

# Source identification and apportionment of $PM_{10}$ and $PM_{2.5}$ in Hastings and Auckland

NIWA Client Report: CHC2007-137 November 2007

NIWA Project: PCCA075



# Source identification and apportionment of $PM_{10}$ and $PM_{2.5}$ in Hastings and Auckland

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# Foundation for Science, Research and Technology

NIWA Client Report: CHC2007-137 November 2007 NIWA Project:

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# **Executive Summary**

The contribution of different sources to  $PM_{10}$  and  $PM_{2.5}$  concentrations was examined in Hastings and Auckland using receptor modelling. The research was carried out for the FRST programme "Protecting New Zealand's Clean Air" with assistance from Auckland Regional Council (provision of results and analysis for the Kowhai Auckland site) and Hawke's Bay Regional Council (filter collection and provision of BAM and meteorological data from the Hastings site). The research objectives were to:

- 1. show how results from receptor modelling studies may be used to check emission inventory results.
- 2. demonstrate a method for determining the contribution of natural sources to  $PM_{10}$  concentrations.
- 3. expand existing information on source profiles for New Zealand.

Receptor model studies provide for implementation of current ambient air quality standards by identifying and quantifying contributions of various source types to ambient particulate matter concentrations. The receptor modelling technique involves measuring concentrations of chemical elements or compounds that particulate matter is composed of, and using statistical models to determine the contributions of different sources to a sample of particles collected on a filter. The filter measurements at Hastings included  $PM_{10}$  and  $PM_{2.5}$  samples collected over a 24-hour period from midnight to midnight, on approximately a one-day-in-three basis between April 2006 and May 2007. A one-day-in-three sampling basis was also adopted for  $PM_{10}$  and  $PM_{2.5}$  at the Kowhai site in Auckland, with 24-hour samples of  $PM_{2.5}$  collected between July 2004 and December 2006, and  $PM_{10}$  samples collected from December 2005 to December 2006.

All data were analysed using the EPA.PMF 1.1 receptor modelling software. Because  $PM_{10}$  exceedances are invariably a winter phenomenon at most New Zealand urban areas where breaches of the NES occur, analyses were focused on sources of  $PM_{10}$  during winter.

In Hastings, five sources were found to contribute to the  $PM_{10}$  concentrations. These were identified as domestic heating, marine aerosol, motor vehicles, sulphate and soil. For this report, domestic heating sources also include outdoor burning of domestic waste biomass. The main contributor to  $PM_{10}$  in Hastings was domestic heating, which was responsible for most of the annual peak concentrations.

Domestic heating was also identified as the dominant source of  $PM_{10}$  during winter in Hastings by emission inventory and an airshed dispersion model. This demonstrates the successful application of a receptor modelling study as a tool for comparing and checking emission inventory results.



While the results and conclusions for Hastings may not be directly applicable to other urban areas in New Zealand, this study has demonstrated how receptor modelling may be used at other locations as a complementary tool to emission inventories. Receptor modelling determines the contribution of different sources to the ambient concentrations measured at a particular location whereas emissions inventories estimate emissions to atmosphere from various sources. Depending on meteorological characteristics, site location, source characteristics and atmospheric chemistry, source contributions identified by receptor modelling may or may not be in broad and general agreement with emission contributions, as was observed for the Hastings study. If there is no broad and general agreement, the use of an airshed model would be appropriate for investigating the link between emissions and concentrations from different sources.

The second objective of the study was to evaluate the contribution of natural sources to  $PM_{10}$  concentrations which cannot be estimated by emissions inventories in urban areas. Depending on whether sulphate is treated as non-anthropogenic, or is a secondary source from industrial emissions, the total contribution from natural sources during winter in Hastings may be estimated between 13-15% of total  $PM_{10}$ . However, on days when  $PM_{10}$  concentrations exceeded the NES, the combined contributions of soil and marine aerosol sources to  $PM_{10}$  concentrations was around 8%. This information is particularly relevant for air quality management in Hastings because the background component of the  $PM_{10}$  cannot be managed, yet needs to be accounted for when developing models and strategies for mitigating  $PM_{10}$  concentrations.

The winter sources of  $PM_{10}$  at Kowhai, Auckland, are somewhat different from those at Hastings. Whereas domestic heating was the dominant source at Hastings during winter, at Kowhai there are also substantial contributions from motor vehicles and sea salt during the winter. The receptor modelling was particularly useful for identifying the contribution of the natural sea salt source. Peak  $PM_{10}$  concentrations were also observed during the summer at Kowhai and on these days marine aerosol sources were found to be dominant. Depending on whether sulphate is treated as natural or anthropogenic, the average contribution from natural sources during winter at Kowhai may be estimated between 26–32% of total  $PM_{10}$ . Identification of the large contribution of natural sources to  $PM_{10}$  concentrations at Kowhai demonstrates the value of receptor modelling for air quality management in Auckland.

The third objective of the research was to contribute to the existing database of source profiles for particulate air pollution in New Zealand. The profiles identified in this study help characterise the composition of particulate matter from different sources and will assist researchers in evaluating future receptor modelling results. Some variability in the elements present and their contributions across the different datasets was observed. This may be explained by local influences and by the size distributions of different components, although further studies may be required to confirm the latter.

Prior to this work no receptor modelling had been carried out on  $PM_{10}$  in New Zealand. A more common approach is to measure the  $PM_{2.5}$  and  $PM_{10-2.5}$  size fractions and combine the receptor



modelling results to provide source contributions to  $PM_{10}$ . Sampling for  $PM_{2.5}$  and  $PM_{10-2.5}$  requires a specific sampler set up and the analysis of two filters for each sample day. Receptor modelling studies in New Zealand and overseas have shown that anthropogenic combustion sources (motor vehicles, domestic solid fuel fires) and secondary particulate matter sources are the main contributors to the  $PM_{2.5}$  fraction, while natural sources (marine aerosol, crustal matter) primarily contribute to the  $PM_{10}$ .  $_{2.5}$  or coarse fraction. An analysis of the  $PM_{2.5}$  size fraction was provided by GNS for this report, primarily because of concerns about how well  $PM_{10}$  would respond to receptor modelling due to the potentially larger number of sources requiring identification on  $PM_{10}$  filters compared with  $PM_{10-2.5}$  or  $PM_{2.5}$  filters.

Following analysis, the  $PM_{2.5}$  results were largely consistent with the  $PM_{10}$  analysis. Differences that did exist, such as the absence of a soil profile and lower marine aerosol contributions in the  $PM_{2.5}$  results, may be explained by the variation of source contributions to the coarse versus fine size fractions.

The ability to determine sources of specifically the  $PM_{10}$  size fraction is particularly useful for air quality managers in New Zealand who wish to determine contributions, including background sources, to ambient particulate matter concentrations and make comparisons with  $PM_{10}$  emission inventories. A key benefit of analysing  $PM_{10}$  is that knowledge of sources is required to assist regulatory authorities to achieve NES requirements relating to management of  $PM_{10}$ . In New Zealand, receptor modelling has been carried out on the  $PM_{10}$  size fraction (e.g., Hastings), the  $PM_{2.5}$  and  $PM_{10-2.5}$  size fractions (which can be collated to give  $PM_{10}$  (e.g., Davy, 2007)) and the  $PM_{2.5}$  size fraction (e.g., Scott, 2006). While the  $PM_{10}$  receptor modelling analysis was successful here, this may not always be the case for other locations where different source mixes occur. Therefore it should not be assumed that acceptable results would always be achieved using the  $PM_{10}$  alone. While more expensive, if an appropriate budget is available, there may be less risk in sampling both  $PM_{10-2.5}$  and  $PM_{2.5}$  as the results can be pooled to provide estimates of combined  $PM_{10}$  sources.



## 1. Introduction

The National Environmental Standard for air quality (NES) requires that ambient concentrations of particulate matter smaller than 10 microns ( $PM_{10}$ ) shall not exceed 50µg m<sup>-3</sup> when averaged over 24 hours. In airsheds where the NES is not met by 2013, the regulations prohibit regional councils from issuing resource consents for discharge to air. To address this problem, it is important for air quality managers to identify the relative contributions of background and anthropogenic sources of  $PM_{10}$ .

Emission inventories are commonly used for this purpose although, whilst they provide useful information for managing air quality, robust inventory estimations for background sources are not available. For this report, background sources are considered to be of natural genesis, such as crustal matter (soil) or marine aerosols (sea spray). An alternative method for evaluating sources of particles uses the variations in the concentrations of different chemical elements and compounds comprising the particulate matter collected on filters during ambient monitoring. This method is referred to here as receptor modelling and is used to identify the relative contributions of various sources to particulate matter concentrations.

Another issue with inventories is that they are based on emissions, rather than measured concentrations. It is important to determine relative contributions of emissions, because mitigation measures will be based on regulating emission sources. However, the NES is based on ambient  $PM_{10}$  concentrations. While the magnitude of  $PM_{10}$  concentrations are primarily driven by mass of emissions, other variables including meteorological characteristics, atmospheric chemistry, time of day and the height of discharge may also have a substantial impact on ambient concentrations.

Along with providing estimates of background sources, receptor modelling also has the advantage of accounting for the impact of meteorology and atmospheric chemistry, so that contributions to ambient concentrations are quantified. Air quality managers may therefore consider undertaking a receptor modelling investigation to determine sources responsible for peak ambient  $PM_{10}$  concentrations. Airshed modelling combined with emissions inventories can also be used as a policy tool for predicting variation of concentrations over space and time, particularly with regard to emissions reduction scenarios and future  $PM_{10}$  concentrations.

To evaluate the effectiveness of management plans to achieve compliance with the National Environmental Standard for  $PM_{10}$ , air quality managers are likely to use ambient monitoring of  $PM_{10}$  to determine trends over time. Identifying the contribution of background sources is important when developing air quality



management plans because, without this knowledge, the background contribution may be ignored or underestimated. Consequently, there is a risk of overestimating the impact of strategies to reduce ambient  $PM_{10}$  concentrations via reductions of anthropogenic emissions.

Exceedances of the NES for  $PM_{10}$  occur only in winter for most airsheds in New Zealand. This is understood to be a consequence of domestic home heating being the dominant source of emissions in these airsheds combined with meteorological conditions conducive to elevated pollution occurring during these months. Source apportionment used for the purpose of assisting with NES attainment in New Zealand would therefore usually be of most benefit if the investigation focused on data from winter months and high pollution days.

The Foundation for Research Science and Technology's (FRST) Protecting New Zealand's Clean Air Programme (Contract number C01X0405) includes a number of objectives to assist Councils in meeting the requirements of the NES for  $PM_{10}$  as effectively as possible. The milestones and outputs relating to the research detailed in this report are as follows:

- 1. Validation of emissions inventories for New Zealand cities using monitoring data, inverse modelling techniques and other approaches.
- 2. A report or workshop that presents an analysis of air quality and source apportionment monitoring data which aims to determine the contribution of background air pollution to urban air quality
- 3. A report or workshop that provides a method by which background air quality can be estimated for the major urban areas in New Zealand

Prior to the studies detailed in this report, receptor modelling of  $PM_{10}$  or  $PM_{2.5}$  had been carried out in Christchurch (Scott 2005, Wilton 2003) and a number of locations in the Wellington Region (Davy, 2007) using a range of techniques for both monitoring and analysis. These studies form a good baseline for evaluating sources and profiles. However, further receptor modelling for New Zealand is required to assist in establishing typical source profiles and for providing information from other areas of New Zealand.



#### 1.1 Receptor modelling in New Zealand

A number of receptor modelling studies have been carried out in New Zealand. These include two source apportionment studies carried out in Christchurch (Scott, 2006; Wilton, 2003). These studies had different objectives and analysis methods. Scott (2006) used positive matrix factorisation (PMF) to apportion 24-hour average  $PM_{2.5}$  concentrations measured at an ambient air monitoring site in Christchurch. In contrast, Wilton (2003) used principal components analysis (PCA) to apportion sources of daytime particulate (measured from 8am to 1pm) and regressed these against light scattering and absorption to determine sources contributing to visibility degradation in Christchurch. Source apportionment studies have also been carried out on the coarse ( $PM_{10-2.5}$ ) and fine ( $PM_{2.5}$ ) size fractions in Masterton, Upper Hutt and Lower Hutt using a range of techniques including PCA and PMF (Davy, 2007).

The results from these three studies provide an indication of source profiles for a range of sources in New Zealand. Five sources were identified in Scott (2006) and these were classified as domestic heating, motor vehicles, secondary particulate, marine aerosol and aged marine aerosol. The latter source included what appeared to be aged (chlorine depleted) marine aerosol that had reacted with urban sources to give sodium sulphate as well as other sources such as soil. Appendix A (from Scott, 2006) compares the presence of different elements in these profiles to other source apportionment studies.

Wilton (2003) identified six profiles although one of these comprised only a few metals. The classifications were soil, secondary particulate, domestic heating, motor vehicles, marine aerosol and metals, although the results suggested some crossover between soil and marine aerosol profiles which were attributed to uncertainties in the Na measurements. The motor vehicle profile contained elemental carbon (BC), S, Fe, Cl and Si.

In Upper Hutt, PMF analysis of 142 samples identified three sources in the coarse  $(PM_{10-2.5})$  size fraction and four sources in the  $PM_{2.5}$  size fraction (Davy, 2007). These were classified as sea salt, soil and road dust (coarse fraction) and sulphate, motor vehicles, wood burning and sea salt ( $PM_{2.5}$  size fraction). Both the soil and the marine aerosol profiles were dominated by Cl, possibly also suggesting some overlap in the soil versus marine aerosol profiles.

In Seaview, an industrial area in Lower Hutt, four factors were identified in the coarse  $(PM_{10}-PM_{2.5})$  size fraction and five factors in the fine  $(PM_{2.5})$  size fraction (Davy, 2007). Both size fractions contained factors identified as sea salt, road dust, soil and zinc with the fine fraction containing another factor identified as motor vehicles.



The Masterton study was more extensive than both Upper and Lower Hutt (Davy, 2007). Filters were collected over a number of years and a total of 200 filters were obtained for both the  $PM_{10-2.5}$  and  $PM_{2.5}$  size fractions. Four sources were identified in the coarse ( $PM_{10-2.5}$ ) size fraction and five in the  $PM_{2.5}$  size fraction. These were classified as sea salt, soil, road dust, wood combustion and motor vehicles with the latter present in the  $PM_{2.5}$  size fraction only.

Specific source profiles have also been determined for marine aerosol (samples from Baring Head), motor vehicles (samples from Mt Victoria Tunnel) and wood burner emissions (Davy 2007).

#### **1.2** Natural sources of particles

The contribution of natural sources to  $PM_{10}$  is an important consideration in airshed management. This is because reduction strategies may fall short of targets if the contribution of natural sources is not accounted for. Natural sources of  $PM_{10}$  typically include marine aerosol and wind-blown soils. Due to the mechanisms by which the particles are produced, natural sources are more relevant in the coarser ( $PM_{10-2.5}$ ) size fraction, although they can also contribute to the fine  $PM_{2.5}$  size fraction.

The contribution of natural sources to  $PM_{10}$  concentrations will vary with location and with meteorological conditions. Typically, natural source contributions will be greater when wind speed is high and from the direction of the sea or specific dust sources. Geographical influences include distance from the sea, type of coastline and the presence of dust generating sources such as gravel riverbeds or open dry areas.

Receptor modelling is one of the few methods available for determining the relative contribution of natural sources to particulate matter concentrations. An added advantage of this method is the ability to compare contributions during different seasons for different concentration ranges and under different meteorological conditions.

Receptor modelling studies in New Zealand to date have shown marine sources to contribute up to 5% of the  $PM_{10}$  size fraction in Masterton on high pollution days (Davy, 2007) and 8% of the  $PM_{2.5}$  size fraction in Christchurch on days when  $PM_{10}$  concentrations were elevated during the winter months (Scott, 2006). In Masterton, soil contributed 6 to 14% of the  $PM_{10}$  on the winter high pollution days. No separate soil profile was found in the Christchurch study (Scott, 2006) possibly because the contribution in the smaller  $PM_{2.5}$  size fraction was negligible or it was not resolved by the receptor modelling.



#### 1.3 Objectives

The key objectives of this study are as follows:

- 1. To show how results from receptor modelling studies may be used to check emission inventory results.
- 2. To demonstrate a method for determining the contribution of natural sources to  $PM_{10}$  concentrations.
- 3. To expand on the existing information on source profiles for New Zealand.

The location of the monitoring sites was an important consideration in the design of the programme with respect to the meeting the objectives. The following location variables were considered desirable to achieve the objectives of the research:

- A range of sources representative of urban air quality in New Zealand.
- An ambient air quality monitoring site likely to be representative of average source contributions within the airshed.
- A location where a recent emission inventory has been conducted.
- A location where natural sources are likely to be a notable contributor to  $PM_{10}$ .

Hastings was considered to be a suitable location for the study because of the existence of a recent air emission inventory, the potential for a range of anthropogenic sources (e.g., domestic heating, motor vehicles, and industry), the likely contribution of natural sources and high  $PM_{10}$  concentrations in excess of the NES (Wilton, 2005). Auckland was also considered a good location for the work because of the potential for a variety of sources and the likely prevalence of marine aerosol. Hastings was chosen as a location suitable for investigating all of the key objectives. Auckland was included because the diversity of sources was considered particularly useful for meeting Objective 3 and source apportionment data were already available from the Auckland regional Council (ARC).



### 2. Methodology

#### 2.1 Site selection and locations

A source apportionment monitoring site was established in Hastings. The programme was funded by FRST with contributions in-kind by GNS and Hawke's Bay Regional Council. The FRST programme focused on the  $PM_{10}$  size fraction because of the air quality management requirements of the NES. The GNS contribution involved the analysis and reporting of the  $PM_{2.5}$  size fraction. This was done because of concern about conducting source apportionment analysis on the  $PM_{10}$  alone, without consideration of the bimodal distribution (and by inference the contributing sources) of urban particles in the coarse ( $PM_{10-2.5}$ ) and fine ( $PM_{2.5}$ ) size fractions.

Receptor modelling studies in New Zealand and overseas have shown that anthropogenic combustion sources (motor vehicles, domestic solid fuel fires) and secondary particulate matter sources are the main contributors to the  $PM_{2.5}$  fraction while natural sources (marine aerosol, crustal matter) primarily contribute to the  $PM_{10}$ . <sub>2.5</sub> fraction. Therefore, separating these sources by sampling for the two different size fractions improves the resolution of the receptor modelling.

The objectives to be met by the Hastings study were an evaluation of the contribution of background sources to  $PM_{10}$  in an urban location where NES breaches occur and to compare receptor modelling results with an air emission inventory. The general approach was measurement of  $PM_{10}$  and  $PM_{2.5}$  size fraction and determination of elemental concentrations by ion beam analysis methods. These methods are detailed in section 2.2.5. No organic carbon or inorganic ion assessment was included in the Hastings study. This limits the assessment of secondary particulate to estimates of sulphate based on sulphur concentrations with no assessment made of the nitrate contribution. The significance of this has yet to be determined, although nitrate sources are not expected to be a dominant contributor of  $PM_{10}$  in New Zealand urban environments.

Information from an existing ambient monitoring site in Kingsland, Auckland (Kowhai) was provided by ARC for use in this study. In addition to supplying the data, the analysis of sources was also provided by ARC. The Kowhai investigation is part of a broader receptor modelling project that includes many sites at various locations within the Auckland airshed, where both  $PM_{10}$  and the  $PM_{2.5}$  size fraction are being measured. The results of the wider investigation will be reported by ARC at a later date.



#### 2.1.1 Hastings (St Johns College Monitoring site)

Hastings is a small urban area located approximately 20 kilometres south of Napier in Hawke's Bay on the east coast of the North Island of New Zealand. Figure 2-1 illustrates the distance and direction to sea, neighbouring areas and the largely flat topography of the immediate area.



**Figure 2-1:** Topography surrounding Hastings, showing nearby hills, Napier to the north and Pacific Ocean to the east. Grids are 10km<sup>2</sup> (NZMG).

The ambient sampling monitoring equipment was situated at the St Johns Ambient Air Quality monitoring site located at St Johns College in Jervois Street, Hastings (Figure 2-2). The NZTM site co-ordinates are Easting: 1931169 and Northing: 5605196.

Existing monitoring equipment owned and operated by Hawke's Bay Regional Council at the site includes a FH62-C14 beta attenuation monitor (BAM) recording hourly average  $PM_{10}$  concentrations, a Vaisala WXT510 Weather Transmitter measuring wind speed, wind direction, relative humidity and ambient temperature. Meteorological data were logged as 10 minute averages on an IQUEST DS4483 Data Logger. BAM data were also logged as hourly and 24-hour averages.





**Figure 2-2:** Location of the Hastings Air Quality Monitoring Site. Grids are 1km<sup>2</sup>.

#### 2.1.2 Auckland

Samples of airborne particles were collected by Auckland Regional Council at an ambient air quality monitoring station located within the grounds of Kowhai Intermediate School, off Sandringham Road, Kingsland (NZTM 1755691 E; 5197772 N). Figure 2-3 shows a map of the wider Auckland area, while Figure 2-4 is a map of the local neighbourhood.

The Kowhai Intermediate School monitoring site is operated by Watercare Services for the ARC Regional Air Quality Monitoring Network and the Ministry for the Environment as part of the Global Environmental Monitoring System / Air Pollution Programme (GEMS/AIR) conducted in conjunction with the World Health Organisation. The site was established in early 2004 and is classed as a residential – peak site (http://www.mfe.govt.nz/publications/air/gems/). Pollutants monitored at the site include nitrogen dioxide (NO<sub>2</sub>), ozone, volatile organic compounds (VOC), total suspended particulate (TSP), lead (Pb), PM<sub>10</sub> and PM<sub>2.5</sub>, along with meteorological parameters.







The Kowhai site is approximately 3.5 kilometres southwest from the central business district of Auckland City. Land use in the area is predominantly residential with some light industrial and commercial activities. The northern side of the monitoring station was adjacent to a 2 m fence next to the school swimming pool and beyond that, approximately 50 m to the northeast, are the school buildings. 30 m to the west is Sandringham Road, with residential housing to the southwest and beyond them Eden Park stadium is 300 m southwest. To the east are open fields and beyond that are residential properties. To the south of the monitoring station are more school fields then beyond that are residential properties. The land around the site at Kowhai Intermediate School is flat to rolling, however, 300 m to the north it drops away into the Newton valley through which the north-western motorway passes.





Figure 2-4: Map showing location of Kowhai monitoring site

#### 2.2 Conceptual receptor model

An important part of the receptor modelling process is to formulate a conceptual model of the receptor site. This means understanding and identifying the major sources that may influence ambient particulate matter concentrations at the site. A conceptual receptor model includes:

- An understanding of source categories and their temporal trends (day-of-week, seasonal, annual);
- An understanding of regional and local meteorological transport patterns and the sources that contribute to particulate matter at the monitoring location;

The conceptual receptor model for sources of  $PM_{10}$  and  $PM_{2.5}$  at the Hastings and Auckland monitoring sites is likely to include contributions from:

1. Combustion products from motor vehicle emissions and re-entrained road dust (all year);



- 2. Combustion products from domestic solid fuel fires (winter) and other domestic activities such as lawn mowing and backyard fires (all year);
- 3. The coarse and fine fractions of marine aerosol (sea spray) and possibly some crustal (soil) matter (these sources are likely to be wind speed and direction dependent)
- 4. Commercial/industrial activities such as boiler emissions;
- 5. Secondary aerosols from atmospheric gas-to-particle conversion processes (mainly during summer due to increased solar radiation driving atmospheric chemistry);
- 6. Hastings may also have some contribution from agricultural or horticultural practices such as rural burning and ammonia (to form ammonium particle species) from livestock wastes.

Of these and more minor contributing sources, not all are likely to be resolved by the receptor modelling. However, of primary importance is the determination of sources contributing to elevated  $PM_{10}$  concentrations.

#### 2.3 Sampling method

#### 2.3.1 Hastings PM<sub>10</sub>

The instrument used to collect particulate matter at the Hastings site was a GENT. The GENT sampler was designed by the University of Ghent in Belgium and has been used extensively throughout the world for source apportionment studies. It is a relatively simplistic sampler in that it measures on one air stream, but has the advantage of a stacked filter unit which allows for the measurement of both the coarse  $(PM_{10}-PM_{2.5})$  and  $PM_{2.5}$  size fractions. In this study, the dual size fraction option was not utilised and the GENT was used to measure the  $PM_{10}$  size fraction alone. Samples were collected on Teflon filters.

#### 2.3.2 Hastings PM<sub>2.5</sub>

The Hastings  $PM_{2.5}$  samples were collected on a 24-hour basis using an ANSTO ASP sampler with a  $PM_{2.5}$  cyclone-type size selective inlet.



#### 2.3.3 Sample period Hasting PM<sub>10</sub> and PM<sub>2.5</sub>

Filters from the GENT and ANSTO samplers were collected in Hastings from April 2006 to May 2007. Table 2-1 shows the number of  $PM_{10}$  filters collected during each month and the number of these excluded from the analysis. More detail on sample dates and the duration of the sampling period are appended. The sample programme was based on a frequency of one day in three with an intensive one day in two sampling regime for a one month period during both the winter and summer months. Actual sampling frequency was somewhat variable but a representation of each season was achieved.

	Total Filters	No. Invalid
January (2007)	9	
February (2007)	10	
March (2007)	15	1
April (2006 & 2007)	17	1
May (2006 & 2007)	9	3
June (2006)	10	
July (2006)	9	1
August (2006)	14	1
September (2006)	11	2
October (2006)	7	1
November (2006)	4	1
December (2006)	6	
Total	121	11

#### Table 2-1:PM10 sample distribution by month of year

 $PM_{2.5}$  sampling began in April 2006 and ended in May 2007, with a total of 130 samples collected. Filters for all size fractions were exposed for a 24-hour period from midnight to midnight as specified in the NES for ambient  $PM_{10}$  monitoring (MfE, 2004).

Throughout the source apportionment sampling period, concentrations of  $PM_{10}$  were also continuously measured at the St Johns monitoring site using a FH62-C14 BAM.

#### 2.3.4 Auckland

Filter samples, results and analyses from various instruments located at the Kowhai air quality monitoring station were supplied by ARC. Samples were collected on a one-



day-in-three sampling basis with the monitoring period and number of filters analysed as follows:

- 240 PM<sub>2.5</sub> samples from RAAS (Andersen Instruments Inc.) and Partisol 2300 (Rupprecht and Patashnick Inc.) speciation samplers for the period July 2004 – December 2006;
- 2. 115  $PM_{10}$  samples from a Partisol 2000 for the period December 2005 December 2006;

Separate receptor modelling studies were carried out for ARC by GNS for each of these sample sets. Along with the gravimetric samplers, a BAM (ThermoAndersen FH62-C14) recorded continuous  $PM_{10}$  observations at the Kowhai air monitoring station. A summary of the results are reported here for information.

#### 2.4 Analytical methods

A range of ion beam analysis methods were used to determine concentrations of elements within the samples. These included proton induced X-ray emission (PIXE), particle induced gamma ray emissions (PIGE) and particle elastic scattering analysis (PESA).

Concentrations of the majority of the elements in the particulate samples were measured using PIXE. When protons in a 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 elements present in the specimen. The energy emitted is specific to each element allowing quantification of the concentration of that element within any given sample. The proton beam passes through a portion of the filter. Concentration estimates are based on the assumption of uniform distribution of the element on the filter surface. PIXE was used for the measurement of elements ranging from Mg to Pb.

PIGE was used to measure concentrations of Na in the samples and can also be used for other elements with low atomic weights. With PIGE, protons interact with the nuclei rather than the electrons and gamma ray energies are measured.

Hydrogen in the sample was measured using PESA. The method is based on measurements of elastically scattered protons when a proton beam is passed through the filter. The measurement is made in forward direction for a scattering angle of  $45^{\circ}$ .



Further details of the ion beam analysis methods used in this study are provided by Trompetter and Davy (2007).

Measurement of elemental carbon (soot) on filters was by light reflection. Determination of carbon by these methods is referred to as Black Carbon (BC) or light absorbing carbon (LAC). The absorption and reflection of visible light on particles in the atmosphere or collected on filters depends on the particle concentration, density, refractive index and size. For atmospheric particles, elemental carbon (EC) is the most highly absorbing component in the visible light spectrum with very much smaller components coming from soils, sulphates and nitrates. Hence, to the first order it can be assumed that all the absorption on atmospheric filters is due to EC. The main sources of atmospheric EC are anthropogenic combustion sources and include biomass burning, motor vehicles and industrial emissions.

When measuring BC by light reflection/transmission, light from a source is transmitted through a filter onto a photocell. The amount of light absorption is proportional to the amount of elemental carbon present and provides a value that is a measure of the elemental carbon on the filter. Conversion of the absorbance value to an atmospheric concentration value of BC requires the use of an empirically derived equation.

#### 2.5 Statistical analysis

A three tiered approach to each analysis was implemented for the Hawke's Bay samples:

- Preliminary evaluation.
- Principal Components Analysis.
- Positive Matrix Factorisation.

A similar approach was also used by GNS for the Auckland dataset.

The preliminary evaluation involved an examination of 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.



Principal Components Analysis (PCA) 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. While historically PCA has been used as a source apportionment tool, there are a number of limitations in the application of the results to determining source contributions. The main advantage of carrying out the PCA analysis as a part of the PMF process is the identification of the eigenvalue distribution of factors. This can assist in understanding the dataset and potentially the number of factors to use. It should be noted, however, that PMF is a more sensitive method and may be able to distinguish between factors that are combined in the PCA approach (e.g., motor vehicles and domestic heating). PCA was carried out on the datasets using Systat 12 and STATGRAPHICS XV.

Positive Matrix Factorisation (PMF) is a factor analysis tool based on least square regression that has been designed to overcome the limitations associated with using PCA for source apportionment studies, in particular the determination of the contributions of sources. It also provides a more sensitive analysis as 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 applies a lesser weighting to their significance and reduces 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).

#### 2.6 Receptor modelling of PM<sub>2.5</sub> and PM<sub>10</sub>

A number of design issues can impact on the data collected in a source apportionment study. The selection of particulate matter size fraction and the species to be included in the analysis are important considerations.

Speciation samplers, which collect particulate matter on a variety of filter media to allow for analysis of inorganic ions and organic and elemental carbon (EC), as well as PIXE analysis for elements, may be equipped with a  $PM_{2.5}$  size selection inlet. This can be problematic in that additional studies of the coarse size fraction may be necessary to evaluate the contributions to  $PM_{10}$  for air quality management purposes.

The ability to determine sources of specifically the  $PM_{10}$  size fraction is particularly useful for air quality managers in New Zealand who wish to determine contributions, including background sources, to ambient particulate matter concentrations and make comparisons with  $PM_{10}$  emission inventories. A key benefit of analysing  $PM_{10}$  is that knowledge of sources is required to assist regulatory authorities to achieve NES



requirements relating to management of  $PM_{10}$ . An evaluation of the  $PM_{10}$  size fraction could be made based on collecting particulate matter as  $PM_{10}$ , or on two separate filters as  $PM_{2.5}$  and  $PM_{10-2.5}$ . Improved results are likely to occur as a result of using the latter method, because the statistical analysis may be simplified as a result of the physical separation of fine and coarse mode sources. However, in some cases resources may not allow for the collection and analysis of two size fractions. For example,  $PM_{10}$  filters may be available from gravimetric sampling conducted as a requirement of the NES. A third option of using  $PM_{2.5}$  as a proxy for  $PM_{10}$  is less useful and may lead to false assumptions being made about the ability to achieve air quality targets.

#### 2.7 Limitations

An important factor to consider when interpreting data from source apportionment studies is that results are for a specific site and may not be indicative of average airshed contributions. In an area with minimal topographical and meteorological complexity (such as Hastings, Christchurch or Masterton) a site representative of average air quality is likely to provide a good indication of average source contributions across a wider area. If the topography and meteorology is more complex, or the monitoring location is more consistent with a "peak" monitoring site, results may reflect contributions that are not applicable beyond the vicinity of the site.

As with any modelling and analysis technique there are uncertainties associated with the source contribution values. These stem from physical measurements (gravimetric determination, volumetric flows, timers and elemental determinations) and the receptor model fitting itself, as demonstrated by  $r^2$  values and the bootstrapping process. Therefore the values and percentages quoted throughout this document are likely to have an associated relative error of around  $\pm$  10% (Davy 2007).

Furthermore, the GENT or ANSTO samplers collect particulate matter on one or two filters (fine and coarse size fractions) and the analysis focuses on elements that can be identified on Teflon or Polycarbonate filters. With this configuration, inorganic ions and organic carbon are unable to be identified, although inclusion of hydrogen in conjunction with black carbon can be an indicator of the latter.

# 3. Hastings Monitoring Data

Figure 3-1 shows 24-hour average  $PM_{10}$  concentrations measured using the BAM, GENT and ANSTO samplers from April 2006 to May 2007. All three methods show that elevated concentrations occurred during the winter months and peak  $PM_{10}$ 



concentrations exceeded the NES regularly. Highest  $PM_{10}$  concentrations in Hastings occur on calm winter days when low wind speeds and cold temperatures create conditions that trap emissions near to the ground. An air emission inventory for Hastings (Wilton 2005) determined that solid fuel burning for domestic heating is the main source of  $PM_{10}$  emissions during the winter months.



**Figure 3-1:**  $PM_{10}$  and  $PM_{2.5}$  concentrations measured using three different sampling methods for the duration of the sample period.



The relationship between the  $PM_{10}$  concentrations measured using the BAM and the GENT is shown in Figure 3-2. This shows a good correlation with 87% of the variability in concentrations explainable by the relationship. On three days GENT  $PM_{10}$  concentrations were elevated (40 to 70 µg m<sup>-3</sup>) when BAM concentrations were less than 30 µg m<sup>-3</sup>. The dates for these outlying data points were 12 May, 26 July and 31 July 2006. The main sources of  $PM_{10}$  on these days as indicated by the analysis in Chapter 4 of this report is domestic home heating.



**Figure 3-2:** Comparison of BAM and GENT PM<sub>10</sub> concentrations from April 06 to May 07

### 4. Hastings $PM_{10}$

#### 4.1 Source Profiles

Five sources were identified and labelled as domestic heating, sulphate, sea spray, motor vehicles and soil. For this report, domestic home heating includes solid fuel heating sources, along with outdoor burning of garden waste and biomass burning activities. Figure 4-1 compares the concentration profiles for each source. Details of the method used to derive these profiles 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  $PM_{10}$  mass showed a strong correlation ( $r^2 = 0.89$ ) and similar  $PM_{10}$  values (RM = 1.05 x  $PM_{10} + 1.26$ ).

The source labelled domestic heating profile is dominated by black carbon and contains the majority of the hydrogen, potassium, zinc and arsenic. The first two elements are consistent with emissions from wood burning. Zinc has also been



included in wood burning profiles in New Zealand before (Wilton, 2003; Scott 2005) and may be a consequence of galvanising (zinc plating) being released from woodburner flues. The contribution of arsenic may occur as a result of the burning of treated timber.



**Figure 4-1:** Source profiles for PM<sub>10</sub> at Hastings



The sulphate profile is dominated by black carbon (BC) and sulphur with small quantities of H, Na and K. The combination suggests the presence of ammonium sulphate, sodium sulphate and potassium sulphate.

The sea spray factor is dominated by Cl and Na and has smaller amounts of Mg, S and BC. The motor vehicle profile was dominated by BC with smaller contributions of Ca, Cl, Fe, Si, and S. Based on the elements present, the profile appears to include both exhaust emissions and those associated with road dust and brake and tyre wear (e.g., Si, Al, Fe, and Ca).

The soil profile was dominated by Si, with moderate contributions from Al, C and Na and smaller contributions from Fe, Mg, Ca, K, H and Ti. These elements are consistent with a soil profile (e.g. Scott, 2005).

#### 4.2 Source contributions

Figure 4-2 shows the estimated contribution of the different sources to annual average  $PM_{10}$  concentrations<sup>1</sup>. This indicates the domestic heating contribution to annual average  $PM_{10}$  concentrations is around 59% with sea spray contributing 21% and motor vehicles 7%.



**Figure 4-2:** Contribution of sources to annual PM<sub>10</sub> concentrations at Hastings

<sup>&</sup>lt;sup>1</sup> 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  $PM_{10}$  mass shown in Appendix A.



The daily contributions of sources to  $PM_{10}$  concentrations for each sample day are shown in Figure 4-3 (by source) and Figure 4-4 (combined). The high  $PM_{10}$ concentrations observed during the winter occur as a result of domestic home heating. Sea spray is responsible for over half of the  $PM_{10}$  on one day during the winter, although the mass  $PM_{10}$  concentration on this day does not exceed 50 µg m<sup>-3</sup>. Overall domestic heating is the main source of  $PM_{10}$  on most days from April to October. A small 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 biomass burning (e.g. garden waste) sources which are also included in this profile.



**Figure 4-3:** Daily PM<sub>10</sub> contributions at Hastings by source

Seasonal trends in other sources are limited. Sulphate contributions are minimal throughout the year with a slight tendency towards higher concentrations during the summer. Sea spray also occurs more consistently during the summer months, although the highest sea spray contribution occurs during one day in July.





**Figure 4-4:** Source contributions to reconstructed PM<sub>10</sub> at Hastings



#### 4.3 Comparison with emission inventory results

An air emission inventory for Hastings was completed during 2005 (Wilton, 2005) and results are included in Table 4-1. The emission inventory indicated that domestic heating was the dominant contributor of  $PM_{10}$  during the winter and other anthropogenic sources including motor vehicles and industry were minor contributors for that time of year. The origin of the sulphate source identified by the receptor modelling (Figure 4-3) is uncertain, but may be a combination of sea spray and industrial emissions. In any case, sulphate was not included in the emission estimates, so it is not appropriate to include the receptor model sulphate estimates in a comparison with inventory results.

Receptor modelling results can be compared with the inventory contributions if the background source contributions are removed and this has been done for the receptor modelling results in Table 4-1. The receptor modelling results showed that domestic heating is the dominant contributor to  $PM_{10}$  concentrations and this is broadly consistent with the emission inventory.

**Table 4-1:**Contributions of anthropogenic  $PM_{10}$  sources during winter at Hastings, identified by<br/>emission inventory (Wilton 2005), receptor modelling and an airshed dispersion<br/>model (Gimson 2006).

	Evaluation methodology		
Source	Emission inventory	Receptor modelling	Airshed model
Domestic*	94%	96%	92%
Motor vehicles	4%	4%	2%
Industry	2%	0%	6%

 $^{\ast}$  Domestic sources include both solid fuel heating and outdoor burning of domestic waste and biomass

The results from the emission inventory and receptor modelling collated in Table 4-1 therefore show that the two methods are in agreement for broadly identifying contributions to  $PM_{10}$  sources during winter at Hastings, while keeping in mind that the former method relates to estimated emissions while the latter relates to contributions to measured ambient concentrations. A direct comparison ideally needs to account for meteorology, atmospheric chemistry and temporal variations.

An airshed dispersion model developed by Gimson (2006) for Hastings was based on the emission inventory data and also identified domestic heating as the dominant contributor to  $PM_{10}$  concentrations (Table 4-1). Airshed model results would be



particularly useful for investigating links between emissions and concentrations for studies where inventory estimates fail to provide a broad and general match with receptor modelling results. While the inventory and receptor modelling were in broad and general agreement for the Hastings investigation, in this case the airshed model provides confidence that the agreement of inventory and receptor modelling results is not a result of coincidence.

Minor contributions from motor vehicles and industry were identified by the emission inventory. The receptor modelling also estimated a minor contribution from motor vehicles, however no industry contribution to  $PM_{10}$  concentrations was identified. The most likely explanation is that industrial emissions do not impact at the location of the sampling site or, alternatively, the receptor modelling was unable to resolve an industry source profile. An analysis of wind direction associated with the  $PM_{2.5}$  sources suggests that at least some of the sulphate may be associated with industrial emissions of SO<sub>2</sub> up-wind from the site (see Section 5 and Appendix C).

Gimson (2006) notes that the airshed model results for industry sources are not reliable, because there is uncertainty regarding the estimates of industry emissions and the emissions are also not input to the model as elevated stacks. In any case, motor vehicles and industry are only minor contributors to winter  $PM_{10}$  emissions and it is most noteworthy that the domestic heating contribution was consistently identified as dominant by emission inventory, airshed modelling and receptor modelling techniques.

The comparison of winter emission inventory data and the receptor modelling will be of particular interest to air quality managers, because the winter season is when exceedances of the NES for  $PM_{10}$  typically occur. It is encouraging that results from the techniques are in agreement because this provides confidence, when developing management plans to achieve NES targets, that reductions in domestic  $PM_{10}$  emissions will be effective at reducing ambient  $PM_{10}$  concentrations.

#### 4.4 Seasonal variations

Figure 4-5 shows that the main source of  $PM_{10}$  concentrations during the winter time when NES breaches occur in Hastings is domestic heating. Note that this differs from the results in Table 4-1 because natural sources are included in Figure 4-5. The versatility of the receptor modelling for identifying intra-annual variation of  $PM_{10}$ sources is demonstrated in Figure 4-5. The dominance of sea spray as the main contributor during summer shows how natural sources may be especially important at different times of the year. Conclusions regarding management of  $PM_{10}$  in winter may therefore not be valid for other times of the year.





**Figure 4-5:** Seasonal variations of the percentage contribution of sources to PM<sub>10</sub> concentrations at Hastings. Seasonally averaged 24hr PM<sub>10</sub> concentrations are shown at top left of each plot.

While Figure 4-5 indicates that the percentage contribution of sea spray to total  $PM_{10}$  is very much greater in summer (53%) than winter (9%), the average  $PM_{10}$  concentration in summer (12 µg m<sup>-3</sup>) is much lower than the winter average  $PM_{10}$  concentration (44 µg m<sup>-3</sup>) at Hastings.

Relationships between meteorological conditions and sources of  $PM_{10}$  in Hastings were also examined and results are appended for information (Appendix B).

#### 4.5 High pollution days

Figure 4.6 shows the average contribution of sources to  $PM_{10}$  concentrations on days when concentrations exceeded 50 µg m<sup>-3</sup>. The domestic heating contribution on these days increases from 82% (winter average) to 87% on the highest pollution days.

It is very useful to identify the contribution of natural sources to  $PM_{10}$  concentrations, because this needs to be accounted for when management strategies are being developed. Failure to effectively account for natural sources may create a risk of overestimating the ability to achieve air quality targets via reductions of anthropogenic emissions.





**Figure 4-6:** Average source contributions on days when  $PM_{10}$  concentrations exceed 50 µg m<sup>-3</sup> in Hastings. The average 24hr  $PM_{10}$  concentration for the high pollution days was 63 µg m<sup>-3</sup>.

Gimson (2006) estimated that natural sources contributed 5–10  $\mu$ g m<sup>-3</sup> of PM<sub>10</sub> concentrations in Hastings when NES exceedances occur and implications of the modelling are based on this assumption. Receptor modelling shows that at least 8% (i.e. 5  $\mu$ g m-3) of PM<sub>10</sub> may be from non-anthropogenic sources on high pollution days (Figure 4-6) and would be 9.5% (i.e. 6  $\mu$ g m-3) if sulphate is entirely from natural sources. Natural sources of PM<sub>10</sub> may therefore be confidently accounted for as 5–6  $\mu$ g m<sup>-3</sup> when future airshed models or management strategies are developed for high pollution days at Hastings.

# 5. Hastings PM<sub>2.5</sub>

An analysis of the  $PM_{2.5}$  size fraction was also carried out for Hastings, primarily because of concerns about how well receptor modelling would perform with  $PM_{10}$ . (Refer to Section 2.1 and Section 2.6 for discussion on this).

#### 5.1 Source profiles

Figure 5-1 shows the source profiles extracted from the PMF analysis of Hastings  $PM_{2.5}$  data. Details of the method used to derive these profiles and the PMF model diagnostics are contained in Appendix C. A comparison of the reconstructed mass (RM) based on the contributions from these profiles to the measured  $PM_{10}$  mass showed a strong correlation ( $r^2 = 0.86$ ) and similar  $PM_{10}$  values ( $RM = 1.3 \times PM_{2.5} - 0.4$ ).










Figure 5-1: Source profiles and elemental concentrations in PM<sub>2.5</sub> at Hastings



The first  $PM_{2.5}$  source profile is that for marine aerosol, as it is dominated by sodium and chlorine, while the second profile is for a secondary sulphate aerosol source. The third source profile has been labelled domestic heating as it clearly includes BC and K with some S and Cl. The fourth source contribution was identified to be from motor vehicle emissions with a road dust component included.

Zinc and arsenic were also highly correlated with the domestic heating source signature but present at low concentrations. Arsenic was only detected above the limit of detection ( $\approx 3-5 \text{ ng/m}^3$ ) during winter as shown in Figure 5-2.

The presence of As may be associated with burning of copper chrome arsenic (CCA) treated timber in domestic wood burning appliances. A similar phenomenon was observed in winter  $PM_{2.5}$  at Upper Hutt (Davy 2007).





#### 5.2 Source contributions

Figure 5.3 presents the average (over the entire monitoring period) source contributions to ambient  $PM_{2.5}$  concentrations at Hastings.

The average source contributions estimated by the receptor modelling indicate that wood burning emissions from domestic heating is the most significant contributor to  $PM_{2.5}$  concentrations at Hastings. Other sources contributing to  $PM_{2.5}$  were marine





aerosol, secondary sulphate particles and motor vehicle emissions, although these are estimated to contribute only around 10% each.

**Figure 5-3:** Average relative source contributions to PM<sub>2.5</sub> at Hastings

The temporal variation in source contribution estimates is useful for source identification and demonstrating seasonal trends. Figure 5-4 shows the relative contribution of sources to  $PM_{2.5}$  mass for each sample collected at Hastings with average monthly contributions as the inset. Figure 5-5 presents the daily contributions of individual sources to  $PM_{2.5}$  mass.

The domestic heating source had a distinct seasonality with higher concentrations during winter months. The receptor modelling results also suggest that the secondary sulphate and marine aerosol sources were present in higher concentrations during summer.

#### 5.3 Seasonal variations

Figure 5-6 shows that the primary source of  $PM_{2.5}$  during the winter (June-August) at Hastings, when average  $PM_{2.5}$  concentrations were high (> 24 µg m<sup>-3</sup>), was emissions from domestic heating. This source also dominated during autumn (April-May) and spring (September-November). During the summer (December-March) when  $PM_{2.5}$  concentrations were low (5 µg m<sup>-3</sup>), the contribution from domestic heating is much less and sources of  $PM_{2.5}$  are primarily from marine aerosol and secondary sulphate.





**Figure 5-4:** Source contributions to reconstructed PM<sub>2.5</sub> at Hastings (Inset: Monthly contributions)





Figure 5-5: Daily contributions by source to PM<sub>2.5</sub> at Hastings



Figure 5-6: Seasonal variations in relative contributions to PM<sub>2.5</sub> sources at Hastings



Figure 5-7 shows the contribution of these sources as  $PM_{2.5}$  concentrations and demonstrates that while sea salt and sulphate are the dominant contributors during summer, the actual concentrations are relatively small compared with the domestic heating contribution during winter.





More detailed analyses of  $PM_{2.5}$  on high pollution days are included in Appendix C for information purposes, along with an investigation of source contributions with wind direction. Peak  $PM_{2.5}$  concentrations in Hastings were found to be primarily due to emissions from domestic solid fuel fires.

# 5.4 Hastings comparison of size fractions

The relationship between the  $PM_{10}$  and  $PM_{2.5}$  mass concentrations measured at Hastings is shown in Figure 5-8. This shows a reduced contribution of  $PM_{2.5}$  at high  $PM_{10}$  concentrations. This relationship is inconsistent with observations from Christchurch (Foster, 1997) which indicate an increasing  $PM_{2.5}$  contribution (around 90%) at high  $PM_{10}$  concentrations. Like Hastings, the main source of Christchurch  $PM_{10}$  at peak concentrations was domestic heating.





**Figure 5-8:** Comparison of  $PM_{2.5}$  and  $PM_{10}$  mass concentrations measured using the ANSTO and GENT samplers respectively

The estimated source contribution on days when  $PM_{10}$  concentrations were high and  $PM_{2.5}$  concentrations were low was examined to determine whether sources of particulate could explain the poorer relationships on these days (8 June and 26 July 2006). On both occasions the predominant source of particulate in both size fractions was domestic home heating. Similarly the main source of both  $PM_{2.5}$  and  $PM_{10}$  concentrations on the days when  $PM_{10}$  concentrations were highest was domestic heating. Because this source produces predominantly fine mode ( $PM_{2.5}$ ) particulate, the difference in measured concentrations cannot be readily explained by particulate composition.

Examination of the BAM versus GENT data shows that the 26 July was an outlier in this comparison and that an overestimate by the GENT is a likely explanation of the poor  $PM_{10}$  and  $PM_{2.5}$  relationship on this day.

Daily variations in the contribution of  $PM_{2.5}$  and  $PM_{10-2.5}$  (GENT  $PM_{10}$  – Ansto  $PM_{2.5}$ ) are shown in Figure 5-9.

The evaluation of sources within each size fraction is similar, with domestic heating contributing the majority of the  $PM_{10}$  and  $PM_{2.5}$  concentrations. During the winter months the average  $PM_{2.5}$  concentration was 24 µg m<sup>-3</sup> and the estimated domestic contribution was 89%. In the  $PM_{10}$  size fraction, the average winter  $PM_{10}$  concentration was 44 µg m<sup>-3</sup> and the domestic heating contribution was estimated at 82%.





**Figure 5-9:** Daily estimates of PM<sub>2.5</sub> and PM<sub>10-2.5</sub> concentrations at Hastings

This suggests that, either more than 10  $\mu$ g m<sup>-3</sup> of domestic heating particulate emissions was occurring within the coarse PM<sub>10-2.5</sub> size fraction, or there is some measurement issue with the monitoring data.

Notwithstanding differences in absolute concentrations for domestic heating, the receptor modelling results were well correlated. A plot of the reconstructed  $PM_{10}$  and  $PM_{2.5}$  mass from domestic heating shows a good relationship ( $r^2 = 0.75$ ) with the largest variations in the relationship observed on the days identified above which had poor correlations of mass (e.g., 8 June, 26 July). The correlation between the reconstructed  $PM_{2.5}$  and  $PM_{10}$  mass from other sources was poor. However, this is not surprising given the low concentrations from these sources (typically less than 7 µg m<sup>-3</sup>) relative to the precision of the monitoring methods.

The main difference in the profiles is the presence of a soil factor in the  $PM_{10}$  size fraction and a higher marine aerosol contribution in the  $PM_{10}$  size fraction. This is expected because both sources produce predominantly coarse mode particulate and should have a greater presence in the  $PM_{10-2.5}$  size fraction.

Overall the results for the  $PM_{10}$  and  $PM_{2.5}$  size fractions are generally consistent, with both showing domestic heating as the dominant source, smaller contributions from motor vehicles and sulphate and a larger contribution from coarse mode sources (marine aerosol and soil) in the  $PM_{10}$  size fraction.

While on this occasion a reasonable result was achieved from the investigation of winter sources of  $PM_{10}$  concentrations, this is not necessarily the norm and it should not be assumed that acceptable results would necessarily always be achieved using the  $PM_{10}$  size fraction alone for receptor modelling. Success of receptor modelling on



 $PM_{10}$  may depend on factors including location and the mix of sources. While more expensive, there may be less risk in sampling both  $PM_{10-2.5}$  and  $PM_{2.5}$ , as the results can be pooled to provide estimates of combined  $PM_{10}$  sources.

# 6. Auckland (Kowhai) monitoring data

The Auckland data presented here are from one predominantly residential urban site and the investigation is not expected to infer source contributions for Auckland urban area as a whole, but rather shows a small part of a much larger picture. This study is a component of a much wider receptor modelling programme being undertaken by the Auckland Regional Council and the reader is referred to that organisation for further information. The analysis for this section of the report was carried out by GNS for ARC and provides examples of the results obtained in Auckland and discusses them in relation to the Hawke's Bay study.

The particulate matter gravimetric results from a BAM at Kowhai, presented in Figure 6-1, show that  $PM_{10}$  concentrations tended to be highest during winter months (May-August). A smaller secondary maximum in  $PM_{10}$  concentrations is evident during summer (December-January) and the summer-winter variations may be explained by the relative contributions to ambient concentrations from different sources at different times of the year.



Apr-04 Jun-04 Aug-04 Oct-04 Dec-04 Feb-05 Apr-05 Jun-05 Aug-05 Oct-05 Dec-05 Feb-06 Apr-06 Jun-06 Aug-06 Oct-06 Dec-06

**Figure 6-1:** 24 hour average  $PM_{10}$  concentrations at Kowhai, measured by FH62 BAM (source: ARC)



# 7. Kowhai $PM_{10}$

The Partisol  $PM_{10}$  samples from Kowhai refer to those  $PM_{10}$  samples collected using a Partisol 2000 Sampler from December 2005 to December 2006. The Partisol 2000  $PM_{10}$  sampler was located alongside a RAAS Speciation Sampler until April 2006. The RAAS was replaced by a Partisol 2300 Speciation Sampler from June 2006 onwards. Analyses of  $PM_{10}$  were provided for elements and black carbon only. The Partisol  $PM_{10}$  sampler was operated as a satellite to a main  $PM_{2.5}$  hub system and, by necessity, sampled on alternate days to  $PM_{2.5}$ , therefore, few sample days were coincident for the  $PM_{10}$  and  $PM_{2.5}$  samples.

Gravimetric results for the Partisol  $PM_{10}$  samples, presented in Figure 7-1, show distinct peaks in  $PM_{10}$  concentrations during winter months at Kowhai similar to the BAM  $PM_{10}$ , along with several peaks above 25 µg m<sup>-3</sup> during the summer.



**Figure 7-1:** 24 hour average PM<sub>10</sub> concentrations measured by a gravimetric Partisol sampler at Kowhai (Source: ARC)

Figure 7-2 presents the source profiles extracted from the PMF analysis of Kowhai Partisol  $PM_{10}$  data.

The first factor has been identified as derived from marine aerosol. The second factor is likely to be due to secondary sulphate although it may represent an aged marine











**Motor Vehicles** 1400 Concentration (ng/m<sup>3</sup>) 1200 1000 800 600 400 200 0 н вс Na Si S Element СІ κ Ca Fe

**Figure 7-2:** Source profiles and elemental concentrations for Partisol PM<sub>10</sub> at Kowhai (Source: ARC)



aerosol source due to the presence of Na and Cl along with S, Mg, K and Ca. The third source contribution has been identified as originating from biomass burning due to the presence of BC, K and Cl in the profile. The fourth factor represents a crustal matter source (soil) and the fifth factor has been labelled motor vehicle emissions due to the presence of BC, S Ca and Fe.

Figure 7-3 presents the relative source contributions to ambient  $PM_{10}$  concentrations at Kowhai. For all Auckland results, the source labelled biomass burning is identical to the domestic heating category for the Hastings results and includes both domestic heating and outdoor burning contributions. The relative source contributions estimated by the receptor modelling indicate that marine aerosol is the most significant contributor on an annual basis. The remaining sources, when listed from greatest to least magnitude of  $PM_{10}$  contribution, are: biomass burning, motor vehicles, secondary sulphate and soil.





#### 7.1 Seasonal variations in PM<sub>10</sub> source contributions at Kowhai

Figure 7-4 shows that the primary source of  $PM_{10}$  during the winter, when average  $PM_{10}$  concentrations at Kowhai were elevated ( $20\mu g/m^3$ ), was domestic heating. Sea salt and motor vehicles are also considerable sources during winter, while sulphate and soil are minor contributors. For the rest of the year, sea salt dominates  $PM_{10}$  source contributions. Average  $PM_{10}$  concentrations during autumn, spring and summer are



relatively similar  $(15-16\mu g/m^3)$  and, during these months, the contribution from biomass burning is lower and sources of PM<sub>10</sub> are primarily from sea salt, motor vehicles and secondary sulphate.



#### **Figure 7-4:** Seasonal variation in PM<sub>10</sub> source contributions at Kowhai (Source: ARC)

Figure 7-5 shows the contribution of these sources as  $PM_{10}$  concentrations. While sea salt is the dominant contributor in summer,  $PM_{10}$  concentrations from sea salt are less during winter and domestic heating is the dominant  $PM_{10}$  concentration source during the colder months.

Analyses of two peak  $PM_{10}$  (>30 µg m<sup>-3</sup>) events at Kowhai, including meteorological phenomena, are included in Appendix D for information purposes. These show that on the peak winter day, biomass burning was a major contributor to the elevated  $PM_{10}$  concentrations, but on the peak summer day the dominant contributor was sea salt.





**Figure 7-5:** Seasonal variations in PM<sub>10</sub> concentrations from various sources at Kowhai (Source: ARC)

# 8. Auckland (Kowhai) PM<sub>2.5</sub>

The  $PM_{2.5}$  samples from the Kowhai Intermediate School site in Kingsland were collected with a RAAS Speciation Sampler from July 2004 – April 2006 and replaced by the Partisol 2300 Speciation Sampler from June 2006 onwards. Both speciation samplers have 4 different sample collection 'channels' for analysis of the various  $PM_{2.5}$  component species of interest. For the Kowhai speciated  $PM_{2.5}$  study, analyses were provided for elemental and black carbon (BC) concentrations.

Gravimetric results for the  $PM_{2.5}$  samples, as presented in Figure 8-1, show distinct peaks in  $PM_{2.5}$  concentrations during winter months at Kowhai. Note that the gaps are due to missed sample days. The peak concentrations in Figure 8-1 correspond with the peaks in BAM  $PM_{10}$  concentrations, with the exception that  $PM_{10}$  also exhibits a smaller secondary maximum during summer (Figure 7-1). The slightly different seasonal variation of  $PM_{10}$  concentrations compared to  $PM_{2.5}$  may be explained by the relative contributions of various sources.





**Figure 8-1:** Gravimetric results for PM<sub>2.5</sub> at Kowhai (Source: ARC)

Figure 8-2 presents the source profiles extracted from the PMF analysis of Kowhai  $PM_{2.5}$  data.

The first factor in Figure 8-2 has been labelled biomass burning due to the presence of BC, K and Cl in the profile. This factor is equivalent to the domestic heating factor identified for Hastings and includes combustion sources from solid fuel heating and outdoor burning of domestic garden waste and other biomass burning activities. The second source contribution is from secondary atmospheric aerosol due to the dominance of sulphur in the profile. The third source contribution is from crustal matter (soil). The fourth source contribution has been identified as originating from motor vehicle emissions due to the presence of BC, S, Ca and Fe. The fifth factor has been identified as a marine aerosol (marine aerosol) source due to the presence of Na and Cl along with some Mg, and Ca.

Figure 8-3 presents the relative source contributions to ambient  $PM_{2.5}$  concentrations at Kowhai averaged over the entire sampling period.

The relative source contributions estimated by the receptor modelling indicate that biomass burning and motor vehicle emissions are the most significant contributors to fine particle concentrations at Kowhai, followed by the contribution from secondary sulphate particles. Marine aerosol and crustal sources are minor contributors of PM<sub>2.5</sub>.





**Figure 8-2:** Source profiles and elemental concentrations for PM<sub>2.5</sub> at Kowhai (Source: ARC)





Figure 8-3: Average (2004 - 2006) relative source contributions to  $PM_{2.5}$  at Kowhai (Source: ARC)

#### 8.1 Seasonal variations in source contributions to PM<sub>2.5</sub> at Kowhai

Figure 8-4 shows that the primary source of  $PM_{2.5}$  during the winter at Kowhai was due to biomass burning, and this was most likely due to emissions from solid fuel appliances for domestic heating. Average  $PM_{2.5}$  concentrations were found to be higher in winter (11 µg m<sup>-3</sup>) than other seasons. During the other seasons, emissions from motor vehicles are the predominant source contributor to  $PM_{2.5}$ . Average  $PM_{2.5}$  concentrations (5–7 µg m<sup>-3</sup>) during autumn, spring and summer are relatively similar when the concentrations apportioned to biomass burning are lower (Figure 8-5).

Biomass burning during the summer is attributed to backyard fires such as burning of garden wastes.

An analysis of  $PM_{2.5}$  sources on a high pollution day in July at Kowhai is included in Appendix D for information purposes. Biomass burning was found to be the dominant source contributor to  $PM_{2.5}$  (91%) and meteorological conditions were cold and calm on the high pollution day.





**Figure 8-4:** Seasonal variations in PM2.5 source contributions at Kowhai (Source: ARC)



**Figure 8-5:** Seasonal variations in PM<sub>2.5</sub> concentrations from various sources at Kowhai (Source: ARC)



# 9. Auckland (Kowhai) comparison of size fractions

## 9.1 Mass comparisons

Analysis of the gravimetric results for the  $PM_{2.5}$  dataset compared to BAM  $PM_{10}$  shows scatter at lower concentrations, but indicates that  $PM_{2.5}$  is largely responsible for elevated  $PM_{10}$  concentrations (i.e. >30 µg m<sup>-3</sup>) as shown in Figure 9-1.





The comparison of Partisol  $PM_{10}$  and  $BAM PM_{10}$  shows good correlation as shown in Figure 9.2.



**Figure 9-2:** Partisol PM<sub>10</sub> versus BAM PM<sub>10</sub> (24-hour average) at Kowhai, December 2005 – December 2006 (Source: ARC)



## 9.2 Factor comparisons

Similar factors were derived for both the  $PM_{2.5}$  and  $PM_{10}$  datasets. Only two of the sample days for each of the size fractions coincided due to instrument configurations so that a correlation analysis could not be made between the source apportionment profiles.

## 9.3 Source contributions

Contributions to  $PM_{10}$  from the marine aerosol and soil sources were approximately ten times their respective contributions to the  $PM_{2.5}$  fractions, confirming that most marine aerosol and crustal matter particles sizes are in the coarse mode ( $PM_{10-2.5}$ ). Motor vehicle emissions were found to contribute similar mass to  $PM_{10}$  and  $PM_{2.5}$ , suggesting they are largely fine fraction particles (<2.5 µm). The biomass source contributions were higher in  $PM_{10}$  (4.1 µg m<sup>-3</sup>) than  $PM_{2.5}$  (2.7 µg m<sup>-3</sup>) which suggests that some agglomeration or coagulation to coarser particle sizes (>2.5 µm) may occur for particles from this combustion source. The secondary sulphate source was found to have a higher contribution to  $PM_{10}$  but this may also be due to a contribution from aged marine aerosol unresolved from the  $PM_{2.5}$  secondary sulphate by the  $PM_{10}$ receptor modelling analysis.

Table 9-1 presents the source contributions for  $PM_{10}$  and  $PM_{2.5}$  when averaged over the entire study period.

Source	Seasalt	Sulphate	Biomass burning	Soil	Motor vehicles
Size fraction	Average Mass µg/m <sup>3</sup>				
<b>PM</b> <sub>10</sub>	6.1	2.1	4.1	1.1	2.3
PM <sub>2.5</sub>	0.6	1.2	2.7	0.08	2.5

**Table 9-1:**Mass contributions by sources to PM10 and PM2.5 at Kowhai

#### 9.3.1 Background versus anthropogenic sources

In order to examine the difference between contributions from natural or background sources (in this case marine aerosol, sulphate and soil) and those of anthropogenic origin (biomass combustion, motor vehicles) the mass contributions were combined for each category. Figure 9-3 shows that anthropogenic sources (average 5  $\mu$ g m<sup>-3</sup>) are significant contributors to PM<sub>2.5</sub>, primarily during winter months, with background contributions (average 2  $\mu$ g m<sup>-3</sup>) generally less than 5  $\mu$ g m<sup>-3</sup> PM<sub>2.5</sub>.





**Figure 9-3:** Background and anthropogenic contributions to PM<sub>2.5</sub> at Kowhai (Source: ARC)

Figure 9-4 presents the  $PM_{10}$  anthropogenic and background source contributions. The contributions of background (10 µg m<sup>-3</sup>) and anthropogenic sources (7 µg m<sup>-3</sup>) to  $PM_{10}$  show a greater influence from coarse fraction particles ( $PM_{10-2.5}$ ). While only one year of data was available for the  $PM_{10}$  analysis, it shows that anthropogenic sources still dominate during winter, but background sources can contribute a significant proportion of  $PM_{10}$  not ascertained by gravimetric analysis or emissions inventories alone.



**Figure 9-4:** Background and anthropogenic contributions to PM<sub>10</sub> at Kowhai (Source: ARC)



# **10.** Discussion and conclusions

#### **10.1** Comparison with an air emission inventory for Hastings

The first objective was to compare receptor model results with emission sources identified by an inventory. Because  $PM_{10}$  exceedances are invariably a winter phenomenon at most New Zealand urban areas where breaches of the NES occur, this analysis focused on sources of  $PM_{10}$  during winter.

The dominant source of  $PM_{10}$  during winter in Hastings was domestic home heating. This conclusion was verified by emission inventory, receptor modelling and an airshed dispersion model. This demonstrates the successful application of a receptor modelling study as a tool for determining sources responsible for peak ambient  $PM_{10}$ concentrations. The receptor modelling approach is also useful to make broad comparisons with emissions inventories: both methods are considered complimentary tools for air quality management and policy formulation, particularly where intervention strategies may be required.

It should be noted that this comparison is valid for Hastings  $PM_{10}$  during winter and the conclusions are not necessarily appropriate for use in other urban areas. The link between emission inventories and ambient concentrations used for receptor modelling depends on meteorology, atmospheric chemistry, and temporal variations. However, this study has demonstrated how receptor modelling might be used at other locations as a check of emission inventory results. The concentration of sources identified by receptor modelling at other airsheds may not be in broad and general agreement with emission contributions, as was observed for the Hastings study. In this case, the use of an airshed model would be appropriate for investigating the link between source emissions and ambient concentrations.

#### **10.2** Contribution of natural sources to PM<sub>10</sub>

The second objective of the study was to evaluate the contribution of natural sources to  $PM_{10}$  concentrations in urban areas. Of particular relevance is the contribution of natural, and therefore unmanageable, sources during winter, because it is during winter when  $PM_{10}$  concentrations typically exceed the NES.

Marine aerosol and crustal matter (soil) were the two key sources that could be considered natural background. The main non-anthropogenic source in Hastings was marine aerosol, which contributed around 9% to  $PM_{10}$  concentrations on average during winter. The combined contributions of soil and marine aerosol sources to  $PM_{10}$  concentrations in Hastings were 13% on average during the winter months and 8%



when  $PM_{10}$  concentrations exceeded the NES. This information is particularly relevant for air quality managers in Hawke's Bay because the background component of the  $PM_{10}$  is essentially unmanageable, yet needs to be accounted for when developing models and strategies for reducing ambient  $PM_{10}$  concentrations.

One area of uncertainty in the study is the extent to which the sulphate source reflects an anthropogenic contribution, or is caused by background sources such as marine aerosol, or is a combination of both. Fertiliser manufacturing in Awatoto to the north of Hastings is the main source of sulphur emissions in the Hawke's Bay Region and may contribute to the sulphate measured in Hastings. If the sulphate source was entirely non-anthropogenic, the background source contribution is estimated at around 9.5% on high pollution days during winter. If the sulphate was entirely a secondary source from industrial emissions, the background contribution may be around 8% on high pollution days. Natural sources of PM<sub>10</sub> may therefore be confidently accounted for as 5–6  $\mu$ g m<sup>-3</sup> when future airshed models or management strategies are developed for high pollution days at Hastings.

The winter sources of  $PM_{10}$  at Kowhai, Auckland, are somewhat different from those at Hastings. Whereas domestic heating was the dominant source at Hastings during winter, at Kowhai there are also substantial contributions from motor vehicles and sea salt during the winter. The more substantial contribution from motor vehicles in Auckland, compared to the Hastings results, is obviously a consequence of the much greater volume of traffic in the larger city of Auckland. The North-western Motorway is not far from the Kowhai monitoring site and, combined with the close proximity of other busy roads, would result in the total vehicle kilometres travelled (VKT) being higher than at the Hastings monitoring site.

The receptor modelling was particularly useful for identifying the contribution of the natural marine aerosol and crustal matter sources. If the background sources were underestimated, the effectiveness of strategies to mitigate anthropogenic emissions would be overestimated. Peak  $PM_{10}$  concentrations were also observed during the summer at Kowhai and these days were found to be dominated by marine aerosol sources. Identification of the relative contributions of natural sources and anthropogenic sources to  $PM_{10}$  concentrations at Kowhai demonstrates the utility of receptor modelling for air quality management in Auckland.

## **10.3** Source profiles for PM<sub>10</sub> and PM<sub>2.5</sub> for New Zealand

The third objective of the research was to contribute to the existing database of source profiles for  $PM_{10}$  in New Zealand. In this respect, the study is extremely valuable as it provides additional information on source profiles for  $PM_{10}$ . Previous studies have



focused on the  $PM_{2.5}$  size fraction (Scott, 2005, Davy 2007) and the coarse ( $PM_{10-2.5}$ ) size fraction (Davy, 2007).

Source profiles for motor vehicles, domestic heating (biomass combustion), marine aerosol and sulphate were found for all four datasets and soil profiles were found for the  $PM_{10}$  datasets at both Hastings and Auckland (Kowhai). The relative proportion of different elements comprising the profiles for each site are appended. The domestic heating source profile was relatively consistent across sites with minimal variability in the elements included and the relative contributions. This source was dominated by black carbon (range 62% to 70%) with hydrogen (range 9% to 20%) providing an indication of a significant contribution from organic carbon compounds derived from incomplete combustion of fuels. The S, Cl and K contributions to the domestic heating source were identical for both  $PM_{10}$  size fractions at 1%, 5% and 4% respectively with the  $PM_{2.5}$  size fractions being slightly higher. The consistency of this profile between sites and size fractions provides valuable information on a domestic heating source profile for New Zealand.

More variability is observed in the elemental profiles for motor vehicles. The Hastings  $PM_{10}$  and  $PM_{2.5}$  size fractions showed contributions from Si (around 10%) and Al (3%) indicating the probability of road dusts contributing to this profile. In Auckland however, the motor vehicle profile was dominated by black carbon in both size fractions and included only 2% Si in the  $PM_{10}$  size fraction and less than 1% in the  $PM_{2.5}$  size fraction.

Sulphur (S) in the motor vehicle profile may occur as a result of emissions from diesel fuelled vehicles and may vary from site to site depending on the vehicle fleet profile of the area. The proportion of S in each ranged from 0% (Hastings  $PM_{2.5}$ ) to 6% (Hastings  $PM_{10}$ ). The percentage of S was higher in the  $PM_{10}$  size fractions (6% and 3%) than the  $PM_{2.5}$  size fractions (0% and 1%), although the sample size is too small to determine the significance of this. The Hastings motor vehicle profile for  $PM_{10}$  also contained higher percentages of both Ca and Cl.

The sulphate profile generally contains the same elements across the four datasets, although the contribution of black carbon varies with location and size fraction and the Kowhai  $PM_{10}$  sulphate profile appears to include some marine aerosol. Marine aerosol profiles were similar containing the main components of sea water (Cl, Na, Mg and S) with smaller amounts of K and Ca, although both Hastings size fractions included some black carbon. The soil profile at Hastings ( $PM_{10}$  only) was dominated by Si (43%) with smaller amounts of Na and Al (both 13%) and Fe (8%). In Auckland the Si proportion was lower at 25%, with NaCl (47%) being the significant other



contributor. This indicates either a combined soil and marine aerosol profile or the resuspension of deposited marine aerosol.

The information on sources obtained through this study adds considerably to the existing database of source profiles for New Zealand. These help characterise the composition of particulate from different sources in New Zealand and will assist researchers in evaluating future receptor modelling results. The profiles obtained were generally robust and in most cases appeared to represent distinct sources. Some variability in the elements present and their contributions across the different datasets may be explained by local influences (e.g., Si in motor vehicles) and by the size distributions of different components (e.g., S in motor vehicles), although further studies may be required to confirm the latter.

## **10.4** Overall conclusions

From the source apportionment undertaken in Hastings and Kowhai (Auckland), the following overall conclusions were obtained:

- Sources resolved using PCA/PMF for Hastings and Kowhai (Auckland) included seasalt, soil, vehicle emissions, domestic home heating emissions and sulphates (assumed to be secondary particulate). The source profiles will assist with future source apportionment studies that may be carried out in NZ. It was not possible to distinguish the different types of fuels for home heating (e.g. coal/wood) or vehicle sources (e.g. diesel/petrol).
- The methodology helped to identify the main sources to peak concentrations of  $PM_{10}$  and  $PM_{2.5}$ . In Hastings, peak concentrations were generally attributed to home heating but at Kowhai (Auckland), seasalt was also a significant contributor to the summer high concentration episodes.
- Overall, the results from the source apportionment study confirmed the conclusions drawn from emissions inventory and modelling investigations in Hastings and provided information about background levels of PM<sub>10</sub> and PM<sub>2.5</sub>. This information is critical for air quality management so that reduction targets can be set for anthropogenic (i.e. 'manageable') sources of PM<sub>10</sub> and PM<sub>2.5</sub>, allowing for background levels.
- It was possible to estimate the contributions to background levels of PM<sub>10</sub> in Hastings and Kowhai (Auckland) by using source apportionment. The natural component of PM<sub>10</sub> concentrations from soil and sea spray averaged 6.7 μg m<sup>-</sup>



 $^{3}$  in Hastings and 7.2 µg m<sup>-3</sup> in Kowhai. Sulphate PM<sub>10</sub> sources contributed an average of 1.1 µg m<sup>-3</sup> and 2.1 µg m<sup>-3</sup> at Hastings and Kowhai respectively, although it is uncertain whether these sources are of natural or anthropogenic origin.

• It was possible to estimate the contributions to background levels of  $PM_{2.5}$  in Hastings and Kowhai (Auckland) by using source apportionment. The natural component of  $PM_{2.5}$  concentrations from soil and sea spray averaged 1.3 µg m<sup>-3</sup> in Hastings and 0.7 µg m<sup>-3</sup> in Kowhai. Sulphate  $PM_{2.5}$  sources contributed an average of 1.2 µg m<sup>-3</sup> at both Hastings and Kowhai, although it is uncertain whether these sources are of natural or industrial genesis.

# 11. Summary

As a first tool in  $PM_{10}$  investigations at New Zealand urban areas, ambient monitoring is often conducted to identify where and when  $PM_{10}$  exceedances occur. For airsheds where  $PM_{10}$  pollution is apparent, emission inventories are often undertaken to evaluate anthropogenic sources for identifying appropriate mitigation strategies. This report has demonstrated the value of receptor modelling for quantifying source contributions to ambient concentrations of  $PM_{10}$ , particularly with regard to contributions from background sources.

Airshed models may be used to investigate the link between emissions and concentrations. Airshed models are also useful for policy development and predicting concentrations over space and time but themselves rely on emission inventory estimates. Factors to consider when evaluating the likelihood of natural source contributions may include distance from the coastal marine aerosol sources, the extent and distance from agricultural activities, along with meteorological data as an assessment of the long-range transport background  $PM_{10}$ .

The report demonstrates the successful application of receptor modelling to the  $PM_{10}$  size fraction in both Hastings and Auckland. Prior to this work no receptor modelling had been carried out on  $PM_{10}$  in New Zealand, although a common approach is to measure the  $PM_{2.5}$  and  $PM_{10-2.5}$  size fractions and combine the receptor modelling results to provide source contributions to  $PM_{10}$ . In this study the analysis of  $PM_{2.5}$  size fractions were more robust (as indicated by bootstrapping), however  $PM_{10}$  results were acceptable.

The ability to apply receptor modelling tools to understand the  $PM_{10}$  variability is particularly useful for air quality managers in New Zealand who wish to determine



contributions, including background sources, to ambient particulate matter concentrations and make comparisons with  $PM_{10}$  emission inventories. A key benefit of analysing  $PM_{10}$  is that knowledge of sources is required to assist regulatory authorities to achieve NES requirements relating to management of  $PM_{10}$ . Using  $PM_{2.5}$  as a proxy for  $PM_{10}$  may lead to false assumptions being made about the ability to achieve air quality targets.

Furthermore,  $PM_{10}$  filters may be available from gravimetric sampling conducted as a requirement of the NES. However, while on this occasion reasonable results were achieved for the  $PM_{10}$  analysis, this is not necessarily the norm and it should not be assumed that acceptable results would always be achieved using the  $PM_{10}$  alone. An advantage of separating sources by sampling for the two different size fractions is that the resolution of the receptor modelling is often improved. While more expensive, there may be less risk in sampling both  $PM_{10-2.5}$  and  $PM_{2.5}$ , as the results can be pooled to provide estimates of combined  $PM_{10}$  sources.

# **12.** Acknowledgements

This work was conducted under the Foundation for Research, Science and Technology programme "Protecting New Zealand's Clean Air", contract CO1X0405.

John Phillips and the team at Hawke's Bay Regional Council are thanked for the many hours changing and collecting filters.

Auckland Regional Council supplied data from the Kowhai site. Janet Petersen is thanked for advice and assistance with data provision.

GNS Science conducted elemental analyses of all filter samples and funded the Hastings  $PM_{2.5}$  analysis. Bill Trompetter and Andreas Markwitz of GNS Science contributed to the receptor modelling and conditional probability function analysis for the Hastings  $PM_{2.5}$  and Auckland Regional Council datasets.

Lou Reddish from NIWA is thanked for site setup and instrument support.

Janet Petersen (Auckland Regional Council), John Phillips (Hawke's Bay Regional Council), Gustavo Olivares (NIWA), Paul Franklin (Ministry for the Environment) Louise Wickham (Ministry for the Environment) and Kevin Mahon (Auckland Regional Council) provided useful comments on drafts of this report.



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# Appendix A: Hasting PM<sub>10</sub> and PM<sub>2.5</sub> sampling details

Run date	Run Hours Run date		Run Hours	Run date	Run Hours
5 April 2006	24	19 August 2006	24	25 January 2007	24
9 April 2006	24	21 August 2006	24	28 January 2007	24
11 April 2006	24	23 August 2006	24	31 January 2007	24
14 April 2006	24	25 August 2006	24	3 February 2007	24
17 April 2006	24	27 August 2006	24	6 February 2007	24
20 April 2006	24	29 August 2006	24	9 February 2007	24
24 April 2006	24	31 August 2006	24	12 February 2007	24
3 May 2006	24	2 September 2006	24	15 February 2007	24
6 May 2006	24	4 September 2006	24	18 February 2007	24
12 May 2006	24	6 September 2006	24	21 February 2007	24
13 May 2006	24	8 September 2006	24	23 February 2007	24
17 May 2006	24	10 September 2006	24	25 February 2007	24
20 May 2006	24	14 September 2006	24	27 February 2007	24
Unknown	54	16 September 2006	24	1 March 2007	24
Unknown	33	20 September 2006	24	3 March 2007	24
8 June 2006	24	24 September 2006	24	5 March 2007	24
10 June 2006	24	26 September 2006	48	7 March 2007	24
Unknown	24	28 September 2006	24	9 March 2007	24
16 June 2006	24	4 October 2006	24	11 March 2007	24
18 June 2006	24	4 October 2006	24	15 March 2007	24
20 June 2006	24	6 October 2006	24	17 March 2007	24
22 June 2006	24	9 October 2006	24	19 March 2007	24
24 June 2006	24	12 October 2006	63	21 March 2007	24
26 June 2006	24	18 October 2006	24	23 March 2007	24
28 June 2006	24	30 October 2006	24	25 March 2007	24
2 July 2006	24	2 November 2006	24	27 March 2007	24
7 July 2006	24	5 November 2006	24	29 March 2007	24
8 July 2006	37	12 November 2006	24	31 March 2007	24
16 July 2006	24	21 November 2006	24	2 April 2007	24
18 July 2006	24	1 December 2006	24	4 April 2007	24
22 July 2006	24	7 December 2006	24	6 April 2007	24
24 July 2006	24	10 December 2006	36	8 April 2007	24
26 July 2006	24	13 December 2006	24	15 April 2007	24
31 July 2006	24	19 December 2006	24	16 April 2007	24
1 August 2006	24	21 December 2006	24	18 April 2007	24
2 August 2006	24	4 January 2007	24	20 April 2007	24
5 August 2006	24	7 January 2007	24	22 April 2007	24
9 August 2006	24	13 January 2007	24	24 April 2007	24
13 August 2006	24	16 January 2007	24	26 April 2007	24
15 August 2006	24	19 January 2007	24	28 April 2007	24
17 August 2006	24	22 January 2007	24	30 April 2007	24
				2 May 2007	24



# Appendix B: Data Analysis Hastings PM<sub>10</sub>

## Data validation

Data validation included an assessment of  $PM_{10}$  mass concentrations, elemental concentrations, run durations and flow rates. Quality assurance procedures used for this data set included:

- Exclusion of filters/runs with run times outside  $24 \pm 1$  hour.
- Exclusion of filters/runs with sample volumes greater than 27 m<sup>3</sup>.
- Removal of elements with 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. However a small number of data points were identified as unusual. These data points were dealt with by increasing the error values associated with the specific elements and days of concern. Table B.1 shows the summary information for concentrations of elements.

Element	Average concentration ng/m <sup>3</sup>	Max ng/m <sup>3</sup>	Min ng/m <sup>3</sup>	Std dev	Average % Error	Av LOD ng/m <sup>3</sup>	No. of samples > LOD
Н	485	3820	9	709	34	20	109
BC	3468	12087	206	3059	262	150	111
Na	707	2733	52	560	97	124	104
Mg	96	359	8	60	14	20	108
AI	121	451	7	104	8	11	106
Si	426	1595	35	355	12	8	111
Р	12	49	0	9	11	12	41
S	324	744	37	146	13	8	111
CI	1671	7931	163	1261	44	7	111
К	234	1194	18	227	8	5	111
Са	177	610	15	116	7	6	111
Ti	9	48	0	8	5	5	51
Mn	4	21	0	3	5	4	30
Fe	108	352	8	79	6	4	111
Cu	6	55	1	6	7	10	24
Zn	18	85	1	19	6	6	65
As	18	102	2	19	21	24	28
Se	13	30	2	5	26	27	12
Br	18	121	3	12	30	23	19
Ва	14	50	1	9	22	20	18
Pb	34	162	4	23	71	57	14

# Table B.1PM10 elemental concentrations and statistics



## **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<sub>10</sub> 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 with a ratio of near 1:2. A strong correlation between Mg and both Na and Cl is also observed. These correlations are associated with PM<sub>10</sub> from marine aerosol.
- The relationship between Al and Si is also very strong  $(r^2 = 0.98)$  and indicative of a soil based source. Other elements strongly correlated with both of these and with each other include Fe and Ca.
- A seemingly exponential relationship between BC and K ( $r^2 = 0.7$ ) and between both elements and Zn and both elements and As. The BC and K relationship is a good indicator of wood burning, most probably for domestic home heating, although the apparent exponential aspect of this may reflect more than one type of wood combustion (with one having a stronger K to BC ratio). The presence of Zn in a wood burning profile is not uncommon and may be a reflection of the material (galvanising) used in the flues or the burning of painted wood. The presence of As may be associated with burning of copper chrome arsenic (CCA) treated timber in domestic wood burning appliances.
- The relationship between Zn and As is not illustrated but has an  $r^2$  of 0.6 indicating that 60% of the variation in concentrations of these elements can be explained by their relationship.

Principal components analysis was carried out on the dataset. Eigenvector analysis returned 15 clusters with values greater than 1 (Figure B.1). Evaluation of the analysis showed three key factors, the relationships within which were able to explain 93% of



the variability in the elemental mass. The strongest factor (explaining 74% of the variability) was consistent with combustion but did not differentiate between combustion types or fuel. The other two profiles were consistent with marine aerosol (16% of the variation) and soil (3%) of the variation.





Figure B.1: Scree plot of Eigenvalues from PCA of Hastings PM<sub>10</sub> 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 four factors and 197 runs for one factor (sulphate). This indicates that the derived profiles are reproducible but that the sulphate profile is slightly less robust than the other sources.

Species	Intercept	Slope	RMSE	r <sup>2</sup>
PM <sub>10</sub> Mass	430.76	0.87	3288.78	0.96
Н	60.64	0.87	92.98	0.98
BC	-813.15	1.32	1399.8	0.89
Na	44	0.9	147.64	0.92
Mg	2.94	0.97	15.89	0.93
AI	1.48	0.98	7.86	0.99
Si	2.25	0.99	17.32	1
S	0.82	1	4	1
CI	5.75	0.98	178.48	0.98
К	1.49	0.98	21.65	0.99
Са	1.59	0.99	6.45	1
Ti	3.23	0.69	4.65	0.59
Fe	0.38	0.99	14.17	0.97
Zn	1.84	0.84	7.07	0.83
As	2.05	0.8	8.66	0.75

#### Table B.2:PMF diagnostics for PM10 at Hastings

 $Q_{Theoretical} = 1221; Q_{Robust} = 1015.35; Q_{True} = 1041.69$ 

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 : 201 Number of bootstrapped factors mapped to original factor 2 : 200 Number of bootstrapped factors mapped to original factor 3 : 197

Number of bootstrapped factors mapped to original factor 4 : 200

Number of bootstrapped factors mapped to original factor 5 : 200

Number of bootstrapped factors mapped to no original factor : 2

The average contribution of each element to the profiles is shown in Table B.3. The  $PM_{10}$  mass is included in the table because the PMF contribution outputs for  $PM_{10}$  mass indicate the amount of  $PM_{10}$  from each source on average.

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 motor vehicles responsible for just over 10%. Hydrogen, which provides an indication of the organic carbon component, is also dominated by domestic heating. Na and Cl are both dominated by marine aerosol and Si, Al, Ti and Fe by soil.



	Marine aerosol	Domestic Heating	Sulphate	Soil	Motor Vehicles
	ng/m³	ng/m³	ng/m <sup>3</sup>	ng/m³	ng/m <sup>3</sup>
PM <sub>10</sub> mass	4006	11441	870	1843	1404
н	18.9	403.4	35.7	16.5	0.0
BC	179.9	2751.5	239.9	60.6	415.3
Na	559.2	0.0	17.3	92.7	0.0
Mg	65.4	3.8	7.2	14.5	4.7
AI	0.8	6.0	0.0	92.6	21.9
Si	1.5	28.1	2.7	302.4	94.4
S	85.5	33.7	155.2	0.0	47.0
CI	1352.7	172.8	0.0	0.0	82.1
К	27.5	143.3	10.6	37.8	6.9
Са	28.9	2.6	6.1	18.2	118.0
Ті	0.2	1.7	0.5	6.0	1.4
Fe	0.0	20.0	4.0	55.6	27.9
Zn	1.2	11.4	0.7	2.5	0.7
As	2.0	11.5	1.5	0.0	0.9

Table B.3:	Factor	identification	and	contributions
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Figure B.2: Distribution of elements by source



Two methods can be used to estimate the relative contribution of each source to  $PM_{10}$  concentrations. These include integration of the  $PM_{10}$  mass data into the PMF model or multiple linear regression (MLR) of the PMF source contributions outputs. Integration of the  $PM_{10}$  mass into the PMF analysis gives a profile for  $PM_{10}$  mass (see Table B.3) similar to the output of the MLR. Results from the integration of  $PM_{10}$  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  $PM_{10}$  mass (Figure B.3) gave an  $r^2$  of 0.9 indicating all but 10% of the variability in concentrations could be explained by the relationships.



**Figure B.3:** Reconstructed versus measured PM<sub>10</sub> mass at Hastings

#### Meteorological analysis of Hastings PM<sub>10</sub> sources

The relationship between meteorological conditions and sources of  $PM_{10}$  in Hastings was examined by comparing daily variations in wind speed, wind direction and temperature on days when the highest concentrations from each source occurred. This method provides more detailed information than comparing 24-hour average meteorology with source contributions but is limited in that it only considers the relationships on a small number of days.

Table B.4 summarises the days examined and the corresponding source contributions and  $PM_{10}$  concentrations. The reconstructed  $PM_{10}$  refers to the sum of the source contributions estimating using the PMF source apportionment evaluation. The measured  $PM_{10}$  refers to the mass concentration measured using the GENT sampler and the BAM concentration is the 24-hour average concentration measured at the site for NES compliance monitoring purposes. Figures B.5 to B.9 illustrate daily variations in meteorological variables and  $PM_{10}$  concentrations on days when the highest concentrations from each source were measured.



	EC	Na	Mq	Al	Si	S
ЕC		4000 2000 0 10000 20000	400 200 0 0 10000 20000	500		
Na		4000 2000 0 0 2000 4000		500 0 0 2000 4000		
Mg				500 0 0 200 400		
AI		4000 2000 0 0 500		500 0 0 500	2000 1000 0 0 500	
Si		3000 2000 1000 0 1000 2000		600 400 200 0 0 1000 2000	2000 1000 0 0 1000 2000	
















		Source PM <sub>10</sub>	Reconstructed*	Measured PM <sub>10</sub>	
Date	Source	µg m⁻³	PM₁₀ µg m⁻³	µg m⁻³	µg m⁻³
8-Jun-06	Domestic	74	83	78	65
10-Jun-06	Domestic	88	94	94	86
24-Jul-06	Domestic	85	94	112	94
24-Apr-06	Marine aerosol	18	19	13	18
16-Jul-06	Marine aerosol	22	22	20	34
17-Apr-06	Sulphate	3	13	11	15
3-Mar-07	Sulphate	2	7	19	11
31-Mar-07	Motor vehicles	3	13	11	11
20-Apr-07	Motor vehicles	4	30	17	31
31-Aug-06	Soil	8	27	25	23
20-Sep-06	Soil	7	20	26	15

# **Table B.4:**Summary PM10 data for peak source days

\* The reconstructed  $PM_{10}$  mass is the amount of  $PM_{10}$  estimated for that day based on the PMF analysis of sources. Note this may be higher or lower than the measured  $PM_{10}$  mass and represents the sum of the estimated individual source contributions ( $\mu g m^{-3}$ ) to  $PM_{10}$  on the day.

Strong diurnal variations in hourly average  $PM_{10}$  concentrations are apparent on days when the domestic heating contribution was greatest, with peak concentrations occurring during the evening from 5pm to midnight (Figure B.5). A smaller mid morning peak is also apparent and relates to both meteorological conditions and emissions at this time. On these days the wind direction was predominantly south to south west during the evening and morning periods when the elevated  $PM_{10}$ concentrations occurred. A northerly wind shift during the afternoon on these days also occurs but is not associated with elevated  $PM_{10}$  concentrations.

Figure B.6 shows winds were from the north and around 8-10 ms<sup>-1</sup> on one of the high marine aerosol days and from the east and around 3-10 ms<sup>-1</sup> on the second. Easterly winds are the likely the most common direction for this source although other directions are possible with variable wind trajectories.

High sulphate days were characterised by variable wind directions, temperatures of around 18 to 20 degrees and wind speeds ranging from 0 to 10 ms<sup>-1</sup> (Figure B.7). Although these days represent the greatest mass and percentage contributions from sulphate, on 17 April domestic heating was the greatest contributor to total  $PM_{10}$  concentration and on 3 March marine aerosol was the greatest contributor.





**Figure B.5:** Daily variations in meteorological parameters and  $PM_{10}$  concentrations on days when the domestic heating contribution was greatest in Hastings.





**Figure B.6:** Daily variations in meteorological parameters and PM<sub>10</sub> concentrations on days when the marine aerosol contribution was greatest in Hastings.



**Figure B.7:** Daily variations in meteorological parameters and  $PM_{10}$  concentrations on days when the sulphate contribution was greatest in Hastings.





**Figure B.8:** Daily variations in meteorological parameters and  $PM_{10}$  concentrations on days when the motor vehicle contribution was greatest in Hastings.



**Figure B.9:** Daily variations in meteorological parameters and  $PM_{10}$  concentrations on days when the soil contribution was greatest in Hastings.



Figure B.8 shows that on 31 March 06 when elevated motor vehicle contributions were observed, wind was mainly from a northerly direction and wind speed was 5 to 12 m s<sup>-1</sup> for most of the day. A decrease in wind speed and change in direction after 7pm did not result in significant changes in  $PM_{10}$  concentrations. On 20 April 2007, wind was from the southerly direction during the morning, northerly direction during the afternoon and southerly direction during the evening. Wind speed was low during the morning and evening periods and up to around 10 m s<sup>-1</sup> during the afternoon. The main source of  $PM_{10}$  on 20 April 2007 was domestic heating (81%).

It is worth noting that the morning peak in  $PM_{10}$  concentrations (around 9am as observed on high pollution days: e.g. Figure B.5) is non-existent or minimal on the two days when  $PM_{10}$  concentrations from motor vehicles were highest. Because of the timing of the pollution peak relative to patterns in vehicle movements, this peak has often been referred to as a motor vehicle peak, but may alternatively be due to relighting of domestic fires for heating in the morning. On the days when this peak occurs (e.g. Figure B.5) the motor vehicle contribution is minimal (1-3%).

The highest soil contributions to  $PM_{10}$  concentrations occurred on the 31 August and the 20 September 2006. Figure B.9 shows southerly wind directions on both days with a brief change to northerly in the afternoon on the 31 August and the evening of the 20 September. On both days wind speeds were high at around 8 to 10 m s<sup>-1</sup> for extended periods.



# Appendix C: Data Analysis Hastings PM<sub>2.5</sub>

# Elemental analysis of Hastings PM<sub>2.5</sub>

Table C.1. presents the data for the elemental concentrations determined by IBA for  $PM_{2.5}$  at Hastings.

Element	Average concentration ng/m <sup>3</sup>	Max ng/m <sup>3</sup>	Min ng/m³	Std dev	Average % Error	Av LOD ng/m <sup>3</sup>	No. of samples > LOD
Н	278	1160	26	283	3	5	130
BC	1321	3313	308	681	2	38	130
Na	347	1215	32	239	11	69	128
Mg	46	150	7	29	11	7	129
AI	19	79	1	15	13	3	125
Si	58	224	7	43	4	2	130
Р	4	14	0	3	101	4	73
S	232	818	25	147	3	2	130
CI	603	2649	10	493	3	2	130
К	115	1287	16	133	3	1	130
Ca	35	86	5	17	5	1	130
Ti	1	7	0	1	69	2	55
Mn	1	14	0	2	94	1	48
Fe	22	93	2	15	8	1	130
Cu	3	43	0	5	52	1	85
Zn	9	62	0	9	27	1	124
As	6	29	0	8	40	3	71
Se	1	5	0	1	51	4	14
Br	3	77	0	7	63	5	42
Ва	5	129	0	12	73	5	47
Pb	7	70	0	10	100	14	24

 Table C.1:
 PM<sub>2.5</sub> elemental concentrations and statistics

A number of elements were measured at low concentrations at or near the limits of detection (LOD) and these were excluded from the receptor modelling process. Research suggests that those elements with less than 70 % values above the LOD should be excluded from factor analysis and where a particular element is considered a crucial tracer for a source, measured values should be at a minimum of 50% above the LOD. The effect of these low concentration species on the receptor modelling should be examined in detail.



#### **Factor Identification**

Principal components analysis (PCA) of the data was conducted in order to determine relationships between  $PM_{2.5}$  species and examine the number of factors (sources) that can be appropriately derived from the speciated data.

The PCA provides estimated communalities for each element (which can be interpreted as estimating the proportion of the variability in each variable attributable to the extracted factors), and the scree plot of the Eigenvalues for each factor which provides an indication of the significance of extracted factors. Figure C.1 shows the scree plot derived from the PCA analysis which indicates four to five significant factors are present.



**Figure C.1:** Scree plot of Eigenvalues from PCA of Hastings PM<sub>2.5</sub> elemental composition

A total of 120 samples were included in the PCA of Hastings  $PM_{2.5}$  elemental data and four factors extracted which, between them, explained 93% of the variability in the original data. Other minor sources may contribute to  $PM_{2.5}$  but were not resolved by PCA. For the purposes of the source apportionment of  $PM_{2.5}$  mass by PMF, the statistical data provided by PCA suggested that a four or five factor (contributing sources) solution may be appropriate.

#### Source contributions to PM<sub>2.5</sub> at Hastings

Four primary source contributors were found to be the most robust solution to the PMF analysis of the  $PM_{2.5}$  elemental data. These are identified as presented in Table C.2. The PMF modelling diagnostics are listed in Table C.3.



	Factor 1	Factor 2	Factor 3	Factor 4	
	Motor Vehicles	Sulphate	Biomass Burning	Seasalt	
Species	Average Mass ng/m <sup>3</sup>	Average Mass ng/m <sup>3</sup>	Average Mass ng/m <sup>3</sup>	Average Mass ng/m <sup>3</sup>	
PM2.5	1072	1140	7608	1193	
Н	24	17	220	1	
BC	300	103	694	139	
Na	21	60	0	268	
Mg	4	8	2	32	
AI	14	2	1	0	
Si	44	5	6	1	
S	0	171	37	14	
CI	0	0	69	513	
К	15	2	76	11	
Са	14	4	3	13	
Fe	15	1	4	0	
Zn	2	0	5	0	
As	1	0	5	0	

# Table C.2: Elemental composition of source profiles and contribution to PM<sub>2.5</sub> at Hastings

# Table C.3PMF diagnostics for PM2.5 at Hastings

Species	Intercept	Slope	RMSE	r <sup>2</sup>
PM <sub>2.5</sub>	1402.21	0.73	2387.34	0.85
н	18.23	0.89	37.99	0.98
BC	-71.31	1	331.78	0.81
Na	-14.56	1.03	45.41	0.97
Mg	-1.19	1.01	5.44	0.96
AI	1.92	0.86	3.45	0.93
Si	5.46	0.87	9.19	0.94
S	9.88	0.94	24.68	0.97
CI	44.16	0.89	57.39	0.98
К	-4.51	1.04	14.92	0.97
Ca	5.27	0.81	5.55	0.87
Fe	2.75	0.82	4.72	0.87
Zn	2.15	0.62	3.56	0.68
As	1.25	0.75	2.74	0.8
Q <sub>Theoretical</sub> = 80	0; Q <sub>Robust</sub> = 533.17; Q-	<sub>Frue</sub> = 533.17		

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 : 200 Number of bootstrapped factors mapped to original factor 3 : 200 Number of bootstrapped factors mapped to original factor 4 : 200 Number of bootstrapped factors mapped to no original factor 5 0



The PMF analysis has satisfactorily modelled the elemental mass concentrations and the bootstrapping shows that the derived profiles are reproducible. There were no standardised residuals beyond -3 or +3.

# 

### Hasting PM<sub>2.5</sub> elemental scatter plots

#### Source contributions on high pollution days

High concentrations of air particulate matter are of concern due to adverse effects on human health. Four peak pollution days where  $PM_{2.5}$  concentrations exceeded 40 µg m<sup>-3</sup> and  $PM_{10}$  exceeded 50 µg m<sup>-3</sup> were chosen for detailed analysis of the contributing sources and the air pollution meteorology on those days. Monitoring results from these days are displayed in Table C.4.

# Analysis of PM<sub>2.5</sub> source contributions on 10 June 2006

Domestic heating was found to be the dominant source contributor to  $PM_{2.5}$  (98%) on 10 June 2006 as the relative source contributions derived from the factor analysis shows in Figure C.2.



Date	ANSTO ASP PM₂.₅ (μg m⁻³)	GENT PM <sub>10</sub> (µg m <sup>-3</sup> )	BAM PM₁₀ (µg m⁻³)	% PM <sub>2.5</sub>
10/06/2006	41	94	86	48
04/07/2006	40	60	51	78
18/07/2006	48	55	43	112
24/07/2006	41	112	93	44

#### **Table C.4:** Concentration data for PM<sub>2.5</sub> events at Hastings



St Johns PM<sub>2.5</sub> source contributions

**Figure C.2:** Source contributions to PM<sub>2.5</sub> on 10 June 2006 at Hastings

Meteorological conditions at the Hastings air quality monitoring site during 10 June 2006 were characterised by cold overnight temperatures (minimum -1  $^{0}$ C) and low wind speeds (< 2 m s<sup>-1</sup>) from the southerly quarter (Figure C.3). Two peaks in 1-hour BAM PM<sub>10</sub> concentrations occurred, the first between 0:00 and 03:00 (~ 175 µg m<sup>-3</sup>) in the morning and the other between 17:00 and 24:00 in the evening (~ 200 µg m<sup>-3</sup>). Synoptic meteorological conditions were anticyclonic as shown in the mean sea level pressure (MSLP) chart presented in Figure C.3.

#### Analysis of PM<sub>2.5</sub> source contributions on 4 July 2006

Domestic heating was again found to be the dominant source contributor to  $PM_{2.5}$  (98%) on 4 July 2006, as shown in Figure C.4.





**Figure C.3:** Meteorological analysis for 10 June 2006: Clockwise from top left - Synoptic MSLP analysis; Temperature trace; wind speed and direction; 1-hour average BAM PM<sub>10</sub>



#### Figure C.4: Source contributions to PM<sub>2.5</sub> on 4 July 2006 at Hastings

Meteorological conditions at Hastings on this day were characterised by cool temperatures (minimum 3  $^{0}$ C) around midnight, and low wind speeds from the northerly quarter (Figure C.5). One-hour BAM PM<sub>10</sub> concentrations peaked at midnight (~ 300 µg m<sup>-3</sup>) and decreased through the early morning. PM<sub>10</sub>



concentrations dropped to low levels as a southerly wind increased during the day due to an approaching trough from the southwest as indicated by the MSLP analysis in Figure C.5.



**Figure C.5:** Meteorological analysis for 4 July 2006: Clockwise from top left - Synoptic MSLP analysis for midday; Temperature trace; wind speed and direction; 1-hour average BAM PM<sub>10</sub>

#### Analysis of PM<sub>2.5</sub> Source contributions on 18 July 2006

Domestic heating (79%) was again the primary source of  $PM_{2.5}$  on 18 July 2006 with a contribution also from motor vehicle emission sources (15%) as shown in Figure C.6.



Figure C.6: Source contributions to PM<sub>2.5</sub> on 18 July 2006 at Hastings



Meteorological conditions at Hastings for this period were characterised by cool overnight temperatures (minimum 6  $^{0}$ C), with a gentle south to southeast breeze (1 - 2 m s<sup>-1</sup>) that swung more northerly during the day and then dropped away in the evening of 18 July (Figure C.7). One-hour BAM PM<sub>10</sub> concentrations increased during the evening to peak (180 µg m<sup>-3</sup>) at approximately 10pm. Synoptic meteorological conditions were anticyclonic, bringing a northerly flow over Hawke's Bay as shown in Figure C.7



**Figure C.7:** Meteorological analysis for 18 July 2006: Clockwise from top left - Synoptic MSLP analysis; Temperature trace; wind speed and direction; 1-hour average BAM PM<sub>10</sub>

The peak BAM  $PM_{10}$  concentrations at night suggest that solid fuel fire emissions were the main source of air particulate matter pollution as indicated by the receptor modelling.

#### Analysis of PM<sub>2.5</sub> Source contributions on 24 July 2006

Receptor modelling results determined that domestic heating (97%) was the primary source of  $PM_{2.5}$  on 24 July 2006 with a minor contribution from motor vehicle emission sources (2%) and marine aerosol (1%) as shown in Figure C.8.





#### Figure C.8: Source contributions to PM<sub>2.5</sub> on 24 July 2006 at Hastings

Meteorological conditions at Hastings for this period were characterised by cold overnight temperatures (minimum -1  $^{0}$ C), and low wind speeds (> 2 m s<sup>-1</sup>) from the southwest. Two peaks in 1-hour BAM PM<sub>10</sub> concentrations occurred, the first between 00:00 and 04:00 (~ 250 µg m<sup>-3</sup>) in the morning and the other between 19:00 and 24:00 in the evening (~ 250 µg m<sup>-3</sup>). Synoptic meteorological conditions were anticyclonic due to a high pressure area to the west of the North Island bringing the south-westerly flow over Hastings as indicated by the MSLP analysis in Figure C.9.

#### Summary of high pollution days

Peak  $PM_{2.5}$  concentrations in Hastings were found to be primarily due to emissions from domestic solid fuel fires. The highest concentrations occurred on cold calm nights when dispersion conditions were poorest and significant temperature inversions were likely to have formed. Synoptic conditions were generally found to be anticyclonic with a general southerly flow over the area. Where peak  $PM_{2.5}$ concentrations occurred during a more northerly flow, a significant motor vehicle contribution was also present. Further analysis of source contributions with wind direction is provided in the following section.





**Figure C.9:** Meteorological analysis for 24 July 2006: Clockwise from top left - Synoptic MSLP analysis; Temperature trace; wind speed and direction; 1-hour average BAM PM<sub>10</sub>

#### **Meteorological variations**

A useful data analysis method is to investigate if there is a relationship between the source contributions and wind direction. Conditional Probability Function (CPF) analysis provides a method to determine the directions for which high values of estimated source contributions are likely to be related with the source directions.

The probability that a source contribution originates from a given wind direction is estimated by comparing the wind direction distribution for the upper 25% of source contribution relative to the total wind direction distribution.

$$CPF_{\Delta\theta} = \frac{m_{\Delta\theta}}{n_{\Delta\theta}}$$

Where:

 $m_{\Delta\theta}$ : Number of occurrences from wind sector  $\Delta\theta$  for the upper 25% of source contributions



### $n_{\Lambda\theta}$ : Total number of occurrences from the same wind sector

Analysis was based on the data where the wind speed is  $\geq 2 \text{ ms}^{-1}$ . 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 C.10. 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.



Figure C.10: CPF analyses of relative source contributions with wind direction in Hastings

The following sections discuss the results for each source contributor for the Hastings  $PM_{2.5}$  dataset.

# **Motor Vehicles**

The motor vehicle contribution originates primarily from the north and westerly sectors in the direction of Hastings' CBD and State Highway 2, where traffic (and consequent vehicle emissions) is likely to be the densest.



#### Sulphate

The sulphate contribution primarily originates from the northerly sector. As sulphate is formed in the atmosphere due to homogeneous chemical reactions the process takes some time and the sulphate presence is normally considered to be a consequence of long-range transport from some originating source of precursor gases (e.g.  $SO_2$ , dimethyl-sulphide) up-wind. In this case the originating source could be  $SO_2$  emissions in Napier to the north of Hastings. Some sulphate will also be due to non-sea salt sulphate, associated with emissions of dimethyl sulphide from marine organisms and therefore there is an easterly component as well.

#### Marine aerosol

The marine aerosol contribution primarily originates from the northeast to southeast sectors in the direction of the Pacific Ocean.

#### **Domestic heating**

The domestic heating contribution appears to have an association with southerly wind directions. The meteorological assessment of peak  $PM_{2.5}$  days shows that biomass burning (due to domestic fire emissions) dominates during calm (wind speed <2 m s<sup>-1</sup>) and cold anticyclonic conditions when atmospheric dispersion conditions are poorest. Hence the wind direction is not a considered major influence on this source and the directionality may be more aligned with katabatic drainage flows.



# Appendix D: Additional analyses for Kowhai

#### Analysis of elevated PM<sub>10</sub> events at Kowhai

Two peak  $PM_{10}$  (>30 µg m<sup>-3</sup>) events at Kowhai, one during the summer and the other during the winter have been chosen for further analysis. These events occurred on 14 December 2005 and 3 July 2006 respectively.

# Analysis of $PM_{10}$ source contributions on 23 December 2005

Receptor modelling results determined that marine aerosol was the primary the source (85 %) of  $PM_{10}$  on Friday 23 December 2005.as shown in Figure D1.



#### **Figure D1:** Source contributions to PM<sub>10</sub> on 23 December 2005 at Kowhai (Source: ARC)

Meteorological conditions at Kowhai on 23 December 2005 were characterised by relatively constant temperatures (15–22°C) and moderate wind speeds from the southwest. 1-hour BAM PM<sub>10</sub> concentrations were relatively constant between 25 and 40  $\mu$ g/m3. Synoptic meteorological conditions were cyclonic with low pressure system to the southeast of New Zealand as depicted by the MSLP chart in Figure D2. This brought a southwest flow over the Auckland region and a long fetch over the Tasman Sea. It is likely that there was significant surf activity on Auckland's west coast generating salt spray during this period.





**Figure D2** Meteorological analysis for 23 December 2005: Clockwise from top left - Synoptic MSLP analysis for midday; Temperature trace; windrose; 1 hour average BAM PM<sub>10</sub>. (Source: ARC)

#### Analysis of PM<sub>10</sub> source contributions on 30 July 2006

Receptor modelling results determined that biomass burning was the primary source of  $PM_{10}$  on 30 July 2006, with a lesser contribution from motor vehicle sources as shown in Figure D.3.

Meteorological conditions at Kowhai on this day were characterised by cool temperatures on the early hours of 30 July (minimum 4°C), calm conditions and peak 1-hour average BAM PM<sub>10</sub> concentrations around 80  $\mu$ g m<sup>-3</sup> (Figure D.4). During the day, wind speeds increased from the north-easterly quarter and PM<sub>10</sub> dropped away to background concentrations (~15  $\mu$ g/m<sup>3</sup>). Synoptic meteorological conditions were anticyclonic due to a high pressure area northeast of New Zealand with a low pressure system approaching from the Tasman as indicated by the MSLP analysis in Figure D.4.





**Figure D.3:** Source contributions to PM<sub>10</sub> on 30 July 2006 at Kowhai (Source: ARC)



**Figure D.4** Meteorological analysis for 30 July 2006: Clockwise from top left - Synoptic MSLP analysis for midday; Temperature trace; windrose; 1-hour average BAM PM<sub>10</sub> (Source: ARC)



#### Analysis of an individual PM<sub>2.5</sub> event at Kowhai

One peak  $PM_{2.5}$  event at Kowhai during the monitoring period has been chosen for further analysis. The BAM 24hr  $PM_{10}$  results also indicate elevated concentrations for the same period as shown in Table D.1, although it did not exceed the NES (50  $\mu$ g/m<sup>3</sup>).

# **Table D.1:** Concentration data for a PM<sub>2.5</sub> event at Kowhai

Date	PM <sub>2.5</sub> (µg m <sup>-3</sup> )	BAM PM <sub>10</sub> (μg m <sup>-3</sup> )	% PM <sub>2.5</sub>
12/07/2004	27	34	79

#### Analysis of PM<sub>2.5</sub> source contributions on 12 July 2004

Biomass burning was found to be the dominant source contributor to  $PM_{2.5}$  (91%) on 12 July 2004 as the relative source contributions derived from the factor analysis shows in Figure D.5. Motor vehicle emissions were not observed as a source on 12 July 2004.





#### **Figure D.5:** Source contributions to PM<sub>2.5</sub> on 12 July 2004 at Kowhai (Source: ARC)

Meteorological conditions at Kowhai on this winters day were characterised by low overnight temperatures (minimum 4  $^{0}$ C), clear skies, and low wind speeds from the south-easterly quarter with calm winds (< 1 m s<sup>-1</sup>) for 50% of the period (Figure D.6). Two peaks in 1 hour BAM PM<sub>10</sub> concentrations occurred: the first between 07:00 and 11:00 Peak (~50 µg m<sup>-3</sup>) in the morning and the other between 22:00 and 24:00 in the evening (~100 µg m<sup>-3</sup>). Synoptic meteorological conditions were anticyclonic,





bringing cool air from the southern oceans up towards Auckland as depicted by the mean sea level pressure (MSLP) chart shown in Figure D.6.

**Figure D.6:** Meteorological analysis for 12 July 2004: Clockwise from top - Synoptic MSLP analysis for midday; Temperature trace; windrose; 1 hour average BAM PM<sub>10</sub>(Source: ARC)

Wind direction was such that traffic emissions from the north-western motorway and other busy roads to the north and west would have dispersed away from the monitoring site. However, the wind direction would have brought air to the monitoring station from across the residential areas to the southeast, which would explain why domestic fires were the major source of particulate matter on that particular day.