Evaluation of New Zealand's background particulate matter sources

PK Davy WJ Trompetter
LE Revell C Hardacre

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EXECUTIVE SUMMARY

This report presents an analysis of the natural sources (background concentrations) of airborne particulate matter to assess the achievability of air-quality standards and guidelines for each gazetted New Zealand airshed or air quality management area. Specifically, the report addresses three over-arching questions relating to natural sources of particulate matter:

1. What are the estimated natural-source contributions (including concentrations) for all 89 airsheds (73 gazetted + 16 regional/unitary boundaries) in New Zealand?

2. Are there any trends observable in the natural-source contributions within each of the airsheds?

3. What are the implications for these natural-source contributions under climate-change scenarios?

The report draws on data and information generated from 20 years of particulate matter monitoring to provide answers or identify the knowledge gaps.

Overview of Natural Sources of Airborne Particulate Matter and Approach Used in this Report

Natural (or background) sources of particulate matter are the emissions and processes that produce airborne material that does not arise from direct or indirect human activity. Natural sources of particulate matter are of interest for air-quality management purposes because, while they contribute to ambient particulate matter mass concentrations, little can be done to control their presence.

Quantifying the contribution of natural sources to daily and annual average particulate matter concentrations is vital for air-quality management. The proportion of particle mass from natural and other (uncontrollable) sources needs to be factored into any air pollution reduction strategy. This information identifies the level of control required for anthropogenic-source emissions if ambient concentrations exceed or approach relevant air-quality guidelines and standards designed to protect the health of exposed populations.

Compositional data from filter-based particulate matter samples has been collected for approximately 40 airshed-based air-quality-monitoring sites across New Zealand[1]. This dataset has provided the basis to assess the contribution of natural sources of particulate matter in New Zealand urban environments.

Natural Sources that Contribute to New Zealand Urban Atmospheres

Our findings from the analysis of particulate matter show that marine (sea salt) and secondary aerosol are the most significant natural sources of particulate matter in New Zealand urban areas.

Key findings across sites in New Zealand show that:

*   Marine aerosol (sea salt) is the primary natural-source contributor to particulate matter concentrations.

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1   The Institute of Geological & Nuclear Sciences (GNS Science) has measured elemental concentrations in New Zealand particulate matter samples since 1996 and holds an archive of filter-based, time-integrated particulate matter samples that forms part of the National Air Particulate Speciation Database: https://doi.org/10.21420/R58Q-FZ78

- Secondary sulphate dominates the secondary aerosol contribution, with secondary nitrate species likely to be present at lower (five to ten times less) concentrations. Secondary sulphate and nitrate also have anthropogenic sources.

- Crustal matter (soil) in urban atmospheres was primarily due to anthropogenic emissions, apart from occasional transboundary events associated with Australian desert dust storms.

- There is a lack of data on biogenic organic aerosol components and the relative contributions to urban particulate matter concentrations.

The data for natural-source contributions show that 24-hour average marine aerosol and secondary sulphate contributions to $PM_{2.5}$ were reasonably uniform across the country for both coastal and inland locations. This suggests that both sources are well mixed in the regional air mass and likely the result of long-range transport rather than localised emission sources.

By examining long-range atmospheric transport of natural particulate matter, it was shown that:

- For locations north of about Christchurch, secondary sulphate contributions above the mean are heavily influenced by emissions of precursor gases from the Taupō Volcanic Zone (TVZ), with Whakaari / White Island being the most significant source of SO_2 emissions.[2]

- For locations in the south of the South Island, it is more likely that oceanic sources of secondary sulphate predominate natural-source contributions.

- Marine aerosol contributions to urban particulate matter concentrations are ubiquitous across the country, with sea-salt particles measured at all monitoring locations, whether inland or coastal, for both short and longer sampling campaigns.

- There is more variability for marine aerosol contributions to PM_{10}, with coastal locations experiencing higher concentrations than those monitoring locations further inland; this is likely to be due to topographical sheltering effects (wet and dry deposition) for the coarse (and heavier) fraction of sea-salt particles.

Figures ES.1 and ES.2 present examples of the likely source locations for the highest concentrations of marine aerosol and natural secondary sulphate, respectively, as measured at New Zealand urban locations.

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2   The TVZ emissions of precursor gases for secondary sulphate are estimated to be three times the total New Zealand anthropogenic (annual average) output.
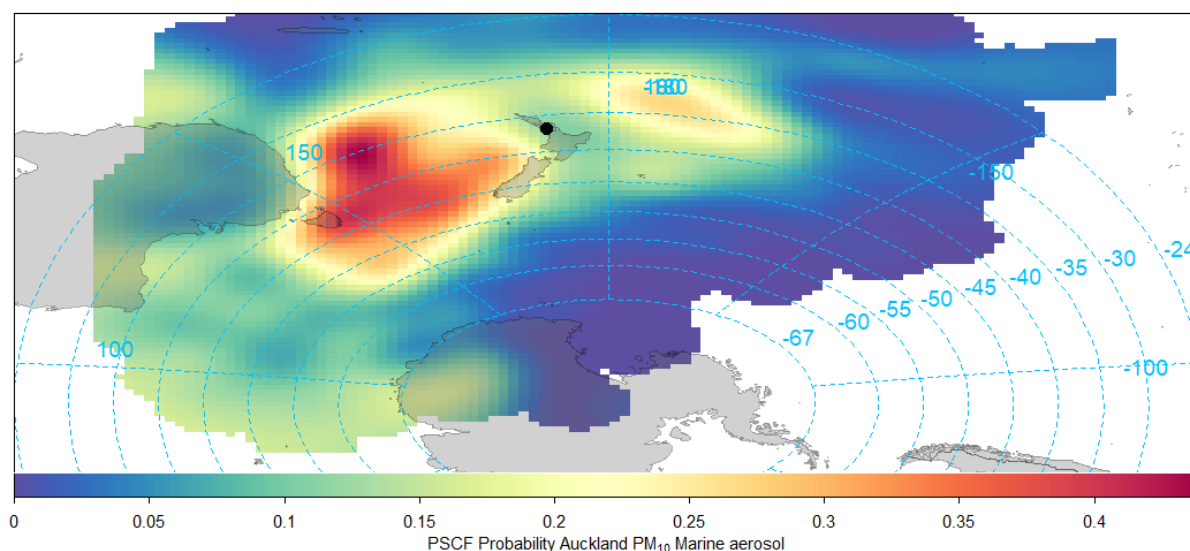
Figure ES.1   Probability map showing the most likely oceanic emissions locations (southern Tasman Sea and Southern Ocean) for the highest concentrations of sea salt as measured at Auckland sites.
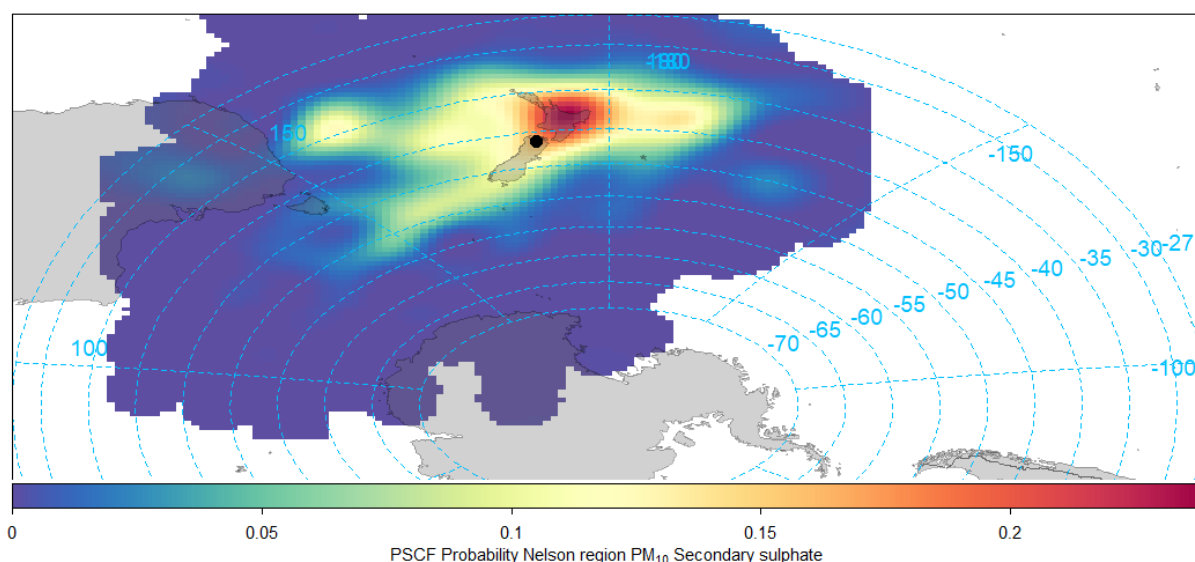
Figure ES.2   Probability map showing the most likely emissions location (centred on the Taupō Volcanic Zone) for the highest concentrations of natural secondary sulphate as measured at Nelson sites.

These effects have been taken into account to provide an estimate of the mean and likely peak (24-hour average) natural-source contributions that could be expected at all 73 gazetted airsheds for the purposes of air-quality management.

Airshed Exceedances of Air-Quality Standards or Guidelines and Relationship with Natural-Source Contributions

The data was analysed to identify any airsheds that have, or may be likely to, exceed particulate matter air-quality standards or guidelines due to natural-source contributions. Across the database of 24-hour particulate matter samples collected in New Zealand for compositional analysis to date:

- For $PM_{2.5}$ (n = 6680, timespan = 20 years), only one natural-source event was identified where the World Health Organization guideline may have been exceeded, suggesting that such events are relatively rare.

- For PM_{10} (n = 12,340; timespan = 20 years), where the marine aerosol contribution has greater impact and transboundary events (Australian desert dust) contribute the most to, there have only been three instances where the PM_{10} National Environmental Standards for Air Quality have been exceeded that were attributable to natural sources in the sample record, also indicating that this is a relatively rare occurrence for this size fraction.

- The stronger winds that give rise to high sea-salt concentration events usually suppress (via dispersion) the anthropogenic contributions to urban particulate matter concentrations at the same time.

The data suggests that it is unlikely that natural sources alone will exceed long-term (annual average) $PM_{2.5}$ or PM_{10} Ambient Air Quality Guideline concentrations, but they will contribute to a baseline on top of which anthropogenic sources will have to be managed accordingly.

The Impact of Climate Change on Natural-Source Contributions to Particulate Matter

Climate modelling across a range of policy intervention scenarios generally assume decreases in anthropogenic sources of particulate matter worldwide in response to efforts to improve air quality.[3] However, natural sources of particulate matter are projected to increase over New Zealand.

- Sea-salt aerosol will likely increase, irrespective of the greenhouse gas emissions scenario. Larger increases in greenhouse gas emissions imply larger increases in sea spray aerosol production.

- Dust particulate matter could increase from transboundary transport from Australia; however, models do not consistently agree on the direction of future change.

- Black carbon aerosol is projected to decrease under the SSPs from anthropogenic emissions; wildfires will have localised impacts that are not included in the CMIP6 models.

- Projections of natural sulphate aerosol alone are not possible, as the models only report total (natural and anthropogenic) sulphate aerosol. Anthropogenic sulphur dioxide emissions are assumed to decrease under the range of policy-intervention scenarios, and models disagree over future trends in marine dimethyl sulfide due to uncertainty of climate impacts on phytoplankton productivity. Future volcanic eruptions cannot be predicted and are independent of rising CO_2 levels; however, continued out-gassing of volcanoes in the upper North Island is likely to provide an ongoing natural source of sulphur gas precursors to secondary sulphate aerosol.

Identified Data and Knowledge Gaps

The analysis of natural-source contributions to particulate matter provided in this document was based on data derived from one or two years of monitoring conducted at different times, spread across almost 20 years. The longer-term particulate matter sampling and compositional analysis programmes, such as those in Auckland and Wellington, have provided a benchmark to compare such short-term datasets, assess longer-term trends and guide the conclusions reached. However, the data and coverage are generally more sporadic than desirable to account for many source types. Short-term 'snapshots' of local atmospheric composition do

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3   It should be noted that model uncertainty and scenario uncertainty play important roles in forming future projections. Scenario uncertainty arises because bigger increases in natural particulate matter are seen with larger increases in future greenhouse gas emissions. Model uncertainty arises due to the small number of models (typically five) that provided suitable output for this analysis and their disagreement in the direction of change (i.e. whether particulate matter increased or decreased).

not necessarily provide the means to effectively manage air-quality changes over the longer term and identify the drivers of such change, especially given the seasonal nature of natural aerosol production.

The data and knowledge gaps identified in producing this report comprise three broad categories that are interlinked:

1. Routine monitoring and compositional analysis of source contributions over time is required to track environmental change and the drivers of that change.

2. Deeper research into understanding the fundamental processes and earth system drivers that give rise to the observations we make in our urban monitoring data and the capacity to make future projections.

3. The science capability and capacity to undertake the data gathering and provide the data science necessary to fill those knowledge gaps.

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1.0   INTRODUCTION

The Ministry for the Environment seeks a better understanding of the changes that may be required of existing air-quality management to align with the air-quality guidelines set by the World Health Organization (WHO 2021) and to evaluate what impact background sources will have on achievability of the lower thresholds. This report presents an analysis of the natural sources (background concentrations) of airborne particulate matter to assess the achievability of the new guidelines for each gazetted New Zealand airshed or air-quality management area.

Specifically, the report addresses three over-arching questions relating to natural sources of particulate matter:

1.   What are the estimated natural-source contributions (including concentrations) for all 89 airsheds (73 gazetted + 16 regional/unitary boundaries) in New Zealand?

2.   Are there any trends observable in the natural source contributions within each of the airsheds?

3.   What are the implications for these natural-source contributions under climate-change scenarios?

The report draws on data and information generated from 20 years of particulate matter monitoring to provide answers or identify the knowledge gaps.

1.1   Natural Sources of Particulate Matter

A natural (or background) sources of particulate matter can only be considered 'natural' if it does not arise from direct or indirect human activity (EEA 2012). For example, particulate matter pollution from a wildfire can only be considered natural if it was ignited by lightening or similar. If the ignition source was due to accidental or deliberate human activity, then the fire is considered an anthropogenic source of particulate matter.

Natural sources of particulate matter are of interest for air-quality management purposes because, while they contribute to ambient particulate matter mass concentrations, little can be done to control their presence. Quantifying the contribution of natural sources to daily and annual average particulate matter concentrations is vital for air-quality management. The proportion of particle mass from natural and other (uncontrollable) sources needs to be factored into any air pollution reduction strategy such that it identifies the level of control required for anthropogenic-source emissions to meet relevant air-quality guidelines and standards designed to protect the health of exposed populations.

Furthermore, with climate change, it is likely that New Zealand will experience increased severe weather events that may lead to episodes of elevated sea salt and windblown dust. Understanding how climate change will impact the trends in natural-source contributions will ensure that any amended regulations and standards can remain achievable into the future.

1.2   Natural-Source Types, Emission-Source Locations, Atmospheric Chemistry and Reaction Pathways

The interaction between the oceans, lithosphere, biosphere and atmosphere are complex and varied, resulting in multiple sources of natural atmospheric aerosol with particle size ranges that span several orders of magnitude (sub-nanometre to sub-millimetre). Disturbance of these domains by human activities and emissions from anthropogenic sources, along with chemical reactions and thermodynamic effects in the atmosphere itself, provide additional

complexity to atmospheric particle composition. Each source or source type of particulate matter produces a distinctive particle size range and chemical composition but, due to the vast number of sources separating them out, a mixture resolution problem occurs. Therefore, to identify and understand those sources that contribute to particulate matter concentrations at any one location requires information on the composition of that aerosol and the atmospheric transport mechanisms that brought it there.

There are four broad categories that give rise to atmospheric aerosol of natural origins; these include:

- Oceanic sources.

- Terrestrial (land-based) sources.

- Volcanic (and geothermal) emissions.

- Aerosol formation in the atmosphere from chemical reactions.

This report does not intend to describe each of these categories in detail, as there is significant scientific literature available on the subject matter. Rather, the focus is on those natural particulate matter sources that can contribute significantly to New Zealand urban aerosol concentrations at times and therefore impact on the ability of regulatory agencies to manage urban air quality for the health of exposed populations.

New Zealand's location as a series of islands arranged north to south in the mid-latitudes between the Pacific and Southern oceans provides an initial understanding that oceanic emissions will be important sources of aerosol in urban atmospheres.

1.3   Report Structure

Aside from the Introduction, this report is comprised of five main sections. The remaining sections cover the following topics:

- **Section 2:** 'Sampling and analysis of airborne particulate matter' provides an overview of the collection of aerosol samples and the analysis of particulate matter composition, along with the derivation of natural sources of particulate matter using geochemical and receptor modelling techniques. Summary statistics are presented for natural-source concentration data currently available from New Zealand air-quality monitoring sites, including seasonal variations and observed inter-annual trends.

- **Section 3:** 'Estimation of natural-source contributions to particulate matter in New Zealand airsheds' describes the methodology used to estimate the natural-source contributions (including concentrations) for all 89 airsheds (73 gazetted + 16 regional/unitary boundaries) in New Zealand. Those airsheds that are, or may be likely to exceed, the WHO (2021) guidelines for $PM_{2.5}$ due to natural sources alone are also identified.

- **Section 4:** 'The impact of climate change on natural-source contributions to particulate matter' examines future climate-change scenarios for meteorological or other factors that may impact the generation of natural sources of air particulate matter and the projected changes for atmospheric concentrations across New Zealand.

- **Section 5:** 'Knowledge gaps in the contributions of natural sources to airborne particulate matter' identifies the gaps in our current knowledge of natural-sources generation and dispersion and the (current) estimated costs of filling those knowledge gaps.

The appendices provide more detailed information on particulate matter elemental speciation measurement techniques, along with monitoring site metadata and quality assurance procedures. Appendix 5 provides a glossary for acronyms used throughout the document.

2.0   SAMPLING AND ANALYSIS OF AIRBORNE PARTICULATE MATTER

Measuring the mass concentration of air particulate matter provides little information on the identity of the contributing sources. Airborne particles are composed of many elements and compounds from a variety of sources. This means a wide range of techniques have been used to analyse particle composition, including real-time (or semi-continuous) monitoring techniques, as well as post-sampling laboratory analyses (Landsberger and Creatchman 1999).

2.1   Collection of Aerosol Samples and Analysis of Particulate Matter Composition

Filter-based particulate matter samples have been collected and the composition analysed for approximately 40 sites across New Zealand, with some urban areas including multiple sites (Figure 2.1). A full list of sites and sampling periods is provided in Appendix 1. Most of the particulate matter sampling and analysis campaigns have been targeted studies commissioned by regional councils that ran for 1–2 years, collecting 24-hour time-integrated particulate matter samples to understand the local drivers of air pollution for air-quality management purposes. The exception to this is the Auckland Council multi-site air particulate matter speciation programme that has been running since mid-2004. This allows for inter-site comparisons, trend analysis and all-of-urban assessment of particulate matter composition and source contributions to both $PM_{2.5}$ and PM_{10} particulate matter size fractions. Longer-term monitoring datasets are also available for Wellington (at Wainuiomata intermittently from 2006 and then continuously since 2014 onward) and a 10-year dataset is available for Nelson (2008–2018). The particulate matter samples have been collected at regulatory authority monitoring sites using National Environmental Standards for Air Quality (NESAQ)-compliant methodologies or alongside NESAQ-compliant particulate matter monitoring systems.

Figure 2.1   Particulate matter sampling sites for compositional analysis (1996–2024).

In addition to the urban monitoring locations, several studies have targeted source-specific particulate matter composition; these include motor vehicle tunnels (Mt Victoria tunnel, Wellington, and the Johnstone Hill Tunnel north of Auckland) (Ancelet et al. 2011; Davy et al. 2011b) and wood burner emissions (Davy et al. 2009; Ancelet et al. 2010) to understand emission source characteristics and composition. For several locations, high-resolution sampling (hourly) and analysis was undertaken as part of research programmes to understand the observed diurnal variation in particulate matter concentrations in New Zealand urban centres (Trompetter et al. 2010; Ancelet et al. 2012, 2014a, 2014b), as well as the impacts of airborne particle infiltration and ventilation on indoor air quality (Trompetter and Davy 2019).

2.2   Analysis of Particulate Matter Composition

Two multi-elemental analysis techniques have been used routinely by GNS Science 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 black carbon concentrations in all samples. These are well-established and internationally accepted methods for determining particulate matter elemental composition (Horvath 1993; Landsberger and Creatchman 1999; Maenhaut and Malmqvist 2001; Bond and Bergstrom 2006). 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). Full descriptions of these techniques are provided in Appendix 2. 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.

As a result of the use of non-destructive analytical techniques, GNS Science holds an archive of filter-based, time-integrated particulate matter samples that forms part of the National Air Particulate Speciation Database.[4]

Several monitoring campaigns have also used additional techniques to quantify other particulate matter components, such as organic compounds, water-soluble ionic components, organic carbon and total carbon, along with the application of electron microscopy for particle size, morphology and composition (Ancelet et al. 2011; Hopke et al. 2011; Cavanagh et al. 2012; Salako et al. 2012; Ancelet et al. 2013b; Davy and Ancelet 2015; Talbot et al. 2022).

2.3   Derivation of Natural Sources of Particulate Matter using Geochemical Principles and Receptor Modelling Techniques

The analysis of air particulate matter sample composition provides the opportunity to assess sources that contribute to the collected samples, and there are a variety of techniques that have been used for this purpose. A fundamental factor for natural sources is that the composition of particles derived from such emissions follow geochemical constraints. The contribution of these components to particulate matter samples can be recognised with the appropriate data analysis techniques, such as a mass reconstruction approach (Cahill et al. 1989; Malm et al. 1994; Cohen 1999): For example, particles derived from crustal matter contain elements (e.g. Al, Si, Ca, Fe, Ti) in the expected ratios for component minerals.

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4   https://doi.org/10.21420/R58Q-FZ78

Similarly, sea-salt particles (also called marine aerosol or sea spray) maintain elemental ratios found in sea water.

As mentioned in Section 1, chemical reactions in the atmosphere can form particles from gaseous and liquid precursors. The composition, size and form of particles are also modified in the atmosphere through a multitude of processes and interactions, for example:

- Adsorption of other species onto particle surfaces.

- Gas-to-particle conversions forming secondary particulate matter, for example, the conversion of sulphur-containing gases to sulphate (SO_4^{2-}) species.

- Volatilisation of particle components, such as organic compounds, or volatilisation of chlorine through reaction with acidic components.

- Interaction with, and transformation by, solar radiation and free radicals in the atmosphere, such as the $OH^.$ and NO_3 species.

These processes occur in the atmosphere for both natural and anthropogenic emissions.

The multivariate analysis of particulate matter compositional data (also known as receptor modelling or source apportionment) provides groupings (or factors) of elements that vary together across multiple samples and over time. This technique effectively delineates source chemical profiles that contribute to airborne particulate matter concentrations and the mass of each element 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 sources of those particles. The chemical profile of each particle type is then used to identify the original emission source and how much that source contributes to the total particle mass sampled.

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). Appendix 1 identifies the specific sampling sites, sampling period and reporting details that included particulate matter elemental speciation, receptor modelling and reporting.

2.4   Contributions of Natural Sources to Urban Particulate Matter

Receptor modelling studies for New Zealand locations (Davy et al. 2011a, 2011c; Davy et al. 2012a; Davy and Ancelet 2014; Davy et al. 2016; Davy and Trompetter 2017b, 2020a, 2024a, 2024b; Boamponsem et al. 2024) have shown that, at urban locations, there are generally five main sources contributing to ambient particulate matter concentrations:

- Motor vehicles, from tailpipe and non-exhaust emissions (e.g. road dust, tyre wear, brake wear).

- Residential heating emissions (mainly wood burning) for winter space heating.

- Secondary aerosol from gas-to-particle atmospheric reactions, which is generally dominated by secondary sulphate aerosol.

- Marine aerosol (sea salt) generated in the oceans.

- Crustal matter (soil) from local dust-generating activities.

Additional sources also contribute to ambient urban concentrations (such as point-source industrial emissions). However, the relative contribution from a particular source depends on local emissions activity and, for receptor modelling analysis, the location of a monitoring site (Boamponsem et al. 2024). The results of receptor modelling are usually summed across all contributing sources and compared to the measured particulate mass concentration as part of the quality assurance process. The data shows that most receptor modelling studies at New Zealand urban locations account for 90–95% of the total mass, with the remainder attributed to secondary nitrate species, biological particles (e.g. pollen, spores, biological detritus) and organic aerosol not associated with the modelled species.

The New Zealand speciation datasets show that marine aerosol (sea salt) is the primary source of natural aerosol present in New Zealand urban atmospheres. Secondary 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 particulate matter that has natural origins is crustal matter, generally referred to as 'Soil' in source apportionment studies. The following sections provide further detail on each of these sources.

2.4.1   Marine Aerosol (Natural Source)

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 PM_{10} mass at New Zealand monitoring sites, along with the more minor components (K, Ca, Mg, S) of sea salt. Sodium and chlorine were highly correlated (as shown for the Auckland dataset in Figure 2.2) and are 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 minor sources of Na and Cl include biomass burning, motor vehicle emissions, crustal matter, fireworks and industrial emissions.
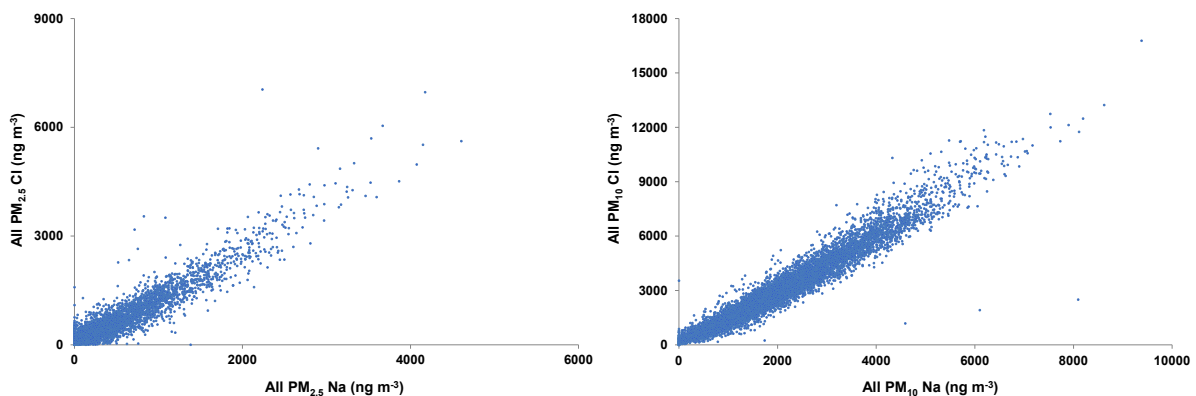
Figure 2.2   Scatterplots for sodium and chlorine in (left) $PM_{2.5}$ and (right) PM_{10} for all Auckland particulate matter samples.

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), with the Auckland data corroborating 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. 2011a). The marine aerosol component of urban air particulate matter is considered to be part of the 'natural' background and therefore is the proportion that cannot be managed.

Daily and seasonal variations in sea-salt concentrations show no bias toward day of the week (Figures 2.3 and 2.4), but winter concentrations tend to be lower at some locations, such as Nelson (Figure 2.4), and there is generally a small October peak likely to be associated with increased spring equinox wind speeds at mid-latitudes for Southern Hemisphere circulation. Further discussion of the observed temporal variations is presented in Section 3.
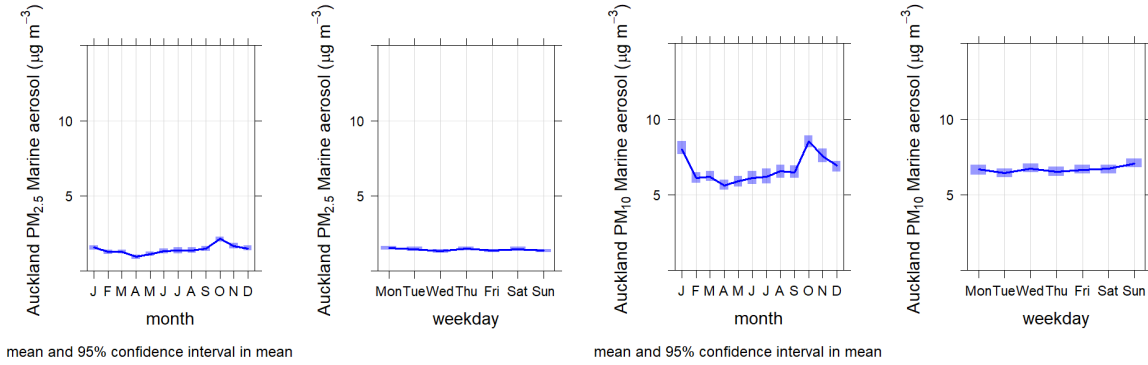
Figure 2.3   Temporal variations in marine aerosol concentrations at Auckland.
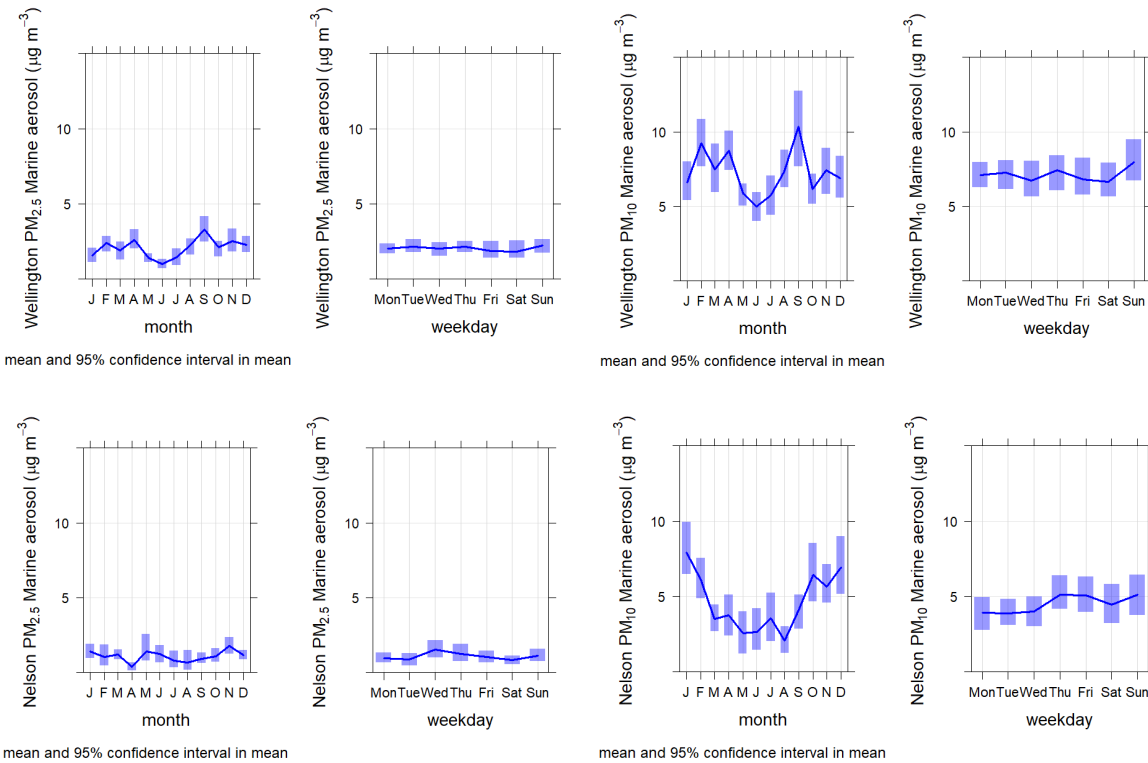
Figure 2.4   Temporal variations in marine aerosol concentrations at Wellington and Nelson.

The Auckland dataset shows that sea-salt concentrations were highly correlated across all monitoring sites (Figure 2.5), indicating that the regional air mass was generally homogenous with respect to marine aerosol.
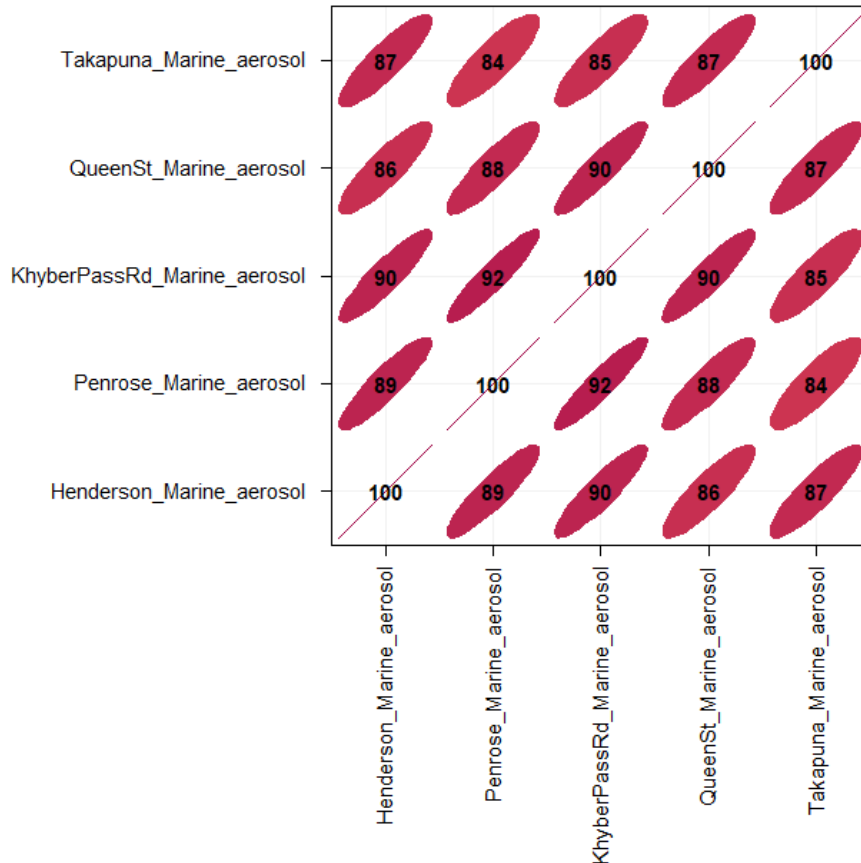
Figure 2.5   Correlation plot for PM_{10} marine aerosol measured at five sites across Auckland.

2.4.2   Secondary Sulphate Aerosol (Primarily Natural Source)

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 and dimethyl sulfide 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 secondary sulphate aerosol 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 2.6), reflecting the relative influence of solar forcing on atmospheric reaction pathways and the influence of emission source activity. The similarity in average monthly secondary sulphate concentrations measured in Auckland and Tokoroa suggest a common source contributor and seasonal aerosol formation pattern.
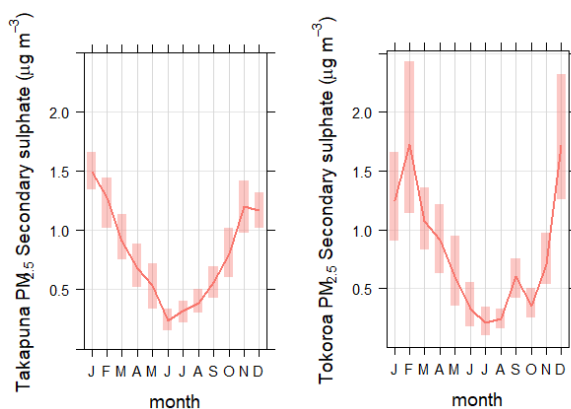
Figure 2.6   Seasonal variation in secondary sulphate concentrations at (left) Takapuna, Auckland (2006–2016), and (right) Tokoroa, Waikato (2016–2017).

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 of secondary sulphate particles to particulate matter concentrations at a given air-quality monitoring site is dependent on:

- Local-source precursor gas emission activity (both anthropogenic and natural).
- Proximity of a particulate matter sampling site to such activities.
- Atmospheric chemical reaction kinetics (i.e. the drivers for the gas-to-particle reaction pathway).
- Long-range transport of natural source (volcanic and oceanic) secondary sulphate.

Receptor modelling studies of particulate matter composition from around New Zealand show that particulate matter monitoring sites near ports are likely to be influenced by secondary sulphate associated with emissions of precursor gases from ship engines. The regulation of sulphur content of automotive fuels has played a significant role in reducing anthropogenic secondary sulphate aerosol in urban environments, as presented for Auckland data in Figure 2.7. The observed peaks in 2015 and 2019 occurred during the summer months and were uniform across all Auckland monitoring sites, suggesting a regional impact. This is likely due to a longer-range natural source with concentrations of secondary sulphate homogeneous in the regional air mass.
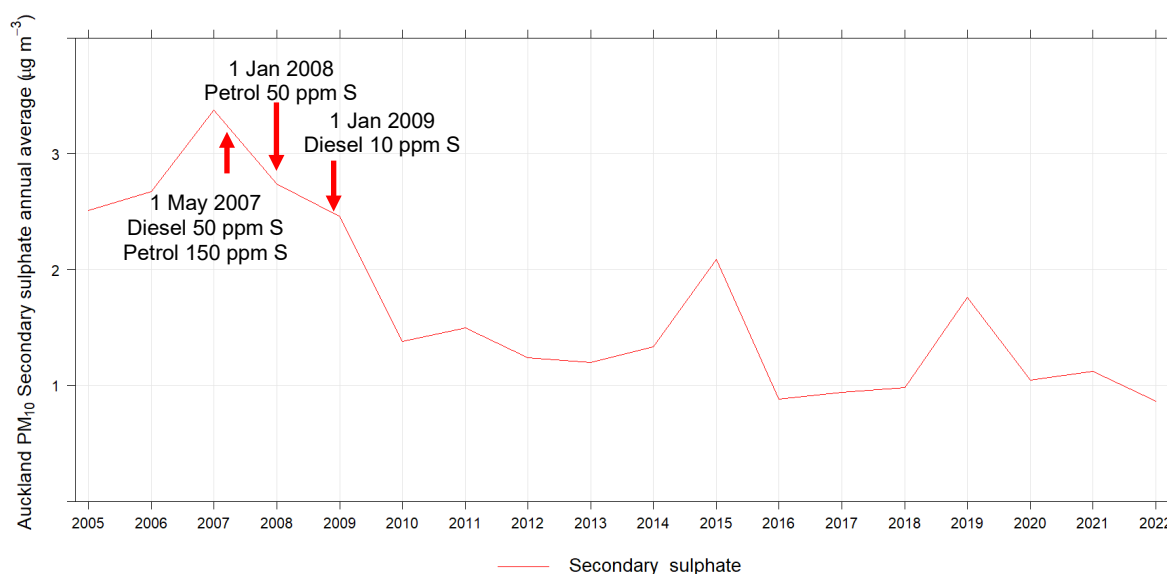
Figure 2.7   Annual average secondary sulphate contributions to Auckland PM_{10} concentrations.

2.4.3 Crustal Matter (Primarily Anthropogenic)

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 PM_{10} 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 re-suspension (Thorpe and Harrison 2008).

The temporal variation for both aluminium and silicon concentrations (Figure 2.8) for Auckland data, as well as the bulk crustal matter contributions to particulate matter, 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. Therefore, crustal matter should not be considered a natural source in urban settings.
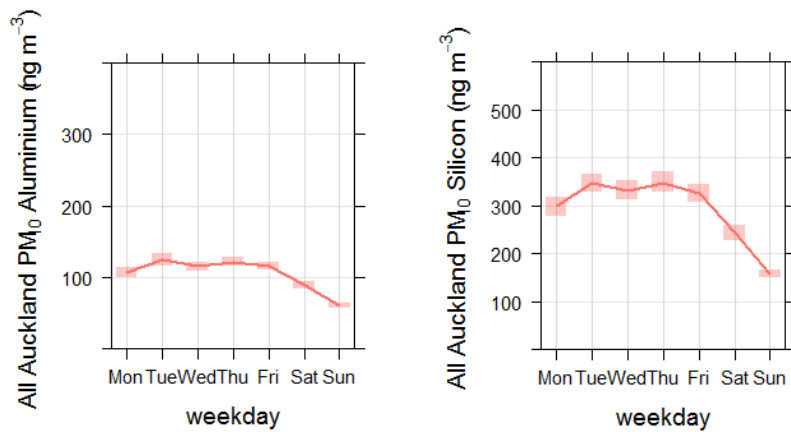
Figure 2.8   Week-day variations in (left) aluminium and (right) silicon in all Auckland PM_{10} samples (n = 9800, 2006–2022) (the shaded bars are the 95 percentile confidence limits in the mean).

Figure 2.9 shows the day-of-the-week dependence for crustal matter (soil) contributions to PM_{10} in Auckland and Hastings.
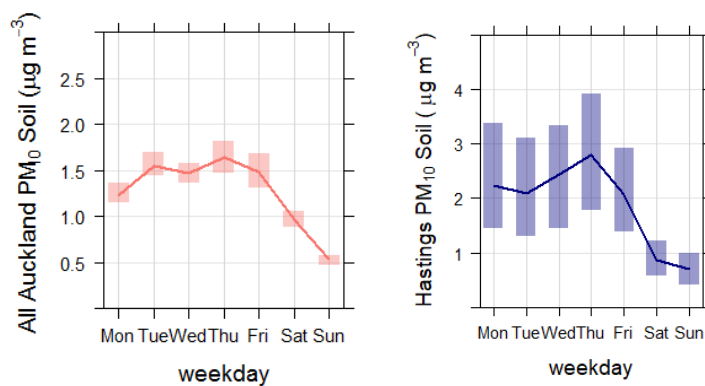
Figure 2.9   Temporal variations in crustal matter contributions for (left) Auckland PM_{10} (n = 9800 samples, 2006–2023) and (right) Hastings PM_{10} (n = 135 samples, 2022–2023) showing lower weekend concentrations (the shaded bars are the 95 percentile confidence limits in the mean).

An analysis of particulate matter compositional data from the Auckland Council background monitoring site at a rural location in Patumāhoe (40 km southwest of the Auckland CBD) found that crustal matter contributions peaked during autumn and were also significantly higher on weekdays than weekends (Davy et al. 2012a). In this case, the higher weekday soil contributions reflect the working-week activity of farm work (such as field ploughing and re-sowing of crops) compared to weekend days, therefore the generation of airborne soil particles was also associated with anthropogenic activities.

At monitoring sites in smaller urban centres, the crustal matter components are often integrated with the motor-vehicle source, as the turbulent passage of motor vehicles over local roads represents the dominant emission mechanism for re-suspension of crustal matter particles into urban atmospheres. Indeed, air pollution emissions (gases and particles) associated with motor vehicles all have higher concentrations on weekdays than weekends due to behavioural factors such as workday commuting and commercial vehicle activity (Boamponsem et al. 2024). An analysis of wind speeds in urban settings suggests that wind-driven re-suspension of urban dusts only becomes significant at speeds greater than 10 m/s (36 km/hr) (Banari et al. 2023).

However, high crustal matter concentrations can cause exceedances of the PM_{10} NESAQ as a result of transboundary incursions driven by extreme dust storm events in Australia. A specific dust event that resulted in PM_{10} 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. 2011a), the influence of which can be seen in the time-series plots for Al and Si in all Auckland PM_{10} samples presented in Figure 2.10. A more recent event in December 2019 was captured by sampling in Wellington, which caused widespread PM_{10} NESAQ exceedances or elevated concentrations across large areas of the country (Davy and Trompetter 2021). Such transboundary events are recognisable by region-wide correlated increases in measured particulate matter concentrations and can be tracked by satellite imagery (Davy and Trompetter 2021).
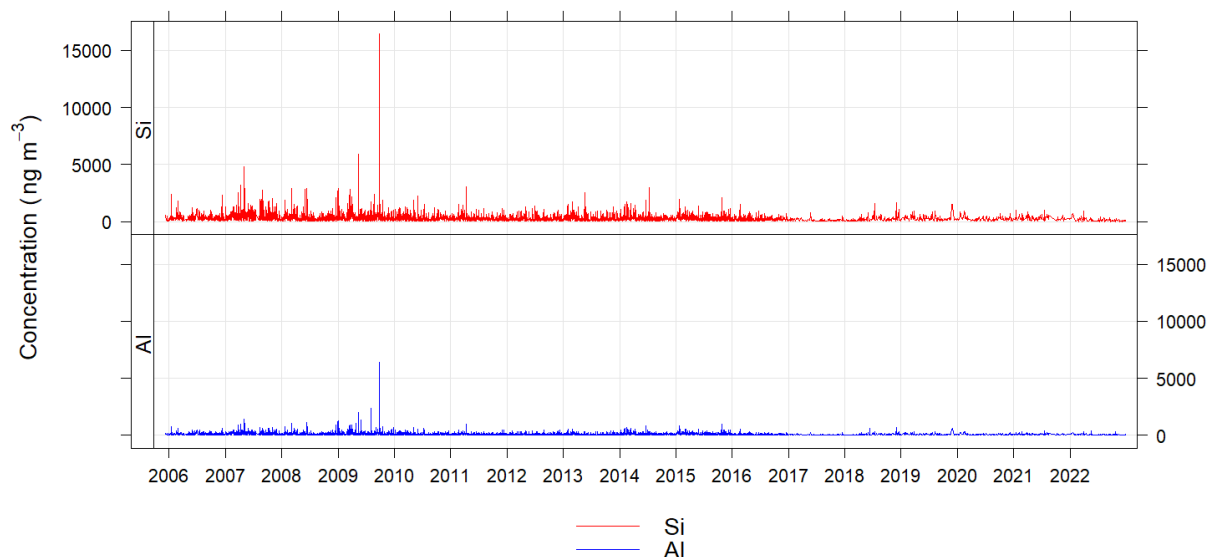
Figure 2.10   Time-series plots for aluminium and silicon in all Auckland PM_{10} samples (n = 9800). Peak concentrations in September 2009 are linked to a dust storm in the Australian desert.

2.4.4 Nitrogen-Containing Aerosol (Natural and Anthropogenic)

Several studies of background inorganic nitrogen-containing aerosol in the Southern Ocean and coastal locations around New Zealand (Kristament et al. 1993; Allen et al. 1997; Wylie and de Mora 1996; Ooki et al. 2007) provide baseline concentrations that are likely to impact across the New Zealand landmass as part of the west to east flow in Southern Hemisphere circulation patterns. Most nitrogenous aerosol was measured as ionic nitrate (NO_3^-) and ammonium (NH_4^+) species, with much of the nitrate present as ammonium salt ($NH_4 NO_3$) (Allen et al. 1997). Figure 2.11 provides a summary of nitrate concentrations measured at New Zealand coastal locations, showing that average concentrations range between 50 and 150 ng m^{-3}.
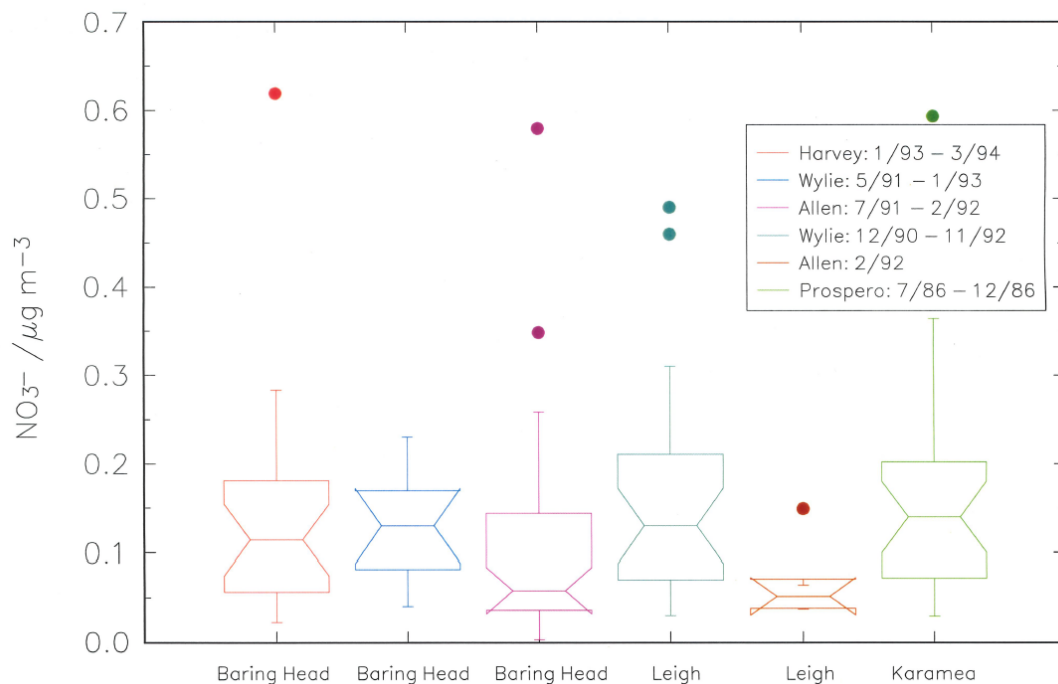
Figure 2.11   Nitrate aerosol concentrations measured at New Zealand coastal locations (Source: MJ Harvey, NIWA).

As a result of sampling campaigns during ship-based voyages across the South Pacific, Jung et al. (2011) found that inorganic nitrogen in aerosols was composed of approximately 32% NO_3^- and 68% NH_4^+, as ammonium ions are also an important component of inorganic sulphate aerosol species [as $(NH_4)_2SO_4$]. Average ammonium ion concentrations in background oceanic air at Baring Head and the Southern Pacific were found to range between 50 and 80 ng m^{-3}, with maximum concentrations during summer (Allen et al. 1997; Ooki et al. 2007; Jung et al. 2011).

2.4.4.1 Monitoring of Nitrogen Aerosol at Urban Locations

There have been relatively few urban monitoring studies in New Zealand that have included nitrogen aerosol, with most being short-duration campaigns. This is partly because of challenges in effective sampling of nitrate aerosol due to its thermodynamic stability and physiochemical properties but primarily due to an urban focus on anthropogenic combustion sources (motor vehicles, fossil fuels, biomass), as those most likely to be responsible for urban air-pollution events. The studies of nitrate aerosol concentrations that have been conducted at various locations do allow for some generalisations about ambient concentrations, seasonality and origins of nitrate and ammonium species in urban areas.

In a series of short-term monitoring campaigns at Auckland and Christchurch between 2000 and 2004, Wang and co-workers analysed and collected particulate matter for nitrate and ammonium species, amongst other parameters. Table 2.1 presents average nitrate and ammonia concentrations in the two cities. It was found that, in general, nitrate was highest during winter at Christchurch and this was ascribed to emissions from solid-fuel (wood) fires for home heating (Wang and Shooter 2001, 2005; Wang et al. 2005).

Table 2.1   Average (numbers in brackets are the maximum) concentrations of nitrate and ammonium species at Auckland and Christchurch (ng m^{-3}) (Source: Wang et al. 2005).

Species (ng m^{-3})	Auckland	Christchurch
Nitrate	233 (1170)	734 (1670)
Ammonium	84 (290)	270 (960)

2.4.4.2   Takapuna, Auckland

Nitrate concentrations were determined as part of a PM$_{2.5}$ dataset from an Auckland Council monitoring site at Takapuna on the North Shore (Davy et al. 2017). Sample collection for analysis, including nitrate and ammonium species, was from January 2009 to December 2013 (Selleck and Keywood 2012). Data for nitrate and ammonium at the Takapuna site show average concentrations of 150 and 106 ng m^{-3}, respectively. When the seasonality of concentrations was examined (Figure 2.12), it showed that ammonium ion concentrations have a summer peak and winter minimum, while, conversely, nitrate had a small winter maximum, which suggests differing sources for the two species.
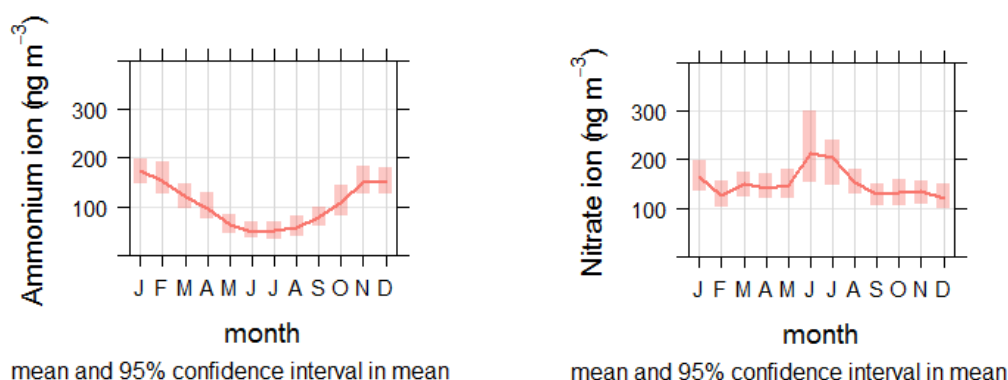
Figure 2.12   Monthly average concentrations for (left) ammonium and (right) nitrate at the Takapuna site.

Analysis of the Takapuna data by receptor modelling techniques was used to apportion the sources of PM$_{2.5}$ (Davy et al. 2017). It showed that most of the ammonium was associated with secondary sulphate aerosol formed from gas-to-particle atmospheric chemical reactions. Nitrate concentrations at Takapuna were found to be dominated by a secondary aerosol source (analogous to the secondary sulphate production mechanism) that may be due to anthropogenic precursor combustion gases (dominated by motor vehicle nitrogen oxide emissions). However, it could also be representative of the oceanic background, given the nitrate concentration associated with this source is around 90 ng m^{-3}.

2.4.4.3   Timaru, Canterbury

A study of PM$_{2.5}$ sources carried out in Timaru from May 2006 to May 2007 also analysed for nitrate and ammonium aerosol species amongst a range of other variables (Scott and Scarrott 2011). Analysis of the Timaru data by receptor modelling techniques (Scott 2014) indicates

that three primary sources of nitrate – biomass burning, motor vehicles and secondary aerosol ammonium nitrate – dominated nitrate concentrations. Average nitrate concentrations at Timaru (493 ng m^{-3}) were significantly higher than Takapuna, Auckland (150 ng m^{-3}), but, as the monitoring periods were not coincident, there can be no direct comparison between the results. When the seasonality of the Timaru nitrate sources was examined, it showed that the biomass burning source was mainly present during the winter months due to the association with solid fuel fires for home heating and that the motor vehicle contribution was at low levels across all months, while the ammonium nitrate source had higher but variable concentrations all year, as shown in Figure 2.13.
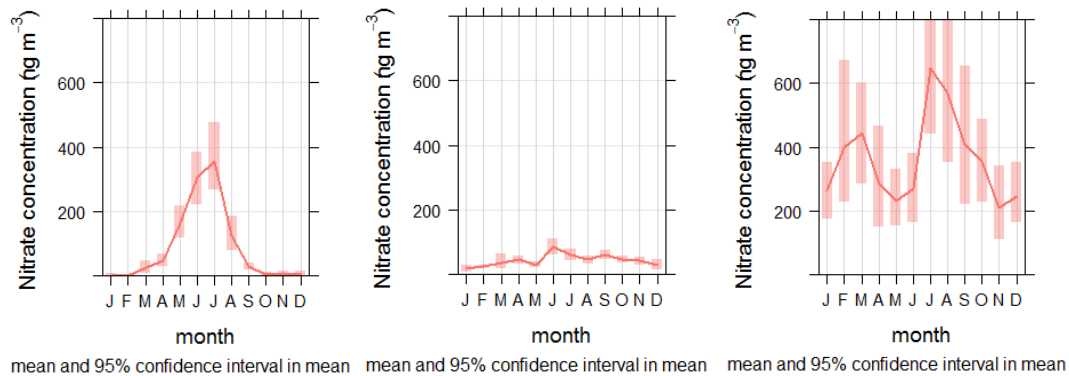
Figure 2.13   Monthly average nitrate concentrations associated with (left) biomass burning, (middle) motor vehicles and (right) ammonium nitrate sources at Timaru.

2.4.4.4   Tokoroa, Waikato

A particulate matter monitoring programme was conducted from May to October 2014 at Tokoroa in order to assess the sources contributing to high winter concentrations of particulate matter pollution (Ancelet and Davy 2015). Nitrate and ammonium species were measured as part of the programme. Receptor modelling of the data found that the nitrate was associated with biomass combustion, secondary sulphate, ammonium nitrate and a minor component with marine aerosol (sea salt). Most of the measured ammonium (92%) was associated with the ammonium nitrate source. Biomass combustion, a major contributor to ambient nitrate concentrations during winter in Tokoroa, represents emissions from solid fuel (wood) fires for home heating and was the primary particulate matter source in the town.

Due to the brevity of the Tokoroa study (winter 2014), it was uncertain as to the exact source of the ammonium nitrate. The study indicated that the ammonium nitrate source contributions peaked under low wind speeds from the north and that it was possible that agricultural emissions, associated with pasture and livestock, were responsible for elevated ammonium nitrate contributions. However, contributions from oceanic background nitrate cannot be ruled out, given that the average concentration of the ammonium nitrate source was 117 ng m^{-3} and was of the same order as those nitrate concentrations for oceanic and background sites.

2.4.4.5   Summary of New Zealand Nitrogen Aerosol Sources

Coastal background and open-ocean monitoring provide an indication of ubiquitous nitrogen aerosol concentrations at New Zealand sites that range between 50 and 80 ng m^{-3}, with maximum (200–600 ng m^{-3}) concentrations during winter. Land-based concentrations from this background are likely to be modified by topographic (orographic) features analogous to marine aerosol (sea salt) data.

Ambient air-quality monitoring at urban sites shows that the primary source of gaseous nitrogen oxides (NOx) are motor vehicles and industrial (combustion) point-source emissions. Urban particulate nitrogen (nitrate, ammonium) was found to be primarily from secondary formation (anthropogenic and natural origin gaseous precursors). Winter peaks in aerosol nitrate coincide with biomass combustion peaks in urban areas, while the relative contribution of rural emission sources to these loadings is unclear from the urban monitoring data. However, it is likely that there is some influence from rural production.

2.4.5 Other Sources of Natural Aerosol

Organic aerosol, secondary organic aerosol (SOA) and biological particles (plant detritus, fibres, bacteria, virus, pollen and spores) from both terrestrial and oceanic sources contribute to atmospheric aerosol concentrations, but relatively little information is available in terms of the total contribution of these sources to New Zealand urban concentrations.

Terrestrial plants emit large quantities of biogenic volatile organic compounds (BVOCs), which play an important role in tropospheric chemistry (Atkinson and Arey 2003). Many BVOCs undergo chemical reactions to form secondary organic aerosols. Emissions of BVOCs are strongly dependent on plant species and meteorological conditions. Few studies have measured BVOC emissions from plants in New Zealand (Effah et al. 2020, 2021), and very little is known about New Zealand's BVOC emission inventory as a whole or the composition of secondary organic aerosols in New Zealand (Paton-Walsh et al. 2022). Given these large knowledge gaps, we do not attempt to quantify secondary organic aerosol over New Zealand but identify it as an area for future investigation.

2.5 Natural-Source Concentration Data Currently Available for New Zealand

Tables 2.2 and 2.3 present the measured mean and maximum natural-source concentration data for $PM_{2.5}$ and PM_{10}, respectively, at locations where there has been at least one year of monitoring to cover any seasonality in source contributions. For comparative purposes, the nitrate aerosol concentrations have been included in the $PM_{2.5}$ table for the three sites where data are available. In the previous sections, the most likely natural-source contributors to particulate matter concentrations at New Zealand airsheds were discussed. It is clear from the data that all sea salt can be considered as a natural source of aerosol. While secondary sulphate and nitrate aerosol have both natural and anthropogenic origins, the similarity in mean concentration data for secondary sulphate across multiple locations (both inland and coastal), presented in Tables 2.2 and 2.3, indicates that the greatest influence on average concentrations is from natural sources, particularly since the reduction of sulphur in automotive fuels. However, urban crustal matter was found to be largely anthropogenic for the purposes of air-quality management, as discussed in Section 2.4.3. Figures 2.14 and 2.15 present the data as box and whisker plots. Note that the monitoring periods vary from site to site; full details on monitoring sites and sample periods are presented in Appendix 1.

The data shows that exposed coastal locations are likely to have higher average and peak PM_{10} marine aerosol concentrations, while $PM_{2.5}$ marine and secondary sulphate aerosol concentrations are more uniform across the country, even for inland locations (e.g. Tokoroa or Masterton). This suggests that there is a common mechanism for size fractionation (i.e. loss of the coarse particles or $PM_{10-2.5}$) for natural aerosol observed at inland locations. Further discussion on the mechanisms for this process is presented in Section 3.

Table 2.2   Measured natural-source contributions (24-hour average) to PM2.5 at New Zealand monitoring sites (n = 6680 samples).

Regional Council Monitoring Site	PM2.5 Marine Aerosol		PM2.5 Secondary Sulphate		PM2.5 Secondary Nitrate (as NH4NO3)	
	Mean (µg m⁻³)	Maximum (µg m⁻³)	Mean (µg m⁻³)	Maximum (µg m⁻³)	Mean (µg m⁻³)	Maximum (µg m⁻³)
AC Queen Street	1.8	12.4	1.0	7.4	-	-
AC Takapuna	2.1	12.5	0.9	4.8	0.19	1.5
AC Khyber Pass Road	1.2	11.1	0.9	6.2	-	-
AC Patumahoe	0.9	5.1	1.0	6.3	-	-
WRC Tokoroa	1.6	8.0	0.8	7.1	0.03	0.09
HBRC Napier	1.2	6.6	1.2	8.8	-	-
HBRC Awatoto	1.2	7.4	0.9	5.2	-	-
HBRC Hastings	1.7	11.5	1.1	5.4	-	-
GWRC Masterton East	1.2	6.2	0.7	11.0	-	-
GWRC Seaview	1.1	5.7	1.1	4.5	-	-
GWRC Wainuiomata	1.4	10.0	1.1	8.2	-	-
GWRC Willis Street	2.1	12.6	1.0	5.0	-	-
NCC Nelson	1.1	9.2	1.0	3.8	-	-
TDC Richmond	1.3	10.8	0.9	5.4	-	-
TDC Motueka	0.8	6.0	0.4	2.2	-	-
ECAN Christchurch	1.8	9.0	1.0	7.5	-	-
ECAN Timaru	0.8	8.5	0.7	4.2	0.7	2.7
ORC Dunedin	1.1	7.4	1.7	6.5	-	-

Table 2.3   Measured natural-source contributions (24-hour average) to PM_{10} at New Zealand monitoring sites (n = 12,340 samples).

Regional Council Monitoring Site	PM_{10} Marine Aerosol		PM_{10} Secondary Sulphate	
	Mean ($\mu g\ m^{-3}$)	Maximum ($\mu g\ m^{-3}$)	Mean ($\mu g\ m^{-3}$)	Maximum ($\mu g\ m^{-3}$)
AC Queen Street	7.2	30.8	0.9	15.1
AC Takapuna	6.7	42.1	1.8	17.3
AC Khyber Pass Road	7.5	35.0	1.5	20.8
AC Penrose	6.5	28.5	1.1	8.6
AC Henderson	6.5	29.0	1.4	14.1
AC Patumahoe	5.3	18.6	1.0	6.3
WRC Tokoroa	3.5	18.0	1.2	10.7
HBRC Napier	4.4	17.7	2.0	12.9
HBRC Awatoto	8.6	40.1	1.2	8.2
HBRC Hastings	6.0	30.6	2.0	9.0
GWRC Masterton	3.8	16.9	0.6	2.3
GWRC Upper Hutt	3.8	8.9	1.2	3.7
GWRC Seaview	6.4	21.7	2.4	6.2
GWRC Wainuiomata	5.2	23.0	1.1	8.2
GWRC Willis Street	7.2	34.6	1.6	8.5
MDC Blenheim	2.0	13.6	1.0	4.2
NCC Nelson	3.7	22.2	2.2	8.9
NCC Tahunanui	3.8	21.4	1.3	5.9
TDC Richmond	2.7	20.9	2.3	9.1
ECAN Christchurch	7.1	33.7	2.3	16.9
ORC Dunedin	4.9	25.8	1.7	6.5
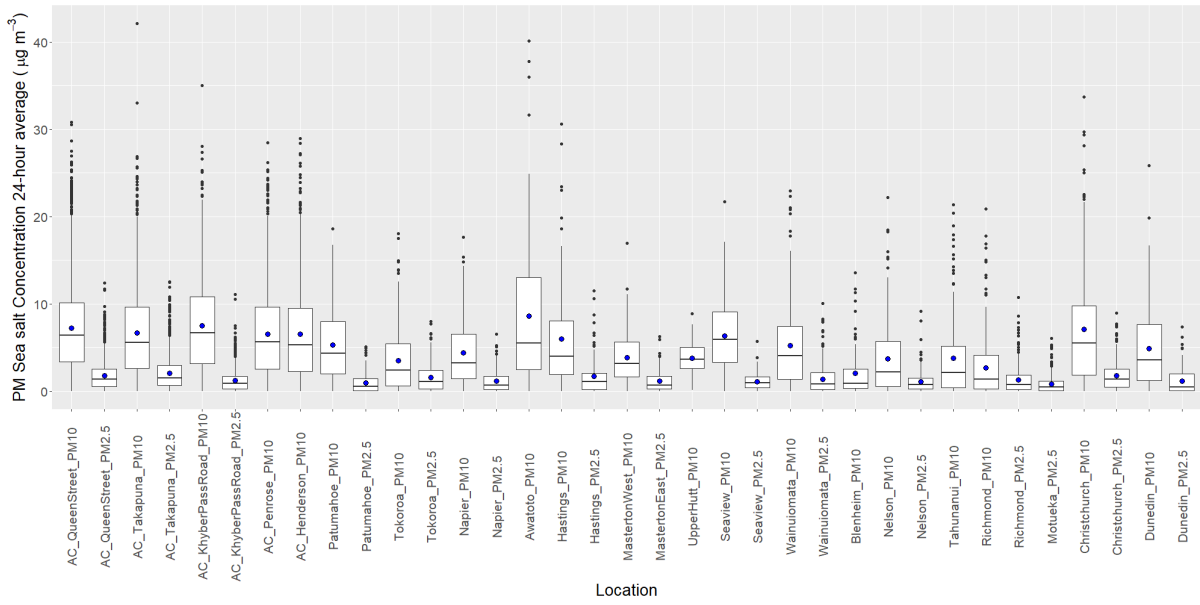
Figure 2.14   Box plots for sea-salt contributions to PM_{10} and $PM_{2.5}$ at New Zealand monitoring locations.
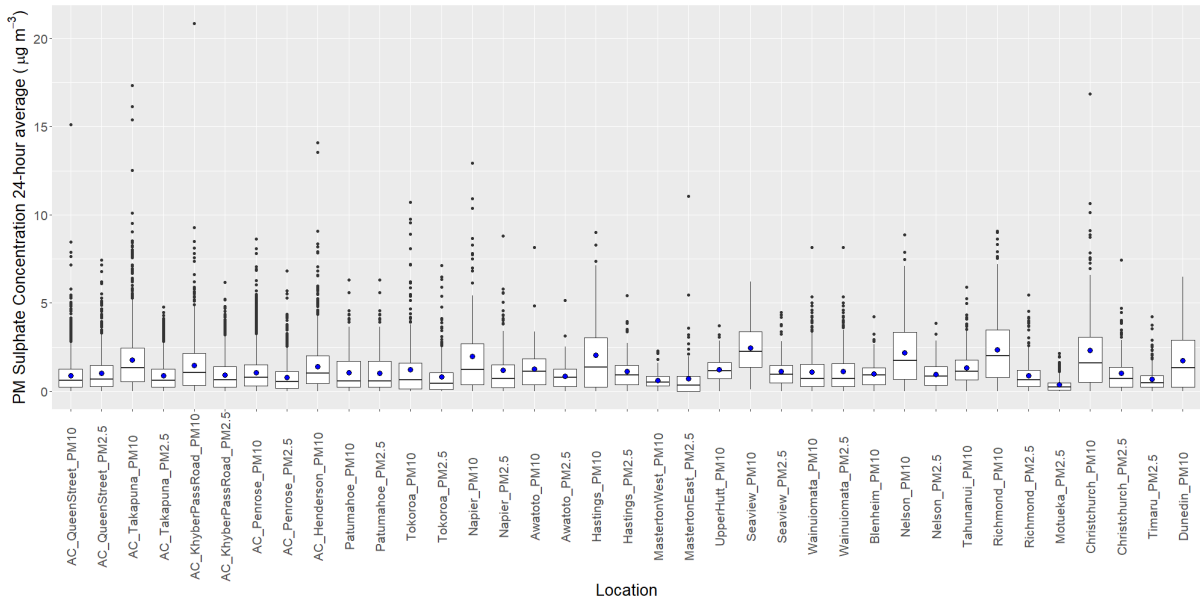
Figure 2.15   Box plots for secondary sulphate contributions to PM_{10} and $PM_{2.5}$ at New Zealand monitoring locations.

2.6 Natural-Source Particle Size Ranges and the Contribution to Regulatory Size Fractions (PM$_{2.5}$, PM$_{10}$)

Several features are evident from the data presented in Section 2.5. The first is that marine aerosol was the most significant natural-source contributor to urban particulate matter concentrations and contributes significantly more to the coarse particle mode (PM$_{10-2.5}$) than PM$_{2.5}$ due to the nature of sea-salt particle formation. The mean ratio of marine aerosol contribution to PM$_{10}$ compared to PM$_{2.5}$ ranged from 2 to 7 depending on the location of the monitoring site. The distance that the marine aerosol has travelled results in size fractionation, as larger particles settle out of the atmosphere sooner due to gravitational effects.

While the gas-to-particle reaction pathway in the atmosphere produces fine particles, some of the sulphate particle size range does extend into the coarse fraction (Anlauf et al. 2006), particularly where heterogeneous atmospheric chemistry takes place on the surface of particles (such as marine aerosol) or in aerosol droplets during the reaction of gaseous sulphur species to form secondary sulphate particle species (Gard et al. 1998; O'Dowd et al. 2000; George and Abbatt 2010). The evidence for some heterogenous particle formation in the New Zealand sample set is based on the inclusion of Na, Mg, K and Ca in the secondary-sulphate-source chemical profiles, indicating that the heterogenous chemistry probably takes place on sea-salt particles, and therefore secondary sulphate concentrations were slightly higher in PM$_{10}$ than PM$_{2.5}$ (mean ratio = 1.6)

None of the natural-source contributions in the samples exceeded either the PM$_{2.5}$ WHO Ambient Air Quality Guidelines (15 µg m^{-3}, 24-hour average) or PM$_{10}$ NESAQ (50 µg m^{-3}, 24-hour average). When the sum of marine aerosol and secondary sulphate contributions to the same samples were calculated across the datasets, none of these values exceeded the respective standard or guideline value:

- **PM$_{2.5}$ sum of natural-source contributions:** mean = 2.2 µg m^{-3}, maximum (Hastings 23 Jan 2023) = 14 µg m^{-3}.

- **PM$_{10}$ sum of natural-source contributions:** mean = 6.5 µg m^{-3}, maximum (Takapuna Jan 2012 = 42 µg m^{-3}).

The data clearly shows that it is unlikely that both secondary sulphate and marine aerosol concentrations will peak at the same time, as these are due to differing atmospheric processes (generation of maximum natural aerosol concentrations) and air-mass transport mechanisms that deliver the aerosol to urban atmospheres.

2.7 Trend Analysis for Natural-Source Contributions to Particulate Matter

For all statistical analyses presented in this report, the *openair* package based on 'R' statistical software has been used to analyse the data for trends (R Core Team 2010; Carslaw 2012; Carslaw and Ropkins 2012). For the trend analysis, the TheilSen function in *openair* was used (Carslaw 2012). The analysis of trends in the particulate matter concentration and source contribution data are accompanied by confidence interval estimates for the observed trends.

The calculation of trends in natural-source data are only possible for longer-term datasets and were therefore limited to those for Auckland, Wainuiomata and Nelson. As presented in Figures 2.16 and 2.17 for the marine aerosol source, concentrations were found to decrease in Auckland and Wellington while, in Nelson, there was no trend evident. Note that, at the top of the trend graphs, the first number is the trend (e.g. decreasing at -0.09 ug/m^3/year), the numbers in brackets are the range (dotted red lines) and the asterisks signify the confidence interval (significant to the 99th percentile for Figure 2.16).

The trend for the Auckland data appears to be driven by $PM_{2.5}$ marine aerosol concentrations (Boamponsem et al. 2024). As sea-salt-aerosol generation is meteorologically driven, it would be expected to be steady-state over the longer term. However, it is possible that inter-decadal oscillations in atmospheric surface-level wind speeds and circulation patterns or a warming climate (see Section 4) could change the amount of marine aerosol delivered to specific locations. This subject area would need to be explored further to determine the likely drivers for the observed trends.
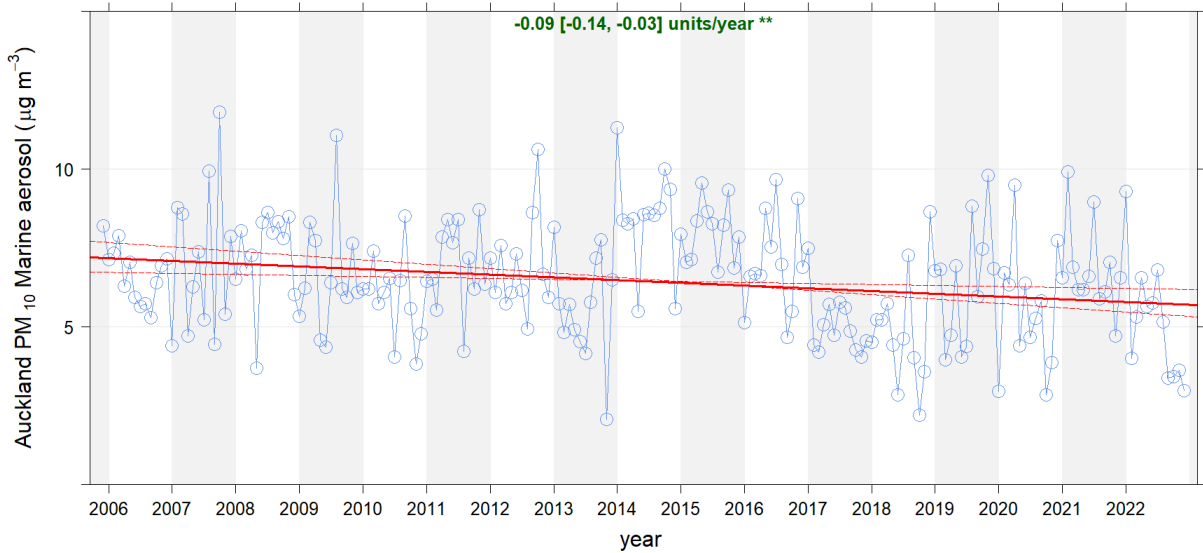
Figure 2.16   Long-term trends in PM_{10} marine aerosol source contributions across all Auckland monitoring sites, showing that concentrations have decreased (statistically significant at the 99% confidence interval).
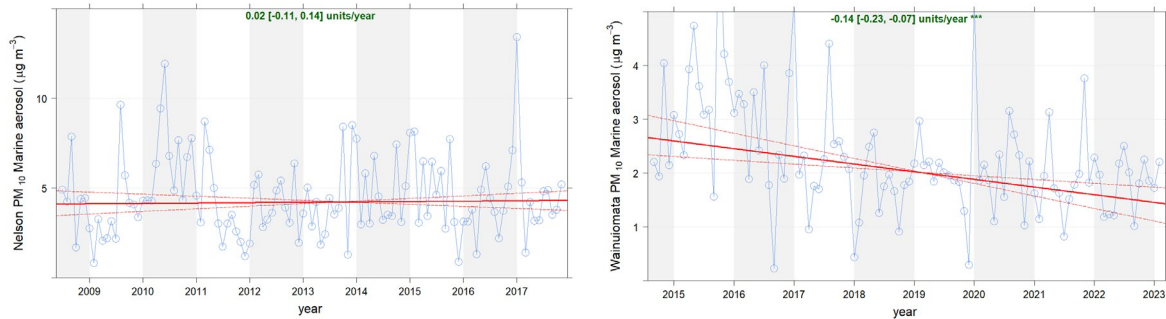
Figure 2.17   Long-term trends in PM_{10} marine aerosol source contributions at the monitoring sites for (left) Nelson, showing no statistically significant trend, and (right) Wainuiomata, showing that concentrations have decreased (statistically significant at the 99.9% confidence interval).

The long-term trends for sulphate aerosol (Figures 2.18 and 2.19) also show a decrease in urban environments. The desulphurisation of automotive fuels has driven a significant decrease in the resulting secondary sulphate from 2006 to 2011, as described in Section 2.4.2, and this can be expected to continue for port locations as shipping emissions of sulphur are also reduced, for example, under the MARPOL Annex VI agreements[5]. It is therefore difficult to separate out the underlying trends in natural-source contributions to sulphate aerosol, but any such trends will be related to marine phytoplankton production, as well as volcanic and geothermal activity.

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5   https://www.transport.govt.nz/area-of-interest/maritime-transport/marpol/
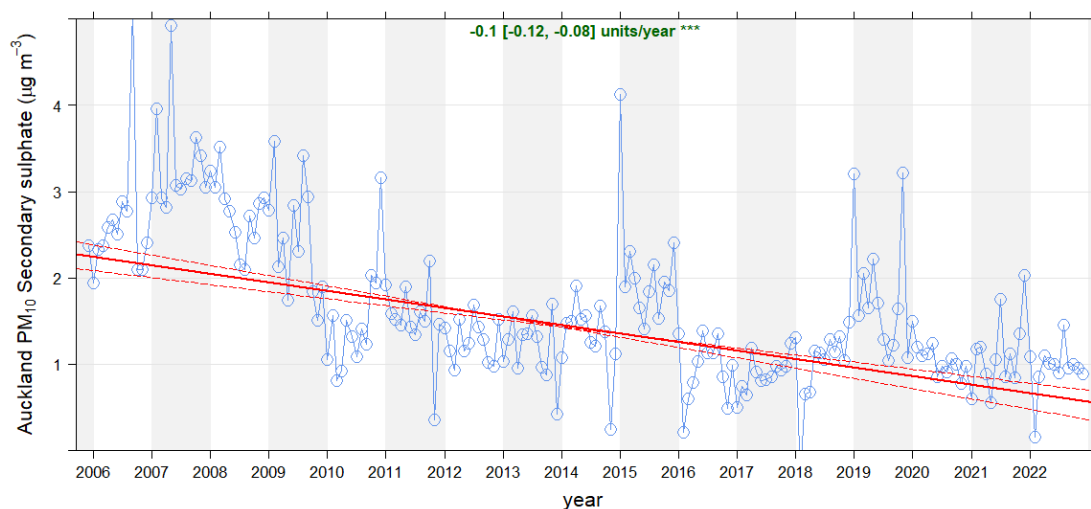
Figure 2.18   Long-term trends in PM_{10} secondary sulphate source contributions across all Auckland monitoring sites, showing that concentrations have decreased (statistically significant at the 99.9% confidence interval).
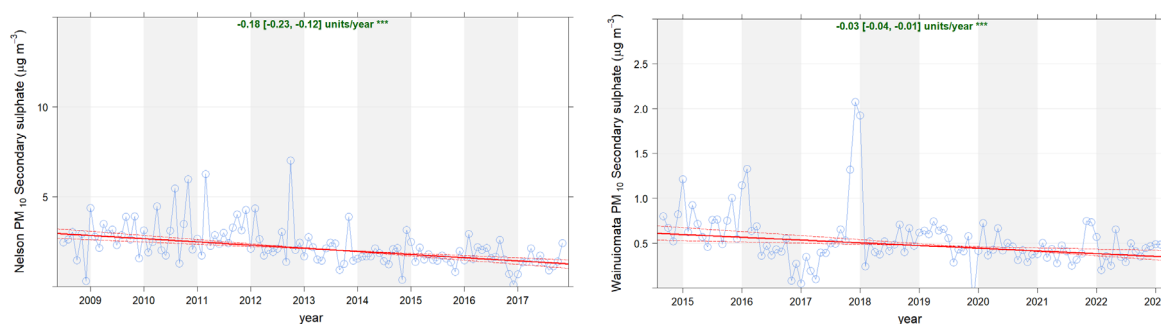
Figure 2.19   Long-term trends in PM_{10} secondary sulphate source contributions at the monitoring sites for (left) Nelson and (right) Wainuiomata, showing that concentrations have decreased at both locations (statistically significant at the 99.9% confidence interval).

2.8   Summary Findings

Marine aerosol (sea salt) and secondary aerosol were found to be the most significant natural sources of particulate matter in New Zealand urban areas. Secondary sulphate dominates the secondary aerosol contribution, with secondary nitrate species likely to be present at lower (five to ten times less) concentrations. Secondary sulphate data shows that average concentrations are relatively similar for large and small urban areas, whether they are inland or coastal, indicating that it is predominantly of natural origin and likely associated with long-range air-mass transport. Apart from transboundary events associated with Australian desert dust storms, crustal matter (soil) in urban locations was primarily associated with anthropogenic emissions, and its presence in urban atmospheres is not regarded as being emitted by natural processes. There is a lack of data on biogenic organic aerosol components and the relative contributions to urban particulate matter concentrations.

While the monitoring periods and timeframes differ across urban locations, the data for natural-source contributions presented in Tables 2.2 and 2.3 show that 24-hour average marine aerosol and secondary sulphate contributions to $PM_{2.5}$ are reasonably uniform across the country for both coastal and inland locations, suggesting that both sources are the result of long-range transport rather than localised emission sources. There is more variability for marine aerosol contributions to PM_{10}, with coastal locations experiencing higher concentrations than those monitoring locations further inland, and this is likely to be due to topographical sheltering effects (wet and dry deposition) for the coarse (and heavier) particle fraction.

3.0 ESTIMATION OF NATURAL-SOURCE CONTRIBUTIONS TO PARTICULATE MATTER IN NEW ZEALAND AIRSHEDS

There are 73 gazetted airsheds across the 12 regional council and four unitary authority territorial areas.[6] There is at least some natural-source contribution data available for all but two regions (Taranaki and Manawatū-Whanganui) and one district (Gisborne), but not all gazetted airsheds. A methodology has therefore been developed to extrapolate the natural-source contribution data and observations to provide an estimate for all airsheds.

Previously, an empirical model was developed using existing receptor modelling data to help define source contributions at those locations where particulate matter concentration monitoring data ($PM_{2.5}$ and PM_{10}) is available, but there was no breakdown by source contributions (Davy and Trompetter 2020b). The empirical model was found to reproduce the peak winter contributions from biomass combustion (wood burning) for residential space heating when compared to the source apportionment data for the same locations. Additionally, it was found that the source apportionment data for motor-vehicle emissions were well correlated with metrics that describe motor-vehicle activity (e.g. emissions density, traffic volumes or vehicle kilometres travelled) (Kuschel et al. 2022).

Further development of the empirical model has included the attribution of non-exhaust emissions in urban areas (Somervell et al., in prep.). The remainder $PM_{2.5}$ and PM_{10} not ascribed to the sources above was attributed to natural sources (Kuschel et al. 2022). The results were such that there was confidence that the empirical model can be used to estimate monthly and annual average contributions at those locations where $PM_{2.5}$ and PM_{10} concentration monitoring data is available (but no breakdown by source) for use in health-effects studies (HAPINZ 3.0; Kuschel et al. 2022) or assessing winter particulate matter concentration trends (Davy and Trompetter 2022). The empirical model can also be applied to estimate annual average natural-source contributions in all airsheds.

The empirical model required the use of monthly and annual averages to smooth out the day-to-day variability in particulate matter concentrations. However, the contributions of natural sources to daily (24-hour) particulate matter concentrations are of interest due to the PM_{10} NESAQ and $PM_{2.5}$ WHO guideline. It was shown in Section 2 that the maximum and mean daily natural-source contributions to $PM_{2.5}$ are reasonably uniform across the country. However, contributions to PM_{10} were more variable, particularly for the marine aerosol PM_{10} contribution. The conclusion from Section 2 indicates that marine aerosol and secondary sulphate are likely long-range sources rather than local to a particular airshed given the similar contributions to $PM_{2.5}$ concentrations across multiple sites (coastal and inland), and the differential of inland versus coastal for coarse particulate matter was likely from wet and dry deposition effects. The following sections explore the meteorological and topographical mechanisms for such observations.

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6   https://data.mfe.govt.nz/layer/98617-nz-airsheds-gazetted/

3.1 Methodological Approach based on Measured Data and Air Mass Back-Trajectory Analysis

As a parcel of air moves across ocean and land, it's composition will be altered by emissions of particulate matter and gases as it does so. At the same time, those particles and gases may undergo chemical and physical transformation as described in Section 2, as well as being deposited out of the atmosphere by wet and dry deposition mechanisms. Air-mass back-trajectory analysis provides an understanding of the pathway that an air parcel takes before delivering the particulate matter within it to a receptor location. There are various statistical methods of analysing such pathways to extract the most likely location of an upwind emission source.

Potential source contribution function (PSCF) analysis is the conditional probability that an air parcel with a certain level of pollutant concentrations arrives at a receptor site after having passed through a specific upwind emission source region (Hsu et al. 2003; Hwang and Hopke 2007). The PSCF values were obtained using the source contributions derived from PMF analyses and air-mass back trajectories produced by the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model.[7] HYSPLIT is a computer model that is used to compute air-parcel trajectories to determine how far and in what direction a parcel of air, and subsequently air pollutants, will travel. $PSCF_{ij}$ is defined as:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}}$$

Equation 3.1

where n_{ij} is the total number of endpoints that fall in the ij^{th} cell and m_{ij} is the number of endpoints in the same cell that exceed a threshold criterion. For this study, the average contribution from each source was used as the threshold criterion. If a trajectory associated with a sample has a mass contribution higher than the criterion, then a high PSCF value in a cell (1° latitude and longitude or 100 km x 100 km) represents a potential source area. For this study, 96-hour (four days) backward trajectories were calculated every three hours (0, 3, 6, 9, 12, 15,18, 21, 24 UTC), starting at 100 m above ground level using the National Center for Environmental Prediction and National Center for Atmospheric Research global re-analysis data. The back-trajectory analysis and PSCF calculations were all conducted within the *openair* package (Carslaw 2012) and conducted for all datasets presented in Tables 2.2 and 2.3. Air-mass back-trajectories were also explored for several of the shorter-term (winter) receptor modelling studies, primarily those for Alexandra, Invercargill and Westport, to understand the source regions that led to peak natural aerosol concentrations during those studies. The PSCF analysis is not designed to capture local flows or urban emissions but rather the longer-range drivers of regional concentration gradients. The meteorological model resolution (1°x1°) may also have difficulty resolving near-field (adjacent-grid cell) emission sources. Therefore, the PSCF analysis for such locations should be interpreted with care, and other sources of information are required to support interpretation for these sites.

3.1.1 Marine Aerosol

In general terms, the PSCF analyses for sea salt showed that the primary source regions were the Tasman Sea, Southern Ocean and Pacific Ocean and were more likely to be further offshore (hundreds to thousands of kilometres) rather than closer to New Zealand coastal regions, as shown for the Auckland and Wellington data in Figures 3.1 and 3.2. Note that the map orientation is such that Antarctica (the South Pole) is at the map centre.

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7   https://www.arl.noaa.gov/hysplit/
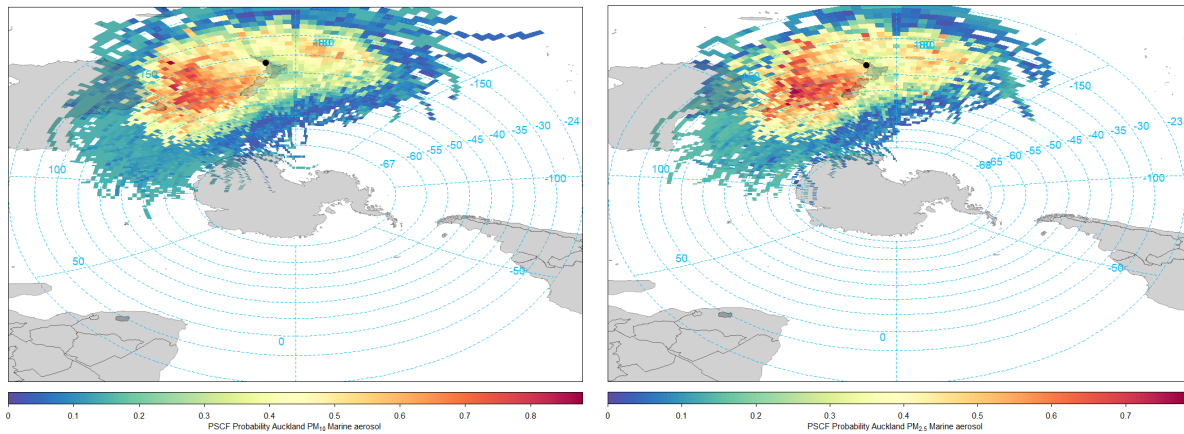
Figure 3.1   Air-mass back-trajectory and potential source contribution function analysis for Auckland marine aerosol source regions for (left) PM$_{10}$ samples (n = 6684, 2006–2022) and (right) PM$_{2.5}$ samples (n = 4405, 2006–2016).

The data presented for marine aerosol concentrations in Tables 2.2 and 2.3 show that Auckland and Wellington have similar average and peak (24-hour) values, and the PSCF value shows that the source regions are also similar. The primary source region represents an area of the southern Tasman Sea and Southern Ocean where there are high wind-field strengths and long oceanic fetches for substantial sea-salt generation by the mechanisms described in Section 2.4.1. Therefore, the delivery of that marine aerosol to Auckland or Wellington largely depends on the trajectory of the air mass once it has gathered the aerosol over that oceanic area. For Wellington, the influx of sea salt from the northeast does not appear to contribute significantly to mean concentrations in contrast to Auckland, which is likely due to topographical 'sheltering' (i.e. by wet and dry deposition of particulate matter) effects of the mountains and hills northeast of Wellington.
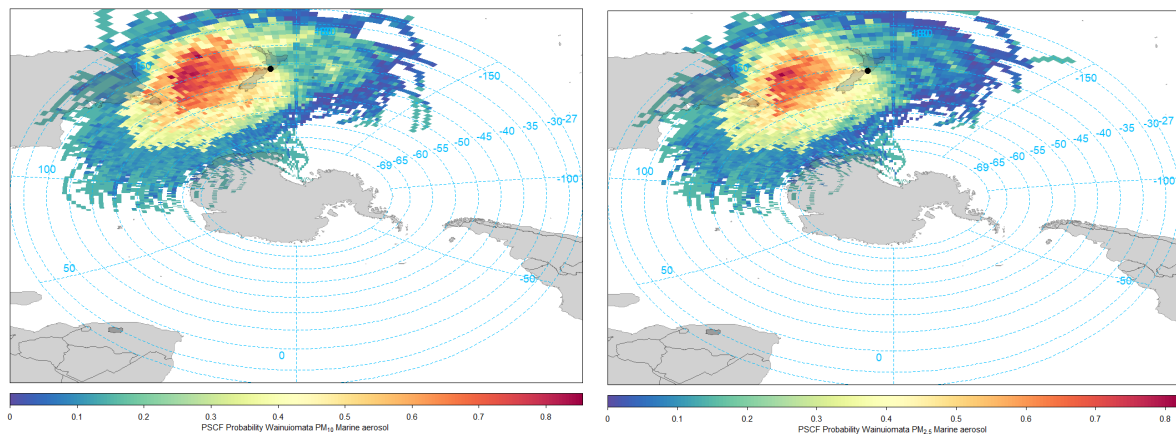
Figure 3.2   Air-mass back-trajectory and PSCF analysis for Wellington (Wainuiomata) marine aerosol source regions for (left) PM$_{10}$ samples (n = 4928) and (right) PM$_{2.5}$ samples (n = 4928).

Inland North Island locations, such as Tokoroa and Masterton, are less exposed to both the W-SW and E-NE onshore wind flows due to surrounding hills and mountains and therefore had lower mean and maximum marine aerosol concentrations. The PSCF analysis shows that the primary source regions for Tokoroa are the same as for the Auckland and Wellington regions, while, for Masterton, the back-trajectories that contribute to concentrations greater than the mean are more likely to approach from the south. Masterton is located in the Wairarapa Valley, surrounded by hills and mountains, but the valley opens out to the ocean to the south, providing the trajectory for unimpeded flow.
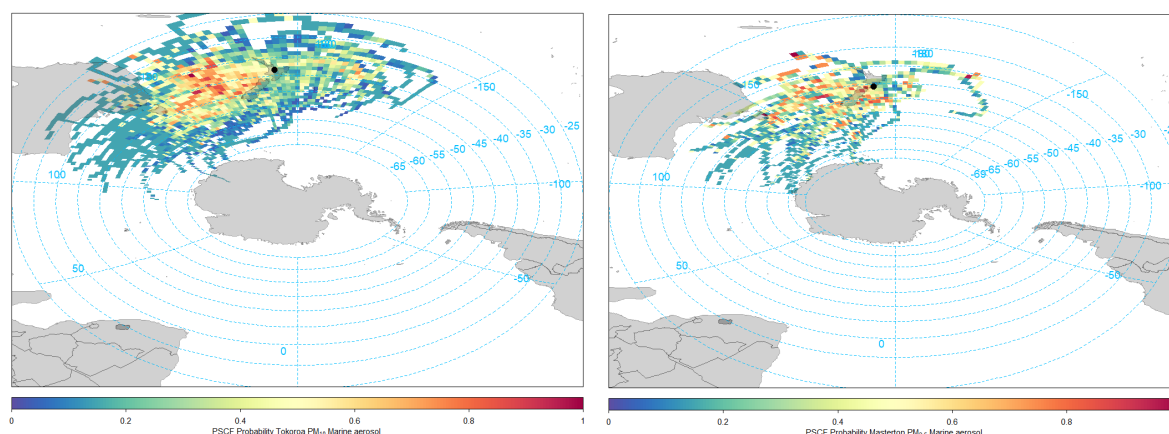
Figure 3.3   Air-mass back-trajectory and PSCF analysis for marine aerosol source regions for (left) Tokoroa PM$_{10}$ samples (n = 361) and (right) Masterton PM$_{2.5}$ samples (n = 180).

The Tokoroa PM$_{10}$ marine aerosol concentration data was matched with the Auckland marine aerosol concentration data, and it was found that the same-day sampling correlation was poor (R^2 = 0.6), likely due to the timing of air-mass trajectories. However, when the data was averaged on a weekly basis, it was found that there was a moderate correlation, as presented in Figure 3.4. This implies that the same air masses (with respect to marine aerosol) impact both locations but the concentrations are attenuated for Tokoroa (Tokoroa marine aerosol = 0.66 x Auckland marine aerosol), most likely due to particle loss from dry deposition and orographic rainfall (wet deposition) on the hills and mountains west of Tokoroa.
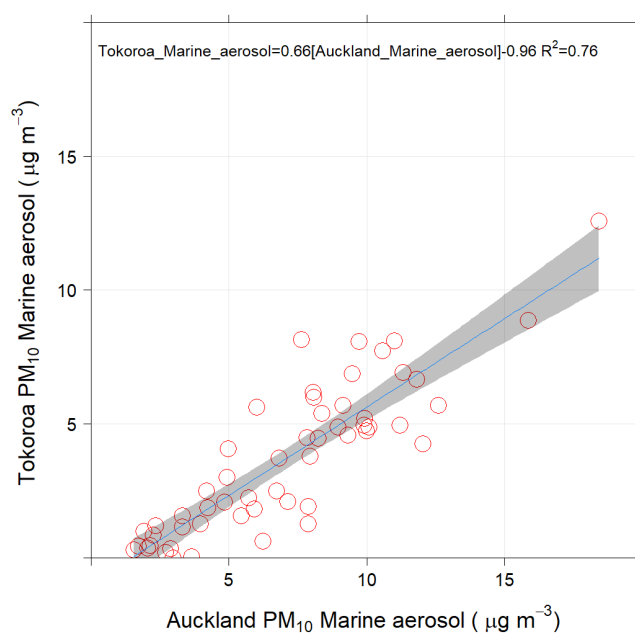
Figure 3.4   Weekly average Tokoroa PM$_{10}$ versus Auckland PM$_{10}$ marine aerosol concentrations, showing that these are moderately correlated (R^2 = 0.76).

The Nelson City, Tahunanui and Richmond monitoring sites are within a 5 km radius of each other, and all have similar PM$_{10}$ and PM$_{2.5}$ marine aerosol contributions to total particulate matter concentrations, as presented in Tables 2.2 and 2.3, with mean PM$_{10}$ marine aerosol concentrations about half of those for Auckland and Wellington. Sea-salt concentrations at the Nelson City and Tahunanui monitoring sites have previously been shown to be highly correlated at the same concentration ratios (Ancelet et al. 2013a). The PSCF for the Nelson data (Figure 3.5) shows a more northwest source region compared to Auckland and Wellington.
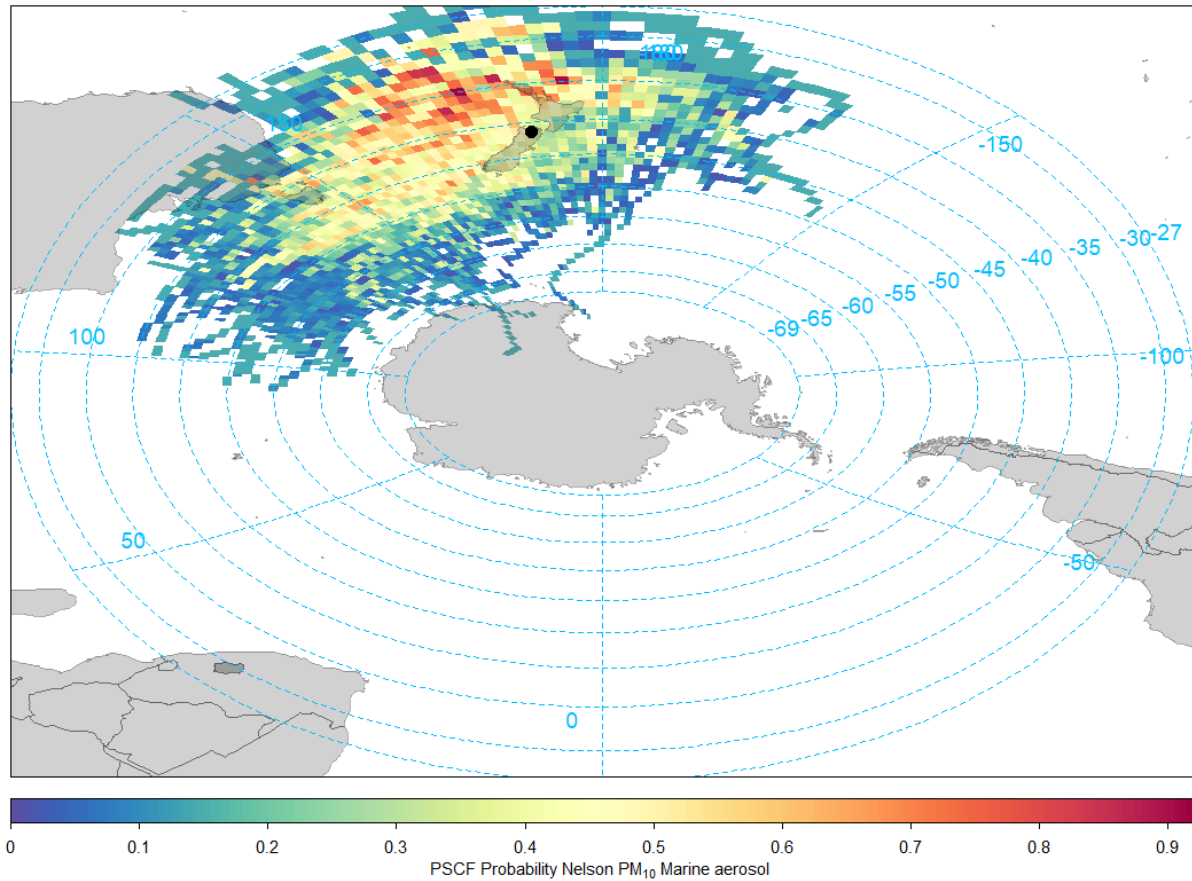
Figure 3.5   Air-mass back-trajectory and PSCF analysis of marine aerosol source regions for Nelson PM_{10} samples (n = 824).

Bivariate polar plots, based on local meteorology combined with source concentration data, can be used to show from which direction the highest concentrations arrive at a monitoring site. Using bivariate polar plots, source contributions can be shown as a function of both wind speed and direction, providing invaluable information about potential source locations.

Conditional Probability Function (CPF) analysis provides a method to find the directions for which high values of source contributions are likely to be related (Ashbaugh et al. 1985). The probability that a source contribution originates from a given wind direction is estimated by comparing the wind direction distribution for the upper 25% of source contributions relative to the total wind direction distribution.

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

where:

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

- $n_{\Delta\theta}$: total number of occurrences from the same wind sector.

Sources are likely to be located in the directions that have high CPF values. To produce the polar plots, wind speeds and directions were vector-averaged using functions available in *openair*. A full description of the vector averaging process can be found in Carslaw (2012).

The CPF plot for Richmond data shows that the highest 25% of sea salt arrives from the northeast sector (Figure 3.6) (Davy and Trompetter 2017b). Because of the smoothing involved, the colour scale is only to provide an indication of overall pattern and should not be interpreted in concentration units.

CPF Polar Plot PM$_{10}$ Marine aerosol Source (TDC Office Met)

CPF at the 75th percentile (=4.1)
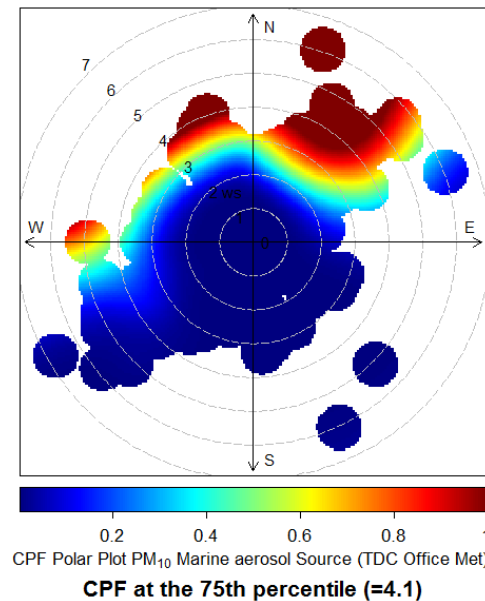
Figure 3.6   Bivariate polar plot of marine aerosol contributions to PM$_{10}$ concentrations at Richmond, Tasman District. The radial dimensions indicate the wind speed in 1 m s^{-1} increments, and the colour contours indicate the average contribution to each wind direction/speed bin.

The Nelson and Tasman districts are sheltered from the general west to southwest wind flows by the Papamoa and Tasman Mountain ranges and from the southeast and east by the Richmond and Kaikoura Mountain Ranges, but the area is open to Tasman Bay, which faces northeast. This explains why the highest marine aerosol concentrations arrive from the northeast for these sites, including Motueka (Figure 3.7), which is located across Tasman Bay from the Richmond and Nelson sites (Davy and Trompetter 2023).

CPF Polar Plot Motueka Marine aerosol

CPF at the 80th percentile (=1.6)
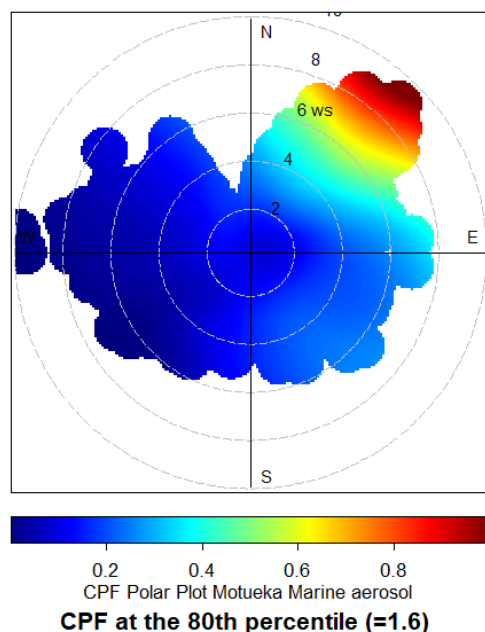
Figure 3.7   Bivariate plot of marine aerosol contributions to PM$_{2.5}$, concentrations at Motueka, Tasman District. The radial dimensions indicate the wind speed in 2 m s^{-1} increments, and the colour contours indicate the relative contribution to each wind direction/speed bin.

The east coasts of the North Island (Tauranga and southwards) and South Island are generally sheltered from the westerly circulation patterns by mountain ranges on the intervening land mass. The PSCF presented in Figure 3.8 shows that Hawke's Bay locations are affected by southwest and northeast source regions out in the Pacific Ocean, while the trajectories for Timaru and Dunedin approach from the south, with the Southern Alps acting as an effective block to westerly trajectories that might contribute to concentrations above the mean.
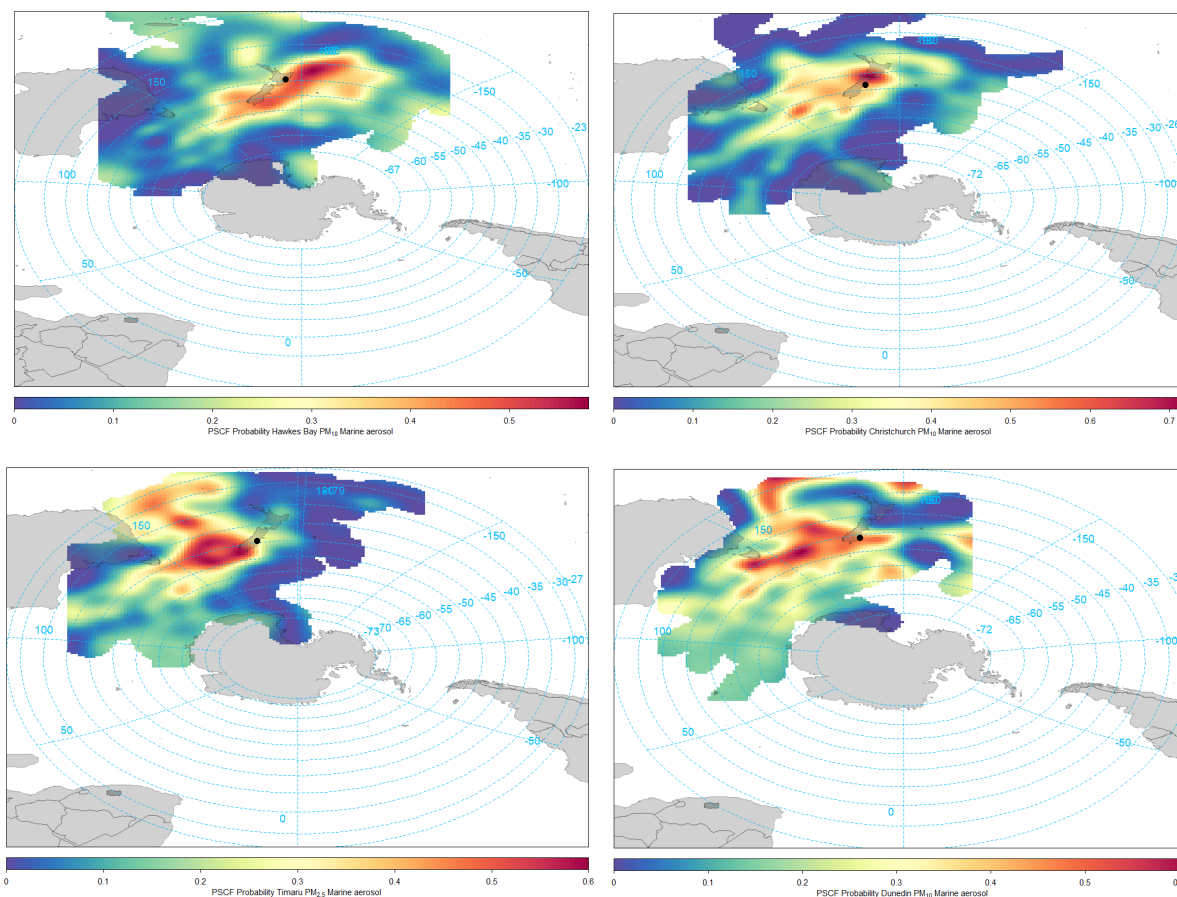
Figure 3.8   Air-mass back-trajectory and PSCF analyses for marine aerosol source regions for (top left) Hawke's Bay PM$_{10}$ samples (n = 386, 2016–2023), (top right) Christchurch PM$_{2.5}$ samples (n = 232, 2013–2015), (bottom left) Timaru PM$_{2.5}$ samples (n = 174, 2006–2007) and (bottom right) Dunedin PM$_{10}$ samples (n = 100, 2010).

The PSCF for Christchurch marine aerosol is interesting, in that it shows a source region around the Cook Strait. This may represent the wind-field strengthening effect (and subsequent sea-salt generation) of the gap between the North and South Islands. Such meteorological conditions are typical for prefrontal northwesterly winds that are accelerated through Cook Strait and then delivered to Christchurch as a northeasterly onshore. An example of such a prefrontal wind flow is depicted by the wind barbs in Figure 3.9. This would also explain why Christchurch experiences similar average PM$_{10}$ marine aerosol concentrations as Wellington (6–7 µg m^{-3}).
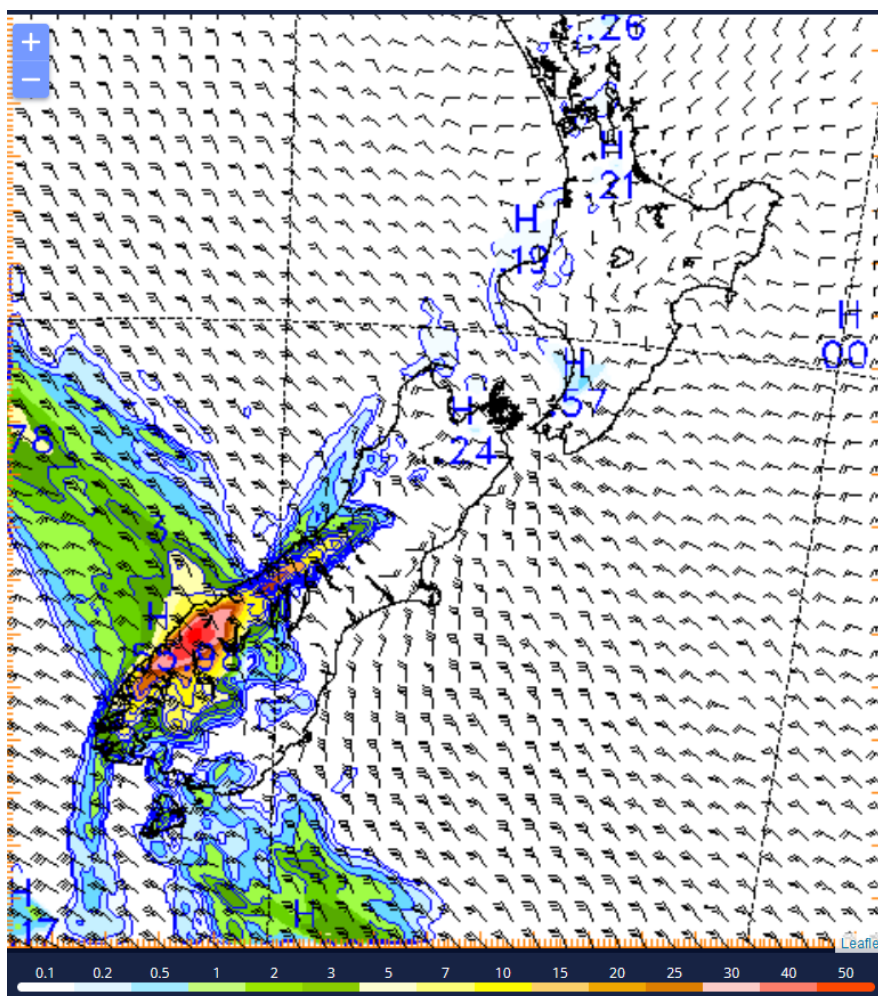
Figure 3.9   Pre-frontal (coloured bands showing rainfall intensity) wind direction depicted by the orientation of the wind barbs, with the number of 'feathers' related to wind speed, showing acceleration through Cook Strait and then the air mass approaching Christchurch from the northeast. Source: MetService, 31 May 2024.[8]

3.1.2   Secondary Sulphate Aerosol

The PSCF analyses for secondary sulphate aerosol formation (which may be somewhere downwind of the original precursor gas emission source location) show that the Bay of Plenty area is a significant source region for North Island and upper South Island locations, as presented in Figures 3.10 and 3.11.

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8   https://www.metservice.com/maps-radar/rain/forecast/3-days
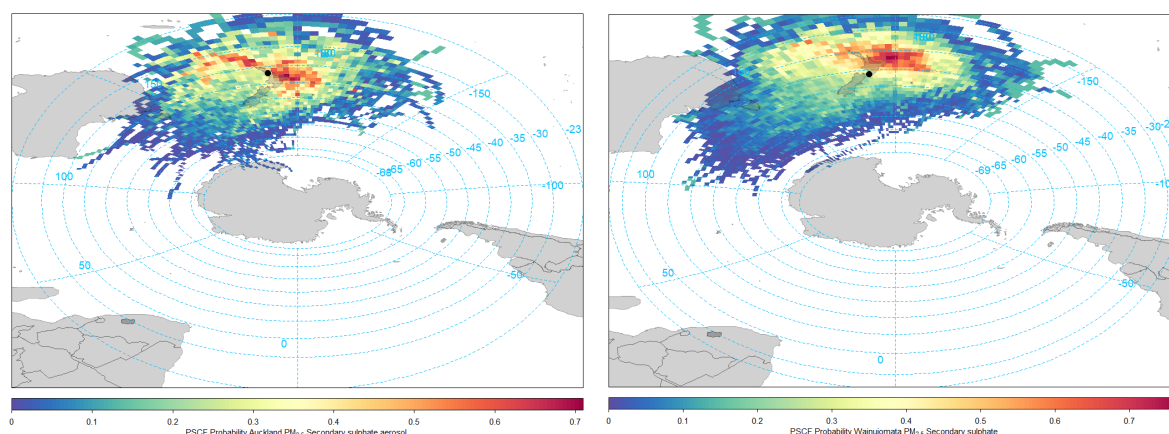
Figure 3.10   Air-mass back-trajectory and PSCF analyses for secondary sulphate aerosol source regions for (top left) Auckland PM$_{2.5}$ samples (n = 4405, 2006–2016) and (top right) Wainuiomata PM$_{2.5}$ samples (n = 4928, 2014–2023).

The TVZ is an area of high volcanic and geothermal activity, with multiple emission sources of sulphur-containing gases (mainly SO$_2$ and H$_2$S). Measurement of SO$_2$ and H$_2$S emissions from Whakaari / White Island off the coast from Tauranga show that, on average, the emission rates were 295 ± 70 tonnes/day, or approximately 109,500 tonnes per year, between 2003 and 2019. Over a similar period, the total TVZ emissions of sulphur gases were estimated to be approximately 144,000 tonnes per year between 1983 and 1999 (Wardell et al. 2001; Christenson et al. 2010, 2017). This contrasts with an emissions inventory estimate of 47,760 tonnes/year for 2019 as the total anthropogenic SO$_2$ emissions for New Zealand, which are distributed across the entire country (Metcalfe and Sridhar 2021). Therefore, the TVZ represents a significant area of natural-source precursor gases for secondary sulphate aerosol (about three times the total anthropogenic emissions) that impacts a wide area of the country. As described in Section 3.1, the meteorological model resolution (1°x1°) may not appropriately resolve the PSCF analysis for inland (Tokoroa) and east coast sites (Hawke's Bay) near the TVZ. However, the quantity of sulphur gas emissions from the TVZ described above support the interpretation that Tokoroa and Hawke's Bay will also be impacted by this natural source of secondary sulphate aerosol.
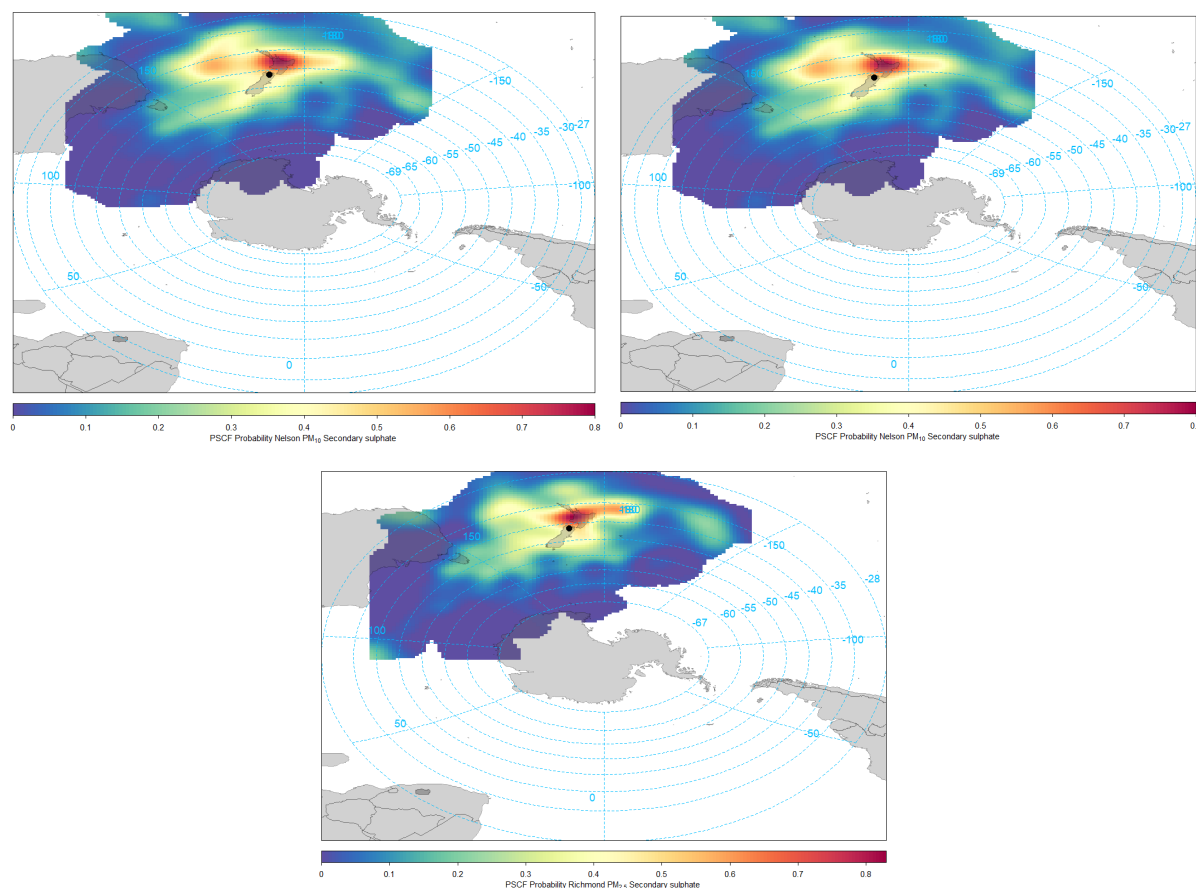
Figure 3.11   Air-mass back-trajectory and PSCF analyses for secondary sulphate aerosol source regions for (top left) Nelson PM$_{10}$ samples (n = 824, 2008–2017), (top right) Motueka PM$_{2.2}$ samples (n = 327, 2022) and (bottom) Richmond PM$_{2.5}$ samples (n = 357, 2015–2016).

For monitoring locations such as Christchurch and further south in the South Island, the PSCF results for secondary sulphate were more ambiguous and likely represent a combination of volcanic emissions and oceanic phytoplankton production of precursor gases for Christchurch and Timaru, as well as primarily phytoplankton production for Dunedin (at least for the monitoring periods in each of those locations), as presented in Figure 3.12.
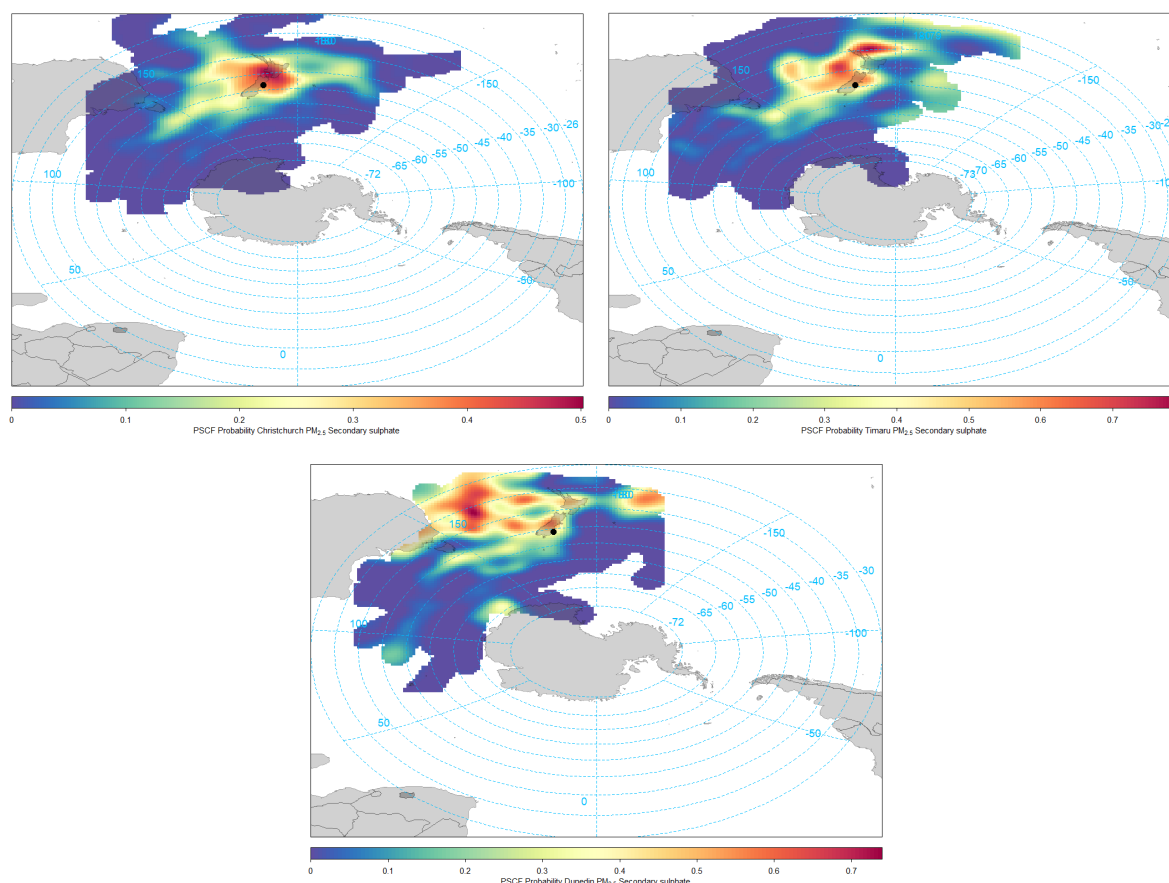
Figure 3.12   Air-mass back-trajectory and PSCF analyses for secondary sulphate aerosol source regions for (top left) Christchurch PM$_{2.5}$ samples (n = 232, 2013–2015), (top right) Timaru PM$_{2.5}$ samples (n = 174, 2006–2007) and (bottom) Dunedin PM$_{2.5}$ samples (n = 100, 2010).

3.2   Natural-Source Contribution Observations for Short-Term Studies

As indicated in Section 2.1, for several locations not covered by longer-term programmes (one year or longer), sampling and compositional analysis have been undertaken primarily during winter as part of research programmes to understand the observed diurnal variation in particulate matter concentrations in New Zealand urban centres. These locations include Alexandra (May–June 2011), Invercargill (June–August 2014) and Westport (May–September 2023). In all of these studies, a marine aerosol contribution was resolved from the data but a secondary sulphate source contribution was not, most likely due to the observed winter minimum (Figure 2.6), and therefore the secondary sulphate contribution falls below the signal-to-noise ratio required for receptor modelling (Paatero and Hopke 2003).

Alexandra is located in central Otago, surrounded by mountains, and is one of the furthest New Zealand speciation monitoring sites from the ocean. The Alexandra data shows that marine aerosol concentrations were relatively low but that there were episodic intrusions of higher concentrations (Ancelet et al. 2014a). The back-trajectory analysis for Alexandra (Figure 3.13) shows that the highest marine aerosol concentrations were in air masses that approached Alexandra from the south, most likely via the Clutha River valley that opens out onto the Southland Plains and the Southern Ocean beyond that. For Invercargill, winter PM$_{10}$ marine aerosol concentrations (mean = 2.6 µg m^{-3}, maximum = 17 µg m^{-3}) were similar to average winter concentrations for Dunedin in 2010. The PSCF back-trajectory (Figure 3.13) shows a similar source region to the southwest of the South Island and that contributions from westerly and northwesterly trajectories were low, most likely due to the blocking effect of the Southern Alps.

Westport is open to the west and southwest and winter (2023) marine aerosol PM_{10} (mean = 5.6 µg m^{-3}, maximum = 15 µg m^{-3}) and $PM_{2.5}$ (mean = 1.3 µg m^{-3}, maximum = 6.5 µg m^{-3}) concentrations were significantly higher than for Alexandra and Invercargill. Based on the observed winter data and PSCF back-trajectories, it is likely that Westport experiences similar sea-salt concentrations to Auckland and Wellington from westerly trajectories, but, during the monitoring period, there was no significant influence from the eastern sector as Westport is sheltered from the east by the Southern Alps.
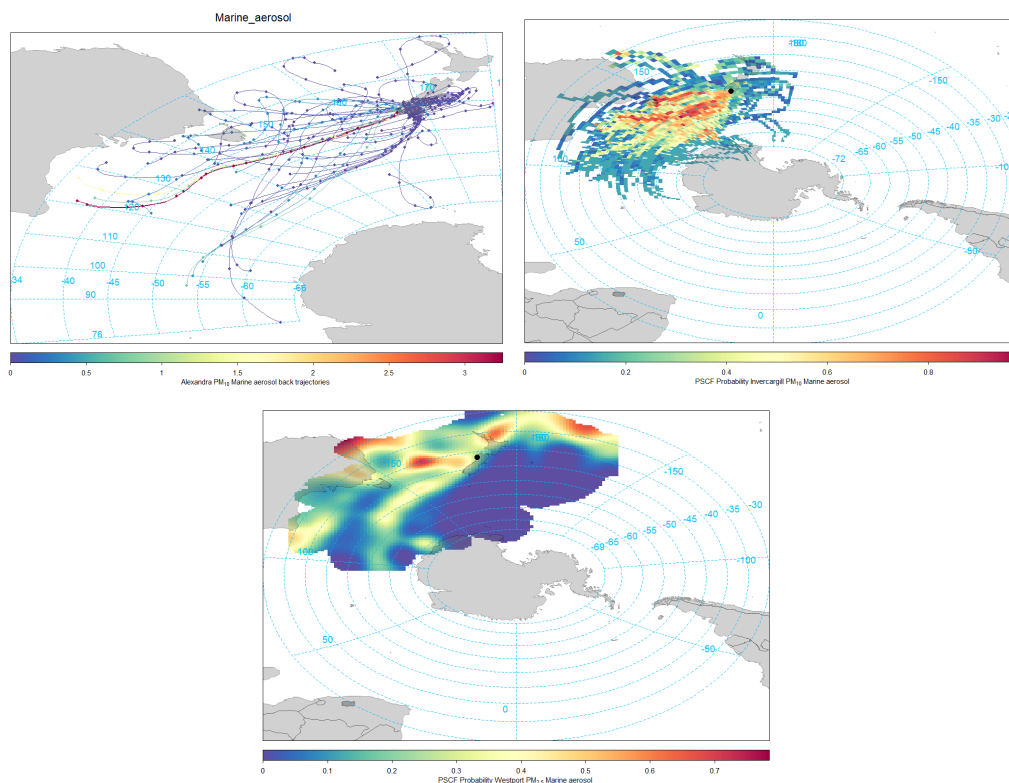
Figure 3.13   Air-mass back-trajectory for marine aerosol source regions for (top left) Alexandra PM_{10} samples (n = 940, April–June 2011), and PSFC analyses for (top right) Invercargill PM_{10} samples (n = 1643, May–August 2014) and (bottom right) Westport PM_{10} samples (n = 70, May–September 2023).

3.3   Natural-Source Contributions to Particulate Matter Concentrations for Gazetted Airsheds in New Zealand

The PSCF back-trajectory analyses have shown that, for locations north of about Christchurch, secondary sulphate contributions above the mean are heavily influenced by emissions of precursor gases from the TVZ, with Whakaari / White Island being the most significant source of SO_2 emissions. Further south in the South Island, it is more likely that oceanic sources of secondary sulphate predominate natural-source contributions. Marine aerosol contributions to urban particulate matter concentrations are ubiquitous across the country, with sea-salt particles measured at all monitoring locations, whether inland or coastal, for both short and longer sampling campaigns. The data also shows that coarse particle marine aerosol concentrations are reduced as the distance from the ocean increases and with the amount of topographical sheltering that a location experiences. These effects have been taken into account to provide an estimate of the mean and likely peak natural-source contributions that could be expected at all 73 gazetted airsheds for the purposes of air-quality management. These impacts are not confined to the airsheds themselves but will also apply to the regions around them. For regions with both coastal and sheltered inland locations, the natural-source contributions will vary accordingly and be primarily delineated by distance from the ocean and the intervening topographical features.

Tables 3.1 and 3.2 present the estimated natural-source contributions to daily (24-hour) concentrations for North Island and South Island airsheds, respectively. Some generalisations in the assigned values have been made, as much of the location data is derived from 1–2-year monitoring programmes conducted at different times spread across almost 20 years. The longer-term particulate matter sampling and compositional analysis programmes, such as those in Auckland and Wellington, have provided the benchmark to compare such short-term datasets and guide the conclusions. The approach taken has been to assign natural-source concentration values based on data from similar location types (coastal, inland, eastern, western, northern or southern), with those values taken from the nearest, most relevant, measured monitoring location. Concentration values have been assigned for marine aerosol (sea salt) and natural sources of secondary sulphate, but, as discussed in Section 2, maximum contributions from the two source types are not additive, as they do not peak at the same time due to different source locations and meteorological conditions under which higher concentrations have been measured.

Table 3.1   Measured or inferred mean and peak natural-source contributions to particulate matter concentrations in North Island airsheds.

North Island		Marine Aerosol PM$_{2.5}$ (µg m^{-3})		Marine Aerosol PM$_{10}$ (µg m^{-3})		Secondary Sulphate PM$_{2.5}$ (µg m^{-3})		Secondary Sulphate PM$_{10}$ (µg m^{-3})	
Airshed	Region	Mean	Peak	Mean	Peak	Mean	Peak	Mean	Peak
Dargaville	Northland	1.7	12	6.9	42	0.9	6.1	1.3	15
Kaitaia	Northland	1.7	12	6.9	42	0.9	6.1	1.3	15
Kerikeri	Northland	1.7	12	6.9	42	0.9	6.1	1.3	15
Marsden Point	Northland	1.7	12	6.9	42	0.9	6.1	1.3	15
Whangārei	Northland	1.7	12	6.9	42	0.9	6.1	1.3	15
Auckland	Auckland	1.7	12	6.9	42	0.9	6.1	1.3	15
Beachlands	Auckland	1.7	12	6.9	42	0.9	6.1	1.3	15
Helensville	Auckland	1.7	12	6.9	42	0.9	6.1	1.3	15
Kumeū	Auckland	1.7	12	6.9	42	0.9	6.1	1.3	15
Maraetai	Auckland	1.7	12	6.9	42	0.9	6.1	1.3	15
Pukekohe	Auckland	1.7	12	6.9	42	0.9	6.1	1.3	15
Riverhead	Auckland	1.7	12	6.9	42	0.9	6.1	1.3	15
Snells Beach	Auckland	1.7	12	6.9	42	0.9	6.1	1.3	15
Waiheke Island	Auckland	1.7	12	6.9	42	0.9	6.1	1.3	15
Waiuku	Auckland	1.7	12	6.9	42	0.9	6.1	1.3	15
Warkworth	Auckland	1.7	12	6.9	42	0.9	6.1	1.3	15
Wellsford	Auckland	1.7	12	6.9	42	0.9	6.1	1.3	15
Cambridge	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Hamilton City	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Huntly	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Matamata	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Morrinsville	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11

North Island		Marine Aerosol PM$_{2.5}$ (µg m^{-3})		Marine Aerosol PM$_{10}$ (µg m^{-3})		Secondary Sulphate PM$_{2.5}$ (µg m^{-3})		Secondary Sulphate PM$_{10}$ (µg m^{-3})	
Airshed	Region	Mean	Peak	Mean	Peak	Mean	Peak	Mean	Peak
Ngāruawāhia	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Ōtorohanga	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Paeroa	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Putāruru	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Taupō	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Te Aroha	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Te Awamutu and Kihikihi	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Te Kūiti	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Thames	Waikato	1.7	12	6.9	42	0.9	6.1	1.3	15
Tokoroa	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Tuakau	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Tūrangi	Waikato	1.6	8	3.5	18	0.8	7.1	1.2	11
Waihi	Waikato	1.7	12	6.9	42	0.9	6.1	1.3	15
Whangamatā	Waikato	1.7	12	6.9	42	0.9	6.1	1.3	15
Whitianga	Waikato	1.7	12	6.9	42	0.9	6.1	1.3	15
Mount Maunganui	Bay of Plenty	1.7	12	6.9	42	0.9	6.1	1.3	15
Rotorua	Bay of Plenty	1.6	8	3.5	18	0.8	7.1	1.2	11
Awatoto	Hawke's Bay	1.2	7	8.6	40	0.9	5.2	1.2	8
Hastings	Hawke's Bay	1.7	12	6.0	31	1.1	5.4	2.0	9
Napier	Hawke's Bay	1.2	7	2.0	13	1.2	8.8	2.0	13
Whirinaki	Hawke's Bay	1.2	7	2.0	13	1.2	8.8	2.0	13
Taihape	Manawatū-Wanganui	1.6	8	3.5	18	0.8	7.1	1.2	11
Taumarunui	Manawatū-Wanganui	1.6	8	3.5	18	0.8	7.1	1.2	11
Kāpiti Coast	Wellington	1.5	11	6.8	35	1.1	5.9	1.3	8
Karori	Wellington	1.5	11	6.8	35	1.1	5.9	1.3	8
Lower Hutt	Wellington	1.5	11	6.8	35	1.1	5.9	1.3	8
Masterton	Wellington	1.2	6	3.8	17	0.7	11.0	0.7	11
Porirua	Wellington	1.5	11	6.8	35	1.1	5.9	1.3	8
Upper Hutt	Wellington	1.4	10	3.8	9	1.2	3.7	1.2	4
Wainuiomata	Wellington	1.4	10	5.2	23	1.1	8.2	1.1	8
Wellington	Wellington	1.5	11	6.8	35	1.1	5.9	1.3	8

Table 3.2   Measured or inferred mean and peak natural-source contributions to particulate matter concentrations in South Island airsheds.

South Island		Marine Aerosol PM$_{2.5}$ (µg m^{-3})		Marine Aerosol PM$_{10}$ (µg m^{-3})		Secondary Sulphate PM$_{2.5}$ (µg m^{-3})		Secondary Sulphate PM$_{10}$ (µg m^{-3})	
Airshed	Region	Mean	Peak	Mean	Peak	Mean	Peak	Mean	Peak
Marlborough	Marlborough	0.8	8	2.0	14	0.7	4.2	1.0	4
Nelson City	Nelson	1.1	9	3.7	22	1.0	3.8	2.2	9
Nelson South	Nelson	1.1	9	3.7	22	1.0	3.8	2.2	9
Tāhunanui Stoke	Nelson	1.1	9	3.8	21	1.0	3.8	1.3	6
Richmond	Tasman	1.3	11	2.7	21	0.9	5.4	2.3	9
Reefton	West Coast	1.3	11	2.4	22	0.9	5.4	2.3	9
Ashburton	Canterbury	0.8	8	4.9	26	0.7	4.2	1.7	6
Christchurch	Canterbury	1.8	9	7.1	34	1.0	7.5	2.3	17
Geraldine	Canterbury	0.8	8	4.9	26	0.7	4.2	1.7	6
Kaiapoi	Canterbury	1.8	9	7.1	34	1.0	7.5	2.3	17
Rangiora	Canterbury	1.8	9	7.1	34	1.0	7.5	2.3	17
Timaru	Canterbury	0.8	8	4.9	26	0.7	4.2	1.7	6
Waimate	Canterbury	0.8	8	4.9	26	0.7	4.2	1.7	6
Washdyke	Canterbury	0.8	8	4.9	26	0.7	4.2	1.7	6
Otago 1	Otago	0.2	1	0.4	9	1.7	6.5	1.7	6
Otago 2	Otago	1.1	7	4.9	26	1.7	6.5	1.7	6
Otago 3	Otago	1.1	7	4.9	26	1.7	6.5	1.7	6
Otago 4	Otago	0.2	1	0.4	9	1.7	6.5	1.7	6
Gore	Southland	1.1	7	2.6	17	1.7	6.5	1.7	6
Invercargill	Southland	1.1	7	2.6	17	1.7	6.5	1.7	6

3.4 Airsheds that May be Subject to Natural-Source Concentrations that Approach or Exceed Short- or Long-Term Air Quality Standards and Guidelines

The monitoring data presented in Section 2, coupled with the PSCF back-trajectory analyses presented in Section 3, show that coastal sites exposed to both westerly and easterly quadrant winds have higher contributions to PM_{10} from natural sources of particulate matter, primarily sea salt. However, contributions from sea salt to $PM_{2.5}$ can also be significant for these locations, such as the 24-hour $PM_{2.5}$ concentration (sea salt = 12 μgm^{-3}, secondary sulphate = 2.6 μgm^{-3}) measured at Hastings during January 2023 (Davy and Trompetter 2024a). Although this does not technically add up to an exceedance of the WHO guideline, it was within the bounds of measurement uncertainty (approximately ±10%). Across the database of 24-hour $PM_{2.5}$ samples (6680) collected in New Zealand for compositional analysis to date, the Hastings event has been the only example where the WHO guideline may have been exceeded, suggesting that such events are relatively rare.

A PM_{10} marine aerosol event was captured on 2 January 2012 in Auckland (Orewa) (Davy et al. 2017). However, as particulate matter samples are not collected in all airsheds every day, there are instances where natural sources (primarily sea salt) have been suspected to have been significant contributors, such as the exceedances of the PM_{10} NESAQ in Auckland and Tauranga on 18 and 19 August 2022. For such occurrences not captured in samples suitable for compositional analyses, a more forensic approach has been taken to provide evidence for the primary source responsible for such exceedances (Davy and Trompetter 2022).

There have been instances where the PM_{10} NESAQ has been exceeded (and captured in the speciation monitoring record) from Australian desert dust incursions, such as on 24–25 September 2009 and 6–7 December 2019 across multiple sites in the North Island and upper South Island (Davy et al. 2011a; Davy and Trompetter 2021). Such transboundary dust storm events will occur from time to time, and there is evidence of such events occurring in the distant past (Brahney et al. 2019). Any airshed in New Zealand may exceed the PM_{10} NESAQ under such conditions. However, there have only been three instances attributable to natural sources in the sample record (n = 12,340) where the PM_{10} NESAQ has been exceeded, also indicting that this is relatively rare for this size fraction. The meteorological- and synoptic-scale conditions that give rise to such events usually suppress (via dispersion) the anthropogenic contributions to urban particulate matter concentrations.

The data suggests that it is unlikely that natural sources alone will exceed long-term (annual average) $PM_{2.5}$ or PM_{10} concentrations, but they will contribute to a baseline on top of which anthropogenic sources will have to be managed accordingly.

4.0   THE IMPACT OF CLIMATE CHANGE ON NATURAL-SOURCE CONTRIBUTIONS TO PARTICULATE MATTER

4.1   Physical Drivers of Natural-Source Particulate Matter Production

4.1.1   Sea Spray Aerosol

Sea spray aerosol is emitted into the atmosphere when waves break and bubbles burst (Saliba et al. 2019). Wind is the most important driver of sea spray aerosol production; large sea spray aerosol concentrations are linked to high wind speeds (Gong 2003; Hartery et al. 2020; Mårtensson et al. 2003). There is some evidence from observations indicating that sea spray production is also influenced by sea surface temperature via changes in the surface tension, density and viscosity of water (Liu et al. 2021; Jaeglé et al. 2011). However, laboratory experiments produce inconclusive results (Christiansen et al. 2019; Salter et al. 2015).

Organic matter at the ocean surface and salinity may also influence sea spray aerosol production (Song et al. 2023). However, these factors are not included in the models used to produce the results shown in Section 4.2.

Wind patterns over New Zealand are expected to change in future as a result of anthropogenic greenhouse gas emissions and the projected recovery of the Antarctic ozone hole (Bodeker et al. 2022). Sea surface temperatures are projected to continue increasing with continued emissions of greenhouse gases (see Bodeker et al. [2022] and references therein).

4.1.2   Natural Sulphate

Secondary sulphate aerosol is formed from gas-to-particle conversion of sulphur-containing gases such as sulphur dioxide (SO_2). As discussed in Section 2.4.2, both natural and anthropogenic sources of secondary sulphate aerosol are present in New Zealand air. Anthropogenic sources include the combustion of sulphur-containing fuels and natural sources include marine biogenic activity and volcanic emissions (Revell et al. 2024). While volcanic activity could significantly contribute to future natural sulphate aerosol burdens in New Zealand (Chim et al. 2023), eruptions are difficult to predict and are not included in the models assessed in Section 4.2.3.

Marine biogenic activity is a significant source of natural sulphate aerosol measured in New Zealand (Revell et al. 2024). Marine biota such as phytoplankton, algae and corals produce dimethylsulfoniopropionate, which is broken down by bacteria in seawater to produce dimethyl sulfide (DMS). DMS is emitted into the atmosphere by wind-induced mixing of surface water (Bell et al. 2015; Blomquist et al. 2017; Szopa et al. 2021). In the atmosphere, DMS is chemically converted to sulphur-containing gases (e.g. SO_2 and methane sulfonic acid [MSA]), which contribute to sulphate aerosol mass and number concentration (von Glasow and Crutzen 2004; Bell et al. 2015; Hoffmann et al. 2016; Blomquist et al. 2017).

In future, atmospheric DMS emissions and the resulting sulphate aerosol production will be influenced by wind speed (as discussed for sea spray), the seawater DMS concentration, sea surface temperature and availability of chemical oxidants.

Future seawater DMS production will be influenced by climate warming, nutrient availability, ocean acidification and solar radiation fluxes (Szopa et al. 2021). However, there are large uncertainties in which factors will be most important for DMS emissions, with recent studies producing conflicting results depending on the assumptions made concerning DMS

production in their models (Schwinger et al. 2017; Wang et al. 2018b; Bock et al. 2021). The Intergovernmental Panel on Climate Change (IPCC)'s Sixth Assessment Report assigned *low confidence* in the magnitude and changes in marine aerosol emissions in response to shifts in climate and marine ecosystem processes (Szopa et al. 2021).

The chemical conversion of DMS to SO_2 in the atmosphere is also complicated and not fully understood (Veres et al. 2020; Cala et al. 2023). The reactions involved can take hours to days depending on the availability of chemical oxidants, atmospheric temperature, relative humidity and solar radiation (Seinfeld and Pandis 2006).

4.1.3   Dust

Mineral dust (rock-derived particles with diameters smaller than 62.5 μm) can be suspended by winds and remain in the atmosphere for minutes to weeks (Kok et al. 2012). Dust emissions are controlled by soil properties, including soil moisture, vegetation and near-surface wind speeds, and are therefore sensitive to climate change and land-use change (Aryal and Evans 2021). Earth system models show an increase in global dust loading through the 21st century due to the sensitivity of dust emissions and precipitation changes (which promote wet deposition) to climate change (Zhao et al. 2023). However, the Sixth Assessment Report of the IPCC reported low confidence in quantitative estimates of dust emission response to climate change (Szopa et al. 2021).

4.1.4   Biogenic Aerosol

Terrestrial plants emit large quantities of biogenic volatile organic compounds (BVOCs), which play an important role in tropospheric chemistry (Atkinson and Arey 2003). Many BVOCs undergo chemical reactions to form secondary organic aerosols. BVOCs are emitted by plants as a protection mechanism against several factors relevant to climate change, such as changes in temperature, carbon dioxide, drought and light (Paton-Walsh et al. 2022). Therefore, we expect BVOC emissions to change in a warming world.

Emissions of BVOCs are strongly dependent on plant species and meteorological conditions. Few studies have measured BVOC emissions from plants in New Zealand (Effah et al. 2020, 2021) and very little is known about New Zealand's BVOC emission inventory as a whole or the composition of secondary organic aerosols in New Zealand (Paton-Walsh et al. 2022). Given these large knowledge gaps, we do not attempt to quantify future changes in secondary organic aerosol over New Zealand. However, ongoing land-use changes in New Zealand (e.g. deforestation and afforestation) are expected to change BVOC emissions and secondary organic aerosol formation. Furthermore, warmer temperatures may affect BVOC emissions depending on plant species and meteorological factors (Wang et al. 2018a; Zhao et al. 2019).

4.1.5   Biomass Burning Aerosol

Open biomass burning produces emissions of black carbon and organic carbon aerosol. While there is an overlap between natural and anthropogenic fires, the spread of fires is more likely in hotter, drier conditions (UNEP 2022). Anthropogenic factors, such as changes in land use, also impact the risk of wildfire occurrence and spread (Veira et al. 2016). In New Zealand, extreme wildfire weather conditions similar to those observed in Australia's 2019/20 'Black Summer' bushfires are possible, even in regions previously unaffected by wildfire (Melia et al. 2022). Wildfires can indirectly create other natural aerosols; for example, the Black Summer fires triggered a phytoplankton bloom in the Southern Ocean (Tang et al. 2021); such blooms are linked with enhanced DMS production (Bell et al. 2015).

4.2 The Impact of Climate Change on Natural-Source Contributions to Particulate Matter

4.2.1 Overview of the CMIP6 Models

The sixth coupled model intercomparison project (CMIP6) is a multi-model intercomparison project designed to inform the sixth assessment of the IPCC (Eyring et al. 2016). CMIP6 focuses on Earth system models, which are global models coupling together the processes and feedbacks occurring between the atmosphere, ocean and land surface; these represent the current best-available models for understanding how climate change will affect the Earth system.

While the CMIP6 Earth system models are state of the art, it is important to be aware of their limitations when interpreting the figures shown in Sections 4.2.2–4.2.5. Improvements in computational power over the past decades have allowed model grid resolution to increase, but the grid sizes are still relatively coarse. As an example, in the UKESM1 model over New Zealand, grid cell areas are approximately 20,000 km^2, meaning that the length of the country spans only 13 grid cells. With that resolution, it is not possible to project future trends at urban scales.

The CMIP6 Earth system models were run for a series of future scenarios, known as the Shared Socioeconomic Pathways (SSPs; O'Neill et al. 2017). The SSPs represent emission scenarios originating from a wide range of socioeconomic drivers. Here, we focus on two scenarios, SSP1-2.6 and SSP5-8.5 (Figure 4.1). SSP1-2.6 is a low-emissions scenario consistent with meeting the 2°C warming target under the Paris Agreement (another scenario, SSP1-1.9, is consistent with 1.5°C; however, fewer models performed this simulation). SSP1-2.6 comprises a 'sustainability' narrative and has an end-of-21st-century global radiative forcing of 2.6 W m^{-2} higher than in pre-industrial times. SSP5-8.5 comprises a 'fossil-fuel intensive' narrative, and global radiative forcing in 2100 is 8.5 W m^{-2} higher than in pre-industrial times (Riahi et al. 2017). Although SSP5-8.5 is not considered a feasible scenario in terms of future population growth, technological development and economic development (Hausfather and Peters 2020), it is useful as an upper bound of likely future responses.

Here, we use outputs from five CMIP6 models that interactively simulate the interactions between aerosol and the climate. This means that the models calculate the impacts of aerosols on climate change via processes involving light scattering and absorption and seeding cloud formation. These processes lead to localised changes in radiative forcing, temperature and rainfall (Forster et al. 2021). The models also simulate how climate change affects emissions of natural aerosols via changes in winds and temperature, as discussed in Section 4.1. Using models that can simulate the bidirectional coupling between aerosols and climate change allows the most realistic projections of natural aerosol emissions to be calculated.

The models used for this report are summarised in Table 4.1. In general, the figures in Sections 4.2.2–4.2.5 show fine- and coarse-model aerosol together. Note that, in this section, 'sulphate aerosol' includes all sources of sulphate (oceanic, volcanic, anthropogenic and so on) because of how the models are configured. In each figure, the five models are used to calculate a multi-model mean. $PM_{2.5}$ plots are shown in Section 4.2.6 for all aerosol sources.

Table 4.1   Coupled Model Intercomparison Project phase 6 (CMIP6) models used.

Model Name*	Modelling Centre/s	Reference
CESM-WACCM	National Center for Atmospheric Research (USA)	Danabasoglu et al. (2020); Gettelman et al. (2019)
GFDL-ESM4	Geophysical Fluid Dynamics Laboratory, National Oceanic and Atmospheric Administration (USA)	Horowitz et al. (2020); Dunne et al. (2020)
MIROC6	Japan Agency for Marine-Earth Science and Technology, Atmosphere and Ocean Research Institute, University of Tokyo, National Institute for Environmental Studies, RIKEN Center for Computational Science (Japan)	Tatebe et al. (2019); Takemura et al. (2018)
MRI-ESM2	Meteorological Research Institute (Japan)	Yukimoto et al. (2019); Oshima et al. (2020)
UKESM1	United Kingdom Met Office (UK)	Sellar et al. (2019); Mulcahy et al. (2020)

* This is used to refer to individual models throughout the report.
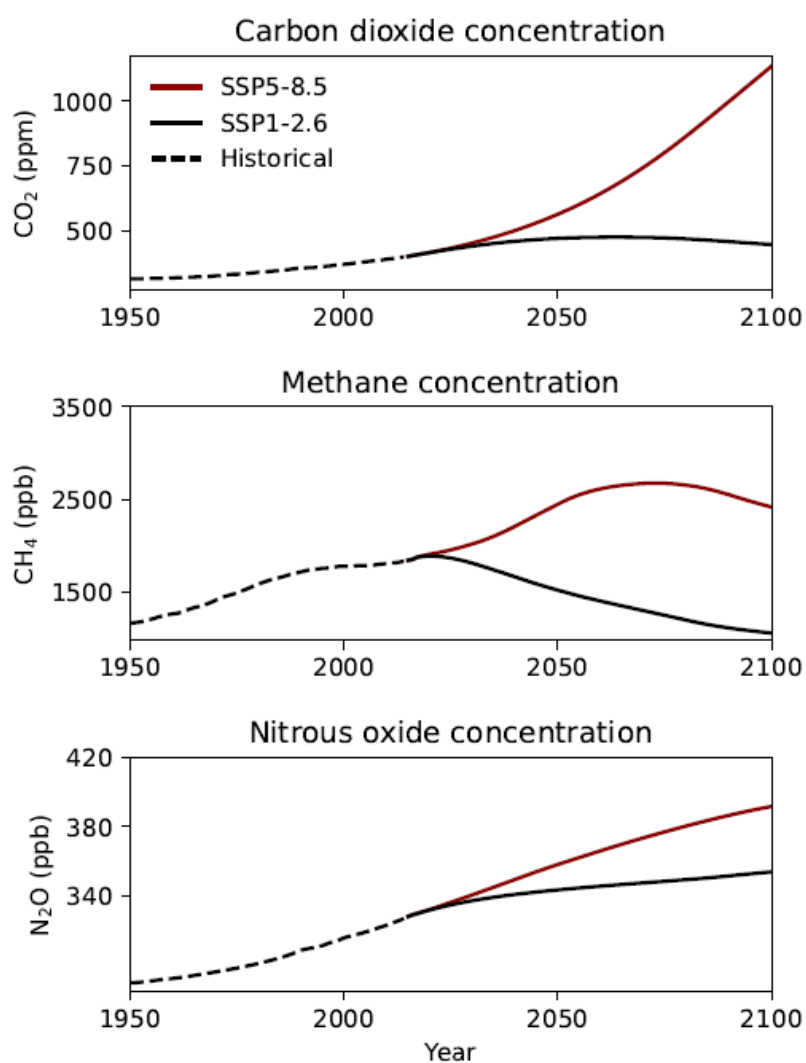
Figure 4.1   Global annual mean greenhouse gas concentrations in the Shared Socioeconomic Pathways (solid lines). Data sourced from Meinshausen et al. (2020).

4.2.2　Future Projections of Sea Spray Aerosol
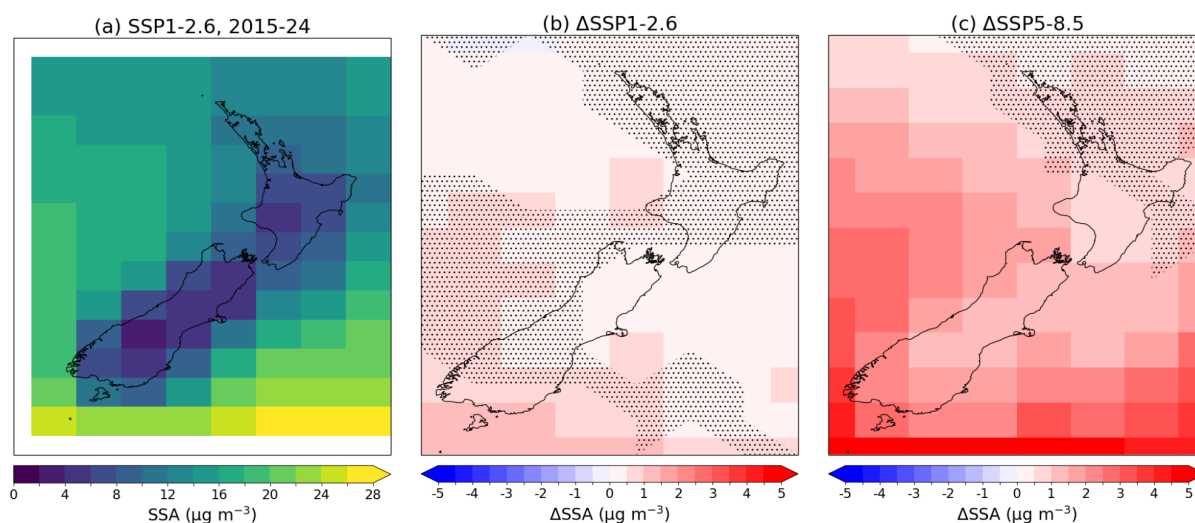
Figure 4.2　Future projections of sea spray aerosol. (a) Sea spray aerosol concentrations in µg m⁻³ averaged over 2015–2024. (b) The change in sea spray aerosol over the 21st century following SSP1-2.6: 2090–2099 minus 2015–2024. Hatching indicates where fewer than four out of five models agree on the sign of the difference. (c) As for (b) but for SSP5-8.5. Models used: CESM-WACCM, GFDL-ESM4, MIROC6, MRI-ESM2, UKESM1.

Figure 4.2a shows sea spray aerosol concentrations averaged over the five CMIP6 models for 2015–2024. As expected, concentrations are higher over the ocean than land, especially the Southern Ocean, where wind speeds are high year-round, leading to large sea spray aerosol fluxes. Sea spray aerosol is projected to increase over New Zealand throughout the 21st century (Figure 4.2b and c) and is scenario-dependent. The multi-model mean shows small increases (up to ~1.5 µg m⁻³) in the low emissions scenario SSP1-2.6. However, over much of the region, the models do not agree well on whether sea spray aerosol concentrations will increase or decrease in this scenario. Larger increases up to ~4.5 µg m⁻³ are seen in the high emissions scenario SSP5-8.5, which is related to increases in wind speed and potentially sea surface temperature (see Section 4.1.1), representing an anthropogenic enhancement of natural emissions (Saiz-Lopez et al. 2023). There is good agreement between the models on the sign of these changes, i.e. sea spray aerosol increases in the future relative to the 2015–2024 period.

4.2.3 Future Projections of Sulphate Aerosol
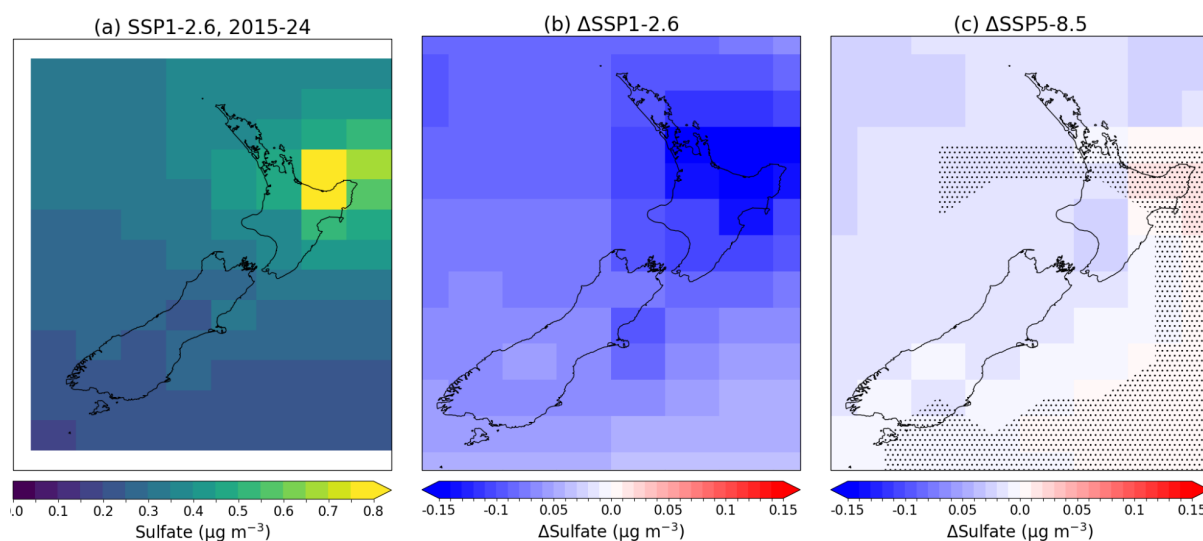
Figure 4.3 Future projections of sulphate aerosol. (a) Sulphate aerosol concentrations in μg m^{-3} averaged over 2015–2024. (b) The change in sulphate aerosol over the 21st century following SSP1-2.6: 2090–2099 minus 2015–2024. Hatching indicates where fewer than four out of five models agree on the sign of the difference. (c) As for (b) but for SSP5-8.5. Models used: CESM-WACCM, GFDL-ESM4, MIROC6, MRI-ESM2, UKESM1.

Figure 4.3a shows sulphate aerosol concentrations averaged over the five CMIP6 models for 2015–2024. Sulphate aerosol concentrations are influenced by anthropogenic and natural sources over the New Zealand region, and there are three main sources of sulphate precursors: (i) DMS from marine biogenic activity, (ii) SO_2 from anthropogenic activity and (iii) SO_2 and H_2S from volcanic sources. The spatial distribution of these sources in present-day and future scenarios is shown in Appendix 4. Figure 4.3a shows that the largest source of sulphate aerosol is from Whakaari / White Island in the Bay of Plenty, which produces about three times as much sulphate as New Zealand's total anthropogenic emissions (Wardell et al. 2001). We note that SO_2 from Whakaari / White Island does not directly contribute to the changes in sulphate in Figure 4.3b and c because the same volcanic emissions are used in the present-day and both future scenarios (Chim et al. 2023).

The models generally agree that sulphate aerosol concentrations will decrease across the New Zealand region in both scenarios, although the decrease is larger in SSP1-2.6 than SSP5-8.5 (Figure 4.3b and c). From this, we infer that reductions in anthropogenic SO_2, which are much larger in SSP1-2.6 than SSP5-8.5, cause the lower future sulphate concentrations.

Marine DMS emissions are predicted to increase over ocean regions to the south and west of New Zealand in both SSP1-2.6 and SSP5-8.5 (see Appendix 4), possibly due to warmer sea surface temperatures. In this region, poor model agreement over whether sulphate concentrations will increase or decrease in SSP5-8.5 (Figure 4.3c) may be caused by increased sulphate concentrations from higher DMS emissions partially offsetting decreases in sulphate concentrations from the smaller SO_2 emissions reductions in SSP5-8.5 compared to SSP1-2.6.

When interpreting the results in Figure 4.33b and c, it is important to consider that DMS emissions and atmospheric sulphur chemistry are presently uncertain and that models simulate these processes differently. For example, Bock et al. (2021) and Bhatti et al. (2023b) found that, for a subset of models considered in Figure 4.3, modelled atmospheric DMS concentrations are more sensitive to the seawater DMS concentration than to the choice of sea-to-air

parameterisation. Atmospheric chemistry is also poorly constrained in these models: the spread in sulphate aerosol burden resulting from uncertainties in atmospheric chemistry is approximately the same as the pre-industrial to present-day change in aerosol burden (Bhatti et al. 2023a). Furthermore, none of the models shown in Figure 4.3 include the recently discovered species relevant to the atmospheric sulphate budget hydroperoxymethyl thioformate (HPMTF; Veres et al. 2020). Inclusion of this species has been shown to have substantial impacts on simulated sulphur species (Cala et al. 2023).

4.2.4   Future Dust Projections
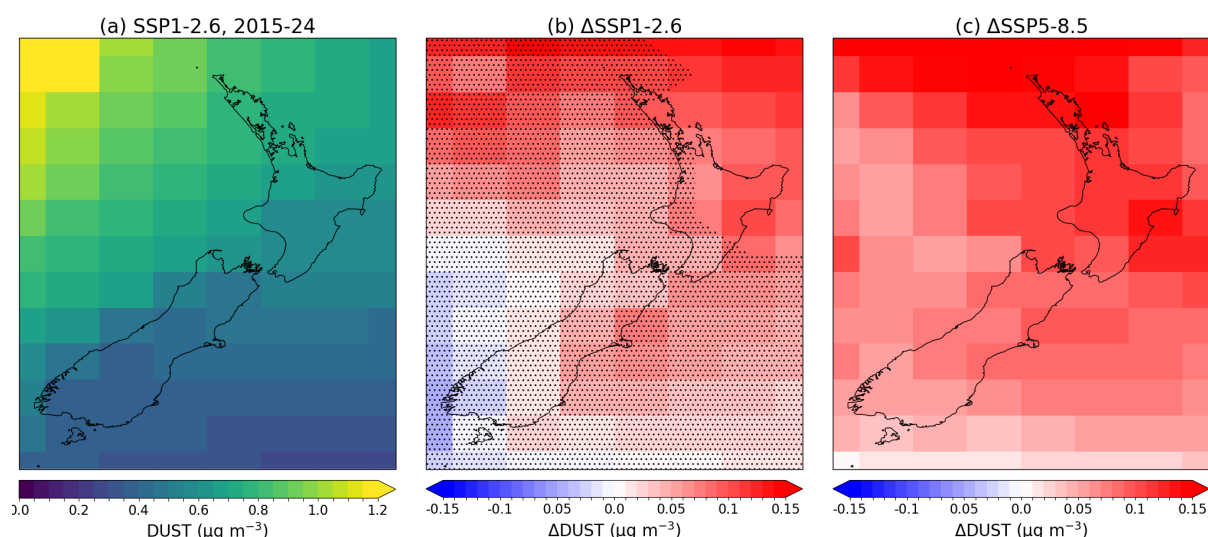
Figure 4.4   Future dust projections. (a) Dust (crustal matter) aerosol concentrations in µg m⁻³ averaged over 2015–2024. (b) The change in dust aerosol over the 21st century following SSP1-2.6: 2090–2099 minus 2015–2024. Hatching indicates where fewer than four out of five models agree on the sign of the difference. (c) As for (b) but for SSP5-8.5. Models used: CESM-WACCM, GFDL-ESM4, MIROC6, MRI-ESM2, UKESM1.

Dust emissions are parameterised in the CMIP6 models as a function of surface wind speed and account for bare soil, soil type and aridity (Thornhill et al. 2021). The models make different assumptions about the dust size distribution, and the land surface components of the models are of varying complexity. Globally, the residence time of atmospheric dust increases in most models as climate change affects its removal by dry and wet deposition (Thornhill et al. 2021).

Figure 4.4a shows that dust aerosol (hereafter referred to as 'dust') concentrations are highest in the north and west of New Zealand due to transboundary transport of dust from Australia – demonstrated previously by Nguyen et al. (2019). Local sources of dust are likely very localised and outside of urban areas, for example, farmland and dry riverbeds, and are not captured in the global-scale CMIP6 models. Globally, there is a large degree of uncertainty in how dust concentrations will change in the future, reflected in Figure 4.4b, which shows that the models used in this study do not agree on whether dust concentrations will increase or decrease in SSP1-2.6. This is because models have differing and poorly constrained emissions and emissions processes. Figure 4.4c shows that the models do agree that dust concentrations will increase by up to 1.5 µg m⁻³ in SSP5-8.5. This may be due to a combination of drier conditions in Australia causing both higher emissions and increased residency time in the atmosphere (less precipitation will mean less dust is washed out during rain). Indeed, reconstructed historical dust deposition in New Zealand is linked to land-use change in Australia (Brahney et al. 2019).

4.2.5 Future Black Carbon Projections (Biomass Burning)
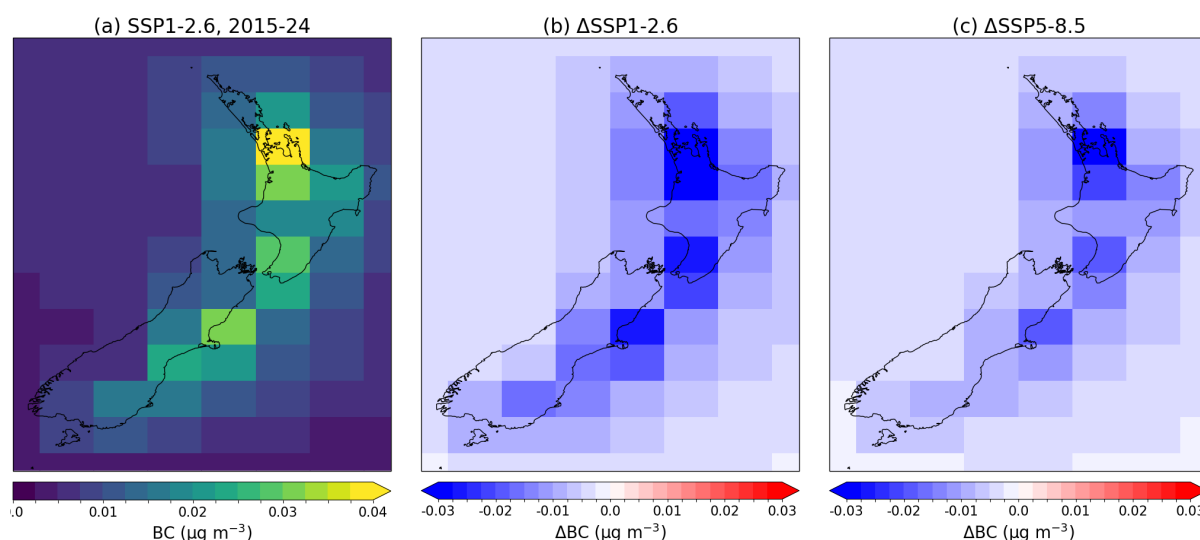
Figure 4.5   Future black carbon projections (biomass burning). (a) Black carbon aerosol concentrations in µg m^{-3} averaged over 2015–2024. (b) The change in black carbon aerosol over the 21st century following SSP1-2.6: 2090–2099 minus 2015–2024. Hatching indicates where fewer than four out of five models agree on the sign of the difference. (c) As for (b) but for SSP5-8.5. Models used: CESM-WACCM, GFDL-ESM4, MIROC6, MRI-ESM2, UKESM1.

The black carbon aerosol in Figure 4.5a is mostly anthropogenic aerosol associated with transport, domestic heating and industry in the main urban regions (note that coarse-model resolution and data interpolation to a common horizontal grid means that the regions of highest black carbon concentrations – Auckland, Wellington and Christchurch – are slightly offset in Figure 4.5). Emissions from open biomass burning represent ~15% of global black carbon emissions and 40% of organic carbon globally (Szopa et al. 2021). In both scenarios, all models agree that black carbon concentrations will be lower in the future, although the reduction is greater in SSP1-2.6 than in SSP5-8.5.

While black carbon aerosol in New Zealand is mostly of anthropogenic origin, contributions from biomass burning and wildfires are also present. During the Black Summer Australian bushfires of 2019/20, modelling by Akdemir et al. (2022) indicates that hourly PM$_{2.5}$ concentrations in Otago were significantly elevated due to long-range smoke transport (Figure 4.5a). Increased wildfire activity in New Zealand and Australia will lead to localised increases in black carbon aerosol measured in New Zealand.

4.2.6 Future PM$_{2.5}$ Projections
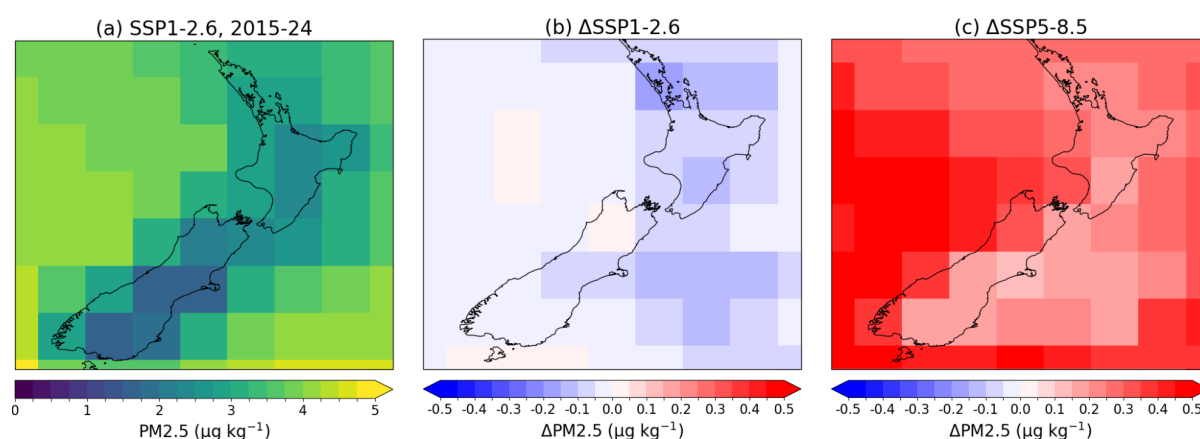
Figure 4.6   Future PM$_{2.5}$ projections. (a) PM$_{2.5}$ concentrations in µg kg^{-1} averaged over 2015–2024. (b) The change in PM$_{2.5}$ over the 21st century following SSP1-2.6: 2090–2099 minus 2015–2024. (c) As for (b) but for SSP5-8.5. Models used: GFDL-ESM4, MIROC6, MRI-ESM2. Note that all aerosol sources (natural plus anthropogenic) are included in calculating PM$_{2.5}$.

Sea spray, sulphate, dust and black carbon all contribute to PM$_{2.5}$ over the New Zealand region, with dust and sea spray being the largest contributors over the ocean, while sulphate and black carbon are more important over the land. In SSP1-2.6, the models agree that PM$_{2.5}$ concentrations reduce in the future, which is likely due to reduced sulphate from anthropogenic sources. In contrast, PM$_{2.5}$ concentrations increase by up to 10% in SSP5-8.5, which is likely due to the large increases in sea spray and dust in this scenario.

4.3   Linkages between Natural Particulate Matter and Extreme Weather Events

Studies reviewed by the IPCC in its Sixth Assessment Report present an uncertain outlook for how climate change will affect particulate matter concentrations globally (Szopa et al. 2021). Some studies projected a small increase in particulate matter related to sulphate and organic aerosols, while others projected a decrease, related to wet deposition and/or precipitation frequency and intensity. Most of these studies used single models, so the results will heavily depend on how aerosol emissions and deposition are parameterised – as discussed earlier, models disagree on the direction of future change. The IPCC reported:

> *"medium confidence that climate-driven changes in meteorological conditions, such as heatwaves or stagnations, will favour extreme air pollution episodes over highly polluted areas, however, the relationship between these meteorological conditions and high concentrations of ozone and PM$_{2.5}$ have been shown to be regionally and metric dependant."* Szopa et al. (2021)

It should be noted that none of the studies reviewed had been carried out for the New Zealand region.

Bodeker et al. (2022) summarised findings from the IPCC Sixth Assessment Report (Masson-Delmotte et al. 2021) relevant to physical climate change in New Zealand and reported the following findings relevant to aerosol emission, transport and deposition:

- Mean air temperatures are projected to increase by the middle and end of the century, with the magnitude of increase dependent on the greenhouse gas emissions scenario. Increased air temperatures have implications for emissions of sea spray and DMS-derived sulphate aerosol. Increased air temperatures may also increase the rates of chemical reactions converting DMS into sulphur dioxide and sulphate aerosol.

- Annual rainfall patterns are expected to change, with increases in the west and south of New Zealand and less rainfall in the east and north. Increased/decreased rainfall is linked to increased/decreased particulate matter wet deposition.

- Fire weather is projected to increase. Biomass burning emissions of black carbon could increase.

- Marine heatwaves are expected to increase. Increased sea surface temperature could affect sea spray and DMS emissions.

Furthermore, increased blocking frequencies could lengthen atmospheric particulate matter residence times, while changes in wind patterns could affect emissions and transport of secondary sulphate, sea spray and dust. Increased frequencies of extreme weather events are also likely to impact atmospheric particulate matter, as was seen with large quantities of silt resuspension following Cyclone Gabrielle in 2023.

4.4 Conclusions for Future Projections of Natural-Source Particulate Matter in New Zealand

The SSP scenarios used by the CMIP6 models generally assume decreases in anthropogenic sources of particulate matter worldwide in response to efforts to improve air quality. However, natural sources of particulate matter are projected to increase over New Zealand. It should be noted that model uncertainty and scenario uncertainty play important roles in forming future projections. Scenario uncertainty arises because bigger increases in natural particulate matter are seen with larger increases in future greenhouse gas emissions. This is effectively an example of anthropogenic enhancement of natural emissions. For example, in the high emissions scenario (SSP5-8.5), Southern Ocean wind speeds, and therefore sea spray aerosol production, increases more in a high-emissions scenario compared with a low-emissions scenario (SSP1-2.6). Model uncertainty arises due to the small number of models (typically five) that provided suitable output for this analysis and their disagreement in the direction of change (i.e. whether particulate matter increased or decreased). This disagreement results from differences in how models parameterise the processes producing natural particulate matter. For example, secondary sulphate aerosol can be produced from marine biogenic activity, which in turn is sensitive to temperature. Some models show that more secondary sulphate aerosol will be produced in a warmer world as a result of increased ocean productivity, while others show that it will decrease.

With those caveats in mind, we can conclude that by the end of the 21st century:

- Sea spray aerosol will likely increase, irrespective of the greenhouse gas emissions scenario. Larger increases in greenhouse gas emissions lead to conditions that result in larger increases in sea spray aerosol production.

- Dust particulate matter could increase from transboundary transport from Australia; however, models do not consistently agree on the direction of future change.

- Black carbon aerosol is projected to decrease under the SSPs from anthropogenic emissions; wildfires will have localised impacts that are not included in the CMIP6 models.

- We cannot make projections of natural sulphate aerosol alone, as the CMIP6 models only report total (natural plus anthropogenic) sulphate aerosol. Sulphate aerosol is affected by anthropogenic emissions and has significant natural sources, including volcanoes and marine DMS. Anthropogenic sulphur dioxide emissions are assumed to decrease under the SSPs, and CMIP6 models disagree over future trends in DMS as discussed above. Future volcanic eruptions cannot be predicted; however, continued outgassing of volcanoes in the upper North Island is likely to provide an ongoing source of sulphur dioxide.

5.0 KNOWLEDGE GAPS IN THE CONTRIBUTIONS OF NATURAL SOURCES TO AIRBORNE PARTICULATE MATTER

5.1 Identified Data Gaps in the Generation, Emission and Dispersion of Background Particulate Matter

The analysis of natural-source contributions to particulate matter concentrations in New Zealand airsheds provided in this document was based on data derived from one or two years of monitoring (except for the Wellington, Auckland and Nelson datasets) conducted at different times spread across almost twenty years. The longer-term particulate matter sampling and compositional analysis programmes, such as those in Auckland and Wellington, have provided a benchmark to compare such short-term datasets, assess longer-term trends and guide the conclusions reached. However, the data and coverage are generally more sporadic than desirable to account for many source types. Short-term 'snapshots' of local atmospheric composition do not necessarily provide the means to effectively manage air-quality changes over the longer term and identify the drivers of such change, especially given the seasonal nature of natural aerosol production. During the work, knowledge gaps in the role that natural sources of aerosol play in our urban atmospheres were identified as follows:

1. As indicated above and described in the body of this work, long-term monitoring and aerosol composition analyses provide the means to assess environmental change over time and the impact that different sources, both anthropogenic (including the effect of policy and regulation) and natural, have on driving those changes. There are significant geographic data gaps across New Zealand for aerosol composition and source contributions, particularly in the lower half of the South Island and inland locations of both islands.

2. Organic aerosol, secondary organic aerosol and other biogenic species are largely unmonitored, and the contributions of natural sources of these species to ambient concentrations are largely unknown across New Zealand. These include secondary organic aerosol from biogenic volatile organic compounds (BVOCs) and primary marine organic aerosol (PMOA). Without any historical or present-day estimates, we cannot say how these might change in the future and we do not know what current BVOC inventories are for New Zealand, nor have there been any field studies to date. Furthermore, we do not know how changes in plant-species distribution, land use and climate will affect BVOC emissions, and these may become more important in future as anthropogenic emissions decrease.

3. Nitrates and other nitrogen containing aerosol are also poorly understood. For example, aerosol nitrate deposition may have implications for nitrogen-cycle management in our freshwater resources.

4. The drivers for the observed trends in marine aerosol (sea salt) are not well understood, yet this species has a profound influence on natural aerosol concentrations everywhere in New Zealand. With regard to the generation of sea-salt aerosol, it is not yet clear what role sea surface temperature has in this or what might be expected in a warming climate. Aerosol originating from the ocean (sea salt + DMS-derived secondary sulphate) is the leading source of natural aerosol to New Zealand – it is unclear how such aerosol production is affected by marine heatwaves, which are becoming more common.

5. The impact of oceanic phytoplankton blooms seeded by fallout from wildfire or dust storm events on the emission of aerosol originating from the ocean (both sea spray and sulphate aerosol) is poorly understood but is likely to become more significant in a warming climate.

6. Recent research in New Zealand and internationally shows that microplastic particles (not a natural source) are also being emitted from our oceans but the relationship with sea-salt aerosol and the emission (or co-emission) mechanisms are not yet understood. For example, the incorporation of microplastic particles in sea salt may have profound implications for the associated health effects resulting from inhalation of such particulate matter. While most sources of anthropogenic particulate matter are projected to decrease in future, microplastic abundances will increase due to degradation of plastic waste that has accumulated in the environment. Similar observations have been made for perfluoroalkyl (PFAS) contamination in sea salt.

7. The lack of understanding of how natural aerosols form in remote Southern Hemisphere regions contributes to uncertainty in how they will change in the future. Earth system models generally produce poor-quality simulations of the atmosphere over the Southern Ocean because there are not sufficient observations (of any type) in and above the Southern Ocean to well constrain the models. Remote Southern Hemisphere areas (including the New Zealand region) are under-studied, and further work is needed to ensure that aerosols are represented appropriately for the New Zealand context. Recognising this problem, the observational effort in the Southern Ocean has increased in the last few years (for example, the Argo floats programme). For sulphate aerosol, the impact of climate change on the DMS precursor emissions is not known. In addition, the chemical processes that convert DMS to sulphate are highly complex and poorly represented in models.

5.2 Recommendations for Further Monitoring or Research and the Likely Costs

The data and knowledge gaps identified in Section 5.1 comprise three broad categories that are interlinked, and it is recommended that:

*   Routine monitoring and compositional analysis of source contributions are undertaken over time to track environmental change and the drivers of that change.

*   Deeper research is conducted into understanding the fundamental processes and earth system drivers that give rise to the observations we make in our urban monitoring data and the capacity to make future projections.

*   The science capability and capacity is ensured to undertake data gathering and provide the data science necessary to fill those knowledge gaps.

The costs for routine monitoring and analyses are well understood and it would therefore be a matter of designing a suitable programme at an appropriate scale to fill those knowledge gaps. How this is cast in the current regional council and unitary authority monitoring regime is a matter for further exploration and discussion.

The deeper research would be at the level of Ministry of Business, Innovation & Employment Endeavour programmes, or platforms such as the Deep South National Science Challenge involving cross-discipline researchers and students. However, Earth system processes and the impacts of human disturbances are best understood through a long-term lens that short-term programme funding will not be able to cover, and some thought needs to be given as to how to address the long-term view and datasets required to inform the science. A longer-term funding approach would also go some way to providing for the sustainable capability and capacity in the New Zealand science system.

6.0 ACKNOWLEDGEMENTS

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APPENDICES

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APPENDIX 1 AIR PARTICULATE MATTER SAMPLING SITES FOR COMPOSITIONAL ANALYSIS AND RECEPTOR MODELLING

Region	Sites	Time Period	Frequency	Size Fraction	Location (Lat; Long)
Northland	Whangārei	2004–2012	1-day-in-6	PM_{10}	-35.7252; 174.3177
Wellington	Masterton	2002–2004	1-day-in-3	$PM_{2.5}$, $PM_{10-2.5}$	-40.9523; 175.6465
	Masterton (two sites)	Winter 2010	Hourly continuous	$PM_{2.5}$, $PM_{10-2.5}$	-40.9593; 175.6531
	Upper Hutt	2000–2002	Variable	$PM_{2.5}$, $PM_{10-2.5}$	-41.1308; 175.0426
	Wainuiomata	2006–2008, 2011–2014	1-day-in-3	$PM_{2.5}$, $PM_{10-2.5}$	-41.2681; 174.9534
	Wainuiomata	2014–onward	6/12-hourly continuous	$PM_{2.5}$, $PM_{10-2.5}$	-41.2681; 174.9534
	Seaview	2002–2004, 2005–2007	1-day-in-3	$PM_{2.5}$, $PM_{10-2.5}$	-41.2405; 174.9140
	Wairarapa (Masterton, Carterton, Featherston)	Winter 2009	Daily (screening)	$PM_{2.5}$, $PM_{10-2.5}$	-
	Mt Victoria Tunnel	Summer 2009	Peak traffic	$PM_{2.5}$, $PM_{10-2.5}$	-41.3035; 174.7892
	Baring Head	1996–1998	Weekly	$PM_{2.5}$, $PM_{10-2.5}$	-41.4082; 174.8714
	Raumati	Winter 2010	12-hourly	$PM_{2.5}$, $PM_{10-2.5}$	-40.9321; 174.9799
	Seven indoor/outdoor sites	Winter 2017	2-hourly continuous	$PM_{2.5}$, $PM_{10-2.5}$	-
	Masterton East	2018	1-day-in-3	$PM_{2.5}$	-40.9593; 175.6531
	Newtown	2016	2-hourly continuous	$PM_{2.5}$, $PM_{10-2.5}$	-41.3111; 174.7797
	Port Nicholson	Dec 2019 – March 2020	6-hourly continuous	$PM_{2.5}$, $PM_{10-2.5}$	-41.2772; 174.7857
	Willis Street	Dec 2019 – March 2020; April 2021 – ongoing	12-hourly continuous	$PM_{2.5}$, $PM_{10-2.5}$	-41.2936; 174.7719

Region	Sites	Time Period	Frequency	Size Fraction	Location (Lat; Long)
Auckland	Kingsland	2004–2007	1-day-in-3	$PM_{2.5}$, PM_{10}	-36.8732; 174.7471
	Takapuna	2007–2016	1-day-in-3	$PM_{2.5}$	-36.7803; 174.7489
	Takapuna	2006–onward	1-day-in-3	PM_{10}	-36.7803; 174.7489
	Takapuna (three sites)	Winter 2012	Hourly continuous	$PM_{2.5}$, $PM_{10–2.5}$	-36.7803; 174.7489
	Queen Street	2006–2016	1-day-in-3	$PM_{2.5}$	-36.8476;174.7655
	Queen Street	2006–onward	Daily	PM_{10}	-36.8476; 174.7655
	Penrose	2006–2016	1-day-in-3	$PM_{2.5}$, PM_{10}	-36.9045; 174.8156
	Khyber Pass Road	2006–2015	1-day-in-3	$PM_{2.5}$, PM_{10}	-36.8662; 174.7705
	Henderson	2006–onward	1-day-in-3	PM_{10}	-36.8681; 174.6284
	Patumāhoe	2010	Daily	$PM_{2.5}$, $PM_{10–2.5}$	-37.2046; 174.8639
	Johnstone Hills tunnel	June 2010	3-hourly	$PM_{2.5}$, $PM_{10–2.5}$	-36.5353; 174.6800
Nelson	Tāhunanui	2005–2019	1-day-in-3	PM_{10}	-41.2949; 173.2431
	Nelson City	2006–2018	1-day-in-3	$PM_{2.5}$, PM_{10}	-41.2783; 173.2735
	Nelson City (three sites)	Winter 2011	Hourly continuous	$PM_{2.5}$, $PM_{10–2.5}$	-41.2783; 173.2735
Marlborough	Blenheim	2007	1-day-in-3	$PM_{2.5}$, $PM_{10–2.5}$	-41.5268; 173.9561
Otago	Dunedin	2010	1-day-in-3	$PM_{2.5}$, $PM_{10–2.5}$	-45.8689; 170.5177
	Alexandra (three sites)	Winter 2011	Hourly continuous	$PM_{2.5}$, $PM_{10–2.5}$	-45.2534; 169.3912
Canterbury	Christchurch	2001–2002	Daily	$PM_{2.5}$	-43.5112; 172.6337
	Timaru	2006–2007	1-day-in-3	$PM_{2.5}$	-44.4046; 171.2496
	Woolston	2013–2014	2-hourly continuous	$PM_{2.5}$, $PM_{10–2.5}$	-43.5572; 172.6811
	Christchurch, Coles Place	2013–2015	1-day-in-3	$PM_{2.5}$, $PM_{10–2.5}$	-43.5112; 172.6337
	Christchurch: Coles Place, Woolston, Riccarton (high-resolution three-site study)	Winter 2014	2-hourly continuous	$PM_{2.5}$, $PM_{10–2.5}$	-43.5112; 172.6337
	Lyttelton Port high resolution study	Summer 2021	6-hourly continuous	$PM_{2.5}$, $PM_{10–2.5}$	-43.6061; 172.7273

Region	Sites	Time Period	Frequency	Size Fraction	Location (Lat; Long)
Hawke's Bay	Hastings	2006–2007	1-day-in-3	$PM_{2.5}$, PM_{10}	-39.6385; 176.8574
	Meanee Rd	2006 + 2008	1-day-in-2 (screening survey)	$PM_{2.5}$, $PM_{10-2.5}$	-
	Napier	2008–2009	1-day-in-3	$PM_{2.5}$, $PM_{10-2.5}$	-
	Awatoto	2016–2017	1-day-in-3	$PM_{2.5}$, $PM_{10-2.5}$	-39.5459; 176.9192
	Marewa Park	2017–2018	1-day-in-3	$PM_{2.5}$, $PM_{10-2.5}$	-39.5002; 176.8971
	Hastings	2022–2023	1-day-in-3	$PM_{2.5}$, PM_{10}	-39.6385; 176.8574
Southland	Invercargill	Winter 2014	Hourly continuous	$PM_{2.5}$, $PM_{10-2.5}$	-46.4305; 168.3711
Waikato	Tokoroa	Winter 2014	Daily	PM_{10}	-38.2216; 175.8589
	Tokoroa	October 2015 – October 2016	Daily	PM_{10}	-38.2216; 175.8589
Bay of Plenty	Rotorua (Whakarewarewa Village)	October 2014 – 2019	1-day-in-3	$PM_{2.5}$, $PM_{10-2.5}$	-38.1625; 176.2571
Tasman	Richmond	2013–2016	1-day-in-3	PM_{10}	-41.3396; 173.1833
	Richmond	2015–2016	Daily	$PM_{2.5}$	-41.3396; 173.1833
	Motueka	2022	Daily	$PM_{2.5}$	-41.3396; 173.1833
West Coast	Westport	Winter 2023	Daily	$PM_{2.5}$, PM_{10}	-41.7511; 171.5998

APPENDIX 2   PARTICULATE MATTER COMPOSITION ANALYSIS TECHNIQUES

A2.1   Elemental Concentrations by Ion Beam Analysis

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; Trompetter et al. 2005). IBA techniques do not require sample preparation and are fast, non-destructive and sensitive (Cohen 1999; Maenhaut and Malmqvist 2001; Trompetter et al. 2005).

IBA measurements for this study were carried out at the New Zealand IBA facility operated by GNS Science. Figure A2.1 shows the particulate matter analysis chamber with its associated X-ray, γ-ray and particle detectors for Particle-Induced X-ray Emission (PIXE), Particle-Induced Gamma-ray Emission (PIGE), Proton Elastic Scattering Analysis (PESA) and Rutherford Back Scattering (RBS) measurements.
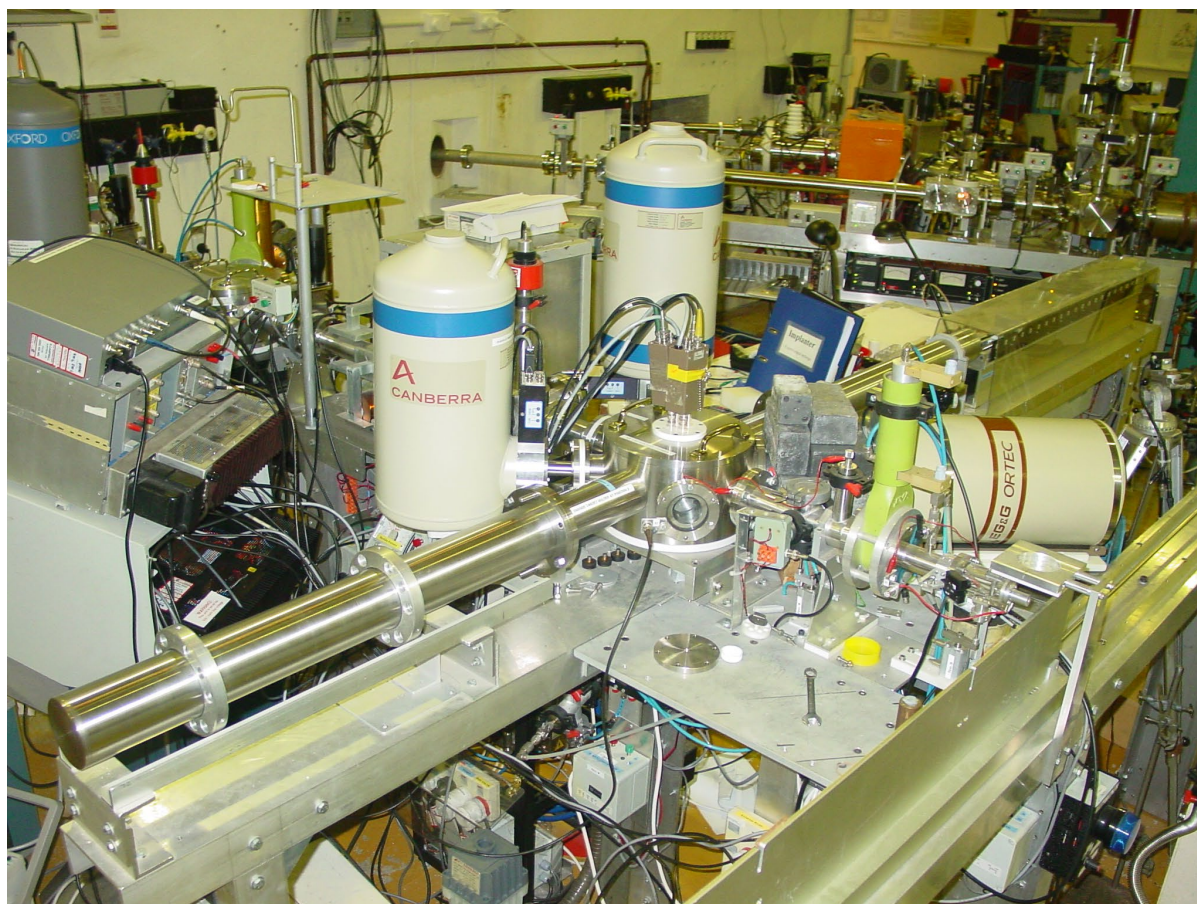
Figure A2.1   Particulate matter analysis chamber with its associated detectors.

The following sections provide a generalised overview of the IBA techniques used for elemental analysis and the analytical set-up at GNS Science (Cohen et al. 1996; Cohen 1998; Trompetter 2004; Trompetter et al. 2005). Figure A2.2 presents a schematic diagram of the typical experimental set-up for IBA of air particulate filters at GNS Science.
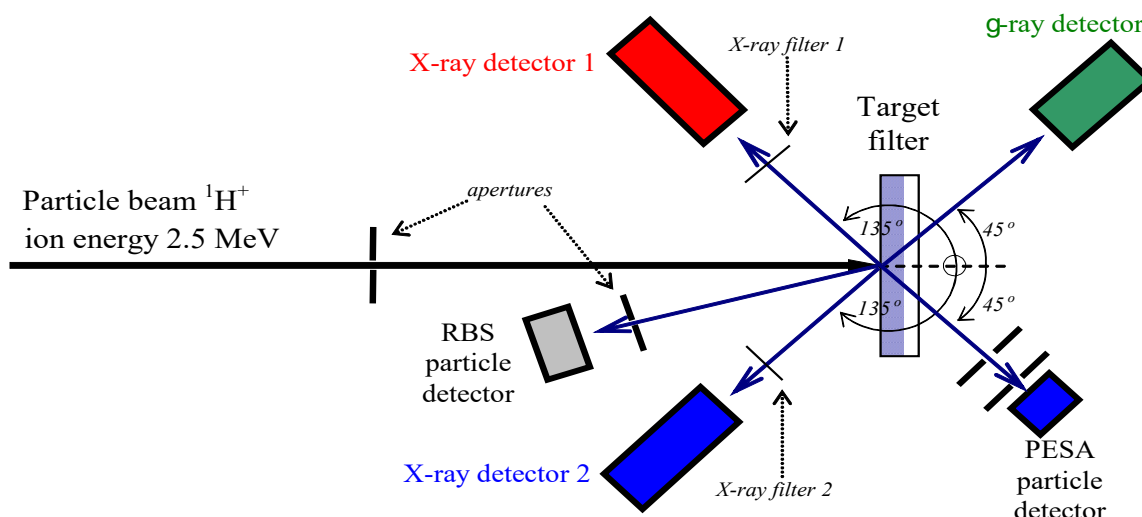
Figure A2.2   Schematic of the typical ion beam analysis experimental set-up at GNS Science.

A2.1.1   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 MeV by the GNS Science 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 practise, 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 A2.3 shows an example of a PIXE spectrum for airborne particles collected on a filter and analysed at the GNS Science IBA facility.
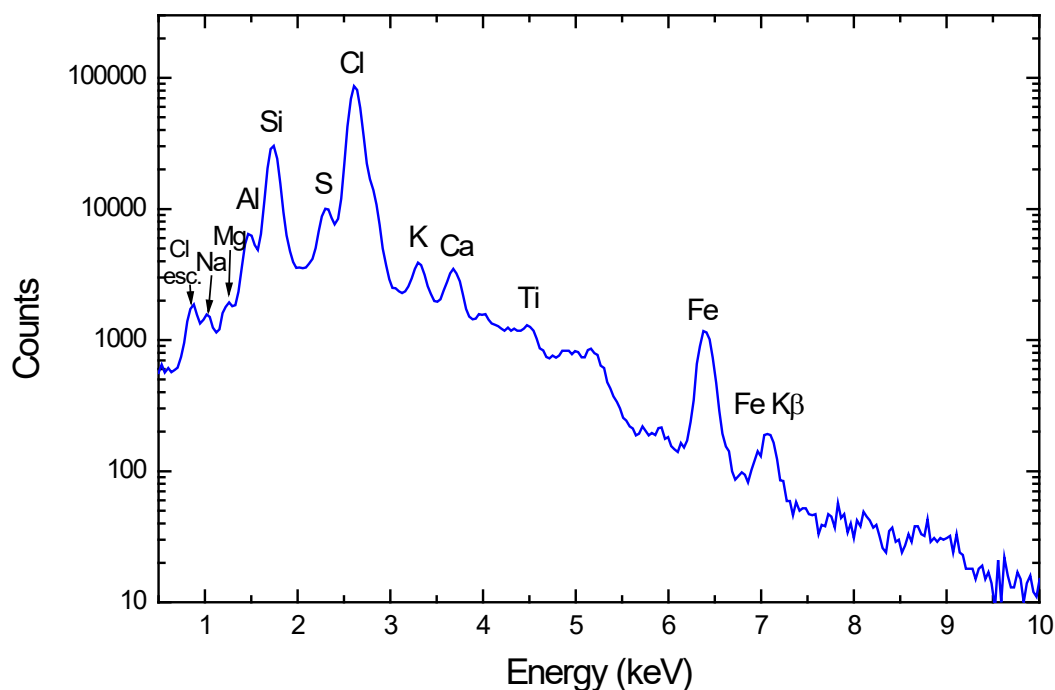
Figure A2.3   Typical particle-induced X-ray emission spectrum for an aerosol sample.

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, 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 limit of detection (LOD). Note that GUPIX provides a specific statistical error and 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. Specific experimental details, where appropriate, are given in the results and analysis section.

A2.1.2 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:

Element	Nuclear Reaction	Gamma Ray Energy (keV)
Sodium	$^{23}Na(p,\alpha\gamma)^{20}Ne$	440, 1634
Fluorine	$^{19}F(p,\alpha\gamma)^{16}O$	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, as the γ-rays are not attenuated to the same extent in the filter matrix or detector material, a problem in the measurement of low-energy X-rays of sodium. Figure A2.4 shows a typical PIGE spectrum.
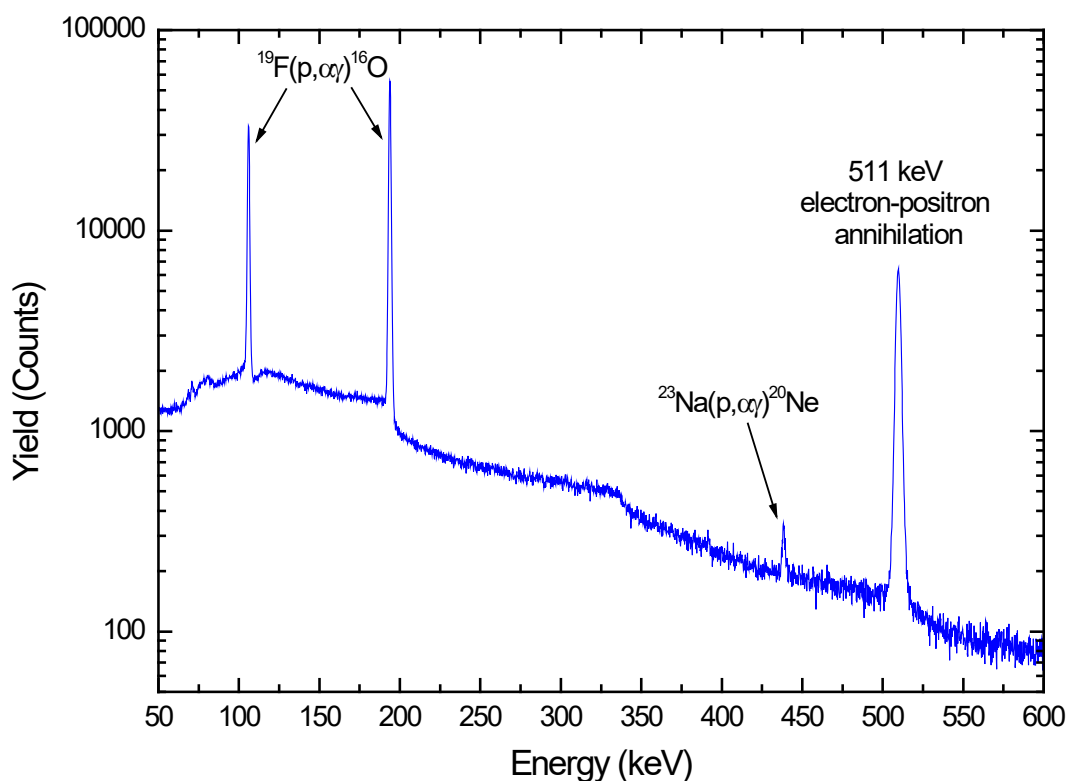
Figure A2.4   Typical particle-induced gamma-ray emission spectrum for an aerosol sample.

A2.2   Elemental Concentrations by X-Ray Fluorescence Spectroscopy

X-ray fluorescence spectroscopy (XRF) was used to measure elemental concentrations in PM_{10} samples collected on Teflon filters at Henderson. 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 A2.5. XRF is a non-destructive and relatively rapid method for the elemental analysis of particulate matter samples.

Figure A2.5   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, the 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 IBA 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 LOD, as 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 A2.6 presents a sample X-ray spectrum.
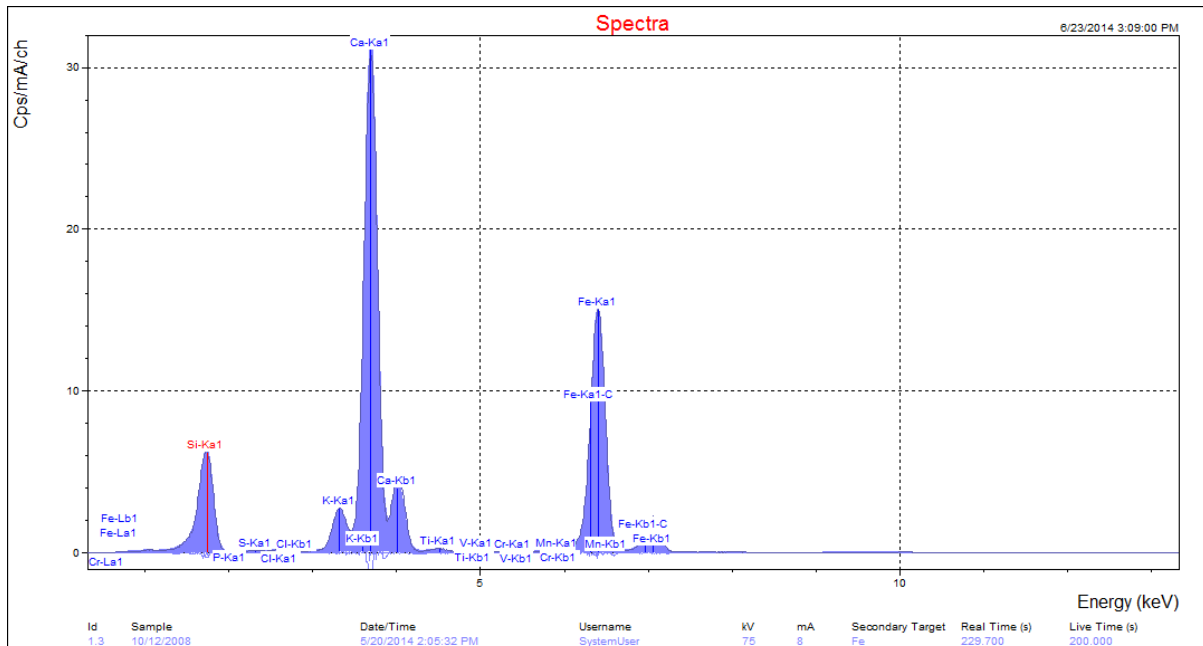
Figure A2.6   Example X-ray spectrum from a PM$_{10}$ sample.

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 National Institute of Standards and Technology reference sample (SRM 2783) and multi-elemental reference standards from the Crocker National Laboratory (University of California, Davis) were also analysed to ensure that the results obtained were robust and accurate.

A2.3   X-Ray Fluorescence Spectroscopy and Ion Beam Analysis Data Reporting

Most filters used to collect particulate matter samples for XRF or IBA analysis are sufficiently thin enough that the X-rays or ion beam penetrate 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 (μg cm^{-2} or 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 47 mm Teflon filters used at monitoring sites. For example, to convert from Cl (ng cm^{-2}) into Cl (ng m^{-3}) for filter samples, the equation is:

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

Equation A2.1

APPENDIX 3   SITE DESCRIPTIONS AND METADATA

The following sections describe the regulatory monitoring sites in airsheds where particulate-matter samples were collected for compositional analysis and receptor modelling. The data from these studies have formed the basis to assess natural-source contributions to total particulate-matter concentrations across New Zealand urban areas and regions. The Potential source contribution function (PSCF) analyses presented in Section 3 should be viewed in conjunction with the individual monitoring location analyses, particularly with respect to the Conditional Probability Function (CPF) plots, which combine local meteorology with source concentrations to produce bivariate polar plots that show the most likely direction from which higher-source concentrations of particulate matter arrive at the monitoring site.

A3.1   Whangārei Monitoring Site

Size-resolved PM_{10} samples were collected with a high-volume sampler from 2004 to 2012 at an ambient air-quality monitoring station located on top of the roof of the Northland Regional Council building at 36 Water Street, Whangārei (Lat. -35.725255, Long. 174.317721; elevation: 6 m). Figure A3.1 presents the site location on a map of the local area (Davy and Ancelet 2014).
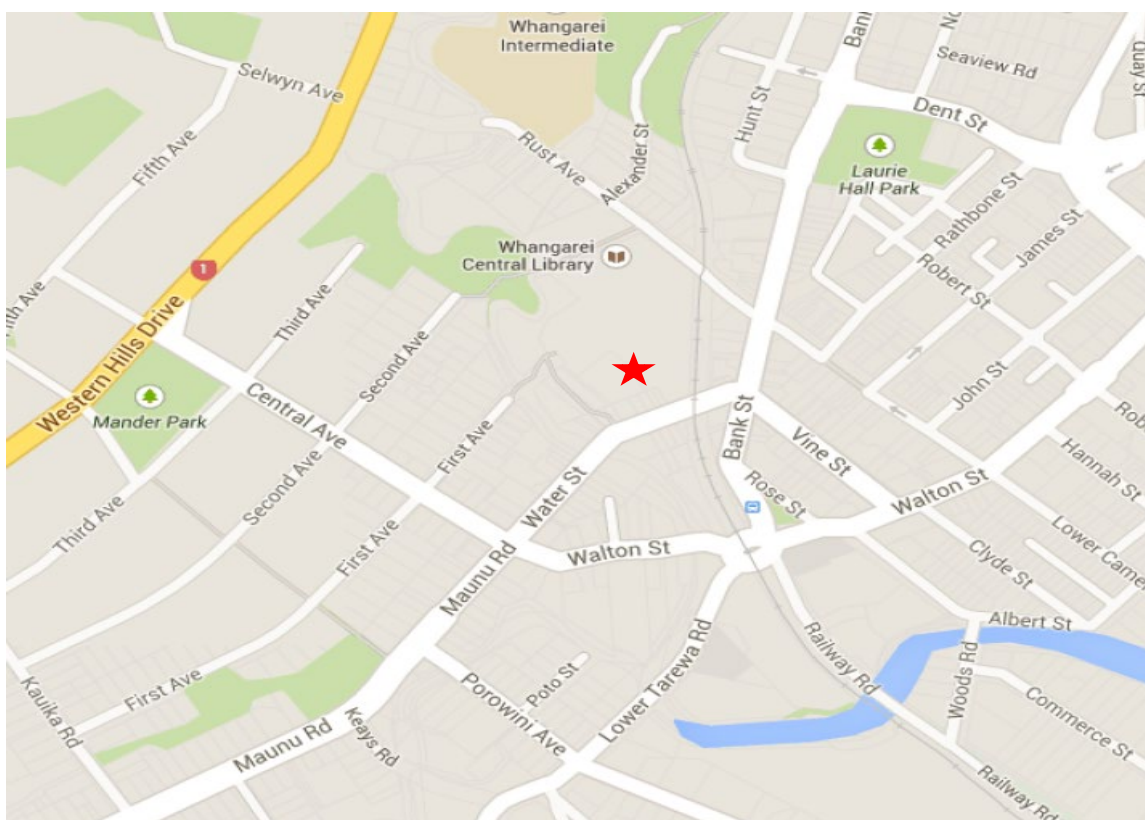
Figure A3.1   Map showing the location of the Water Street monitoring site (★) (Source: Wises Maps).

Water Street is located on the northwestern edge of the Whangārei central business district. The site is 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 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 Whangārei Harbour. The city of Whangārei essentially sits in the confluence of two valleys that drain into the harbour. Figure A3.2 presents the PSCF back-trajectory analyses for marine aerosol and secondary sulphate measured at the Whangārei site.
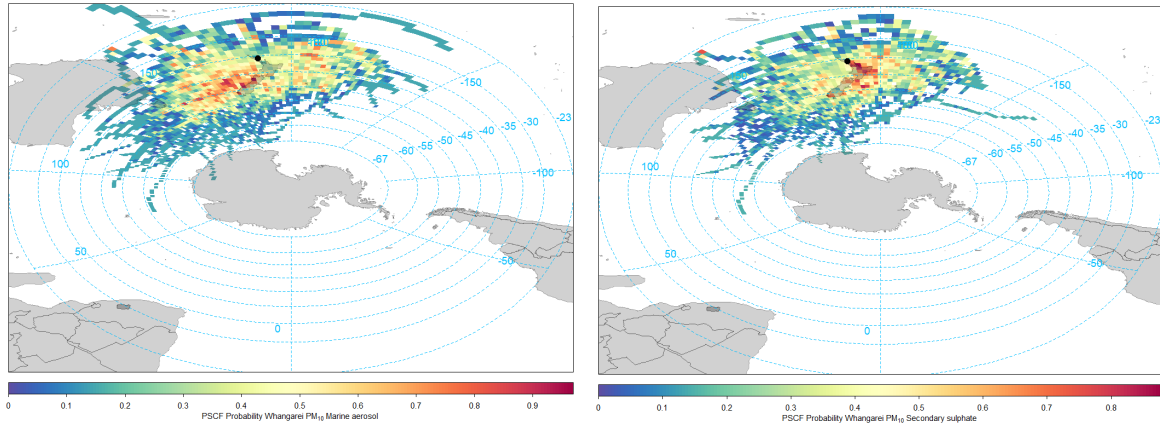
Figure A3.2   Air-mass back-trajectory and PSCF analysis for Whangarei PM_{10} (left) marine aerosol and (right) secondary sulphate source regions.

A3.2   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 A3.3. Full details and site metadata are contained in Davy et al. (2017).
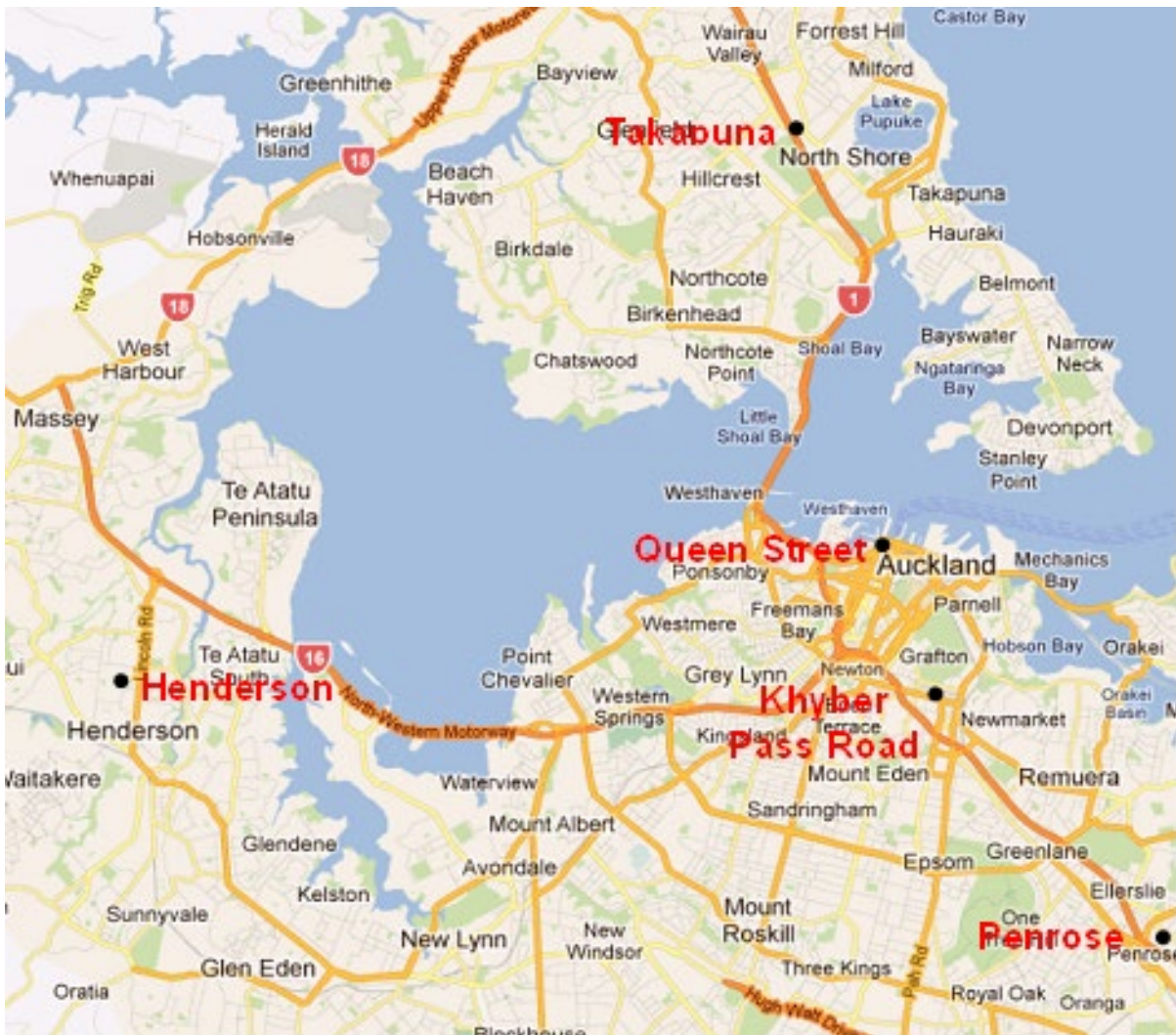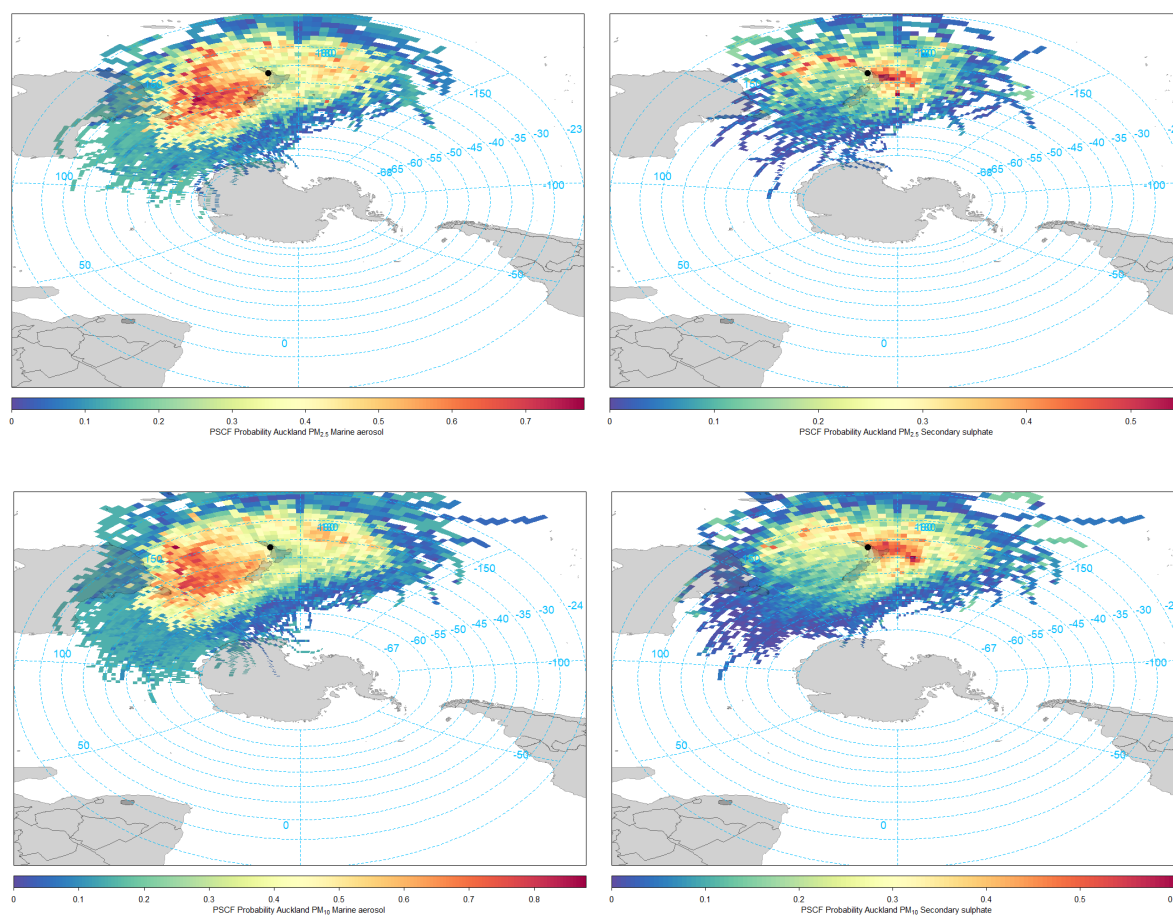

Figure A3.3   Location of the five monitoring sites (●) included in the Auckland receptor modelling study (Source: Wises Maps).

Figure A3.4 presents the PSCF back-trajectory analyses for marine aerosol and secondary sulphate measured across the Auckland sites.

Figure A3.4   Air-mass back-trajectory and PSCF analysis for Auckland (top left) PM$_{2.5}$ marine aerosol, (top right) PM$_{2.5}$ secondary sulphate, (bottom left) PM$_{10}$ marine aerosol and (bottom right) PM$_{10}$ secondary sulphate source regions.

A3.3   Tokoroa Monitoring Site

Daily PM$_{10}$ sampling was undertaken by Waikato Regional Council from September 2015 until October 2016 at its 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 the southeast to the northwest. 24-hour PM$_{10}$ 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 particulate matter sampling and systems maintenance at the air-quality monitoring site was carried out by Waikato Regional Council and, as such, it maintains all records of equipment, flow rates and sampling methodologies used for the particulate matter sampling regime. Filter conditioning, weighing and re-weighing for PM$_{10}$ gravimetric mass determinations was carried out by Hill Laboratories Limited (Davy and Trompetter 2017a).

Figure A3.5   Location of the Billah Street monitoring site in Tokoroa (▲) (Source: Waikato Regional Council).

Figure A3.6 presents the PSCF back-trajectory analyses for marine aerosol and secondary sulphate measured at the Tokoroa site.
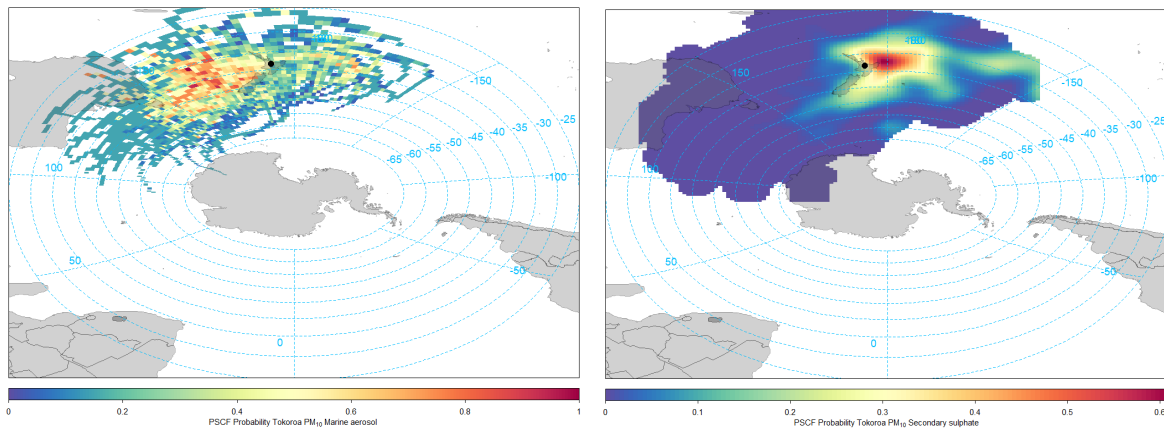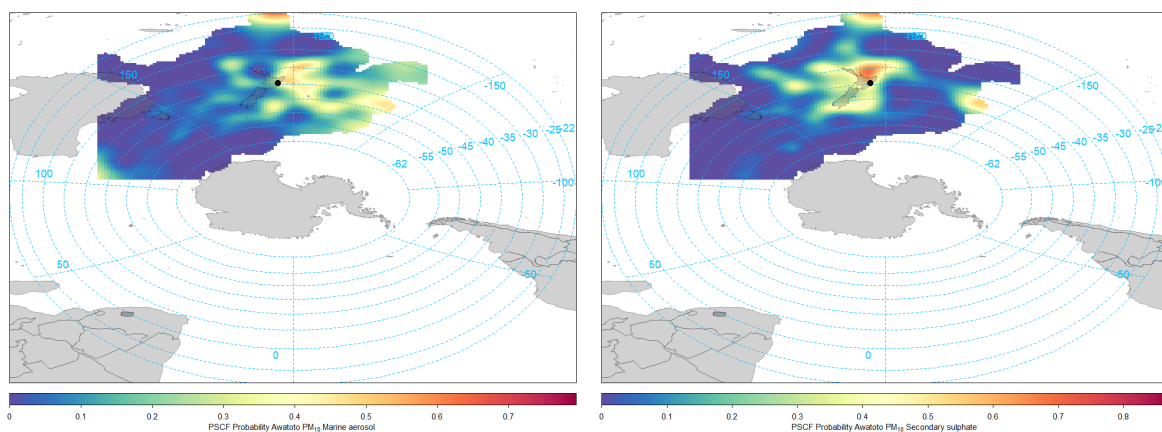

Figure A3.6   Air-mass back-trajectory and PSCF analysis for Tokoroa PM_{10} (left) marine aerosol and (right) secondary sulphate source regions.

A3.4   Hastings (St Johns College) Monitoring Site

Hastings is a small urban area located approximately 20 km south of Napier in Hawke's Bay on the east coast of the North Island of New Zealand. Particulate matter ($PM_{2.5}$ and PM_{10}) sampling was undertaken by Hawke's Bay Regional Council from April 2022 until April 2023 at its air-quality monitoring station on the grounds of St Johns College, Hastings (latitude -39.6390, longitude 176.8588). The site is located in the middle of a residential area, as shown in Figure A3.7 (Davy and Trompetter 2024a).
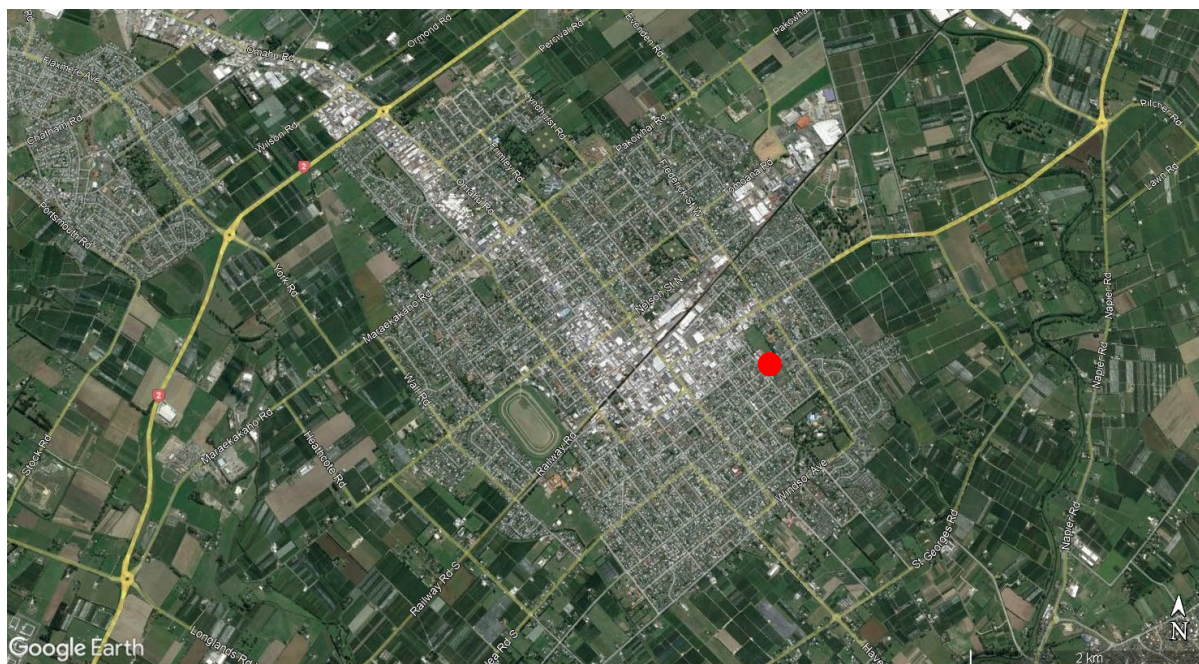
Figure A3.7   Hastings monitoring site location (●) (Source: Hawkes Bay Regional Council).

The area immediately around the site is flat and predominately residential, with local urban road traffic. Hastings town centre and commercial area lies to the west and northwest of the site. Further residential suburbs lie to the north and south. The coast (Hawke Bay) is approximately 10 km directly east. Land use surrounding the Hastings urban area is predominantly agricultural.

Figure A3.8 presents the PSCF back-trajectory analyses for marine aerosol and secondary sulphate measured at the Hastings site.
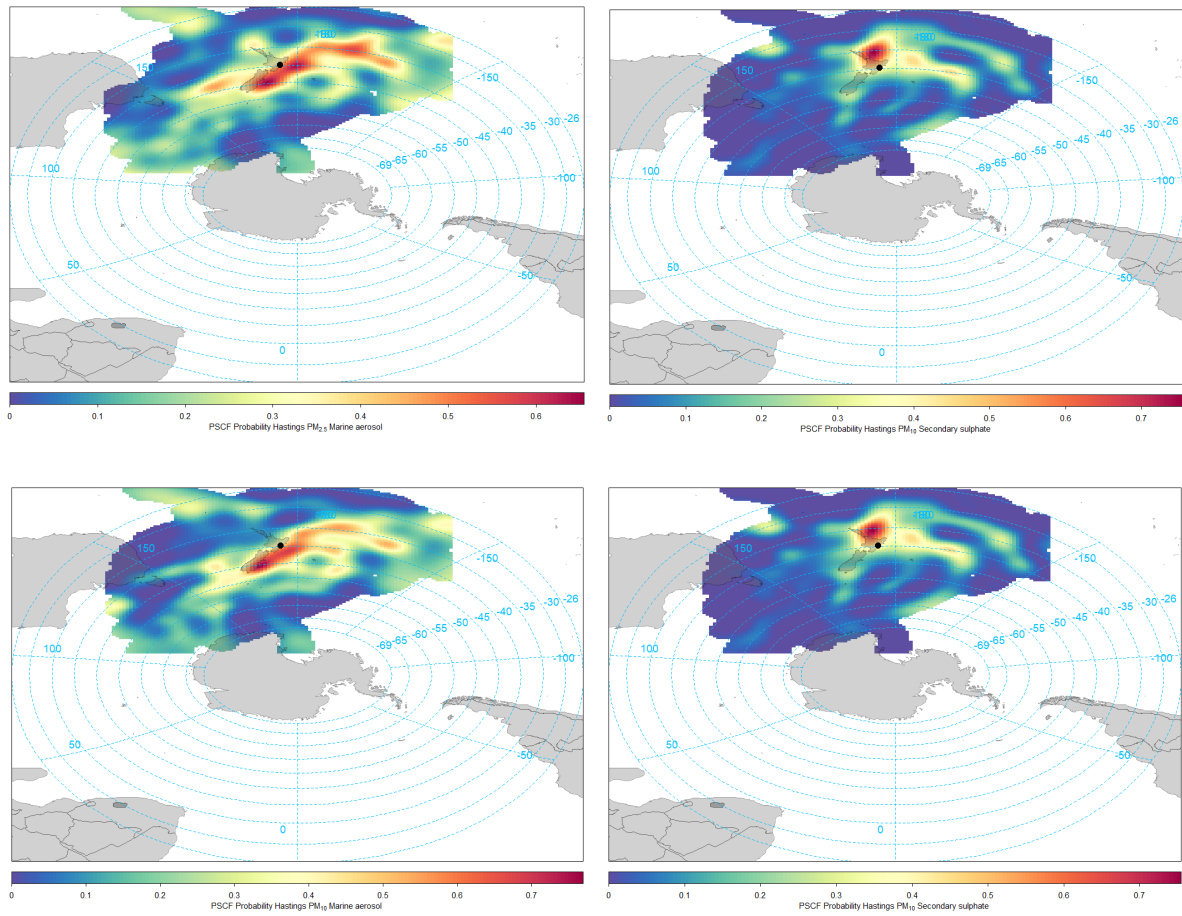
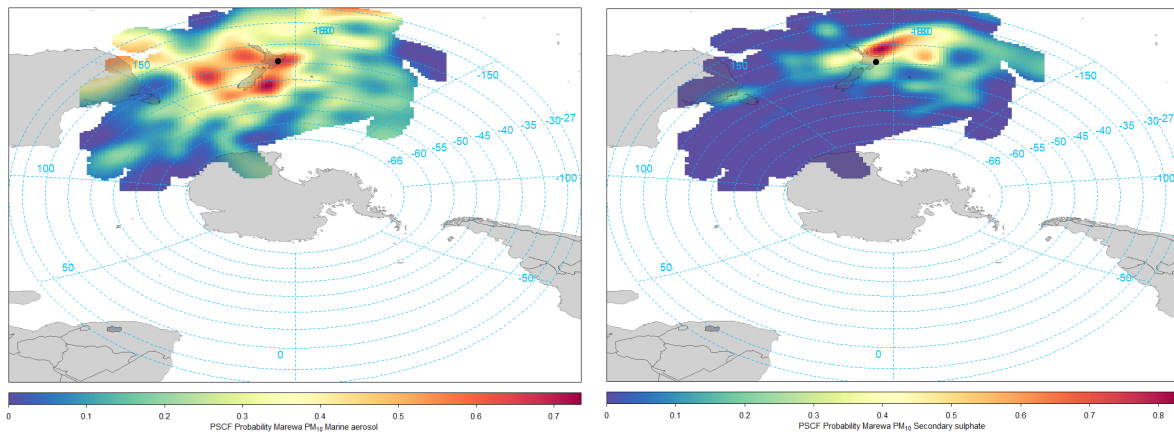Figure A3.8   Air-mass back-trajectory and PSCF analysis for Hastings (top left) PM$_{2.5}$ marine aerosol, (top right) PM$_{2.5}$ secondary sulphate, (bottom left) PM$_{10}$ marine aerosol and (bottom right) PM$_{10}$ secondary sulphate source regions.

A3.5   Awatoto Monitoring Site

$PM_{2.5}$ and $PM_{10–2.5}$ samples were collected at an ambient air-quality monitoring station located at 80 Waitangi Road, Awatoto (Lat. -39.5459, Long. 17.9191; elevation: 4 m). Particulate-matter samples were collected on a 1-day-in-3 basis from April 2016 to May 2017.

Figure A3.9   Aerial image showing the location of the Awatoto air quality monitoring site (●) (Source: Hawke's Bay Regional Council).

Hawke's Bay Regional Council's monitoring site is located approximately 200 m west of the shoreline and 1 km from its northern border. Ravensdown Limited, a fertiliser manufacturer, dominates the area immediately to the south of the monitoring site (Davy and Trompetter 2017c).

Figure A3.10 presents the PSCF back-trajectory analyses for marine aerosol and secondary sulphate measured at the Awatoto site.

Figure A3.10 Air-mass back-trajectory and PSCF analysis for Awatoto PM_{10} (left) marine aerosol and (right) secondary sulphate source regions.

A3.6   Marewa Park, Napier

The air-quality monitoring station on the grounds of Marewa Park is adjacent to the Bowls Napier bowling club at 33 Herrick Street in Marewa Park (Lat. -39.500, Long. 176.897). The site is located in the suburb of Marewa and is the primary national environmental standards (PM_{10}) compliance monitoring site within the Napier airshed, as shown in Figure A3.11. Particulate-matter samples were collected on a 1-day-in-3 basis from May 2017 to May 2018 (Davy and Trompetter 2018).
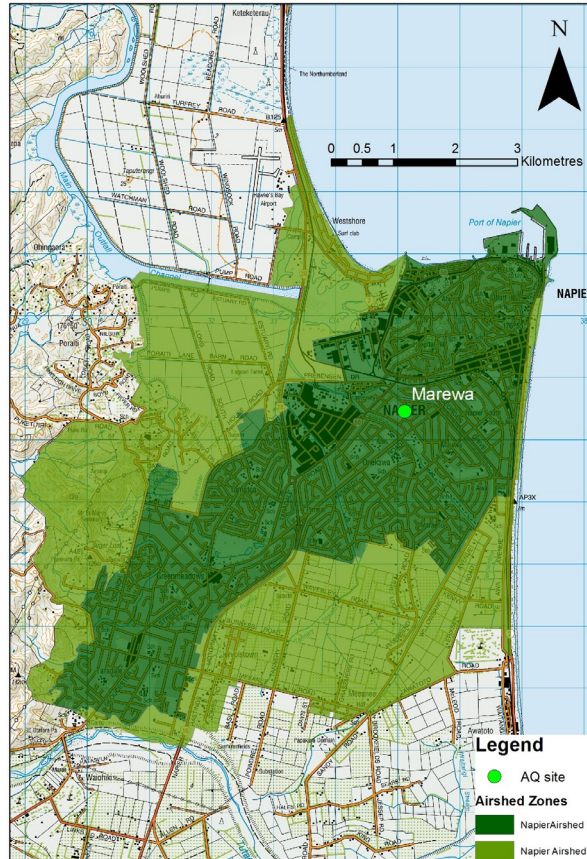
Figure A3.11 Map of the Napier airshed showing the monitoring site in Marewa Park (●) (Source: Hawkes Bay Regional Council).

Figure A3.12 presents the PSCF back-trajectory analyses for marine aerosol and secondary sulphate measured at the Marewa Park site.
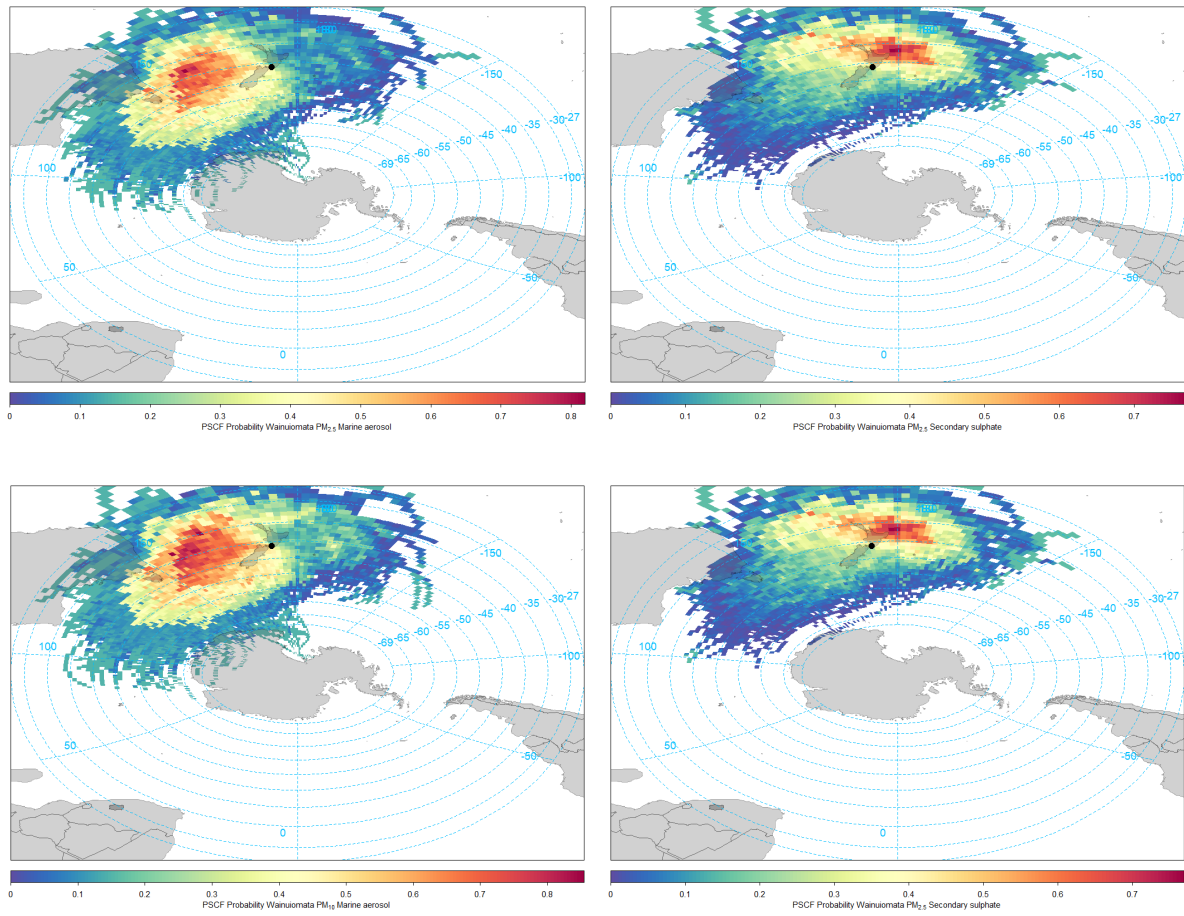

Figure A3.12 Air-mass back-trajectory and PSCF analysis for Marewa Park PM_{10} (left) marine aerosol and (right) secondary sulphate source regions.

A3.7   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. -41.2681, Long. 174.9534). Figure A3.13 shows the site location on a map of the local area (Davy et al. 2012b). Since 2014, a Streaker sampler (Zhou et al. 2016) has been located at the site collecting $PM_{2.5}$ and $PM_{10-2.5}$ samples on a 12-hourly continuous basis for compositional and receptor modelling analysis. This data has been used to generate the PSCF back-trajectory analysis.
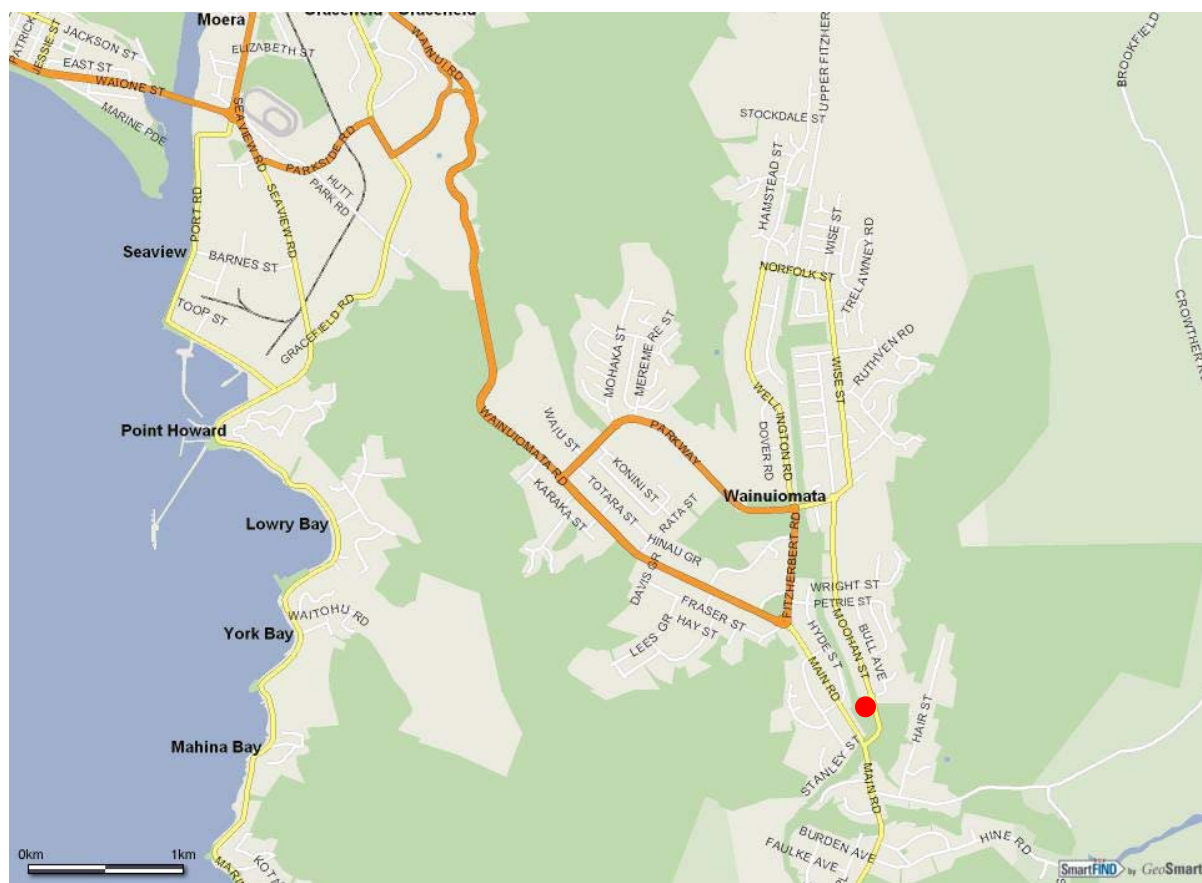
Figure A3.13 Map showing location of the Wainuiomata monitoring site (●) (Source: Wises Maps).

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 Remutaka Range up to 800 m high. The south end of Wainuiomata narrows to a constricted valley that runs 20 km down to the ocean. Wellington City is 15 km to the southwest across the hills and harbour.

Figure A3.14 presents the PSCF back-trajectory analyses for marine aerosol and secondary sulphate measured at the Wainuiomata site.

Figure A3.14 Air-mass back-trajectory and PSCF analysis for Wainuiomata (top left) PM$_{2.5}$ marine aerosol, (top right) PM$_{2.5}$ secondary sulphate, (bottom left) PM$_{10}$ marine aerosol and (bottom right) PM$_{10}$ secondary sulphate source regions.

A3.8   Masterton Monitoring Site

An ambient air-quality monitoring station is located within the grounds of Chanel College in Masterton (Lat. -40.9523; Long. 175.6465; elevation: 100 m) and has been operating since October 2016. Figure A3.15 is a map of the local area surrounding the monitoring site (Ancelet et al. 2012, 2013b). Samples of $PM_{2.5}$ for compositional analysis and receptor modelling were collected at the Chanel College site during 2018.
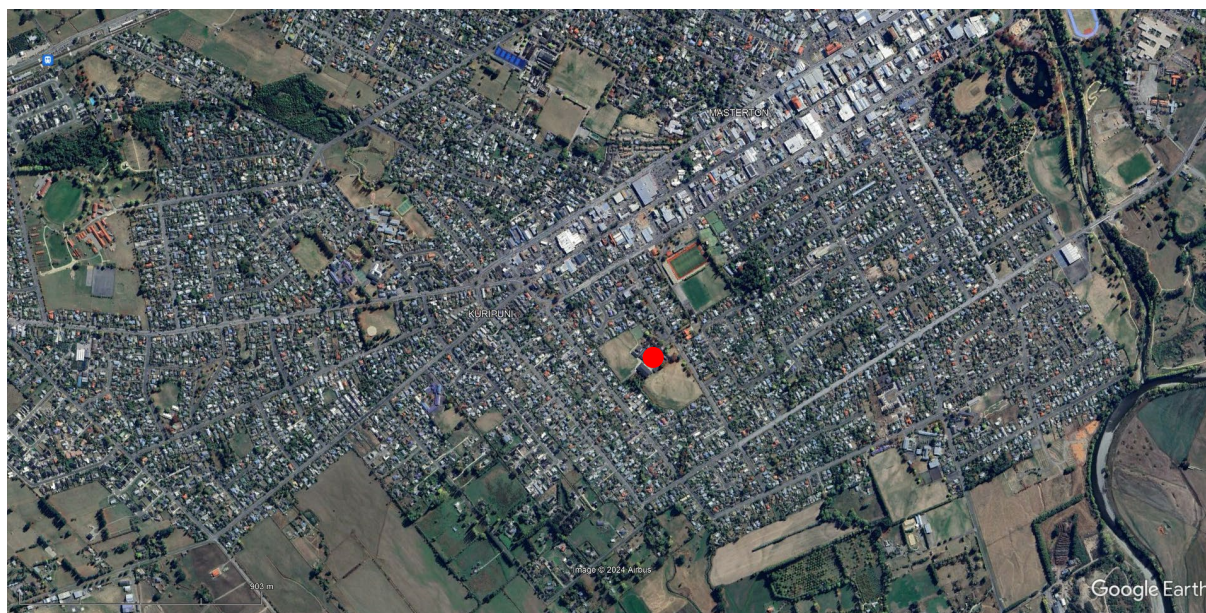
Figure A3.15 Aerial image of Chanel College monitoring site in Masterton (●).

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 Chanel College site was at least 50 m 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.

Figure A3.16 presents the concentration-weighted trajectory analyses for marine aerosol and secondary sulphate measured at the Masterton site.
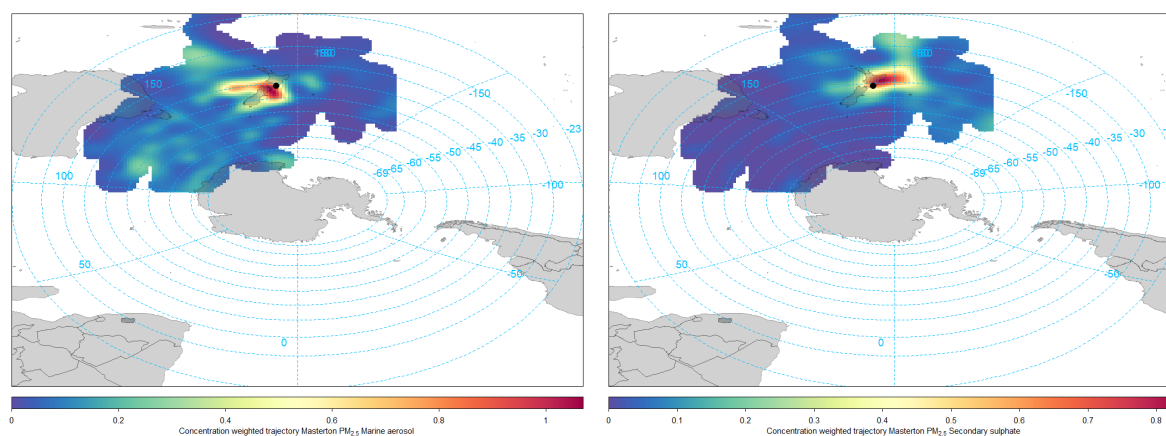
Figure A3.16 Air-mass back-trajectory and concentration-weighted analysis for Chanel College $PM_{2.5}$ (left) marine aerosol and (right) secondary sulphate source regions.

A3.9   St Vincent Street, Nelson Monitoring Site

Size-resolved particulate matter samples (PM_{10} 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 A3.17 presents the site location on a map of the local area. Samples of PM_{10} and $PM_{2.5}$ were collected using a Partisol (satellite and hub) sampler system from July 2008 to November 2017 (Ancelet et al. 2013a, 2014b, 2015).
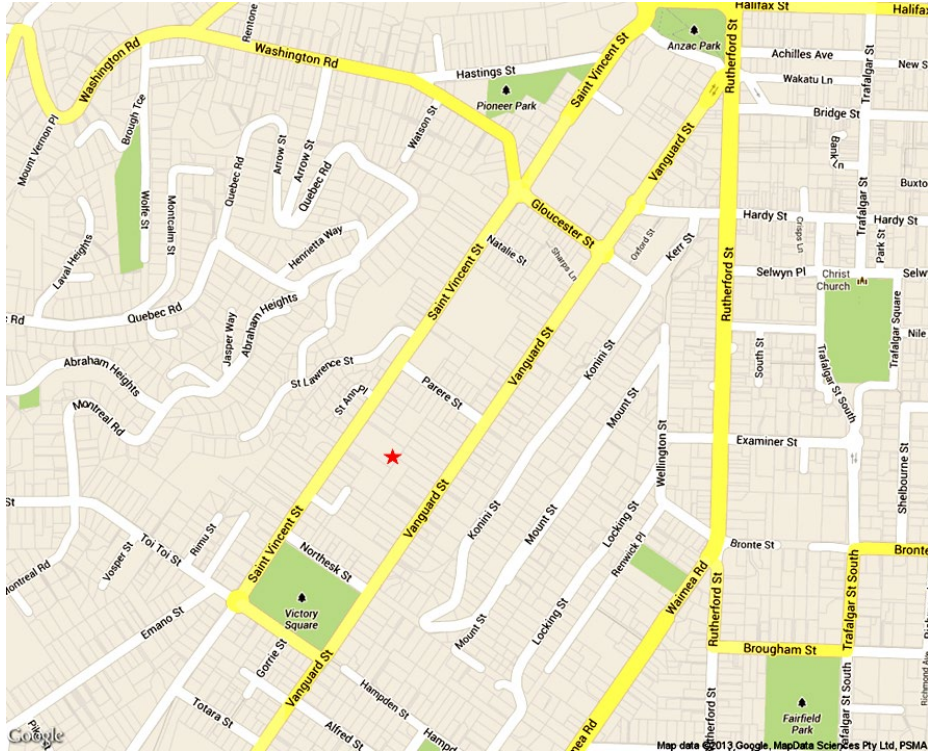

Figure A3.17 Map showing the location of the St Vincent Street monitoring site (★) (Source: Wises Maps).

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

Figure A3.18 presents the PSCF back-trajectory analyses for marine aerosol and secondary sulphate measured at the Nelson site.
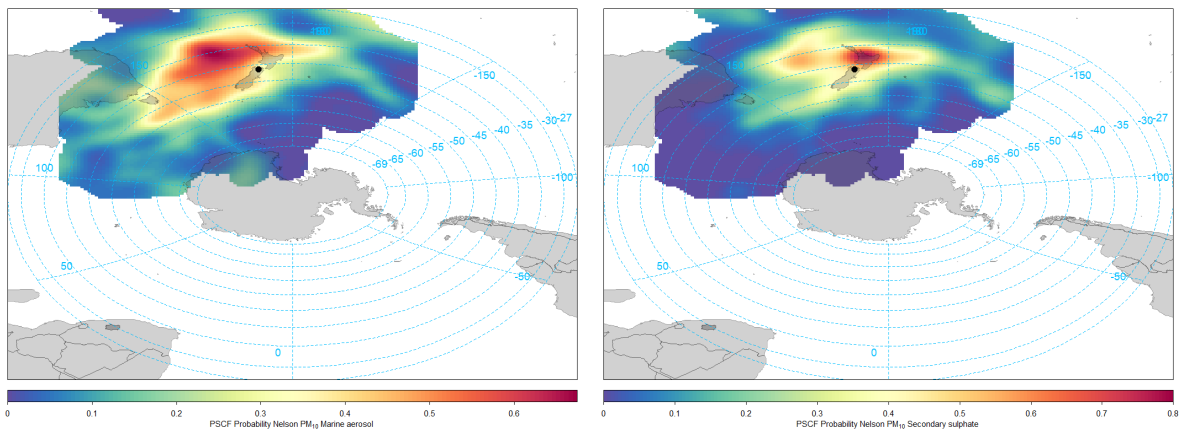
Figure A3.18 Air-mass back-trajectory and PSCF analysis for Nelson PM_{10} (left) marine aerosol and (right) secondary sulphate source regions.

A3.10   Tahunanui Monitoring Site, Nelson

Samples of airborne particles (PM_{10}) were collected between September 2008 and September 2009 at an ambient air-quality monitoring station located on a property off Blackwood Street, Tahunanui (Lat. -41.2949, Long. 173.2431; elevation: 5 m). Figure A3.19 shows the site location on a map of the local area (Davy et al. 2010; Ancelet et al. 2014c).
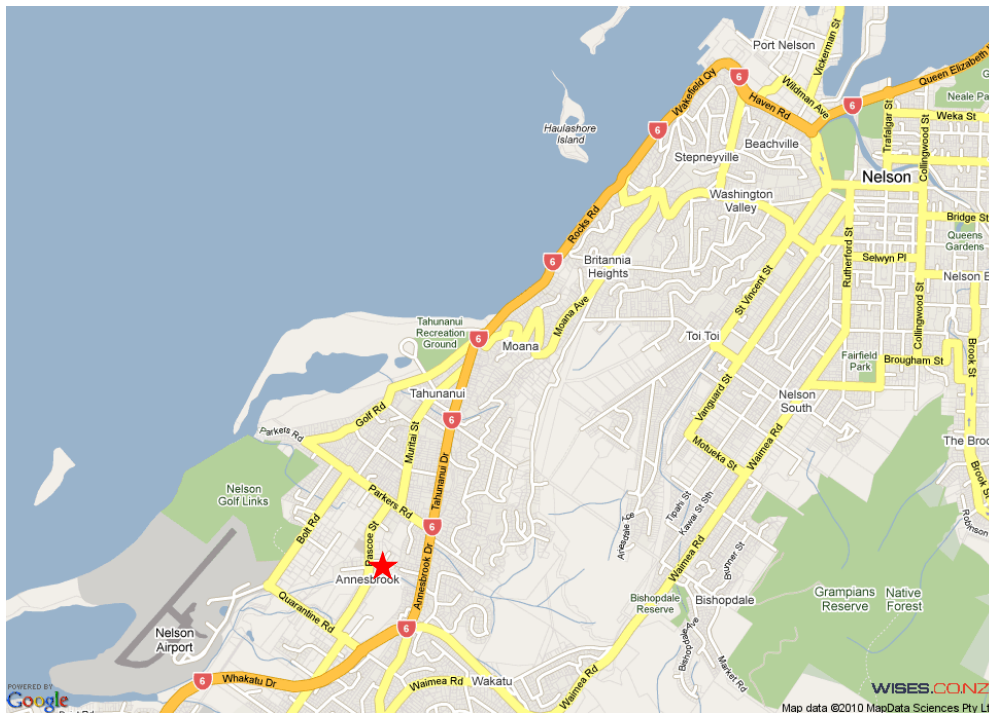

Figure A3.19 Map showing location of Tahunanui monitoring site (★) (Source: Wises Maps).

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.

Figure A3.20 presents the PSCF back-trajectory analyses for marine aerosol and secondary sulphate measured at the Tahunanui site.
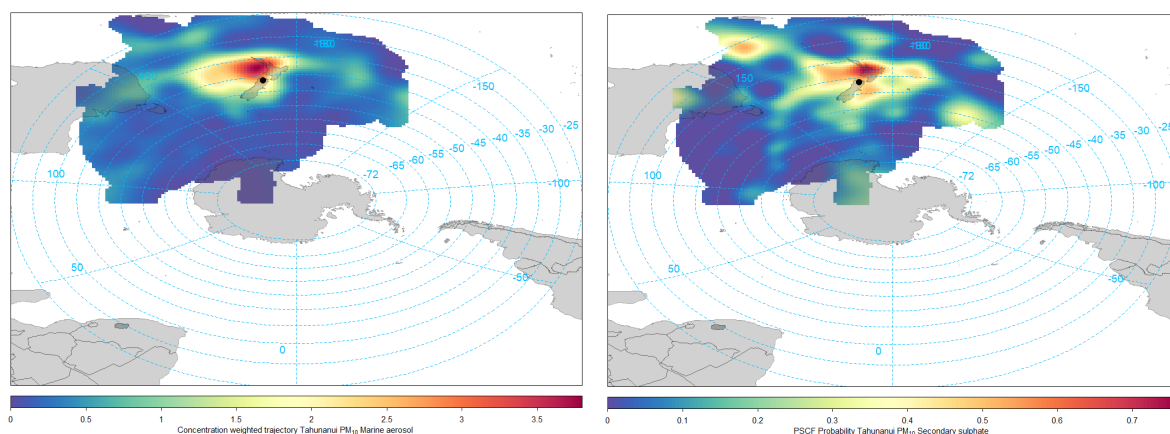
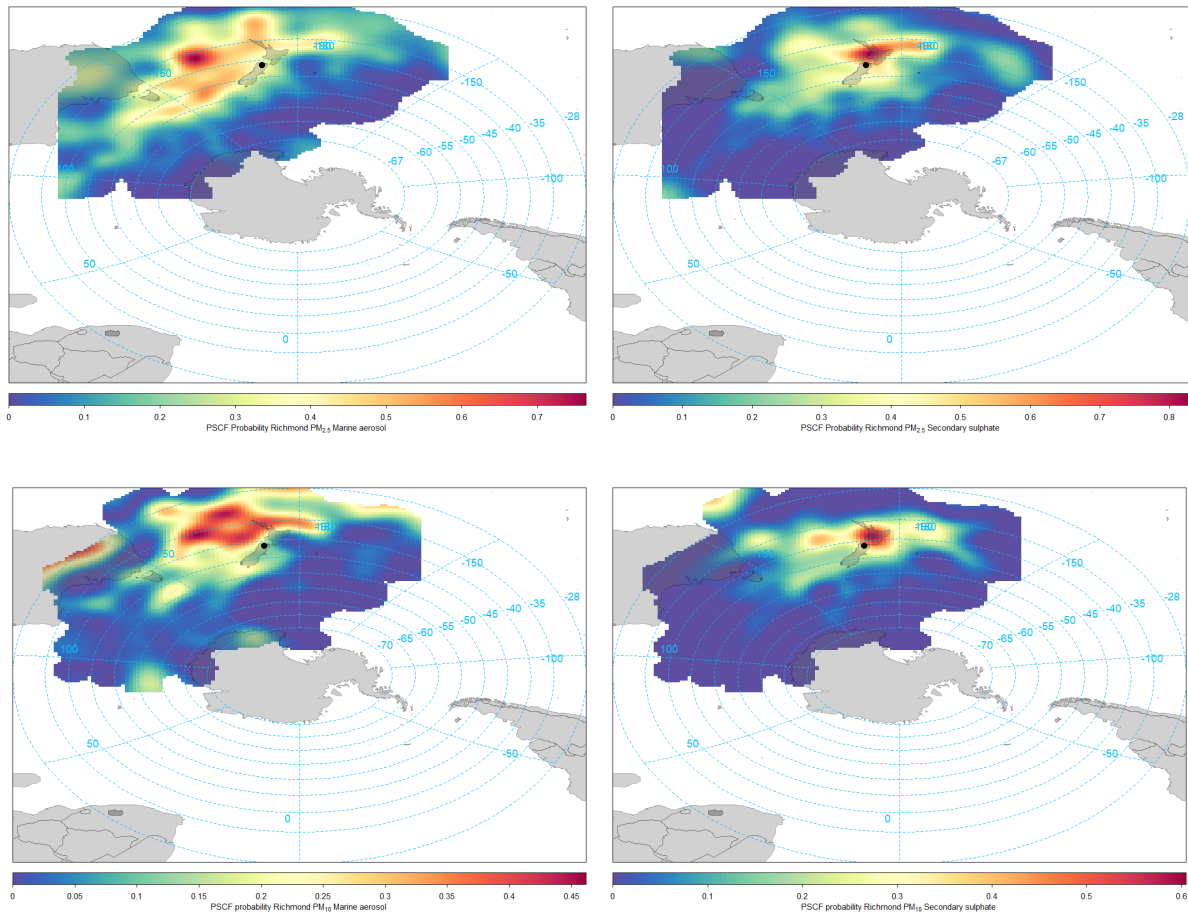Figure A3.20 Air-mass back-trajectory for Tahunanui PM_{10} (left) and concentration-weighted trajectory analysis for marine aerosol, as well as (right) PSCF probability analysis for secondary sulphate source regions.

A3.11   Richmond Monitoring Site, Tasman

PM$_{2.5}$ (daily samples, October 2015 to October 2016) and PM$_{10}$ (1-day-in-6, June 2013 to October 2016) were collected at an ambient air-quality monitoring station located at 56 Oxford Street, Richmond (Lat. -41.2021, Long. 173.1058; elevation: 13 m). Figure A3.21 presents the site location on a map of the local area (Davy and Trompetter 2017b).

Figure A3.21 Map showing the location of the Richmond monitoring site (Source: Tasman District Council).

Oxford Street is located near the Richmond central business district 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.

Figure A3.22 presents the PSCF back-trajectory analyses for marine aerosol and secondary sulphate measured at the Richmond site.

Figure A3.22 Air-mass back-trajectory and PSCF analysis for Richmond (top left) PM$_{2.5}$ marine aerosol, (top right) PM$_{2.5}$ secondary sulphate, (bottom left) PM$_{10}$ marine aerosol and (bottom right) PM$_{10}$ secondary sulphate source regions.

A3.12 Motueka Particulate Matter Speciation Monitoring Site

The Motueka air-quality monitoring station was located on the grounds of Ledger Goodman Park, Motueka (Lat. -41.1117, Long. 173.0170). The site is located in the middle of a residential area, as shown in Figure A3.23. $PM_{2.5}$ samples were collected on a daily basis from January 2022 to January 2023 (Davy and Trompetter 2023).
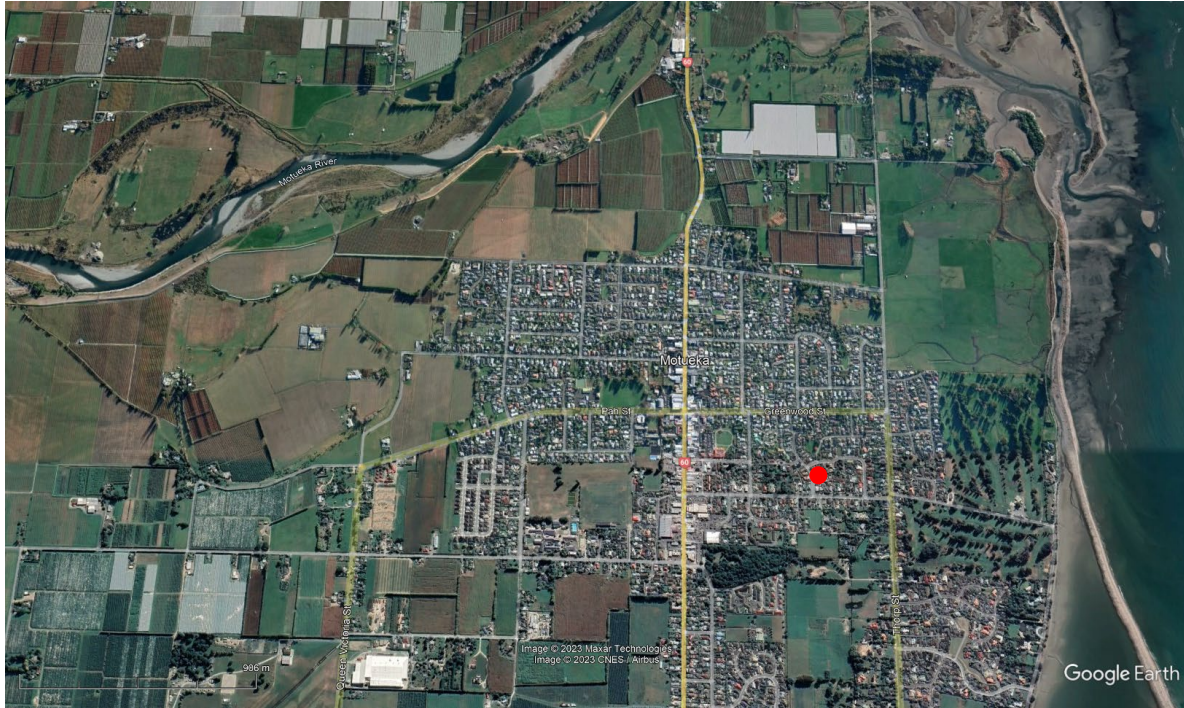
Figure A3.23 Location of Motueka $PM_{2.5}$ monitoring site (●) (Source: Google Earth).

The area immediately around the site is flat and predominately residential, with local urban road traffic. The coast (Tasman Bay) is approximately 1 km directly east, and further residential properties lie to the north and northwest. West of the site, approximately 0.5 km away, is State Highway 60, which runs through the main commercial precinct of Motueka where a variety of commercial, light industrial and engineering activities are located. Land use surrounding Motueka is predominantly agricultural, with the Motueka River to the northwest.

Figure A3.24 presents the concentration-weighted trajectory analyses for marine aerosol and secondary sulphate measured at the Motueka site.
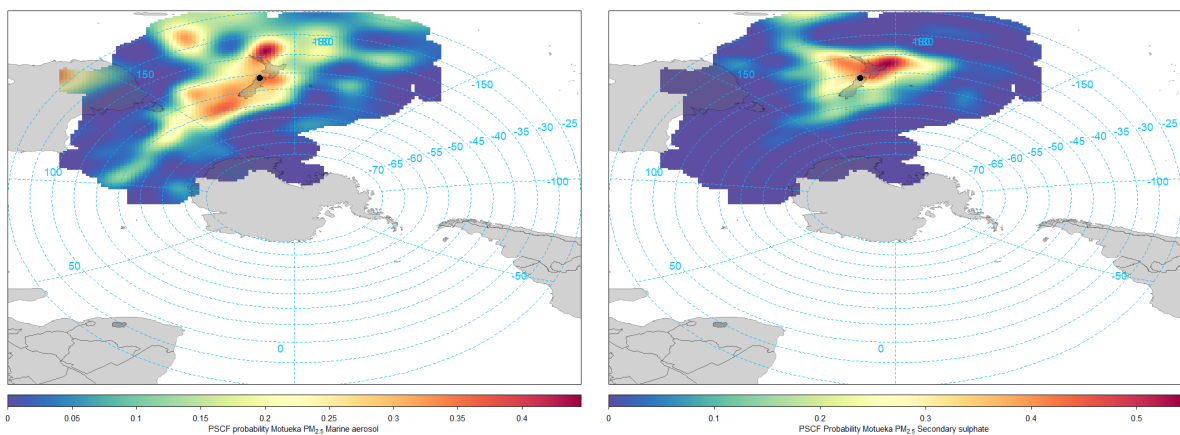

Figure A3.24 Air-mass back-trajectory and PSCF analysis for Motueka $PM_{2.5}$ (left) marine aerosol and (right) secondary sulphate source regions.

A3.13   Westport Monitoring Site

Particulate matter ($PM_{2.5}$ and PM_{10}) winter sampling was undertaken by WCRC from May 2023 until October 2023 at an air quality monitoring site at 44 Queen Street on the grounds of Club Buller, Westport (Lat. -41.7511, Long. 171.5998). The site is located in the middle of a mixed commercial/residential area, as presented in Figure A3.25 (Davy and Trompetter 2024b).

Figure A3.25   Location of Westport monitoring site (●) (Source: Google Earth).

The area immediately around the site is flat and predominately residential, with local urban road traffic. Westport town centre and commercial area lies immediately to the west and southwest of the site, with the Buller River beyond that. Further residential suburbs lie to the north, east and south of the monitoring site. The coast (Buller Bay) is approximately 2 km directly north. Land use surrounding the Westport urban area is predominantly agricultural.

Figure A3.26 presents the back-trajectory analyses for marine aerosol measured at the Westport site.
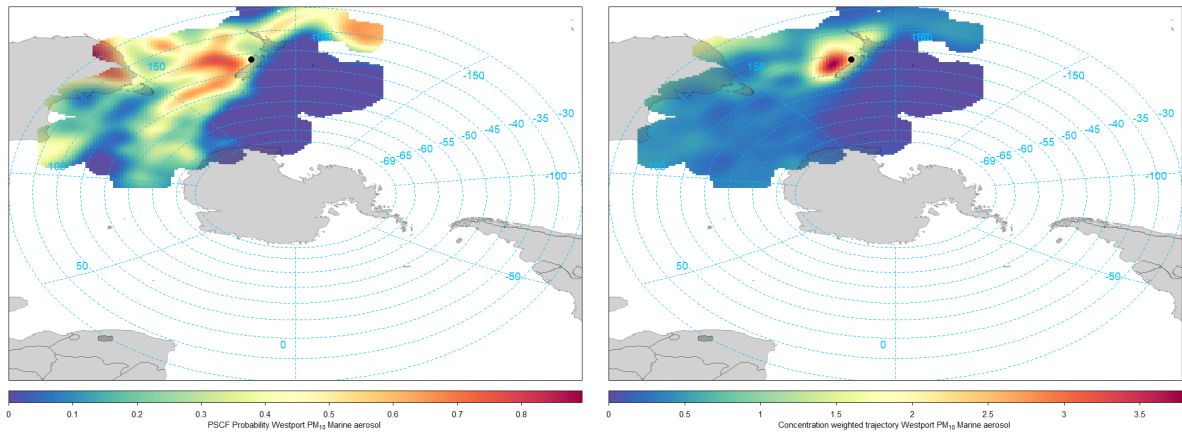
Figure A3.26 Air-mass back-trajectory analysis for Westport marine aerosol source regions (left) PM$_{2.5}$ PSCF analysis and (right) PM$_{10}$ concentration weighted trajectory analysis.

A3.14   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 A3.27 (Davy et al. 2016). Two sampling systems were used to collect particulate matter samples, a MetOne speciation aerosol sampling system (S-SASS) and a Rupprecht & Patashnik (R&P) Dichotomous Partisol-Plus Model 2025 sequential air sampler. Sampling began in January 2013 and ended in February 2015.

Figure A3.27 Location of the Christchurch monitoring site (●) (Source: Google Earth).

As shown in Figure A3.27, 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 (State Highway 74), is approximately 380 m to the east, and 240 m to the south is Edgeware Rd, a busy urban route.

Figure A3.28 presents the PSCF back-trajectory analyses for marine aerosol and secondary sulphate measured at the Christchurch site.
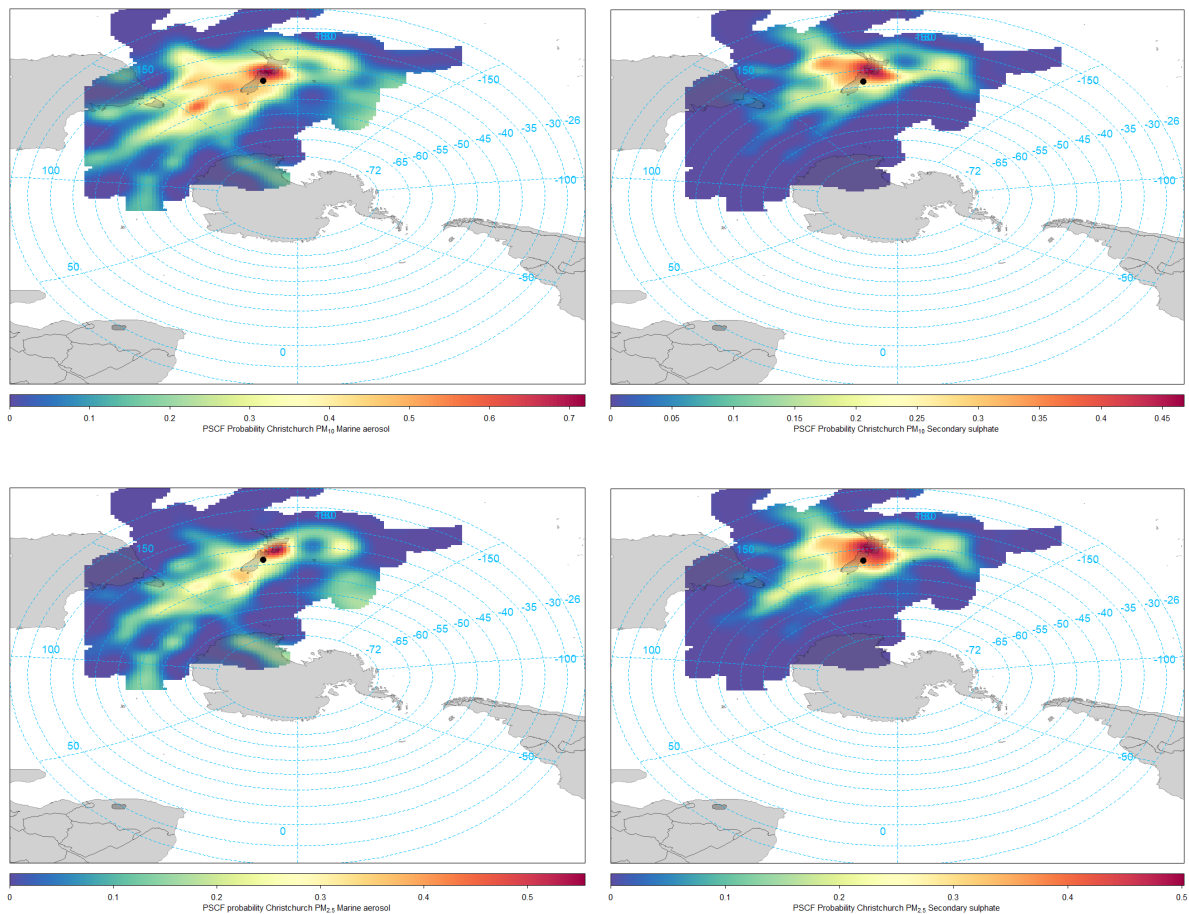
Figure A3.28 Air-mass back-trajectory and PSCF analysis for Christchurch (top left) $PM_{2.5}$ marine aerosol, (top right) $PM_{2.5}$ secondary sulphate, (bottom left) PM_{10} marine aerosol and (bottom right) PM_{10} secondary sulphate source regions.

A3.15   Timaru Monitoring Site

Environment Canterbury's Timaru city air-quality monitoring station is located at Anzac Square, Parkside (Figure A3.29) (Lat. -44.4046, Long. 171.2496). The station is situated in the southeastern 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 the port (<1 km east) (Scott 2014). Twenty-four-hour samples of PM2.5 were collected onto filters for 177 days during April 2006 to May 2007 at the Timaru monitoring site.
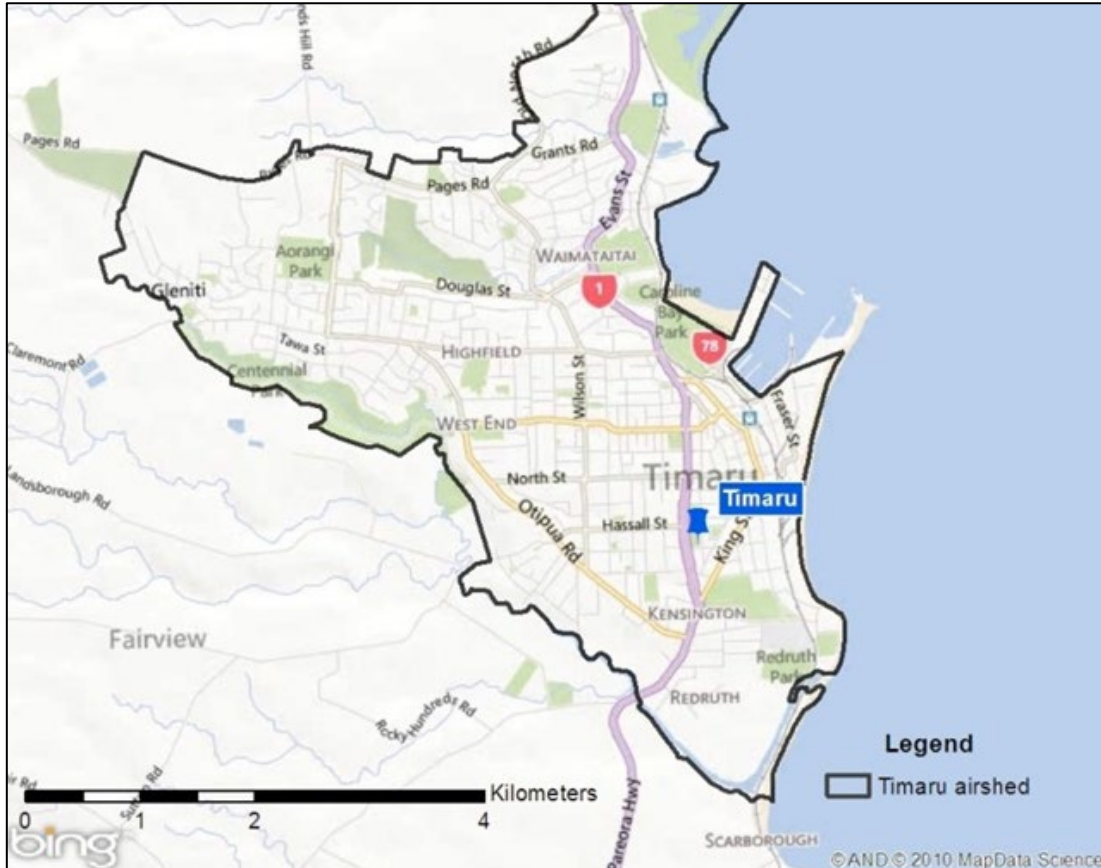
Figure A3.29 Location of the Timaru air-quality monitoring site (Source: Environment Canterbury).

Figure A3.30 presents the concentration-weighted trajectory analyses for marine aerosol and secondary sulphate measured at the Timaru site.
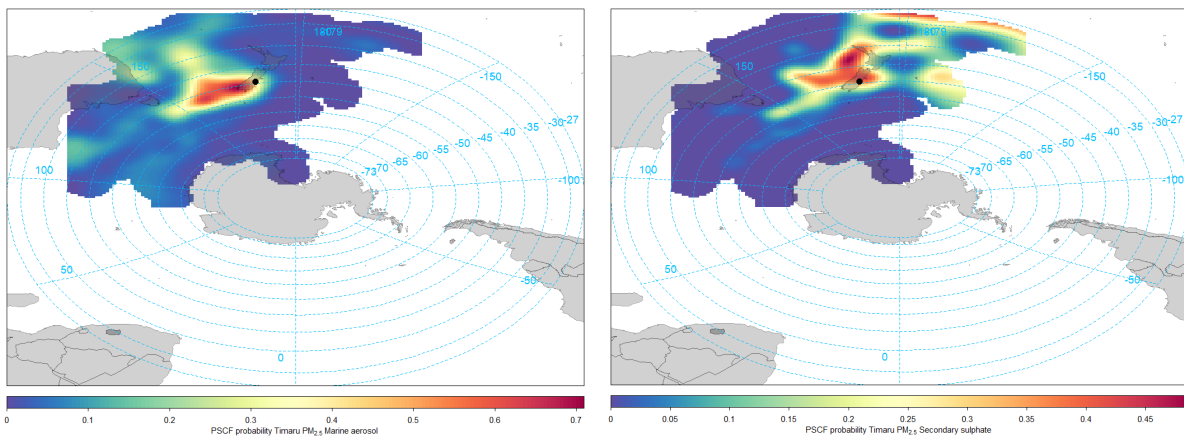
Figure A3.30 Air-mass back-trajectory and PSCF analysis for Timaru PM2.5 (left) marine aerosol and (right) secondary sulphate source regions.

A3.16   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 800 m to the east. Figure A3.31 provides an aerial photo of Dunedin and its immediate environs (Davy et al. 2011d). A total of 102 each of $PM_{2.5}$ and $PM_{10–2.5}$ samples using a GENT Sampler were collected over the period 9 February – 15 December 2010.

Figure A3.31 Aerial view of the Dunedin monitoring site (★) (Source: Google Earth).

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 central business district to the southwest.

Figure A3.32 presents the concentration-weighted trajectory analyses for marine aerosol and secondary sulphate measured at the Dunedin site.
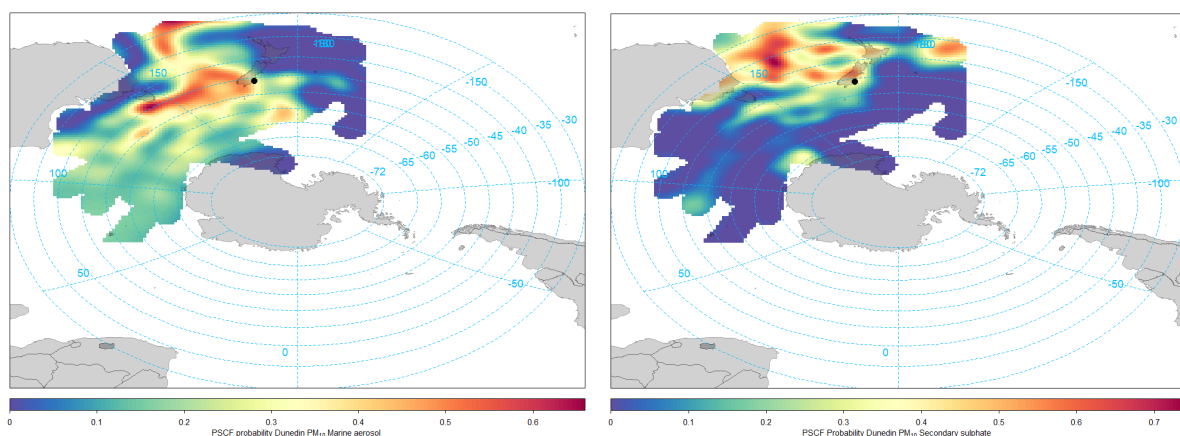

Figure A3.32 Air-mass back-trajectory and PSCF analysis for Dunedin PM_{10} (left) marine aerosol and (right) secondary sulphate source regions.

APPENDIX 4   FUTURE SCENARIOS MODEL PERFORMANCE

A4.1   Sulphate Aerosol – Sources and Inter-Model Variation

Sulphate aerosol over the New Zealand region has sources of both anthropogenic and natural origin. Both the sources themselves and the processes by which they are converted to sulphate can be uncertain. In addition, models may represent the sources and processes differently. Figures A4.1–A4.4 show SO_2 emissions, dimethyl sulfide (DMS) emissions, surface SO_2 concentrations and surface sulphate concentrations for the five CMIP6 models and multi-model mean.

Figure A4.1 shows the oceanic DMS emissions and highlights the uncertainty of the magnitude and spatial distribution of these across the different models. However, there is reasonable agreement that DMS emissions will increase, particularly south of about 40° latitude. Figure A4.2 shows that the SO_2 emissions are co-located with the main urban areas of Auckland, Wellington and Christchurch, indicating that they are anthropogenic. The exception here is the large emissions from Whakaari / White Island. The anthropogenic SO_2 emissions are approximately four times larger than the DMS emissions and decrease in both future scenarios. Figure A4.3 shows how surface SO_2 is distributed, taking into account transport, chemical processing and deposition, which results in an approximately two-day lifetime in the atmosphere. These processes result in elevated SO_2 concentrations over some North Island areas, with the highest concentrations located closer to Whakaari / White Island.
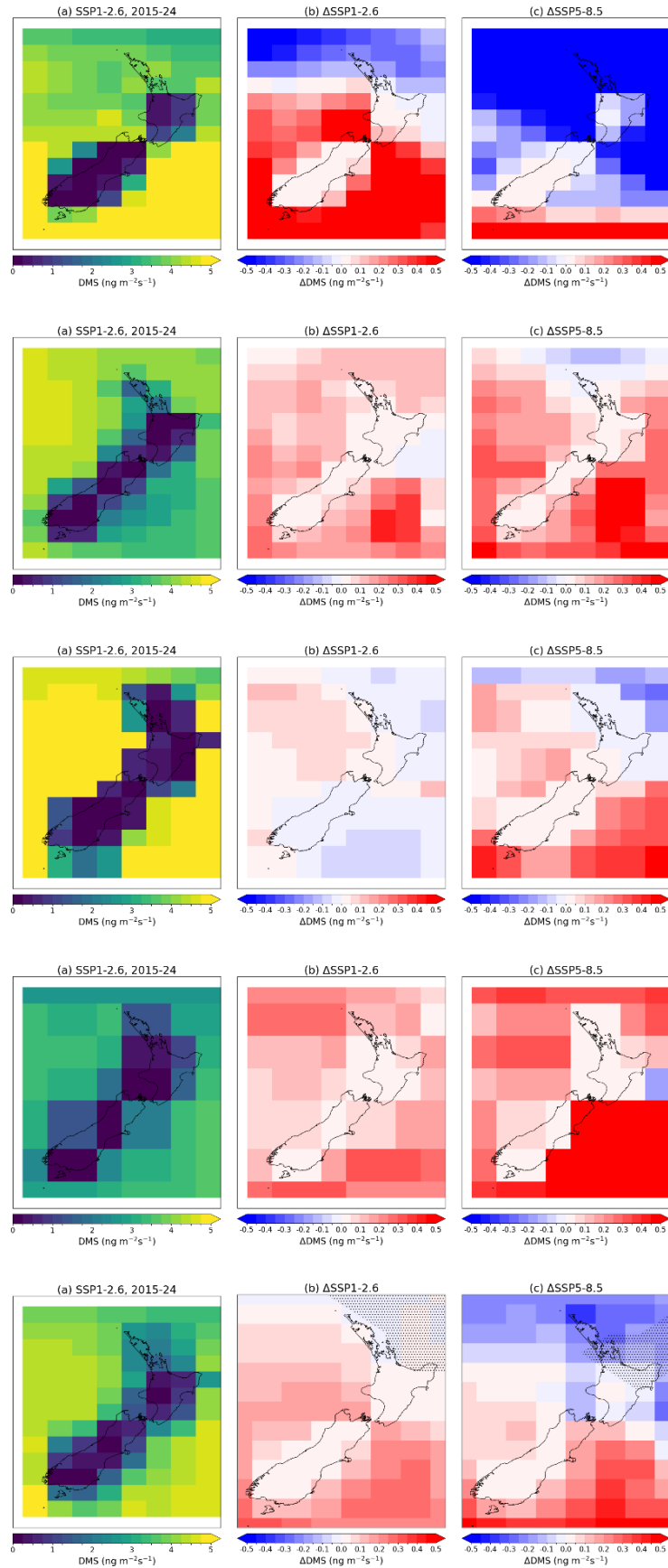
Figure A4.1   Surface dimethyl sulfide (DMS) emissions in ng m^{-2} s^{-1} from individual models. From top to bottom: UKESM1, GFDL-ESM4, CESM-WACCM, MRI-ESM2, MIROC-ES2L, multi-model mean. From left to right: DMS emissions averaged over 2015–2024; the change in DMS emissions over the 21st century following SSP1-2.6: 2090–2099 minus 2015–2024; as previous but for SSP5-8.5.
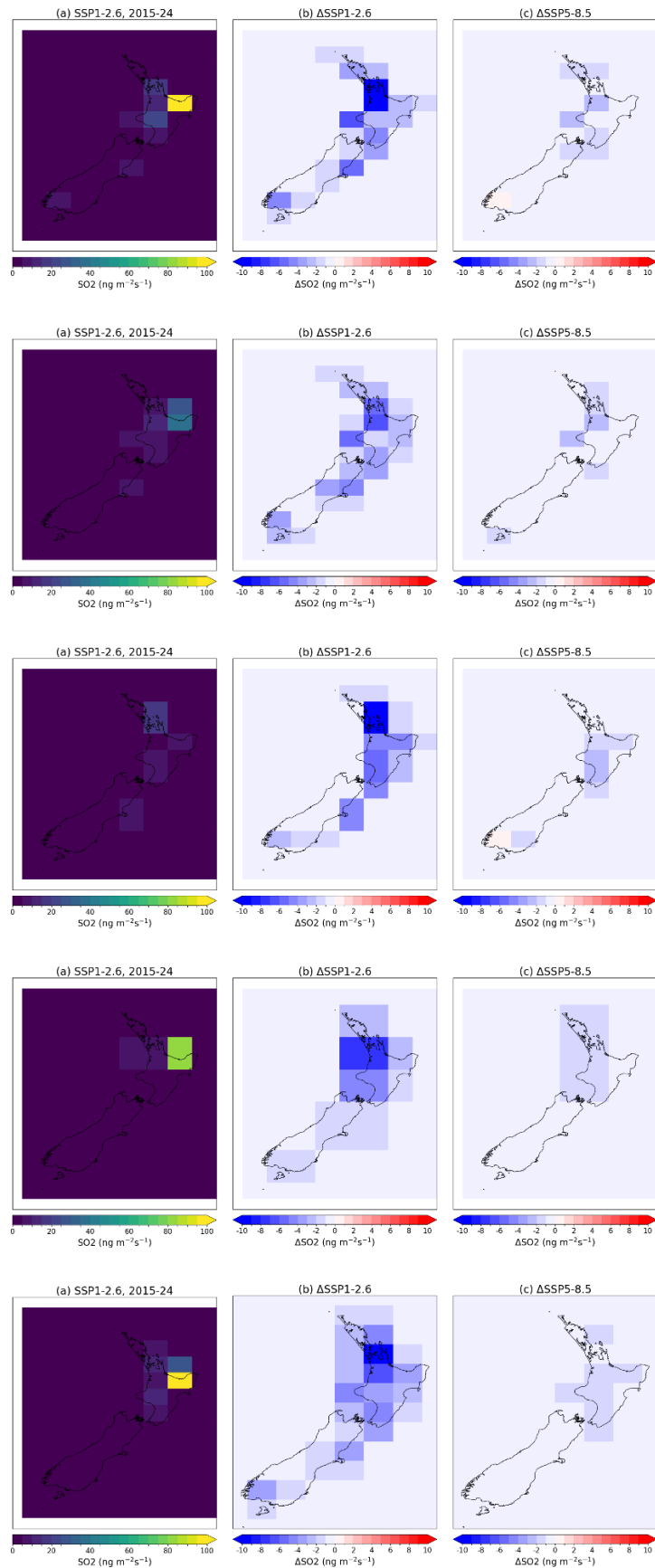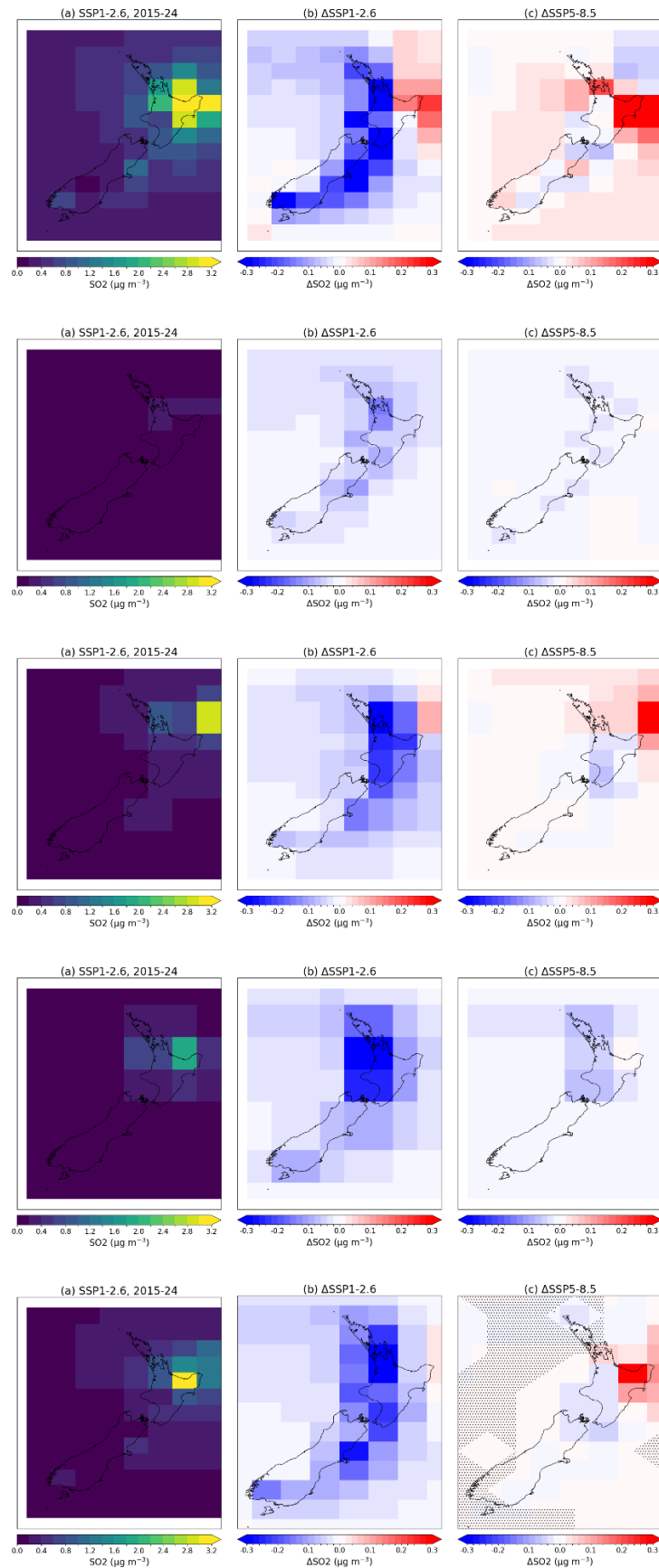
Figure A4.2   Surface SO$_2$ emissions in ng m^{-2} s^{-1} from individual models. From top to bottom: UKESM1, GFDL-ESM4, CESM-WACCM, MRI-ESM2, MIROC-ES2L, multi-model mean. From left to right: SO$_2$ emissions averaged over 2015–2024; the change in SO$_2$ emissions over the 21st century following SSP1-2.6: 2090–2099 minus 2015–2024; as previous but for SSP5-8.5.

Figure A4.3   Surface SO$_2$ concentrations in μg m^{-3} from individual models. From top to bottom: UKESM1, GFDL-ESM4, CESM-WACCM, MRI-ESM2, MIROC-ES2L, multi-model mean. From left to right: SO$_2$ concentrations averaged over 2015–2024; the change in SO$_2$ concentrations emissions over the 21st century following SSP1-2.6: 2090–2099 minus 2015–2024; as previous but for SSP5-8.5.
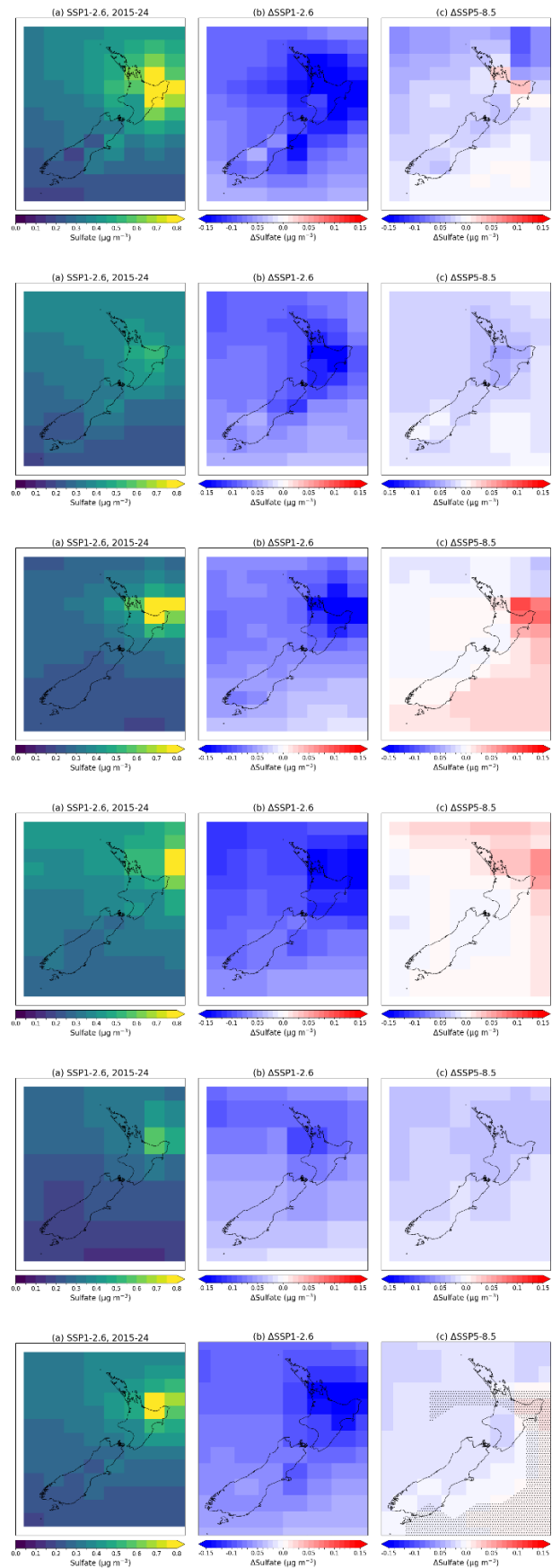
Figure A4.4   Surface sulphate concentrations in μg m⁻³ from individual models. From top to bottom: UKESM1, GFDL-ESM4, CESM-WACCM, MRI-ESM2, MIROC-ES2L, multi-model mean. From left to right; sulphate concentrations averaged over 2015–2024; the change in sulphate concentrations emissions over the 21st century following SSP1-2.6: 2090–2099 minus 2015–2024; as previous but for SSP5-8.5.