



The composition and sources of airborne particulate matter in Greymouth

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PURPOSE

This report uses the composition of airborne particulate matter collected at an urban air quality monitoring site in Greymouth to calculate the contribution of emission sources to the total measured concentrations of particulate matter pollution. The data is intended to be used by West Coast Regional Council to understand airborne particle composition and the sources of air pollution for air quality management and impact assessment purposes.

USE OF DATA

Date that Earth Sciences New Zealand can use associated data:
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EXECUTIVE SUMMARY

This report presents the results of an analysis of particulate-matter concentrations and composition from a winter PM_{2.5} and PM₁₀ sampling campaign at Greymouth on the west coast of the South Island. Particulate-matter samples were collected from June 2025 to September 2025 as part of a winter-time PM_{2.5} and PM₁₀ airborne particle-sampling programme at Greymouth. The sample set formed the basis of a study of particulate-matter composition and the attribution of sources contributing to particulate matter concentrations. The particulate matter elemental composition data showed that black carbon, a product from combustion sources, was a dominant contributor to PM_{2.5} concentrations. For PM₁₀, black carbon, sodium and chlorine were also important components that indicate the primary influence of the PM_{2.5} combustion sources, along with coarse particle marine aerosol (sea salt) sources.

Key results from the study are:

1. Three distinct source types were extracted from the data. These were: home heating, motor vehicles and marine aerosol (sea salt).
2. The primary source of winter anthropogenic PM_{2.5} in Greymouth was the home-heating source, which was attributed to the use of solid-fuel fires for domestic heating. This source contributed 60–70% of the total PM_{2.5} mass during peak concentrations (defined as greater than 15 µg m⁻³, the World Health Organization ambient air-quality guideline 24-hour average for PM_{2.5}). It was also found that marine aerosol (sea salt) contributed significantly on occasion, with two high PM_{2.5} days during the monitoring period dominated by this source, reflecting the exposed west coast location of the Greymouth urban area.
3. PM₁₀ concentrations reflected the influence of PM_{2.5} combustion sources, along with a greater influence of coarse-particle sea salt and motor-vehicle-related sources. With the onset of spring-like conditions and a switch to onshore southwesterly dominated winds in September, marine aerosol was found to be the primary source of PM₁₀ and the main contributor to two exceedances of the National Environmental Standard (NES) for PM₁₀ (50 µg/m³) during the monitoring period.
4. The home-heating source, likely to be a combination of solid-fuel emissions associated with biomass and coal combustion, was found to be contaminated with arsenic and lead, likely due to the opportunistic use of copper chrome arsenate (CCA)-treated timber and old painted timber, respectively, as fuel.

Figures ES.1 and ES.2 present the identified source contributions to PM_{2.5} and PM₁₀, respectively, at Greymouth.

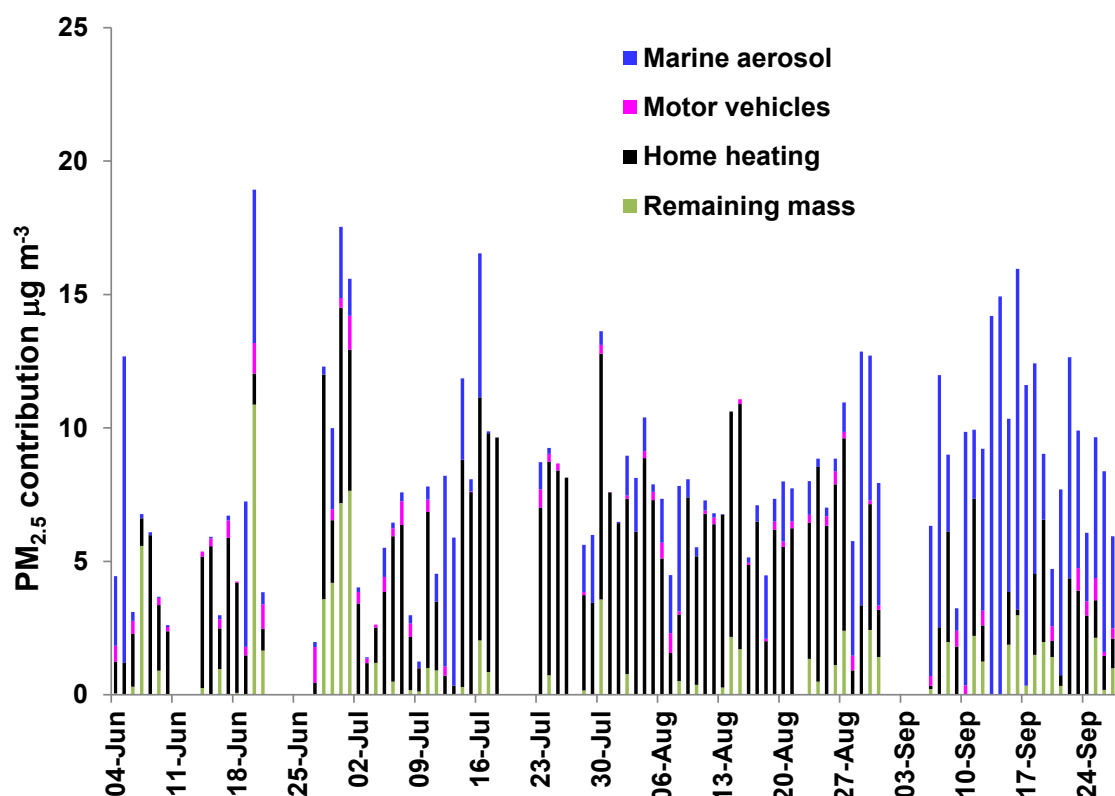


Figure ES.1 Source contributions to PM_{2.5} at Greymouth over the monitoring period (June 2025 to September 2025).

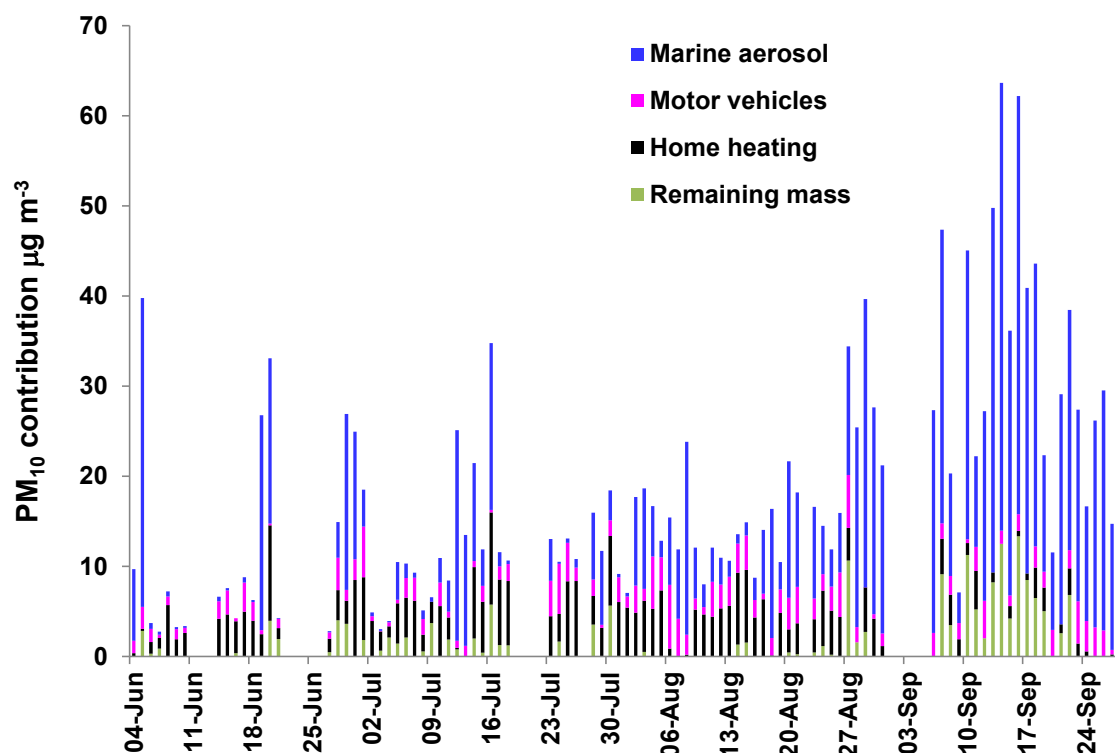


Figure ES.2 Source contributions to PM₁₀ at Greymouth over the monitoring period (June 2025 to September 2025).

Note that ‘*Remaining Mass*’ refers to that particulate-matter gravimetric-mass fraction not explained by the receptor model. This was $1.7 \mu\text{g m}^{-3}$ and $3.3 \mu\text{g m}^{-3}$ on average for PM_{2.5} and PM₁₀ samples, respectively, and likely to be a combination of gravimetric-mass uncertainty (estimated at approximately $0.5 \mu\text{g m}^{-3}$) and those aerosol species not measured, such as nitrate, hydrocarbons and biogenic material.

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1.0 Introduction

This report presents the results of a compositional analysis and receptor-modelling study of airborne particle samples collected during winter 2025 at an ambient air-quality monitoring site in Greymouth. The work was commissioned by West Coast Regional Council to inform its ambient air-quality monitoring programme and requirement to manage air quality in the region. The work was partly funded by an Envirolink Grant (GNS2507 – 2609-WCRC221) from the Ministry of Business, Innovation & Employment.

1.1 Requirement to Manage Airborne Particle Pollution

In response to growing evidence of significant health effects associated with airborne particle pollution, the New Zealand Government introduced in 2004 a National Environmental Standard (NES) of $50 \mu\text{g}/\text{m}^3$ for particles less than $10 \mu\text{m}$ in aerodynamic cross-section (denoted as PM_{10}). The NES places the onus on regional councils to monitor PM_{10} and publicly report whether the air quality in their region exceeds the standard, with a provision for no more than one exceedance annually and a requirement for offsets by industry in PM_{10} -polluted airsheds replacing the restriction on industrial consents (Ministry for the Environment 2011). Air-pollution episodes that are outside regulatory authorities' ability to control may be considered 'exceptional events' by application for exemption (e.g. dust storms, volcanic eruptions).

In areas where the PM_{10} standard is exceeded, information on the sources contributing to those air-pollution episodes is required to:

- identify 'exceptional events' outside of regulatory authority control;
- effectively manage air quality; and
- formulate appropriate mitigation strategies, where necessary.

In addition to the PM_{10} NES, the Ministry for the Environment (2002) issued ambient air-quality guidelines (AAQGs) for air pollutants that included a (monitoring) guideline value of $25 \mu\text{g m}^{-3}$ for $\text{PM}_{2.5}$ (24-hour average). More recently, the World Health Organization (WHO) has confirmed a $\text{PM}_{2.5}$ ambient air-quality guideline value of $15 \mu\text{g m}^{-3}$ (24-hour average) based on the relationship between 24-hour and annual particulate-matter levels (WHO 2021). The WHO annual average guideline for $\text{PM}_{2.5}$ is $5 \mu\text{g m}^{-3}$. These are the lowest levels at which total, cardiopulmonary and lung cancer mortality have been shown to increase, with more than 95% confidence in response to exposure to $\text{PM}_{2.5}$. WHO recommends the use of $\text{PM}_{2.5}$ guidelines over PM_{10} , as epidemiological studies have shown that most of the adverse health effects associated with PM_{10} are due to $\text{PM}_{2.5}$. A recent analysis of the impact of air pollution on human health in New Zealand found that residential wood burning dominated the health effects associated with $\text{PM}_{2.5}$ pollution (Kuschel et al. 2022).

1.1.1 Identifying Sources of Airborne Particulate-Matter Pollution

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 many different sources. Receptor modelling provides a means to determine the relative mass contribution of sources that impact significantly on the total mass of air particulate matter collected at a monitoring site. Elemental concentrations in particulate-matter filter samples were determined using X-Ray Fluorescence spectroscopy (XRF) at the New Zealand Ion Beam Analysis Facility in Gracefield, Lower Hutt. Black carbon concentrations were determined using light-reflectance techniques.

XRF is a mature analytical technique that provides a non-destructive determination of multi-elemental concentrations present in a sample. Using elemental concentrations with appropriate statistical techniques and purpose-designed mathematical models, the sources contributing to each ambient sample can be estimated. Appendix 1 provides a description of the XRF analytical process and receptor-modelling techniques.

1.1.2 Scope of this Study

This report describes sampling, results and outcomes according to the following objectives:

- Identify and quantify elemental concentrations in the particulate-matter samples, including any toxic elements such as arsenic and lead.
- Identify and quantify those sources responsible for any exceedances of the National Environment Standard Air Quality Standard (NESAQ).
- Identify the sources of toxic emissions.
- Examine source contributions to particulate matter with wind speed and direction.
- Identify and quantify the mass contribution to particulate matter from sources that are difficult to quantify by emissions inventories or from natural sources that might fall outside the control of West Coast Regional Council.

2.0 Methodology

2.1 Location of the Greymouth Particulate-Matter Monitoring Site

Particulate matter ($PM_{2.5}$ and PM_{10}) sampling was undertaken by West Coast Regional Council during winter months from June 2025 until September 2025 at an air-quality monitoring site on the grounds of Greymouth High School at 10 Marlborough Street, Greymouth (Lat: -42.4630; Long: 171.1963). The site is located in the middle of a mixed commercial/residential area, as shown in Figure 2.1.

The author has been provided with information about the monitoring site and informed of the typical activities in the surrounding areas that may contribute to particulate-matter concentrations. These details informed the conceptual receptor model described in Section 2.5.



Figure 2.1 Location of Greymouth monitoring site (●) (Image source: Google Earth, 2026).

The area immediately around the site is flat and mixed residential and commercial, with State Highway 6 immediately to the northwest and local urban road traffic on adjacent roads. The Greymouth town centre and commercial area lies to the northeast of the monitoring site alongside the Grey River. Further residential suburbs lie southeast, northeast and south of the monitoring site. Greymouth airport is 500 m west of the site, and the West Coast (Karoro Beach) is approximately 750 m west. Land use surrounding the Greymouth urban area is predominantly agricultural.



Figure 2.2 Location of Greymouth air-quality monitoring site (●) and Greymouth Airport meteorological monitoring site (●) (Image source: West Coast Regional Council, 2025).

2.2 Description of Particulate-Matter Sampling at Greymouth

Particulate-matter samples (24-hour time-integrated sampling period) for analysis were collected onto PTFE filters (TISCH PTFE membrane, 47 mm 0.2 μm) at the site using two MetOne sequential samplers (E-SEQ-FRM sequential reference method particulate sampler) located side by side. A total of 98 $\text{PM}_{2.5}$ and 99 PM_{10} samples (plus field blanks and laboratory blanks) were collected on a daily sampling regime over the monitoring period for compositional analysis. All particulate-matter sampling and systems maintenance at the air-quality monitoring site was carried out by West Coast Regional Council, and, as such, it maintains all records of equipment, flow rates and sampling methodologies used for the particulate-matter sampling regime. Filter supply, conditioning, weighing and re-weighing for particulate-matter gravimetric-mass determinations were carried out by Hills Laboratories, Hamilton, in accordance with AS/NZS 3580.9.10 2006.

2.3 Receptor-Modelling Process

The multivariate analysis of air particulate-matter sample composition (also known as receptor modelling) provides groupings (or factors) of elements that vary together over time. This technique effectively ‘fingerprints’ the sources that are contributing to airborne particulate matter and the mass of each element (as well as the particulate-matter mass) attributed to that source. In this study, the primary source contributors were determined using results from Positive Matrix Factorisation (PMF analysis) of particulate-matter elemental composition data.

A critical point for understanding the receptor-modelling process is that the PMF model can produce any number of solutions, all of which may be mathematically correct (Paatero et al. 2002). The ‘best’ solution (e.g. number of factors, etc.) is generally determined by the practitioner after considering the model diagnostics and a review of the available factor profiles and contributions (to check physical interpretability). 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 profile measured at a monitoring station is resolved mathematically to be the sum of a number of different factors or sources. As with most modelling approaches, receptor models based on the conservation of mass are simplifications of reality and have the following general assumptions:

1. Compositions of source emissions are constant over the period of ambient and source sampling.
2. Chemical species do not react with each other (i.e. they add linearly).
3. All sources with a potential for contributing to the receptor have been identified and have had their emissions characterised.
4. The number of sources or source categories is less than or equal to the number of species measured.
5. The source profiles are linearly independent of each other.
6. Measurement uncertainties are random, uncorrelated and normally distributed.

The effects of deviations from these assumptions are testable and can therefore allow the accuracy of source quantification to be evaluated. Uncertainties in input data can also be propagated to evaluate the uncertainty of source-contribution estimates. There are a number of natural physical restraints that must be considered when developing a model for identifying and apportioning sources of airborne particles (Hopke 2003):

- The model must explain the observations.
- The predicted source compositions must be non-negative.
- The predicted source contributions must also be non-negative.
- The sum of predicted elemental-mass contributions from each source must be less than or equal to measured mass for each element.

These constraints need to be kept in mind when conducting and interpreting any receptor-modelling approach, particularly as a receptor model is still an approximation of the real-world system. Several factors also affect the nature of a source’s particle composition and its contributions to ambient loadings (Brimblecombe 1986; Hopke 1999; Seinfeld and Pandis 2006):

1. The composition of particles emitted from a source may vary over time.
2. The composition of particles is 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, SO₂ gas to SO₄²⁻;
 - volatilisation of particle components, such as organic compounds, or volatilisation of chlorine through reaction with acidic species;
 - interaction with, and transformation by, solar radiation and free radicals in the atmosphere, such as the OH and NO₃ species.

The analytical processes used in this study did not analyse for nitrate (elemental hydrogen, carbon, oxygen and nitrogen are not detectable by XRF techniques), so the missing mass that the analysis is not explaining is likely a combination of nitrate and other unmeasured species such as hydrocarbons and bound water. Measurement of the ionic components in PM₁₀ at other New Zealand sites indicates that aerosol nitrate species (primarily as PM_{2.5}) contribute approximately 0.25 µg m⁻³ in Auckland (Ancelet and Davy 2015) and 0.75 µg m⁻³ in Timaru (Scott 2014) to total particulate-matter mass during winter and somewhat less during other seasons due to atmospheric processing and thermodynamic equilibria (Seinfeld and Pandis 2006).

Analytical noise is also introduced during the species-measurement process, such as analyte interferences and limits of detection for species of interest. These are at least in the order of 5% for species well above the respective detection limit and 20% or more for those species near the analytical method detection limit (Hopke 1999). Further details on data analysis and dataset preparation are provided in Appendix 1.

2.4 Data Analysis and Reporting

The receptor-modelling results within this report have been produced in a manner that provides as much information as possible on the relative contributions of sources to particulate matter concentrations so that this may be used for monitoring strategies, air-quality management and policy development. The data have been analysed to provide the following outputs:

1. Masses of elemental species apportioned to each source.
2. Source elemental profiles.
3. Average particulate-matter mass apportioned to each source.
4. Temporal variations in source-mass contributions (time-series plots).
5. Analysis of source contributions on peak particulate-matter days.

Table 2.1 presents the relevant standards, guidelines and targets for particulate-matter concentrations.

Table 2.1 Standards, guidelines and targets for particulate matter concentrations.

Particle Size	Averaging Time	Ambient Air-Quality Guideline	'Acceptable' Air-Quality Category*	'Alert' Air-Quality Category*	National Environmental Standard
PM ₁₀	24 hours	N/A	<33 µg m ⁻³	>33 <50 µg m ⁻³	50 µg m ⁻³
	Annual	15 µg m ⁻³ (WHO 2021)	<13 µg m ⁻³	>10 <15 µg m ⁻³	N/A
PM _{2.5}	24 hours	15 µg m ⁻³ (WHO 2021)	<10 µg m ⁻³	>10 <15 µg m ⁻³	N/A

* Air-quality categories are taken from Ministry for the Environment (1997).

2.4.1 Conditional Probability Function Analysis

A useful data analysis method is to investigate the relationship between the source contributions and wind direction. Bivariate polar plots using the source contributions to particulate matter were produced using R statistical software and the *openair* package (Carslaw 2012; Carslaw and Ropkins 2012; R Core Team 2015). Using bivariate polar plots, source contributions can be shown as a function of both wind speed and direction, providing invaluable information about potential source regions and how pollution from a specific source builds up. 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).

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. 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.

2.5 Conceptual Receptor Model for Particulate Matter at Greymouth

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

- Domestic activities – likely to be dominated by activities such as emissions from solid-fuel fires (wood and coal) used for domestic heating during the winter.
- Motor vehicles – all roads in the area act as line sources, and roads with higher traffic densities will dominate emissions.
- Industrial emissions from combustion processes (boilers) and dust-generating activities such as excavation, construction and bulk storage handling.
- Local wind-blown soil or road dust sources may also contribute.

Sources that originate further from the monitoring site would also be expected to contribute to ambient particle loadings. These include:

- Marine aerosol (sea salt) generated in the oceanic regions around New Zealand.
- Secondary particulate matter resulting from atmospheric gas-to-particle conversion processes – includes sulphates, nitrate and organic species.

Another category of emission sources that may contribute are those considered to be ‘one-off’ emission sources:

- Fireworks displays and other special events (e.g. Guy Fawkes Day).
- Short-term road works and demolition/construction activities.

The variety of sources described above can be recognised and accounted for using appropriate data-analysis methods, such as the application of geochemical principles, examination of seasonal differences, temporal variations and receptor modelling itself.

2.6 Local Meteorology at Greymouth

Meteorological data were obtained from an automatic weather station located at Greymouth Airport (Greymouth Aero EWS; network number F21425; Lat: -42.4602; Long: 171.1916; operated by Earth Sciences New Zealand), located approximately 0.5 km west of the monitoring site (see Figure 2.2). As shown in Figure 2.3, the predominant wind directions were from the easterly quadrant for June, July and August 2025 and then with a greater proportion from the southwest during September 2025.

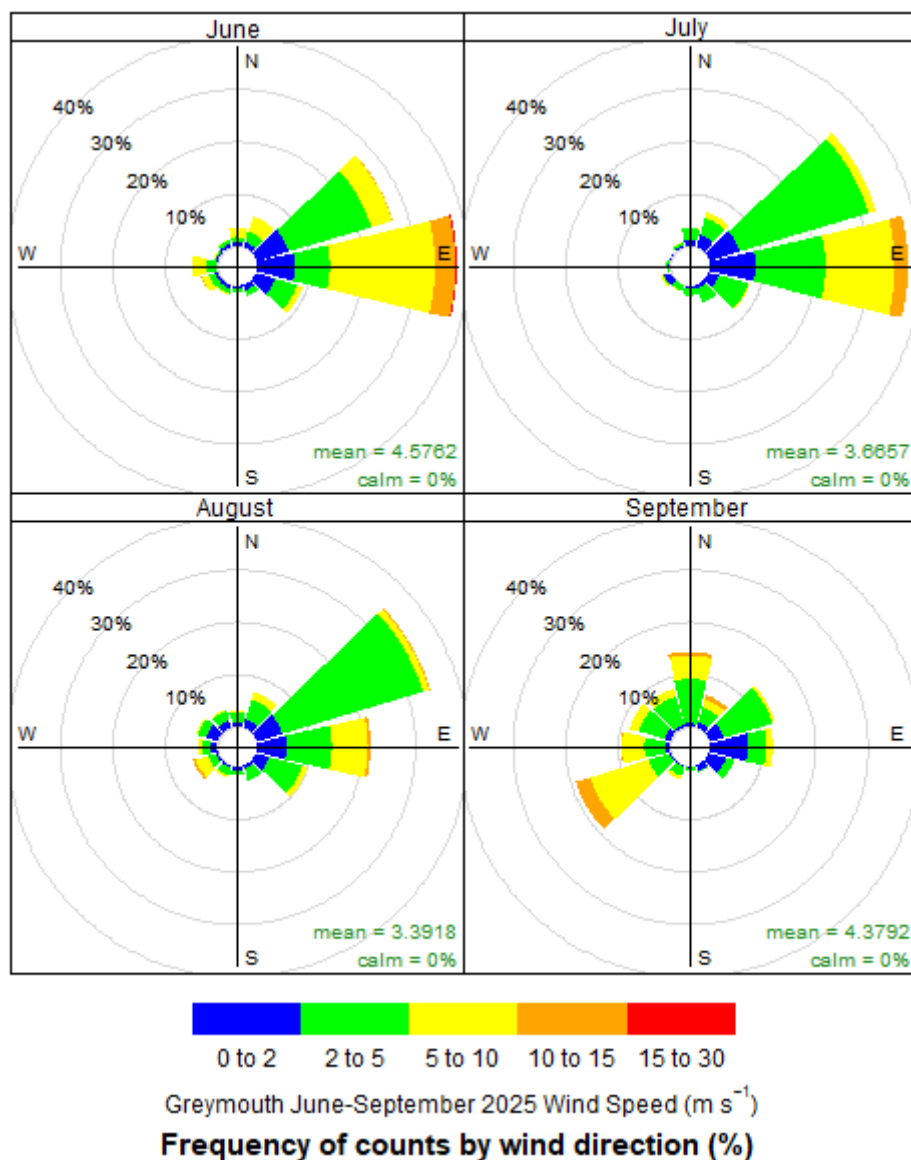


Figure 2.3 Wind rose for each calendar month during the monitoring period at Greymouth (June–September 2025).

2.7 PM_{2.5} and PM₁₀ Concentrations at Greymouth

Mass concentrations were determined gravimetrically by Hills Laboratories for the Greymouth PM_{2.5} and PM₁₀ sample filters. Figures 2.4 and 2.5 present the PM_{2.5} and PM₁₀ monitoring results (24-hour averages, midnight-to-midnight sampling regime) over the monitoring period (June–September 2025). Gaps present in Figures 2.4 and 2.5 are from sampler outages and/or maintenance. The WHO AAQG concentration (15 µg m⁻³ as a 24-hour average) for PM_{2.5} was exceeded on five samples during the monitoring period. The NESAQ for PM₁₀ (50 µg m⁻³ as a 24-hour average) was exceeded on two filter samples during September 2025.

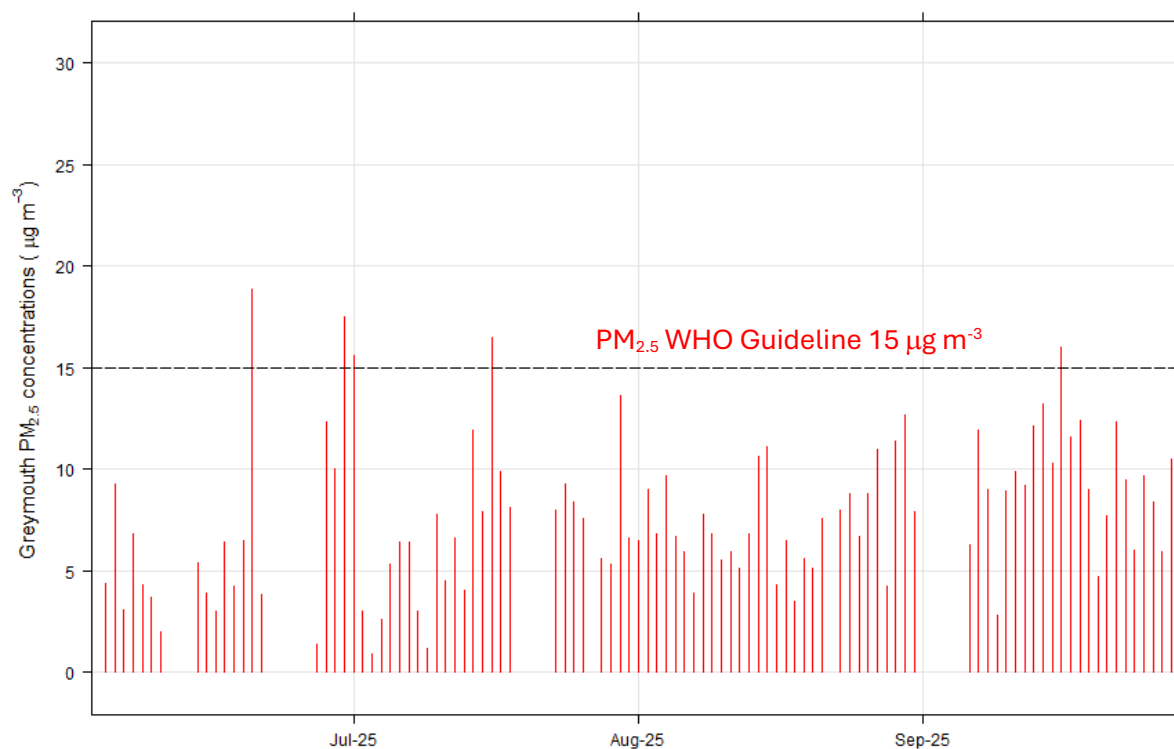


Figure 2.4 Gravimetric PM_{2.5} (24-hour average) concentrations at Greymouth. Note that the gaps in the graph are due to missed sample periods. The dashed line indicates the WHO AAQG concentration (15 $\mu\text{g m}^{-3}$ as a 24-hour average) for PM_{2.5}.

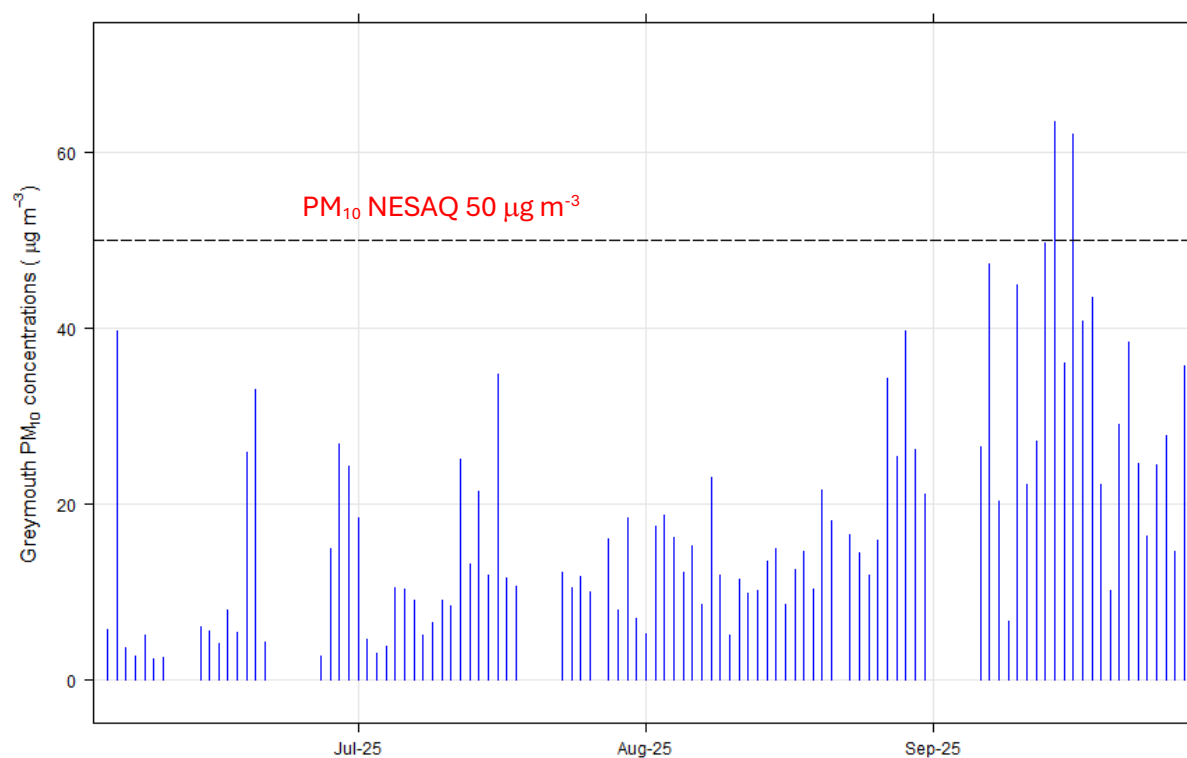


Figure 2.5 Gravimetric PM₁₀ (24-hour average) concentrations at Greymouth. Note that the gaps in the graph are due to missed sample periods. The dashed line indicates the NESAQ for PM₁₀ (50 $\mu\text{g m}^{-3}$ as a 24-hour average).

3.0 Receptor-Modelling Analysis of Greymouth Particulate-Matter Sources

3.1 Analysis of Particulate-Matter Samples Collected at Greymouth

PM_{2.5} and PM₁₀ samples at Greymouth were collected by West Coast Regional Council using a MetOne sequential sampler system on a daily sampling regime over the monitoring period. A total of 98 PM_{2.5} and 99 PM₁₀ samples (plus field blanks and laboratory blanks) were collected on a daily sampling regime over the monitoring period for compositional analysis. Elemental and black carbon concentrations in the particulate-matter samples were determined using XRF and light reflection, respectively, as described in Appendix 1.

3.1.1 Composition of PM_{2.5} at Greymouth

Elemental concentrations in the PM_{2.5} samples collected at the Greymouth monitoring site are presented in Table 3.1. Note that it was found that the PTFE filters used for the Greymouth sampling campaign had a high background of silicon on the field blanks and laboratory blanks. This precluded any sensible data for silicon, and aluminium concentrations had a high uncertainty (aluminium has an X-ray energy peak immediately adjacent silicon) on the sampled filters after blank subtraction. Silicon and aluminium (along with calcium, titanium and iron) are key components of crustal matter (soil), which is usually one of the main sources contributing to ambient particulate-matter at urban locations, particularly to the coarse (PM_{10-2.5}) fraction (Davy et al. 2024). The data show that PM_{2.5} concentrations were dominated by black carbon (BC) during the winter months. Other important elemental constituents included potassium (K), sodium (Na), chlorine (Cl), sulphur (S) and iron (Fe), indicating that combustion sources, marine aerosol and crustal matter were likely to be important contributors to PM_{2.5} concentrations at the monitoring site. Some measured species were close to or below their respective limit of detection in each of the samples. Appendix 1 provides a description of data treatment and detection limits. Elemental correlation plots are provided in Figure A2.2 in Appendix 2.

Table 3.1 Elemental concentrations in PM_{2.5} samples from Greymouth (98 samples). LOD = limit of detection.

	Unit	Average	Maximum	Minimum	Median	Std. Dev.	Average LOD	% > LOD
PM_{2.5}	µg m ⁻³	7	19	0	7	4	-	-
BC	ng m ⁻³	1943	4176	257	2045	1037	153	100
Na	ng m ⁻³	534	2298	4	349	553	4	100
Mg	ng m ⁻³	61	204	0	45	50	8	97
Al	ng m ⁻³	90	267	0	80	65	79	52
Si	ng m ⁻³	272	1433	0	104	387	464	20
P	ng m ⁻³	0	0	0	0	0	2	0
S	ng m ⁻³	97	520	0	89	73	0	97
Cl	ng m ⁻³	732	3932	7	330	904	2	100
K	ng m ⁻³	88	203	11	87	36	1	100
Ca	ng m ⁻³	11	82	0	0	18	2	43
Ti	ng m ⁻³	1	4	0	0	1	1	22
V	ng m ⁻³	0	2	0	0	0	0	15
Cr	ng m ⁻³	1	3	0	1	1	1	47

	Unit	Average	Maximum	Minimum	Median	Std. Dev.	Average LOD	% > LOD
Mn	ng m ⁻³	1	4	0	0	1	1	18
Fe	ng m ⁻³	8	18	0	8	4	3	88
Co	ng m ⁻³	0	1	0	0	0	0	14
Ni	ng m ⁻³	0	2	0	0	0	0	33
Cu	ng m ⁻³	0	5	0	0	1	2	10
Zn	ng m ⁻³	4	33	0	4	5	1	74
Ga	ng m ⁻³	1	3	0	0	1	1	30
As	ng m ⁻³	2	19	0	0	3	1	34
Se	ng m ⁻³	0	4	0	0	1	1	7
Br	ng m ⁻³	2	11	0	2	3	1	61
Sr	ng m ⁻³	1	4	0	0	1	1	28
Mo	ng m ⁻³	1	7	0	0	1	2	18
Cd	ng m ⁻³	6	37	0	1	9	13	15
Sn	ng m ⁻³	2	17	0	0	4	8	11
Sb	ng m ⁻³	2	20	0	0	4	8	8
Te	ng m ⁻³	3	19	0	0	5	9	15
Cs	ng m ⁻³	11	51	0	6	12	11	40
Ba	ng m ⁻³	9	63	0	2	13	14	28
La	ng m ⁻³	11	61	0	0	16	14	28
Ce	ng m ⁻³	44	322	0	0	76	140	13
Sm	ng m ⁻³	45	280	0	9	65	81	24
Pb	ng m ⁻³	8	44	0	6	8	2	74
Hg	ng m ⁻³	1	10	0	0	1	1	17
In	ng m ⁻³	1	11	0	0	2	5	6

3.1.2 Composition of PM₁₀ at Greymouth

Elemental concentrations in the PM₁₀ samples collected at the Greymouth monitoring site are presented in Table 3.2. As PM₁₀ contains the PM_{2.5} fraction, the data show that PM₁₀ black carbon (BC) concentrations were similar to PM_{2.5}. However, elemental constituents such as sodium (Na), chlorine (Cl), sulphur (S), titanium (Ti) and iron (Fe) were significantly higher in PM₁₀, indicating that coarse-particle (PM_{10-2.5} fraction) sources, such as marine aerosol and crustal matter, were likely to be important contributors to PM₁₀ concentrations at the monitoring site, in addition to the PM_{2.5} sources described in Section 3.1.1.

Table 3.2 Elemental concentrations in PM₁₀ samples from Greymouth (99 samples). LOD = limit of detection.

	Unit	Average	Maximum	Minimum	Median	Std. Dev.	Average LOD	% > LOD
PM₁₀	µg m ⁻³	16	64	0	12	14	-	-
BC	ng m ⁻³	2104	4485	331	2144	1068	116	100
Na	ng m ⁻³	2046	7125	10	1570	1843	5	100
Mg	ng m ⁻³	174	689	3	114	167	10	94
Al	ng m ⁻³	148	437	7	121	99	124	49
Si	ng m ⁻³	178	2008	0	41	290	749	4
P	ng m ⁻³	0	0	0	0	0	2	0
S	ng m ⁻³	237	1161	10	163	216	0	100
Cl	ng m ⁻³	2994	13153	12	1679	3204	1	100
K	ng m ⁻³	142	311	20	140	61	10	100
Ca	ng m ⁻³	81	392	0	47	87	1	92
Ti	ng m ⁻³	2	7	0	2	2	1	52
V	ng m ⁻³	0	2	0	0	0	0	19
Cr	ng m ⁻³	1	3	0	0	1	2	11
Mn	ng m ⁻³	1	5	0	1	1	2	37
Fe	ng m ⁻³	38	86	1	37	19	2	99
Co	ng m ⁻³	0	2	0	0	0	0	8
Ni	ng m ⁻³	0	2	0	0	0	1	29
Cu	ng m ⁻³	1	4	0	0	1	2	26
Zn	ng m ⁻³	6	38	0	5	5	1	90
Ga	ng m ⁻³	0	3	0	0	1	1	17
As	ng m ⁻³	2	26	0	0	4	1	40
Se	ng m ⁻³	0	4	0	0	1	1	15
Br	ng m ⁻³	13	73	0	6	15	1	83
Sr	ng m ⁻³	2	11	0	2	2	1	52
Mo	ng m ⁻³	0	5	0	0	1	2	12
Cd	ng m ⁻³	4	25	0	0	7	21	4
Sn	ng m ⁻³	2	14	0	0	3	10	8
Sb	ng m ⁻³	3	21	0	1	4	11	9
Te	ng m ⁻³	4	24	0	0	5	13	8
Cs	ng m ⁻³	6	26	0	3	7	15	15
Ba	ng m ⁻³	8	54	0	3	10	15	20
La	ng m ⁻³	11	65	0	5	14	22	18
Ce	ng m ⁻³	49	335	0	0	76	124	15
Sm	ng m ⁻³	27	213	0	0	45	86	10
Pb	ng m ⁻³	8	46	0	6	8	3	81
Hg	ng m ⁻³	0	5	0	0	1	2	5
In	ng m ⁻³	2	12	0	0	2	5	16

The simultaneous monitoring of the two size fractions ($PM_{2.5}$ and PM_{10}) provides the opportunity to directly compare component species for those samples that were coincident. For example, black carbon concentrations in both $PM_{2.5}$ and PM_{10} were found to be essentially the same as presented in Figure 3.1 (slight differences are due to sampling and measurement uncertainty). This is because black carbon particles, a product of incomplete combustion, are all smaller than $2.5\ \mu m$ and are therefore entirely contained in the $PM_{2.5}$ fraction (a subset of PM_{10}).

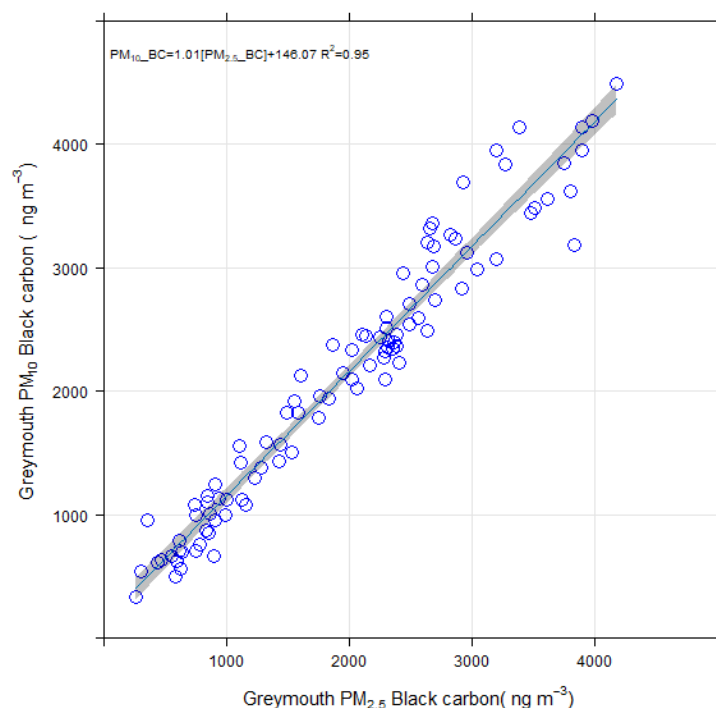


Figure 3.1 Black carbon concentrations in $PM_{2.5}$ versus PM_{10} samples from Greymouth.

Of the measured heavy metals, lead was found to have similar concentrations in $PM_{2.5}$ and PM_{10} , as presented in Figure 3.2, indicating that the metal was derived from a fine-particle emission source.

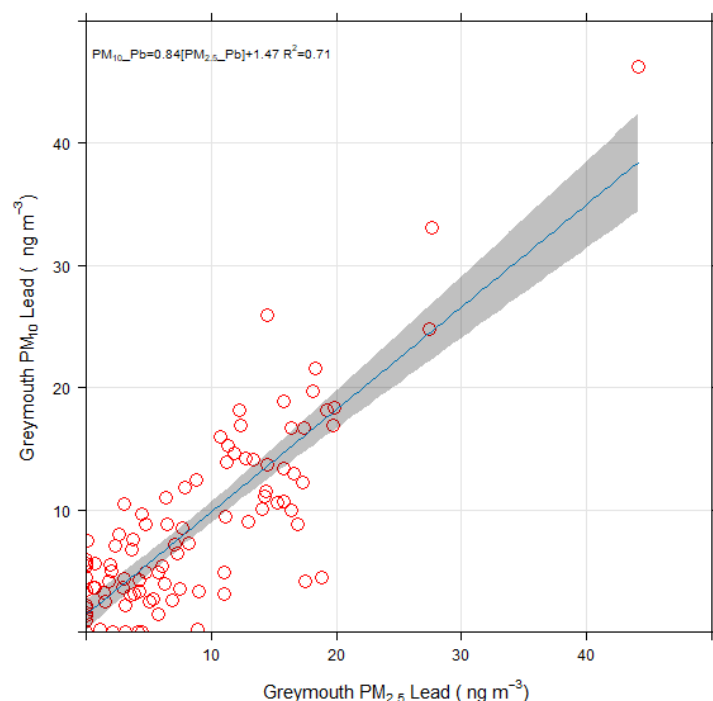


Figure 3.2 Lead concentrations in $PM_{2.5}$ versus PM_{10} samples from Greymouth.

Inhalation of lead-contaminated air particulate matter provides a pathway for lead to enter the bloodstream, resulting in biological up-take in humans. There is no known safe concentration of lead in blood; such concentrations as low as 3.5 µg/dL may be associated with decreased intelligence in children, behavioural difficulties and learning problems (CDC 2024).

3.2 Source Contributions to Particulate Matter at Greymouth

The PM_{2.5} and PM₁₀ compositional data were analysed to provide information on contributing sources using PMF with multiple re-iterations such that robust solutions and source attributions were arrived at. Sources of particulate-matter emissions or generation include particles across the size-range spectrum and therefore contribute to both fine and coarse size fractions, although some source types will contribute more to one size fraction than the other. For example, combustion sources, such as domestic solid-fuel fires or motor-vehicle tailpipe emissions, produce particles in the sub-micron size range and are therefore largely confined to the PM_{2.5} fraction. Windblown dust; non-exhaust emissions generated from brakes, tyres and by the turbulent passage of vehicles over local roads; sea salt; or industrial processes that involve mechanical grinding, sorting, storage and transport of bulk materials, predominantly produce particles in the larger size ranges (greater than PM_{2.5}), although some ‘tail’ of particle sizes does extend down into the PM_{2.5} size fraction.

3.2.1 Sources of PM_{2.5} and PM₁₀ at Greymouth

Three source types were identified from PMF receptor-modelling analysis of the Greymouth PM_{2.5} and PM₁₀ elemental data. The source contributors identified were found to explain 94% of the PM_{2.5} and 93% of the PM₁₀ mass on average.

The sources identified were:

- **Home heating:** The first factor was identified as a home-heating source, likely to be emissions from solid-fuel fires (biomass combustion and coal) based on the dominance of black carbon and potassium in the profile, along with sulphur (Fine et al. 2001; Khalil and Rasmussen 2003). Trace amounts of arsenic and lead were also strongly associated with the biomass combustion profile. This phenomenon is consistent throughout New Zealand and indicates co-combustion of copper chrome arsenate (CCA)-treated timber and old painted timber, respectively (Davy et al. 2014).
- **Motor vehicles:** The second factor was identified as motor vehicles because of the presence of black carbon, iron, copper and zinc as significant elemental components. This profile is likely a combination of tailpipe (black carbon and zinc from fuel combustion) and re-entrained road dust emissions (calcium, titanium and iron from crustal-matter components; copper from brake dust; zinc from tyre wear).
- **Marine aerosol:** The third factor was identified as a marine-aerosol source because of the predominance of sodium and chlorine, along with some magnesium, sulphur, potassium and calcium in similar ratios to sea water.

Figure 3.3 presents the source elemental profiles for the PM_{2.5} and PM₁₀ source contributors.

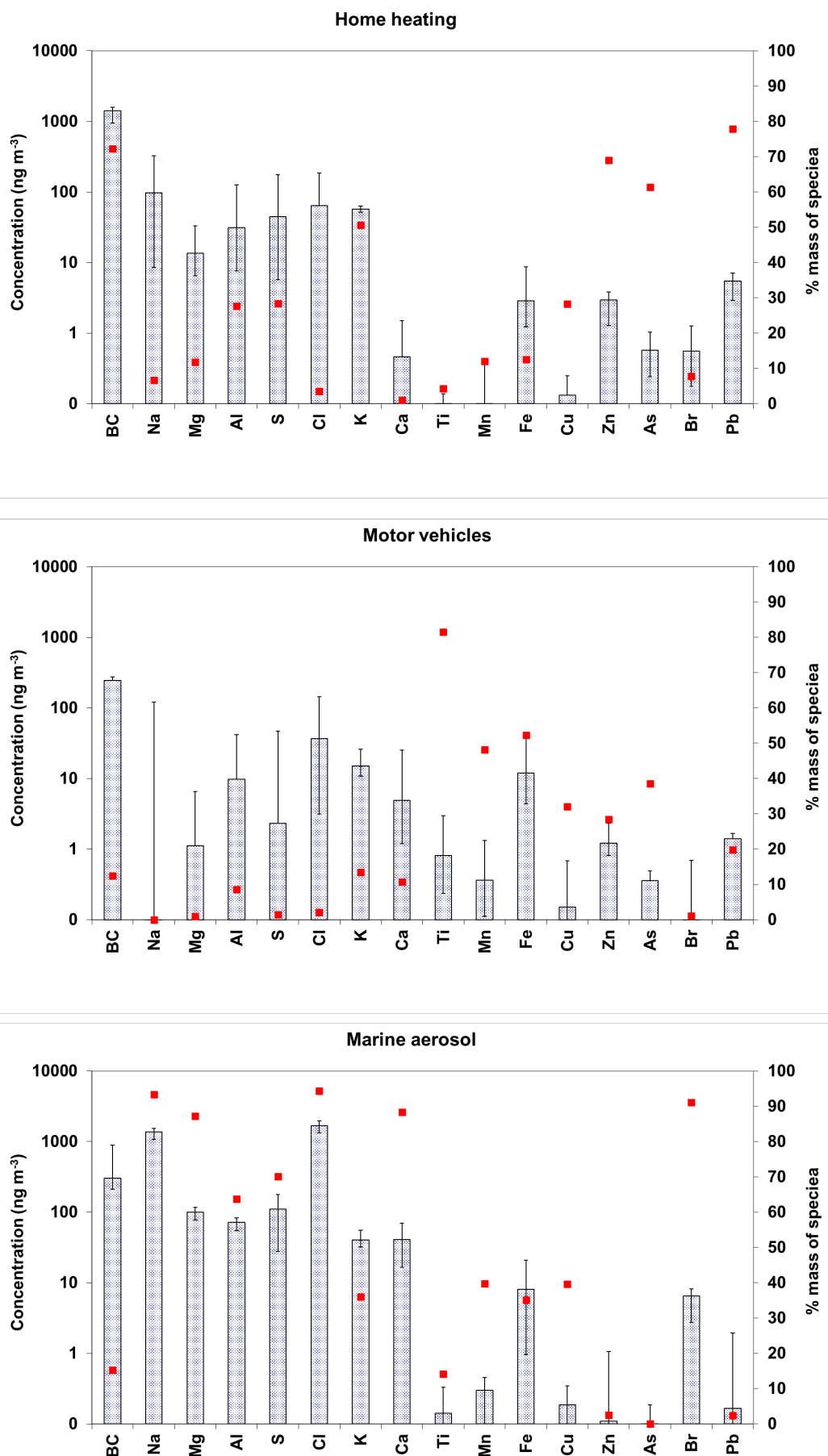


Figure 3.3 Source elemental-concentration profiles for particulate-matter samples from Greymouth. The red dots represent the percentage of each chemical species attributed to each source.

Table 3.3 presents the average source elemental-concentration profiles for PM_{2.5} samples derived from the PMF analysis.

Table 3.3 Average source elemental-concentration profiles for PM_{2.5} samples from Greymouth (based on 98 samples).

	Home Heating (ng m ⁻³)	Motor Vehicles (ng m ⁻³)	Marine Aerosol (ng m ⁻³)
PM_{2.5}	4183	261	2787
BC	1403	242	298
Na	35.3	0.0	498.9
Mg	7.2	0.6	53.3
Al	25.0	7.8	57.5
S	27.5	1.4	67.7
Cl	26.3	15.1	690.9
K	44.6	11.8	31.8
Ca	0.1	1.2	9.6
Ti	0.0	0.5	0.1
Mn	0.1	0.3	0.2
Fe	1.0	4.0	2.7
Cu	0.1	0.1	0.2
Zn	3.1	1.3	0.1
As	0.9	0.6	0.0
Br	0.2	0.0	2.1
Pb	6.5	1.6	0.2

Table 3.3 shows that home heating was the dominant contributing source to average PM_{2.5} concentrations at Greymouth during the monitoring period and that this source was contaminated with lead, most likely from the use of contaminated fuels, such as old painted timber. Note that the summation of elemental components does not equal particulate-matter mass, as this analysis was not for compounds (which includes oxides and other unmeasured species as described in Section 2.1) but for proportional elemental covariance and the proportion of particulate-matter mass that is also covariant with those elemental species.

Figure 3.4 presents the relative source contributions to PM_{2.5} in Greymouth. Also included are the 5th and 95th percentile confidence limits (bottom and top of error bar, respectively) in average mass contributions attributed to each of the sources, indicating the variability in average mass contributions over the monitoring period.

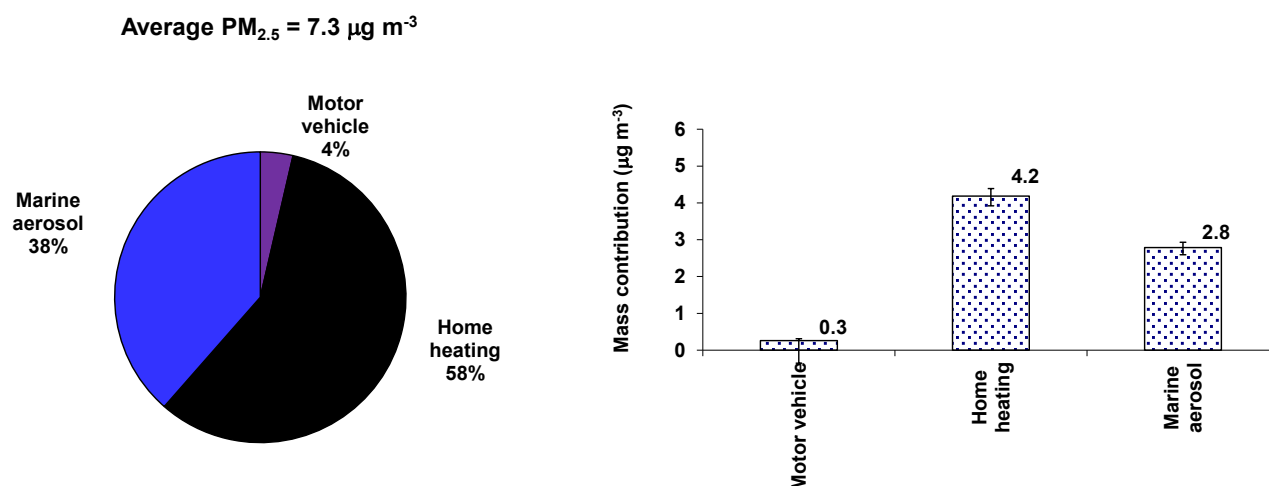


Figure 3.4 Average source-mass contributions to $PM_{2.5}$ at Greymouth over the monitoring period.

The average $PM_{2.5}$ source contributions over the monitoring period estimated from the PMF analysis showed that home heating (58%) was the most significant contributor to $PM_{2.5}$ mass and marine aerosol (38%) the next highest, while motor vehicles (4%) had the lowest contribution to $PM_{2.5}$ mass.

Table 3.4 presents the average source elemental-concentration profiles for PM_{10} samples derived from the PMF analysis.

Table 3.4 Average source elemental-concentration profiles for PM_{10} samples from Greymouth (based on 99 samples).

	Home Heating ($ng m^{-3}$)	Motor Vehicles ($ng m^{-3}$)	Marine Aerosol ($ng m^{-3}$)
PM_{10}	3536	2081	11025
BC	1520	262	322
Na	135.4	0.0	1910.6
Mg	20.6	1.7	152.0
Al	41.1	12.8	94.5
S	67.3	3.5	165.9
Cl	107.5	61.8	2824.9
K	71.9	19.0	51.2
Ca	0.8	8.7	71.8
Ti	0.1	1.5	0.3
Mn	0.2	0.7	0.6
Fe	4.8	20.0	13.4
Cu	0.2	0.3	0.3
Zn	4.0	1.6	0.1
As	1.2	0.8	0.0
Br	1.0	0.1	11.5
Pb	6.5	1.7	0.2

Table 3.4 also shows that marine aerosol (sea salt) and home heating were the dominant contributing sources to average PM_{10} concentrations at Greymouth.

Figure 3.5 presents the relative source contributions to PM₁₀ in Greymouth. Also included are the 5th and 95th percentile confidence limits (bottom and top of error bar, respectively) in average mass contributions attributed to each of the sources, indicating the variability in mass contributions over the monitoring period.

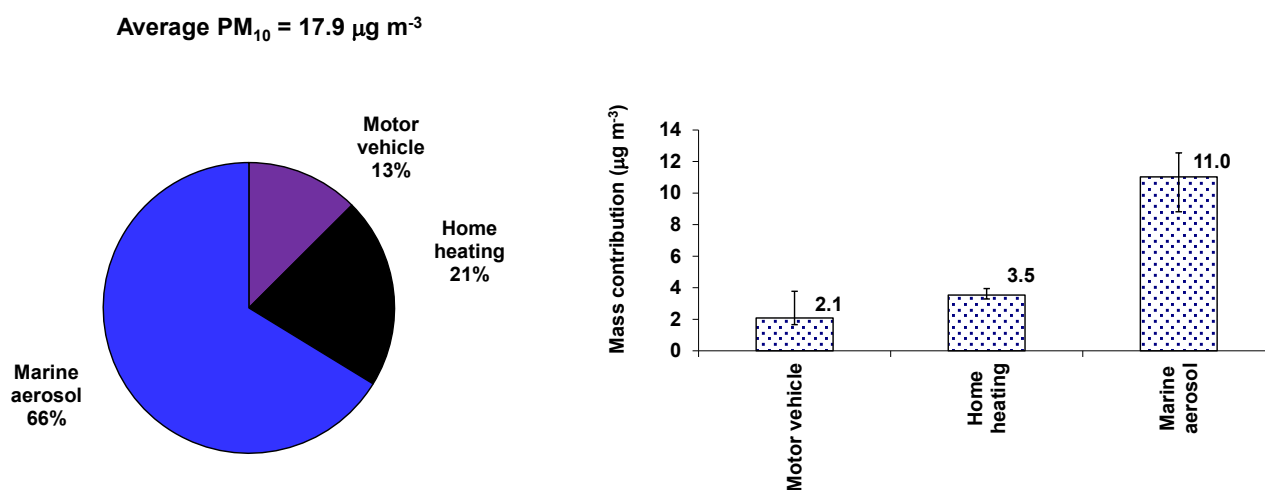


Figure 3.5 Average source-mass contributions to PM₁₀ at Greymouth over the monitoring period.

The average PM₁₀ source contributions over the monitoring period estimated from the PMF analysis showed that marine aerosol (66%) was the most significant contributor to PM₁₀ mass, with home heating (21%) the second highest, while motor vehicles (13%) had the lowest contributions to PM₁₀ mass.

3.3 Temporal Variations in Source Contributions to Particulate Matter at Greymouth

Temporal variations in the source contributions to PM_{2.5} and PM₁₀ at Greymouth are presented in Figures 3.6 and 3.7, respectively. It was evident from the data that PM_{2.5} mass is dominated by the home-heating source during key winter months (June to August), which arises primarily from solid-fuel fire emissions used for domestic space heating. It is also evident that significantly higher marine aerosol concentrations were present in PM_{2.5} through September as winter transitioned to spring and equinoctial winds were dominated by onshore southwesterlies.

Peak PM₁₀ mass was dominated by the marine-aerosol source over the monitoring period with increased contributions from motor vehicles compared to PM_{2.5}, indicating the relative influence of the coarse-particle fraction for those sources. Coarse-particle contributions to the motor-vehicle source include tyre and brake wear, as well as re-suspended crustal matter and other dusts on roadways representing the non-exhaust emission component in urban locations. As with PM_{2.5}, marine-aerosol contributions to PM₁₀ increased significantly during September 2025. Note that '*Remaining Mass*' refers to that particulate-matter gravimetric-mass fraction not explained by the receptor model. This was 1.7 µg m⁻³ and 3.3 µg m⁻³ on average for PM_{2.5} and PM₁₀ samples, respectively, and likely to be a combination of gravimetric-mass uncertainty (estimated at approximately 0.5 µg m⁻³) and those aerosol species not measured, such as nitrate, hydrocarbons and bound water, as described in Section 2.3.

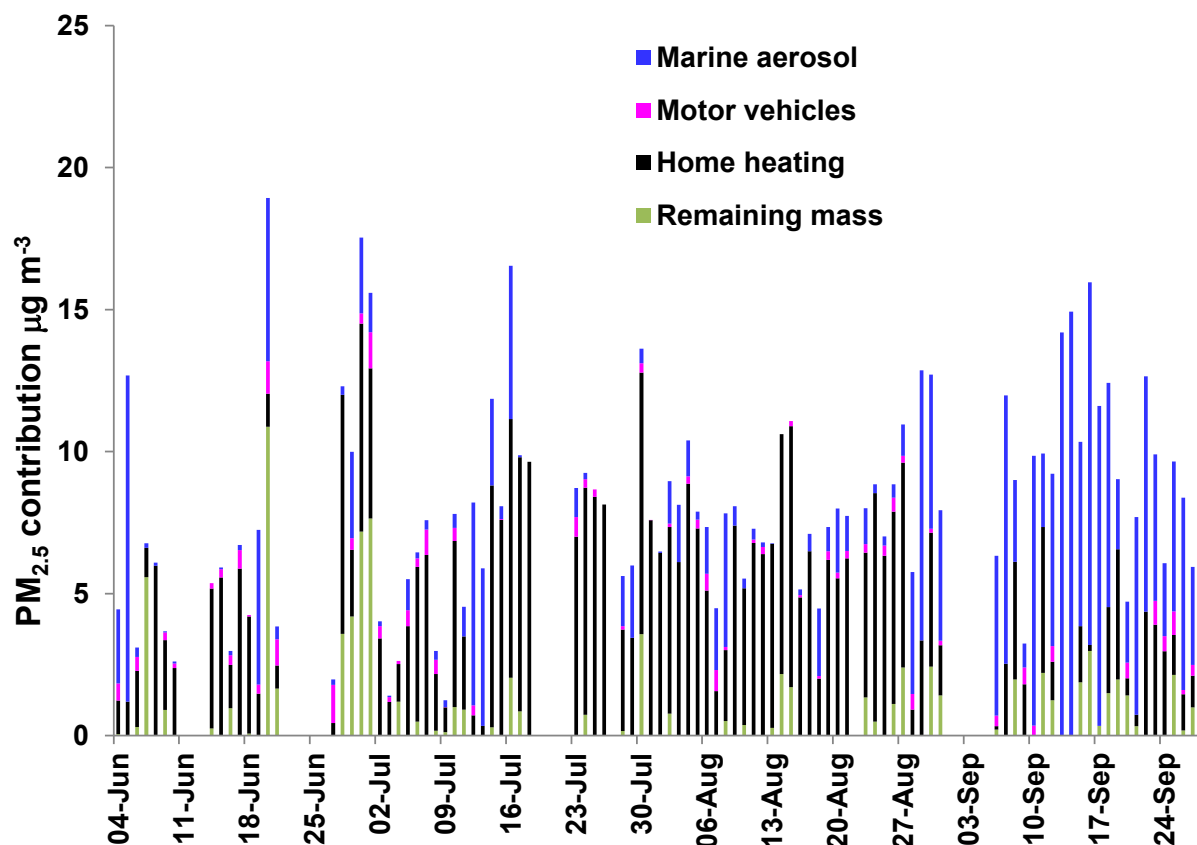


Figure 3.6 Temporal variations in relative source contributions to PM_{2.5} mass (24-hour average) at the Greymouth site.

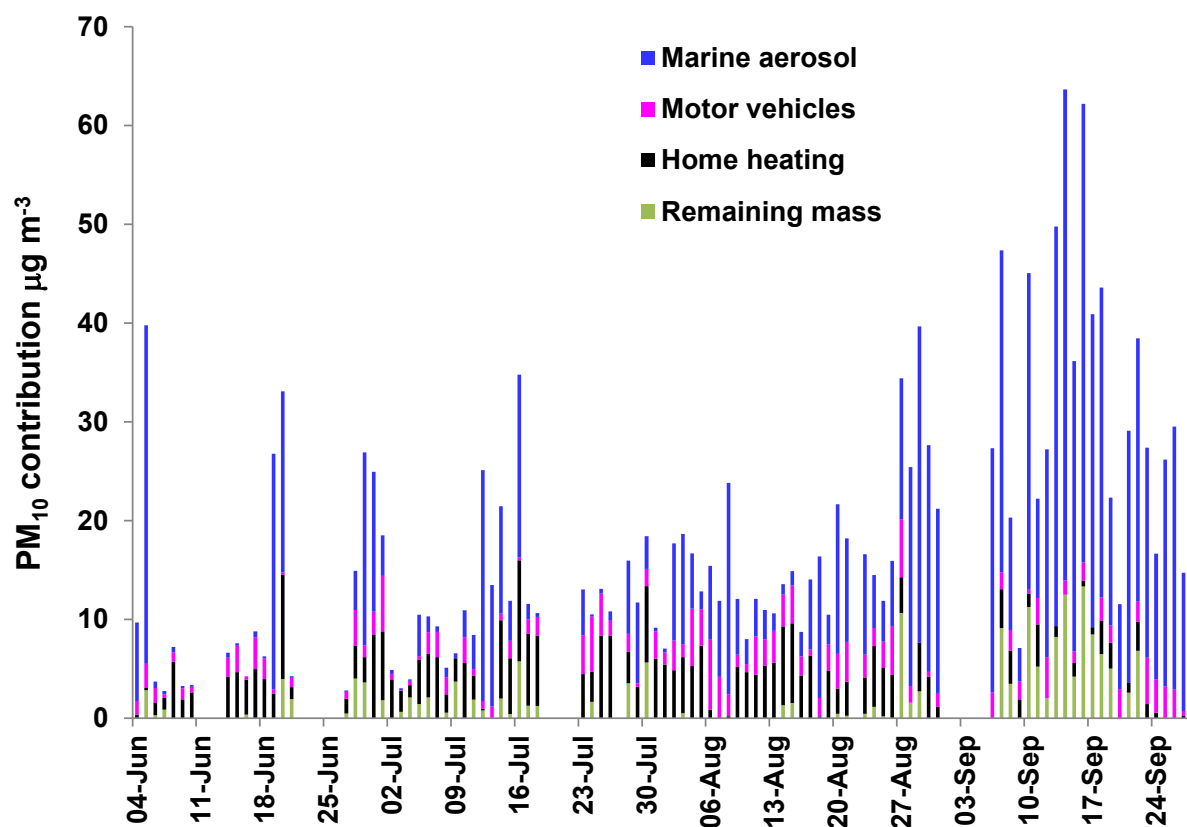


Figure 3.7 Temporal variations in relative source contributions to PM₁₀ mass (24-hour average) at the Greymouth site.

3.4 Variations in Source Contributions with Wind Direction at Greymouth

Bivariate polar plots using the source contributions to $PM_{2.5}$ were produced using R statistical software and the *openair* package (Carslaw 2012; Carslaw and Ropkins 2012; R Core Team 2015). Using bivariate polar plots, source contributions can be shown as a function of both wind speed and direction, providing invaluable information about potential source regions and how pollution from a specific source builds up. 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 conditional probability function statistic = 'cpf' has been used here, as described in Section 2.2.1. Because of the smoothing involved, the colour scale used in the plots is only to provide an indication of overall pattern and should not be interpreted in concentration units. The meteorological data used for the polar plot analysis was that supplied by West Coast Regional Council from the Greymouth Aerodrome EWS operated by Earth Sciences New Zealand (see Section 2.6).

3.4.1 Home Heating

Home-heating source contributions to $PM_{2.5}$ and PM_{10} were primarily from domestic solid-fuel fire emissions. Figure 3.8 presents a bivariate polar plot of home-heating combustion contributions to particulate matter at the monitoring site and shows that peak home-heating contributions occurred under light winds (less than 5 m/s) from the southeast. This suggests that light winds, most likely katabatic (cold air) drainage flows down the Sawyers Creek Valley, coupled with domestic fire emissions and poor dispersion, were responsible for elevated particulate-matter concentrations associated with home-heating emissions. Similar meteorological conditions, along with domestic solid-fuel heating emissions into an airshed, have been observed to lead elevated particulate-matter concentrations at other New Zealand locations (Trompetter et al. 2010; Ancelet et al. 2012; Grange et al. 2013; Ancelet et al. 2014a).

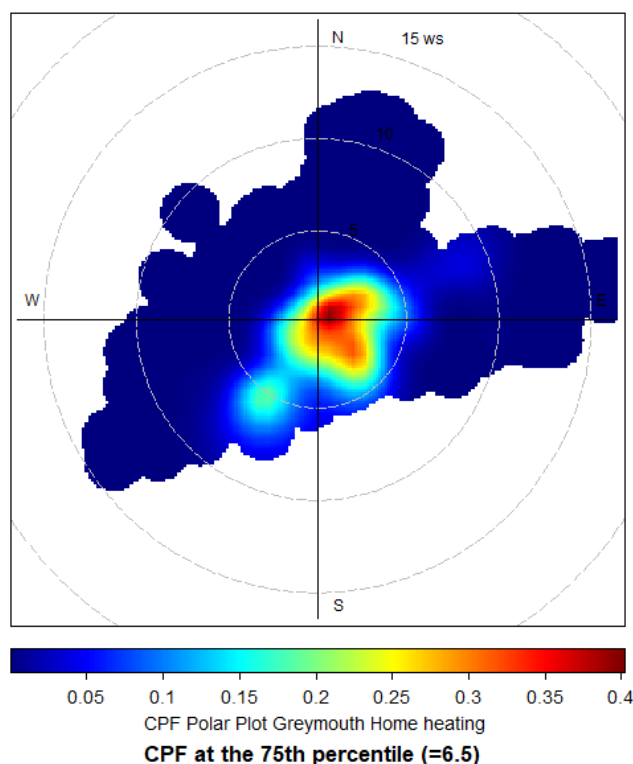


Figure 3.8 Polar plot of home-heating contributions to $PM_{2.5}$ and PM_{10} concentrations. The radial dimensions indicate the wind speed in 5 m s^{-1} increments, and the colour contours indicate the relative contribution to each wind direction / speed bin. Because of the smoothing involved, the colour scale used in the plots is only to provide an indication of overall pattern and should not be interpreted in concentration units.

3.4.2 Motor Vehicles

Peak motor-vehicle contributions at the monitoring site occurred under winds from the northeast quadrant (Figure 3.9). This is likely to represent the contribution from motor vehicles on the local road network and activity in the commercial centre to the north and northeast of the monitoring site. When wind direction aligns with the centreline of roadways, the road acts as a line source and will convey the highest concentrations of motor-vehicle emissions. State Highway 6 (the main West Coast road) runs from northeast to southwest immediately in front of the monitoring site at Greytown.

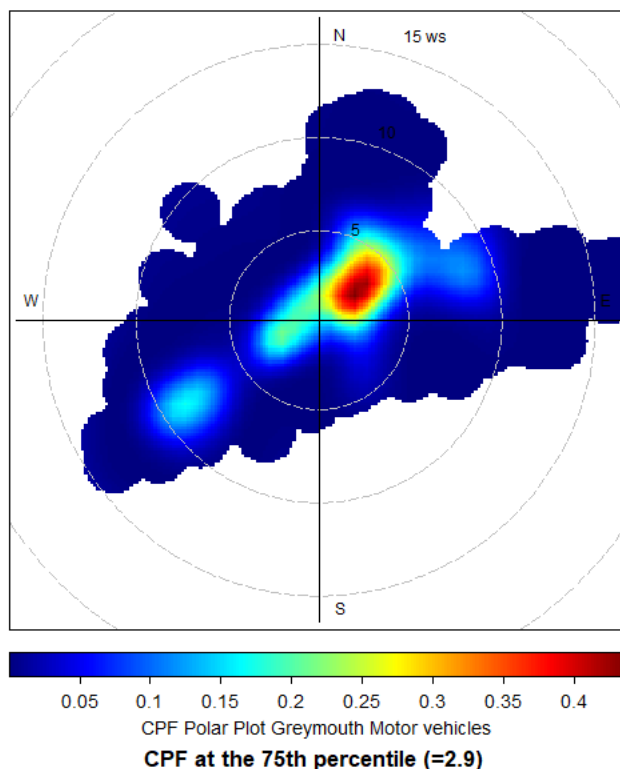


Figure 3.9 Polar plot of motor-vehicle contributions to $PM_{2.5}$ and PM_{10} concentrations. The radial dimensions indicate the wind speed in 5 m s^{-1} increments, and the colour contours indicate the relative contribution to each wind direction / speed bin. Because of the smoothing involved, the colour scale used in the plots is only to provide an indication of overall pattern and should not be interpreted in concentration units.

3.4.3 Marine Aerosol

Marine-aerosol contributions in Greymouth peaked under higher wind speeds from the northwest to southwest sectors, which aligns with the significant oceanic wind fetch relative to Greymouth's exposed West Coast location. Figure 3.10 shows the peak marine-aerosol contributions on a monthly basis (June to September) and illustrates the significant increase in overall concentrations during September 2025. The marine aerosol (sea salt) source concentrations were likely to be primarily a meteorologically generated source (wind field strength over oceanic fetch) (Fitzgerald 1991). The most likely source of marine aerosol was the Tasman Sea and Southern Ocean.

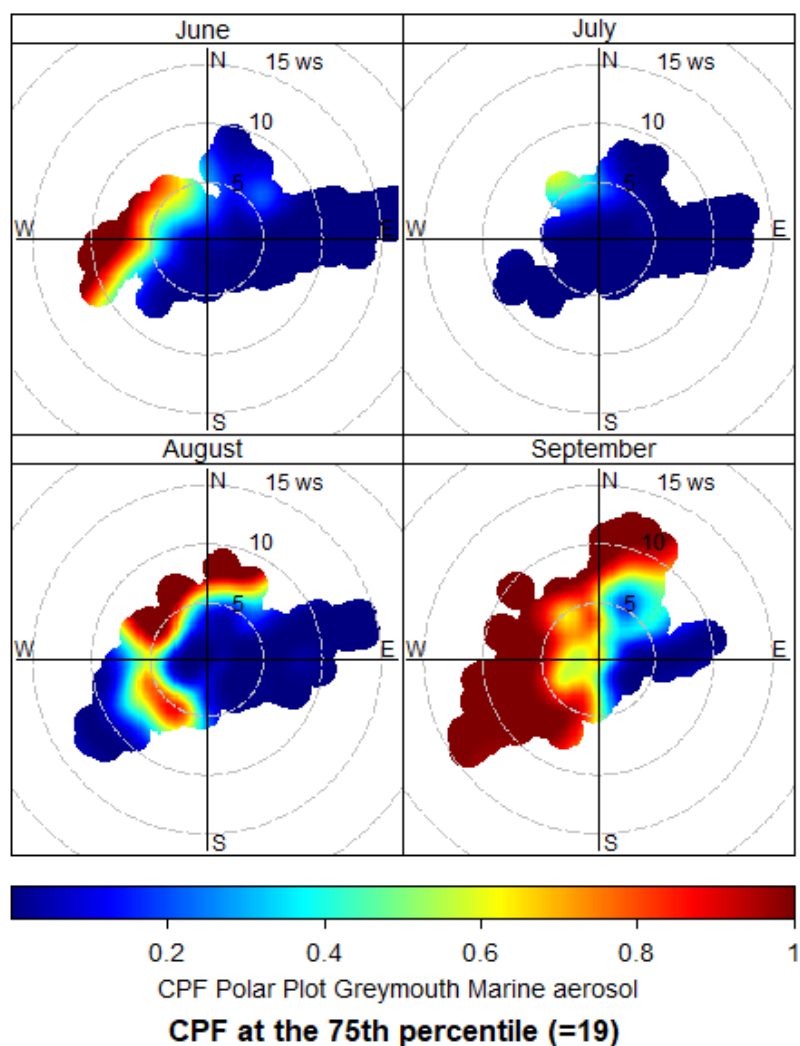


Figure 3.10 Polar plot of marine-aerosol contributions to $PM_{2.5}$ and PM_{10} concentrations for each month of the monitoring period (June to September 2025). The radial dimensions indicate the wind speed in 5 m s^{-1} increments, and the colour contours indicate the relative contribution to each wind direction / speed bin. Because of the smoothing involved, the colour scale used in the plots is only to provide an indication of overall pattern and should not be interpreted in concentration units.

4.0 Discussion of the Greymouth Receptor-Modelling Results

Three primary source contributors to PM_{2.5} and PM₁₀ concentrations at Greymouth were identified from receptor modelling of particulate-matter sample composition. The simultaneous collection of PM_{2.5} and PM₁₀ at the Greymouth monitoring site has provided the means to intercompare source contributions to each size fraction and examine any differences. The receptor-modelling analysis showed that peak winter PM_{2.5} concentrations were primarily influenced by home-heating sources, while marine aerosol and home heating dominated PM₁₀ concentrations.

4.1 Sources of Particulate Matter at Greymouth

4.1.1 Home Heating

The home-heating source was most likely to have originated from domestic solid-fuel fires for home heating and included traces of arsenic and lead in the source chemical profile, suggesting that CCA-treated wood and old painted timber were being used as fuel. The use of such contaminated timber as fuel for domestic fires is common throughout New Zealand (Davy et al. 2012; Ancelet et al. 2013a; Mitchell et al. 2013; Ancelet et al. 2014a, 2014b; Davy et al. 2014, 2016; Davy and Trompetter 2017a, 2017b, 2018, 2020). The home-heating source chemical profile also shows that average sulphur concentrations were elevated (45 ng m⁻³) compared to other urban areas (15 ng m⁻³) in New Zealand, suggesting that coal (a high-sulphur fuel) may be used with greater prevalence as fuel in domestic heating appliances in Greymouth, as presented in Figure 4.1. A similar result was obtained for Westport air-quality monitoring during 2023 (Davy and Trompetter 2024). Due to the covariant nature of both wood and coal emissions from domestic fires, it is difficult to separate source contributions from the different fuels over a short study period.

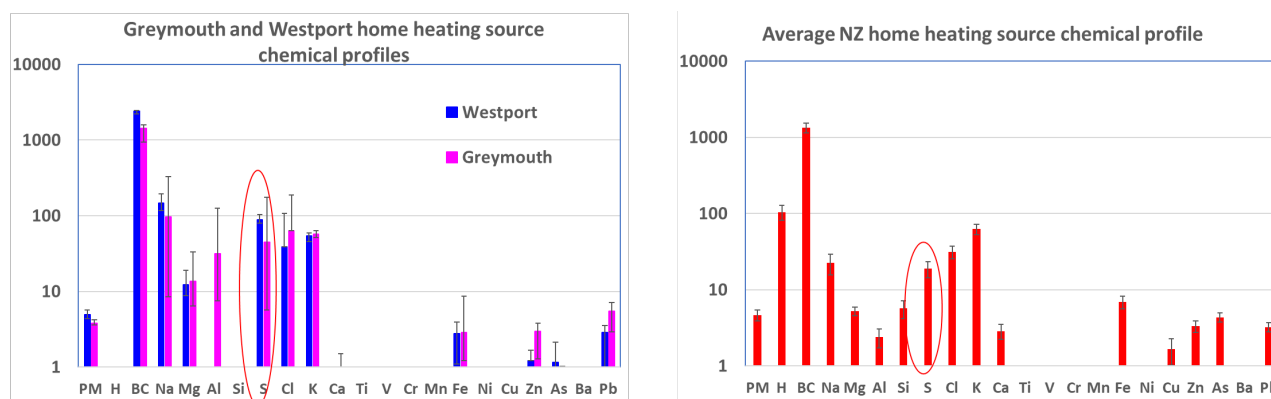


Figure 4.1 Greymouth and Westport (left) urban home-heating-source chemical profiles, showing higher sulphur content (circled) compared to the average profile for New Zealand (right).

An interesting feature of the Greymouth elemental data were the concentrations of lead in both PM_{2.5} and PM₁₀. Lead was found to be higher and more consistently present than for the corresponding Westport data. Figure 3.2 shows that concentrations of the heavy metal were highly correlated between the two size fractions, indicating that the lead was associated with fine-particle source emissions, and the receptor modelling showed that lead, along with lower quantities of arsenic, were associated with emissions of home-heating particles.

4.1.2 Motor Vehicles

The motor-vehicle source was identified as a minor contributor to PM_{2.5} (4%) and PM₁₀ (13%) at Greymouth. As indicated in the previous sections, the motor-vehicle source is likely to be a combination of vehicular tailpipe emissions (fine particles) and re-suspended material (coarse particles), including crustal matter, brake wear and tyre wear generated by the turbulent passage of vehicles on roads,

carparking areas and unsealed yards. At other urban locations in New Zealand, the motor-vehicle and non-exhaust sources have been found to be closely associated (Davy 2026). The evidence for this is based on a weekday/weekend difference in source contributions for both source types (Davy and Trompetter 2021). A similar statistical temporal-variation analysis was not possible for the Greymouth data due to the short (winter only) duration of the sampling.

4.1.3 Marine Aerosol

Marine aerosol was found to be a significant contributor to $PM_{2.5}$ (38%) and a major contributor to PM_{10} (66%) in Greymouth. It is generally a primary particle source in New Zealand airsheds due to the isolated oceanic location of the landmass. Figure 4.2 shows that marine-aerosol contributions were highly correlated between the two size fractions, as the generation of sea salt results in a primarily coarse particle-size range that extends down to $PM_{2.5}$.

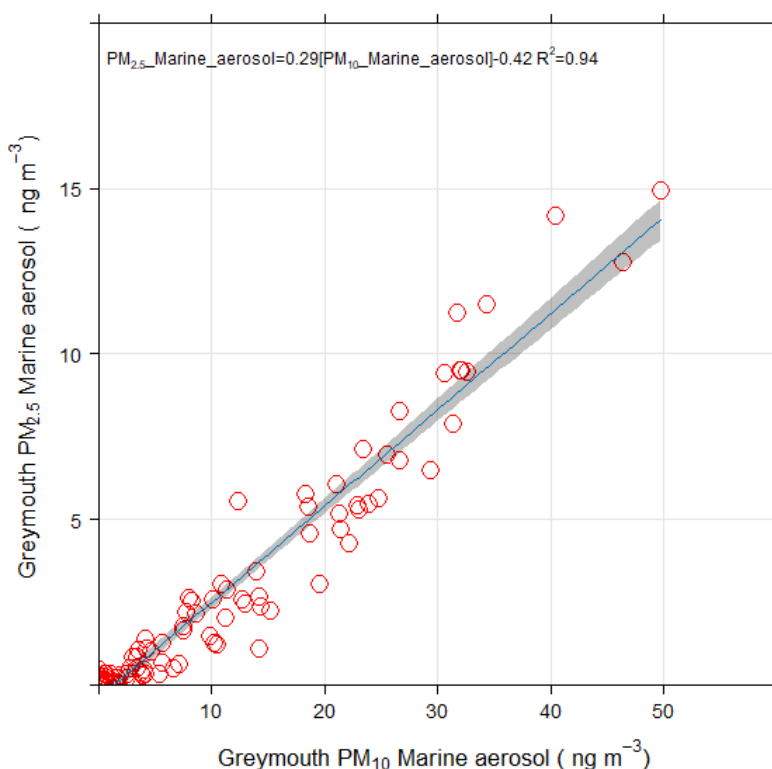


Figure 4.2 Marine aerosol contributions to $PM_{2.5}$ compared to PM_{10} for Greymouth.

The elemental composition for the marine-aerosol source closely resembles that of seawater (Lide 1992), and the source profile is therefore dominated by chlorine and sodium. Analysis of peak marine-aerosol contributions to particulate-matter concentrations (Figure 3.10) showed distinct northwest to southwest directionality during higher wind speeds at Greymouth, which was consistent with the most significant oceanic wind directions.

4.2 Analysis of Contributions to Particulate Matter on Peak Days

For air-quality management purposes and the protection of human health, contributions from the various sources to peak particulate-matter concentration events are of most interest. Of the days when samples were collected during the monitoring period, there were five days when $PM_{2.5}$ concentrations were higher than $15 \mu g m^{-3}$, the WHO AAQG for $PM_{2.5}$. The relative source contributions to $PM_{2.5}$ on those peak days are presented in Figure 4.3.

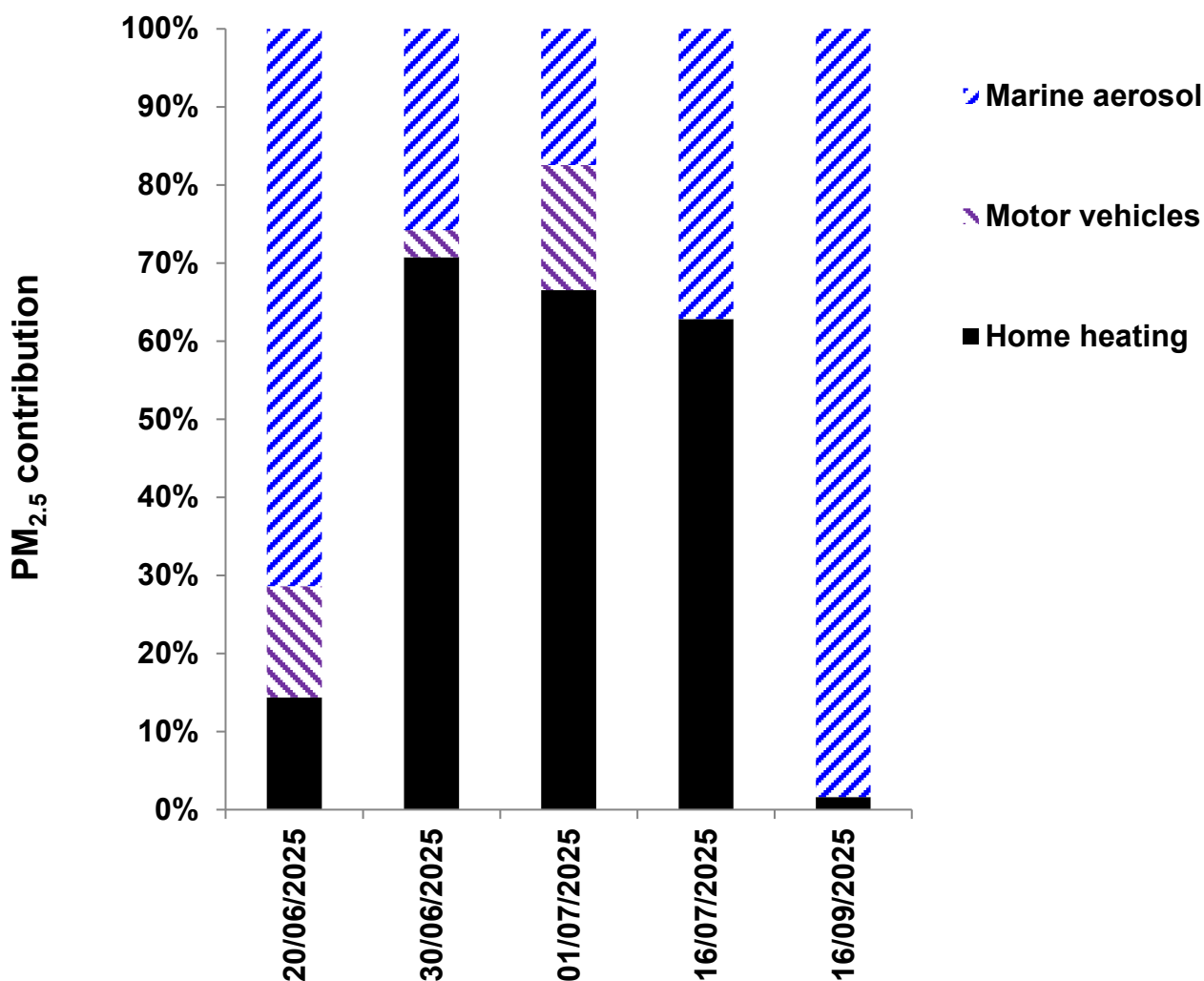


Figure 4.3 Source-mass contributions to peak $\text{PM}_{2.5}$ events ($>15 \mu\text{g m}^{-3}$) at Greymouth.

Figure 4.3 shows that home-heating emissions were responsible for an average of 60–70% of $\text{PM}_{2.5}$ mass on high concentration days during winter. The result is consistent with the location of the Greymouth monitoring site in a residential area where solid-fuel fires are used for home heating during winter. In New Zealand urban areas, high-particulate-matter events are generally dominated by home-heating emissions during winter. The results from Greymouth are interesting in that marine aerosol was still present in significant amounts, and two of the high $\text{PM}_{2.5}$ sample days were dominated by this source.

For PM_{10} , peak concentration days are concentrations above $33 \mu\text{g m}^{-3}$ (the ‘Alert’ category, as described in Table 2.1). There were 16 sampling days during the monitoring campaign where PM_{10} exceeded the Alert category, and two of those days (14 and 16 September 2025) exceeded the PM_{10} NESAQ of $50 \mu\text{g m}^{-3}$ (24-hour average). The data indicate that marine aerosol dominated PM_{10} source contributions on those days (97% and 95%, respectively), as shown in Figure 4.4. $\text{PM}_{2.5}$ was also high in marine aerosol for those sample days (100% and 98%, respectively).

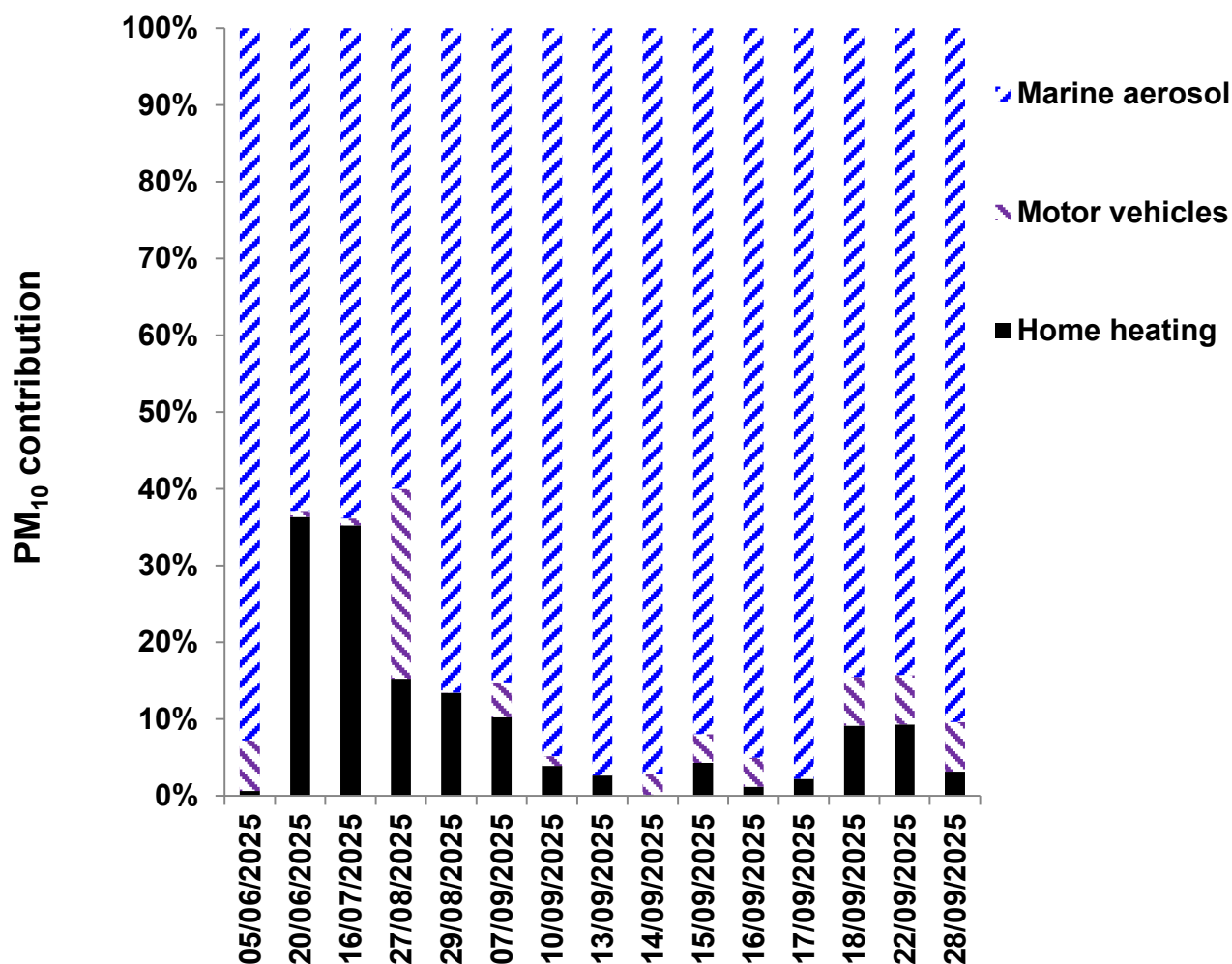


Figure 4.4 Source-mass contributions to the peak PM₁₀ events (>33 µg m⁻³) at Greymouth.

The particulate-matter monitoring and data analyses for the Greymouth site indicate that the open aspect of the location to the west coast and Tasman Sea, along with winter-time down-valley airflows (katabatic drainage), provide a moderating factor for the build-up of combustion-related pollutants (i.e. anthropogenic sources). Sea salt drives peak particulate matter on winds from the southwest to northwest sectors. Peak PM_{2.5} is affected by sea salt and combustion, while peak PM₁₀ is heavily influenced by sea salt. The role of combustion-related particulate matter is characterised by black carbon concentrations, which are a key indicator of motor-vehicle and home-heating combustion emissions. As presented in Figure 4.5, the CPF for black carbon (left-most plot) shows that peak concentrations occur during light winds (<5 m s⁻¹) associated with the down-valley flow, as found for the home-heating (Figure 3.8) and motor-vehicle sources (Figure 3.9). The CPF bivariate polar plots for PM_{2.5} and PM₁₀ show the influence of sea salt from the westerly sector.

The data clearly show that, if high PM_{2.5} concentrations in Greymouth occur during winter under low wind speeds (<5 m s⁻¹) from the easterly sector, then the likely source is home-heating emissions, whereas higher PM_{2.5} and PM₁₀ concentrations occurring during stronger winds (>5 m s⁻¹) from the westerly sector are likely to have marine aerosol as the source.

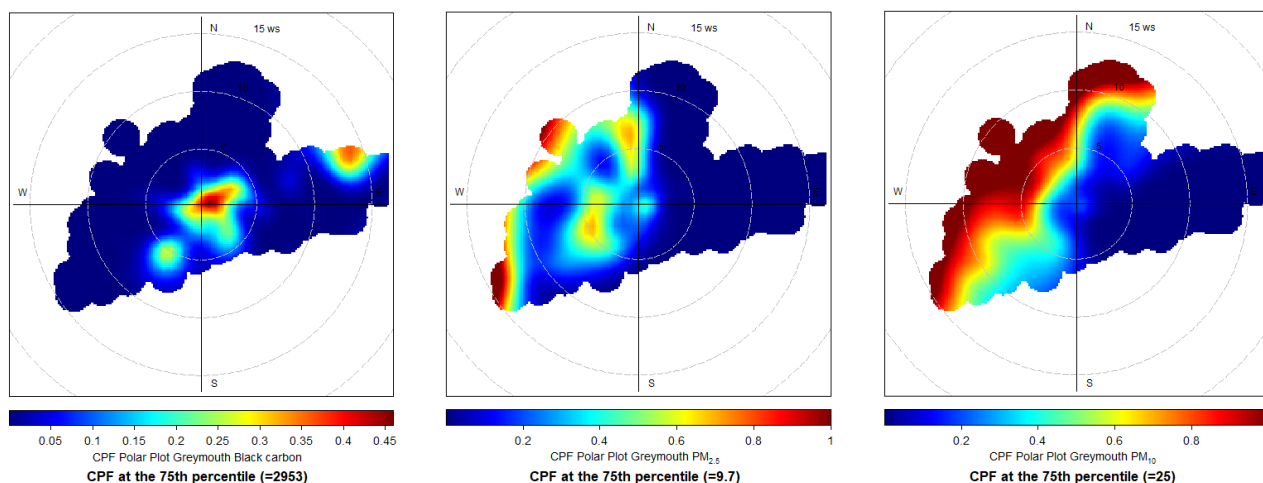


Figure 4.5 Polar plot of Greymouth black carbon concentrations (left) for the monitoring period (June to September 2025) alongside those for PM_{2.5} (centre) and PM₁₀ (right). The radial dimensions indicate the wind speed in 5 m s⁻¹ increments, and the colour contours indicate the relative contribution to each wind direction / speed bin. Because of the smoothing involved, the colour scale used in the plots is only to provide an indication of overall pattern and should not be interpreted in concentration units.

5.0 Summary of Greymouth Particulate-Matter Composition and Source Contributions

A winter (June–September 2025) PM_{2.5} and PM₁₀ airborne particle-sampling programme at Greymouth formed the basis of a study of particulate-matter composition and the attribution of sources contributing to measured particulate-matter concentrations. The particulate-matter elemental-composition data showed that black carbon, a product from combustion sources, was a dominant contributor to PM_{2.5} concentrations. For PM₁₀, black carbon, sodium and chlorine were important components that indicate the primary influence of the PM_{2.5} combustion sources, along with coarse-particle marine aerosol (sea salt) sources.

Three main source types of particulate matter were extracted from the data by receptor-modelling techniques (using PMF): these were home heating, motor vehicles and marine aerosol. The primary source of peak winter anthropogenic PM_{2.5} in Greymouth was the home-heating source, which was attributed to the use of solid-fuel fires for domestic space heating. It was also found that sea salt can also have a significant effect on local PM_{2.5} concentrations. Contributions to peak PM₁₀ concentrations reflected the influence of PM_{2.5} combustion sources, along with a greater influence of coarse-particle sea salt and motor-vehicle sources, to the extent that the two sampling days (14 and 16 September 2025) that exceeded the PM₁₀ NESAQ of 50 µg m⁻³ (24-hour average) were entirely dominated by marine aerosol. The home-heating source associated with solid-fuel fire emissions was also found to be contaminated with arsenic and lead, likely due to the opportunistic use of CCA-treated timber and old painted timber, respectively, as fuel.

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APPENDICES

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APPENDIX 1 Analysis Techniques

A1.1 X-Ray Fluorescence Spectroscopy

X-Ray Fluorescence spectroscopy (XRF) was used to measure elemental concentrations in PM_{2.5} and PM₁₀ samples collected on PTFE filters (TISCH PTFE membrane, 47 mm 0.2 µm) at Greymouth. XRF measurements in this study were carried out at the Earth Sciences New Zealand XRF facility, and the spectrometer used was a PANalytical Epsilon 5 (PANalytical, the Netherlands). The Epsilon 5 is shown in Figure A1.1. XRF is a non-destructive and relatively rapid method for the elemental analysis of particulate-matter samples.



Figure A1.1 The PANalytical Epsilon 5 spectrometer.

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

To eject inner-shell electrons from atoms in a sample, the XRF spectrometer at Earth Sciences New Zealand 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 sodium to uranium. Unlike ion-beam-analysis techniques, which are similar to XRF, the PANalytical Epsilon 5 is able to use characteristic K-lines produced by each element for quantification. This is crucial for optimising limits of detection, 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 germanium detector, which further improves the detection limits. Figure A1.2 presents a sample X-ray spectrum.

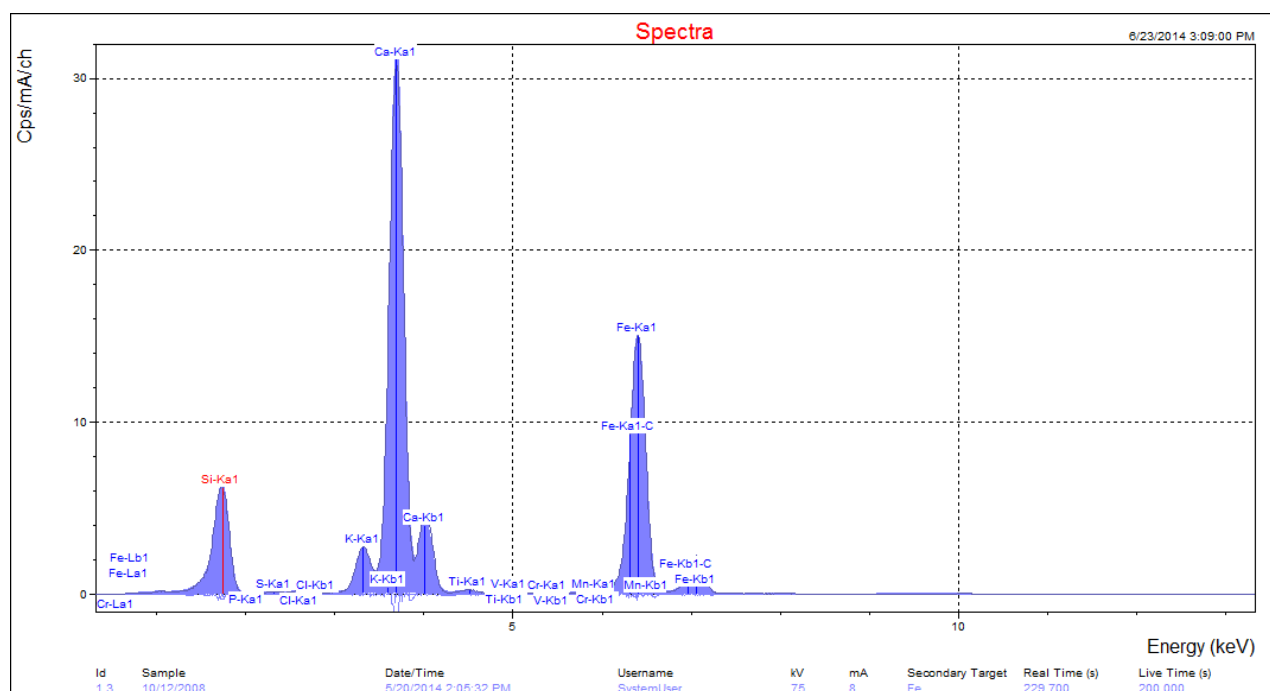


Figure A1.2 Example X-ray spectrum from a PM₁₀ sample.

In this study, 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 the Greymouth samples. Multi-elemental reference standards were also analysed to ensure that the results obtained were robust and accurate (Hyslop et al. 2019; Yarkin et al. 2020).

A1.2 Black Carbon Measurements

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

Black carbon particle-size ranges have been well characterised over a variety of emission sources, both in New Zealand (Davy et al. 2007, Ancelet et al. 2011a, 2011b; Davy et al. 2012; Salako et al. 2012; Ancelet et al. 2013b; Trompetter et al. 2013) and internationally (Ke et al. 2007; Schneider et al. 2008; Lack et al. 2009; Hays et al. 2011; Lopez-Reyes et al. 2016) and are invariably found to be in the sub-micrometre size range. Black carbon particles can consist of individual spherules (10–30 nm in diameter) to larger agglomerations (300–500 nm diameter) of individual particles. Black carbon (often called 'soot') is usually formed under conditions in which insufficient oxygen is present for complete oxidation of carbonaceous fuel to CO₂ (fuel-rich) (Bond et al. 2004). The characteristics of the combustion source therefore have an important bearing on particle size and carbonaceous

composition, with high-temperature combustion conditions (diesel engines, power stations) producing smaller, graphitic carbon particle entities (Allen et al. 2001; Huang et al. 2006; Ancelet et al. 2011a; Hung et al. 2014), whereas lower-temperature biomass combustion (wood fires for home heating, wild fire, forest fires) produce a mixture of carbon agglomerations and larger particles (500–900 nm), composed of a soot core and coated in organic ‘tar’ from incomplete combustion (Pósfai et al. 2003, 2004; Davy et al. 2007).

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

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

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

where:

- BC is black carbon.
- ε is the mass absorbent coefficient for ($\text{m}^2 \text{g}^{-1}$) at a given wavelength.
- F is a correction factor to account for other absorbing factors such as sulphates, nitrate, shadowing and filter loading. These effects are generally assumed to be negligible, and F is set at 1.00.
- R_0 , R are the pre- and post-reflection intensity measurements, respectively.

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

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

where:

- R_{blank} is the average reflectance for a series of blank filters and is close (but not identical) to 100 (Earth Sciences New Zealand always use the same blank filter for adjusting to 100);
- R_{sample} is the reflectance for a filter sample (normally lower than 100);

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

A1.3 Positive Matrix Factorization (PMF)

PMF is a linear least-squares approach to factor analysis and was designed to overcome the receptor-modelling problems associated with techniques like principal components analysis (PCA) and the *a priori* knowledge required for chemical mass balance approaches (Paatero et al. 2005). With PMF, sources are constrained to have non-negative species concentrations, no sample can have a negative source contribution, and error estimates for each observed data point are used as point-by-point weights. This feature is a distinct advantage in that it can accommodate missing and below-detection-limit data, which is a common feature of environmental monitoring results (Song et al. 2001). In fact, the signal-to-noise ratio for an individual elemental measurement can have a significant influence on a receptor model and modelling results. For the weakest (closest to detection limit) species, the variance may be entirely from noise (Paatero and Hopke 2003). Paatero and Hopke (2003) strongly suggest down-weighting or discarding noisy variables that are always below their detection limit or species that have a lot of error in their measurements relative to the magnitude of their concentrations. The distinct advantage of PMF is that mass concentrations can be included in the model and the results are directly interpretable as mass contributions from each factor (source).

A1.4 PMF Model Outline

The mathematical basis for PMF is described in detail by Paatero (Paatero 1997, 2000). Briefly, PMF uses a weighted least-squares fit with the known error estimates of measured elemental concentrations used to derive the weights. In matrix notation, this is indicated as:

$$X = GF + E \quad \text{Equation A1.3}$$

where:

- X is the known $n \times m$ matrix of m measured elemental species in n samples.
- G is an $n \times p$ matrix of source contributions to the samples.
- F is a $p \times m$ matrix of source compositions (source profiles).
- E is a residual matrix – the difference between measurement X and model Y .

E can be defined as a function of factors G and F :

$$e_{ij} = x_{ij} - y_{ij} = x_{ij} - \sum_{k=1}^p g_{ik} f_{kj} \quad \text{Equation A1.4}$$

where:

- $i = 1, \dots, n$ elements.
- $j = 1, \dots, m$ samples.
- $k = 1, \dots, p$ sources.

PMF constrains all elements of G and F to be non-negative, meaning that elements cannot have negative concentrations and samples cannot have negative source contributions as in real space. The task of PMF is to minimise the function Q such that:

$$Q(E) = \sum_{i=1}^n \sum_{j=1}^m (e_{ik} / \sigma_{kj})^2 \quad \text{Equation A1.5}$$

where σ_{kj} is the error estimate for x_{ij} . Another advantage of PMF is the ability to handle extreme values typical of air-pollutant concentrations, as well as true outliers that would normally skew PCA. In either case, such high values would have significant influence on the solution (commonly referred to as leverage). PMF has been successfully applied to receptor-modelling studies in a number of countries around the world (Hopke et al. 1999; Lee et al. 1999; Chueinta et al. 2000; Song et al. 2001; Lee et al. 2002; Kim et al. 2003, 2004; Jeong et al. 2004; Begum et al. 2005), including New Zealand (Ancelet et al. 2012; Davy et al. 2012; Ancelet et al. 2014b; Bennett et al. 2019; Davy and Trompeter 2020; Patel et al. 2020).

A1.4.1 PMF Model Used

Two programs have been written to implement different algorithms for solving the least squares PMF problem; these are PMF2 and EPAPMF. The latter incorporates the Multilinear Engine (ME-2) (Hopke et al. 1999; Ramadan et al. 2003). In effect, the EPAPMF program provides a more flexible framework than PMF2 for controlling the solutions of the factor analysis, with the ability of imposing explicit external constraints.

This study used EPAPMF 5.0 (version 14.0), which incorporates a graphical user interface (GUI) based on the ME-2 program. Both PMF2 and EPAPMF programs can be operated in a robust mode, meaning that ‘outliers’ are not allowed to overly influence the fitting of the contributions and profiles (Eberly 2005). The user specifies two input files, one file with the concentrations and one with the uncertainties associated with those concentrations. The methodology for developing an uncertainty matrix associated with the elemental concentrations for this work is discussed in Section A1.4.2.

A1.4.2 PMF Model Inputs

The PMF programs provide the user with a number of choices in model parameters that can influence the final solution. Two parameters, the ‘signal-to-noise ratio’ and the ‘species category’ are of particular importance and are described below.

Signal-to-noise ratio (S/N) – this is a useful diagnostic statistic estimated from the input data and uncertainty files. Two calculations are performed to determine S/N, where concentrations below uncertainty are determined to have no signal, and, for concentrations above uncertainty, the difference between concentration (x_i) and uncertainty (s_i) is used as the signal.

$$d_{ij} = \left(\frac{x_{ij} - s_{ij}}{s_{ij}} \right) \quad \text{if } x_{ij} > s_{ij}$$

$$d_{ij} = 0 \quad \text{if } x_{ij} \leq s_{ij}$$

S/N is then calculated using Equation A1.6:

$$\left(\frac{S}{N} \right)_j = 1/n \sum_{i=1}^n d_{ij}$$

Equation A1.6

The result with this S/N calculation is that species with concentrations always below their uncertainty have a S/N of 0. Species with concentrations that are twice the uncertainty value have a S/N of 1. S/N greater than 1 may often indicate a species with a ‘good’ signal, although this depends on how uncertainties were determined. Negative concentration values do not contribute to the S/N, and species with a handful of high-concentration events will not have artificially high S/N (Norris et al. 2014).

Species category – this enables the user to specify whether the elemental species should be considered:

- Strong – whereby the element is generally present in concentrations well above the limit of detection (high signal-to-noise ratio) and the uncertainty matrix is a reasonable representation of the errors.
- Weak – where the element may be present in concentrations near the limit of detection (low signal-to-noise ratio), where there is doubt about some of the measurements and/or the error estimates, or where the elemental species is only detected some of the time. If ‘Weak’ is chosen, EPAPMF increases the user-provided uncertainties for that variable by a factor of 3.
- Bad – that variable is excluded from the model run.

For this work, an element with concentrations at least three times above the limit of detection, high signal-to-noise ratio (>2) and present in all samples was generally considered ‘Strong’. Variables were labelled as ‘Weak’ if their concentrations were generally low, had a low signal-to-noise ratio, were only present in a few samples or where there was a lower level of confidence in their measurement. Mass-concentration gravimetric measurements and black carbon were also down weighted as ‘Weak’ depending on the dataset, as their concentrations are generally several orders of magnitude above other species and can have the tendency to ‘pull’ the model. Paatero and Hopke (2003) recommend that such variables be down-weighted, as well as that it does not particularly affect the model fitting if those variables are from real sources. What does affect the model severely is if a dubious variable is over-weighted. Elements that had a low signal-to-noise ratio (<0.5) were examined using bivariate correlation plots to determine interspecies relationships. Those low S/N variables with little or no association with other species, or that had mostly zero values, or that were doubtful for any reason, were labelled as ‘Bad’ and were subsequently not included in the analyses.

If the model is appropriate for the data and if the uncertainties specified are truly reflective of the uncertainties in the data, then Q (according to Eberly [2005]) should be approximately equal to the number of data points in the concentration dataset:

$$\text{Theoretical } Q = \# \text{ samples } \times \# \text{ species measured} \quad \text{Equation A1.7}$$

However, a slightly different approach to calculating the Theoretical Q value was recommended by Brown and Hafner (2005), which takes into account the degrees of freedom in the PMF model and the additional constraints in place for each model run. This theoretical Q calculation Q_{th} is given as:

$$Q_{th} = (\# \text{ samples } \times \# \text{ good species}) + [(\# \text{ samples } \times \# \text{ weak species})/3] - (\# \text{ samples } \times \text{factors estimated}) \quad \text{Equation A1.8}$$

Both approaches have been taken into account for this study, and it is likely that the actual value lies somewhere between the two. Further guidance has more recently been provided by Paatero et al. (2014) and Brown et al. (2015), where a third parameter, $Q_{expected}$, should also be calculated, but only the ‘good’ or non-weak variables should be taken into account:

$$\text{The expected value of } Q \text{ is approximately} = (\text{number of non-weak data values in } X) - (\text{numbers of elements in } G \text{ and } F, \text{ taken together}) \quad \text{Equation A1.9}$$

A down-weighted weak variable has only a small, rarely significant contribution to $Q_{expected}$ and, for simplicity, is excluded here. If the Q value of the chosen model differs significantly from what is expected (e.g. by a factor of 10 or more), then DISP error analysis becomes invalid and BS-DISP is likely questionable.

In PMF, it is assumed that only the x_{ij} 's are known and that the goal is to estimate the contributions (g_{ik}) and factors (or profiles) (f_{kj}). It is assumed that the contributions and mass fractions are all non-negative, hence the 'constrained' part of the least-squares. Additionally, EPAPMF allows the user to say how much uncertainty there is in each x_{ij} . Species-days with lots of uncertainty are not allowed to influence the estimation of the contributions and profiles as much as those with small uncertainty, hence the 'weighted' part of the least squares and advantage of this approach over PCA.

Diagnostic outputs from the PMF models were used to guide the appropriateness of the number of factors generated and how well the receptor modelling was accounting for the input data. Where necessary, initial solutions have been 'rotated' to provide a better separation of factors (sources) that were considered physically reasonable (Paatero et al. 2002). Each PMF model run reported in this study is accompanied by the modelling statistics, along with comments where appropriate.

A1.5 Dataset Quality Assurance

Quality assurance of sample elemental datasets is vital so that any dubious samples, measurements and outliers are removed, as these will invariably affect the results of receptor modelling. In general, the larger the dataset used for receptor modelling, the more robust the analysis. The following sections describe the methodology used to check data integrity and provide a quality-assurance process that ensured that the data being used in subsequent factor analysis was as robust as possible.

A1.5.1 Mass Reconstruction and Mass Closure

Once the sample analysis for the range of analytes has been carried out, it is important to check that total measured mass does not exceed gravimetric mass (Cohen 1999). Ideally, when elemental analysis and organic compound analysis has been undertaken on the same sample, one can reconstruct the mass using the following general equation for ambient samples as a first approximation (Cahill et al. 1989; Malm et al. 1994; Cohen 1999):

$$\text{Reconstructed mass} = [\text{Soil}] + [\text{OC}] + [\text{BC}] + [\text{Smoke}] + [\text{Sulphate}] + [\text{Sea salt}] \quad \text{Equation A1.10}$$

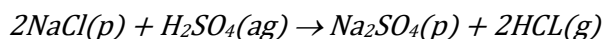
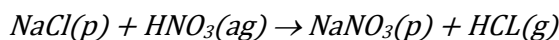
where:

- $[\text{Soil}] = 2.20[\text{Al}] + 2.49[\text{Si}] + 1.63[\text{Ca}] + 2.42[\text{Fe}] + 1.94[\text{Ti}]$
- $[\text{OC}] = \Sigma[\text{Concentrations of organic compounds}]$
- $[\text{BC}] = \text{Concentration of black carbon (soot)}$
- $[\text{Smoke}] = [\text{K}] - 0.6[\text{Fe}]$
- $[\text{Sea salt}] = 2.54[\text{Na}]$
- $[\text{Sulphate}] = 4.125[\text{S}]$

The reconstructed mass is based on the fact that the six composite variables, or 'pseudo' sources, given in Equation A1.10 are generally the major contributors to fine- and coarse-particle mass and are based on geochemical principles and constraints. The $[\text{Soil}]$ factor contains elements predominantly found in crustal matter (aluminium, silicon, calcium, titanium, iron) and includes a multiplier to correct for oxygen content and an additional multiplier of 1.16 to correct for the fact that three major oxide contributors (MgO, K₂O, Na₂O), carbonate and bound water are excluded from the equation.

$[\text{BC}]$ is the concentration of black carbon, measured in this case by light reflectance/absorbance. $[\text{Smoke}]$ represents potassium not included as part of crustal matter and tends to be an indicator of biomass burning.

[*Sea salt*] represents the marine-aerosol contribution and assumes that the NaCl weight is 2.54 times the sodium concentration. Sodium is used, as it is well known that chlorine can be volatilised from aerosol or from filters in the presence of acidic aerosol, particularly in the fine fraction via the following reactions (Lee et al. 1999):



Alternatively, where chlorine loss is likely to be minimal, such as in the coarse fraction or for both size fractions near coastal locations and relatively clean air in the absence of acid aerosol, then the reciprocal calculation of [*Sea salt*] = 1.65[*Cl*] can be substituted, particularly where sodium concentrations are uncertain.

Most fine sulphate particles are the result of oxidation of SO₂ gas to sulphate particles in the atmosphere (Malm et al. 1994). It is assumed that sulphate is present in fully neutralised form as ammonium sulphate. [*Sulphate*] therefore represents the ammonium sulphate contribution to aerosol mass with the multiplicative factor of 4.125[S] to account for ammonium ion and oxygen mass [i.e. (NH₄)₂SO₄ = ((14 + 4)2 + 32 + (16 × 4)/32)].

Additionally, the sulphate component not associated with sea salt can be calculated from Equation A1.11 (Cohen 1999):

$$\text{Non-sea salt sulphate (NSS-Sulphate)} = 4.125 ([S_{\text{tot}}] - 0.0543[\text{Cl}]) \quad \text{Equation A1.11}$$

where the sulphur concentrations contributed by sea salt are inferred from the chlorine concentrations, i.e. [*S/Cl*] sea salt = 0.0543, and the factor of 4.125 assumes that the sulphate has been fully neutralised and is generally present as (NH₄)₂SO₄ (Cahill et al. 1989; Malm et al. 1994; Cohen 1999).

The reconstructed mass and mass-closure calculations using the pseudo-source and pseudo-element approach are a useful way to examine initial relationships in the data and how the measured mass of species in samples compares to gravimetric mass. Note that some scatter is possible because not all aerosols are necessarily measured and accounted for, such as all organic compounds, ammonium species, nitrates and unbound water.

A1.5.2 Dataset Preparation

Careful preparation of a dataset is required because serious errors in data analysis and receptor-modelling results can be caused by erroneous individual data values. The general methodology followed for dataset preparation was as recommended by Brown and Hafner (2005) and the EPAPMF 5.0 User Guide (Norris et al. 2014). For this study, all data were checked for consistency with the following parameters:

- Individual sample collection validation.
- Gravimetric-mass validation.
- Analysis of reconstructed mass versus gravimetric mass to assess mass closure and linearity.
- Identification of unusual values, including noticeably extreme values and values that normally track with other species (e.g. aluminium and silicon) but deviate in one or two samples. Scatter plots and time-series plots were used to identify unusual values. One-off events such as fireworks displays, forest fires or vegetative burn-offs may affect a receptor model, as it is forced to find a profile that matches only that day.

- Species were included in a dataset if at least 70% of data were above the limit of detection, and signal-to-noise ratios were checked to ensure that data had sufficient variability. Important tracers of a source where less than 70% of data were above the limit of detection were included, but model runs with and without the data were used to assess the effect.

In practise, during data analyses, the above steps were a re-iterative process of cross-checking as issues were identified and corrected for, or certain data excluded, and the effects of this were then studied.

A1.5.2.1 PMF Data Matrix Population

The following steps were followed to produce a final dataset for use in the PMF receptor model (Brown and Hafner 2005).

- Below detection limit data:** For given values, the reported concentration used and the corresponding uncertainty was checked to ensure that it had a high value.
- Missing data:** Substituted with the dataset median value for that species.

A1.5.2.2 PMF Uncertainty Matrix Population

Uncertainties can have a large effect on model results, so these must be carefully compiled. The effect of under-estimating uncertainties can be severe, while over-estimating uncertainties does not do too much harm (Paatero and Hopke 2003).

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

- $\sigma_{ij} = x_{ij} + 2/3(DL_j)$ for samples below limit of detection, and
- $\sigma_{ij} = 0.2x_{ij} + 2/3(DL_j)$; $DL_j < x_{ij} < 3DL_j$ and $\sigma_{ij} = 0.1x_{ij} + 2/3(DL_j)$; $x_{ij} > 3DL_j$ for detected values,

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

Missing data: Uncertainty was calculated as $4 \times \text{median value}$ over the entire species dataset.

Particulate matter gravimetric mass: Uncertainty given as $4 \times \text{mass value}$ to down-weight the variable.

Re-iterative model runs were used to examine the effect of including species with high uncertainties or low concentrations. In general, it was found that the initial uncertainty estimations were sufficient and that adjusting the ‘additional modelling uncertainty’ function accommodated any issues with modelled variables, such as those with residuals outside ± 3 standard deviations.

APPENDIX 2 Greymouth 2025 Particulate-Matter Data-Analysis Summary

Using the methodology outlined in Section A1.4.1, Figure A2.1 presents the mass reconstruction results for Greymouth PM_{2.5} and PM₁₀. Figure A2.2 presents a correlation matrix plot for key elemental species in the two size fractions.

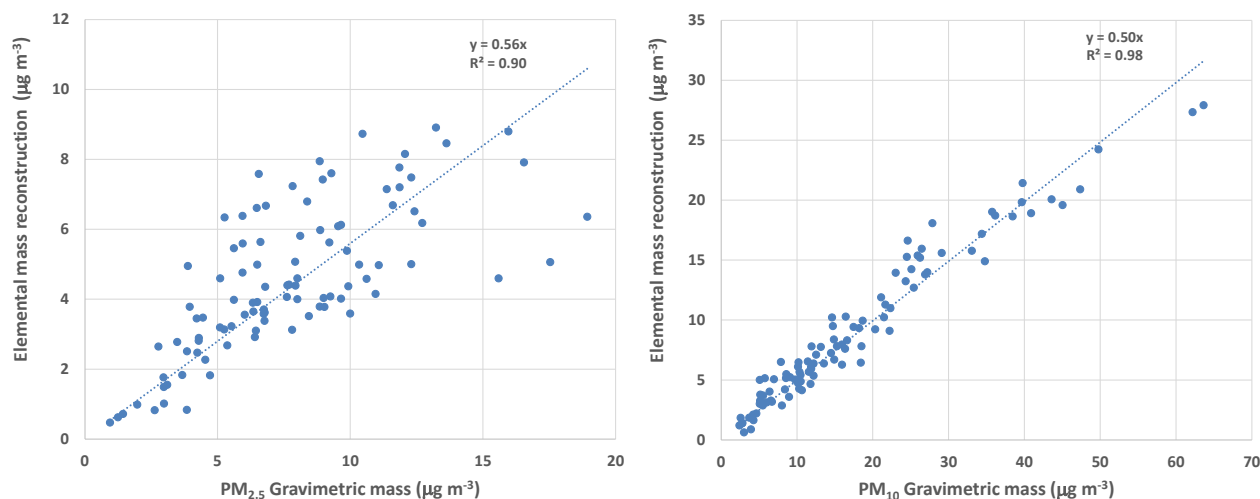


Figure A2.1 Plot of Greymouth PM_{2.5} and PM₁₀ elemental mass reconstruction against gravimetric mass.

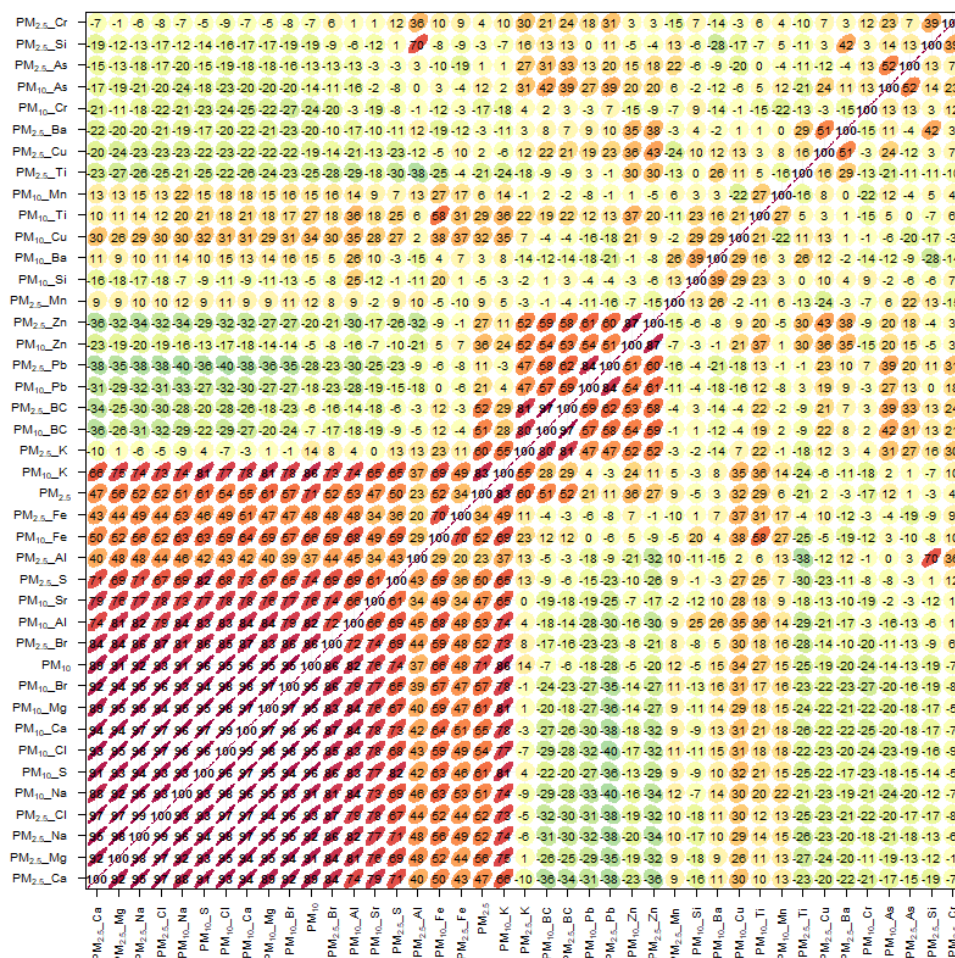


Figure A2.2 Particulate-matter and key elemental-composition correlation plot for Greymouth PM_{2.5} and PM₁₀ samples.

A2.1 Greymouth PMF Receptor Modelling Diagnostics

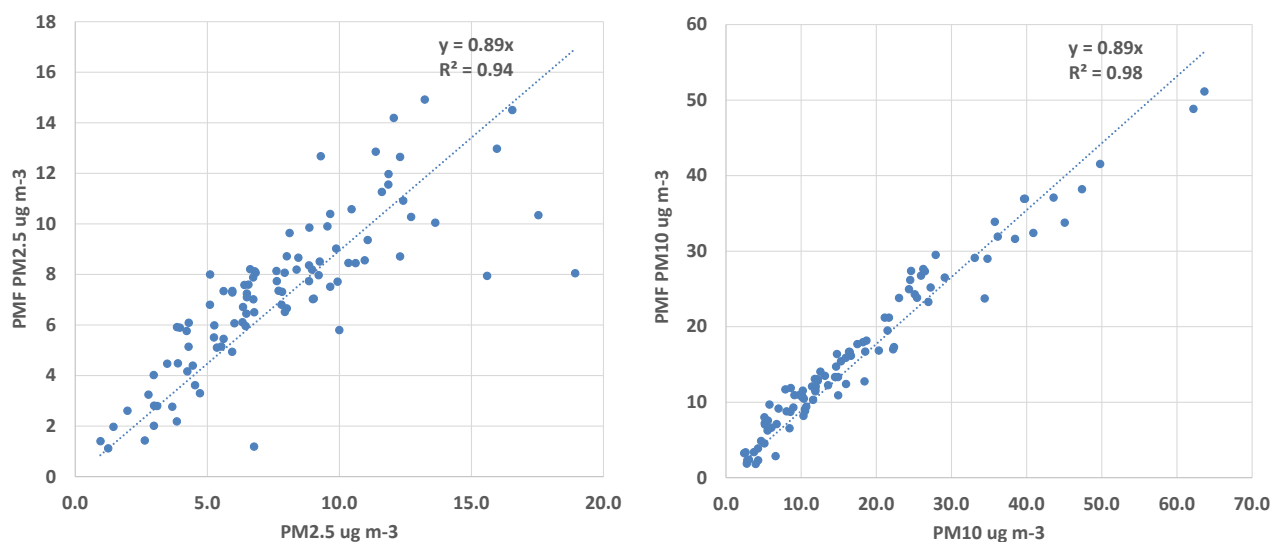
PMF analyses involve many details about the development of the data, decisions of what data to include/exclude, determination of a solution and evaluation of robustness of that solution. The following diagnostics for the PMF solutions are reported as recommended by Paatero et al. (2014) and Brown et al. (2015) and should be read in conjunction with Section 2.1 and Appendix 1. A critical factor in the success of receptor modelling is the ability to reproduce observed versus predicted (modelled) mass. This was achieved to an acceptable level in the case of Greymouth PM_{2.5} and PM₁₀, as presented in Figure A2.3.

Table A2.1 Summary of EPAPMF settings for receptor modelling of Greymouth PM_{2.5} and PM₁₀.

Parameter	Setting
Data type; averaging timeframe	PM ₁₀ , PM _{2.5} 24-hour
Number of samples	197
Number of factors	4
Treatment of missing data	No missing data
Treatment of data below detection limit (BDL)	Data used as reported, no modification or censoring of BDL data
Lower limit for normalised factor contributions gik	-0.2
Robust mode	Yes
Constraints	None
Seed value	Random
Number of bootstraps in BS	200
r ² for BS	0.6
DISP dQmax	4, 8, 16, 32
DISP active species	PM ₁₀ , PM _{2.5} , BC, Na, Mg, Cl, K, Ca, Ti, Fe
Number of bootstraps; r ² for BS in BS-DISP	200; 0.6
BS-DISP active species	PM ₁₀ , PM _{2.5} , BC, Na, Mg, Cl, K, Ca, Ti, Fe
BS-DISP dQmax	0.5, 1, 2, 4
Extra modelling uncertainty	15%

Table A2.2 Output diagnostics for receptor modelling of Greymouth PM_{2.5} and PM₁₀.

Diagnostic	Four Factors
Q _{Theoretical}	1550
Q _{Expected}	1258
Q _{true}	859
Q _{robust}	859
Q _{robust} /Q _{expected}	0.707
DISP Diagnostics	
Error code	0
Largest Decrease in Q	0
DISP % dQ	0
DISP swaps by factor	0
BS-DISP Diagnostics	
BS mapping (Fpeak BS) – unmapped	91% (96%) – 0
BS-DISP % cases accepted	86%
Largest decrease in Q	-12.08
BS-DISP % dQ	0
No. of decreases in Q	9
No. of swaps in best fit	54
No. of swaps in DISP	0
BS-DISP swaps by factor	2, 4, 1, 3

Figure A2.3 Plot of Greymouth PM_{2.5} (left) and PM₁₀ (right) versus predicted (PMF mass).



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