



Source Apportionment of PM₁₀ in Blenheim.

Marlborough District Council

Acknowledgement

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Executive Summary

The purpose of this report was to determine background contributions to PM₁₀ concentrations in Blenheim by using receptor modelling source apportionment. The research was funded by the FRST funded EnviroLink programme and Marlborough District Council.

The method involves measuring concentrations of chemical elements in particulate matter collected on a filter and the application of statistics to determine the contributions of different sources. The filter measurements included PM₁₀ collected over a 24-hour period from midnight to midnight, intermittently from June 2006 to August 2007 using a GENT PM₁₀ sampler. Marlborough District Council staff collected around 120 samples. Data were analysed using the EPA.PMF 1.1 source apportionment software.

In Blenheim, five main sources were found to contribute to the PM₁₀ concentrations. These were identified as domestic heating, sea salt, sulphate, and two soil profiles, one of which was mixed with combustion and had high concentrations of K and Ca. For this report, domestic heating sources also include outdoor burning of domestic waste biomass. The main contributor to PM₁₀ concentrations in Blenheim was domestic heating, which was responsible for 71% of the daily winter average concentrations and typically 78% of the PM₁₀ on high pollution days.

The study also evaluated the contributions of natural sources to PM₁₀ concentrations in Blenheim. During winter around 5% of the PM₁₀ on average was from sea salt and 10% from soil. The average natural source contribution on days when PM₁₀ concentrations breached the NES during the study period was 11%. This suggests that around 6 µg m⁻³ of PM₁₀ may come from these sources on days when PM₁₀ concentrations are around 50 µg m⁻³. It is uncertain whether the sulphate originates from natural or anthropogenic sources.

This information is particularly relevant for air quality managers in Blenheim because the background component of the PM₁₀ is essentially unmanageable, yet needs to be accounted for when developing models and strategies for mitigating PM₁₀ concentrations.

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1 Introduction

The National Environmental Standard for air quality (NES) requires that ambient concentrations of particulate smaller than 10 microns (PM₁₀) shall not exceed 50 µg m⁻³ when averaged over 24 hours. In airsheds where the NES is not met by 2013, the Marlborough District Council (MDC) will not be able to issue resource consents for discharges to air. At present, Blenheim is the only airshed in Marlborough known to exceed the NES for PM₁₀.

Work has already been undertaken by MDC towards the development of a management framework to improve air quality in Blenheim. An emissions inventory was undertaken in 2005 to determine the sources of PM₁₀ concentrations (Wilton, 2005) as well as an assessment of the management options to reduce PM₁₀ concentrations in Blenheim (Wilton, 2006).

In this report further work is undertaken using source apportionment to identify the relative contributions of background and anthropogenic sources of PM₁₀ to assist with the development of a management framework to reduce PM₁₀ concentrations in Blenheim.

1.1 Air Quality Monitoring

Historically, air quality monitoring has been carried out at a number of sites in Blenheim. The main contaminant of concern has been identified as PM₁₀. The longest record of PM₁₀ data (2000 to 2007) is available from the Middle Renwick Road monitoring site. Only two breaches of 50 µg m⁻³ have been measured at the Middle Renwick Road monitoring site.

An additional monitoring site was established in Redwoodtown in 2002. This became a permanent monitoring site in 2005 and in 2006 became an NES compliant¹ PM₁₀ monitoring site as PM₁₀ concentrations in this locality are higher than at Middle Renwick Road. In addition, some survey monitoring for PM₁₀ was carried out in Renwick during 2002. Other air quality monitoring in Blenheim includes visibility surveys and passive sampling for nitrogen oxides and sulphur oxides.

The frequency of PM₁₀ breaches in Blenheim ranges from around 10 to 34 per year, and depends largely on the prevalence of meteorological conditions conducive to elevated pollution. In Blenheim PM₁₀ concentrations in excess of the NES occur during the winter months when low wind speeds and temperature inversions trap pollution near the earth's surface.

¹ The NES specifies appropriate monitoring methods and sampling protocols and frequencies.

Table 1.1 shows summary details of PM₁₀ concentrations measured at the Redwoodtown air quality monitoring site since 2002.

Table 1.1: Summary of PM₁₀ concentrations measured at Redwoodtown from 2002-2006

	2002	2003	2004	2005	2006
"Good" 0-33% of guideline	18%	22%	46%	63%	66%
"Acceptable" 33-66% of guideline	62%	30%	22%	17%	21%
"Alert" 66-100% of guideline	10%	26%	20%	17%	10%
"Action" >Guideline	10%	22%	12%	3%	3%
Percentage of valid data	14%	7%	22%	32%	68%
Annual average ($\mu\text{g m}^{-3}$)	-	-	22	18	17
Measured exceedences	5	6	10	3	6
Guideline exceedences (extrapolated for missing data)	16	34	31	9	10
Annual maximum ($\mu\text{g m}^{-3}$)	58	60	81	58	59

1.2 Emissions inventory

An emissions inventory to determine the sources of PM₁₀ in Blenheim was undertaken in 2005 (Wilton 2005b). The results indicated that domestic home heating is the main source of PM₁₀ emissions, contributing around 85% of the daily wintertime PM₁₀ (Wilton, 2005b). Other sources of PM₁₀ in the urban areas of Blenheim include outdoor burning (6%), motor vehicles (7%) and industry (2%).

As part of the inventory work, a domestic heating survey was undertaken that showed around 52% of households in Blenheim used wood burners for domestic home heating, with 5% using open fires and 7% using multi fuel burners. On an average winter's day around 95 tonnes of wood (including wood pellets) and two tonnes of coal are burnt in Blenheim.

1.3 Management Options for Reducing PM₁₀ in Blenheim

A report on various management options to reduce PM₁₀ concentrations in Blenheim was prepared in 2005 (Wilton 2006). Based on the maximum measured PM₁₀ concentration in Blenheim of 81 $\mu\text{g m}^{-3}$ (24-hour average) that was recorded at

Redwoodtown during 2004, a 37% decrease in PM₁₀ concentrations was estimated to be required to meet the NES by 2013.

The methodology used to assess the impact of different management options on PM₁₀ emissions in Blenheim used an estimate of background contributions that contained a significant degree of uncertainty. Blenheim is located around 5-10 kilometres from the east coast so it is possible that sea salt may contribute to PM₁₀ concentrations. Based on studies in Christchurch and Masterton, it was assumed that around 6% of the PM₁₀ measured in Blenheim is from natural sources such as sea salt. These concentrations would not be influenced by the implementation of management options to reduce PM₁₀ in Blenheim.

Management measures focused largely on domestic home heating as the primary source of PM₁₀, although prohibitions on outdoor rubbish burning were also considered. A number of management options were evaluated including a ban on outdoor rubbish burning, the use of open fires, setting an emission criterion for the installation of new multi fuel burners, a prohibition of the installation of solid fuel burners in new dwellings and existing dwellings using other heating methods and incentives for the replacement of burners with non-solid fuel alternatives. Management options were evaluated based on an assumed wood burner life of 15 years and for an assumed burner life of 20 years.

The report found that consideration could be given to a combination of management options including a ban on outdoor rubbish burning, the use of open fires, prohibiting the installation of new multi fuel burners not meeting the NES design criteria for wood burners and incentives to encourage households replacing solid fuel burners to select non-solid fuel alternatives. It is likely that the implementation of these measures would achieve the NES by 2013.

1.4 Natural sources of particulates

Previous source apportionment studies showed that the two main natural sources of PM₁₀ in urban areas of New Zealand are sea salt and soil (Wilton, 2007). The contribution of these sources to PM₁₀ is an important consideration in airshed management. This is because strategies to reduce PM₁₀ may be inadequate if the contribution of natural sources is not accounted for. Both sea salt and soil are coarse mode particulate formed through abrasive and mechanistic processes and are therefore more prevalent in the coarser (PM_{10-2.5}) size fraction, although they can also occur within the fine PM_{2.5} size fraction.

The contribution of natural sources to PM₁₀ concentrations will vary with location and with meteorological conditions. The Blenheim urban area is around six kilometres to

the west of the east coast of New Zealand. In Blenheim sea salt contributions to PM₁₀ are likely to be greater when the wind speed is high and from an easterly direction.

The potential for crustal matter (soil) contributions to PM₁₀ is high in Blenheim because of the proximity of gravel river bed (Wairau River), the surrounding land use (largely vineyard) and the prevalence of strong north west winds.

Receptor modelling is one of the few methods available for determining the relative contribution of natural sources to PM₁₀.

A number of receptor modelling studies have been carried out in New Zealand and have identified sea salt contributions and crustal matter sources. A recent study for Hastings (Wilton et al., 2007) found sea salt contributed 53% of the PM₁₀ measured during the summer (average concentration 12 µg m⁻³) and soil contributed 17% of the summer concentrations. In winter (average concentration 44 µg m⁻³) sea salt contributed 9% and soil 4% of the PM₁₀ concentrations. In Masterton, marine sources contribute up to 5% of the PM₁₀ size fraction on high pollution days (Davy, 2007) and 8% of the PM_{2.5} size fraction in Christchurch on days when PM₁₀ concentrations were elevated during the winter months (Scott, 2005). In Masterton, soil contributed 6 to 14% of the PM₁₀ on the winter high pollution days.

2 Methodology

2.1 Site location

The urban area of Blenheim and surrounding topography is shown in Figure 2.1. The Redwoodtown monitoring site was used for the receptor modelling work in this study. This site is situated at the Blenheim Bowling Club on Weld Street and is an existing and permanent air quality monitoring site for Blenheim. Figure 2.2 shows the site layout and neighbouring areas.

Air quality measurements at the Redwoodtown monitoring site included hourly average PM₁₀ (measured using an FH62 Beta Attenuation Monitor (BAM)), 24 hour PM₁₀ (measured using a gravimetric high volume sampler) and 24 hour PM₁₀ measured using the GENT sampler. Hourly average meteorological data, including temperature, wind speed and wind direction, were obtained from a NIWA site on the outskirts of Blenheim.

Interpretation of the results of the modelling is also influenced by characteristics of the monitoring location, in particular seasonal impacts of sources and meteorology. The location is an urban area that is largely surrounded by vineyards. The Wairau River with gravel beds flows to the north and meets the coast to the east of Blenheim. The Redwoodtown monitoring site is likely to be influenced by PM₁₀ concentrations from:

1. Combustion products from domestic solid fuel fires (winter) and other domestic activities such backyard fires (all year).
2. Combustion products from motor vehicle emissions and re-entrained road dust (all year).
3. The coarse and fine fractions of marine aerosol (sea salt) and crustal (soil) matter (these source are likely to be wind speed and direction dependent).
4. Possibly some commercial/industrial combustion, in particular it is possible that a wood fired boiler to the west of the monitoring site may contribute.
5. Secondary aerosols from atmospheric gas-to-particle conversion processes.
6. Agricultural or horticultural practices such as rural burning and potentially some spray accumulation from vineyard spraying.

Of these sources and more minor contributors, not all are likely to be resolved by the receptor modelling. However, of primary importance is the determination of sources contributing to elevated PM₁₀ concentrations.

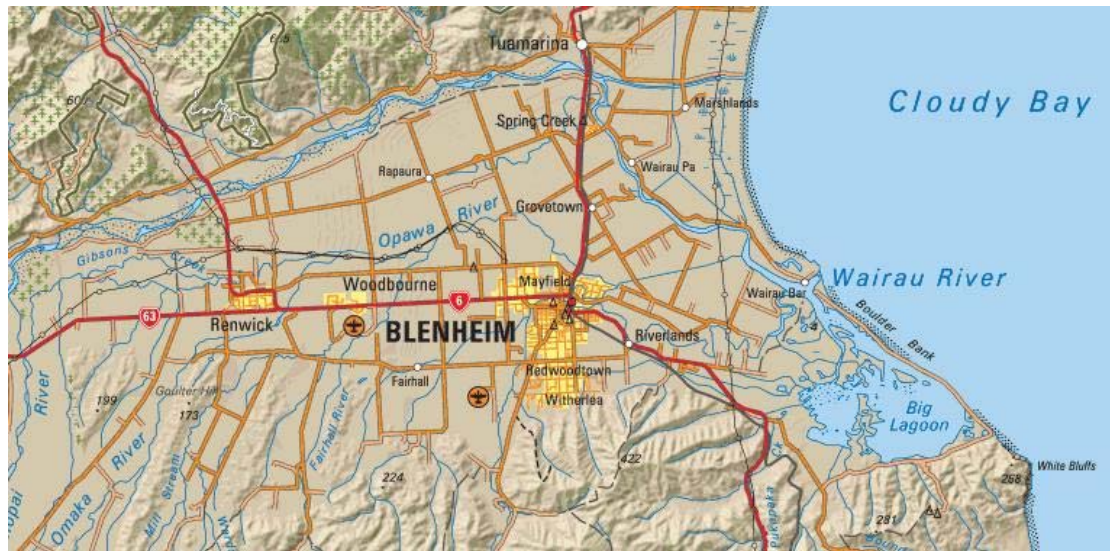


Figure 2.1: Blenheim urban area and surrounds



Figure 2.2: Aerial photo of the Redwoodtown air quality monitoring site



Figure 2.3: GENT monitor at the Redwoodtown air quality monitoring site

2.2 Sampling method

The instrument used to collect particulate matter for this study at the Blenheim site was a GENT (Figure 2.3). The GENT sampler was designed by the University of Ghent in Belgium and has been used extensively throughout the world for source apportionment studies. In this study, the dual size fraction option was not utilised and the GENT was used to measure the PM₁₀ size fraction alone. Samples were collected on Teflon filters.

2.3 Sampling period Blenheim PM₁₀

Filters from the GENT samplers were collected in Blenheim from May 2006 to August 2007. Table 2.1 shows the number of filters collected during each month that were included in the PM₁₀ analysis. A small number of filters were excluded from the analysis because of quality assurance issues. More detail on sample dates and the duration of the sampling period are shown in Appendix A. The sample programme was based on a frequency of one day in three sampling.

Table 2.1 Sample distribution by month of year

	Total Filters
January	5
February	5
March	5
April	2
May	12
June	21
July	15
August	15
September	11
October	9
November	10
December	10
Total	120

Throughout the source apportionment sampling period, concentrations of PM₁₀ were also continuously measured at the Redwoodtown monitoring site using a BAM.

2.4 Analytical methods

Details of the gravimetric and elemental analysis results of the PM₁₀ filters used in this study are reported in a supporting document (Trompetter et al 2007). The main ion beam analysis method used to determine concentrations of elements within the samples was proton induced X-ray emission (PIXE). This was used to measure concentrations of elements from Mg to Pb. In addition, particle induced gamma ray emissions (PIGE) was used to measure Na and particle elastic scattering analysis (PESA) to measure H.

In the case of PIXE, a proton beam passes through a portion of the filter. When the protons in the high energy ion beam collide with atoms in the sample, atomic electrons are ejected from their orbital and X-rays are emitted as other electrons fill the vacancy. The X-ray energy spectrum consists of a background together with the characteristic X-ray lines of the atoms present in the specimen. The energy emitted is specific to each element allowing an estimate of the concentration of that element within any given sample. Concentration estimates are then made based on the good assumption that there is a uniform distribution of the air particulate matter on the filter surface.

The PIGE method is similar to PIXE except the protons interact with the nuclei rather than the electrons and gamma rays are measured. PESA measures elastically

scattered protons when a proton beam is passed through the filter. The measurement is made in forward direction for a scattering angle of 45° . Further details of the ion beam analysis methods used in this study are provided in Davy (2007) and Trompeter et al (2005).

2.5 Statistical analysis

The main analytical method used to analyse data was Positive Matrix Factorisation (PMF). This is a factor analysis tool based on least square regression and has been designed specifically for air quality applications to overcome the limitations associated with using PCA for source apportionment studies. In particular, it provides a method for determining the contributions of sources with increased sensitivity because it allows each concentration to be weighted by the use of an error matrix. This allows concentrations that have low signal to noise ratios or are less than detection limits to be included but down weights their significance, reducing their impact on the analysis. The PMF software used in this study was EPA.PMF 1.1. Further details on the model, method and input variables are given in EPA (2005).

Other methods used include Principal Components Analysis (PCA) which was carried out on the data to further understand the relationships between elements and to provide an initial indication of the number and nature of factors and the amount of variability in the data that can be explained by each.

Summary data and scatter plots were also prepared to examine the distribution of concentrations of elements and linear relationships between each variable. The purpose of this stage is familiarisation with the data and identification of outliers and unusual events.

3 Blenheim PM₁₀ concentrations

The study monitoring period for the source apportionment project was May 2006 until August 2007. During this time air quality monitoring for PM₁₀ was also carried out at Redwoodtown using two further monitoring methods. These included gravimetric sampling using a high-volume sampler (a 24-hour based measurement for the period midnight to midnight) and a continuous Met One Beta Attenuation Monitor (BAM). The latter provided hourly average PM₁₀ concentrations for the Redwoodtown monitoring site and daily PM₁₀ concentrations as required by the NES. The sampling frequency for the gravimetric sampling was one day in three and the purpose was comparative sampling for historical purposes and to allow for adjustments of BAM data to reference method equivalents, should they be required.

Monitoring results from June 2006 to September 2007 show that there were ten exceedances of the NES recorded by the BAM at Redwoodtown (Figure 3.1). Of these, two were coincided with sample days for this study (11 August 2006 and 25 June 2007). A NES breach was also likely on 28 June 2007 (BAM concentration of 47 $\mu\text{g m}^{-3}$) because the BAM was found to under report PM₁₀ concentrations relative to the reference method by around 7% in Blenheim (Wilton, 2007).

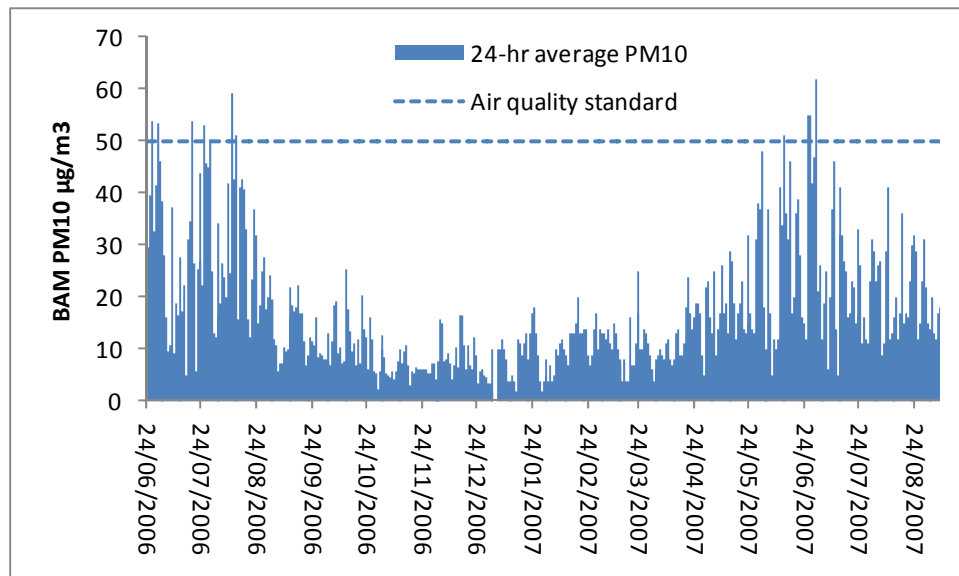


Figure 3.1: 24-hour average PM₁₀ concentrations measured at Redwoodtown from May 2006 – September 2007

4 Results

4.1 Source Profile

Five factors were identified and labelled as domestic heating, sea salt, soil, soil/combustion and sulphate. Two profiles (sulphate and soil/combustion) appear also to contain some PM₁₀ from combustion sources. The concentration profiles for each source are shown in

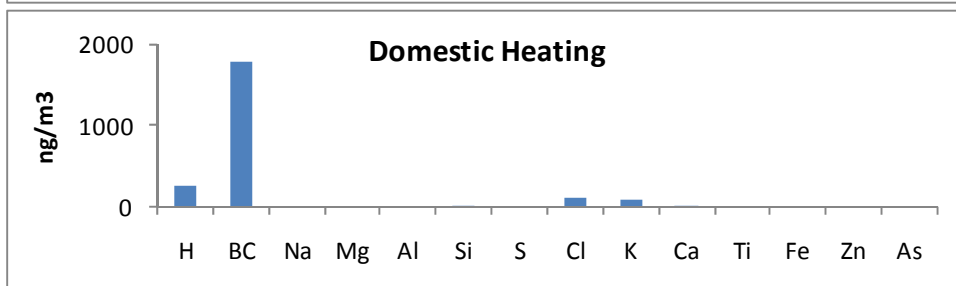
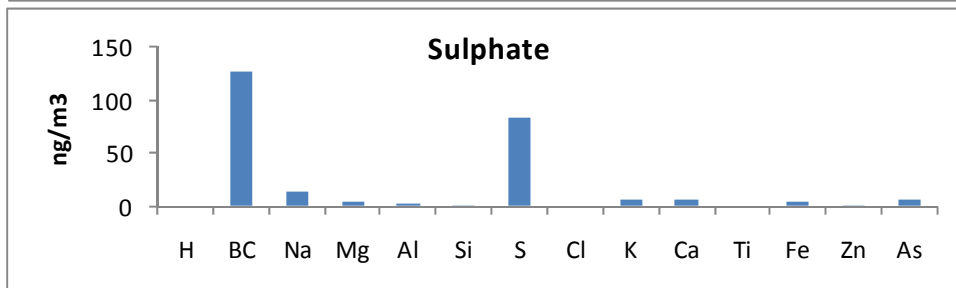
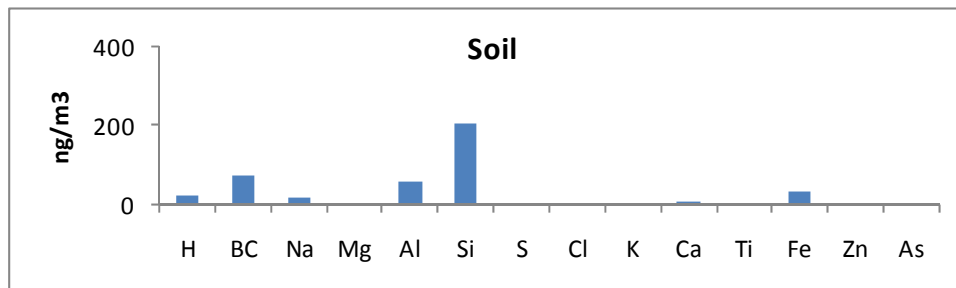
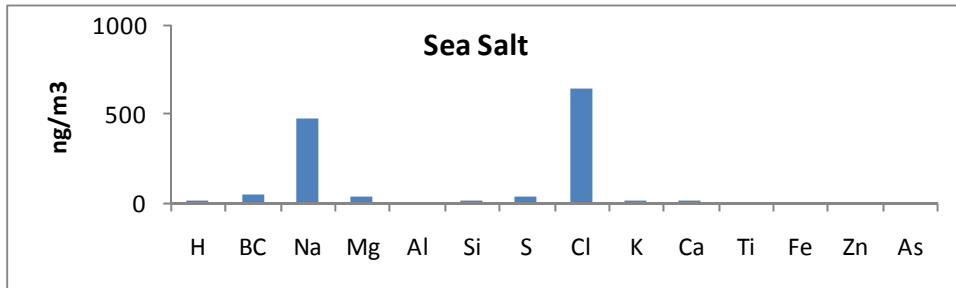
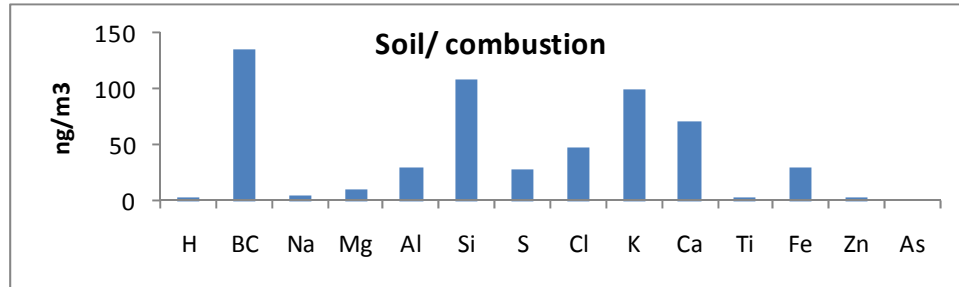


Figure 4.1. Further details of the profiles, the method of deriving them and the PMF model diagnostics are contained in Appendix B. A comparison of the reconstructed mass (RM) based on the contributions from these profiles to the measured PM₁₀ mass shows a coefficient of determination (r^2) of 0.9. This is a good result for the concentration range of the sample (maximum 41 $\mu\text{g m}^{-3}$). A similar study carried out in Hasting (Wilton, et. al., 2007) gave an r^2 of 0.9 for a concentration range up to 112 $\mu\text{g m}^{-3}$ but the r^2 for the same data was 0.57 for concentrations less than 41 $\mu\text{g m}^{-3}$.

The source labelled domestic heating profile is dominated by black carbon (BC) and contains the majority of the hydrogen, and around half of the potassium and zinc. The profile also includes Cl in a similar proportion to K. This combination is consistent with wood burning profiles in New Zealand. In this profile, the hydrogen is an indicator of organic carbon, which otherwise has not been measured. Although labelled as domestic heating, this profile may also include PM₁₀ from outdoor burning.

The sulphate profile is dominated by BC (51%) and sulphur (33%) with small quantities of Na (5%), K (3%), As (2%) and Ca (2%). The combination suggests the potential for two sources, one combustion related (EC, K and potentially As and Ca) and the other sulphate most probably as sodium sulphate (Na_2SO_4) and possibly gypsum (CaSO_4). Sulphate formation is common in coastal areas where sulphuric acid has been neutralised by NaCl in sea salt.

The sea salt factor is dominated by Cl and Na and has smaller amounts of Mg (3%), S (2%) and BC (3%). The soil profile was dominated by Si, with smaller amounts of BC (17%) Al (14%), Fe (8%), Na (4%), Ca (2%) and H (5%).

The soil/combustion profile contains the elements typical of biomass burning (e.g., BC and K) and those typical of soil (e.g., Si, Al, Fe). The proportion of K in this profile is excessive both in terms of K to BC (0.7:1) and K to Si (0.9:1). The K:BC ratio compares to a more typical proportion of (0.06:1) in the biomass burning profile. Similarly the proportion of Ca to Si is high (0.6:1). There are a number of environmental sources of K and Ca including fertiliser (e.g., KCl, K_2SO_4 , K_2CO_3) and lime (CaCO_3). This source shows some correlation with domestic heating ($r^2 = 0.3$) and with soil ($r^2 = 0.2$).

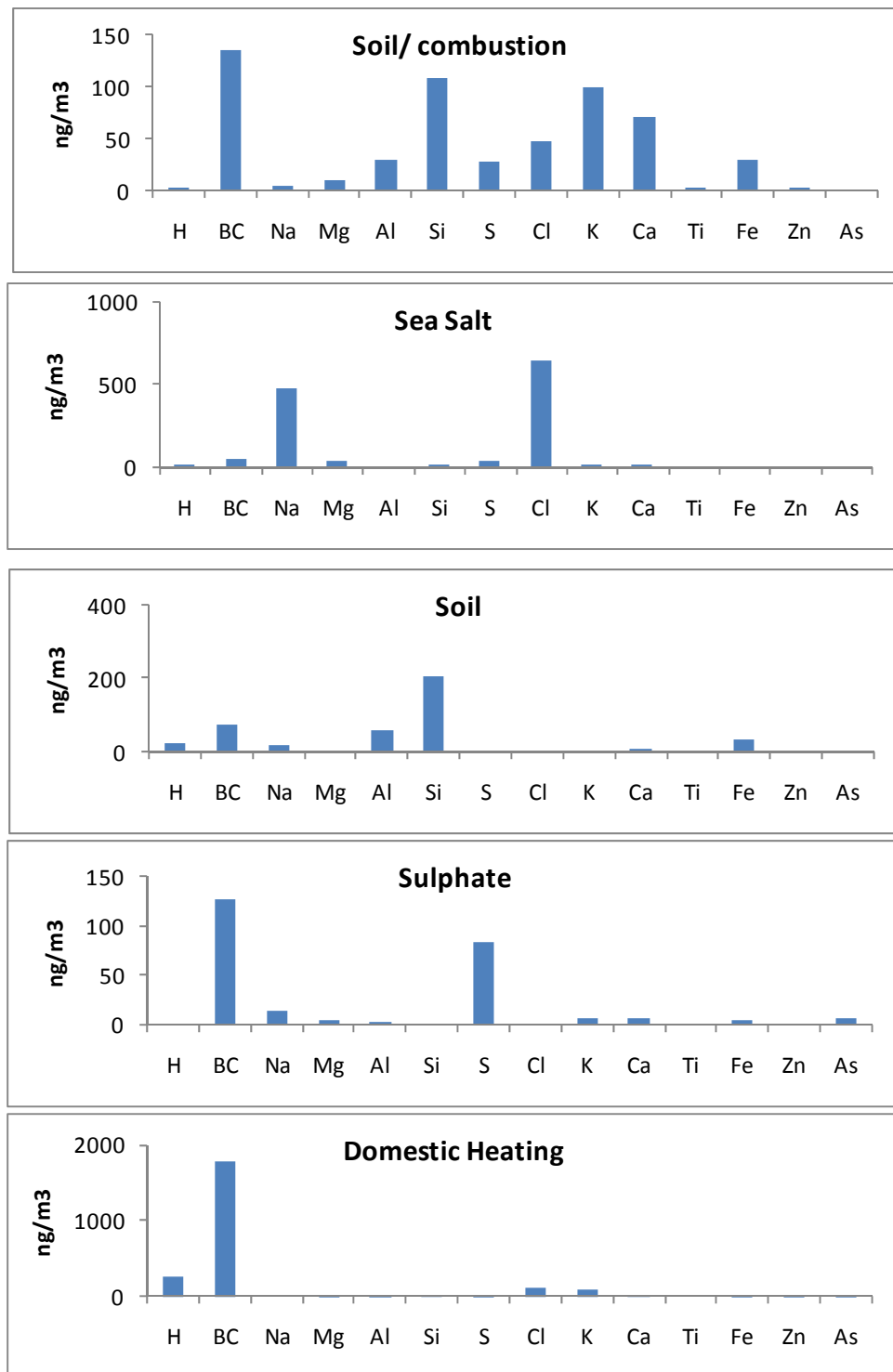


Figure .4.1: Source profiles for PM₁₀ at Blenheim

4.2 Source contribution

The relative contribution of the five different profiles to annual PM₁₀ concentrations is shown in Figure 4.2². Around 44% of the PM₁₀ is from domestic heating with around 23% from sea salt. The pure soil profile contributes 13% and the soil/ combustion profile around 10%, although it is roughly estimated that at around 50% of the latter may be from an alternative combustion source such as industry or motor vehicles³. The total soil contribution is estimated at around 18% of the annual PM₁₀. This is consistent with soil contribution estimates made using the reconstructed mass method described in Davy (2007) which suggest that around 17% of the annual PM₁₀ is from soil.

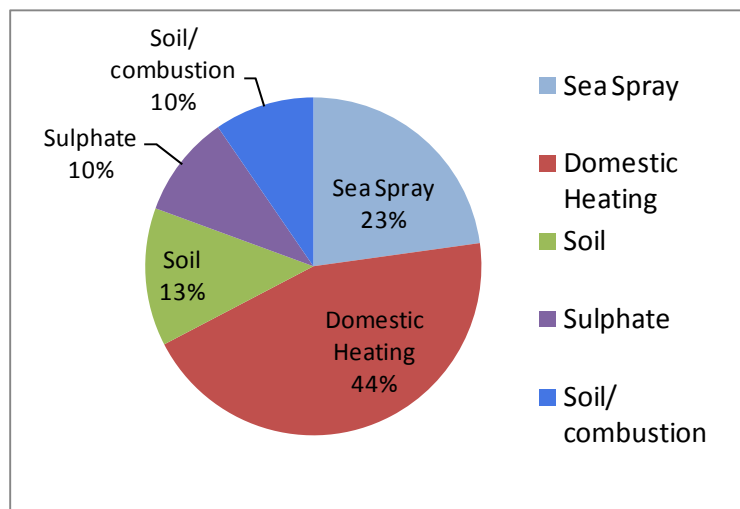


Figure 4.2 Contribution of sources to annual PM₁₀ concentrations

Figure 4.3 shows the estimated daily contributions of different sources and reconstructed PM₁₀ concentrations for the duration of the study period. The individual source contributions are illustrated in Figures 4.4 and 4.5.

Seasonal variations in sources of PM₁₀ are apparent with large contributions from domestic heating during the winter months when PM₁₀ concentrations are highest. Sea salt is the main source of PM₁₀ during the summer months. Overall, domestic heating is the main source of PM₁₀ on most days from April to October. A small

² This was based on an average of the monthly contributions to remove any bias in the sampling regime and therefore differs slightly to the distribution based on the concentration distribution for PM₁₀ mass shown in Appendix A.

³ This is an approximate estimate based on the proportion of BC in the sample and an estimate of the proportion of unmeasured components for this source that may belong to wood burning versus soil.

contribution from this source occurs also during the summer months. This may be a consequence of some households continuing to use domestic heating during the summer months or may be from outdoor burning (e.g., garden waste) sources which are also likely to be included in this profile.

Soil and sea salt contributions tend to be higher during the summer months. This is likely to be related to the prevalence of windy days which assist in the generation of emissions from these sources.

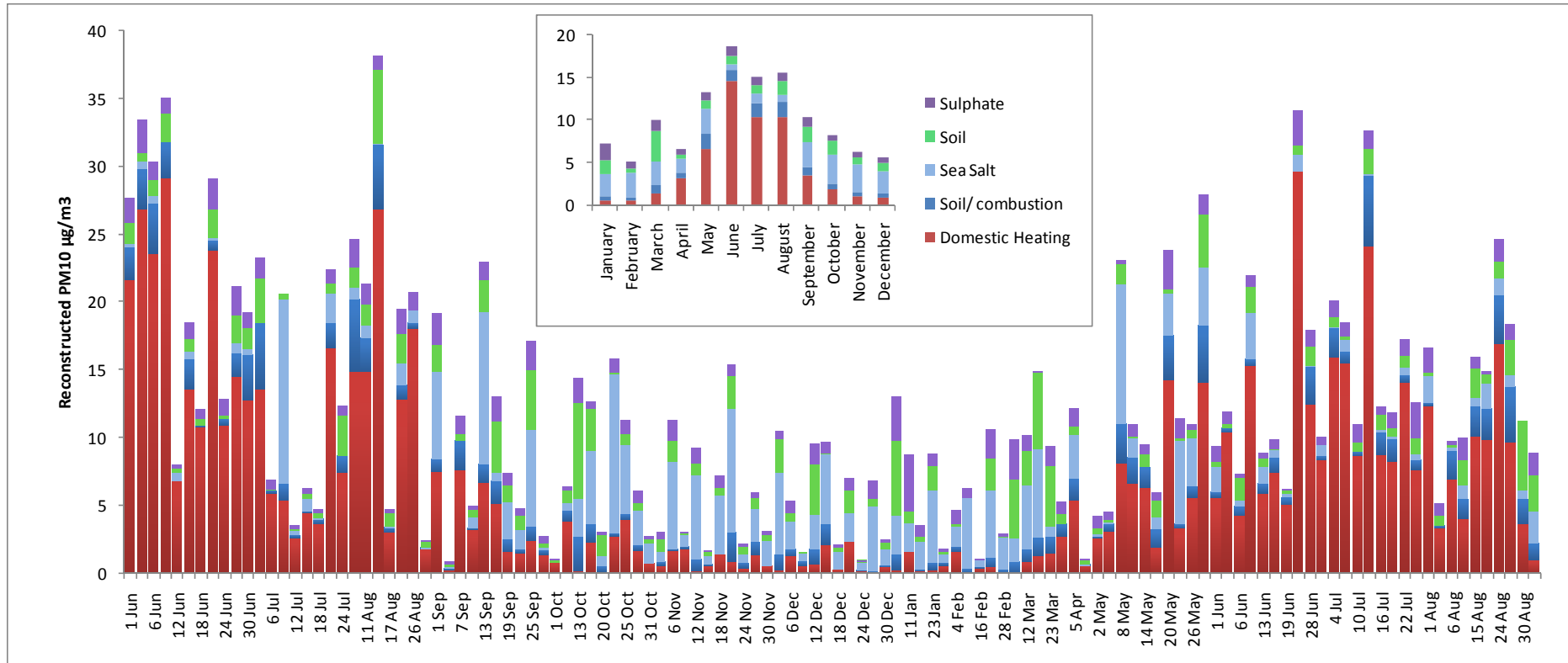


Figure 4.3 Source contributions to reconstructed PM₁₀

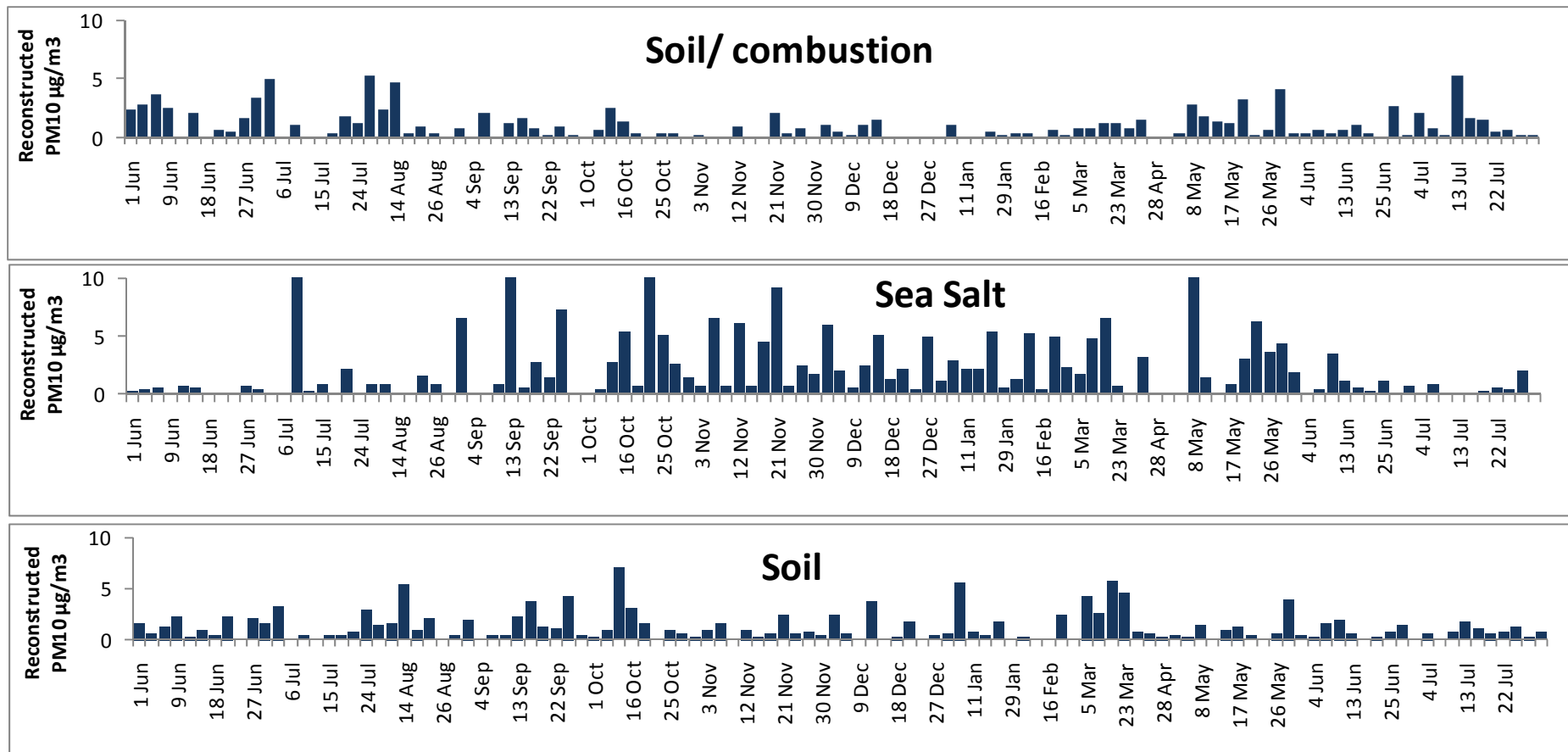


Figure 4.4: Reconstructed PM₁₀ mass by source (soil/ combustion, sea salt and soil)

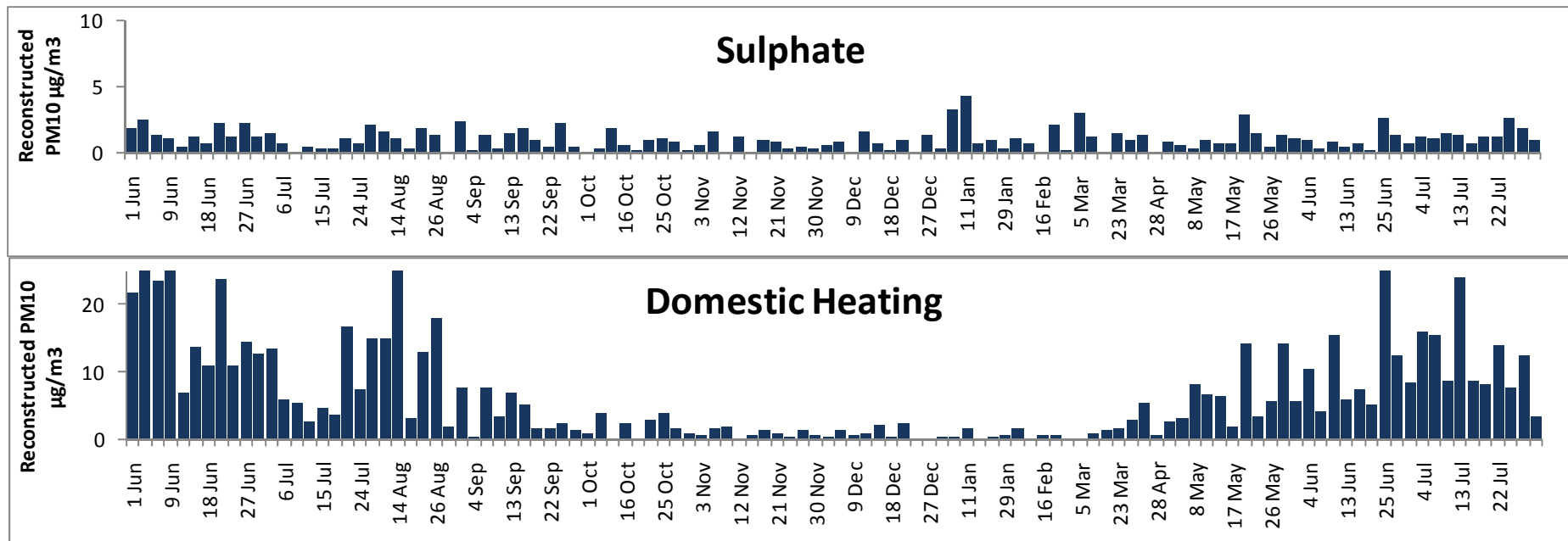


Figure 4.5: Reconstructed PM₁₀ mass by source (sulphate and domestic heating)

4.3 Seasonal variations

The main source of PM₁₀ concentrations during the winter time when NES breaches occur in Blenheim is solid fuel burning for domestic heating which contributes at least 71%⁴ (Figure 4.6). During the non-winter months, sea salt is the dominant source of PM₁₀. While concentrations during these months are typically low and do not require reduction to meet the NES, a small number of elevated concentrations (>40 µg m⁻³) have been recorded in November/ December 2005. As these episodes were not captured by the study period it is uncertain whether sea salt was a major contributor.

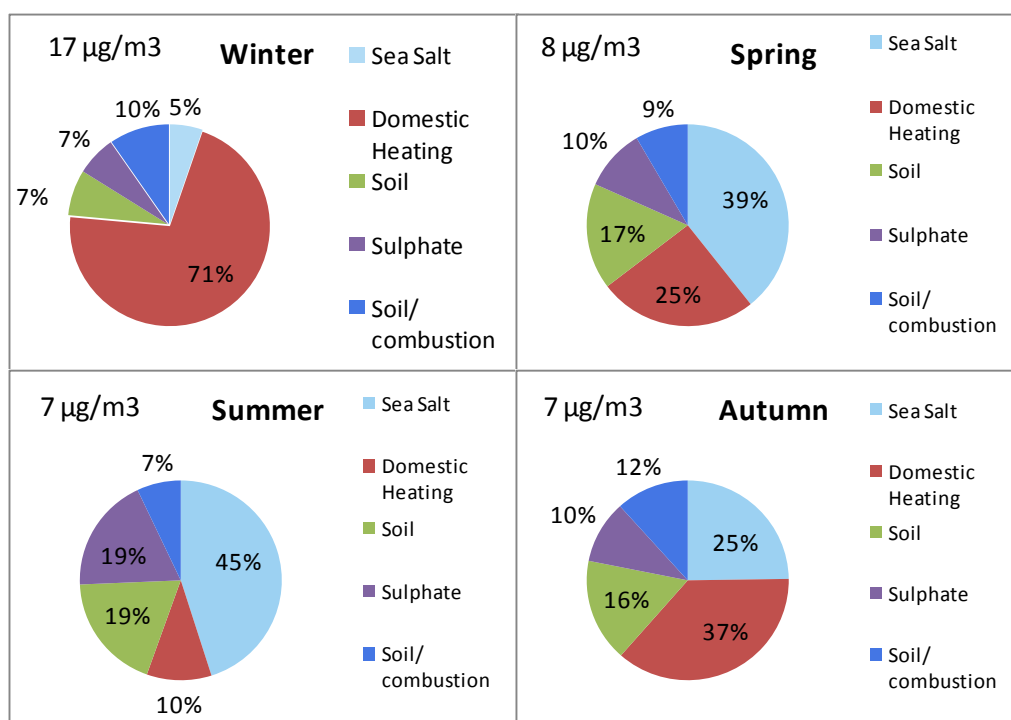


Figure 4.6 Seasonal variations in the contribution of sources to PM₁₀ concentrations at Blenheim

4.4 High pollution days

Figure 4.7 shows the average contribution of sources to PM₁₀ concentrations on days when PM₁₀ concentrations measured by the BAM exceeded 47 µg m⁻³. This value was used instead of 50 µg m⁻³ because BAM concentrations in 2006 were found to be around 7% less than the reference method in Blenheim (Wilton, 2007). From June 2006 to September 2007, there were three sample days when BAM concentrations exceeded 47 µg m⁻³. The domestic heating contribution on these days was around 78%.

⁴ Some combustion contribution appears likely within the soil/combustion and sulphate sources, although this may be from sources other than domestic heating.

The natural sources contribution is most relevant on days when the NES is breached. Based on the assumption that around 50% of the combined soil/combustion profile is natural (soil), the natural source contribution is estimated at around 11% of the daily PM₁₀ on high pollution days. This equates to around 6 µg m⁻³ for PM₁₀ concentrations around 50 µg m⁻³ or around 7 µg m⁻³ for PM₁₀ concentrations around 66 µg m⁻³ (proposed revised starting point for the Blenheim straight line path).

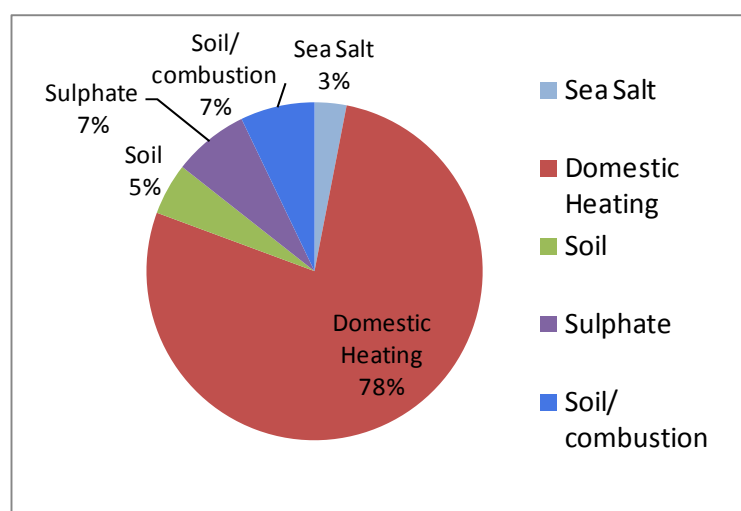


Figure 4.7 Average source contributions on high pollution days when PM₁₀ concentrations exceed 50 µg m⁻³

4.5 Meteorological variation

The relationship between meteorological conditions and sources of PM₁₀ in Blenheim was examined using a conditional probability function (CPF). This method illustrates the wind directions from which the upper quartile of each source profiles originates. Figure 4.8 shows the CPF plots for each source.

Analysis was based on the data where the wind speed is $\geq 1 \text{ ms}^{-1}$. Sources are likely to be located in the directions that have high CPF values. The CPF analyses for each source are shown as a radial plot in Figure 4.8. The radial divisions are in degrees (0 = north; 180 = south) and the vertical axes are in relative units. Therefore, the greater the distance from the origin, the higher the mass contribution for a given wind direction.

Results suggest that high concentrations from biomass burning/ domestic heating occur when the wind is from the south west quadrant. As emissions from this source occur in all directions, and are most common under winds of less than 1 ms⁻¹, it is likely that the dominance of this wind direction reflects the prevalence of meteorological conditions conducive to elevated pollution rather than any particular source directionality.

The sulphate/ combustion source originates from the north with a smaller profiles to the west and east. Potential origins to the north include sea salt from the Tasman Sea. Industry and vineyard spraying are both potential sources located to the west of the monitoring site. It is uncertain how relevant the directionality is for this source, however, because some of it may be of secondary origin.

Figure 4.6 shows that the soil profile is more common when the wind is from the north and the west with a smaller peak to the east. Likely origins of dusts include unsealed roads, river beds, exposed soils and brake and tyre wear.

Sea salt is most prevalent when the wind is from the east, north and northwest. The smaller prevalence of this source from the north west quadrant may reflect wind recirculation patterns (i.e., the wind trajectory originates from the east but appears from the north west owing to the recirculation) or may be from longer range transportation from the Tasman Sea.

The soil/ combustion profile shows a strong westerly peak with contributions also from the north, south and a north east peak. This is consistent with the direction of a large industrial combustion activity and viticulture activity.

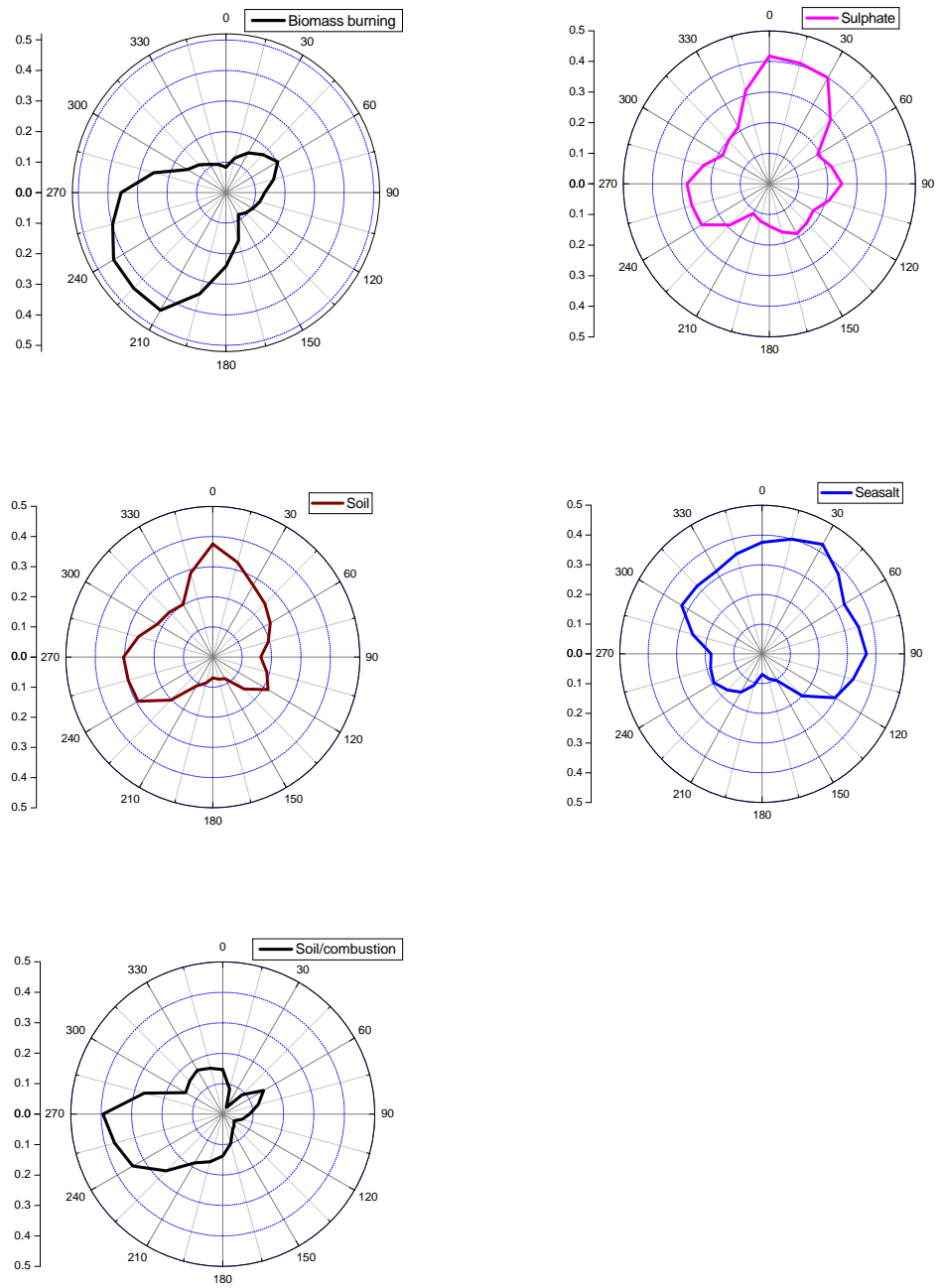


Figure 4.8: Meteorological profile for each source

5 Discussion

Generally the source profiles were well resolved and consistent with other New Zealand source apportionment studies. The main difference was the high concentrations of K and Ca in the profile that included both soil and combustion. It is possible that separate analysis of the coarse and fine components of PM₁₀ would have separated out the soil from the combustion and provided more insight into potential sources. Similarly inclusion of a greater number of samples may have assisted with the separation of the combustion components from the soil components. The unusual aspect of this profile is that the high K and to a lesser extent Ca, would have been likely to persist and results indicate it may relate to location specific sources.

The domestic heating contribution is estimated at around 71% of the average winter PM₁₀ concentrations and around 78% of PM₁₀ concentrations on high pollution nights. Other combustion sources likely to be present in smaller concentrations include motor vehicles and industrial emissions. One potential exception with respect to the latter is Flight Timbers Limited which burns significant quantities of wood in an industrial boiler and is located around 1.5 kilometers to the west of the monitoring site. While the products of combustion from this source would be similar to domestic heating, the meteorological conditions under which high concentrations occur are likely to differ. It is possible that the combustion contribution of the soil/ combustion source originates from industry such as Flight Timbers. The CPF analysis shows a strong westerly profile for this source although soil sources to the west will also contribute.

Around 11% of the PM₁₀ on high pollution days is estimated to originate from natural sources. This is important for air quality managers as this contribution is essentially unmanageable and must be accounted for in scenario modelling. This estimate excludes the sulphate source which seems to contain a reasonable proportion of combustion emissions. The origin of the combustion emissions is uncertain. Possible sources include motor vehicles, industry, outdoor burning and to a less extent domestic heating. Unlike domestic heating, the CPF profile for this source shows little contribution from the southerly direction.

One potential limitation in applying the results of this study is the difference between the GENT data relative to BAM concentrations (as detailed in Appendix B). It is uncertain what is causing the difference as other studies (e.g., Wilton, et. al., 2007) have reported consistent results between GENT and BAM PM₁₀. Previous comparisons of the BAM to gravimetric high volume

sampling showed a good correlation with BAM concentrations under measuring by around 7% compared with the gravimetric reference method (Wilton, 2007). It has been assumed here that concentrations are being under measured but that there is no source specificity in the under measurement. Results in this study have generally been presented as reconstructed PM₁₀ mass, with the exception being the estimate of natural source contributions on high pollution days. In the absence of information to the contrary it would seem reasonable to assume the percentage contributions estimated here could be applied to PM₁₀ concentrations measured by the BAM and high volume samplers.

6 Conclusion

The main natural sources of PM_{10} in Blenheim are soil and sea salt. Soil is the main natural source contributor during the winter months with an estimated contribution of 10% (7% soil profile, 3% soil/combustion assuming 50% is soil). Sea salt is the dominant natural source contributor during the other months, contributing around 40% of the daily PM_{10} during spring and summer. During these months natural sources are responsible for around two thirds of the daily PM_{10} on average.

Anthropogenic sources are responsible for the majority (at least 76%) of the PM_{10} during the winter months and around two thirds of the PM_{10} during autumn. During winter, sea salt contributes around 5% of the PM_{10} and soil around 10%. On nights when PM_{10} concentrations exceeded the NES the soil contribution was around 8% and the sea salt reduced to 3%.

Results for combustion are consistent with emissions from domestic home heating, although this profile is also likely to include outdoor rubbish burning. This source appears responsible for the majority of the anthropogenic PM_{10} in Blenheim. This work supports the development of management strategies targeting domestic home heating in Blenheim and highlights the need to adequately account for natural sources in evaluating the effectiveness of any such measures.

7 References

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Appendix A: Blenheim PM₁₀ sampling details

Run date	Run Hours	Run date	Run Hours	Run date	Run Hours
1-Jun-06	24	22-Oct-06	24	28-Apr-07	24
3-Jun-06	24	25-Oct-06	24	2-May-07	24
6-Jun-06	24	28-Oct-06	24	5-May-07	24
9-Jun-06	24	31-Oct-06	24	8-May-07	24
12-Jun-06	24	3-Nov-06	24	10-May-07	24
15-Jun-06	24	6-Nov-06	24	14-May-07	24
18-Jun-06	24	9-Nov-06	24	17-May-07	24
21-Jun-06	24	12-Nov-06	24	20-May-07	24
24-Jun-06	24	15-Nov-06	24	23-May-07	24
27-Jun-06	24	18-Nov-06	24	26-May-07	24
30-Jun-06	24	21-Nov-06	24	29-May-07	24
3-Jul-06	24	24-Nov-06	24	1-Jun-07	24
6-Jul-06	24	27-Nov-06	24	4-Jun-07	24
9-Jul-06	24	30-Nov-06	24	6-Jun-07	24
12-Jul-06	24	3-Dec-06	24	9-Jun-07	24
15-Jul-06	24	6-Dec-06	24	13-Jun-07	24
18-Jul-06	24	9-Dec-06	24	16-Jun-07	24
21-Jul-06	24	12-Dec-06	24	19-Jun-07	24
24-Jul-06	24	15-Dec-06	24	25-Jun-07	24
27-Jul-06	14	18-Dec-06	24	28-Jun-07	24
11-Aug-06	24	21-Dec-06	24	1-Jul-07	24
14-Aug-06	24	24-Dec-06	24	4-Jul-07	24
17-Aug-06	24	27-Dec-06	24	5-Jul-07	24
20-Aug-06	24	30-Dec-06	24	10-Jul-07	24
26-Aug-06	24	5-Jan-07	22	13-Jul-07	24
29-Aug-06	24	11-Jan-07	24	16-Jul-07	24
1-Sep-06	24	17-Jan-07	24	19-Jul-07	24
4-Sep-06	24	23-Jan-07	24	22-Jul-07	25
7-Sep-06	24	29-Jan-07	24	25-Jul-07	24
10-Sep-06	24	4-Feb-07	24	27-Jul-07	24
13-Sep-06	24	10-Feb-07	24	1-Aug-07	24
16-Sep-06	24	16-Feb-07	24	3-Aug-07	24
19-Sep-06	36	22-Feb-07	24	6-Aug-07	23
22-Sep-06	24	28-Feb-07	24	8-Aug-07	24
25-Sep-06	24	5-Mar-07	24	15-Aug-07	24
28-Sep-06	24	12-Mar-07	24	18-Aug-07	134
1-Oct-06	24	18-Mar-07	24	24-Aug-07	24
10-Oct-06	24	23-Mar-07	24	27-Aug-07	24

Source Apportionment of PM₁₀ in Blenheim

13-Oct-06	24	30-Mar-07	24	30-Aug-07	24
16-Oct-06	24	5-Apr-07	24	1-Sep-07	24
20-Oct-06	24	17-Apr-07	24		
1-Jun-06	24	22-Oct-06	24	28-Apr-07	24

Appendix B: Data Analysis

Data validation

Data validation included an assessment of PM₁₀ mass concentrations, elemental concentrations, run durations and flow rates. Quality assurance procedures used for this data set included:

- Exclusion of filters returning negative gravimetric concentrations (2 filters)
- Removal of elements with around 50% or more concentrations below detection limit.

Scatter plots and summary statistics were carried out to examine relationships, determine unusual data point and generally assess the validity of the data. No data were considered invalid as a result of this exercise. Table B.1 shows the summary information for concentrations of elements.

Table B.1 PM₁₀ elemental concentrations and statistics

Element	Average concentration ng/m ³	Max ng/m ³	Min ng/m ³	Std dev	Average % Error	Av LOD ng/m ³	No. of samples > LOD
H	251	1242	0	243	85	20	118
BC	1944	7743	230	1787	12	151	120
Na	485	3536	0	743	59	197	53
Mg	55	245	0	54	83	24	84
Al	97	403	8	88	15	12	117
Si	338	1416	28	311	5	8	120
P	6	36	0	9	190	18	23
S	153	388	1	97	13	10	118
Cl	859	4451	0	868	4	8	119
K	204	835	1	183	8	6	119
Ca	118	786	0	120	9	6	119
Ti	7	72	0	10	96	6	52
Mn	4	18	0	4	105	5	52
Fe	76	513	0	77	12	4	115
Cu	3	16	0	4	75	8	30
Zn	13	99	0	19	63	9	65
As	8	59	0	12	69	22	33
Se	6	34	0	7	105	28	9
Br	7	43	0	12	68	37	14
Ba	6	36	0	8	166	22	10
Pb	12	122	0	24	111	66	9

Preliminary assessment

Preliminary assessment of a PMF dataset includes a comparison of the relationships between individual elements, comparison of mass of elements to PM_{10} mass and conducting an initial PCA.

A good relationship is observed ($r^2 = 0.8$) between mass of elements measured and the PM_{10} mass.

Four pages of scatter plots (Figure B.4) show the relationships between key elements in the PM_{10} size fraction measured at Hastings. The element noted on the left of the page is on the horizontal axis of each plot. Scatter plots of the data were carried out in the preliminary stages of the analysis to observe key relationships between elements. The notable relationships observed in these data include:

- A strong correlation is observed between Na and Cl ($r^2=0.9$) with a ratio of around 0.7:1. A strong correlation between Mg and both Na and Cl is also observed. These correlations are associated with PM_{10} from marine aerosol.
- The relationship between Al and Si is also very strong ($r^2 = 0.98$) and indicative of a soil based source. Fe is also strongly correlated with both Si and Al.
- A linear relationship between BC and K ($r^2 = 0.8$) which is typical of biomass burning.
- Concentrations of S and Cl are both split between two or more sources, one of which appears to include BC.

Principal components analysis was carried out on the dataset. Eigenvector analysis returned 3 clusters with values greater than 1 but results indicate that around 5 factors is appropriate (Figure B.1). Evaluation of the analysis showed that the first three factors were able to explain 78% of the variability in the elemental mass. The first factor (explaining 27% of the variability) was consistent with combustion, the second included crustal matter (28% of the variability) and the third (23% of the variability) was consistent with sea salt.

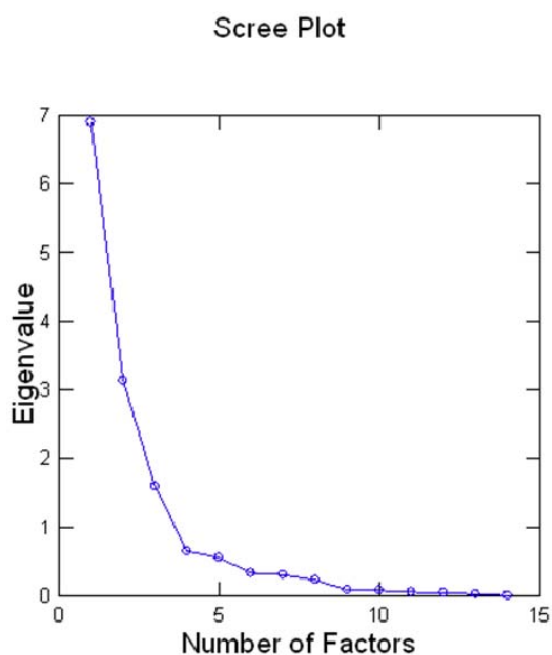


Figure B.1 Scree plot of Eigenvalues from PCA of Blenheim PM_{10} elemental composition

Factor Identification

Positive Matrix Factorisation (PMF) was conducted using EPA.PMF, a windows based version of the PMF software adapted by the USEPA.

Table B.2 shows the model diagnostics for the PMF analysis. The high r^2 values indicate that most of the variability in the concentrations of elements was explained by the source profiles identified. With the exception of titanium, all factors had an r^2 value of greater than 0.7. The amount of variability explained by the relationships for titanium was 59%. The slope for the BC concentrations is 1.32 indicating that the predicted BC concentrations are higher than those measured. For most other elements predicted concentrations are lower than measured concentrations. The high RMSE for BC indicates that there is still variability in concentrations of this element that is not explained by the relationships observed.

The robustness and repeatability of the model was tested using the EPA.PMF bootstrapping procedure. The model was run 200 times based on the default correlation setting of 0.6. All bootstrap runs converged and each factor mapped to the original factor for all of the 200 runs for three factors, 193 runs for one factor (sea salt) and 207 runs for one factor (sulphate). This indicates that the derived profiles are reproducible but that the sulphate and sea salt profiles are slightly less robust than the other sources.

Table B.3 PMF diagnostics for PM₁₀ at Blenheim

Species	Intercept	Slope	RMSE	r ²
PM ₁₀ Mass	132.98	0.91	2255.58	0.93
H	11.35	0.96	57.88	0.96
BC	-96.02	1.03	502.93	0.94
Na	68.88	0.88	166.46	0.93
Mg	8.33	0.86	17.18	0.87
Al	-0.93	1	8.08	0.99
Si	0.35	1	14.45	1
S	-0.02	1	1.67	1
Cl	-10.68	1.02	24.82	1
K	1.05	0.99	22.92	0.99
Ca	30.27	0.65	44.98	0.77
Ti	3.23	0.52	4.67	0.55
Fe	18.08	0.69	28.4	0.8
Zn	6.72	0.36	8.14	0.38
As	5.96	0.52	8.76	0.25

$Q_{\text{Theoretical}} = 1320$; $Q_{\text{Robust}} = 751.04$; $Q_{\text{True}} = 751.04$

Number of bootstrap runs that converged and are summarized: 200

Number of bootstrap runs that did not converge: 0

Number of bootstrapped factors mapped to original factor 1 :200

Number of bootstrapped factors mapped to original factor 2 : 207

Number of bootstrapped factors mapped to original factor 3 : 200

Number of bootstrapped factors mapped to original factor 4 : 193

Number of bootstrapped factors mapped to original factor 5 : 200

Number of bootstrapped factors mapped to no original factor : 0

The average contribution of each element to the profiles is shown in Table B.4. The PM₁₀ mass is included in the table because the PMF contribution outputs for PM₁₀ mass indicate the amount of PM₁₀ from each source on average.

Table B.4 Factor identification and contributions

	Soil & smoke ng/m ³	Sea salt ng/m ³	Soil ng/m ³	Sulphate & smoke ng/m ³	Domestic heating ng/m ³
PM ₁₀ mass	1136	2013	1291	995	6541
H	3.8	10.0	21.2	0.0	259.7
BC	136.2	42.2	76.5	126.9	1780.3
Na	5.4	470.5	19.3	13.2	0.0
Mg	10.5	32.4	4.7	4.4	3.8
Al	30.0	2.7	60.3	1.9	3.7

Si	109.1	8.3	207.4	0.0	19.7
S	27.8	31.4	3.2	83.0	11.1
Cl	47.4	643.8	2.8	0.0	131.0
K	99.9	12.9	0.0	6.4	106.8
Ca	70.6	13.1	6.8	5.3	16.6
Ti	2.7	0.2	4.7	0.0	0.0
Fe	29.5	0.3	34.9	3.0	5.6
Zn	3.3	0.0	2.6	0.3	6.1
As	0.0	0.0	2.8	6.1	5.6

Figure B.2 shows the distribution of the concentrations of each element by source. The majority of the black carbon is attributed to domestic heating, with small amounts to sulphate and K enriched soil, both of which appear to be mixed with some combustion. Hydrogen, which provides an indication of the organic carbon component, is also dominated by domestic heating. Potassium is split between domestic heating (where it contributes around 3% of the profile) and the soil/ combustion source (where it contributes 17% of the profile). Na and Cl are both dominated by marine aerosol and Si, Al, Ti and Fe by the two soil related profiles.

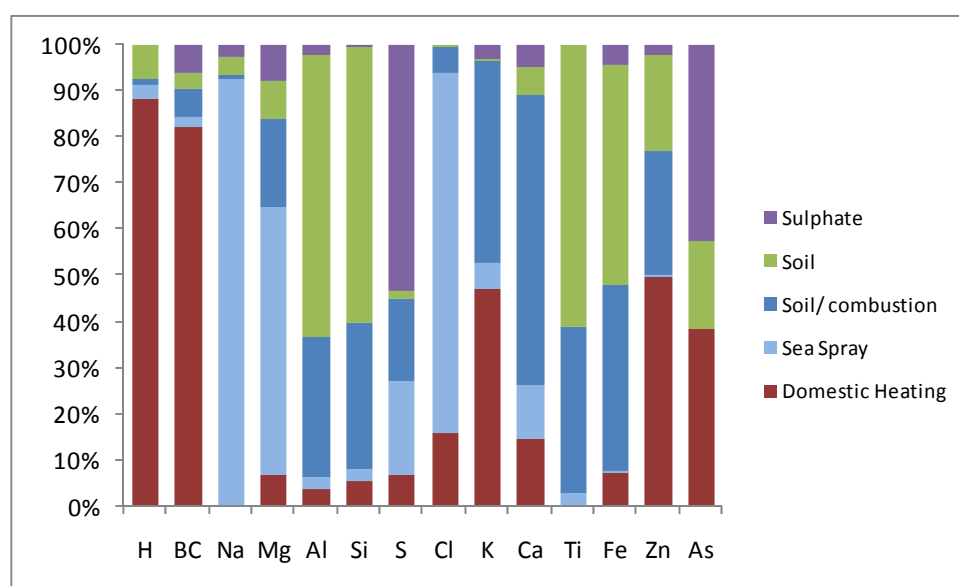


Figure B.2 Distribution of elements by source

Two methods can be used to estimate the relative contribution of each source to PM₁₀ concentrations. These include integration of the PM₁₀ mass data into the PMF model or multiple linear regression (MLR) of the PMF source contributions outputs. Integration of the PM₁₀ mass into the PMF analysis gives a profile for PM₁₀ mass (see Table B.3) similar to the output of the MLR. Results from the integration of PM₁₀ mass into the PMF analysis were used for this report and MLR was used as a cross check. The resulting relationship

between reconstructed and measured PM₁₀ mass (Figure B.3) gave an r^2 of 0.93 indicating all around 93% of the variability in concentrations could be explained by the relationships.

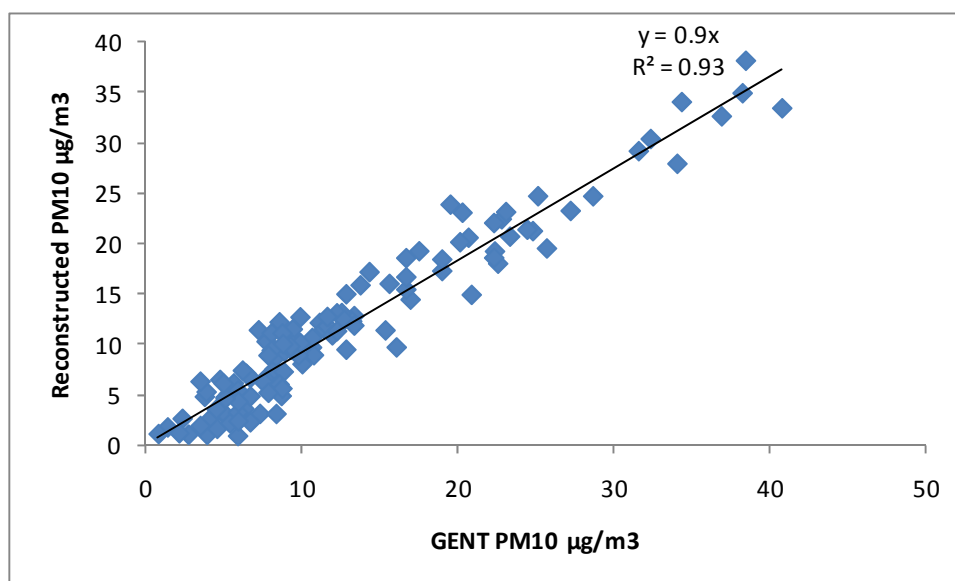


Figure B.3 Reconstructed versus measured PM₁₀ mass at Blenheim

With the exception of the soil/ combustion source, all profiles were readily identifiable and generally consistent with other source profiles from source apportionment studies in New Zealand (e.g., Wilton, et. al., 2007). The soil/ combustion profile differs in the concentrations of K and Ca which are higher than would be expected for either a soil or combustion profile. This source was examined in greater detail to determine whether a local source of K and Ca was contributing to this profile or whether the profiles were anomalous. To minimise the potential impact of the combustion component, results from the summer months were examined on days when the soil/ combustion contribution was high. Figure B4 illustrates daily variations in meteorological parameters, hourly average PM₁₀ and daily source contributions based on the PMF analysis for three of five days examined during 2006. On two of these days the main contributor to PM₁₀ is sea salt and on one day it is soil. All days experience elevated wind conditions, generally westerly with some patches of easterly winds.

The source profile clearly contains soil and combustion but the main point of difference is the high K and Ca concentrations which are apparent in this profile. Typically a biomass burning/ domestic heating PM₁₀ profile in New Zealand would contain around 5% potassium and less than 5% Ca. Potassium is also present in soil profiles at around the same proportion. Ratios of K to BC and K to Si for biomass burning and soil of around 5-10%

and 12% were recorded in recent source apportionment studies for Hastings and Kowhai (Wilton, et. al., 2007).

Table B5 shows concentrations of BC, Si, K and Ca measured in Blenheim on four days when this source was strongest during spring/ summer 2006. Concentrations of both K and Ca are elevated relative to the main elements measured that are present in combustion (carbon) and soil (Si). Possible sources of K and Ca include fertiliser, either as enrichment of the soil or directly from application.

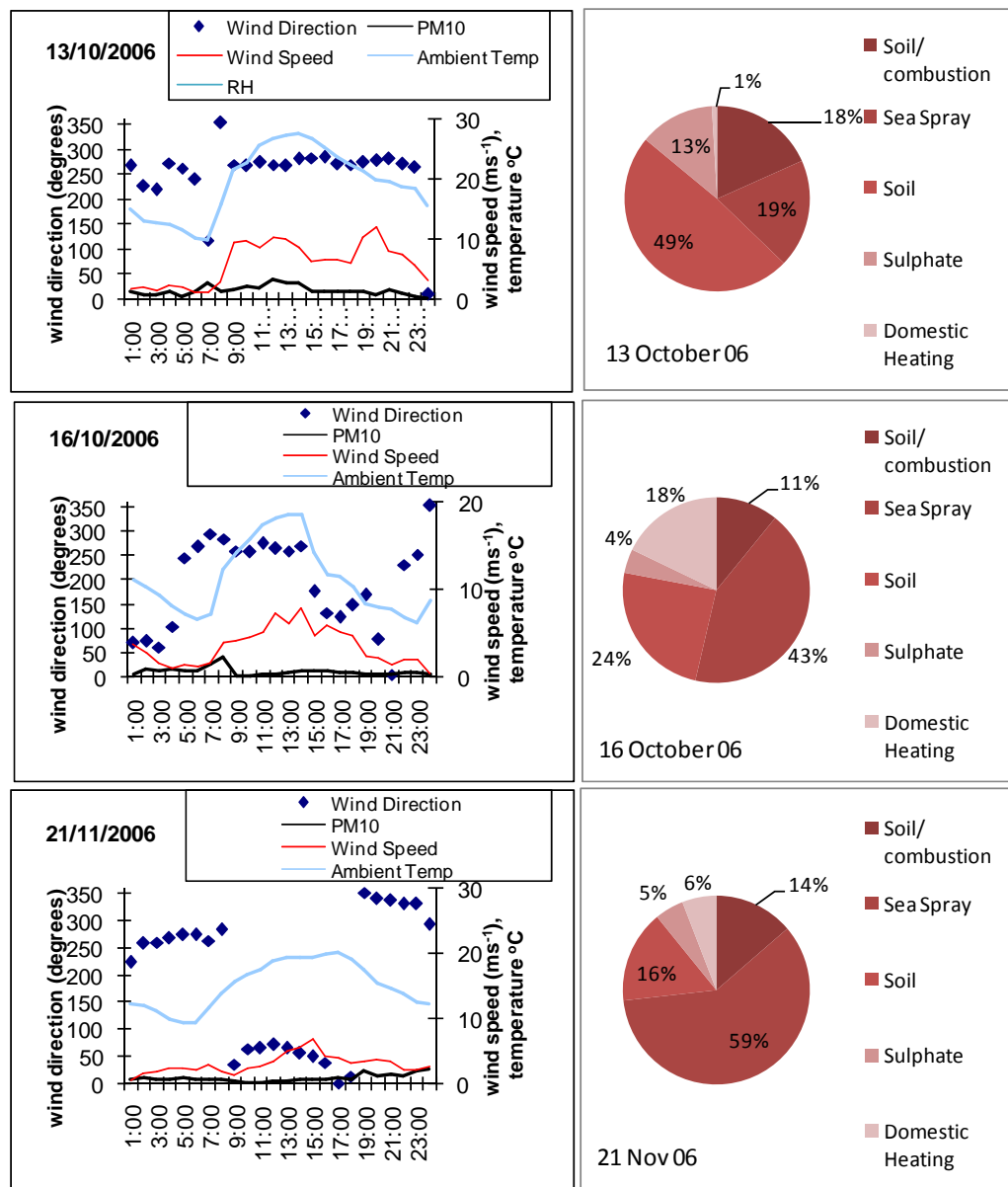


Figure B4: Daily variations in meteorological parameters, PM₁₀ and daily source contributions on high soil/ combustion days during spring 2006.

Table B.5: Daily average concentrations of elements on high soil/combustion days during spring 2006

	BC ng/m ³	Si ng/m ³	K ng/m ³	Ca ng/m ³	K:BC	Ca:BC	K:Si	Ca:Si
16 September	1628	813	250	149	15%	9%	31%	18%
13 October	1417	1416	284	205	20%	14%	20%	14%
16 October	1117	664	193	380	17%	34%	29%	57%
21 November	684	627	278	197	41%	29%	44%	31%

Figure B.5 compares 24-hour average PM₁₀ concentrations measured by the GENT and BAM PM₁₀ monitors for the study period. Results indicate the GENT sampler underestimates PM₁₀ concentrations relative to the BAM and there is a reasonable amount of unexplained variability. This result was unexpected as the GENT sampler has previously performed well relative to NES compliant methods such as the BAM (e.g., Wilton et. al., 2007). The poor correlation is unlikely to be associated with measurement errors by the BAM because a good relationship was observed between the BAM and gravimetric high volume sampler during the study period.

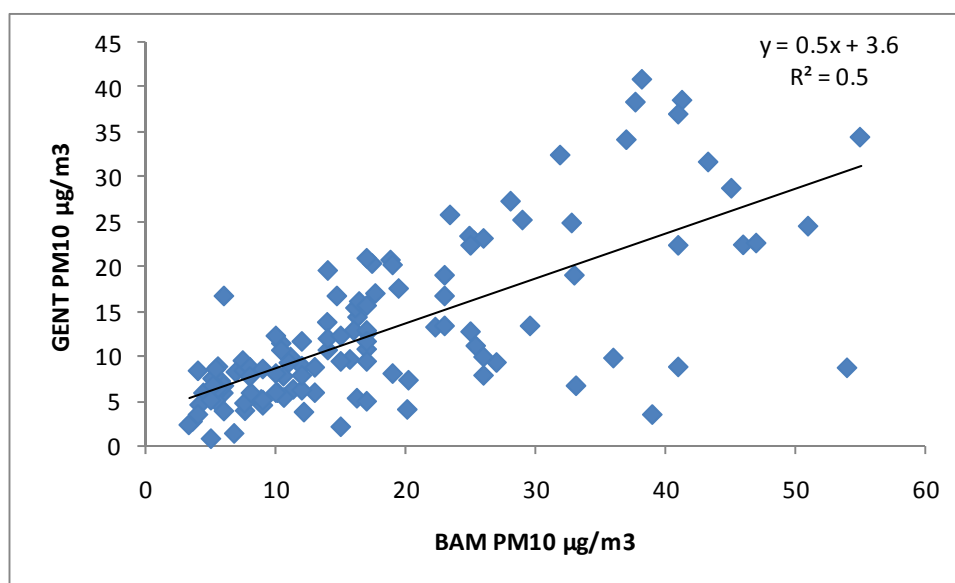
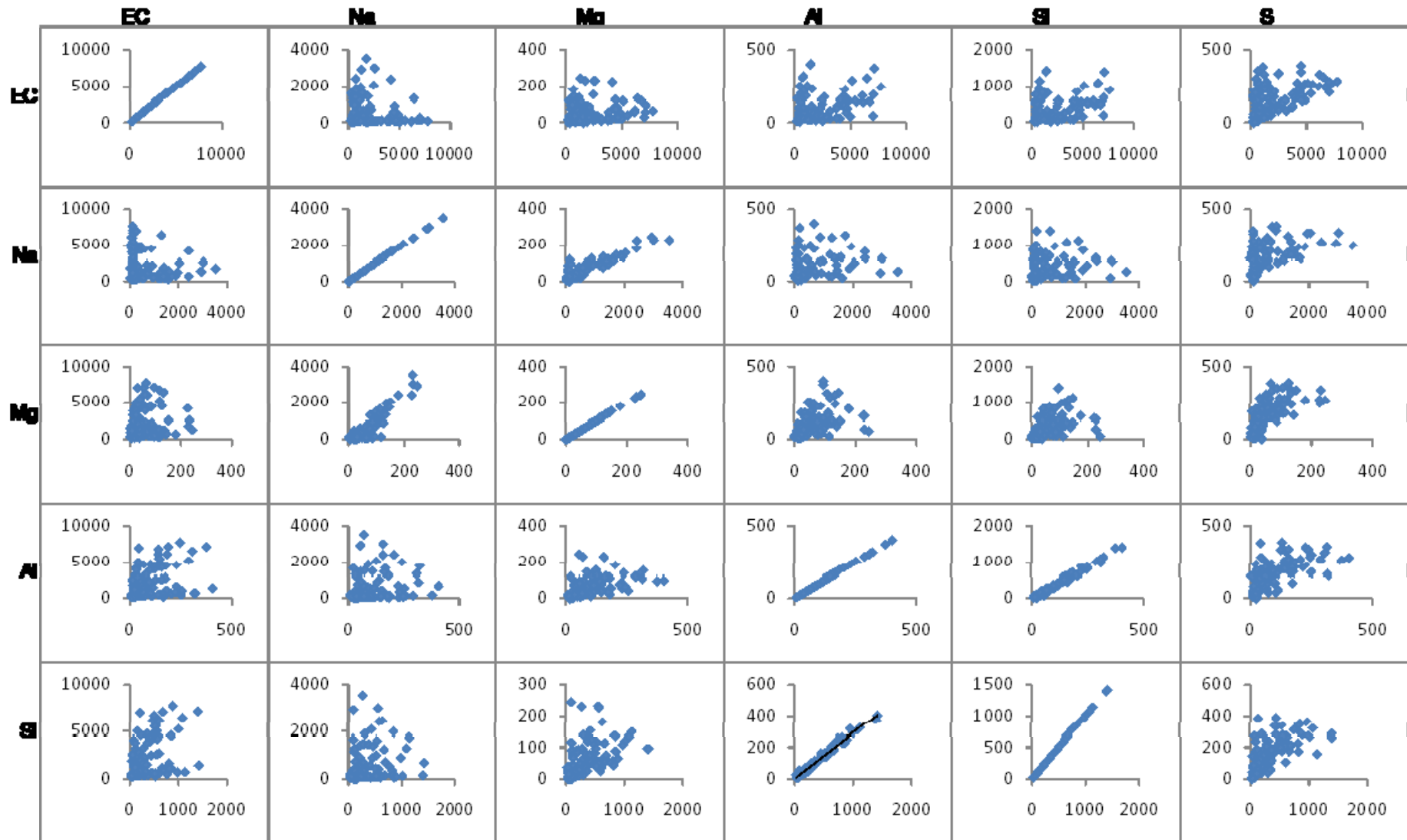
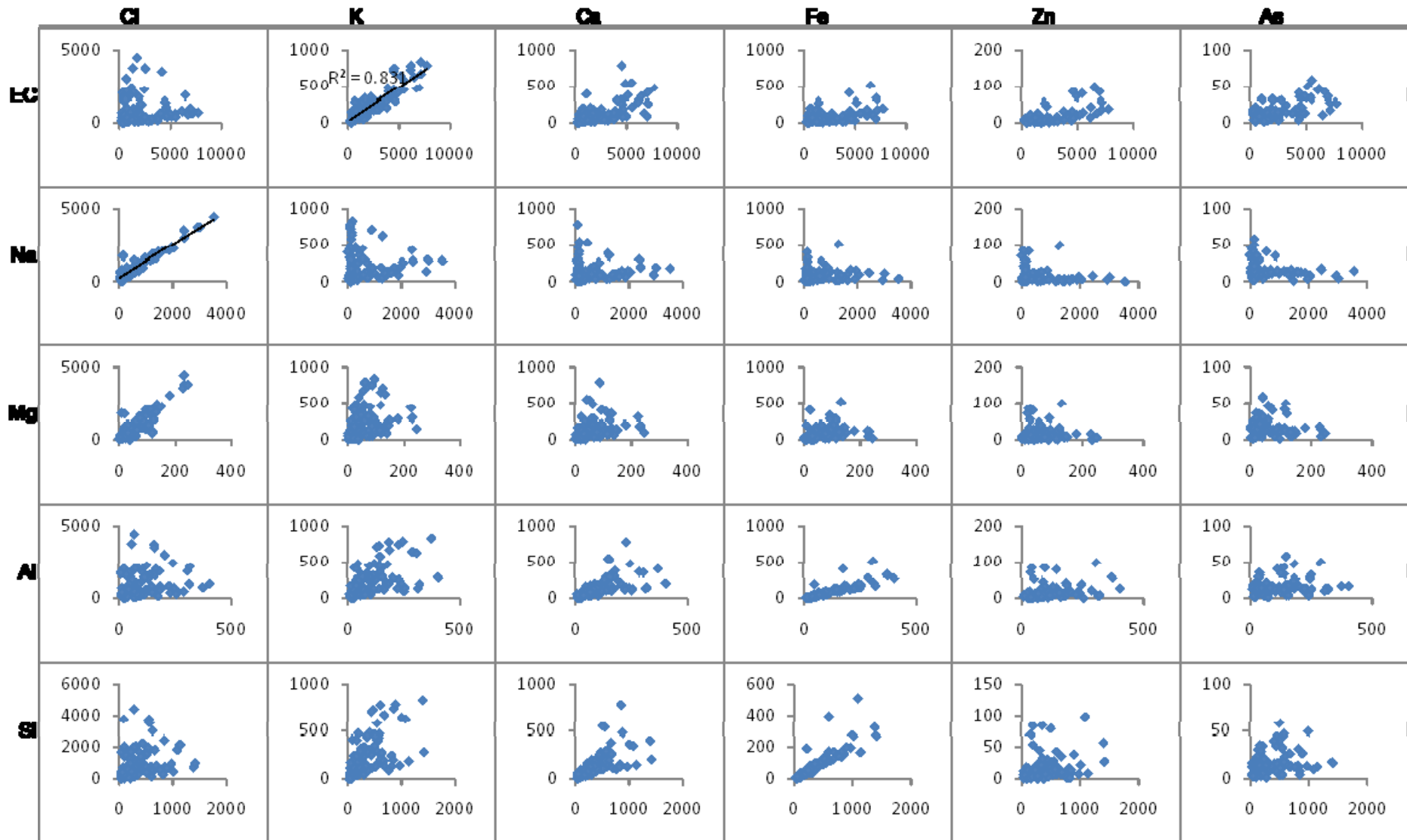
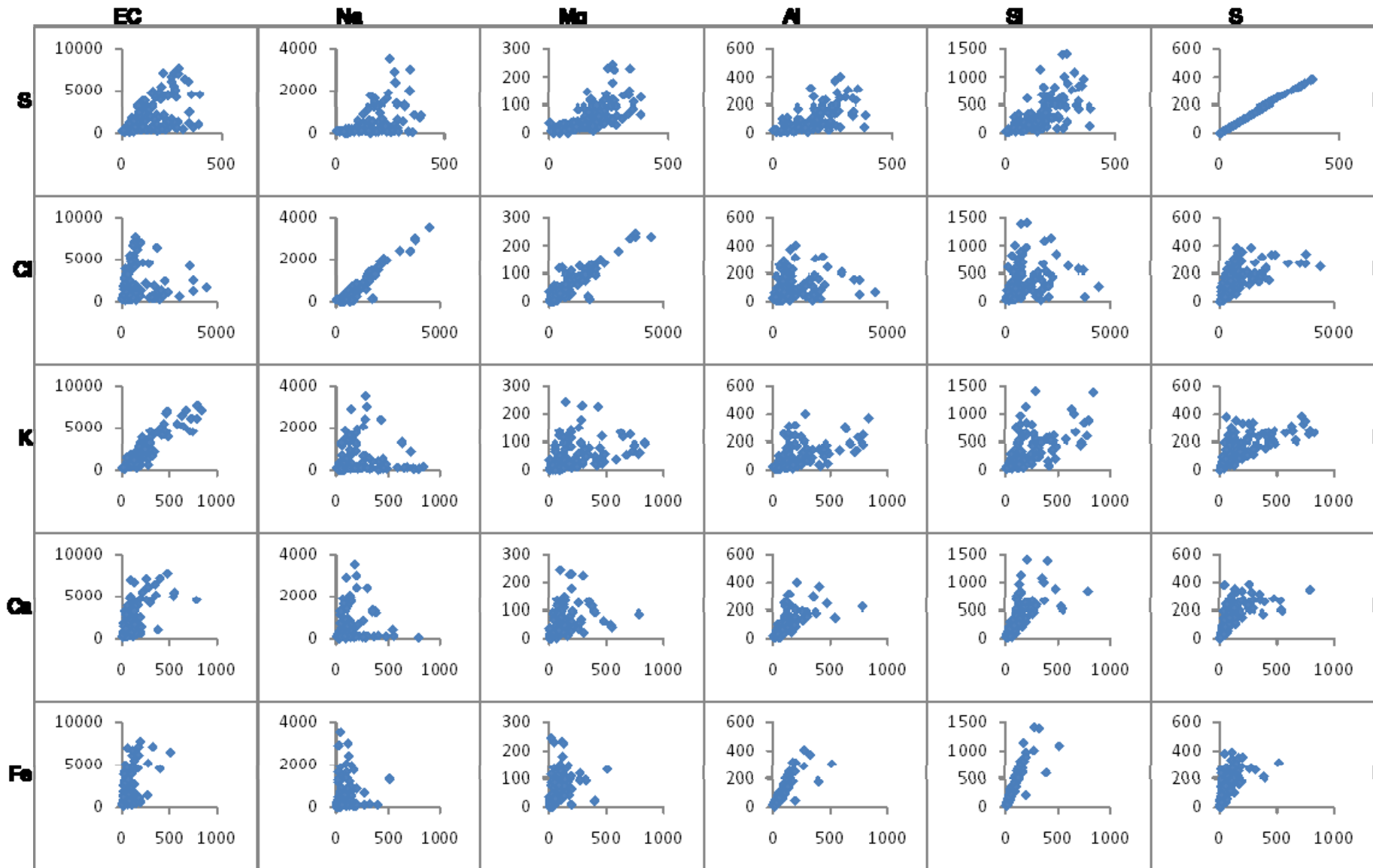


Figure B.5: Comparison of PM₁₀ concentrations measured using the BAM and GENT samplers from June 2006 to September 2007 in Blenheim.







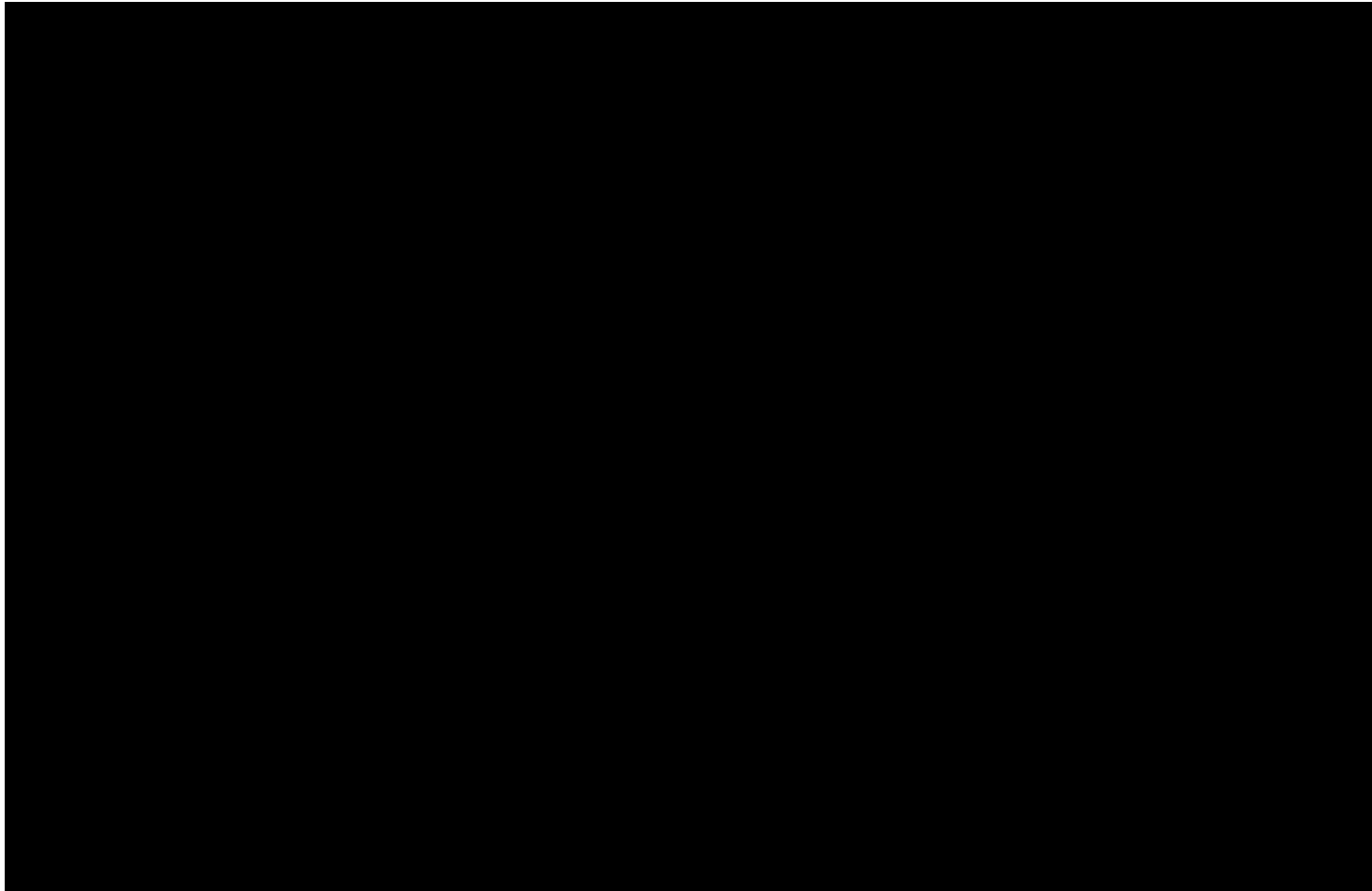


Figure B.4 Relationships between key elements in the PM_{10} size fraction measured at Blenheim

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