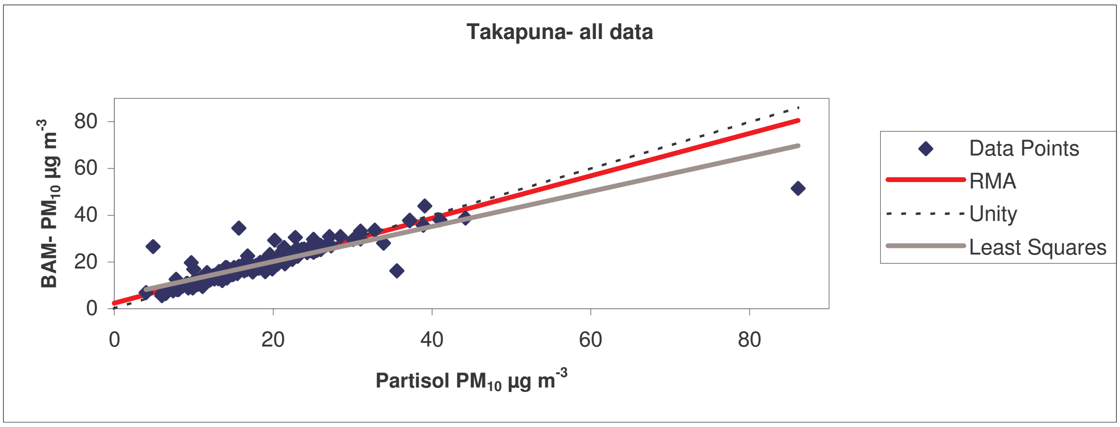


Figure A2.9: Correlation plot for 24-hour average BAM versus gravimetric measurements – Takapuna, Auckland

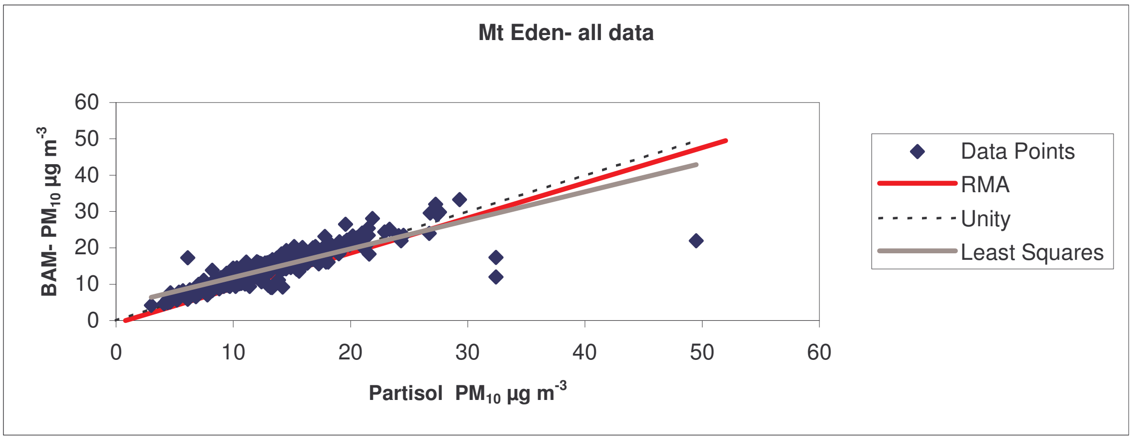


Figure A2.10: Correlation plot for 24-hour average BAM versus gravimetric measurements – Mount Eden, Auckland

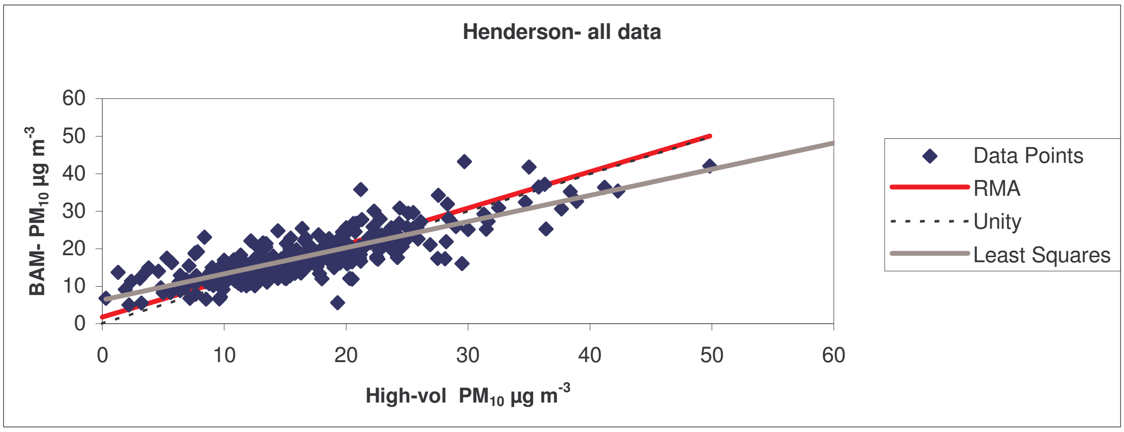


Figure A2.11: Correlation plot for 24-hour average BAM versus gravimetric measurements – Henderson, Auckland

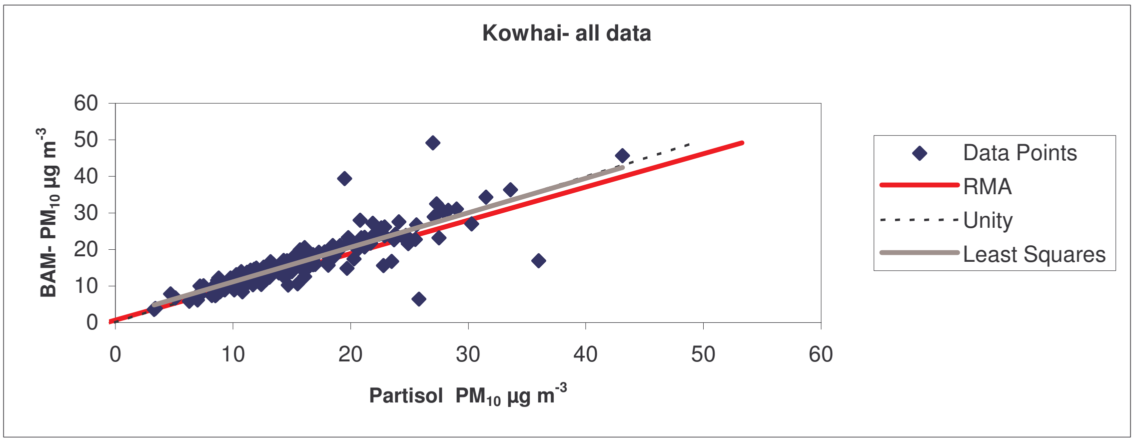


Figure A2.12: Correlation plot for 24-hour average BAM versus gravimetric measurements – Kowhai, Auckland

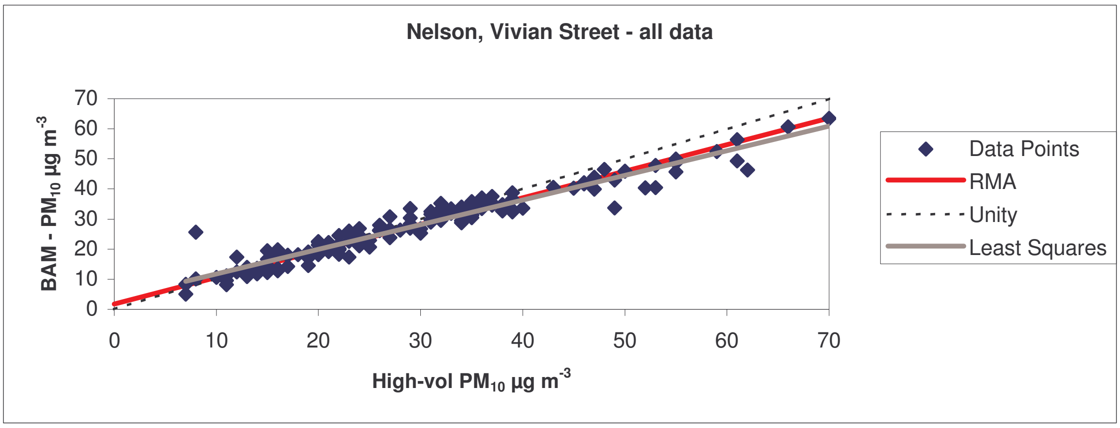


Figure A2.13: Correlation plot for 24-hour average BAM versus gravimetric measurements – Vivian Street, Nelson

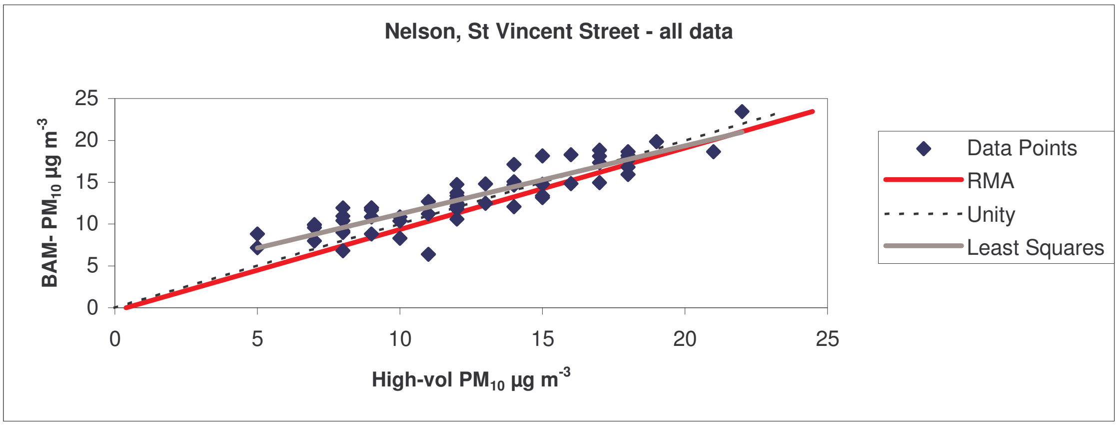


Figure A2.14: Correlation plot for 24-hour average BAM versus gravimetric measurements – St Vincent Street, Nelson

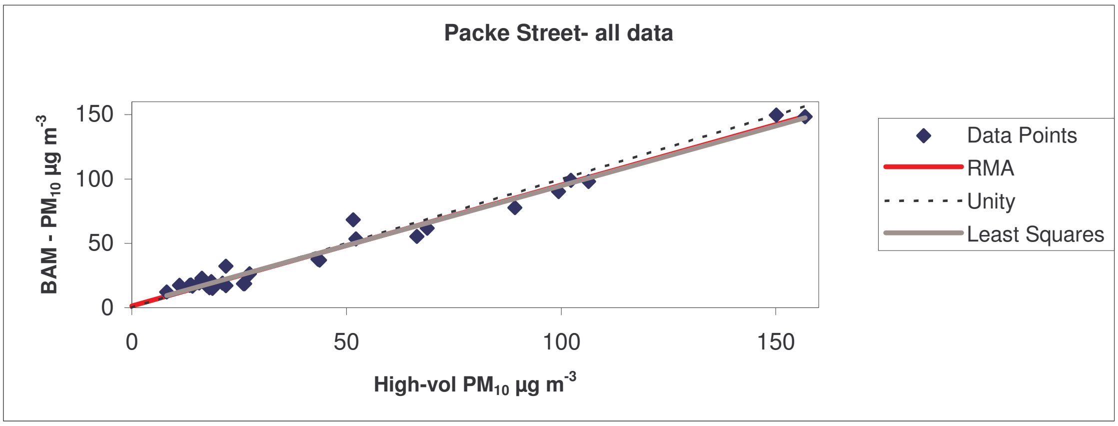


Figure A2.15: Correlation plot for 24-hour average BAM versus gravimetric measurements – Packe Street, Christchurch

Note – this BAM does not have a heated inlet

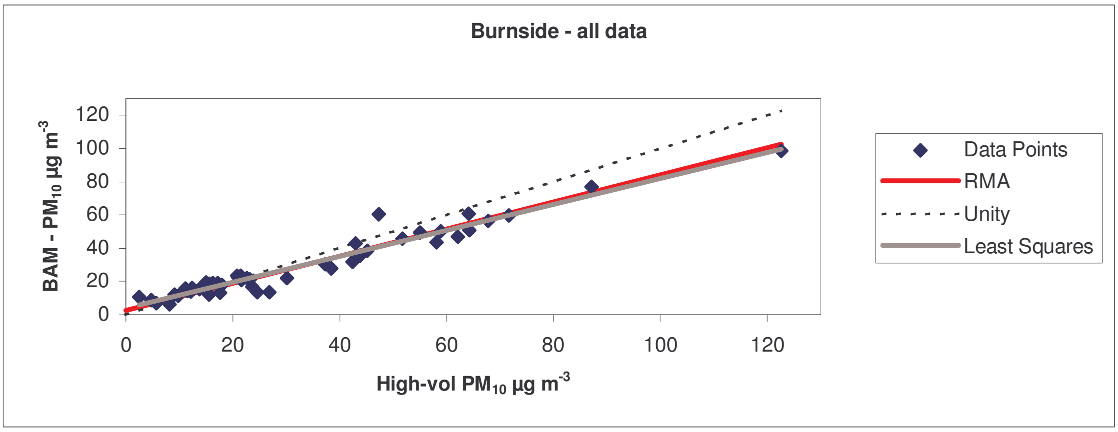


Figure A2.16: Correlation plot for 24-hour average BAM versus gravimetric measurements – Burnside, Christchurch

Appendix 3: Analysis of TEOM(50) Data

Summary tables were prepared for each data set. RMA results are shown in the following data tables based on season, concentration (high > 20 µg m^{-3} , low < 20 µg m^{-3}) and season and concentration. R^2 values are only shown if at least 6 data points were used.

Packe Street TEOM50 vs Hi-vol	RMA Slope	Intercept	R2	No. of datapoints
All	0.61	2.0	0.96	28
All high	0.56	6.9	0.93	13
All low	0.70	-0.4	0.22	15
Winter	0.61	2.0	0.96	28
Winter high	0.56	6.9	0.93	13
Winter low	0.68	-0.1	0.91	15

Mt Eden TEOM - Partisol	RMA Slope	Intercept	R2	No. of data points
All	1.03	0.4	0.63	50
All high	0.66	8.9		5
All low	1.02	0.5	0.58	45
Winter	1.07	0.1	0.80	22
Winter high	0.30	17.8		3
Winter low	1.07	0.0	0.80	19
Summer	0.98	0.7	0.56	28
Summer high	0.21	16.3		2
Summer low	0.97	0.7	0.91	26

Penrose TEOM - High-vol	RMA Slope	Intercept	R2	No. of data points
All	1.00	1.8	0.08	55
All high	0.54	17.2	0.52	30
All low	0.65	1.4	0.16	25
Winter	1.03	1.7	0.20	44
Winter high	0.55	16.9	0.54	24
Winter low	0.75	0.8	0.16	20
Summer	0.88	2.3	0.14	11
Summer high	0.45	19.2		6
Summer low	0.45	1.7		5

Takapuna TEOM - High-vol	RMA Slope	Intercept	R2	No. of data points
All	0.92	2.1	0.60	142
All high	0.56	11.5	0.47	43
All low	0.98	0.9	0.35	99
Winter	0.86	2.9	0.70	91
Winter high	0.60	8.8	0.62	26
Winter low	1.01	0.4	0.11	39
Summer	1.12	0.1	0.35	78
Summer high	0.84	8.5	0.23	17
Summer low	1.04	0.3	0.93	61

A3.1 All data

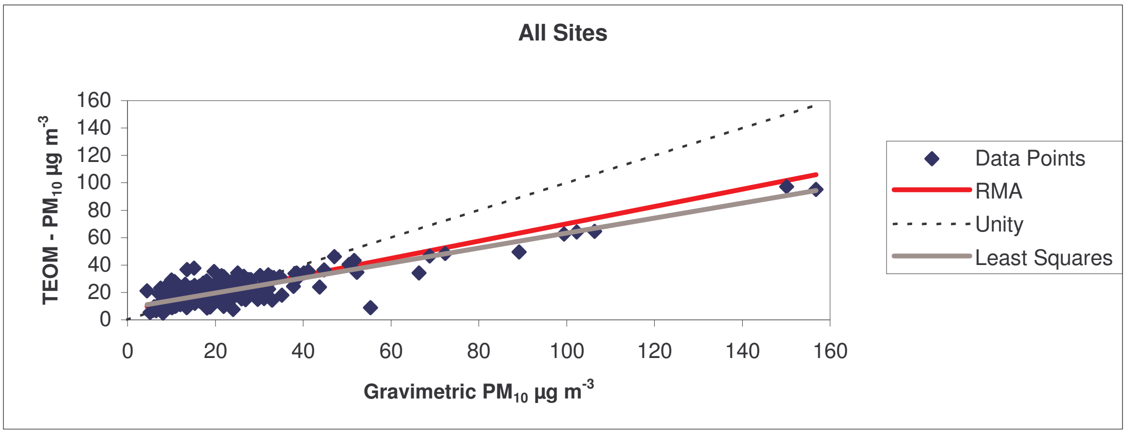


Figure A3.1: Correlation plot for 24-hour average TEOM(50) versus gravimetric measurements – all data

A3.2 Effect of Season

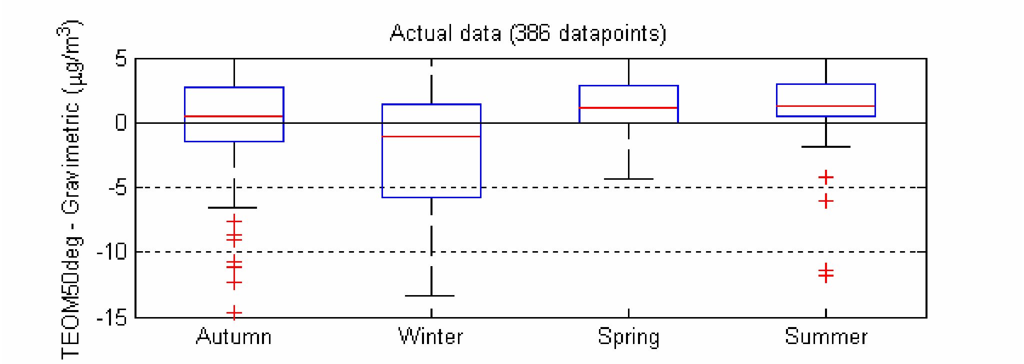


Figure A3.2: Residuals of 24-hour average TEOM(50) to gravimetric measurements by season

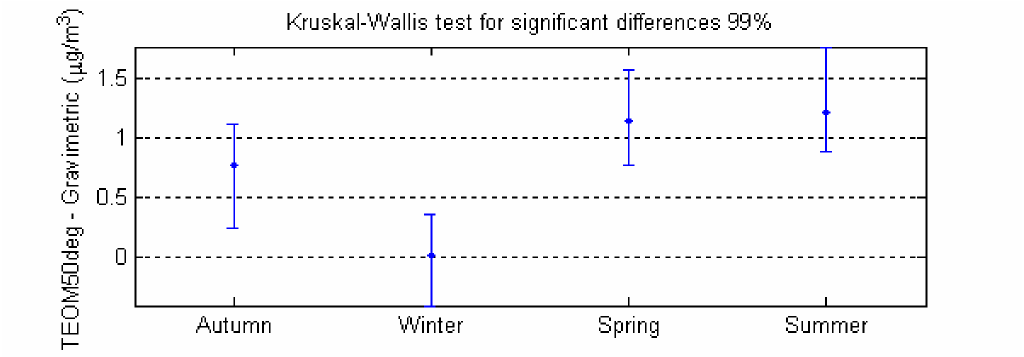


Figure A3.3: Kruskal-Wallis test for significance of season at the 99% confidence level for 24-hour average TEOM(50) versus gravimetric residuals

A3.3 Effect of Location

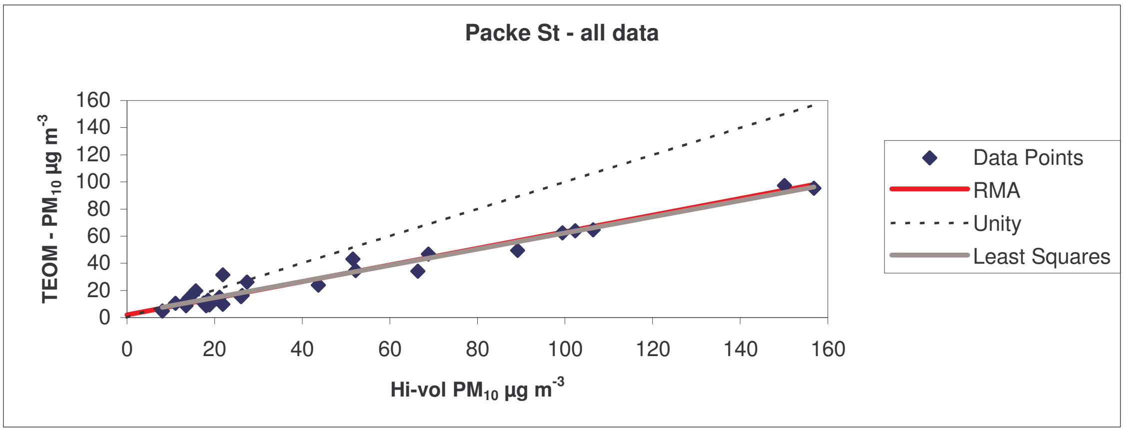


Figure A3.4: Correlation plot for 24-hour average TEOM(50) versus gravimetric measurements – Packe Street, Christchurch.

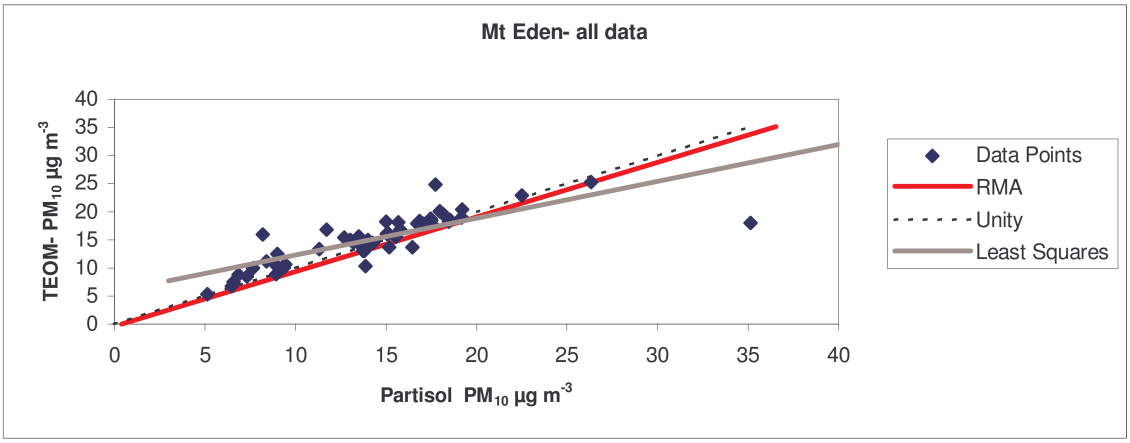


Figure A3.5: Correlation plot for 24-hour average TEOM(50) verses gravimetric measurements – Mt Eden, Auckland

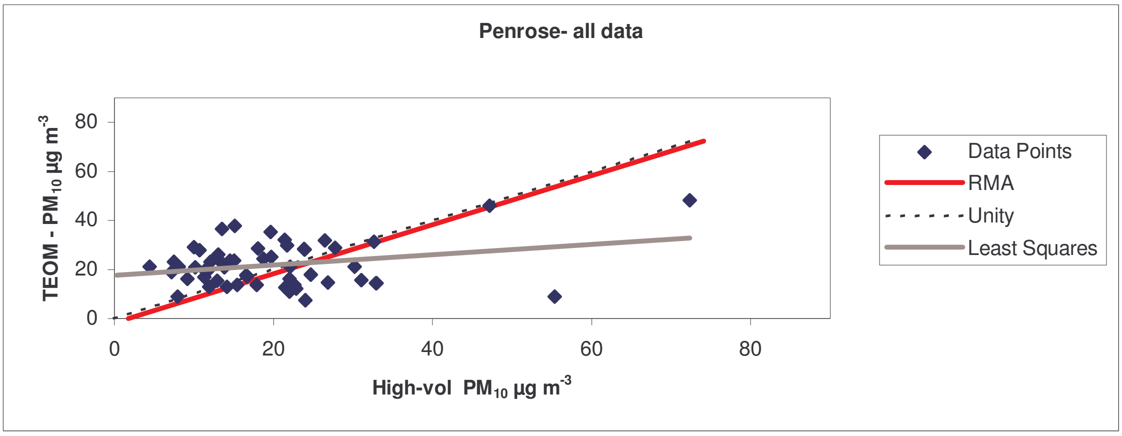


Figure A3.6: Correlation plot for 24-hour average TEOM(50) versus gravimetric measurements – Penrose Auckland

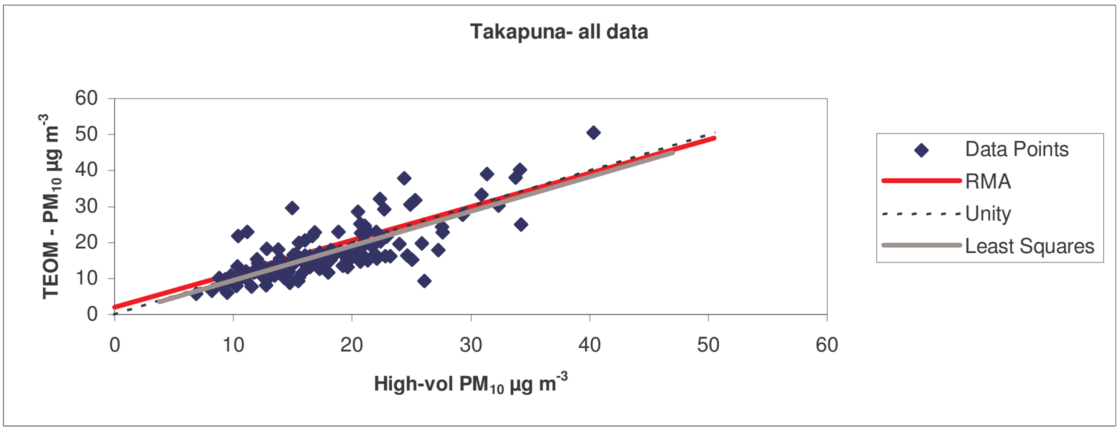


Figure A3.7: Correlation plot for 24-hour average TEOM(50) versus gravimetric measurements – Takapuna, Auckland

A3.3 Effect of Location

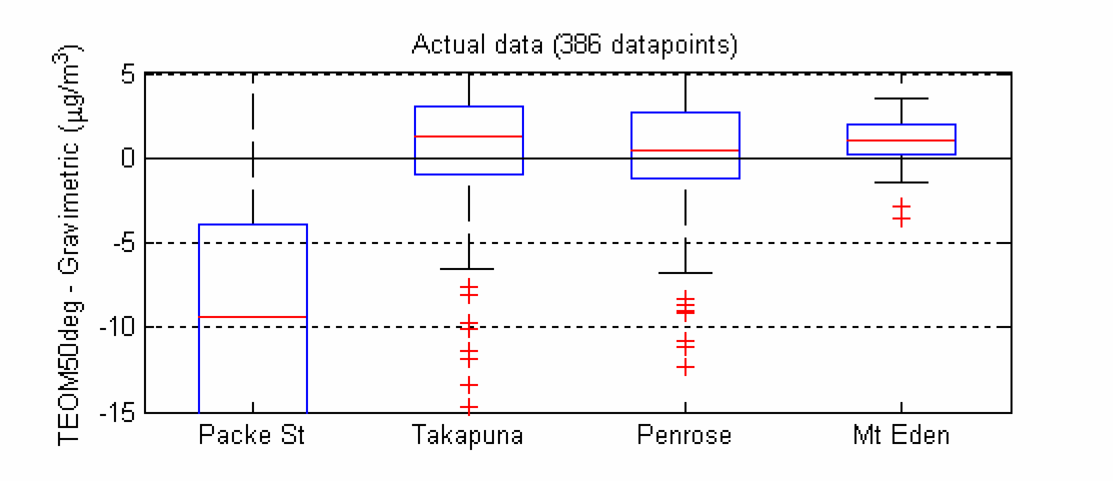


Figure A3.8 Residuals of 24-hour average TEOM(50) to gravimetric measurements by site

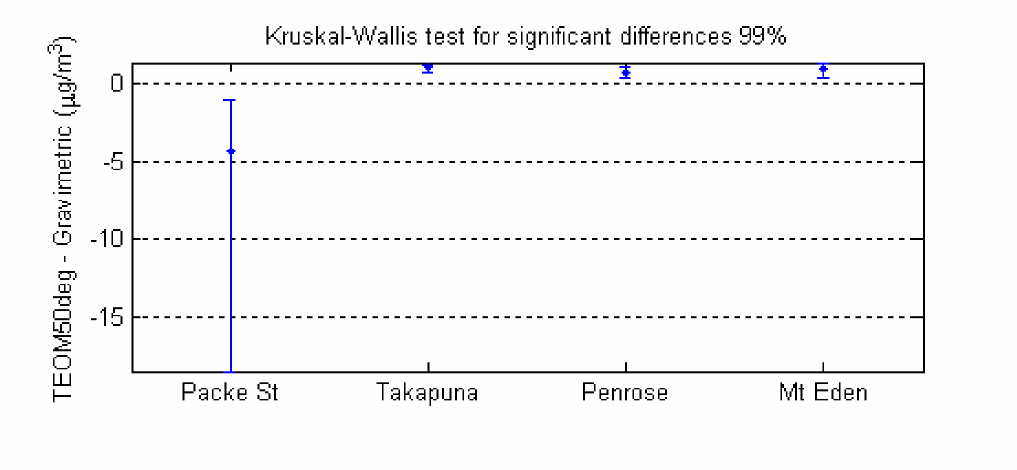


Figure A3.9: Kruskal-Wallis test for significance of site at the 99% confidence level for 24-hour average TEOM(50) versus gravimetric residuals

A3.4 Effect of Meteorological factors for TEOM(50)

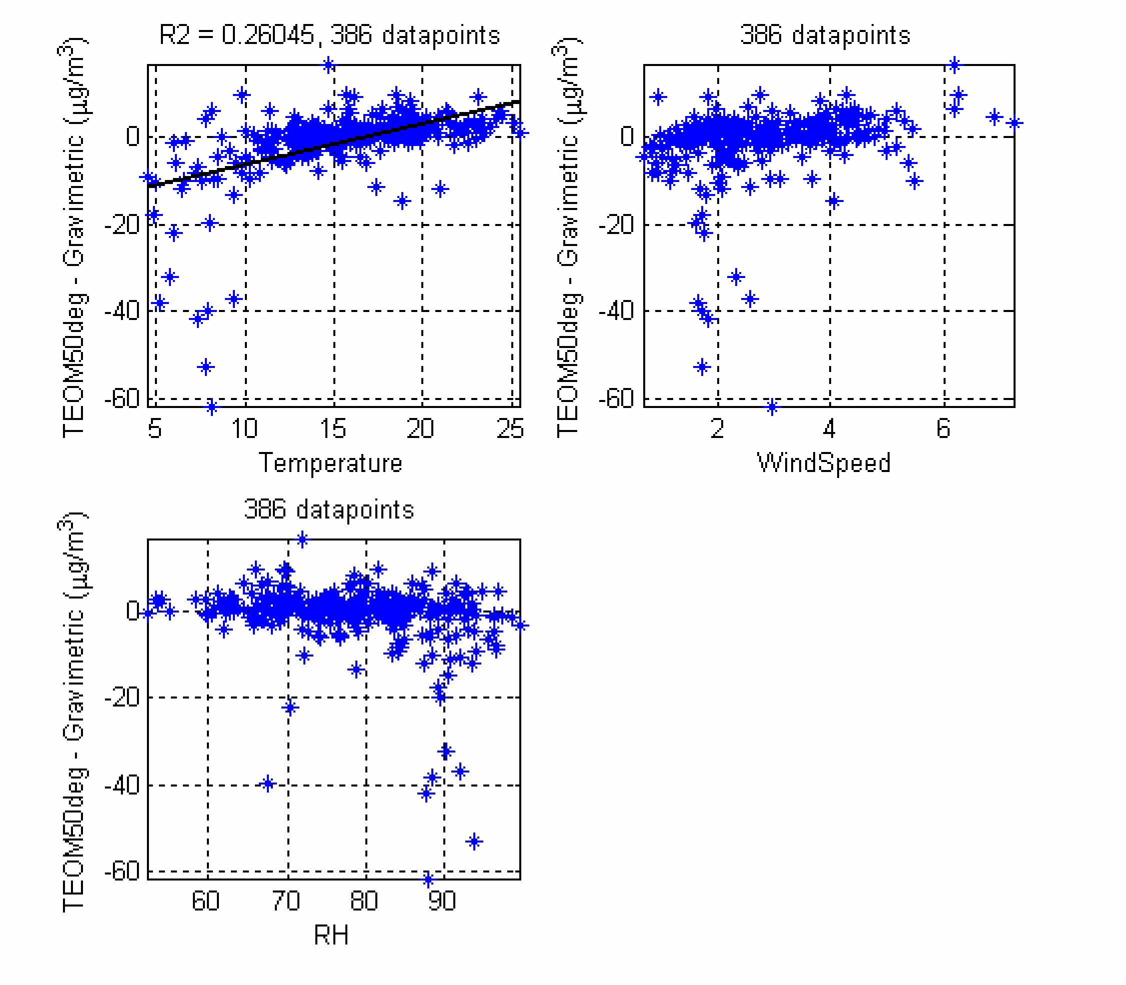


Figure A3.10: Variation of the residuals of 24-hour average TEOM(50) and gravimetric measurements with temperature, wind speed and relative humidity

A3.5: Adjustment Factors for TEOM(50) data.

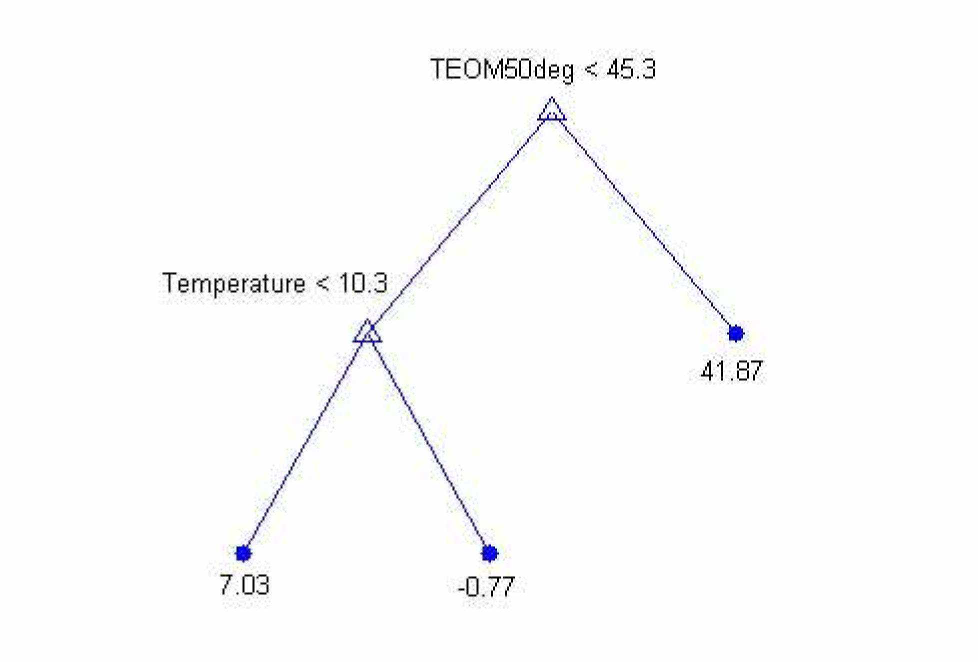


Figure A3.11: Regression Tree for TEOM(50) data with TEOM(50) data and ambient temperature as predictor variables.

TEOM(50) >45 add 41.87

TEOM(50)<45 and temperature <10.3 add 7.03

TEOM(50)<45 and temperature >10.3 subtract 0.76

Appendix 4: Gravimetric Method Comparisons

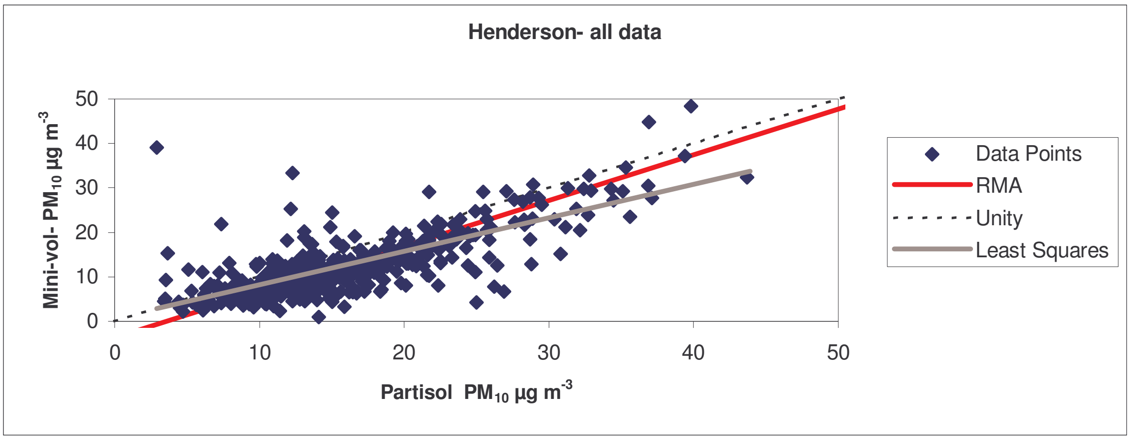


Figure A4.1: Correlation plot for 24-hour average Partisol versus Mini-vol gravimetric measurements – Henderson Auckland

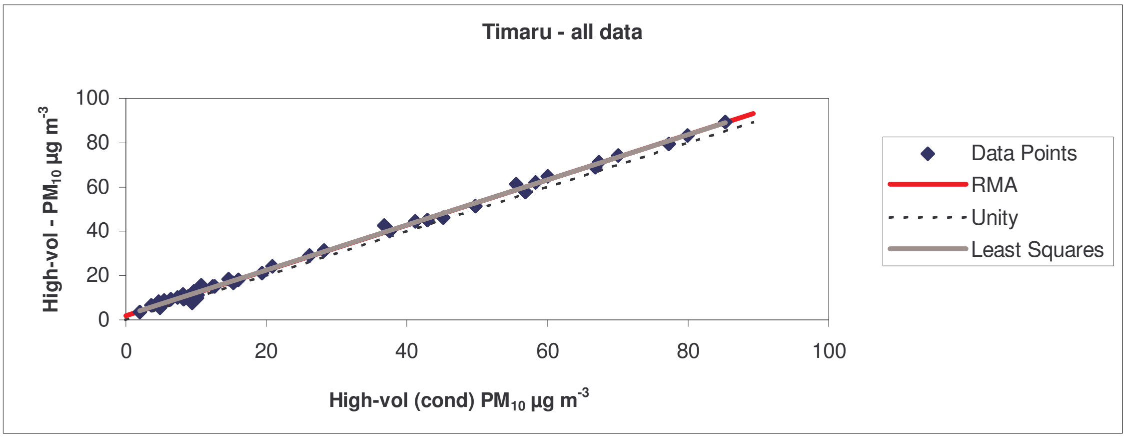


Figure A4.2: Correlation plot for 24-hour average Hi-vol concentrations – Timaru. N.B. the gravimetric analysis on each filter was done twice by two different laboratories, one with climate control and one without.

Appendix 5: Descriptions of Monitoring Site Types

Table A5.1 outlines different site classifications used for air quality monitoring sites in New Zealand.

Table A5.1: Monitoring site descriptions and scales (MfE, 2000)

Recommended Site Category (EPI)	Site Scale Equivalent (AS)	Typical Area
Recommended Site Category	Site Scale Equivalent (AS)	Typical Area
Traffic	Peak1 (metres to 10s of metres)	Typically very close to high traffic use roads and intersections. Site should be between 2 to 5 metres from the roadside.
Industrial	Peak (metres to 10s of metres) or Dense2 (10s of metres to 0.5 km)	Peak - close to one large point source or fugitive emissions- typically used for compliance monitoring. Dense - with large and varied point source industry emissions, and high population density. Such areas may contain heavy commercial and processing industries.
Residential	Peak (metres to 10s of metres) or Neighbourhood3 (0.5 to 10s of kilometres)	Peak - a monitoring site located somewhere not truly representative (so it's not neighbourhood scale) but does not exactly fit the "traffic' or 'industrial' peak site descriptions. Neighbourhood - suburban areas in larger cities with a relatively high population density, but not in the immediate vicinity of congested roads or industry. This category also includes residential areas in smaller rural areas.
Special (site description)	Regional4 10s to 100s of kilometres	Airsheds which are distinct in their geographical, meteorological and emissions characteristics. Included are the effects of any point sources or urban plumes on the regional air quality. Could include places where natural emissions are significant, eg, Rotorua in which case the category would be Special (Geothermal).
Special (site description)	National5	National background sites which contribute to the global network.

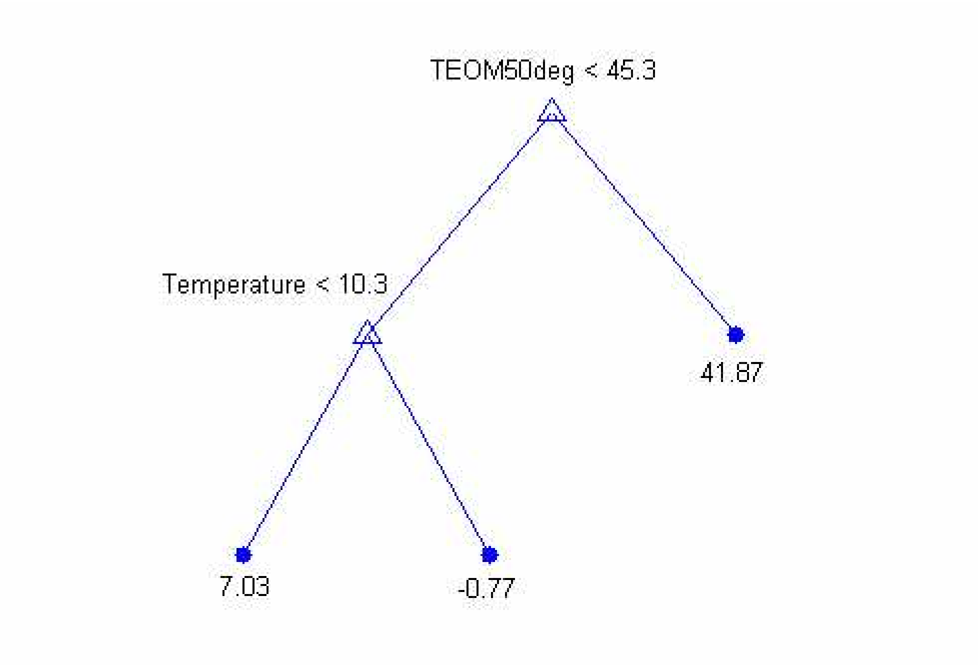
1. The Peak scale is used here in a slightly different way to Peak scales elsewhere. It is needed in New Zealand to describe monitoring, which is conducted in truly peak areas, such as road intersections.
2. The Dense scale includes the US's Micro and Middle scales (USEPA, 1992), and is identical to the Australian Peak scale (AS 2922,1987). Dense rather than Peak is used because the scale peak (highest concentration) measurements are made on depends on the contaminant.
3. The Neighbourhood scale includes the US's Neighbourhood and Urban scales (USEPA, 1992), and is identical to the Australian Neighbourhood scale (AS 2922, 1987).
4. The Regional scale is the same as the US's Regional scale (USEPA, 1992), and is identical to the Australian Background scale (AS 2922, 1987). Regional rather than Background is used because the scale background measurements are made on depends on the scale of concern.
5. The National scale is the same as the US's National scale (USEPA, 1992)

Appendix 6: Description of Multivariate Regression Trees

We used tree model function in Matlab to find whether any of the available variables explained the observed differences between PM measurement methods. Tree models make few assumptions about variable data distribution and relationships. The response variable (the variable we want to explain) is the adjustment required to the TEOM50 data. The predictor variables (the variables we would like to use to do the explaining) are the TEOM50 data itself and season.

Example of outputs:

Graphical example of a tree model:



Basic interpretation of this tree model:

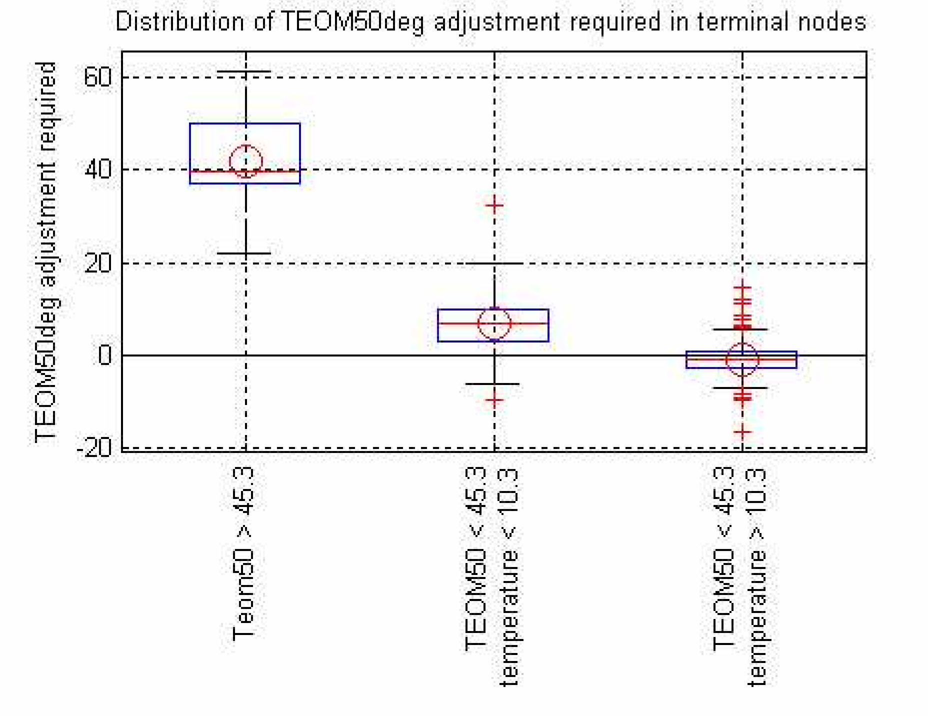
This tree clusters the data into 3 groups (there are 3 terminal nodes on the tree). The average values of adjustment required to the TEOM50 data in each group are shown below each terminal node. The clustering criteria are defined by the predictor variables (TEOM50 and temperature).

More detailed reading of the tree model:

All data starts in one big group at the top node. The first split is " TEOM50deg < 45.3". Data for which this condition is true (lower Teom50 readings) go left. All other data (higher TEOM50 readings) go right. The right node does not split again and these data have an average adjustment value of 41.87. The data that went left are next split on temperature. Data for which the temperature condition is true (low temperatures) go left and require an average adjustment of 7.03. All other data go right and required an average adjustment of -0.77.

The tree can be used to make a prediction about the likely adjustment required for some new TEOM50 data. Let's take a new TEOM50 measurement of 40 µg/m^3 taken when the temperature is 15 degrees. This data starts at the top of the tree. The first criteria (TEOM50<45.3) is true so the data moves left. The next criteria (temperature < 10.3) is false so the data goes right. The predicted adjustment is given by the average value of this group i.e. subtract 0.77.

The figure below shows the range of response (required adjustment) values in each of the 3 groups formed by the tree.



The adjustment required is largest in the group containing high TEOM50 values because this is where the TEOM50 under-measures by the largest amount. The middle group under-measures slightly so requires a small positive adjustment and the last group requires very little adjustment.

Appendix 7: Results of the Kruskal-Wallis Test for Significant Difference

The following figures show the results of the Kruskal-Wallis test for significant difference of season at the 99% confidence level (CL). If the blue confidence interval bars **do not** overlap, then the difference between the seasons is significant. If the bars **do** overlap there is no significant difference at the 99% CL. These figures can only be used to determine if there is a significant difference between seasons. The bars do not give a good indication of the true range of the data. That information is provided in the graphs in Section 5.2.

A7.1: Effect of Season

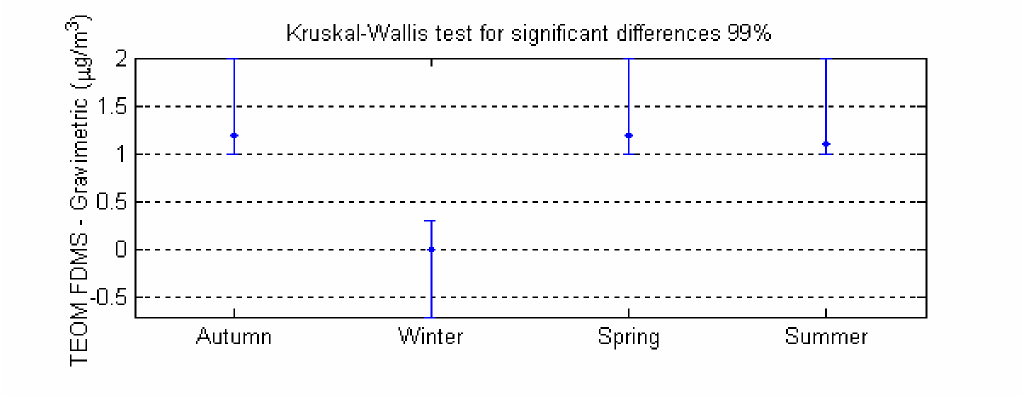


Figure A7.1: Kruskal-Wallis test for significant difference of season at the 99% confidence level for 24-hour average TEOM-FDMS to gravimetric residuals

Figure A7.1 shows that the performance of the TEOM-FDMS varies with season. Winter performance is significantly different to spring and summer and autumn (the blue bar for winter does not overlap the blue bars for the other three seasons). Spring, summer and autumn are not significantly different from each other (their blue lines overlap).

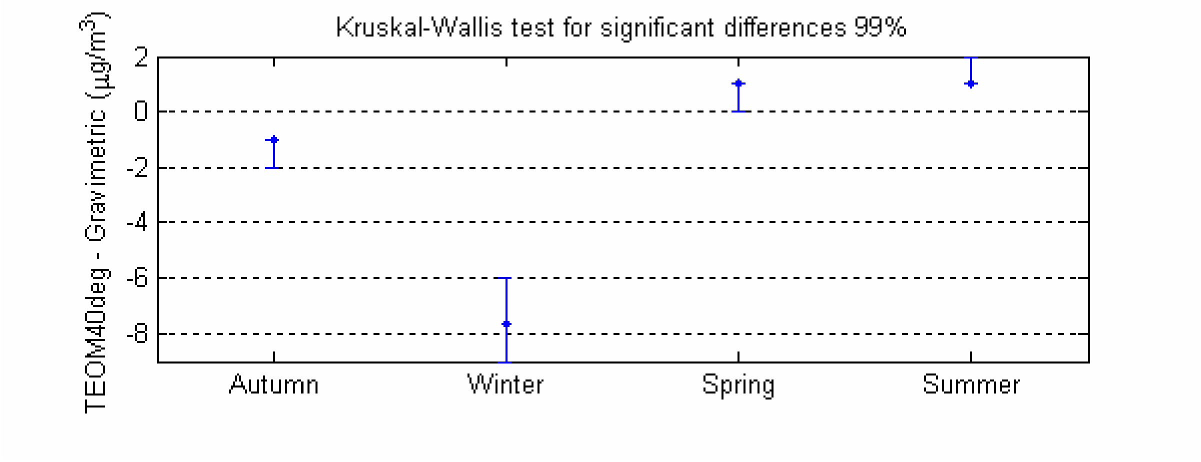


Figure A7.2: Kruskal-Wallis test for significant difference by season at the 99% confidence level of 24-hour average TEOM(40) to gravimetric residuals

Figure A7.2 shows that the performance of the TEOM(40) is significantly different in all four seasons.

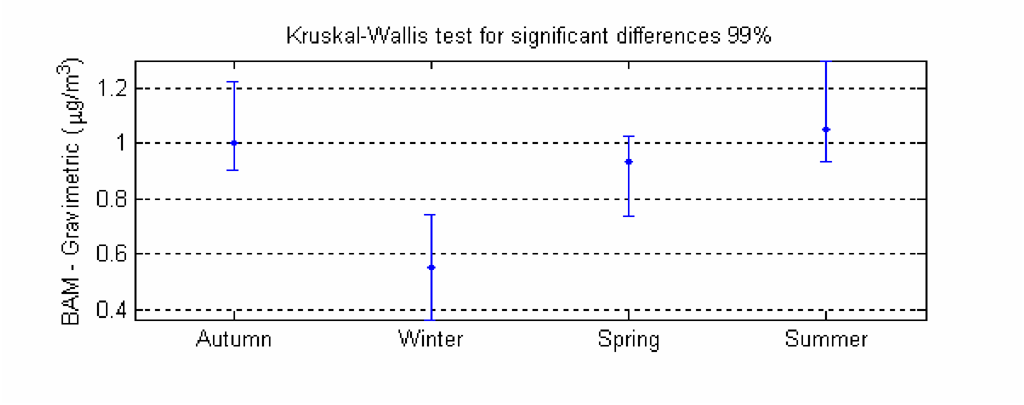


Figure A7.3: Kruskal-Wallis test for significant difference by season at the 99% confidence level of 24-hour average BAM to gravimetric residuals

Figure A7.3 shows that the performance of the BAM compared to gravimetric varies with season. Winter is significantly different to autumn and summer. But there is no significant difference between the performance of the BAM compared to gravimetric during autumn, spring and summer.

A7.2 Effect of Location

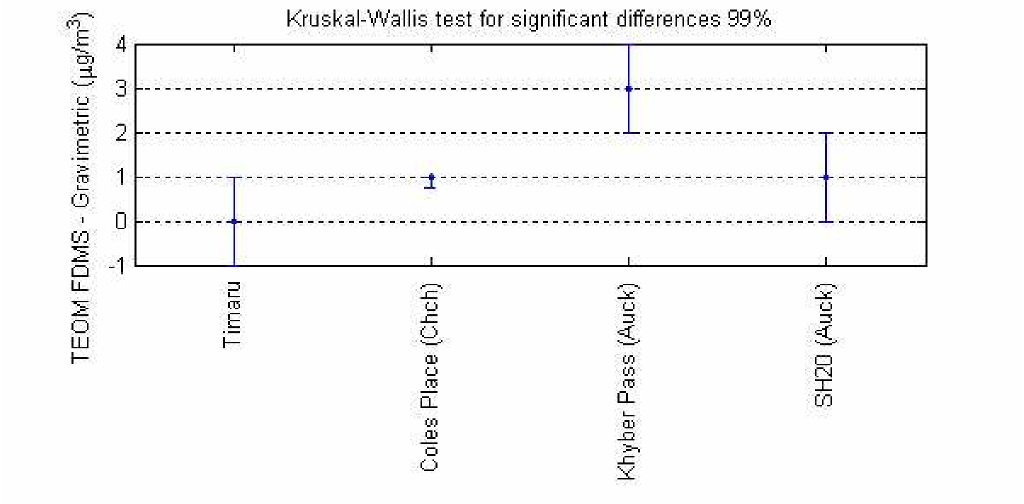


Figure A7.4: Kruskal-Wallis test for significant difference of site at the 99% confidence level for 24-hour average TEOM-FDMS to gravimetric residuals

Figure A7.4 shows that. Khyber Pass measurements are significantly different to those taken at the other three 3 sites, which cannot be distinguished from each other.

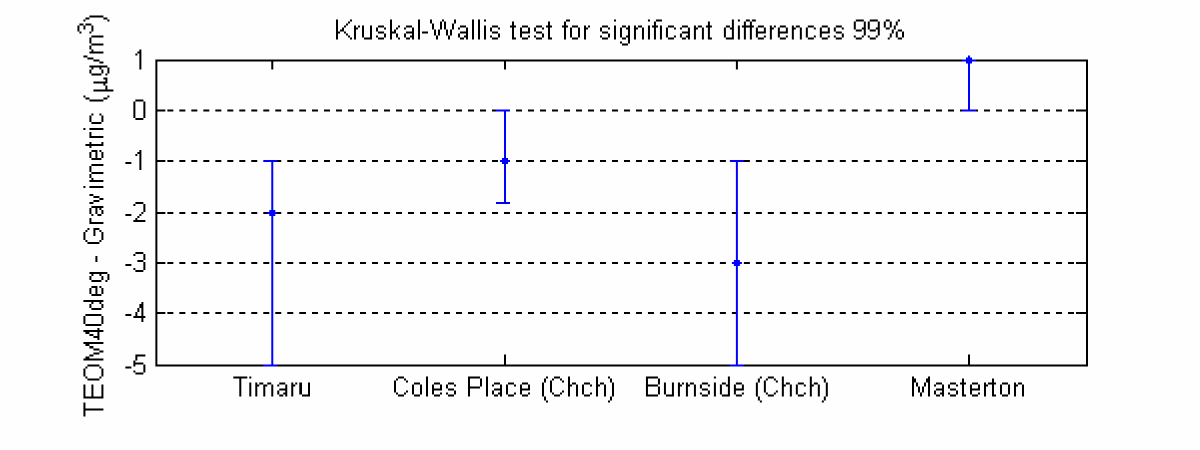


Figure A7.5: Kruskal-Wallis test for significant difference by site at the 99% confidence level of 24-hour average TEOM(40) to gravimetric residuals

Figure A7.5 show that the relationship between the TEOM(40) and gravimetric methods appears to differ with location. However, with the exception of the Masterton, the differences are not statistically significant.

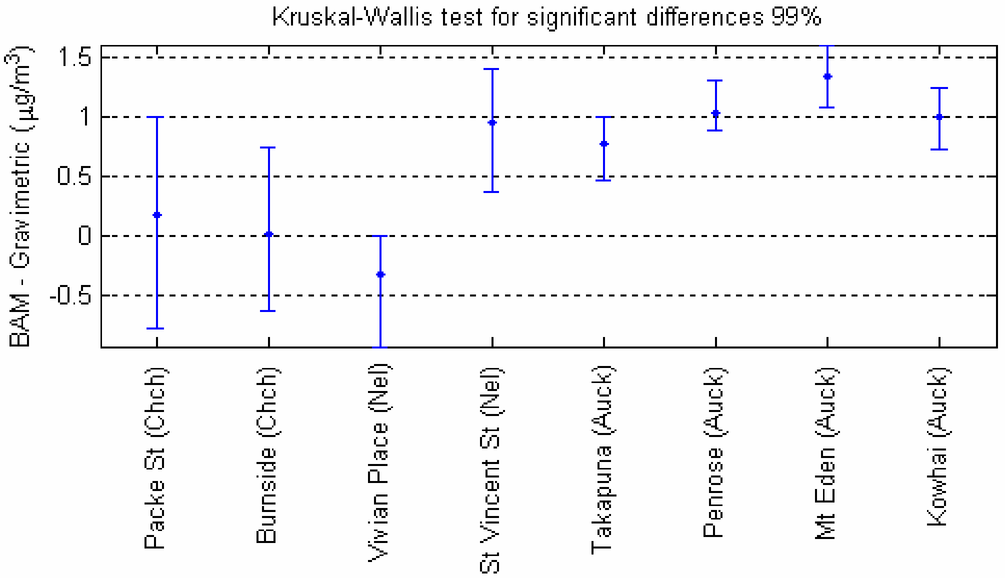


Figure A7.6: Kruskal-Wallis test for significant difference by locatoin at the 99% confidence level of 24-hour average BAM to gravimetric residuals

Figure A7.6 shows that the under-measurement observed at the Christchurch - Burnside and Nelson -Vivian Place locations is significantly different to the over-measurement observed at the two Auckland locations - Penrose and Mount Eden. The performance of the BAMs at the other two Auckland locations – Takapuna and Kowhai, Nelson – St Vincent Street and Christchurch – Packe Street is not significantly different to the groups of instruments which have stronger tendencies to under- or over-measure.