

**Heavy metals, black carbon and natural sources
of particulate matter in New Zealand**

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EXECUTIVE SUMMARY

This report presents summary information and statistics on the composition and sources of airborne particulate matter (PM) samples collected at air quality monitoring sites around New Zealand. The primary focus of the report is on concentrations of black carbon, heavy metals and the natural source contributions to urban PM concentrations. The data represents 20 years of monitoring and analyses by regulatory authorities and GNS Science.

Black carbon particles are produced during the combustion of fuels which, in the New Zealand context, are dominated by motor vehicle emissions and solid fuel fires used for domestic space heating and for this reason concentrations peak during winter. The heavy metal data is of interest from an environmental toxicology perspective and the analyses provided by GNS Science also show the sources (domestic fires, motor vehicles, shipping emissions and fireworks) responsible for emissions of PM containing heavy metals.

The natural source contributions to urban PM concentrations represents the proportion that cannot be managed by air quality mitigation strategies. The predominant natural PM source in New Zealand is of oceanic origins (primarily sea salt), which is unsurprising given our Southern Hemisphere location in the 'roaring forties'.

1.0 INTRODUCTION

This report presents summary information and statistics on the composition and sources of airborne particulate matter (PM) samples collected at air quality monitoring sites around New Zealand. In particular, the focus is on concentrations of black carbon, heavy metals and the natural source contributions to urban PM concentrations. The report summarises the methodologies used to obtain these data, any limitations associated with the data, and presents metadata describing the data, how it was collected and how it was analysed.

GNS Science has used a particulate matter composition analysis and receptor modelling approach to identify sources (including natural sources) of particulate matter in New Zealand airsheds. The particulate matter compositional data held by GNS Science have been generated consistently using internationally accepted methodologies (USEPA) and quality assurance procedures with traceable standards including successful participation in international inter-laboratory comparisons. The elemental concentrations have been determined by Ion Beam Analysis (IBA) and/or X-ray fluorescence (XRF) with black carbon concentrations by light absorption analysis of filter-based particulate matter samples. All elemental (heavy metal) and black carbon data is accompanied by analytical uncertainty estimations and limits of detection. The receptor modelling based on the compositional data provides the natural source contributions such that the proportion that natural sources contribute to total PM mass and the relative uncertainty associated with those estimations have been determined. A direct result of using this technique is that the sources of BC and heavy metals were also derived and the mass contributions of each emission source to atmospheric BC and heavy metal concentrations were determined. Therefore, this report not only presents the concentrations of BC and heavy metals measured in New Zealand urban environments but also the primary sources of those particulate matter component species.

1.1 Black Carbon

Black carbon is a combustion-derived atmospheric aerosol that has important implications for human health and the Earth's climate. Exposure to ambient concentrations of black carbon (BC) has been associated with significant negative impacts on human health, including increased hospital admissions and mortality due to cardiovascular diseases (Dockery et al., 2005, Zanobetti and Schwartz, 2006, Geng et al., 2013). Black carbon also plays a unique role in the Earth's climate system. While most aerosols in the atmosphere scatter incoming solar radiation, resulting in a net cooling effect on the atmosphere, BC absorbs significantly more light than it reflects, resulting in a net warming effect. Light absorbing particles radiate long-wave energy that heats the surrounding air. This results in a positive (warming) forcing (Jacobson, 2001). The magnitude of BC's warming has recently been estimated to trail only the greenhouse gas carbon dioxide (Bond et al., 2013). Research regarding the concentrations and effects of BC is ongoing, and as more research is undertaken, it is likely that these and other effects will be further quantified.

1.2 Heavy Metals

Heavy metals is a generic term that is used to define metallic elements with relatively high densities, atomic weights or atomic numbers. The criteria used to define them varies but it is really the chemical behaviour that is of interest in the environmental context, particularly in relation to the interaction of heavy metals with living organisms along with the general environmental toxicity and availability of those metallic elements. This report focuses on the

concentrations of lead, arsenic, nickel and vanadium in PM due to the local emission sources and environmental toxicity associated with these metals, but reference to other metallic elements measured in PM is also made where they are an important component of PM and considered relevant to emission sources in the New Zealand context.

1.3 Natural Sources of Particulate Matter

Natural sources of particulate matter are of interest for air quality management purposes because, while they contribute to ambient PM mass concentrations, little can be done to control their presence. One of the key results from receptor modelling analyses is the derivation of mass contributions to ambient aerosol concentrations from natural sources and sources for which little useful information is available from other methods of source apportionment such as emissions inventories. The information is vital for air quality management as the proportion of particle mass from natural and other (uncontrollable) sources needs to be factored into any air pollution reduction strategy.

1.4 Report Structure

This report is comprised of 3 main chapters. The remaining chapters have been broken down as follows:

1. Chapter 2 provides an overview of the collection of BC and heavy metal PM samples, their measurement and the predominant sources, along with the derivation of natural sources of PM by receptor modelling techniques.
2. Chapter 3 presents summary statistics for the BC, heavy metal and natural source concentration data currently available from New Zealand air quality monitoring sites, including seasonal variations and observed inter-annual trends.

The appendices provide more detailed information on PM elemental speciation and BC measurement techniques along with monitoring site metadata and quality assurance procedures.

2.0 PARTICULATE MATTER MONITORING SITES IN NEW ZEALAND

GNS Science holds an archive of filter-based, time-integrated particulate matter samples that have firstly been analysed gravimetrically to provide ambient particulate matter concentrations then by appropriate analytical techniques to provide elemental composition data. The PM samples have been collected and analysed for approximately 40 sites across New Zealand, with some urban areas including multiple sites. The particulate matter compositional data has been derived from particulate matter samples collected at regulatory authority monitoring sites using National Environmental Standard (NES) compliant methodologies or alongside NES compliant particulate matter monitoring systems. The PM compositional data has been used to determine source contributions to ambient PM concentrations by receptor modelling techniques which includes the derivation of natural source contributions.

The majority of particulate matter sampling and analysis campaigns have been targeted studies that ran for 1-2 years collecting 24-hour time integrated particulate matter samples in order to better understand the local drivers of air pollution for air quality management purposes. The exception to this is the Auckland multi-site air particulate matter speciation database that has been running since mid-2004 which allows for inter-site comparisons, trend analysis and all-of-urban assessment of PM composition and natural source contributions to both PM_{2.5} and PM₁₀ particulate matter size fractions.

Figure 2.1 presents the PM speciation sampling locations in New Zealand to date. All the sampling sites shown also included PM elemental speciation with the accompanying receptor modelling and reporting. Appendix 2 identifies the specific locations, sampling period and reporting details.



Figure 2.1 Particulate matter sampling locations in New Zealand.

In addition to the urban monitoring locations, several studies have targeted source specific particulate matter composition, these include motor vehicle tunnels (Ancelet et al., 2011a, Davy et al., 2011a) and wood burner emissions (Davy et al., 2009, Ancelet et al., 2010, Ancelet et al., 2011b) in order to better understand emission source characteristics and composition. For several locations, high-resolution sampling (hourly) and analysis was undertaken as part of a research programme¹ to understand the observed diurnal variation in particulate matter concentrations in New Zealand urban centres (Ancelet et al., 2012, Ancelet et al., 2014d, Ancelet et al., 2014c, Trompetter et al., 2010).

2.1 Analysis of Particulate Matter Composition

Two multi-elemental analysis techniques have been used routinely to provide the particulate matter composition analysis, these are accelerator based ion beam analysis (IBA) and X-ray fluorescence analysis (XRF), while light reflectance has been used to determine BC concentrations in all samples. These are well established and internationally accepted methods for determining PM elemental composition (Horvath, 1993a, Landsberger and Creatchman, 1999, Maenhaut and Malmqvist, 2001, Bond and Bergstrom, 2006). Full descriptions of these techniques are provided in Appendix 1. IBA and XRF are both non-destructive analytical techniques and provide complimentary elemental results where XRF is more sensitive (lower limits of analytical detection) for heavier elements, particularly heavy metals, and IBA is more sensitive for lighter elements (Na to K) with the ability to determine hydrogen concentrations, a useful marker for hydrocarbon and secondary aerosol species.

GNS Science has used the accelerator based IBA techniques to measure elemental concentrations in New Zealand particulate matter samples since 1996, then in 2013 the analysis capability was extended by acquiring the XRF analytical facility (Epsilon 5, Panalytical Pty, Netherlands). Details of both techniques are provided in Appendix 1.

2.2 Receptor Modelling of Particulate Matter Composition

The multivariate analysis of air particulate matter sample composition (also known as receptor modelling or source apportionment) provides groupings (or factors) of elements that vary together over time. This technique effectively 'fingerprints' the sources that are contributing to airborne particulate matter concentrations and the mass of each element (including BC) attributed to that source. Most commonly used receptor models are based on conservation of mass from the point of emission to the point of sampling and measurement (Hopke, 1999). Their mathematical formulations express ambient chemical concentrations as the sum of products of species abundances in source emissions and source contributions. In other words, the chemical composition of filter based samples of particulate matter collected at a monitoring station is resolved mathematically to be the sum of a number of different factors or sources of those particles.

GNS Science has used the receptor modelling approach to identify sources of particulate matter in New Zealand airsheds by applying a technique known as Positive Matrix Factorisation (PMF) analysis to particulate matter composition data (Paatero and Tapper, 1994, Hopke et al., 1999). A direct result of using this technique is that the sources of BC and heavy metals (or any other variable) were also derived and the mass contribution of each emission source to atmospheric BC and heavy metal concentrations was determined.

¹ MBIE Contract C05X0903: Understanding air particulate matter pollution
Sources, patterns and transport of air particulate matter in polluted New Zealand urban environments

Therefore, this report not only presents the concentrations of BC and metals measured in New Zealand urban environments but also the primary sources of those species.

2.2.1 Derivation of Natural Sources of Particulate Matter

One of the key results from receptor modelling analyses is the derivation of mass contributions to ambient aerosol concentrations from natural sources and sources for which little useful information is available from other methods of source apportionment such as emissions inventories. The information is vital for air quality management as the proportion of particle mass from natural and other (uncontrollable) sources needs to be factored into any air pollution reduction strategy. A straightforward definition of natural sources of particulate matter is that the source can only be considered 'natural' if it involves no direct or indirect human activity². For example particulate matter pollution from a wildfire can only be considered natural if it was ignited by lightning or similar. If the fire was due to accidental or deliberate human activity as the ignition source then it is considered anthropogenic an anthropogenic source.

The New Zealand datasets show that oceanic or marine aerosol (sea salt) is the primary source of natural aerosol present in New Zealand urban atmospheres. Secondary sulphate aerosol formed from gas-to-particle atmospheric reactions has both natural (oceanic phytoplankton, volcanic emissions) and anthropogenic (combustion of sulphur containing fuels, industrial emissions) gaseous precursor sources. The third component of urban PM that has natural origins is crustal matter, generally referred to as 'Soil' in source apportionment studies. However, time-variation analyses across multiple datasets show that urban Soil PM concentrations are lower on weekends than weekdays indicating that the generation of airborne crustal matter in urban locations is largely the result of human activities (construction/demolition, earthworks, roadworks, passage of vehicles on roads and unpaved areas) and therefore does not meet the 'natural source' criteria discussed above. The following sections provide further detail on each of these sources.

2.2.1.1 Marine Aerosol

Sodium and chlorine are the primary constituents of marine aerosol or sea salt, and were also significant elemental contributors to both PM_{2.5} and PM₁₀ mass at New Zealand monitoring sites along with the more minor components (K, Ca, Mg, S) of sea salt. The elements were highly correlated (as shown for the Auckland dataset in Figure 2.2) and present in the same ratio at peak concentrations as found in sea salt ([Na] = 0.56[Cl]) (Lide, 1992). The analytical results demonstrate the relative influence of this natural aerosol source on urban particulate matter concentrations in New Zealand, even for inland locations, due to the isolated oceanic location of the New Zealand landmass. Other sources of Na and Cl include biomass burning, motor vehicle emissions, crustal matter, fireworks and industrial emissions.

² *Particulate matter from natural sources and related reporting under the EU Air Quality Directive in 2008 and 2009.* Technical report No. 10/2012. European Union 2012

<https://www.eea.europa.eu/publications/particulate-matter-from-natural-sources>

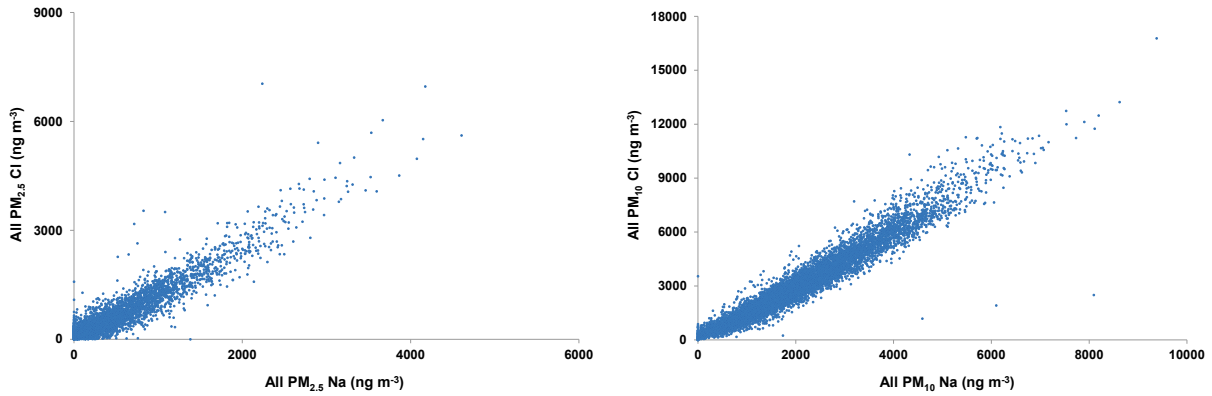


Figure 2.2 Scatterplots for sodium and chlorine in PM_{2.5} (left) and PM₁₀ (right) for all Auckland PM samples.

Research has shown that the concentration of marine aerosol shows a strong dependence on wind speed across the ocean surface and ranges from about 2 µg m⁻³ to as much as 50 µg m⁻³ or more at wind speeds in excess of 15 m s⁻¹ (Fitzgerald, 1991) and the Auckland data corroborates those potential concentration ranges. Therefore, marine aerosol concentrations in New Zealand urban areas are largely influenced by meteorological and long-range transport mechanisms as shown previously (Davy et al., 2011e).

The marine aerosol component of urban air particulate matter is considered to be part of the ‘natural’ background and therefore is that proportion that cannot be managed. It has been shown previously that the primary marine aerosol generation and source regions were in the Southern Ocean below Australia and to the northeast of Auckland out in the Pacific Ocean as shown in the PSCF presented in plot Figure 2.3 (Davy et al., 2011c, Davy et al., 2011e). Similar plots generated for other New Zealand locations show analogous source regions depending of predominant local air mass trajectories.

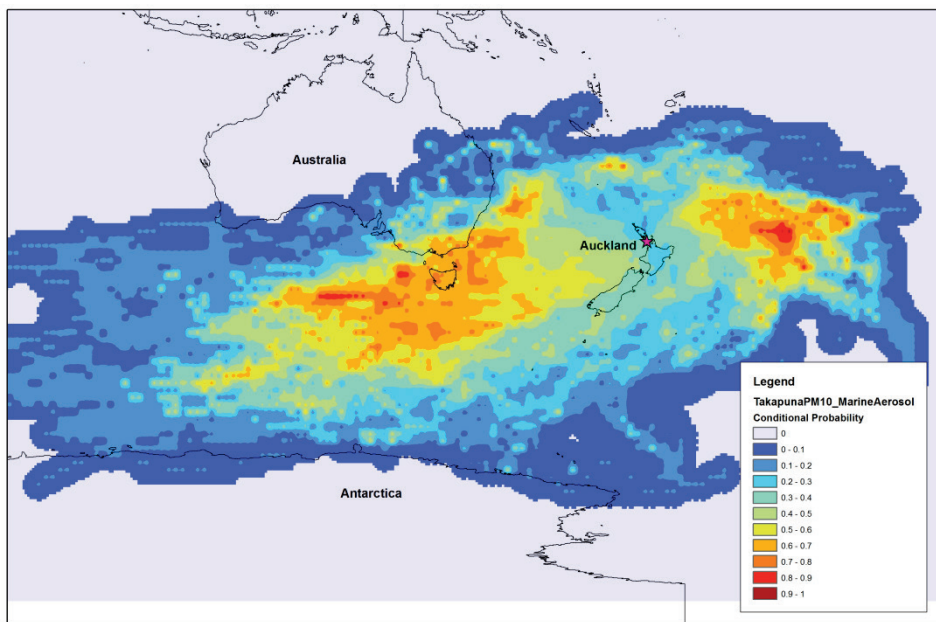


Figure 2.3 PSCF plot (using 96-hour back trajectories) for the Takapuna PM₁₀ marine aerosol source contribution data (2006 – 2013) showing that the most likely source regions are in the Southern Ocean below Australia and Pacific Ocean to the northeast of Auckland.

2.2.1.2 Secondary Sulphate Aerosol

The presence of sulphur in airborne particulate matter is generated from a variety of sources including sulphur incorporated in mineral structures of crustal matter, cell structure of trees (released during biomass combustion), volcanic emissions, marine aerosol, and the combustion of sulphur containing fuels including automotive fuels (petrol, diesel, fuel oils used by ships) and other fossil fuels such as coal. Sulphur containing particulate matter is also derived from precursor gases such as sulphur dioxide, hydrogen sulphide or dimethyl sulphide from the gas-to-particle reaction process in the atmosphere. These reactions can take hours to days depending on the reaction pathway followed, the availability of catalytic metals (e.g. Fe, Mn), relative humidity and the strength of solar radiation (Seinfeld and Pandis, 2006). Therefore, concentrations of sulphur containing particulate matter from secondary sulphate sources are likely to be highest some distance downwind of a precursor gas emission source (Polissar et al., 2001). Seasonal patterns show that secondary sulphate concentrations generally have a summer maximum and a winter minimum (Figure 2.4), reflecting the relative influence of solar forcing on atmospheric reaction pathways.

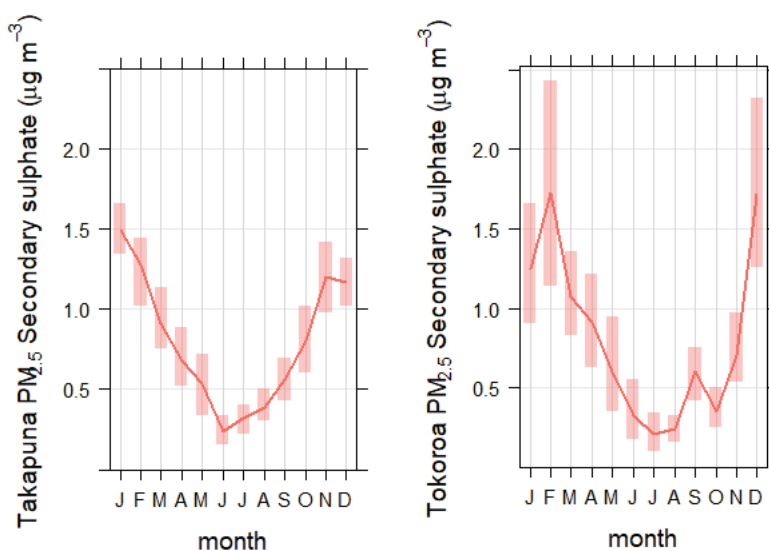


Figure 2.4 Seasonal variation in secondary sulphate concentrations at (left) Takapuna, Auckland (2006-2013) and (right) Tokoroa, Waikato (2016).

The New Zealand source apportionment data indicates that there are both natural (oceanic, volcanic) and anthropogenic (shipping, motor vehicle and industrial emissions) sources of secondary sulphate aerosol. The relative contribution secondary sulphate particles to PM concentrations at a given air quality monitoring site is dependent on:

- local source precursor gas emission activity (both anthropogenic and natural),
- the proximity of a PM sampling site to such activities,
- atmospheric chemical reaction kinetics (i.e. the drivers for the gas-to-particle reaction pathway) and;
- the long-range transport of natural source (volcanic and oceanic) secondary sulphate.

Receptor modelling studies of PM composition from around New Zealand show that PM monitoring sites near ports are likely to be influenced by secondary sulphate associated with emissions of precursor gases from ships engines. Also, some monitoring locations were influenced by direct emissions of combustion-derived particulate matter from ships engines (see also discussion on associated heavy metals in Section 2.3.2).

2.2.1.3 Crustal Matter

Crustal matter is primarily composed of aluminosilicate minerals and the source profiles extracted from receptor modelling reflect this, with Al and Si being the primary constituents and Mg, K, Ca, Ti and Fe commonly present. The mass ratio of Si/Al is consistently about 3:1 for both PM₁₀ and PM_{2.5} size fractions across all New Zealand monitoring sites and is similar to the Si/Al ratio in aluminosilicate minerals. Aluminium and silicon concentrations were primarily associated with crustal matter (synonymous with Soil as a source reference) which is predominantly a coarse particle source generated by mechanical abrasion of surface material. In urban locations, the passage of motor vehicles over roads can be the primary source of crustal matter suspension and resuspension (Thorpe and Harrison, 2008).

A specific dust event that resulted in PM₁₀ exceedances across the Auckland region was identified as originating from a dust storm (a natural event) in the Australian desert during September 2009 (Davy et al., 2011e), the influence of which can be seen in the time-series plots for Al and Si in all Auckland PM₁₀ samples presented in Figure 2.5.

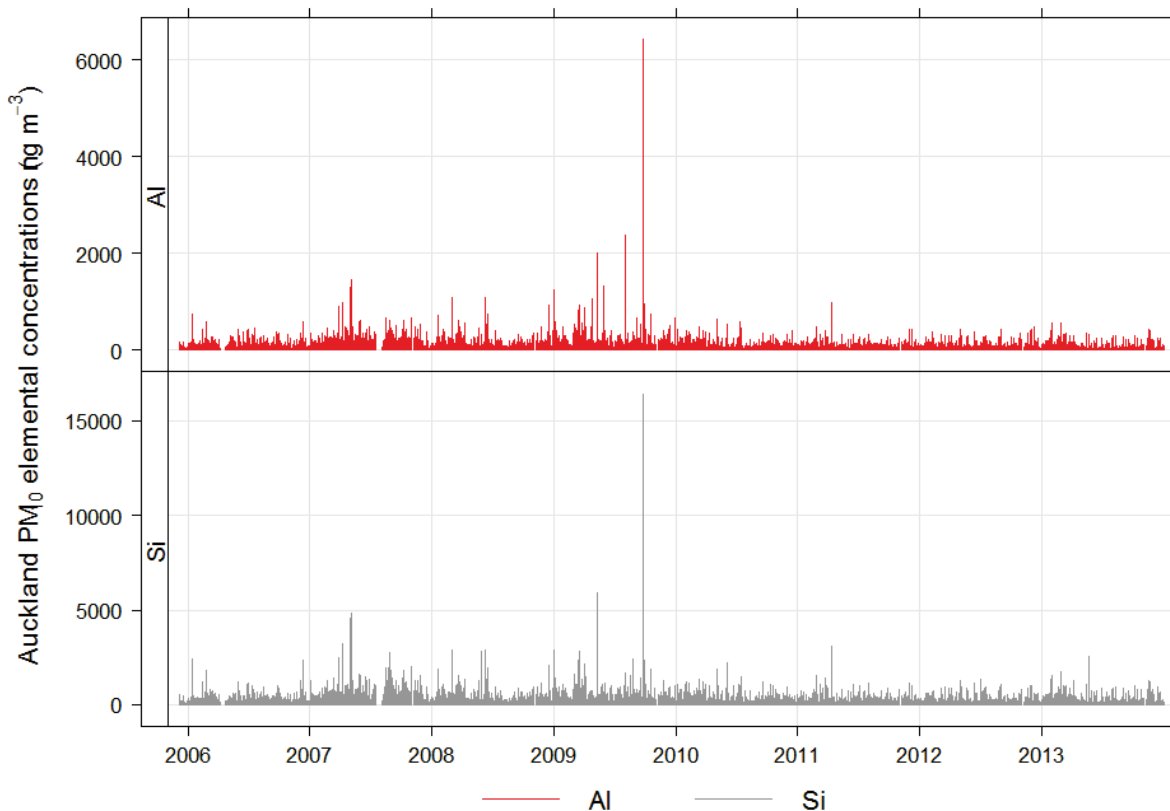


Figure 2.5 Time-series plots for aluminium and silicon in all Auckland PM₁₀ samples.

The temporal variation for both aluminium and silicon concentrations indicate that airborne concentrations are primarily from anthropogenic activities because of the day-of-the-week concentration dependence with weekend concentrations significantly lower than weekdays as presented for Auckland data in Figure 2.6.

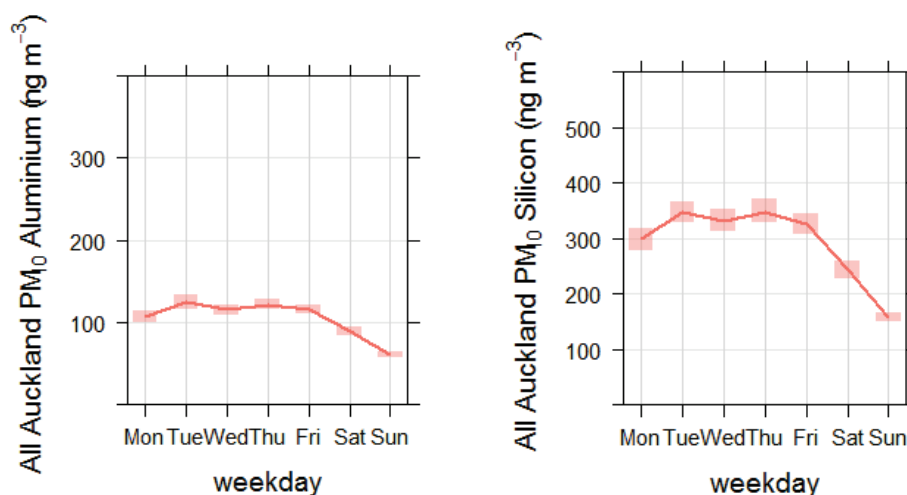


Figure 2.6 Temporal variations in aluminium (left) and silicon (right) in all Auckland PM₁₀ samples (the shaded bars are the 95 percentile confidence limits in the mean).

Crustal matter source contributions at the monitoring sites were likely to be a combination of windblown soil, road dust and dust generated by earthworks, construction and road works. Concentrations were found to vary from site to site depending on meteorological conditions and local dust generating activities. It can be seen from Figure 2.7 that the temporal variation for PM₁₀ crustal matter contributions (Auckland data) that concentrations during the weekend were significantly lower than during weekdays which indicates that crustal matter source emissions were primarily driven by human activity because any randomly generated emissions such as wind-blown dust, would not show a bias for day of the week due to the random nature of meteorological events.

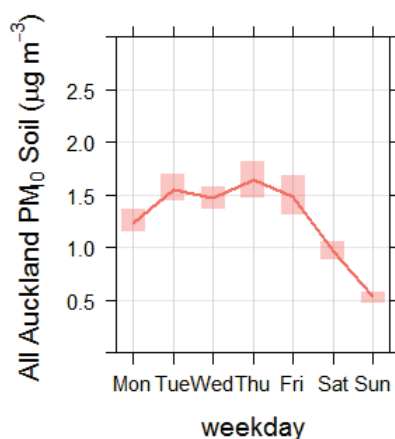


Figure 2.7 Temporal variations in crustal matter contributions for all Auckland PM₁₀ samples showing lower weekend concentrations (the shaded bars are the 95 percentile confidence limits in the mean).

2.3 Sources of Black Carbon and Heavy Metals

2.3.1 Sources of Black Carbon

As indicated in the introduction to this report, the primary global sources of BC are combustion engines (especially diesel), residential burning of wood and coal for home heating, shipping emissions, power stations using heavy oil or coal, field burning of agricultural wastes, as well as forest and vegetation fires (wildfire). While these sources are also present in New Zealand, those such as thermal power stations and agricultural waste burning (stubble or scrub and tree burnoffs) are intermittent and more seasonally based. For example, thermal power stations

burning fossil fuels are generally only brought into the network if necessary to cover peak power usage and this is most likely during winter or when hydro-lake storage levels are low. While forest and vegetation wildfires can release significant quantities of BC and other pollutants to atmosphere, such (accidental) fires are relatively rare and are generally aggressively managed and extinguished to prevent loss of life, property damage and to protect the forestry estate. Another category of combustion sources emitting BC are those stationary industrial heat generation plant used for manufacturing or processing and localised emergency power generation (primarily diesel powered) used to support essential facilities and services during interruptions to normal electricity supply networks.

The most well characterised sources of BC in New Zealand are those combustion sources that are ubiquitous in the urban setting, namely motor vehicle emissions, solid fuel fires (primarily wood) for home heating and shipping emissions in port towns and cities. A more detailed description and analysis of BC sources and concentrations in the New Zealand urban environment has been provided in (Davy and Trompetter, 2017a).

2.3.2 Sources of Heavy Metals

Heavy metals occur naturally in the Earth's crust and are generally located in mineral deposits associated with certain geological structures. It is by mining, processing and use of those metals that they are concentrated and, ultimately are released back into the environment. Concerns regarding health effects due to heavy metals arise when there is a substantive human exposure pathway following any such release into the environment, the most common being via ingestion of contaminated water and food or directly via inhalation of PM emissions containing heavy metal species. A less common exposure risk is the inhalation of vapours or gases associated with certain chemical species of heavy metal, primarily restricted to arsenic as arsine (AsH_3) or mercury vapours.

2.3.2.1 Arsenic and Lead

The analysis of PM samples from New Zealand monitoring sites has shown that arsenic and lead concentrations peaked during winter and were associated with biomass combustion sources (Wilton et al., 2007, Davy et al., 2011d, Ancelet et al., 2012, Cavanagh et al., 2012, Davy et al., 2012, Ancelet et al., 2013, Ancelet et al., 2014a, Ancelet et al., 2014b, Ancelet et al., 2014d, Davy and Ancelet, 2014, Davy et al., 2014a, Ancelet et al., 2015, Davy and Trompetter, 2017b, Davy et al., 2017, Davy and Trompetter, 2017c). This was most likely due to copper chrome arsenate treated timber and old painted wood (for lead) finding its way into the fuel stream for solid fuel fires used for domestic space heating. Figure 2.8 presents the temporal variation for arsenic and lead (by XRF) over two years of monitoring (2013 to 2015) at the Coles Place air quality monitoring site in Christchurch (operated by Environment Canterbury) showing winter maxima for both contaminants.

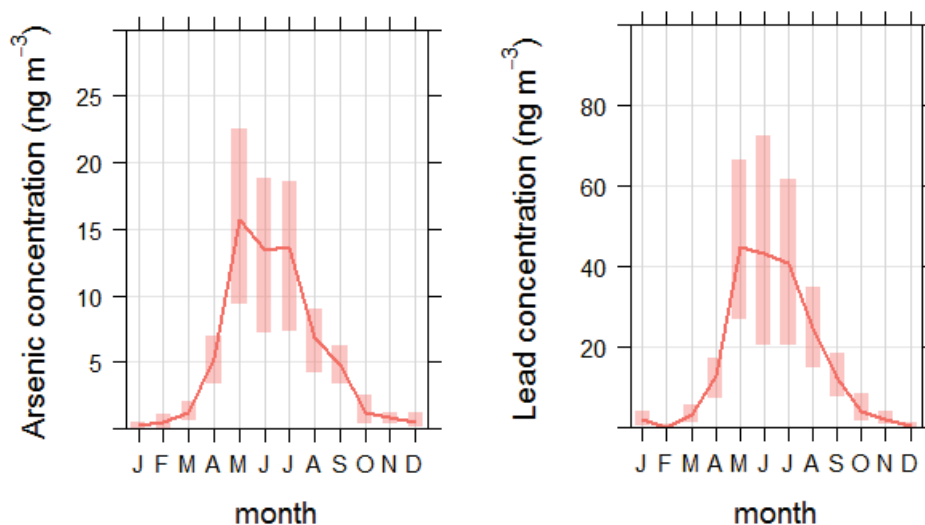


Figure 2.8 Temporal variation for arsenic (left); and lead (right) by XRF showing peak winter concentrations in Christchurch (Shaded areas represent the 95% confidence intervals in the calculated mean).

The New Zealand ambient air quality guidelines (AAQG) and associated background reports contain detailed information on the health effects of arsenic and lead provide guideline values for arsenic (inorganic arsenic is 5.5 ng m^{-3} as an annual average) and lead (200 ng m^{-3} as a 3-month moving average, calculated monthly) in PM_{10} (New Zealand Ministry for the Environment, 2002). It is important to note that, because of the relative limits of detection, only the XRF derived heavy metal data is suitable for comparison to the AAQG. The IBA heavy metal data is suitable as a screening method to identify peak heavy metal concentrations and to examine patterns in the data such as seasonal differences (e.g. monthly averages). Figure 2.9 presents the long-term arsenic and lead time-series measured by XRF for PM_{10} samples collected at Henderson, Auckland and shows the winter peaks in arsenic and lead concentrations.

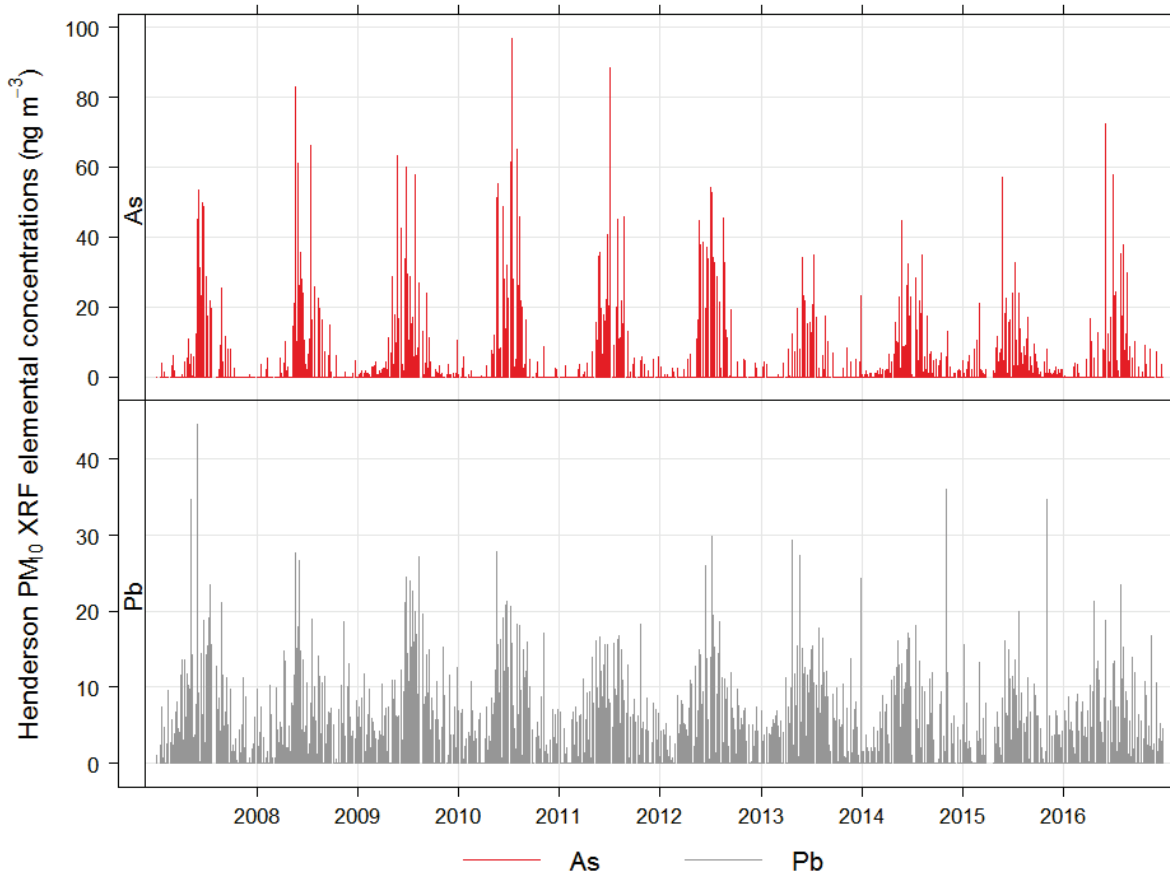


Figure 2.9 XRF Arsenic and lead concentration time-series for Henderson PM₁₀ Samples.

Annual average concentrations for arsenic at Henderson show inter-annual variability around the AAQG (5.5 ng m⁻³) as presented in Figure 2.10. The inter-annual variation was likely to be a combination of meteorological influences and source activity (i.e. the amount of CCA treated timber being burnt in local fireplaces). At other New Zealand urban centres with colder winters and a greater prevalence of domestic solid fuel fires used for home heating, the concentrations of arsenic were found to be commensurately higher than those shown for Henderson (Davy et al., 2014b).

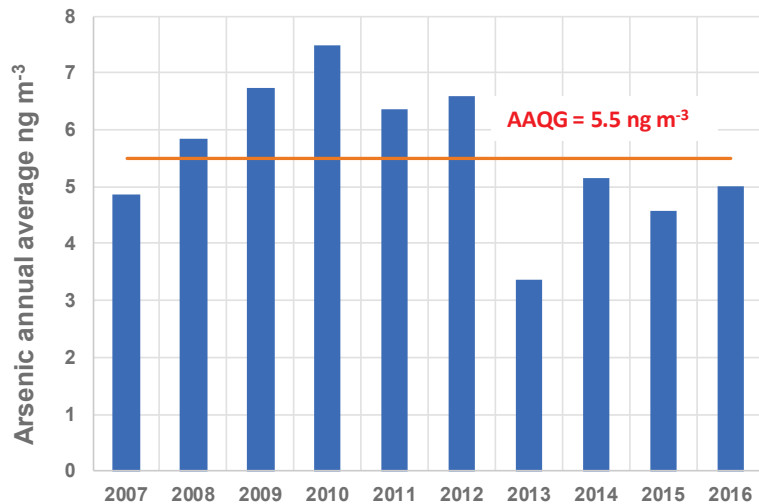


Figure 2.10 Annual average arsenic concentrations at Henderson.

Another more intermittent source of heavy metals in the New Zealand environment appears to be associated with fireworks events as illustrated by the plot for monthly-average lead concentrations (by XRF) in PM₁₀ at Henderson (2007-2016) presented in Figure 2.11. Coincident peaks in Sr, K, Cu, Ba, V, and Ti, all of which are components of pyrotechnics, suggest that lead is used in at least some fireworks products, most likely as lead nitrate due to its properties as an oxidiser when heated³.

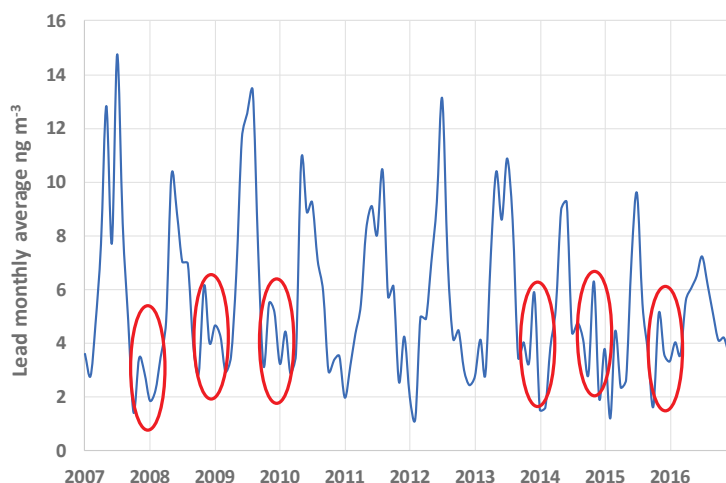


Figure 2.11 Lead (monthly average) concentrations by XRF in PM₁₀ from Henderson, Auckland showing peaks around Guy Fawkes (5 November).

The use of fireworks for Guy Fawkes, New Year's Eve and other public celebrations is widespread in New Zealand and is easily marked by extreme peaks in potassium concentrations (potassium nitrate is a main ingredient of gunpowder) as illustrated by the long-term time series for Auckland (Davy et al., 2017) presented in Figure 2.12.

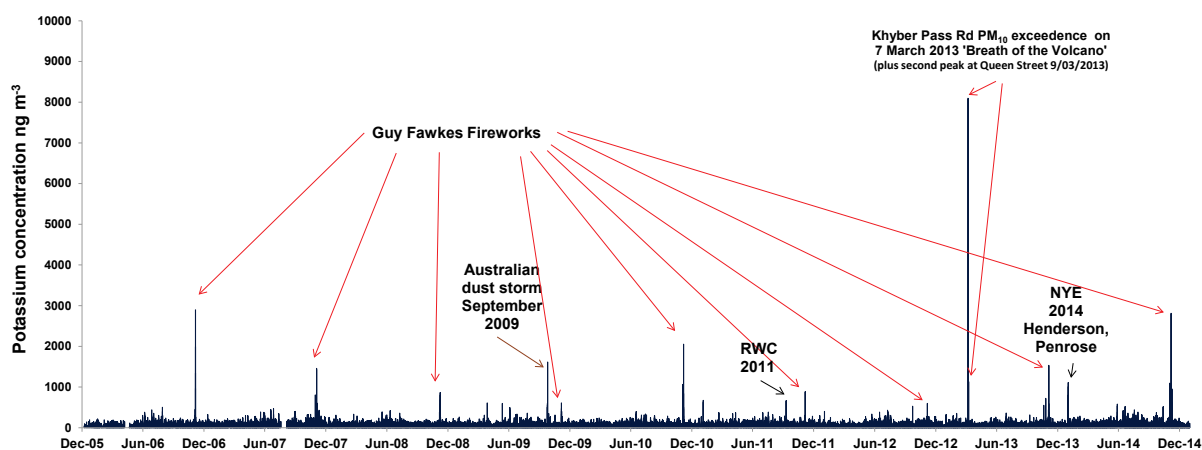


Figure 2.12 Time-series plot of PM_{2.5} potassium at all Auckland sites showing the influence of pyrotechnic events on extreme concentrations (RWC = Rugby World Cup).

2.3.2.2 Vanadium and Nickel

Concentrations of vanadium and nickel were found to be highest in particulate matter samples from monitoring sites near port facilities and were found to be associated with combustion products from ships engines (Davy et al., 2008, Davy et al., 2011d, Davy et al., 2011b, Ancelet et al., 2014d, Davy et al., 2017). The major factor is the use of residual or bunker oil as fuel for

³ Conkling, J. A. 2000. Pyrotechnics. Kirk-Othmer Encyclopedia of Chemical Technology

ships which is generally of poor quality, high in sulphur, PAHs and heavy metals that can result in high sulphate containing particulate matter emissions contaminated with alkali earth and transition metals (V, Ni, Ca, Fe) (Fridell et al., 2008, Moldanová et al., 2009).

Emissions of combustion products from ships engines can impact on local air quality in port areas, regional air quality and global climate (Huebert, 1999, Endresen et al., 2003, Ault et al., 2009, Eyring et al., 2010, Hellebust et al., 2010, Matthias et al., 2010). Species emitted to atmosphere from ships engines include usual combustion products (CO_x, NO_x), gaseous sulphur oxides (SO_x) that relate to fuel composition, volatile organic compounds (VOCs) from incomplete fuel combustion and particulate matter which includes trace heavy metals (e.g. vanadium and nickel) (Healy et al., 2009, Agrawal et al., 2008b, Agrawal et al., 2008a, Fridell et al., 2008).

The analysis of PM data from the Auckland Council Queen Street monitoring site showed that there was an impact on the Auckland CBD due to combustion emissions from ships engines and that there appeared to be an upward trend in concentrations as presented in Figure 2.13 most likely due to increasing shipping activity at the Port of Auckland (Davy et al., 2017).

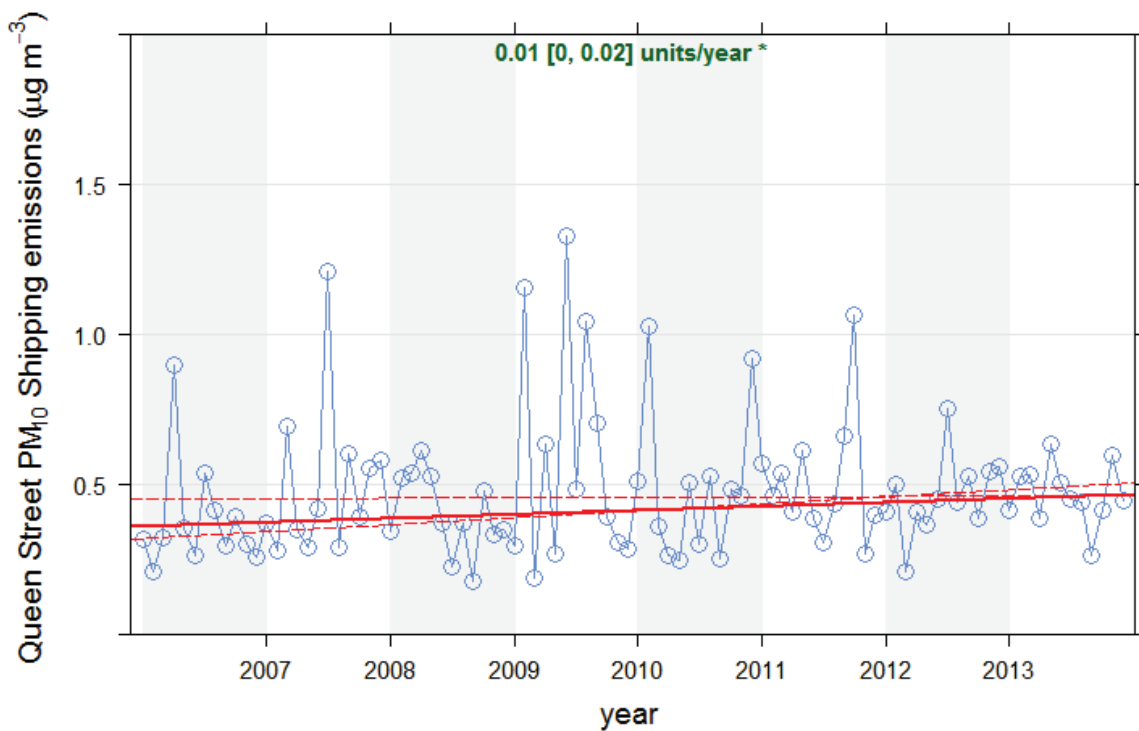


Figure 2.13 Trend in PM₁₀ Shipping emission source concentrations at Queen Street (statistically significant at the 95 % confidence interval).

2.3.2.3 Zinc

Zinc in particulate matter was relatively ubiquitous across New Zealand urban areas and was significantly associated with biomass burning (an important trace element in plant material) and motor vehicle emissions (primarily due to the co-combustion of lubricant oils but is also present in tyre wear particles). Samples of particulate matter from some sites showed that there were significant local industrial emissions of zinc primarily associated with surface coating and anti-corrosion (e.g. hot-dip galvanising) activities.

2.3.2.4 Copper and Barium

Copper was found to be more strongly associated with the coarse particle fraction (i.e. higher concentrations in PM₁₀ than PM_{2.5}) and mostly with motor vehicle sources as part of a 'road dust' component. Copper is a key indicator of brake wear due to brake pad composition containing significant amounts of the metal (Gietl et al., 2009). Other trace heavy metals associated with brake-wear include barium and antimony (Lough et al., 2005).

3.0 SUMMARY STATISTICS FOR BLACK CARBON, HEAVY METALS AND NATURAL SOURCE CONTRIBUTIONS DATA IN PARTICULATE MATTER

This chapter presents summary statistics of the compositional analysis results undertaken by GNS Science for all airborne particulate matter samples collected at New Zealand monitoring sites. Note that only PM samples were collected at each site and the BC and elemental data were generated at GNS Science for all PM samples by subsequent analyses. The natural source data was generated from the compositional data by receptor modelling techniques as described in Section 2.2.1 of this report. Meteorological and climatic variations can have a significant influence on air quality as can variations in source activity (i.e. emissions of particles). It is clear from the 10-year Auckland speciation dataset and the associated source apportionment results that long-term trends are evident for PM, PM composition and the emission sources, including the impact of regulations, policy, macro-economic effects and climatic variability. Short-term datasets (1-2 years) can therefore only be considered as snapshots of what was present in our urban atmospheres at the time monitoring was undertaken.

3.1 Black Carbon and Heavy Metals

The following tables provide summary statistics for black carbon and heavy metal elemental data from speciation monitoring sites around New Zealand. The reported data only includes those samples with a 24-hour integrated sampling regime and at least one year of data. The heavy metal data has been divided into two categories depending on the measurement technique (IBA or XRF) due to the differing limits of detection for the two analytical techniques as described in Section 2.1 and Appendix 1. Briefly, XRF analysis is more sensitive (lower limits of detection) for heavier metallic elements than IBA and can be used to compare the concentration data to the relevant AAQG. Several filter sample sets have been measured by both techniques (Henderson, Auckland and Coles Place, Christchurch) and are presented in both Section 3.1.1 and Section 3.1.2. Black carbon was measured in all samples by light reflection.

3.1.1 Ion Beam Analysis Elemental Data

3.1.1.1 Auckland Sites

Table 3.1 Summary statistics for PM₁₀ samples collected at Henderson, Auckland (2006-2016).

Henderson PM ₁₀	1126 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM10	($\mu\text{g m}^{-3}$)	14	44	2	13	5		
BC	(ng m^{-3})	1919	10463	0	1460	1659	167	97
V	(ng m^{-3})	1	9	0	0	2	10	3
Cr	(ng m^{-3})	1	85	0	0	3	8	6
Mn	(ng m^{-3})	4	33	0	3	4	7	24
Ni	(ng m^{-3})	2	80	0	1	4	9	9
Cu	(ng m^{-3})	6	124	0	4	7	10	28
Zn	(ng m^{-3})	42	2301	0	10	150	11	49
As	(ng m^{-3})	8	95	0	0	13	29	14
Ba	(ng m^{-3})	14	313	0	10	19	30	18
Pb	(ng m^{-3})	14	166	0	0	26	82	6

Table 3.2 Summary statistics for PM_{2.5} samples collected at Takapuna, Auckland (2006-2016).

Takapuna PM _{2.5}	1164 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM2.5	($\mu\text{g m}^{-3}$)	6	35	0	5	4		
BC	(ng m^{-3})	2531	16281	0	2001	2011	178	99
V	(ng m^{-3})	1	12	0	0	2	8	4
Cr	(ng m^{-3})	2	44	0	1	3	7	10
Mn	(ng m^{-3})	2	35	0	1	3	7	10
Ni	(ng m^{-3})	2	20	0	0	3	9	7
Cu	(ng m^{-3})	5	31	0	4	5	10	26
Zn	(ng m^{-3})	14	519	0	8	29	12	40
As	(ng m^{-3})	5	59	0	0	9	30	9
Ba	(ng m^{-3})	8	134	0	4	11	29	10
Pb	(ng m^{-3})	13	144	0	0	23	82	4

Table 3.3 Summary statistics for PM₁₀ samples collected at Takapuna, Auckland (2006-2016).

Takapuna PM ₁₀	1224 Samples	Average	Max	Min	Median	StdDev	Av LOD	% samples > LOD
PM10	($\mu\text{g m}^{-3}$)	16	55	3	15	6		
BC	(ng m^{-3})	2723	11610	95	2367	1704	163	100
V	(ng m^{-3})	1	17	0	0	2	11	3
Cr	(ng m^{-3})	1	16	0	0	2	9	7
Mn	(ng m^{-3})	5	31	0	4	5	7	32
Ni	(ng m^{-3})	2	21	0	1	3	10	9
Cu	(ng m^{-3})	13	97	0	11	10	9	62
Zn	(ng m^{-3})	18	298	0	12	25	12	54
As	(ng m^{-3})	6	83	0	0	11	29	10
Ba	(ng m^{-3})	26	331	0	23	23	31	40
Pb	(ng m^{-3})	13	159	0	0	23	81	5

Table 3.4 Summary statistics for PM_{2.5} samples collected at Queen Street, Auckland (2006-2016).

Queen St PM _{2.5}	1127 Samples	Average	Max	Min	Median	StdDev	Av LOD	% Samples > LOD
PM2.5	($\mu\text{g m}^{-3}$)	9	35	1	8	4	0	0
BC	(ng m^{-3})	3133	7923	432	2965	1362	173	100
V	(ng m^{-3})	4	114	0	1	8	7	24
Cr	(ng m^{-3})	2	11	0	1	2	6	9
Mn	(ng m^{-3})	2	46	0	1	3	6	14
Ni	(ng m^{-3})	3	209	0	1	7	8	15
Cu	(ng m^{-3})	5	221	0	3	8	10	22
Zn	(ng m^{-3})	15	187	0	9	20	11	47
As	(ng m^{-3})	4	45	0	0	8	29	7
Ba	(ng m^{-3})	9	217	0	4	13	27	9
Pb	(ng m^{-3})	12	148	0	0	22	77	5

Table 3.5 Summary statistics for PM₁₀ samples collected at Queen Street, Auckland (2006-2016).

Queen St PM ₁₀	3398 Samples	Average	Max	Min	Median	StdDev	Av LOD	% Samples > LOD
PM10	($\mu\text{g m}^{-3}$)	17	130	2	17	6	0	0
BC	(ng m^{-3})	3883	12651	146	3457	2043	184	100
V	(ng m^{-3})	4	118	0	0	8	10	18
Cr	(ng m^{-3})	2	26	0	0	2	9	8
Mn	(ng m^{-3})	4	99	0	3	5	7	29
Ni	(ng m^{-3})	3	47	0	2	4	9	15
Cu	(ng m^{-3})	11	170	0	10	8	9	59
Zn	(ng m^{-3})	19	750	0	15	24	11	63
As	(ng m^{-3})	4	61	0	0	8	30	7
Ba	(ng m^{-3})	21	143	0	18	19	31	33
Pb	(ng m^{-3})	12	152	0	0	22	79	5

Table 3.6 Summary statistics for PM_{2.5} samples collected at Khyber Pass Road, Auckland (2006-2015).

Khyber Pass Road PM _{2.5}	1072 Samples	Average	Max	Min	Median	StdDev	Av LOD	% Samples > LOD
PM2.5	($\mu\text{g m}^{-3}$)	8	40	0	8	4	0	0
BC	(ng m^{-3})	3719	9152	0	3552	1577	179	100
V	(ng m^{-3})	2	28	0	0	3	7	13
Cr	(ng m^{-3})	2	20	0	1	2	6	9
Mn	(ng m^{-3})	2	26	0	1	2	6	12
Ni	(ng m^{-3})	2	18	0	0	3	8	7
Cu	(ng m^{-3})	5	235	0	5	9	9	30
Zn	(ng m^{-3})	15	162	0	10	18	11	51
As	(ng m^{-3})	4	51	0	0	8	29	7
Ba	(ng m^{-3})	9	364	0	4	17	27	8
Pb	(ng m^{-3})	12	140	0	0	22	77	5

Table 3.7 Summary statistics for PM₁₀ samples collected at Khyber Pass Road, Auckland (2006-2015).

Khyber Pass Road PM ₁₀	1039 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM10	($\mu\text{g m}^{-3}$)	18	53	5	17	6	0	0
BC	(ng m^{-3})	4669	14964	0	4402	2206	188	100
V	(ng m^{-3})	2	36	0	0	4	10	8
Cr	(ng m^{-3})	2	59	0	0	3	8	13
Mn	(ng m^{-3})	6	35	0	5	5	7	42
Ni	(ng m^{-3})	2	56	0	1	3	9	11
Cu	(ng m^{-3})	17	90	0	16	11	9	77
Zn	(ng m^{-3})	24	297	0	17	27	11	69
As	(ng m^{-3})	5	53	0	0	8	29	7
Ba	(ng m^{-3})	24	245	0	22	19	32	38
Pb	(ng m^{-3})	12	111	0	0	21	79	4

Table 3.8 Summary statistics for PM_{2.5} samples collected at Penrose, Auckland (2006-2016).

Penrose PM _{2.5}	1044 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM2.5	(µg m ⁻³)	7	40	0	6	5	0	0
BC	(ng m ⁻³)	2284	9092	0	2037	1466	172	99
V	(ng m ⁻³)	1	12	0	0	2	7	5
Cr	(ng m ⁻³)	2	16	0	1	2	6	12
Mn	(ng m ⁻³)	2	37	0	1	3	6	15
Ni	(ng m ⁻³)	2	13	0	0	2	9	8
Cu	(ng m ⁻³)	3	87	0	2	5	10	14
Zn	(ng m ⁻³)	30	521	0	12	51	11	56
As	(ng m ⁻³)	6	69	0	0	9	29	9
Ba	(ng m ⁻³)	6	120	0	1	10	27	6
Pb	(ng m ⁻³)	15	214	0	0	26	78	7

Table 3.9 Summary statistics for PM₁₀ samples collected at Penrose, Auckland (2006-2016).

Penrose PM ₁₀	1028 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM10	(µg m ⁻³)	16	55	0	16	7	0	0
BC	(ng m ⁻³)	2377	9474	0	2122	1490	176	99
V	(ng m ⁻³)	1	13	0	0	2	11	3
Cr	(ng m ⁻³)	3	401	0	0	14	9	17
Mn	(ng m ⁻³)	6	40	0	4	7	7	36
Ni	(ng m ⁻³)	2	107	0	1	5	9	7
Cu	(ng m ⁻³)	8	117	0	6	8	10	37
Zn	(ng m ⁻³)	46	698	0	17	72	11	64
As	(ng m ⁻³)	6	72	0	0	10	29	11
Ba	(ng m ⁻³)	19	130	0	14	20	34	24
Pb	(ng m ⁻³)	13	257	0	0	25	81	6

Table 3.10 Summary statistics for PM_{2.5} samples collected at Patumahoe, South Auckland (2010).

Patumahoe PM _{2.5}	294 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM2.5	(µg m ⁻³)	3	11	0	3	1		
BC	(ng m ⁻³)	524	2878	30	377	461	123	94
V	(ng m ⁻³)	1	9	0	0	2	8	2
Cr	(ng m ⁻³)	2	11	0	1	2	7	7
Mn	(ng m ⁻³)	1	10	0	0	2	7	6
Ni	(ng m ⁻³)	2	11	0	0	3	9	8
Cu	(ng m ⁻³)	2	16	0	1	3	12	9
Zn	(ng m ⁻³)	11	88	0	8	12	13	41
As	(ng m ⁻³)	4	36	0	0	8	31	7
Ba	(ng m ⁻³)	10	82	0	0	17	67	3
Pb	(ng m ⁻³)	15	135	0	0	26	86	7

Table 3.11 Summary statistics for PM_{10-2.5} samples collected at Patumahoe, South Auckland (2010).

PatumahoePM _{10-2.5}	294 Samples	Average	Max	Min	Median	StdDev	Av LOD	%>LOD
PM10-2.5	($\mu\text{g m}^{-3}$)	7	20	0	7	4		
BC	(ng m^{-3})	83	1430	0	35	165	129	32
V	(ng m^{-3})	1	11	0	0	2	8	3
Cr	(ng m^{-3})	1	8	0	0	2	7	8
Mn	(ng m^{-3})	4	20	0	2	4	7	26
Ni	(ng m^{-3})	2	11	0	0	2	9	8
Cu	(ng m^{-3})	5	704	0	1	40	12	10
Zn	(ng m^{-3})	3	44	0	1	4	13	9
As	(ng m^{-3})	4	36	0	0	7	31	6
Ba	(ng m^{-3})	9	76	0	0	15	67	3
Pb	(ng m^{-3})	10	85	0	0	18	86	3

3.1.1.2 Hawkes Bay

Table 3.12 Summary statistics for PM₁₀ samples collected at Hastings (2006-2007).

Hastings PM ₁₀	124 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM10	($\mu\text{g m}^{-3}$)	22	112	3	16	19		
BC	(ng m^{-3})	3373	12087	206	2264	2963	150	100
V	(ng m^{-3})	1	7	0	0	2	9	2
Cr	(ng m^{-3})	1	6	0	0	1	8	1
Mn	(ng m^{-3})	4	21	0	3	3	6	30
Ni	(ng m^{-3})	1	7	0	0	2	7	8
Cu	(ng m^{-3})	4	55	0	2	7	7	23
Zn	(ng m^{-3})	17	85	0	9	19	7	62
As	(ng m^{-3})	11	102	0	2	21	19	24
Ba	(ng m^{-3})	12	133	0	9	15	23	16
Pb	(ng m^{-3})	19	162	0	2	29	56	15

3.1.1.3 Wellington

Table 3.13 Summary statistics for PM_{2.5} samples collected at Wainuiomata, Lower Hutt (2006-2014).

Wainuiomata PM _{2.5}	488 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM2.5	($\mu\text{g m}^{-3}$)	5	46	0	4	5		
BC	(ng m^{-3})	893	10713	0	324	1367	121	71
V	(ng m^{-3})	1	11	0	0	1	5	5
Cr	(ng m^{-3})	1	9	0	1	2	4	31
Mn	(ng m^{-3})	1	10	0	0	1	4	7
Ni	(ng m^{-3})	1	46	0	1	3	4	16
Cu	(ng m^{-3})	1	30	0	0	3	5	11
Zn	(ng m^{-3})	4	47	0	2	6	7	31
As	(ng m^{-3})	6	91	0	0	11	15	19
Ba	(ng m^{-3})	3	48	0	0	5	17	2
Pb	(ng m^{-3})	9	147	0	0	20	44	6

Table 3.14 Summary statistics for PM_{2.5} samples collected at Masterton (2002-2004).

Masterton PM _{2.5}	139 Samples	Average	Max	Min	Median	Std Dev	Av LOD	% > LOD
PM2.5	($\mu\text{g m}^{-3}$)	9	42	2	6	8		
BC	(ng m^{-3})	1625	7382	0	966	1754	144	88
V	(ng m^{-3})	1	6	0	0	1	6	2
Cr	(ng m^{-3})	5	136	0	2	13	7	40
Mn	(ng m^{-3})	2	13	0	0	2	7	13
Ni	(ng m^{-3})	2	30	0	1	4	7	19
Cu	(ng m^{-3})	4	70	0	2	7	7	31
Zn	(ng m^{-3})	7	37	0	5	7	8	48
As	(ng m^{-3})	6	45	0	2	9	20	27
Pb	(ng m^{-3})	11	123	0	0	21	59	13

Table 3.15 Summary statistics for PM_{10-2.5} samples collected at Masterton (2002-2004).

Masterton PM _{10-2.5}	153 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM10-2.5	($\mu\text{g m}^{-3}$)	8	25	2	7	4		
BC	(ng m^{-3})	331	4401	0	142	550	145	54
V	(ng m^{-3})	1	4	0	0	1	4	3
Cr	(ng m^{-3})	9	542	0	5	45	3	72
Mn	(ng m^{-3})	2	8	0	2	2	3	38
Ni	(ng m^{-3})	3	116	0	1	10	3	47
Cu	(ng m^{-3})	2	15	0	1	3	4	50
Zn	(ng m^{-3})	4	24	0	2	4	5	57
As	(ng m^{-3})	3	27	0	0	5	13	22
Pb	(ng m^{-3})	8	91	0	0	17	35	10

Table 3.16 Summary statistics for PM_{2.5} samples collected at Seaview, Lower Hutt (2005-2007).

Seaview PM _{2.5}	142 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM2.5	(µg m ⁻³)	4.8	10.7	0.4	4.8	1.9		
BC	(ng m ⁻³)	1049	3842	0	874	846	103	84
V	(ng m ⁻³)	1	7	0	0	1	4	5
Cr	(ng m ⁻³)	1	5	0	0	1	3	6
Mn	(ng m ⁻³)	3	13	0	2	3	3	38
Ni	(ng m ⁻³)	1	7	0	1	1	4	9
Cu	(ng m ⁻³)	2	42	0	1	4	5	18
Zn	(ng m ⁻³)	20	448	0	13	39	6	69
As	(ng m ⁻³)	3	33	0	0	5	16	10
Ba	(ng m ⁻³)	4	26	0	2	6	14	9
Pb	(ng m ⁻³)	12	111	0	2	18	42	13

Table 3.17 Summary statistics for PM_{10-2.5} samples collected at Seaview, Lower Hutt (2005-2007).

Seaview PM _{10-2.5}	142 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM10-2.5	(µg m ⁻³)	11.4	23.3	1.5	11.2	4.0		
BC	(ng m ⁻³)	322.5	1554.2	95.6	310.7	150.7	101.6	99
V	(ng m ⁻³)	0.3	21.3	0.0	0.0	1.8	6.6	1
Cr	(ng m ⁻³)	0.7	5.9	0.0	0.0	1.2	5.0	13
Mn	(ng m ⁻³)	4.0	14.3	0.0	3.4	2.7	2.9	62
Ni	(ng m ⁻³)	0.8	4.6	0.0	0.5	1.0	3.1	12
Cu	(ng m ⁻³)	3.4	33.4	0.0	2.5	4.1	2.7	58
Zn	(ng m ⁻³)	19.1	194.6	0.0	13.9	20.7	2.8	95
As	(ng m ⁻³)	2.0	25.9	0.0	0.0	3.4	6.6	16
Ba	(ng m ⁻³)	14.9	59.5	0.0	12.9	11.5	15.3	44
Pb	(ng m ⁻³)	12.5	69.1	0.0	7.2	14.9	15.0	34

3.1.1.4 Nelson

Table 3.18 Summary statistics for PM_{2.5} samples collected at Nelson (2008-2012).

Nelson City PM _{2.5}	200 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM _{2.5}	(µg m ⁻³)	16	70	1	8	16		
BC	(ng m ⁻³)	3208	11310	114	1482	3132	156	100
V	(ng m ⁻³)	1	10	0	1	2	7	9
Cr	(ng m ⁻³)	2	38	0	1	4	6	15
Mn	(ng m ⁻³)	2	13	0	1	2	7	11
Ni	(ng m ⁻³)	2	15	0	1	3	9	8
Cu	(ng m ⁻³)	5	197	0	2	15	10	19
Zn	(ng m ⁻³)	21	131	0	11	25	10	56
As	(ng m ⁻³)	14	88	0	3	20	27	27
Ba	(ng m ⁻³)	6	73	0	1	9	24	6
Pb	(ng m ⁻³)	21	262	0	0	36	81	9

Table 3.19 Summary statistics for PM₁₀ samples collected at Nelson (2008-2012).

Nelson City PM ₁₀	190 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM ₁₀	(µg m ⁻³)	21	78	2	17	13		
BC	(ng m ⁻³)	2907	11158	8	1803	2680	156	98
V	(ng m ⁻³)	2	16	0	1	3	9	11
Cr	(ng m ⁻³)	2	19	0	0	3	8	7
Mn	(ng m ⁻³)	4	19	0	4	4	8	26
Ni	(ng m ⁻³)	2	15	0	1	3	9	9
Cu	(ng m ⁻³)	4	24	0	3	5	11	20
Zn	(ng m ⁻³)	22	155	0	17	24	11	66
As	(ng m ⁻³)	10	66	0	5	14	26	18
Ba	(ng m ⁻³)	13	86	0	8	14	30	16
Pb	(ng m ⁻³)	17	261	0	0	32	80	9

Table 3.20 Summary statistics for PM₁₀ samples collected at Tahunanui, Nelson (2008-2009).

Nelson Tahunanui PM₁₀	185 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM10	($\mu\text{g m}^{-3}$)	21	57	2	19	10		
BC	(ng m^{-3})	3086	10898	175	2188	2638	156	100
V	(ng m^{-3})	3	16	0	2	3	7	16
Cr	(ng m^{-3})	4	25	0	2	5	6	28
Mn	(ng m^{-3})	17	156	0	12	19	5	76
Ni	(ng m^{-3})	2	12	0	1	3	8	16
Cu	(ng m^{-3})	5	20	0	4	5	8	29
Zn	(ng m^{-3})	53	668	0	23	84	9	76
As	(ng m^{-3})	7	48	0	0	10	25	16
Ba	(ng m^{-3})	9	40	0	7	10	26	11
Pb	(ng m^{-3})	13	120	0	0	21	71	4

3.1.1.5 Canterbury

Table 3.21 Summary statistics for PM_{2.5} samples collected at St Albans, Christchurch (2013-2015).

St Albans, Christchurch PM_{2.5}	231 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM2.5	($\mu\text{g m}^{-3}$)	9	52	0	6	8		
BC	(ng m^{-3})	1973	12888	0	907	2557	178	91
V	(ng m^{-3})	1	21	0	0	2	8	3
Cr	(ng m^{-3})	3	16	0	2	3	7	18
Mn	(ng m^{-3})	2	12	0	1	2	8	9
Ni	(ng m^{-3})	2	26	0	1	3	10	11
Cu	(ng m^{-3})	3	16	0	2	4	12	10
Zn	(ng m^{-3})	29	783	0	12	62	13	53
As	(ng m^{-3})	9	188	0	0	18	33	14
Ba	(ng m^{-3})	6	69	0	0	10	30	3
Pb	(ng m^{-3})	17	184	0	0	33	94	7

Table 3.22 Summary statistics for PM_{10-2.5} samples collected at St Albans, Christchurch (2013-2015).

St Albans, Christchurch PM _{10-2.5}	231 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM10-2.5	($\mu\text{g m}^{-3}$)	11.3	63	0	10	7		
BC	(ng m^{-3})	127	1275	0	79	189	160	25
V	(ng m^{-3})	1	8	0	0	2	9	2
Cr	(ng m^{-3})	2	47	0	1	4	7	9
Mn	(ng m^{-3})	3	18	0	2	3	7	17
Ni	(ng m^{-3})	2	10	0	0	2	9	5
Cu	(ng m^{-3})	4	24	0	3	5	10	19
Zn	(ng m^{-3})	8	147	0	6	12	12	36
As	(ng m^{-3})	4	72	0	0	8	30	6
Ba	(ng m^{-3})	8	43	0	4	10	28	5
Pb	(ng m^{-3})	13	131	0	0	24	79	6

Table 3.23 Summary statistics for PM_{2.5} samples collected at Timaru (2006-2007).

Timaru PM _{2.5}	175 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM2.5	($\mu\text{g m}^{-3}$)	16	82	0	10	17		
BC	(ng m^{-3})	3606	17834	120	1835	3931	150	93
V	(ng m^{-3})	3	15	0	0	4	6	1
Cr	(ng m^{-3})	2	19	0	0	4	5	3
Mn	(ng m^{-3})	3	27	0	1	4	5	1
Ni	(ng m^{-3})	12	310	0	3	31	6	16
Cu	(ng m^{-3})	5	30	0	0	7	8	4
Zn	(ng m^{-3})	16	72	0	12	16	9	19
As	(ng m^{-3})	12	108	0	0	21	22	3
Ba	(ng m^{-3})	8	61	0	0	12	19	2
Pb	(ng m^{-3})	37	321	0	0	61	61	4

3.1.1.6 Otago

Table 3.24 Summary statistics for PM_{2.5} samples collected at Dunedin (2010).

Dunedin PM _{2.5}	100 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM2.5	($\mu\text{g m}^{-3}$)	10	26	0	10	5		
BC	(ng m^{-3})	2137	5279	27	1974	1319	206	98
V	(ng m^{-3})	1	8	0	0	2	8	4
Cr	(ng m^{-3})	2	64	0	0	7	7	6
Mn	(ng m^{-3})	3	18	0	1	4	8	20
Ni	(ng m^{-3})	3	25	0	2	4	10	6
Cu	(ng m^{-3})	7	275	0	2	28	12	20
Zn	(ng m^{-3})	10	34	0	9	8	13	42
As	(ng m^{-3})	6	38	0	0	9	32	10
Ba	(ng m^{-3})	8	42	0	5	10	27	8
Pb	(ng m^{-3})	12	107	0	0	23	89	4

Table 3.25 Summary statistics for PM_{10-2.5} samples collected at Dunedin (2010).

Dunedin PM _{10-2.5}	100 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM10-2.5	($\mu\text{g m}^{-3}$)	17	46	1	16	9		
BC	(ng m^{-3})	629	1540	55	543	300	206	95
V	(ng m^{-3})	1	8	0	1	2	6	4
Cr	(ng m^{-3})	1	6	0	1	2	5	9
Mn	(ng m^{-3})	7	36	0	6	6	3	74
Ni	(ng m^{-3})	2	9	0	1	2	4	16
Cu	(ng m^{-3})	7	19	0	6	4	5	68
Zn	(ng m^{-3})	9	42	0	8	8	6	65
As	(ng m^{-3})	1	5	0	0	1	10	0
Ba	(ng m^{-3})	6	30	0	3	8	28	2
Pb	(ng m^{-3})	2	26	0	0	5	24	0

3.1.2 X-ray Fluorescence Elemental Data

3.1.2.1 Northland

Table 3.26 Summary statistics for PM₁₀ samples collected at Whangarei (2004-2012).

Whangarei PM ₁₀	449 Samples	Average	Max	Min	median	StdDev	Av LOD	% > LOD
PM10	($\mu\text{g m}^{-3}$)	12	70	1	11	7		
BC	(ng m^{-3})	1721	6250	50	1340	1174	150	100
V	(ng m^{-3})	2	8	0	1	1	2	20
Cr	(ng m^{-3})	1	17	0	0	1	1	12
Mn	(ng m^{-3})	2	49	0	2	3	1	18
Ni	(ng m^{-3})	2	9	0	2	1	1	0
Cu	(ng m^{-3})	2	15	0	0	2	2	31
Zn	(ng m^{-3})	6	39	0	5	5	2	58
As	(ng m^{-3})	3	18	0	0	3	1	30
Ba	(ng m^{-3})	31	111	0	27	21	12	76
Pb	(ng m^{-3})	12	82	0	8	11	2	36

3.1.2.2 Auckland

Table 3.27 Summary statistics for PM₁₀ samples collected at Henderson, Auckland (2006-2016).

Henderson PM ₁₀	1096 Samples	Average	Max	Min	median	StdDev	Av LOD	% > LOD
PM10	($\mu\text{g m}^{-3}$)	14	44	2	13	5		
BC	(ng m^{-3})	1919	10463	0	1460	1659	167	97
V	(ng m^{-3})	1	25	0	0	1	4	1
Cr	(ng m^{-3})	1	265	0	0	9	2	4
Mn	(ng m^{-3})	3	125	0	2	5	2	48
Ni	(ng m^{-3})	1	131	0	0	5	2	2
Cu	(ng m^{-3})	6	374	0	4	14	4	54
Zn	(ng m^{-3})	43	2283	0	8	147	5	64
As	(ng m^{-3})	6	97	0	1	12	2	35
Ba	(ng m^{-3})	13	293	0	6	21	23	19
Pb	(ng m^{-3})	5	45	0	4	6	4	53

3.1.2.3 Waikato

Table 3.28 Summary statistics for PM₁₀ samples collected at Tokoroa (2015-2016).

Tokoroa PM ₁₀	361 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM ₁₀	(µg m ⁻³)	14	61	3	12	9		
BC	(ng m ⁻³)	1853	9536	150	1002	1931	172	99
V	(ng m ⁻³)	1	6	0	0	1	4	1
Cr	(ng m ⁻³)	1	42	0	0	3	2	27
Mn	(ng m ⁻³)	2	9	0	1	2	2	28
Ni	(ng m ⁻³)	0	7	0	0	1	2	2
Cu	(ng m ⁻³)	3	34	0	2	3	4	31
Zn	(ng m ⁻³)	7	42	0	4	7	5	46
As	(ng m ⁻³)	3	35	0	2	4	2	39
Ba	(ng m ⁻³)	6	56	0	0	10	23	6
Pb	(ng m ⁻³)	4	31	0	3	5	4	44

3.1.2.4 Hawkes Bay

Table 3.29 Summary statistics for PM_{2.5} samples collected at Awatoto, Hawkes Bay (2016-2017).

Awatoto PM _{2.5}	111 Samples	Average	Max	Min	Median	StdDev	Av LOD	% >LOD
PM _{2.5}	(µg m ⁻³)	4	12	0	3	2		
BC	(ng m ⁻³)	155	2079	0	36	269	184	62
V	(ng m ⁻³)	0	7	0	0	1	2	2
Cr	(ng m ⁻³)	0	9	0	0	1	1	5
Mn	(ng m ⁻³)	1	7	0	0	2	1	27
Ni	(ng m ⁻³)	0	2	0	0	0	1	1
Cu	(ng m ⁻³)	2	13	0	1	2	2	37
Zn	(ng m ⁻³)	4	28	0	2	5	2	47
As	(ng m ⁻³)	0	3	0	0	1	1	10
Ba	(ng m ⁻³)	2	77	0	0	8	12	5
Pb	(ng m ⁻³)	1	29	0	0	4	2	17

Table 3.30 Summary statistics for PM_{10-2.5} samples collected at Awatoto, Hawkes Bay (2016-2017).

Awatoto PM _{10-2.5}	111 Samples	Average	Max	Min	Median	StdDev	Av LOD	% >LOD
PM10-2.5	($\mu\text{g m}^{-3}$)	10	43	0	9	6		
BC	(ng m^{-3})	144	289	16	142	59	184	26
V	(ng m^{-3})	0	3	0	0	0	2	1
Cr	(ng m^{-3})	5	371	0	2	35	1	58
Mn	(ng m^{-3})	2	23	0	0	3	1	45
Ni	(ng m^{-3})	0	11	0	0	1	1	1
Cu	(ng m^{-3})	4	20	0	4	3	2	76
Zn	(ng m^{-3})	5	33	0	4	5	2	69
As	(ng m^{-3})	0	4	0	0	0	1	3
Ba	(ng m^{-3})	1	32	0	0	4	12	2
Pb	(ng m^{-3})	1	37	0	0	4	2	8

3.1.2.5 Tasman

Table 3.31 Summary statistics for PM_{2.5} samples collected at Richmond (2015-2016).

Richmond PM _{2.5}	356 samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM2.5	($\mu\text{g m}^{-3}$)	11	50	0	6	10		
BC	(ng m^{-3})	2949	12279	8	1505	2868	159	99
V	(ng m^{-3})	0	33	0	0	2	4	1
Cr	(ng m^{-3})	8	137	0	2	17	2	42
Mn	(ng m^{-3})	2	16	0	1	2	2	39
Ni	(ng m^{-3})	1	5	0	0	1	2	6
Cu	(ng m^{-3})	7	110	0	3	11	4	42
Zn	(ng m^{-3})	10	47	0	7	10	5	60
As	(ng m^{-3})	13	171	0	5	19	2	66
Ba	(ng m^{-3})	4	395	0	0	22	23	3
Pb	(ng m^{-3})	7	31	0	5	6	4	61

Table 3.32 Summary statistics for PM₁₀ samples collected at Richmond (2013-2016).

Richmond PM ₁₀	313 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM10	($\mu\text{g m}^{-3}$)	18	59	1	14	11		
BC	(ng m^{-3})	3866	12665	297	2855	3245	162	100
V	(ng m^{-3})	1	8	0	0	1	4	6
Cr	(ng m^{-3})	14	215	0	1	35	2	42
Mn	(ng m^{-3})	5	17	0	5	4	2	66
Ni	(ng m^{-3})	0	4	0	0	1	2	4
Cu	(ng m^{-3})	13	130	0	6	21	4	75
Zn	(ng m^{-3})	18	109	0	13	16	5	84
As	(ng m^{-3})	14	131	0	6	21	2	62
Ba	(ng m^{-3})	9	72	0	3	13	23	14
Pb	(ng m^{-3})	7	34	0	6	7	4	65

3.1.2.6 Canterbury

Table 3.33 Summary statistics for PM_{2.5} samples collected at St Albans, Christchurch (2013-2015).

St Albans, Christchurch PM _{2.5}	245 Samples	Average	Max	Min	Median	StdDev	Av LOD	% > LOD
PM2.5	($\mu\text{g m}^{-3}$)	10	52	0	8	9		
BC	(ng m^{-3})	2334	16441	0	1038	3127	371	82
V	(ng m^{-3})	0	4	0	0	1	4	0
Cr	(ng m^{-3})	16	344	0	2	47	2	40
Mn	(ng m^{-3})	6	62	0	4	8	2	53
Ni	(ng m^{-3})	3	19	0	2	2	2	40
Cu	(ng m^{-3})	4	21	0	2	4	4	35
Zn	(ng m^{-3})	31	283	0	15	44	5	72
As	(ng m^{-3})	5	52	0	1	10	2	38
Ba	(ng m^{-3})	10	96	0	0	18	23	17
Pb	(ng m^{-3})	16	205	0	0	33	4	39

3.2 Temporal Variations in Natural Source Contributions to Particulate Matter

The natural source contribution data has been summarised and presented as temporal variation plots in the following sections as this provides an overview of the relative influence of the various sources on PM concentrations depending on the size fraction. Note that only datasets with at least one year of PM monitoring samples have been included here.

3.2.1 Auckland

3.2.1.1 Auckland PM₁₀

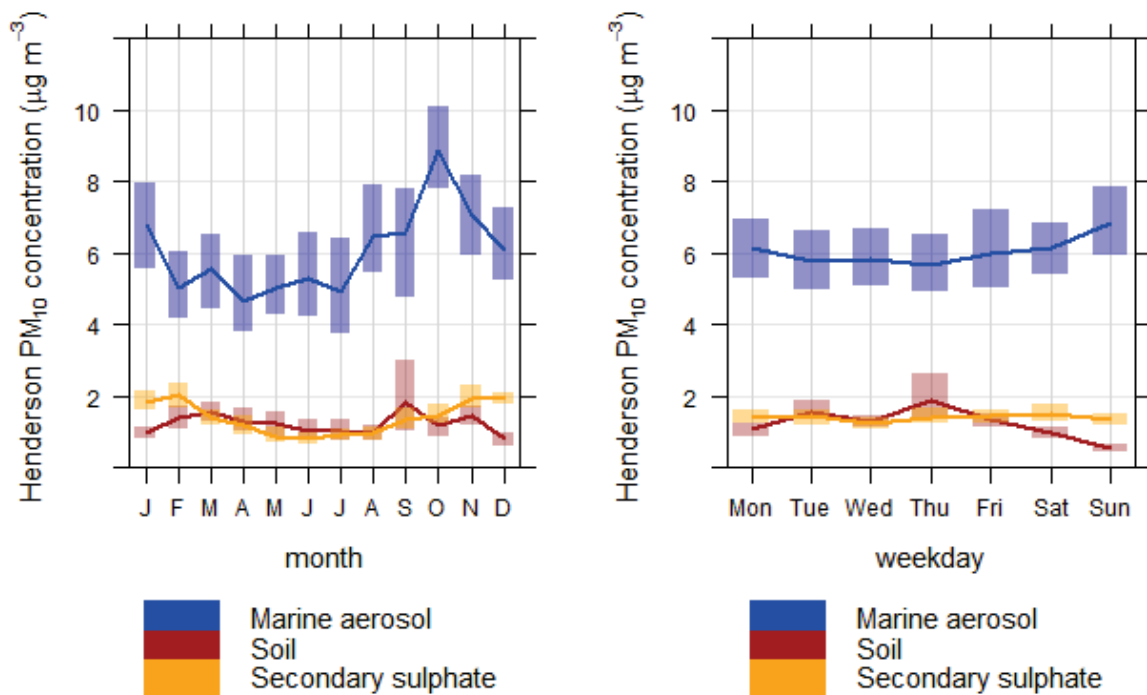


Figure 3.1 Temporal variation in natural source contributions to PM₁₀ at Henderson, Auckland (2006-2013). Shaded areas represent the 95% confidence intervals in the calculated mean.

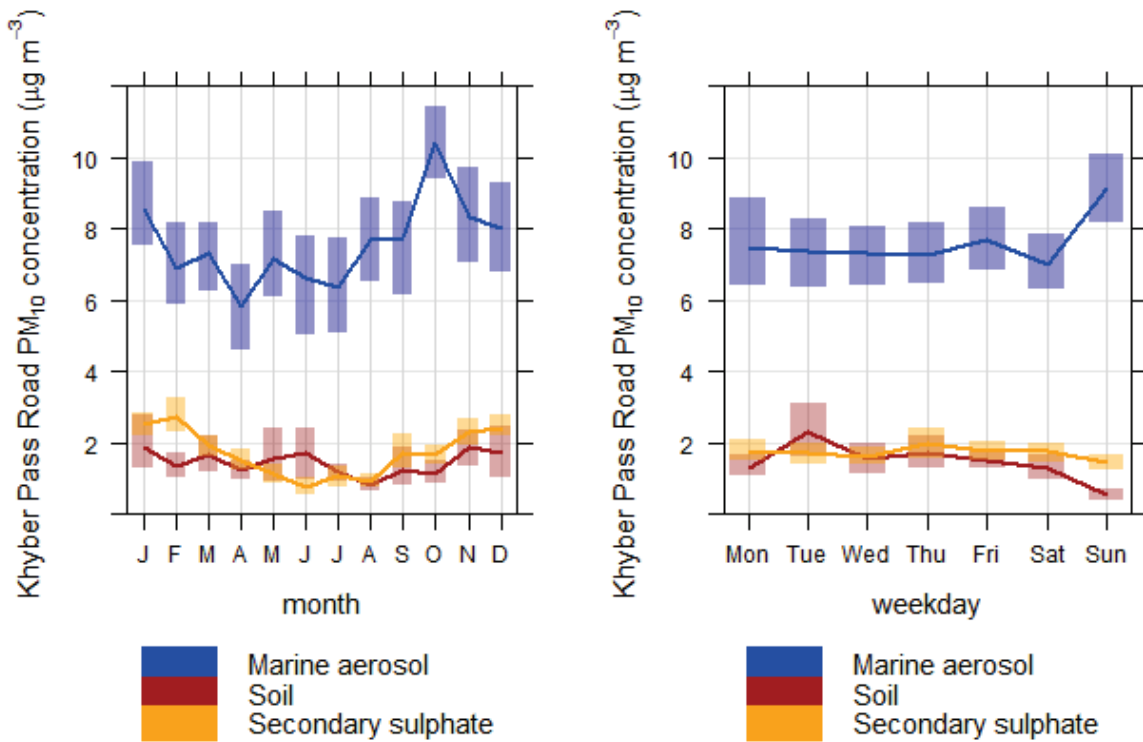


Figure 3.2 Temporal variation in natural source contributions to PM₁₀ at Khyber Pass Road, Auckland (2006-2013). Shaded areas represent the 95% confidence intervals in the calculated mean.

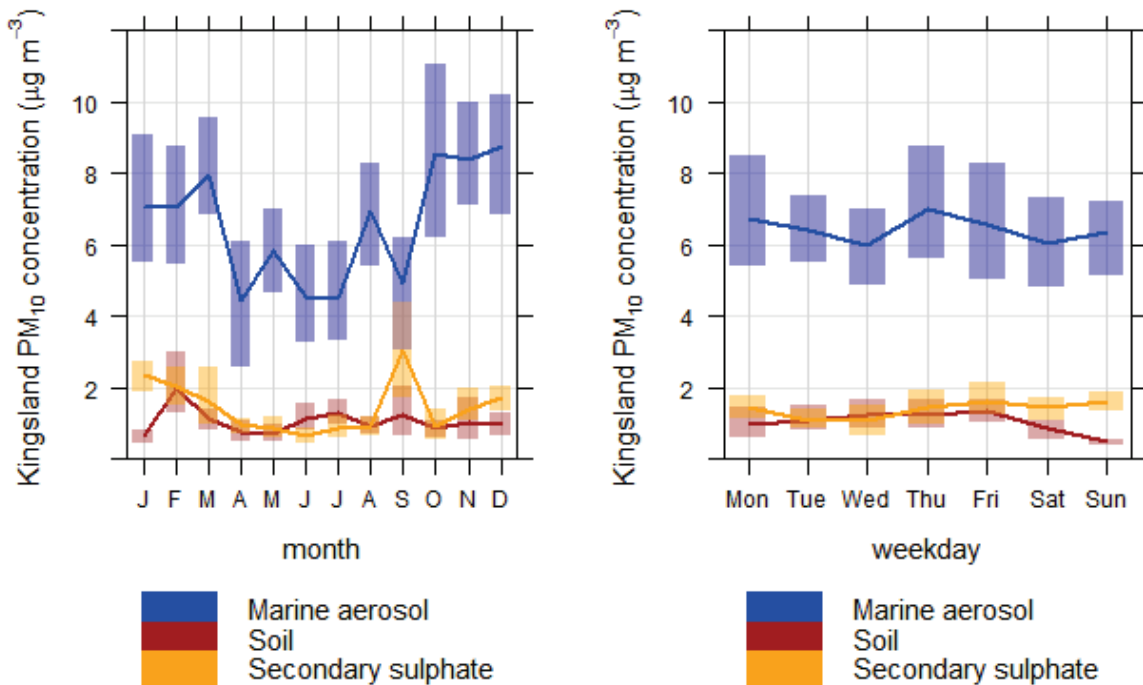


Figure 3.3 Temporal variation in natural source contributions to PM₁₀ at Kingsland, Auckland (2004-2007). Shaded areas represent the 95% confidence intervals in the calculated mean.

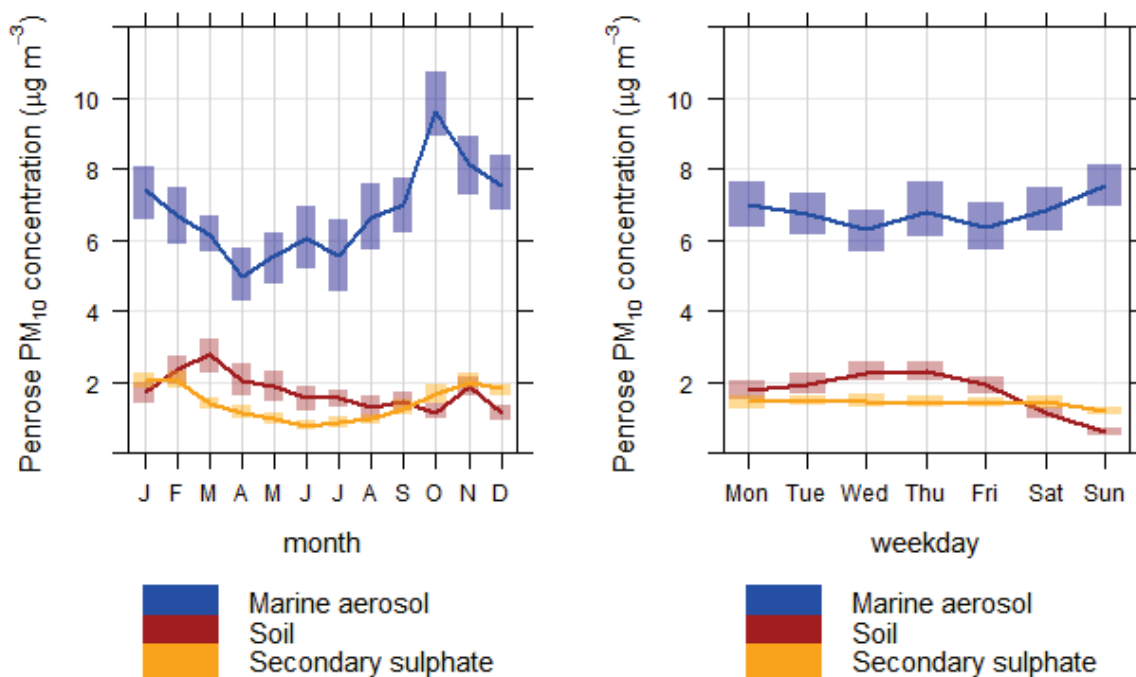


Figure 3.4 Temporal variation in natural source contributions to PM₁₀ at Penrose, Auckland (2006-2013). Shaded areas represent the 95% confidence intervals in the calculated mean.

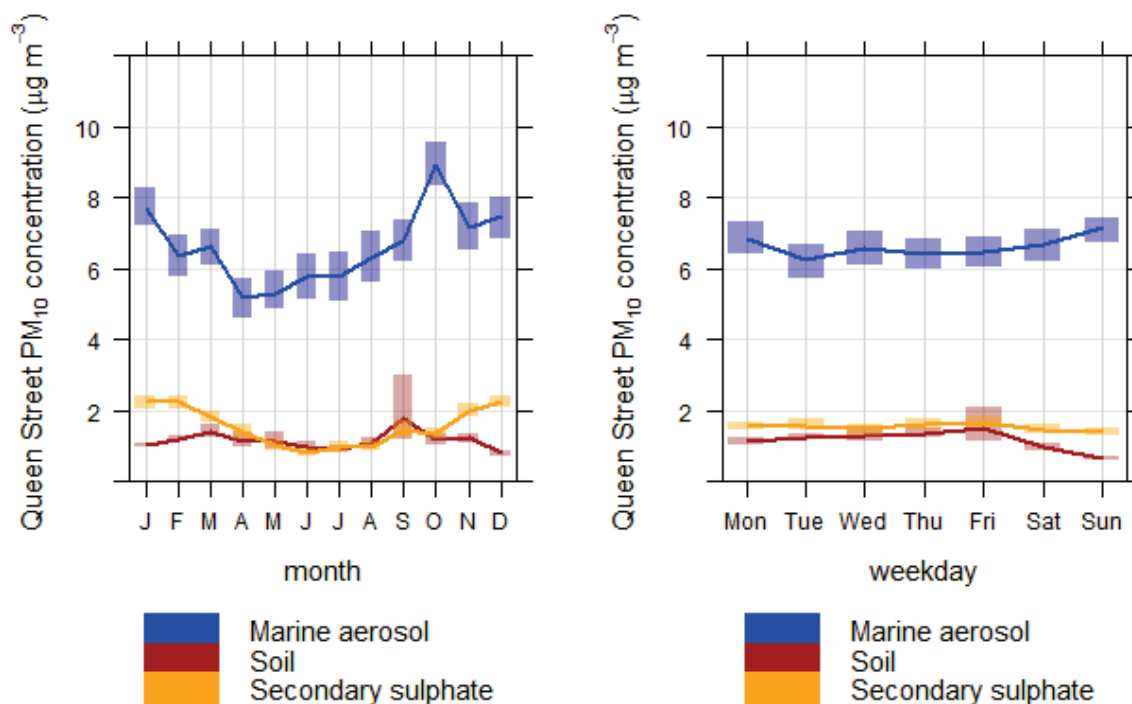


Figure 3.5 Temporal variation in natural source contributions to PM₁₀ at Queen Street, Auckland (2006-2013). Shaded areas represent the 95% confidence intervals in the calculated mean.

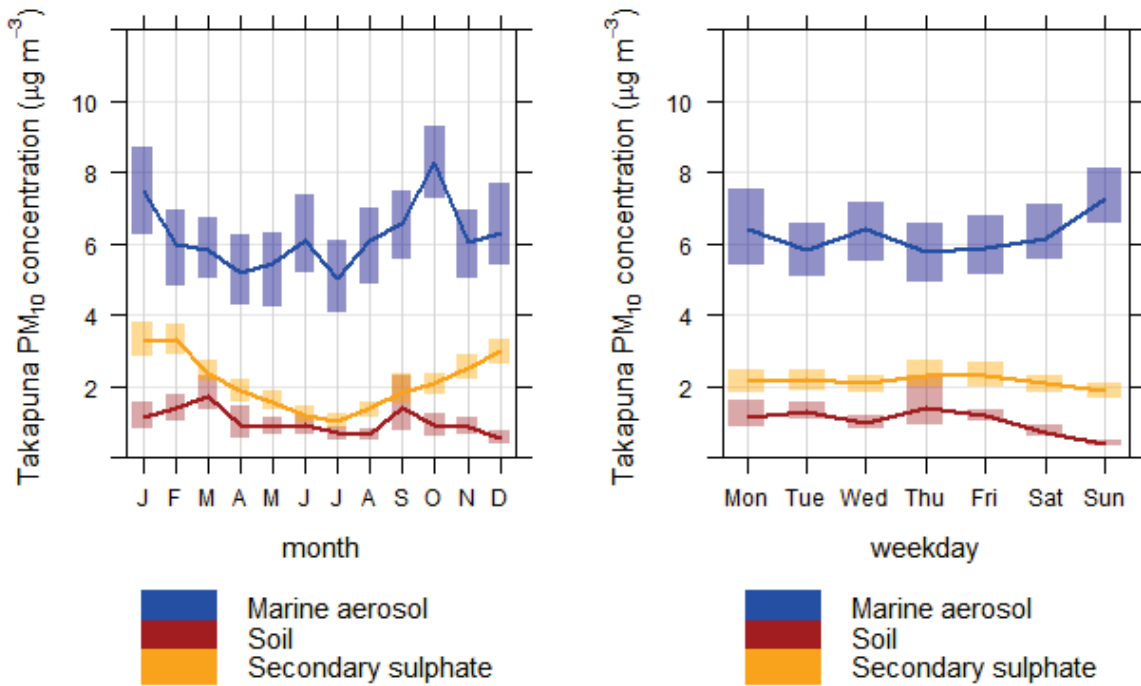


Figure 3.6 Temporal variation in natural source contributions to PM₁₀ at Takapuna, Auckland (2006-2013). Shaded areas represent the 95% confidence intervals in the calculated mean.

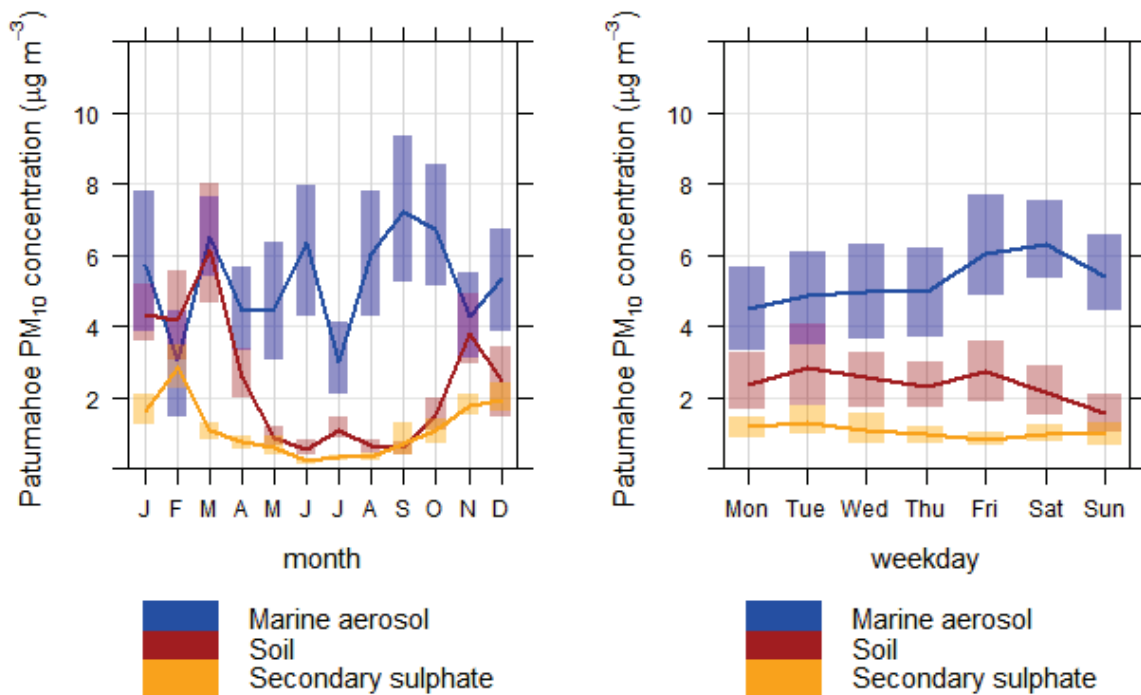


Figure 3.7 Temporal variation in natural source contributions to PM₁₀ at Patumahoe, South Auckland (2010). Shaded areas represent the 95% confidence intervals in the calculated mean.

3.2.1.2 Auckland PM_{2.5}

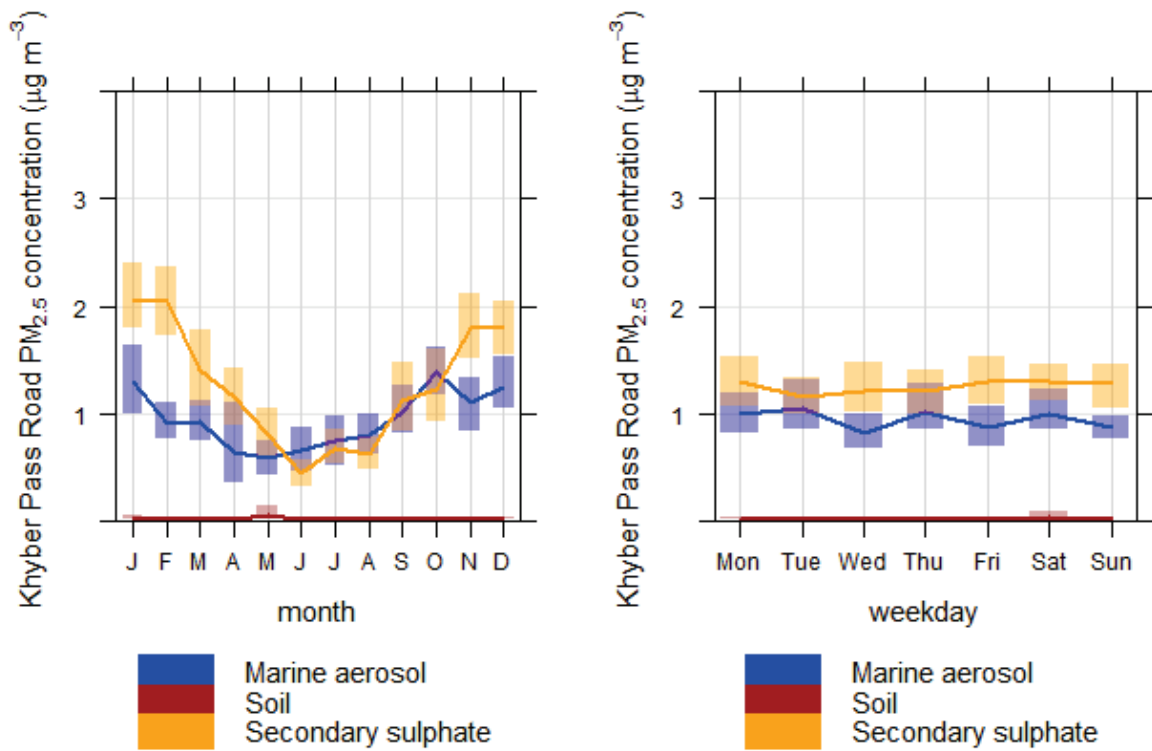


Figure 3.8 Temporal variation in natural source contributions to PM_{2.5} at Khyber Pass Road, Auckland (2006-2013). Shaded areas represent the 95% confidence intervals in the calculated mean.

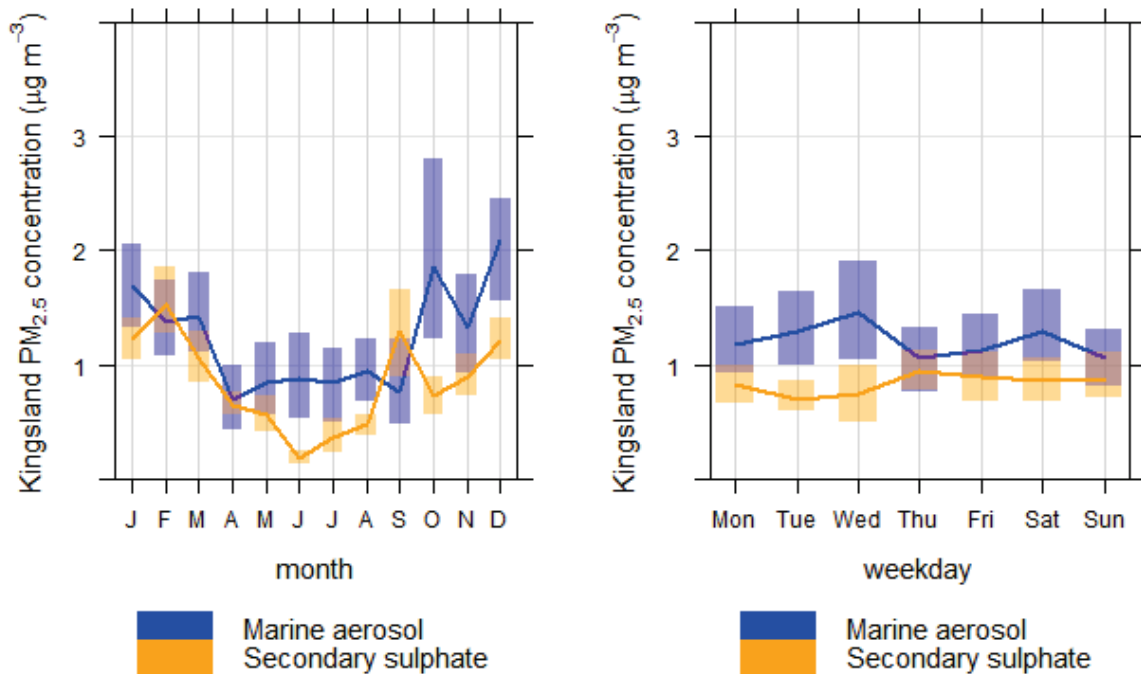


Figure 3.9 Temporal variation in natural source contributions to PM_{2.5} at Kingsland, Auckland (200-2007). Shaded areas represent the 95% confidence intervals in the calculated mean.

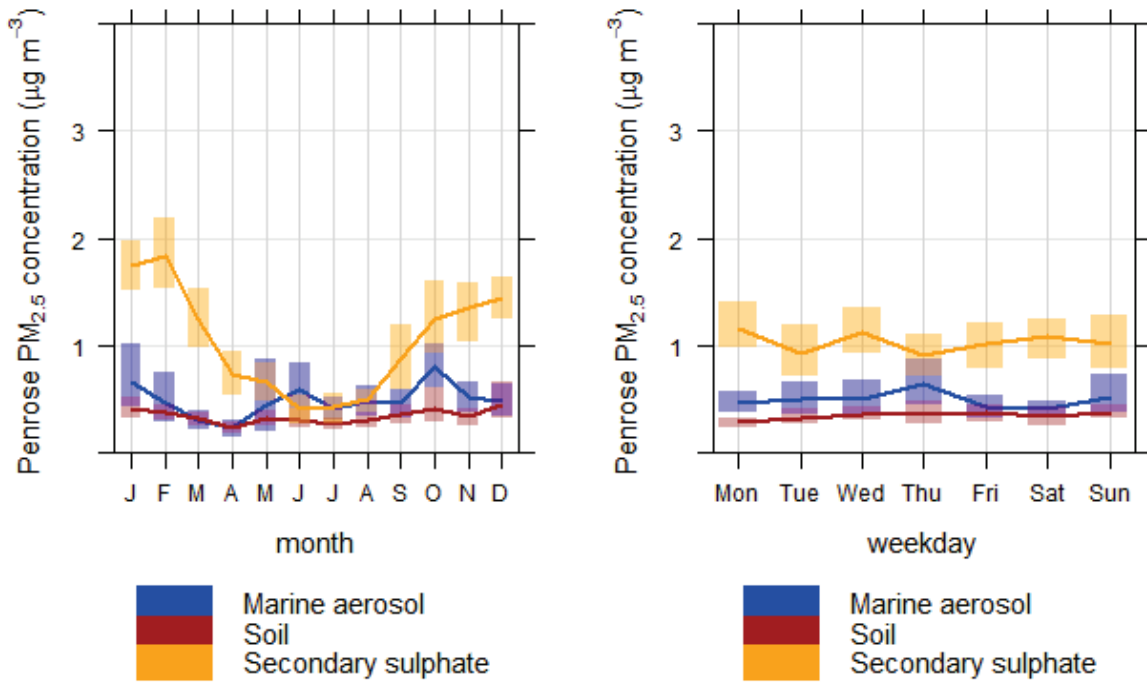


Figure 3.10 Temporal variation in natural source contributions to PM_{2.5} at Penrose, Auckland (2006-2013). Shaded areas represent the 95% confidence intervals in the calculated mean.

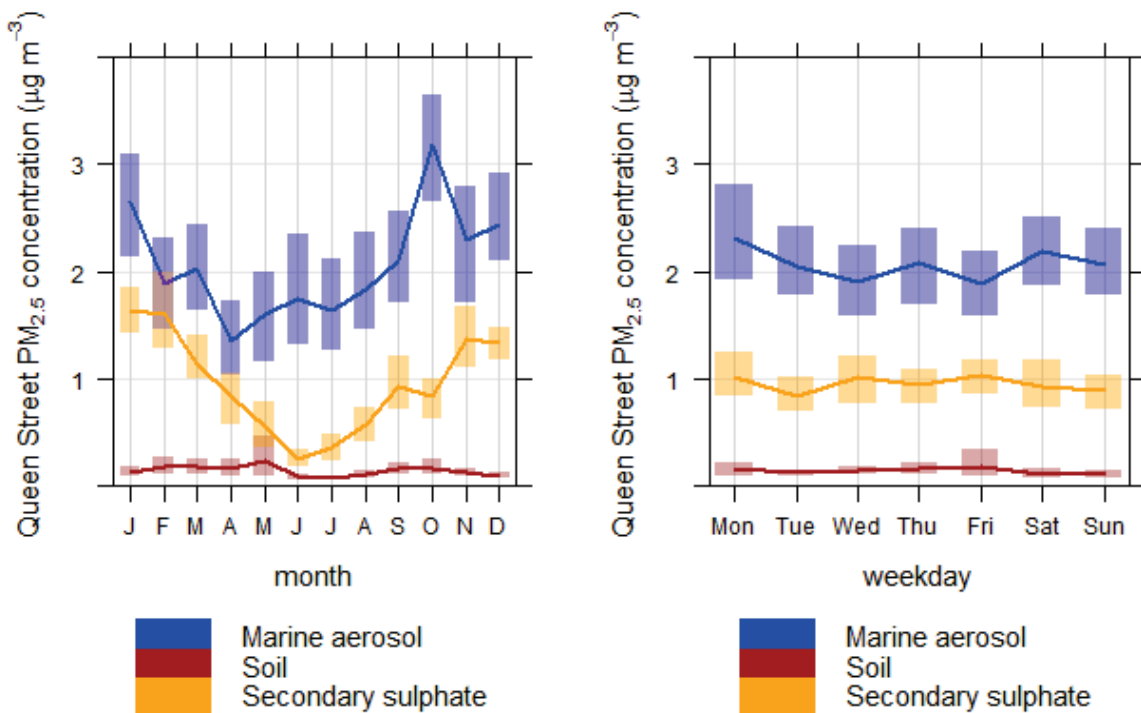


Figure 3.11 Temporal variation in natural source contributions to PM_{2.5} at Queen Street, Auckland (2006-2013). Shaded areas represent the 95% confidence intervals in the calculated mean.

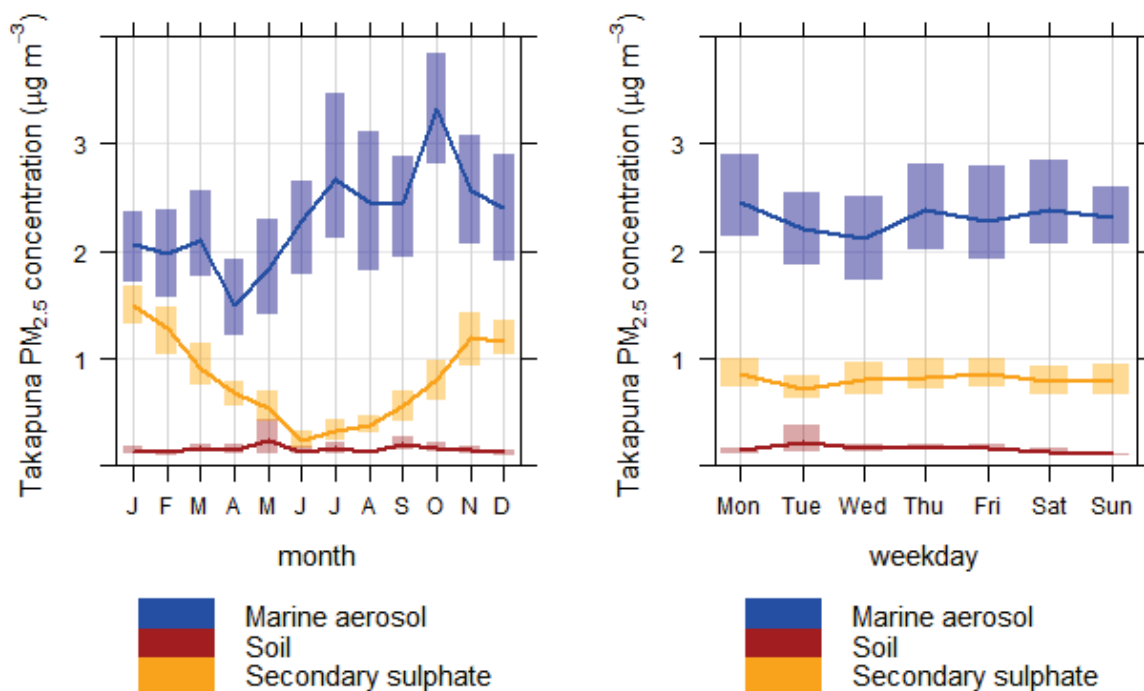


Figure 3.12 Temporal variation in natural source contributions to PM_{2.5} at Takapuna, Auckland (2006-2013). Shaded areas represent the 95% confidence intervals in the calculated mean.

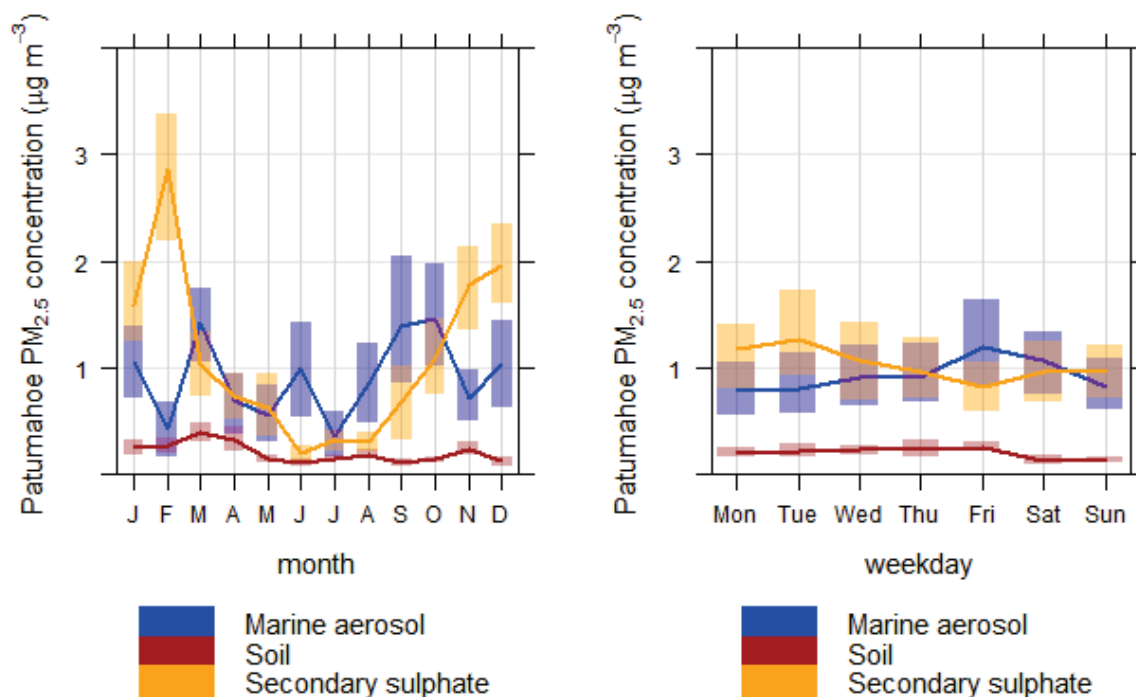


Figure 3.13 Temporal variation in natural source contributions to PM_{2.5} at Patumahoe, South Auckland (2010). Shaded areas represent the 95% confidence intervals in the calculated mean.

3.2.2 Waikato

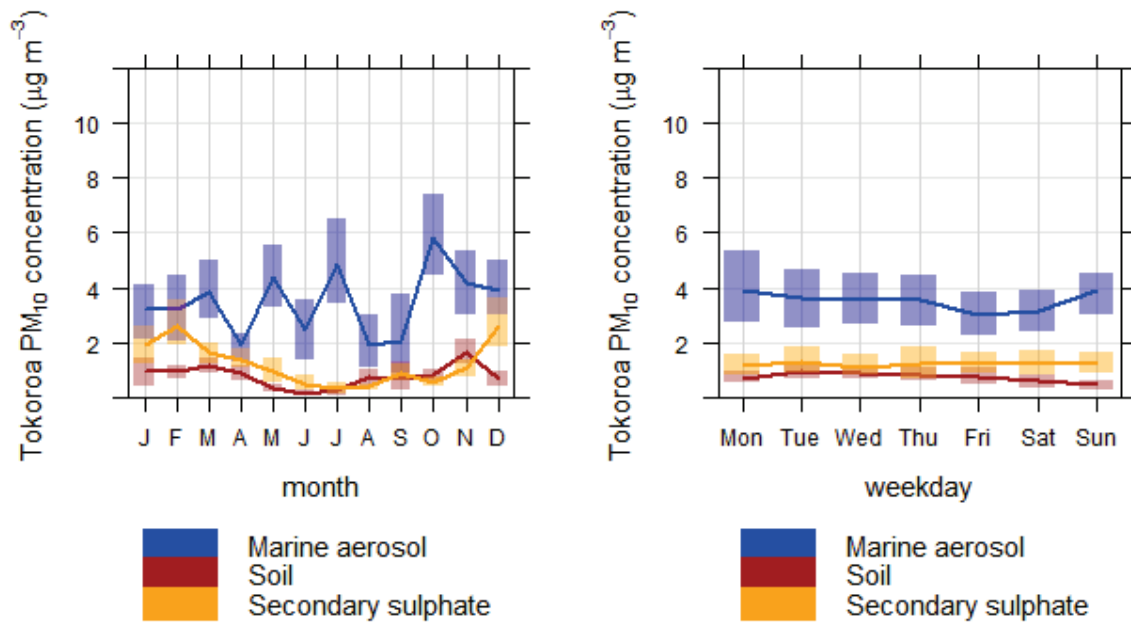


Figure 3.14 Temporal variation in natural source contributions to PM₁₀ at Tokoroa, (2015-2016). Shaded areas represent the 95% confidence intervals in the calculated mean.

3.2.3 Hawkes Bay

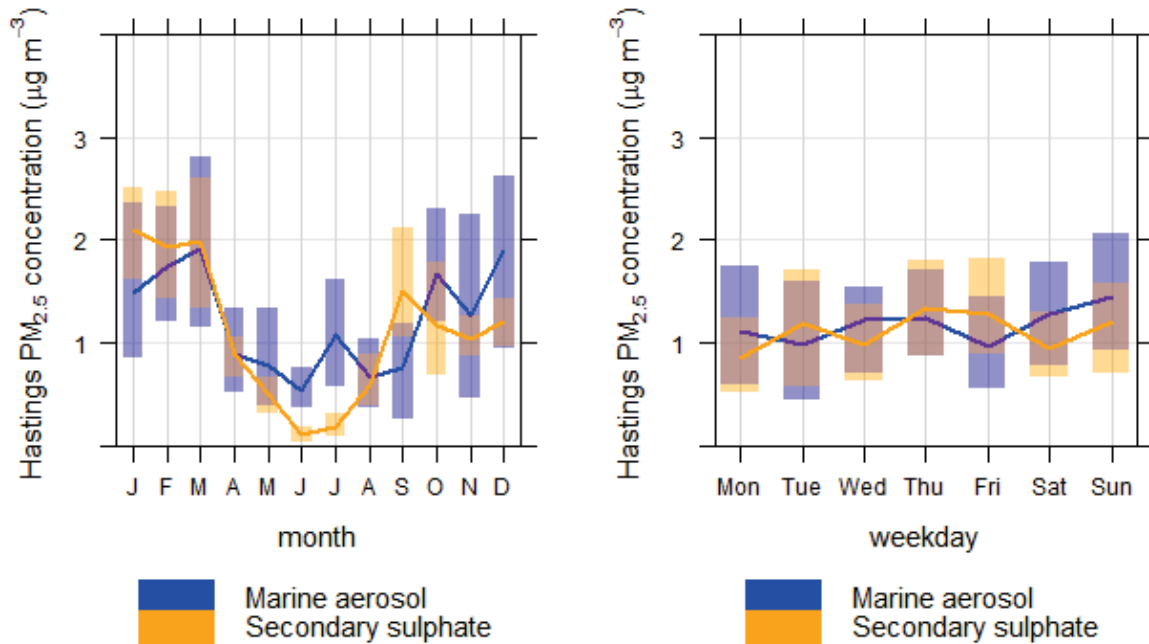


Figure 3.15 Temporal variation in natural source contributions to PM_{2.5} at Hastings, (2006-2007). Shaded areas represent the 95% confidence intervals in the calculated mean.

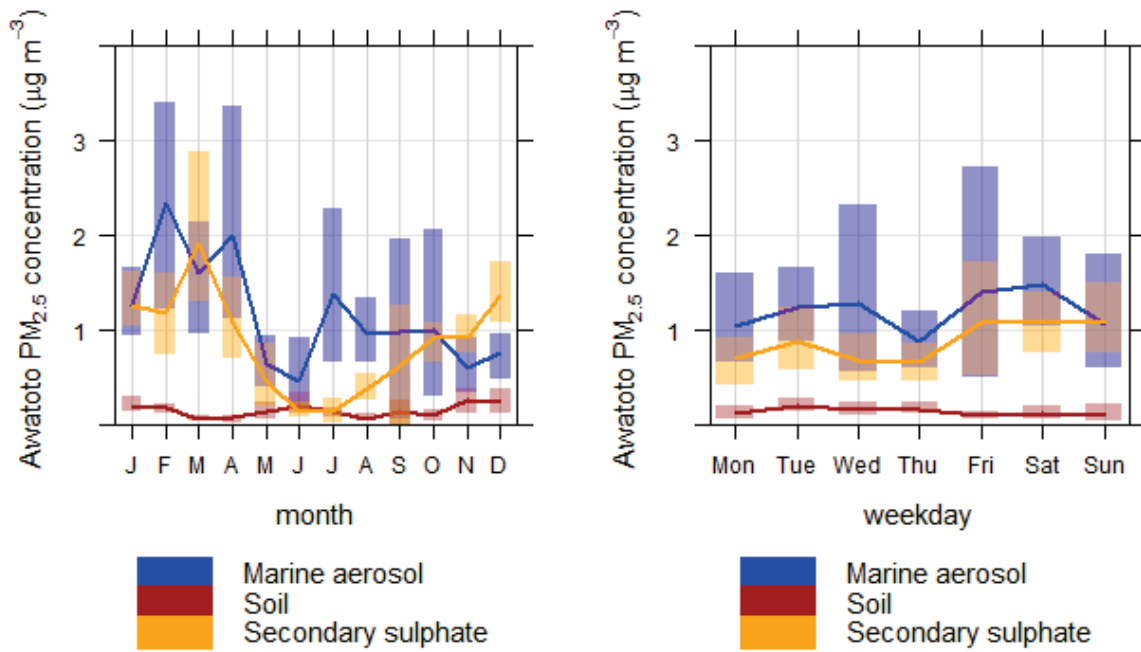


Figure 3.16 Temporal variation in natural source contributions to PM_{2.5} at Awatoto, Hawkes Bay, (2016-2017). Shaded areas represent the 95% confidence intervals in the calculated mean.

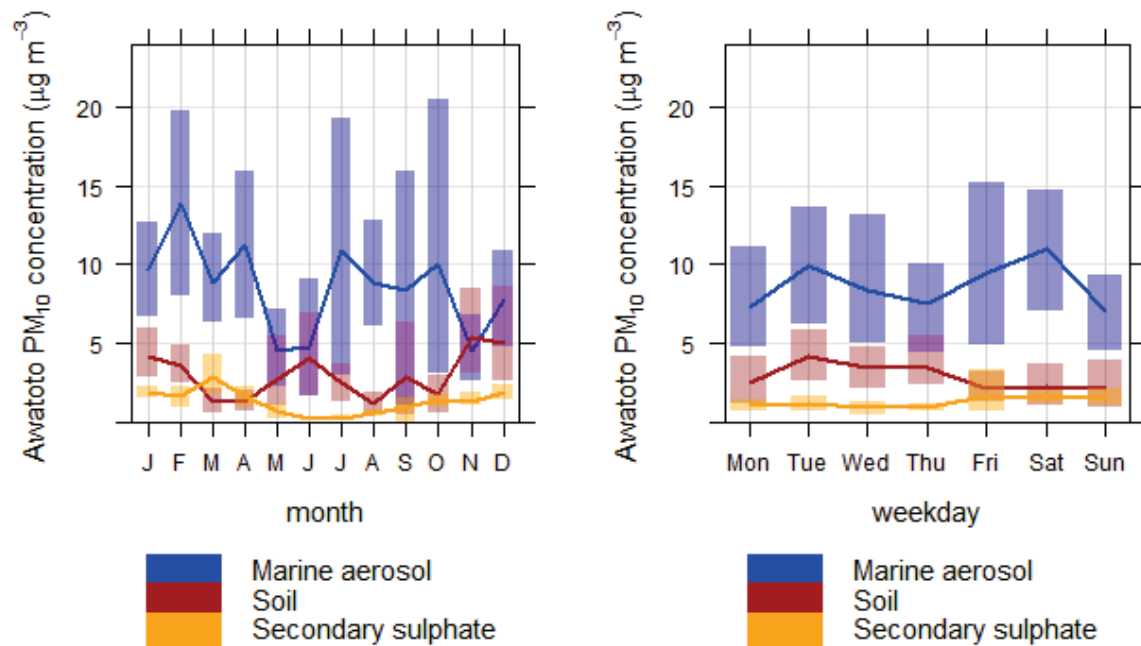


Figure 3.17 Temporal variation in natural source contributions to PM₁₀ at Awatoto, Hawkes Bay, (2016-2017). Shaded areas represent the 95% confidence intervals in the calculated mean.

3.2.4 Wellington

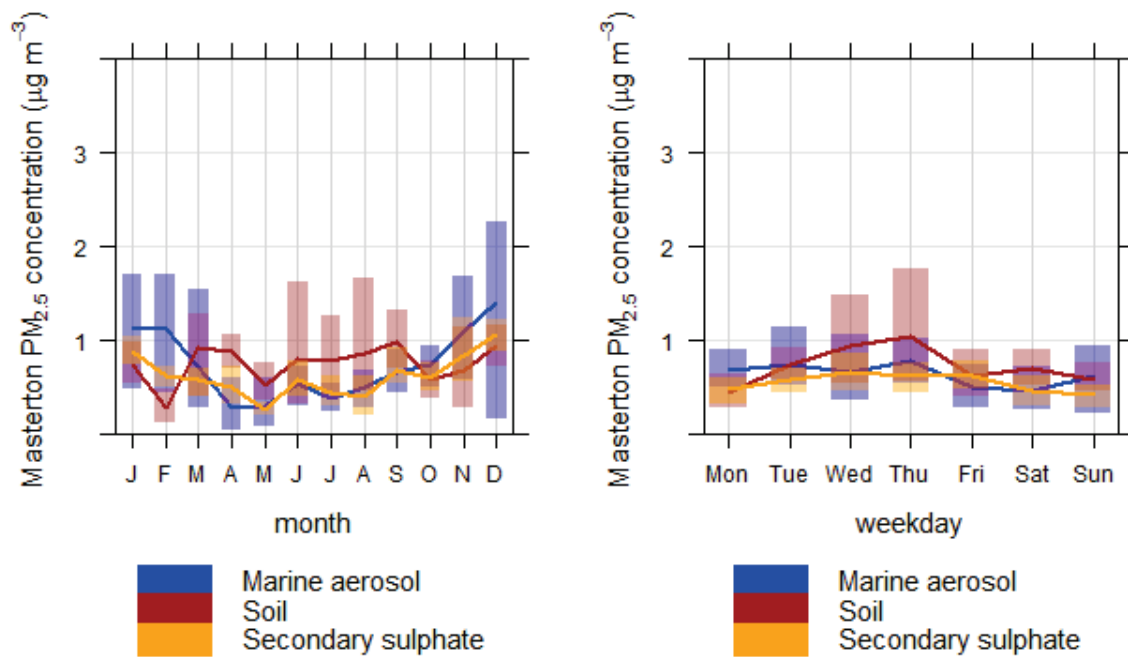


Figure 3.18 Temporal variation in natural source contributions to PM_{2.5} at Masterton (2002-2004). Shaded areas represent the 95% confidence intervals in the calculated mean.

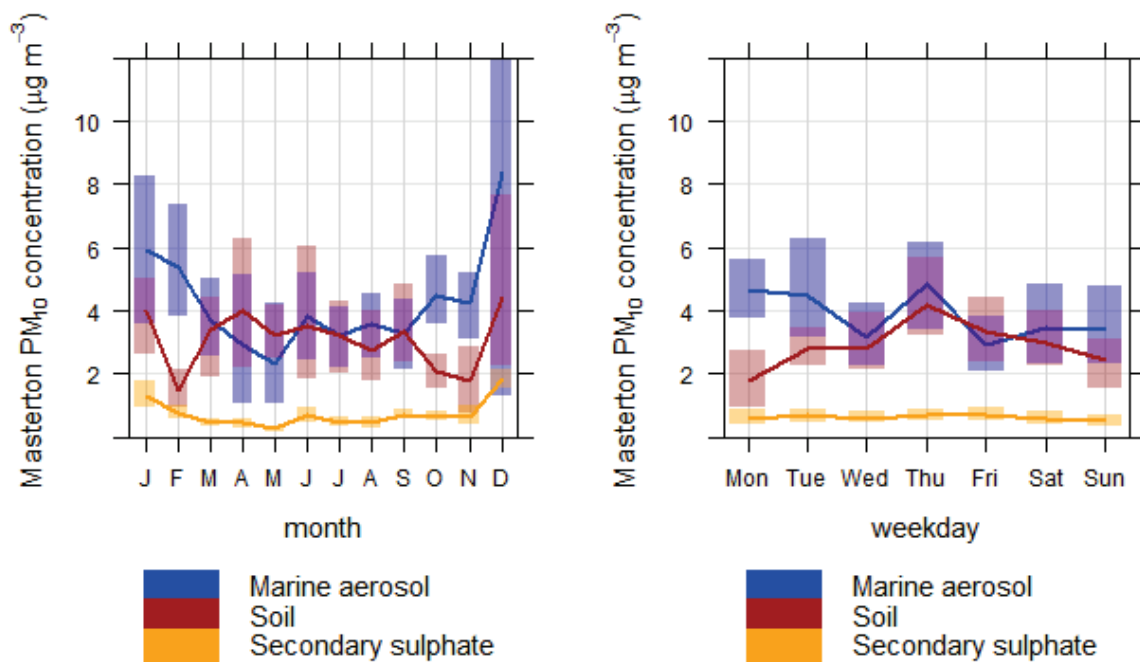


Figure 3.19 Temporal variation in natural source contributions to PM₁₀ at Masterton (2002-2004). Shaded areas represent the 95% confidence intervals in the calculated mean.

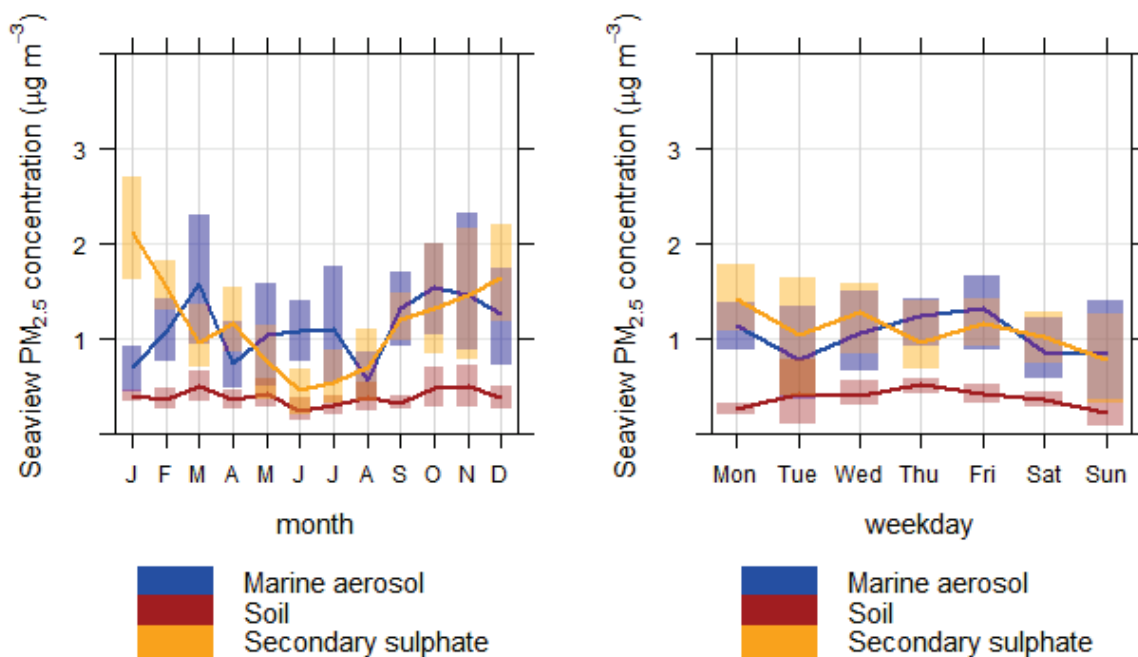


Figure 3.20 Temporal variation in natural source contributions to PM_{2.5} at Seaview, Lower Hutt (2005-2007). Shaded areas represent the 95% confidence intervals in the calculated mean.

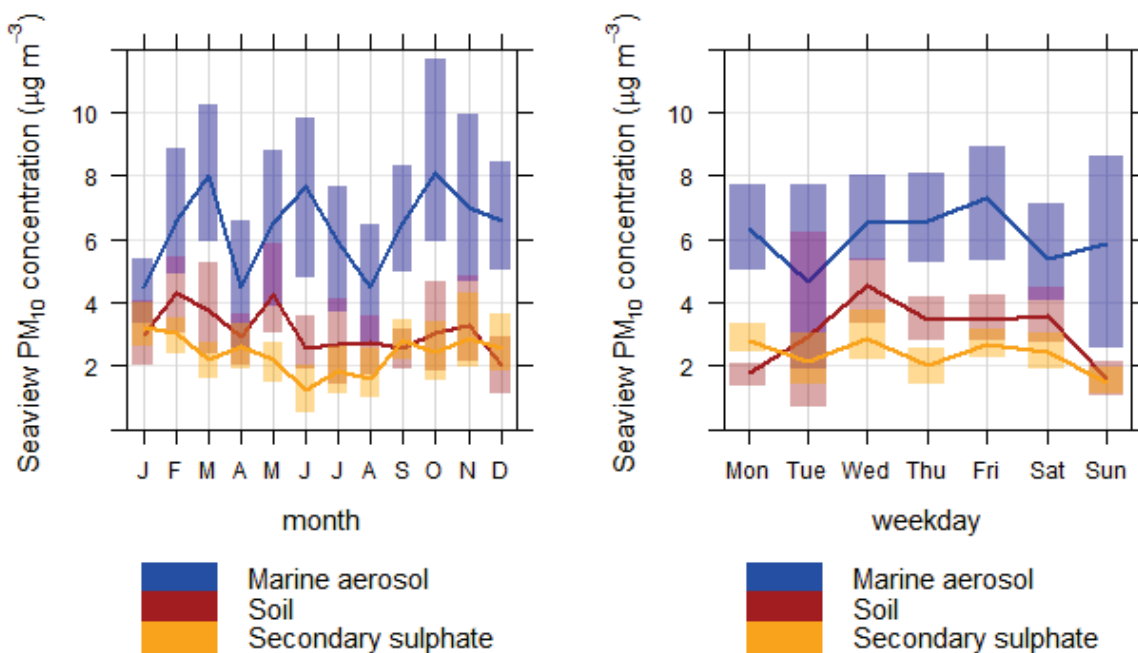


Figure 3.21 Temporal variation in natural source contributions to PM₁₀ at Seaview, Lower Hutt (2005-2007). Shaded areas represent the 95% confidence intervals in the calculated mean.

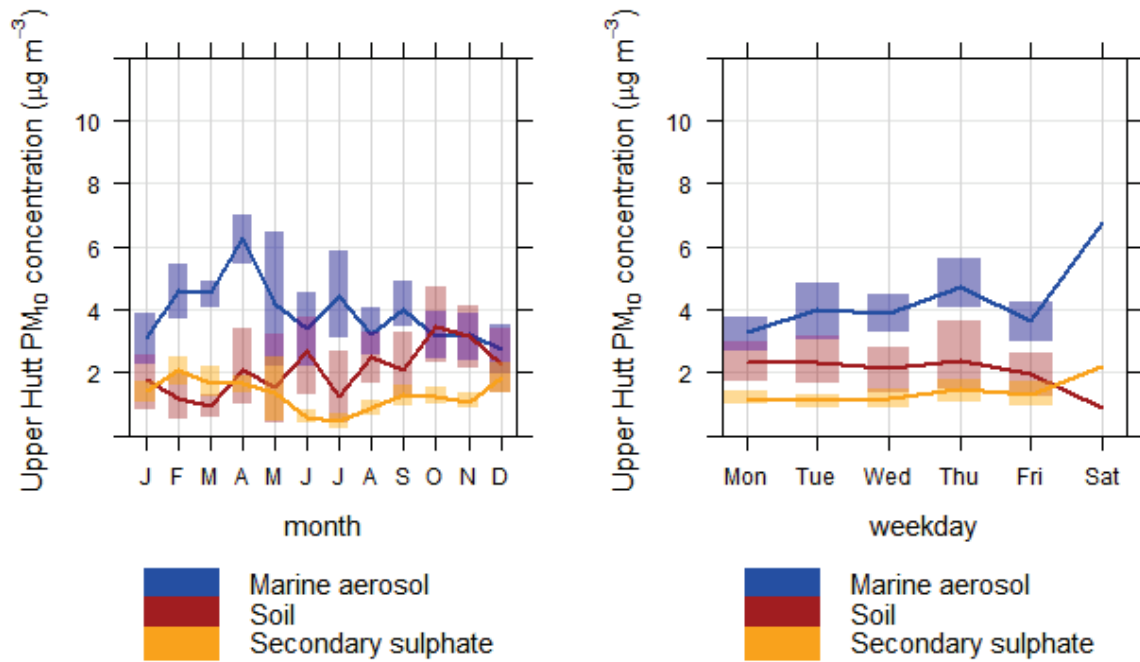


Figure 3.22 Temporal variation in natural source contributions to PM₁₀ at Upper Hutt (2000-2002). Shaded areas represent the 95% confidence intervals in the calculated mean.

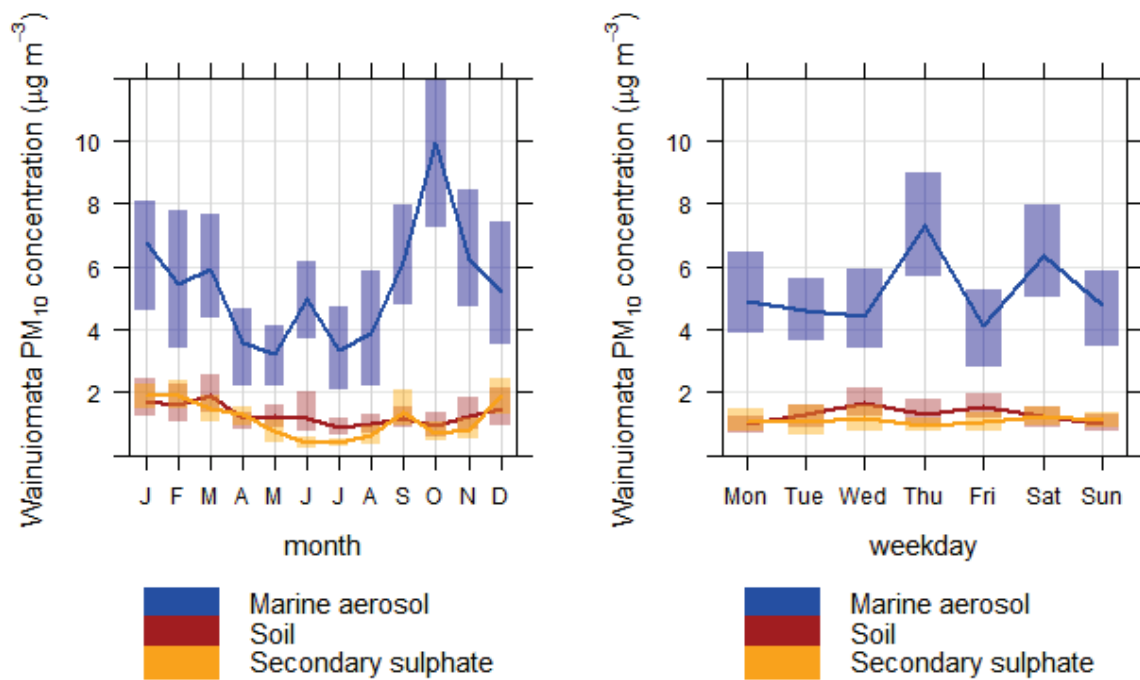


Figure 3.23 Temporal variation in natural source contributions to PM₁₀ at Wainuiomata, Lower Hutt (2000-2002). Shaded areas represent the 95% confidence intervals in the calculated mean.

3.2.5 Marlborough

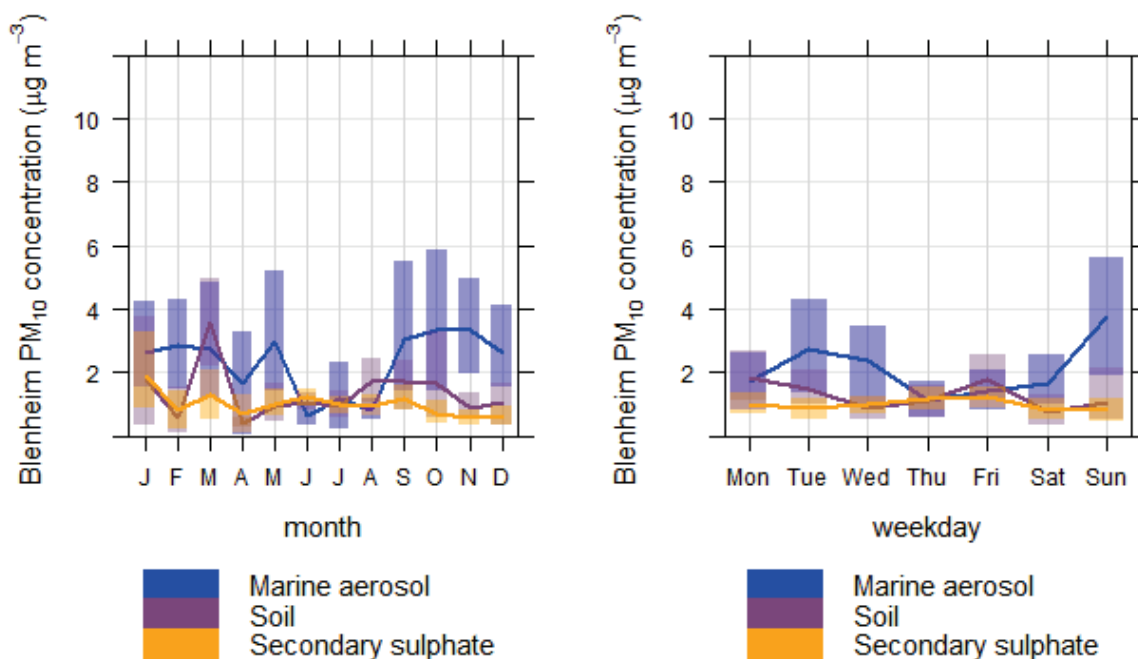


Figure 3.24 Temporal variation in natural source contributions to PM₁₀ at Blenheim (2006-2007). Shaded areas represent the 95% confidence intervals in the calculated mean.

3.2.6 Nelson

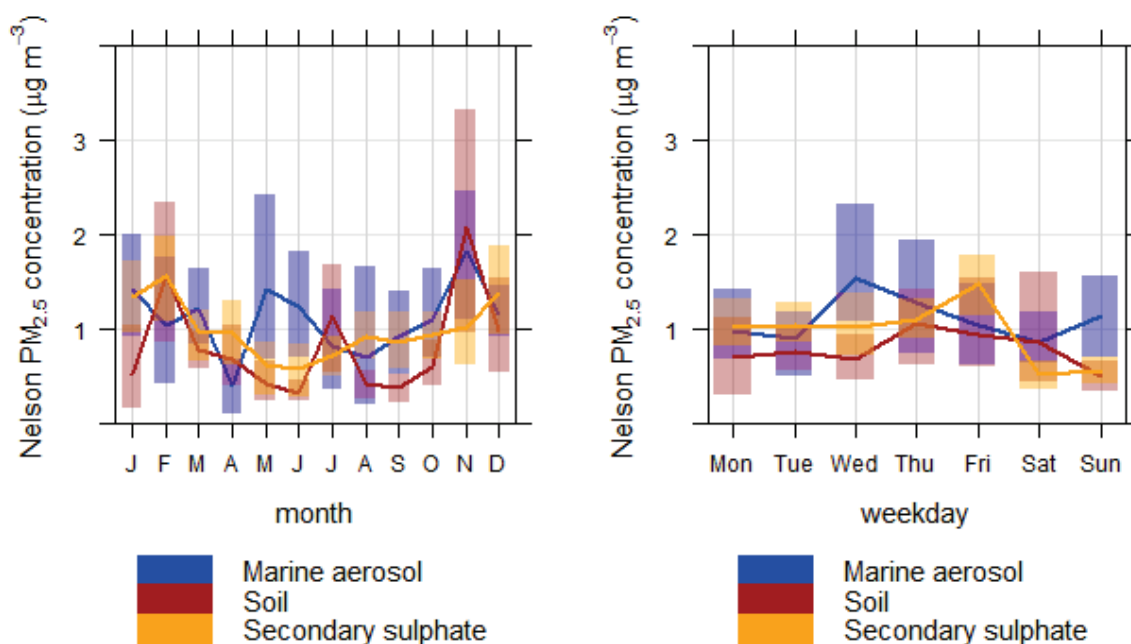


Figure 3.25 Temporal variation in natural source contributions to PM_{2.5} at Nelson (2008-2012). Shaded areas represent the 95% confidence intervals in the calculated mean.

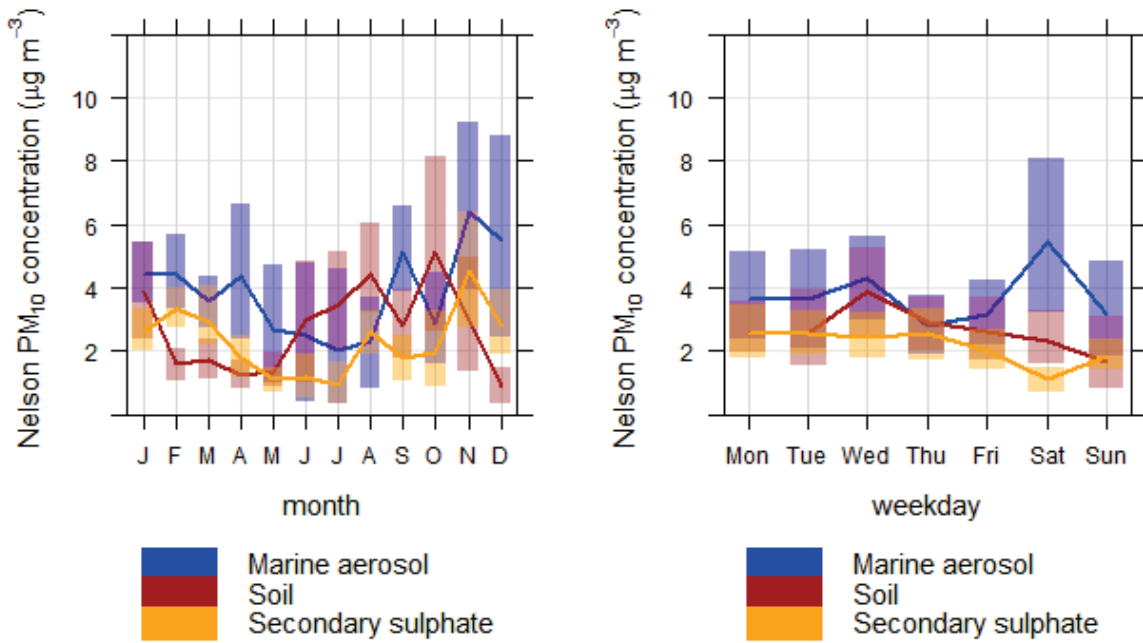


Figure 3.26 Temporal variation in natural source contributions to PM₁₀ at Nelson (2008-2012). Shaded areas represent the 95% confidence intervals in the calculated mean.

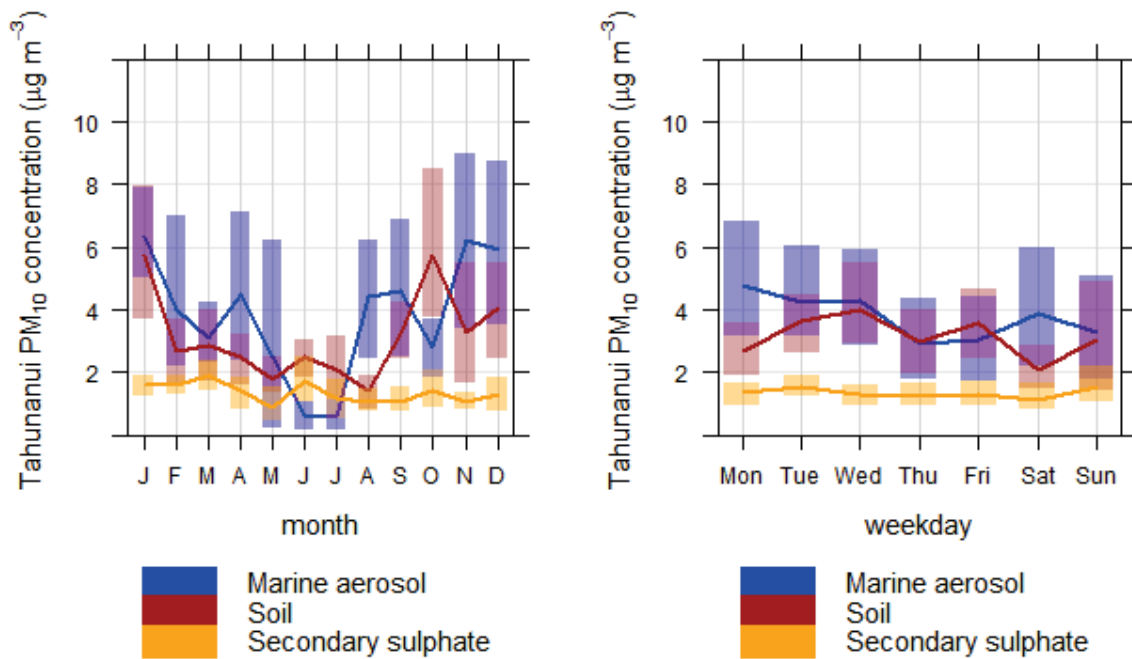


Figure 3.27 Temporal variation in natural source contributions to PM_{2.5} at Tahunanui, Nelson (2008-2009). Shaded areas represent the 95% confidence intervals in the calculated mean.

3.2.7 Tasman

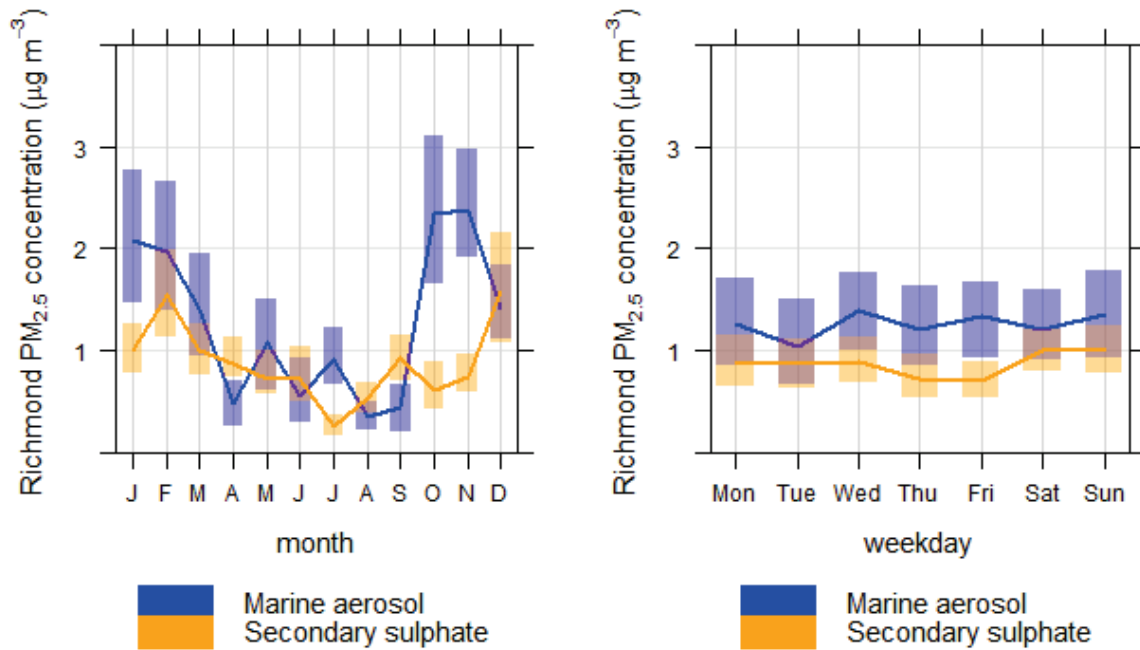


Figure 3.28 Temporal variation in natural source contributions to PM_{2.5} at Richmond (2015-2016). Shaded areas represent the 95% confidence intervals in the calculated mean.

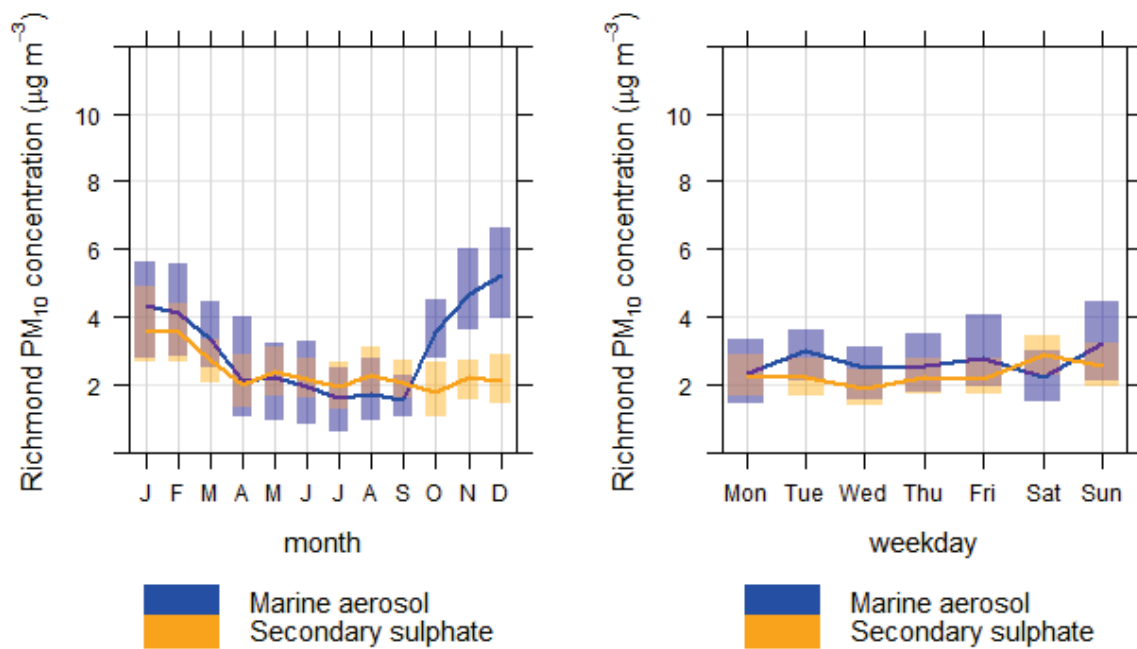


Figure 3.29 Temporal variation in natural source contributions to PM₁₀ at Richmond (2013-2016). Shaded areas represent the 95% confidence intervals in the calculated mean.

3.2.8 Canterbury

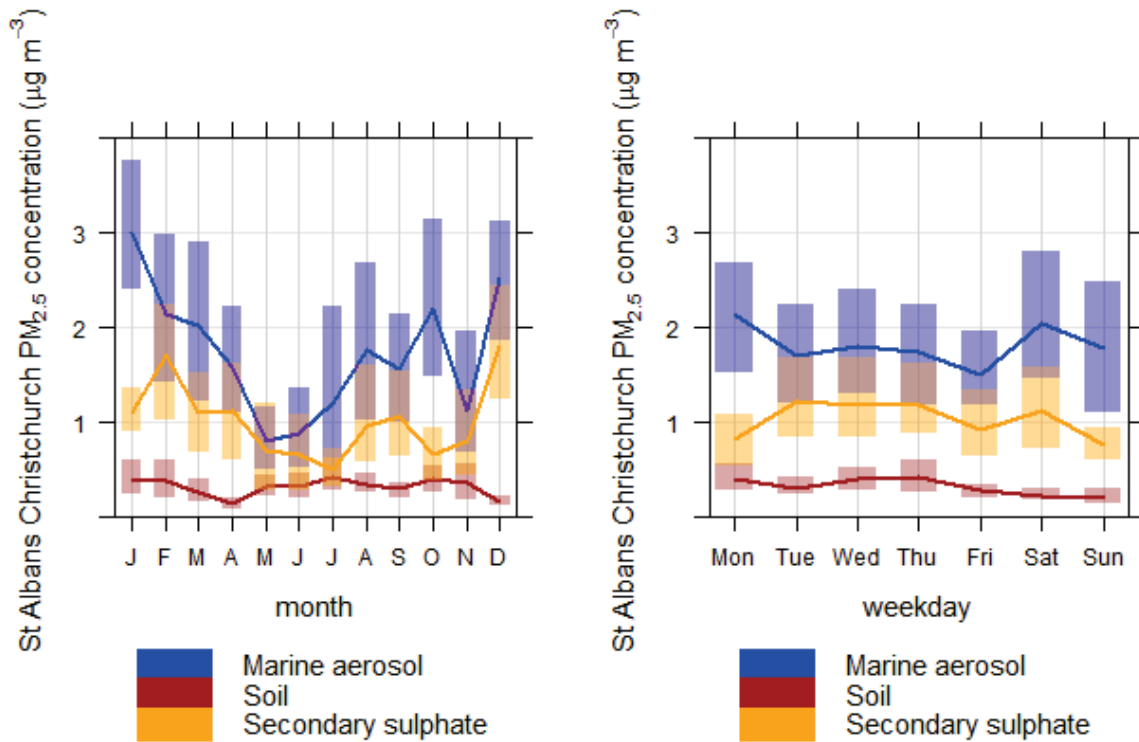


Figure 3.30 Temporal variation in natural source contributions to PM_{2.5} at St Albans, Christchurch (2013-2015). Shaded areas represent the 95% confidence intervals in the calculated mean.

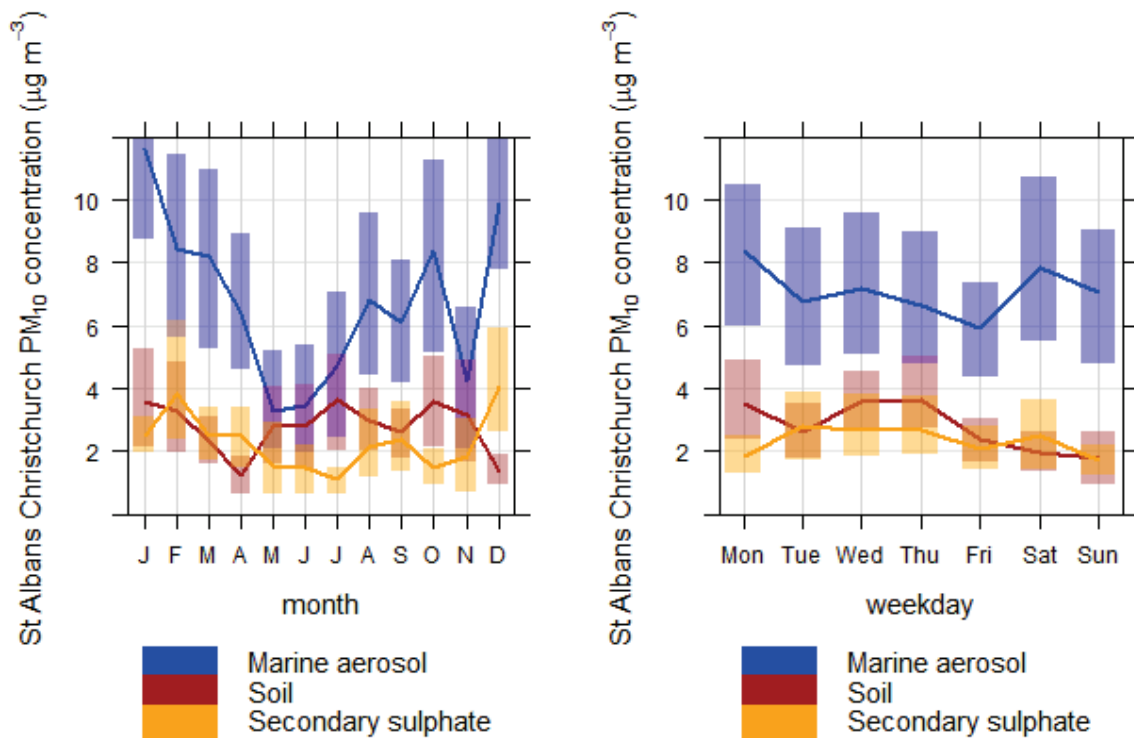


Figure 3.31 Temporal variation in natural source contributions to PM₁₀ at St Albans, Christchurch (2013-2015). Shaded areas represent the 95% confidence intervals in the calculated mean.

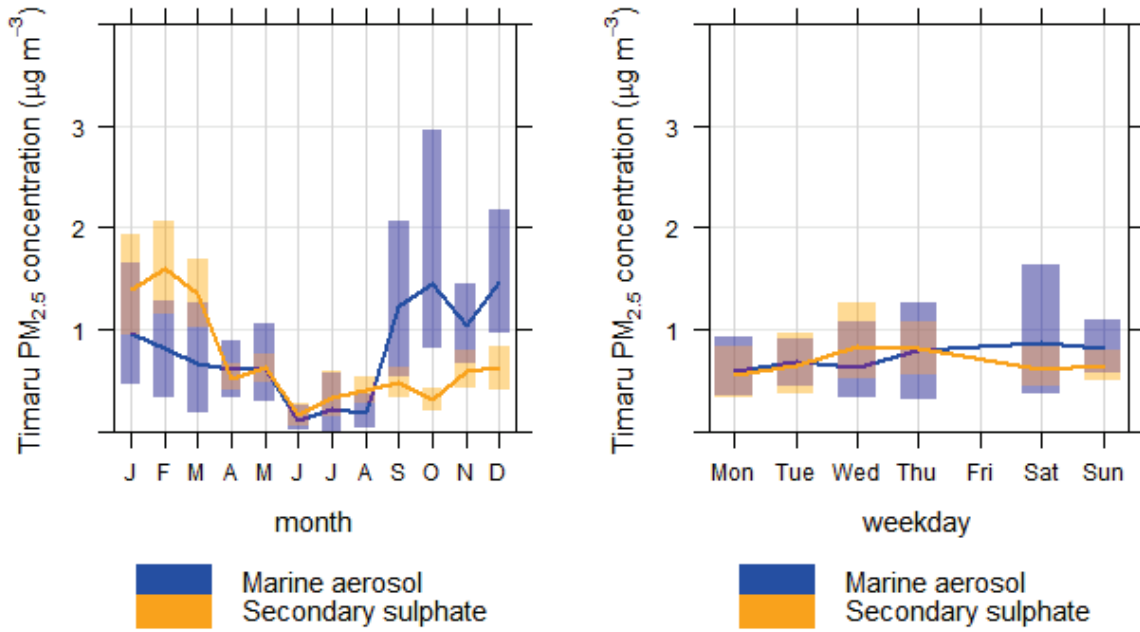


Figure 3.32 Temporal variation in natural source contributions to PM_{2.5} at Timaru (2013-2015). Shaded areas represent the 95% confidence intervals in the calculated mean.

3.2.9 Otago

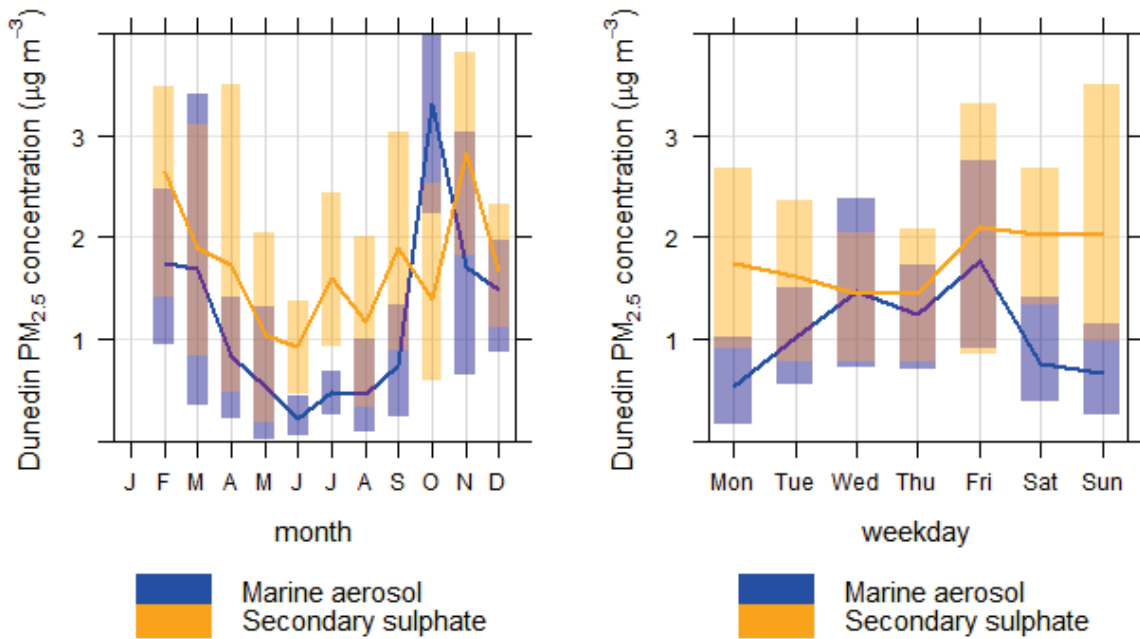


Figure 3.33 Temporal variation in natural source contributions to PM_{2.5} at Dunedin (2010). Shaded areas represent the 95% confidence intervals in the calculated mean.

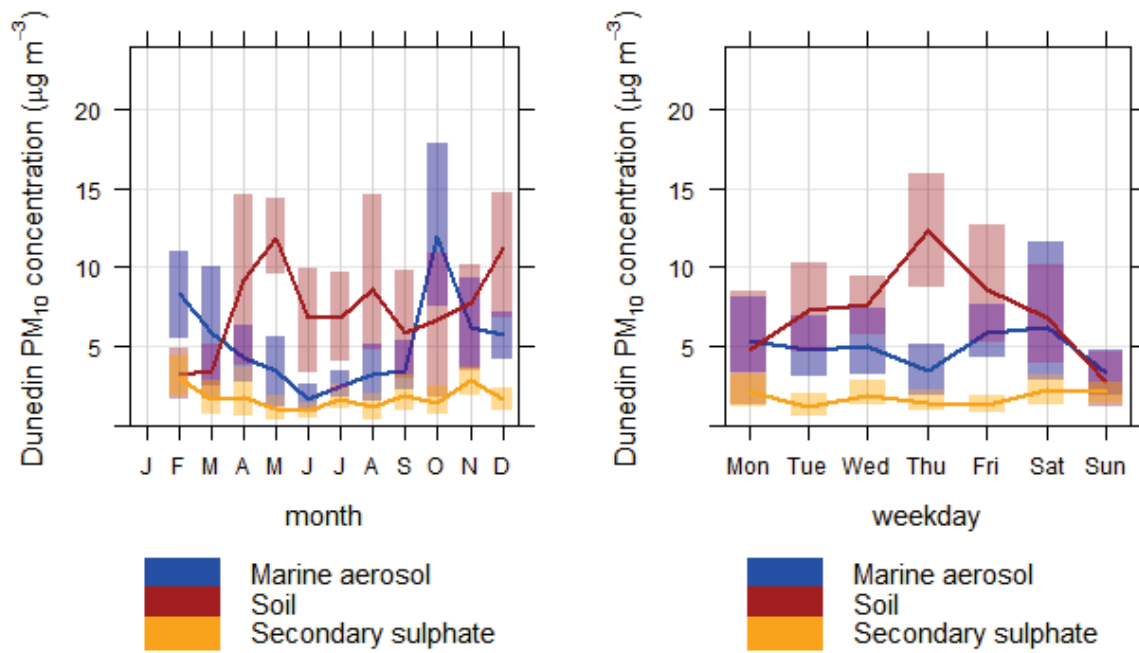


Figure 3.34 Temporal variation in natural source contributions to PM₁₀ at Dunedin (2010). Shaded areas represent the 95% confidence intervals in the calculated mean.

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APPENDICES

A1.0 AIR PARTICULATE MATTER ANALYSIS TECHNIQUES

A1.1 Black Carbon

Black carbon (BC) has been studied extensively, but it is still not clear to what degree it is elemental carbon (EC (or graphitic) C(0)) or high molecular weight refractory weight organic species or a combination of both (Jacobson et al., 2000). Current literature suggests that BC is likely a combination of both, and that for combustion sources such as petrol and diesel fuelled vehicles and Biomass burning (wood burning, coal burning), EC and organic carbon compounds (OC) are the principle aerosol components emitted (Fine et al., 2001, Jacobson et al., 2000, Salma et al., 2004, Watson et al., 2002).

Determination of carbon (soot) on filters was performed by light reflection to provide the BC concentration. The absorption and reflection of visible light on particles in the atmosphere or collected on filters is dependent on the particle concentration, density, refractive index and size. For atmospheric particles, BC is the most highly absorbing component in the visible light spectrum with very much smaller components coming from soils, sulphates and nitrate (Horvath, 1993b, Horvath, 1997). Hence, to the first order it can be assumed that all the absorption on atmospheric filters is due to BC. The main sources of atmospheric BC are anthropogenic combustion sources and include biomass burning, motor vehicles and industrial emissions (Cohen et al., 2000). Cohen and co-workers found that BC is typically 10–40% of the fine mass (PM_{2.5}) fraction in many urban areas of Australia.

When measuring BC by light reflection/transmission, light from a light source is transmitted through a filter onto a photocell. The amount of light absorption is proportional to the amount of black carbon present and provides a value that is a measure of the black carbon on the filter. Conversion of the absorbance value to an atmospheric concentration value of BC requires the use of an empirically derived equation (Cohen et al., 2000):

$$BC (\mu\text{g cm}^{-2}) = (100/2(F\varepsilon)) \ln[R_0/R] \quad \text{A1.1}$$

where:

ε is the mass absorbent coefficient for BC ($\text{m}^2 \text{g}^{-1}$) at a given wavelength;

F is a correction factor to account for other absorbing factors such as sulphates, nitrates, shadowing and filter loading. These effects are generally assumed to be negligible and F is set at 1.00;

R_0, R are the pre- and post-reflection intensity measurements, respectively.

Black carbon was measured at GNS Science using the M43D Digital Smoke Stain Reflectometer. The following equation (from Willy Maenhaut, Institute for Nuclear Sciences, University of Gent Proeftuinstraat 86, B-9000 GENT, Belgium) was used for obtaining BC from reflectance measurements on Nucleopore polycarbonate filters or Pall Life Sciences Teflon filters:

$$BC (\mu\text{g cm}^{-2}) = [1000 \times \text{LOG}(R_{\text{blank}}/R_{\text{sample}}) + 2.39] / 45.8 \quad \text{A1.2}$$

where:

R_{blank} : the average reflectance for a series of blank filters; R_{blank} is close (but not identical) to 100. GNS always use the same blank filter for adjusting to 100.

R_{sample} : the reflectance for a filter sample (normally lower than 100).

With: 2.39 and 45.8 constants derived using a series of 100 Nuclepore polycarbonate filter samples which served as secondary standards; the BC loading (in $\mu\text{g cm}^{-2}$) for these samples had been determined by Prof. Dr. M.O. Andreae (Max Planck Institute of Chemistry, Mainz, Germany) relative to standards that were prepared by collecting burning acetylene soot on filters and determining the mass concentration gravimetrically (Trompeter, 2004).

A1.2 Elemental Concentrations by X-Ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence spectroscopy (XRF) was used to measure elemental concentrations in $\text{PM}_{2.5}$ and $\text{PM}_{10-2.5}$ samples collected on polycarbonate filters at Awatoto. XRF measurements in this study were carried out at the GNS Science XRF facility and the spectrometer used was a PANalytical Epsilon 5 (PANalytical, the Netherlands). The Epsilon 5 is shown in Figure A1.1. XRF is a non-destructive and relatively rapid method for the elemental analysis of particulate matter samples.



Figure A1.1 The PANalytical Epsilon 5 spectrometer.

XRF is based on the measurement of characteristic X-rays produced by the ejection of an inner shell electron from an atom in the sample, creating a vacancy in the inner atomic shell. A higher energy electron then drops into the lower energy orbital and releases a fluorescent X-ray to remove excess energy (Watson et al., 1999). The energy of the released X-ray is characteristic of the emitting element and the area of the fluorescent X-ray peak (intensity of the peak) is proportional to the number of emitting atoms in the sample. From the intensity it is possible to calculate a specific element's concentration by direct comparison with standards.

To eject inner shell electrons from atoms in a sample, XRF spectrometer at GNS Science uses a 100 kV Sc/W X-ray tube. The 100 kV X-rays produced by this tube are able to provide elemental information for elements from Na–U. Unlike ion beam analysis techniques, which are similar to XRF, the PANalytical Epsilon 5 is able to use characteristic K-lines produced by each element for quantification. This is crucial for optimising limits of detection because K-lines have higher intensities and are located in less crowded regions of the X-ray spectrum. The X-rays emitted by the sample are detected using a high performance Ge detector, which further improves the detection limits. Figure A1.2 presents a sample X-ray spectrum.

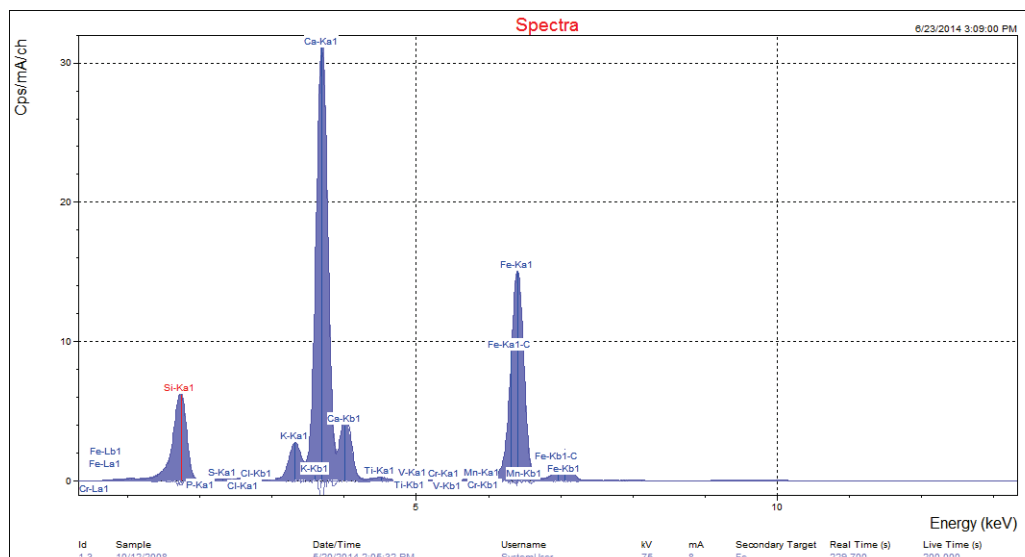


Figure A1.2 Example X-ray spectrum from a PM₁₀ sample.

At GNS Science, calibration standards for each of the elements of interest were analysed prior to the samples being run. Once the calibration standards were analysed, spectral deconvolutions were performed using PANalytical software to correct for line overlaps and ensure that the spectra were accurately fit. Calibration curves for each element of interest were produced and used to determine the elemental concentrations from particulate matter samples. A NIST reference sample (SRM 2783) and multi-elemental reference standards from Crocker National Laboratory (University of California, Davis) were also analysed to ensure that the results obtained were robust and accurate.

A1.3 Elemental Concentrations by Ion Beam Analysis (IBA)

Ion beam analysis (IBA) was used to measure the elemental concentrations of particulate matter on the size-resolved filter samples from the Coles Place monitoring site. IBA is based on the measurement of characteristic X-rays and γ -rays of an element produced by ion-atom interactions using high-energy protons in the 2–5 million electron volt (MeV) range. IBA is a mature and well developed science, with many research groups around the world using IBA in a variety of routine analytical applications, including the analysis of atmospheric aerosols (Maenhaut and Malmqvist, 2001, Trompeter et al., 2005). IBA techniques do not require sample preparation and are fast, non-destructive and sensitive (Cohen, 1999, Maenhaut and Malmqvist, 2001, Trompeter et al., 2005).

IBA measurements for this study were carried out at the New Zealand IBA facility operated by GNS Science. Figure A1.3 shows the PM analysis chamber with its associated X-ray, γ -ray and particle detectors for Proton-Induced X-ray Emission (PIXE), Proton-Induced Gamma-ray

Emission (PIGE), Proton Elastic Scattering Analysis (PESA) and Rutherford Back Scattering (RBS) measurements.

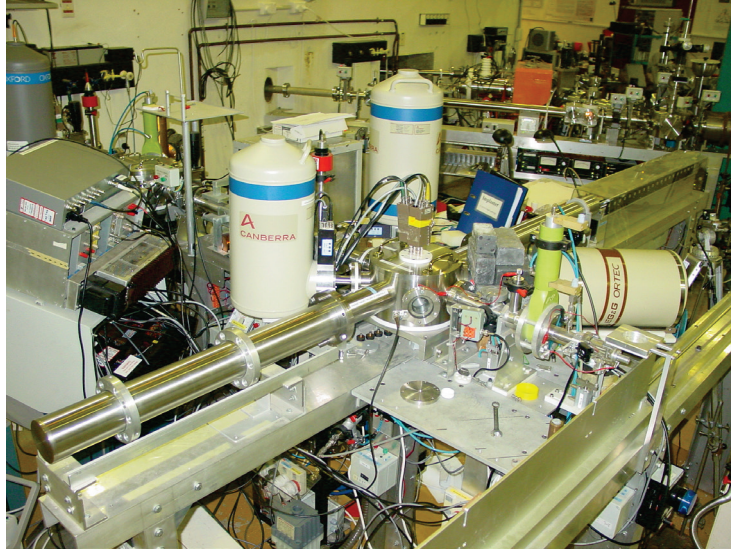


Figure A1.3 Particulate matter analysis chamber with its associated detectors.

The following sections provide a generalised overview of the IBA techniques used for elemental analysis and the analytical setup at GNS Science (Cohen, 1998, Cohen et al., 1996, Trompetter, 2004, Trompetter and Davy, 2005). Figure A1.4 presents a schematic diagram of the typical experimental setup for IBA of air particulate filters at GNS Science.

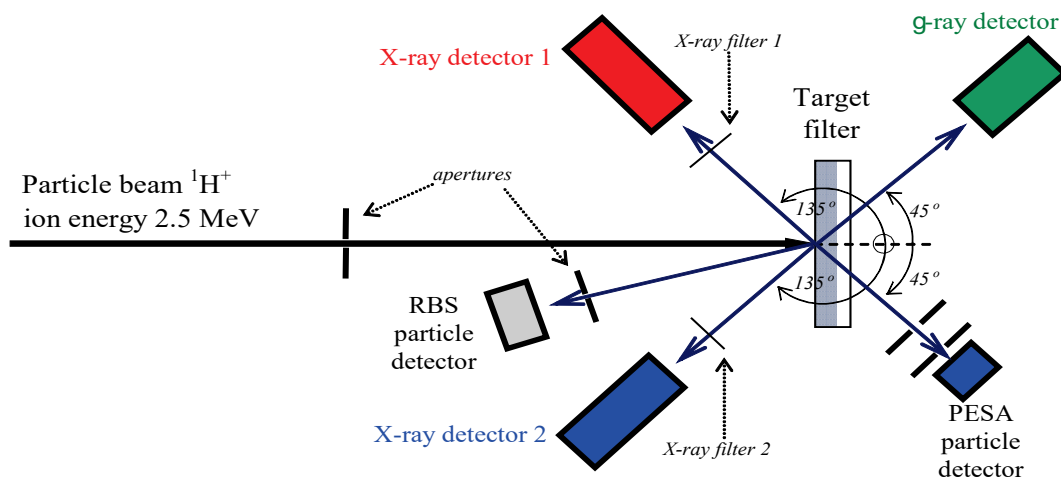


Figure A1.4 Schematic of the typical IBA experimental setup at GNS Science.

A1.3.1 Particle-Induced X-Ray Emission

Particle induced X-ray emission (PIXE), is used to determine elemental concentrations heavier than neon by exposing the filter samples to a proton beam accelerated to 2.5 million volts (MeV) by the GNS 3 MeV van-de-Graaff accelerator. When high energy protons interact with atoms in the sample, characteristic X-rays (from each element) are emitted by ion-electron processes. These X-rays are recorded in an energy spectrum. While all elements heavier than boron emit K X-rays, their production become too few to satisfactorily measure elements heavier than strontium. Elements heavier than strontium are detected via their lower energy L X-rays. The X-rays are detected using a Si(Li) detector and the pulses from the detector are amplified and recorded in a pulse height analyser. In practice, sensitivities are further improved for the lighter

elements by using two X-ray detectors, one for light element X-rays and the other for heavier element X-rays, each with different filtering and collimation. Figure A1.5 shows an example of a PIXE spectrum for airborne particles collected on a filter and analysed at the GNS IBA facility.

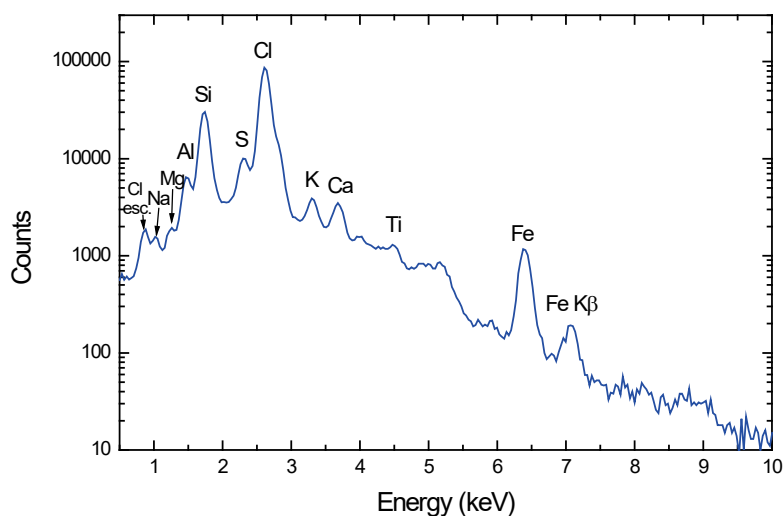


Figure A1.5 Typical PIXE spectrum for an aerosol sample analysed by PIXE.

As the PIXE spectrum consists of many peaks from different elements (and a Bremsstrahlung background), some of them overlapping, the spectrum is analysed with quantitative X-ray analysis software. In the case of this study, Gupix Software was used to perform the deconvolution with high accuracy (Maxwell et al., 1989, Maxwell et al., 1995). The number of pulses (counts) in each peak for a given element is used by the Gupix software to calculate the concentration of that element. The background and neighbouring elements determine the statistical error and the limit of detection. Note, that Gupix provides a specific statistical error and limit of detection (LOD) for each element in any filter, which is essential for source apportionment studies.

Typically 20–25 elements from Mg–Pb are routinely determined above their respective LODs. Sodium (and fluorine) was determined using both PIXE and PIGE (see next section). Specific experimental details, where appropriate, are given in the results and analysis section.

A1.3.2 Particle-Induced Gamma-Ray Emission

Particle Induced Gamma-Ray Emission (PIGE) refers to γ -rays produced when an incident beam of protons interacts with the nuclei of an element in the sample (filter). During the de-excitation process, nuclei emit γ -ray photons of characteristic energies specific to each element. Typical elements measured with γ -ray are:

<i>Element</i>	<i>nuclear reaction</i>	<i>gamma ray energy (keV)</i>
Sodium	$^{23}\text{Na}(p,\alpha\gamma)^{20}\text{Ne}$	440, 1634
Fluorine	$^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$	197, 6129

Gamma rays are higher in energy than X-rays and are detected with a germanium detector. Measurements of a light element such as sodium can be measured more accurately using PIGE because the γ -rays are not attenuated to the same extent in the filter matrix or the detector material, a problem in the measurement of low energy X-rays of sodium. Figure A1.6 shows a typical PIGE spectrum.

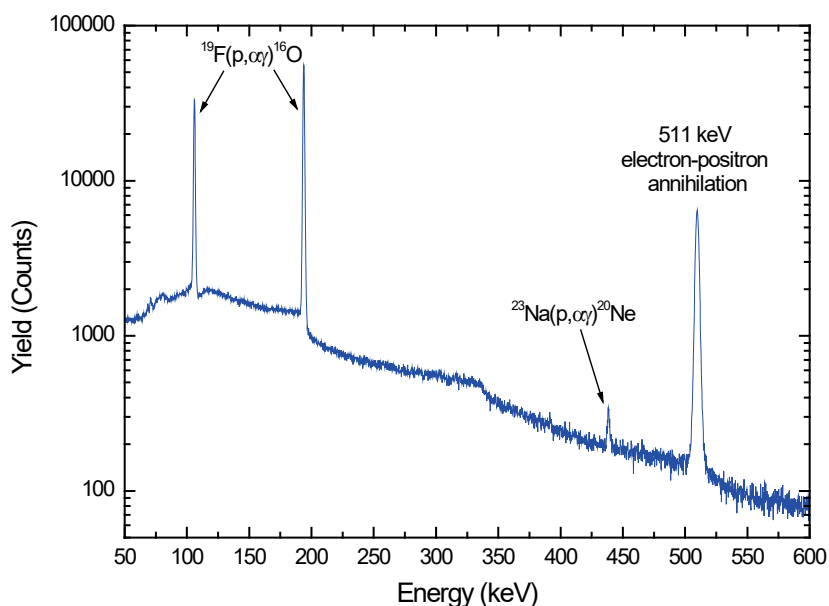


Figure A1.6 Typical PIGE spectrum for an aerosol sample.

A1.4 XRF and IBA Data Reporting

Most filters used to collect particulate matter samples for XRF or IBA analysis are sufficiently thin that the X-rays or ion beam penetrates the entire depth producing a quantitative analysis of elements present. Because of the thin nature of the air particulate matter filters, the concentrations reported from the analyses are therefore in aerial density units (ng cm^{-2}) and the total concentration of each element on the filters is calculated by multiplying with the exposed area of the filter. Typically, the exposed area is approximately 12 cm^2 for the sample deposit on the standard 47mm Teflon or polycarbonate filters used in most studies. For example, to convert from $\text{Cl} (\text{ng cm}^{-2})$ into $\text{Cl} (\text{ng m}^{-3})$ for filter samples, the equation is:

$$\text{Cl} (\text{ng m}^{-3}) = 11.95 (\text{cm}^2) \times \text{Cl} (\text{ng cm}^{-2}) / \text{Vol}(\text{m}^3) \quad \text{A1.3}$$

A1.4.1 Limits of detection and uncertainty reporting for elements

The exact limits of detection and associated analytical uncertainties for the concentration of each element depends on a number of factors such as:

- the method of detection;
- filter composition;
- sample composition;
- the detector resolution;
- spectral interference from other elements.

There are differences on how the analytical limits of detection (LOD) and uncertainties calculated between the XRF and IBA analytical methodologies due the nature of the measurements and the manner in which the sample spectra are deconvoluted by the associated software. Also, where an individual elemental concentration is reported as zero (0) means the measurement value (as derived from the spectral deconvolution) was zero but does not necessarily mean the element was not present but below the method limit of detection and indeterminate. Where this is the case then the corresponding uncertainty value (\pm) can be regarded as $5/6 \text{ LOD}$ (Kara et al., 2015):

The following sections give an overview of this process for XRF and IBA respectively.

A1.4.1.1 Limits of detection and uncertainty reporting for elements determined by XRF

For XRF elemental data, the detection limits are defined in terms of the uncertainty in the blank (1σ) of 10 repeat measurements (USEPA Compendium Method IO-3.3). This ignores the effect of other elements which generally is small due to the use of multiple excitation frequencies except for the light elements (potassium and lower) where overlapping spectral lines will increase the detection limit.

Uncertainties for the XRF elemental data were calculated using the following equations (Kara et al., 2015):

$\sigma_{ij} = x_{ij} + 2/3(DL_j)$ for samples below limit of detection;

$\sigma_{ij} = 0.2x_{ij} + 2/3(DL_j)$; $DL_j < x_{ij} < 3DL_j$ and $\sigma_{ij} = 0.1x_{ij} + 2/3(DL_j)$; $x_{ij} > 3DL_j$: for detected values

where x_{ij} is the determined concentration for species j in the i th sample, and DL_j is the detection limit for species j .

A1.4.1.2 Limits of detection and uncertainty reporting for elements determined by IBA

For IBA, to determine the concentration of each element the background is subtracted and peak areas fitted and calculated. The background occurs through energy loss, scattering and interactions of the ion beam as it passes through the filter material or from γ -rays produced in the target and scattered in the detector system (Cohen, 1999). The peaks of elements in spectra that have interferences or backgrounds from other elements present in the air particulate matter, or filter matrix itself, will have higher limits of detection. The IBA was performed using a 3MeV accelerator proton beam with standards (SrF₂, NaCl, Cr, Ni, SiO, KCl, Al) run before and after each analytical cycle. Spectral X-ray peak deconvolution was performed using Gupix software (Maxwell et al., 1989, 1995). The number of pulses (counts) in each peak for a given element is used by the Gupix software to calculate the concentration of that element. The background and neighbouring elements determine the statistical error and the limit of detection. Note that Gupix provides a specific statistical error (uncertainty) and limit of detection (LOD) for each element in each PM sample. The statistical uncertainty is calculated from the X-ray peak fitting process (called the fit error) and is related to the square root of the peak area. The limit of detection for an element in each sample spectra is defined as three times the error (3σ) obtained for the background and overlap (but not the elements own area) in a 1 full-width-half-maximum region centred about the principal X-ray peak of the element. The summary statistics provided for elemental concentrations in each dataset are therefore averages of the individual uncertainty and LOD values.

Choice of filter material is an important consideration with respect to elements of interest as is avoiding sources of contamination. The GNS IBA laboratory routinely runs filter blanks to correct for filter derived analytical artefacts as part of their QA/QC procedures. Figure A1.7 shows the LODs typically achieved by PIXE for each element at the GNS IBA facility. All IBA elemental concentrations determined in this work were accompanied by their respective LODs. The use of elemental LODs is important in receptor modeling applications.

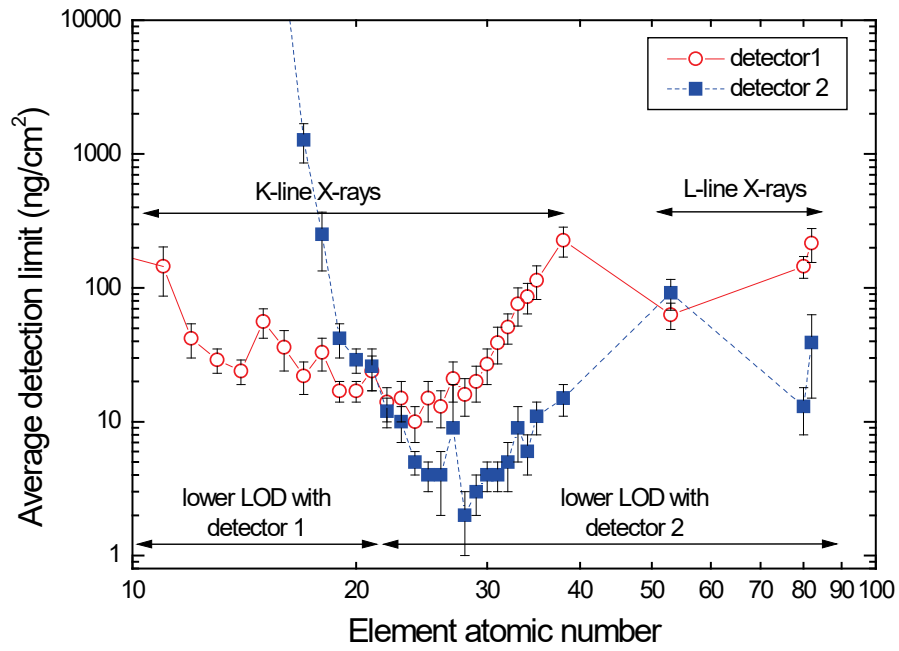


Figure A1.7 Elemental limits of detection for PIXE routinely achieved as the GNS IBA facility for air filters.

A2.0 SITE SUMMARY AND METADATA

Table A2.1 New Zealand Particulate Matter elemental speciation (including heavy metals) and Black Carbon monitoring sites.

Location	Sites	Time period	Frequency	Size fraction	Analytical method	Location Lat; Long	Quality comment
Northland	Whangarei	2004-2012	1 day-in-6	PM10	XRF	-35.7252; 174.3177	Screening/trend
Wellington Region	Masterton	2002-2004	1 day-in-3,	PM2.5, PM10-2.5	IBA	-40.9523; 175.6465	AQM
	Masterton (2 sites)	Winter 2010	Hourly	PM2.5, PM10-2.5	IBA	-40.9593; 175.6531	Research
	Upper Hutt	2000-2002	Variable	PM2.5, PM10-2.5	IBA	-41.1308; 175.0426	Research
	Wainuiomata	2006-2008, 2011-onwards	1 day-in-3	PM2.5, PM10-2.5	IBA	-41.2681; 174.9534	AQM
	Seaview	2002-2004, 2005-2007	1 day-in-3	PM2.5, PM10-2.5	IBA	-41.2405; 174.9140	AQM
	Wairarapa (Masterton, Carterton, Featherston)	Winter 2009	Daily	PM2.5, PM10-2.5	IBA		Screening
	Mt Victoria Tunnel	Summer 2009		PM2.5, PM10-2.5	IBA	-41.3035; 174.7892	Research
	Baring Head	1996-1998		PM2.5, PM10-2.5	IBA	-41.4082; 174.8714	Research
	Raumati	Winter 2010	12-hourly	PM2.5, PM10-2.5	IBA	-40.9321; 174.9799	AQM
Auckland Region	Kingsland	2004-2007	1 day-in-3	PM2.5, PM10	IBA	-36.8732; 174.7471	AQM
	Takapuna	2006-onwards	1 day-in-3	PM2.5, PM10	IBA	-36.7803; 174.7489	AQM
	Takapuna (3 sites)	Winter 2012	Hourly	PM2.5, PM10-2.5	IBA	-36.7803; 174.7489	AQM
	Queen Street	2006-onwards	1 day-in-3	PM2.5	IBA	-36.8476; 174.7655	AQM
	Queen Street	2006-onwards	Daily	PM10	IBA	-36.8476; 174.7655	AQM
	Penrose	2006-onwards	1 day-in-3	PM2.5, PM10	IBA	-36.9045; 174.8156	AQM
	Khyber Pass	2006-onwards	1 day-in-3	PM2.5, PM10	IBA	-36.8662; 174.7705	AQM
	Henderson	2006-onwards	1 day-in-3	PM10	IBA, XRF	-36.8681; 174.6284	AQM
	Patumahoe	2010	Daily	PM2.5, PM10-2.5	IBA	-37.2046; 174.8639	AQM
		Johnstone Hills tunnel	June 2010	3-hourly	PM2.5, PM10-2.5	IBA	-36.5353; 174.6800
Nelson	Tahunanui	2008-2009	1 day-in-3	PM10	IBA	-41.2949; 173.2431	AQM
	Nelson City	2006-2012	1 day-in-6,	PM2.5, PM10	IBA	-41.1642; 173.1624	AQM
	Nelson City (3 sites)	Winter 2011	Hourly	PM2.5, PM10-2.5	IBA		Research
Marlborough	Blenheim	2007	1 day-in-3	PM2.5, PM10-2.5	IBA	-41.5268; 173.9561	AQM
Otago	Dunedin	2010	1 day-in-3	PM2.5, PM10-2.5	IBA	-45.8689; 170.5177	AQM
	Alexandra (3 sites)	Winter 2011	Hourly	PM2.5, PM10-2.5	IBA	-45.2534; 169.3912	Research
Canterbury	Christchurch	2001-2002	Daily	PM2.5	IBA	-43.5112; 172.6337	AQM
	Timaru	2006-2007	1 day-in-3	PM2.5	IBA	-44.4046; 171.2496	AQM
	Woolston	2013-2014	2-hourly	PM2.5, PM10-2.5	IBA	-43.5572; 172.6811	Research
	Christchurch (Coles Place)	2013-2015	1 day-in-3	PM2.5, PM10-2.5	IBA, XRF	-43.5112; 172.6337	AQM
	Christchurch (Coles Place, Woolston, Riccarton 3-site study)	Winter 2014	2-hourly	PM2.5, PM10-2.5	IBA	-43.5112; 172.6337	Research
Hawkes Bay	Hastings	2006-2007	1 day-in-3	PM2.5, PM10	IBA	-39.6385; 176.8574	AQM
	Meanee Rd	2006+2008	1 day-in-2		IBA		Screening
	Napier	2008-2009	1 day-in-3	PM2.5, PM10-2.5	IBA		AQM
	Awatoto	2016-2017	1 day-in-3	PM2.5, PM10-2.5	XRF	-39.5459; 176.9192	AQM
	Marewa Park	2017-2018	1 day-in-3	PM2.5, PM10-2.5	XRF	-39.5002; 176.8971	AQM
Southland	Invercargill	Winter 2014	Hourly	PM2.5, PM10-2.5	IBA	-46.4305; 168.3711	AQM
Waikato	Tokoroa	Winter 2014	Daily	PM10	XRF	-38.2216; 175.8589	Screening
	Tokoroa	October 2015- October 2016	Daily	PM10	XRF	-38.2216; 175.8589	AQM
Bay of Plenty	Rotorua	October 2014 -	1 day-in-3	PM2.5, PM10-2.5	IBA	-38.1625; 176.2571	Research
Tasman	Richmond	2013 - 2016	1 day-in-3	PM10	XRF	-41.3396; 173.1833	AQM
	Richmond	2015 - 2016	Daily	PM2.5	XRF	-41.3396; 173.1833	AQM

Notes on quality comment

Screening

Qualitative analysis for identifying source types and/or sources contributing to ambient particulate matter, may be gaps in data, very short-term dataset or some sources may be significantly underestimated due to missing species - dataset considered incomplete for quantitative analysis

Research

Data used for research purposes, may not cover full seasonal or temporal variation

AQM – Air Quality Management

Data considered appropriate to use for air quality management purposes

A2.1 Site Descriptions and Metadata

A2.1.1 Whangarei monitoring site

Size-resolved PM₁₀ samples were collected at an ambient air quality monitoring station located on top of the roof of the Northland Regional Council building at 35 Water Street, Whangarei (Lat: -35.725255; Long: 174.317721°, elevation: 6 m). Figure A2.1 presents the site location on a map of the local area.

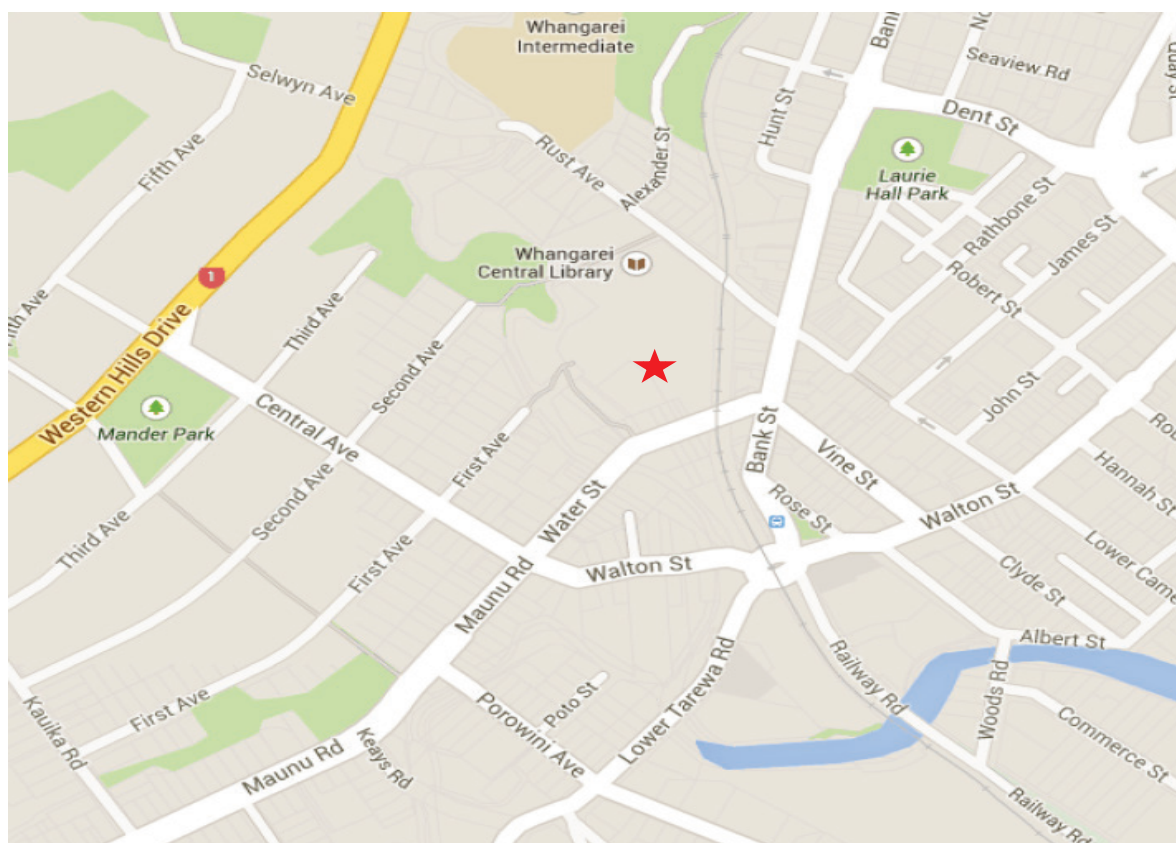


Figure A2.1 Map showing the location of the Water Street monitoring site (★) (source: Wisers Maps www.wisers.co.nz).

Water Street is located on the northwestern edge of the Whangarei CBD. The site was approximately 50 m from the nearest road and surrounded by open space or buildings no more than two stories high. To the northwest of the site is the Whangarei residential suburb of Avenues with bush clad hills further north and west. To the south and southwest the land opens out into the port area and Whangarei Harbour. The city of Whangarei essentially sits in the confluence of two valleys that drain into the harbour.

A2.1.2 Auckland monitoring sites

Samples of airborne particles were collected at five ambient air quality monitoring stations located across the Auckland isthmus as shown in Figure A2.2. Full details and site metadata are contained in (Davy et al., 2017).

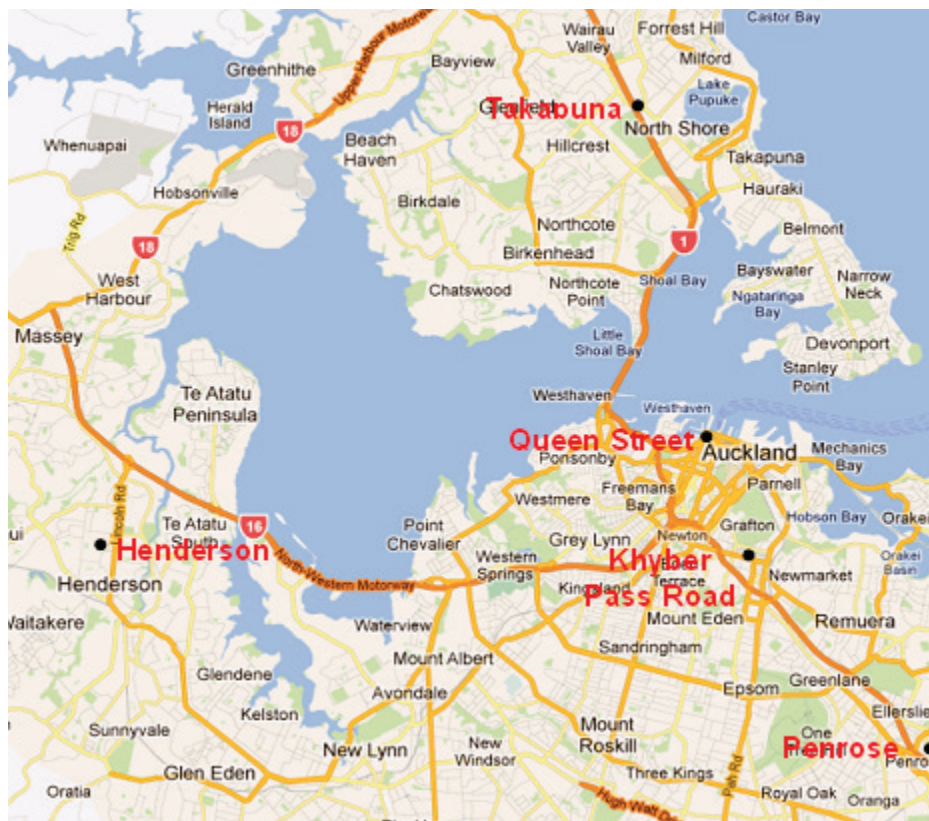


Figure A2.2 Location of the five monitoring sites (●) included in the Auckland receptor modelling study (source: Wisemaps.co.nz)

A2.1.3 Tokoroa monitoring site

Daily PM₁₀ sampling was undertaken by Waikato Regional Council (WRC) from September 2015 until October 2016 at their air quality monitoring station at 80 Billah Street in Tokoroa (NZTM: N5765821; E1850246). The site is classified as residential and is located next to a large water reservoir. The surrounding terrain is flat and Tokoroa lies in a valley that slopes down from southeast to the northwest. Continuous PM₁₀ concentrations for compliance monitoring purposes are recorded at the site using an FH62 beta-attenuation monitor (Thermo-Fisher), and data on wind direction and speed (Vector A101M and W200P) and temperature (PT100) are also collected at the site. 24-hour PM₁₀ samples for analysis were collected onto Teflon filters (Tisch Environmental SF18040) at the site using a sequential Partisol system (Thermo-Fisher 2025). A total of 361 samples (plus field and lab blanks) were collected over this period. All PM sampling and systems maintenance at the air quality monitoring site was carried out by WRC, and as such, WRC maintains all records of equipment, flow rates and sampling methodologies used for the PM sampling regime. Filter conditioning, weighing and re-weighing for PM₁₀ gravimetric mass determinations were carried out by Hill Laboratories Limited.



Figure A2.3 Location of the Billah Street monitoring site in Tokoroa (▲) (source: Waikato Regional Council).

A2.1.4 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 A2.4 illustrates the distance and direction to sea, neighbouring areas and the largely flat topography of the immediate area.



Figure A2.4 Hastings monitoring site location (Source: Hawkes Bay Regional Council).

The ambient sampling monitoring equipment was situated at the St Johns Ambient Air Quality monitoring site located at St Johns College in Jervis Street, Hastings (Figure A2.4) (lat. -39.6385; long. 176.8574).

A2.1.5 Wainuiomata monitoring site, Wellington

Samples of airborne particles were collected at an ambient air quality monitoring station located within the grounds of the Wainuiomata Bowling Club, off Moohan Road, Wainuiomata (Lat: -41.26810, Long: 174.9534). Figure A2.5 shows the site location on a map of the local area.

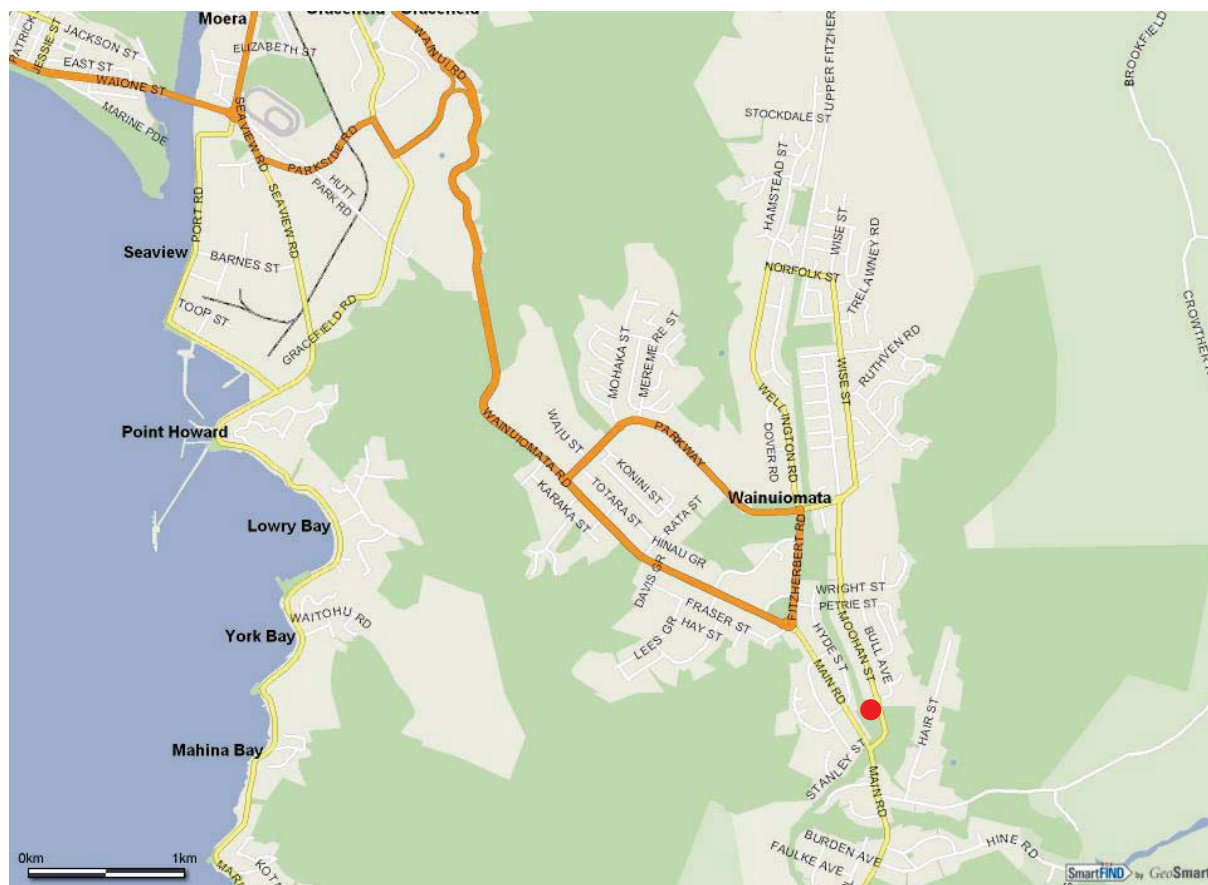


Figure A2.5 Map showing location of Wainuiomata monitoring site (●) (Source: Wisers Maps www.wises.co.nz).

Wainuiomata is located in a valley basin surrounded by hills 200 m high to the north and west, to the east the hills rise into the Rimutaka Range up to 800 m high. The south end of Wainuiomata narrows to a constricted valley which runs 20 km down to the ocean. Wellington City is 15 km to the southwest across the hills and harbour.

A2.1.6 Masterton monitoring site

An ambient air quality monitoring station is located within the grounds of Wairarapa College, in Masterton (lat. -40.9523; long. 175.6465, elevation 100 m) and has been operating since October 2002. Co-located at the site are continuous CO, NO_x and PM₁₀ (TEOM) analysers and a PM₁₀ high-volume sampler as a reference method. Various meteorological parameters were also monitored at the site. Figure A2.6 is a map of the local area surrounding the monitoring site.

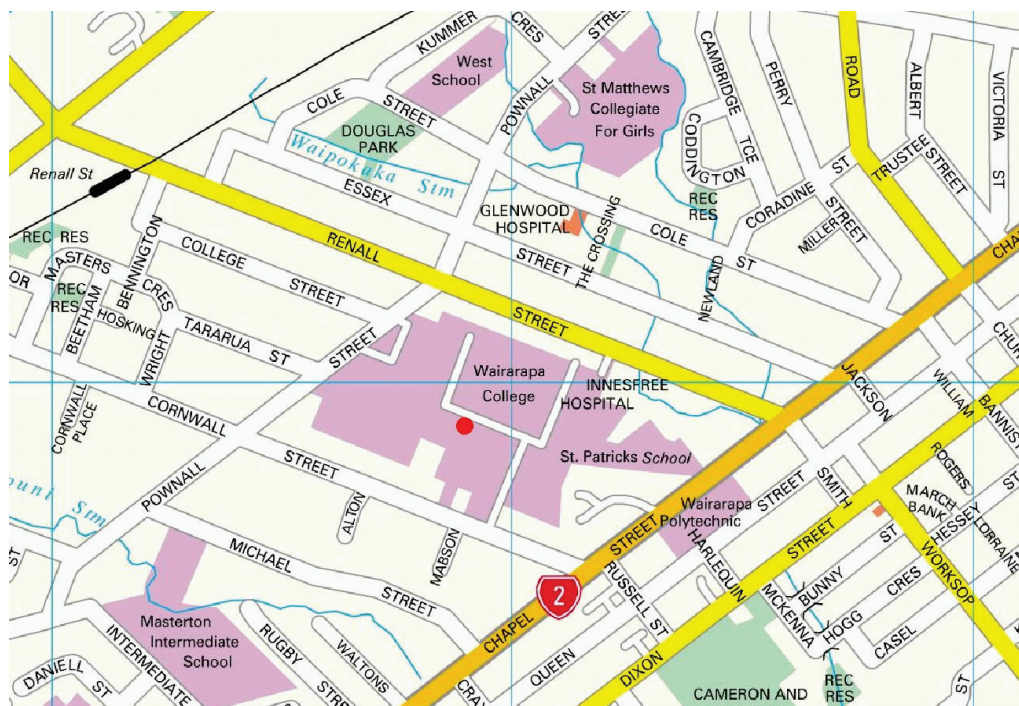


Figure A2.6 Local map of area around Wairarapa College monitoring site (●).

Masterton is a rural town with a population of approximately 20,000 that services the surrounding farming community. Masterton is located on the flat river plain of the Wairarapa Valley which is approximately 20 km wide. The Wairarapa College site was at least 150m from the nearest road and approximately 1 km from the central business district of Masterton. The land around the school site was flat and surrounded by open space or school and residential buildings no more than two storeys high.

A2.1.7 St. Vincent Street, Nelson monitoring site

Size-resolved PM samples (PM₁₀ and PM_{2.5}) were collected at an ambient air quality monitoring station located on a property off of St. Vincent Street, Nelson (Lat: -41.164150°, Long: 173.162447°, elevation: 5 m). Figure A2.7 presents the site location on a map of the local area.

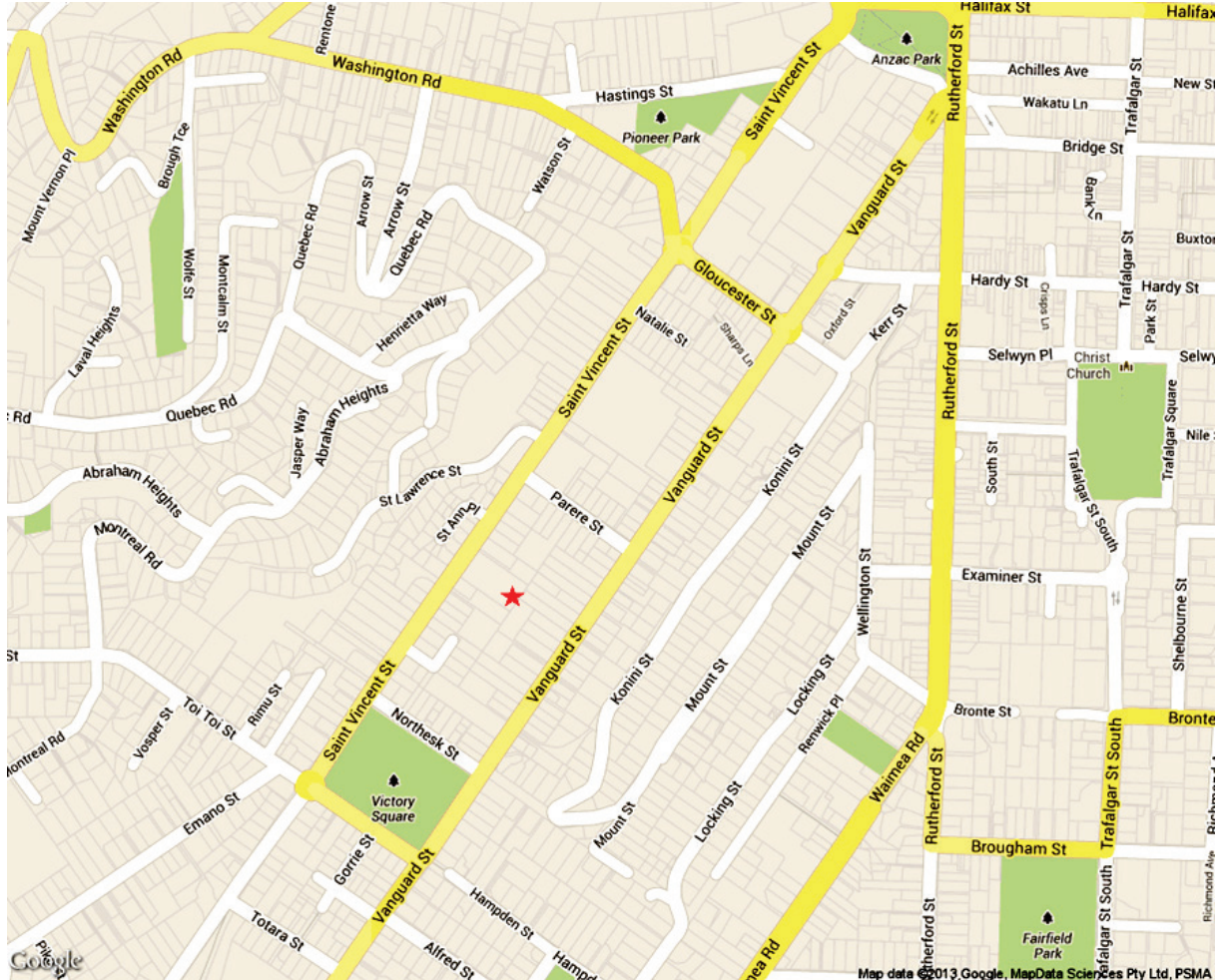


Figure A2.7 Map showing the location of the St. Vincent Street monitoring site (★) (source: Wises Maps www.wises.co.nz).

St. Vincent Street is located near (within 600 m) the Nelson CBD. The site was approximately 90 m from the nearest road and surrounded by open space or buildings no more than two stories high.

A2.1.8 Tahunanui monitoring site, Nelson

Samples of airborne particles (PM₁₀) were collected at an ambient air quality monitoring station located on a property off Blackwood Street, Tahunanui (Lat: -41.2949o, Long: 173.2431, elevation 5 metres). Figure A2.8 shows the site location on a map of the local area.

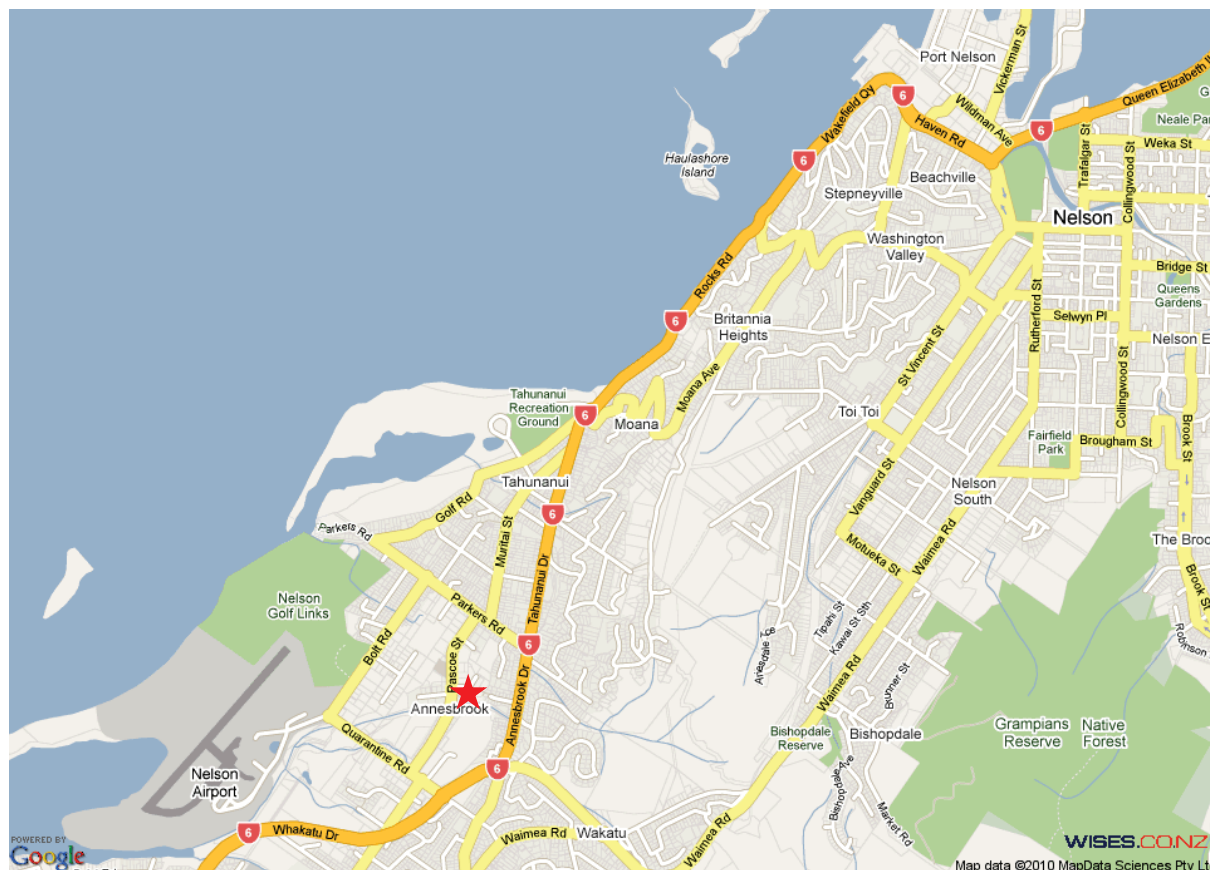


Figure A2.8 Map showing location of Tahunanui monitoring site (★) (Source: Wises Maps www.wises.co.nz).

Tahunanui is located on a narrow coastal plain bordered by hills to the east (200-300 m high) to the north lies Tasman Bay and to the west is the Waimea Inlet. To the southwest is the Waimea Plain. The Blackwood Street site lies on the border between industrial activities to the south and west with Nelson Airport located on the edge of the Tahunanui Inlet west of the monitoring site. Residential activities predominate immediately to the east and north, with State Highway 6 (Annesbrook Drive) 200 m east of the site.

A2.1.9 Richmond monitoring site, Tasman

PM_{2.5} and PM₁₀ samples were collected at an ambient air quality monitoring station located at 56 Oxford street, Richmond (Lat: 41°20'21.46 S; Long: 173°10'58.65 E; elevation: 13 m). Figure A2.9 presents the site location on a map of the local area.



Figure A2.9 Map showing the location of the Richmond monitoring site(source: TDC).Oxford Street is located near the Richmond CBD and the monitoring site was less than 400 m from State Highway 6, the major roadway into and out of Nelson. The site was in a residential area and was surrounded by buildings no higher than two stories. Aside from its immediate environment, the monitoring site was surrounded by hills and farmland, and was less than 5 km south of Tasman Bay.

A2.1.10 St Albans, Christchurch monitoring site

Particulate matter sampling was performed at the Coles Place monitoring site (operated by Environment Canterbury) in St Albans, Christchurch (Lat: -43.304255° ; Long: 172.380231). The site is the primary long-term air quality monitoring site in Christchurch. The sampling location is presented in Figure A2.10.

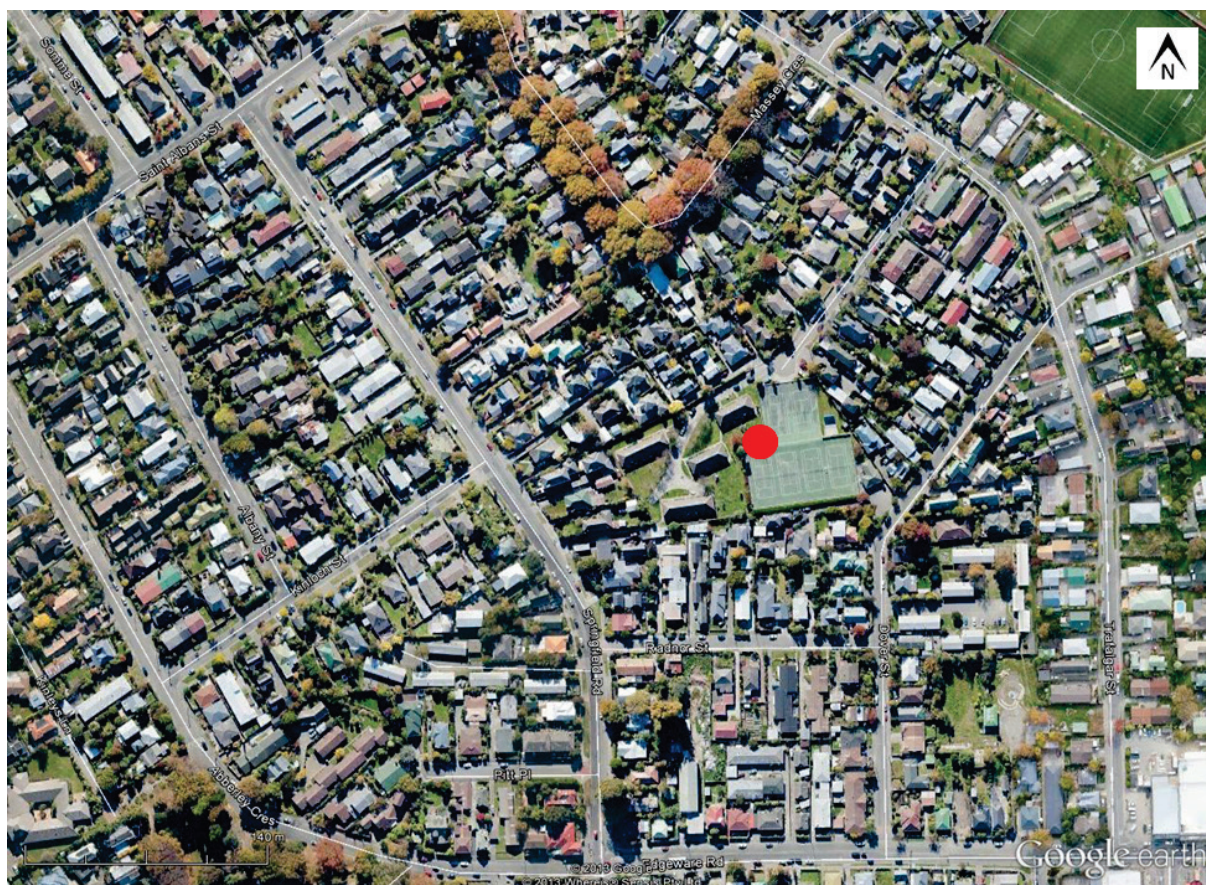


Figure A2.10 Location of the Christchurch monitoring site (●) (Source: Google Maps).

As shown in Figure A2.10, the sampling site is located in a residential area adjacent to tennis courts at the end of a cul-de-sac. The immediate surrounding environment is dominated by older, medium to high-density residential dwellings. The closest arterial road, Cranford St (SH 74), is approximately 380 m to the east, and 240 m to the south is Edgeware Rd, a busy urban route.

A2.1.11 Timaru monitoring site

Environment Canterbury’s Timaru city air quality monitoring station is located at Anzac Square, Parkside (Figure A2.11) (lat. -44.4046; long. 171.2496. The station is situated in the south-eastern corner of the park, a short distance from State Highway 1 (100 m west), Rose St (20 m east), the coast (<1 km east) and port (<1 km east).



Figure A2.11 Location of the Timaru air quality monitoring site (Source: Environment Canterbury).

A2.1.12 Dunedin monitoring site

Samples of airborne particles were collected at an ambient air quality monitoring station located on the corner of Albany Street and Anzac Avenue in Dunedin (Lat: -45.8689; Long: 170.5177). The Albany Street site is located in a mixture of commercial and residential activities with the port area and harbour 800m to the east. Figure A2.12 provides an aerial photo of Dunedin and its immediate environs.



Figure A2.12 Aerial view of Dunedin monitoring site (★) (Source: Google Maps 2011).

Buildings around the Dunedin monitoring site range from single storey up to 7 or 8 storeys which provides for complex terrain that will affect wind speed and direction as measured at the monitoring site. The local topography around the Albany Street air quality monitoring site is flat with hills rising to the north and west and the Dunedin CBD to the southwest.

A3.0 LIST OF ABBREVIATIONS AND DEFINITIONS

AAQG	New Zealand ambient air quality guidelines (2002)
AC	Auckland Council
BAM	beta particle attenuation monitor
BC	black carbon
EC	elemental carbon
GNS Science	Geological and Nuclear Sciences Limited
GUI	graphical user interface
HYSPLIT	hybrid single particle Lagrangian integrated trajectory model
IBA	Ion Beam Analysis
LOD	limit of detection
Marine aerosol	Particulate matter generated from the evaporation of sea water and the primary composition is sodium chloride (sea salt)
ME2	multi-linear engine
MLR	multiple linear regression
NES	New Zealand National Environmental Standard
nss-Sulphate	non-seasalt sulphate
OC	organic carbon
OMH	organic mass from hydrogen
PAHS	polyaromatic hydrocarbons
PCA	principal components analysis
PESA	particle elastic scattering analysis
PIGE	proton induced gamma-ray emission
PIXE	proton induced X-ray emission
PM	particulate matter
PM ₁₀	particulate matter less than 10 micrometres
PM _{10-2.5}	particulate matter between 10 and 2.5 micrometres
PM _{2.5}	particulate matter less than 2.5 micrometres
PMF	positive matrix factorisation

PSCF	potential source contribution function analysis
QA/QC	quality assurance - quality control
Secondary sulphate	Sulphate particles generated from gaseous precursors through atmospheric reaction pathways
S/N	signal-to-noise ratio
TSP	total suspended particulate matter
USEPA	United States Environment Protection Agency
VOCS	volatile organic compounds
WHO	World Health Organisation



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