

**Lyttelton Port Air Particulate Matter
Speciation Analysis**

PK Davy

**GNS Science Consultancy Report 2021/69
August 2021**



Lyttelton Port Air Particulate Matter Speciation Analysis

P K Davy

**GNS Science Consultancy Report 2021/69
August 2021**

DISCLAIMER

This report has been prepared by the Institute of Geological and Nuclear Sciences Limited (GNS Science) exclusively for and under contract to Mote Limited. Unless otherwise agreed in writing by GNS Science, GNS Science accepts no responsibility for any use of or reliance on any contents of this report by any person other than Mote Limited and shall not be liable to any person other than Mote Limited, on any ground, for any loss, damage or expense arising from such use or reliance.

Use of Data:

Client consent required to use data.

BIBLIOGRAPHIC REFERENCE

Davy, P. K. 2021. Lyttelton Port Air Particulate Matter Speciation Analysis. Lower Hutt (NZ): GNS Science. 40 p. Consultancy Report 2021/69.

CONTENTS

EXECUTIVE SUMMARY	III
1.0 INTRODUCTION	1
1.1 Identifying the sources of airborne particle pollution	1
1.2 Report structure.....	1
2.0 SAMPLING AND ANALYSIS	2
2.1 Site location.....	2
2.2 Sampling of airborne particulate matter	2
2.3 Sample analysis	3
2.4 Conceptual model.....	3
2.5 Receptor modeling	4
2.6 Data analysis and reporting	4
3.0 RESULTS AND DISCUSSION	5
3.1 Elemental concentrations in PM _{2.5} and PM _{10-2.5}	5
3.2 Receptor modeling analyses of particulate matter	6
3.2.1 Receptor modelling process.....	6
3.3 Source contributions to PM _{2.5} and PM ₁₀ at the Lyttelton site.....	8
3.3.1 Average source contributions to particulate matter concentrations	9
3.3.2 Temporal variations in source contributions.....	10
4.0 SUMMARY OF THE LYTTELTON RECEPTOR MODELING RESULTS	12
4.1 Sources of Particulate Matter at the Lyttelton monitoring site.....	12
4.1.1 Motor vehicles	12
4.1.2 Soil.....	12
4.1.3 Cement.....	12
4.1.4 Ship emissions	12
4.1.5 Marine Aerosol	12
4.1.6 Coal dust	13
5.0 REFERENCES	14

FIGURES

Figure ES1	Average source contributions to PM _{2.5} at the Lyttelton monitoring site.....	iii
Figure ES2	Average source contributions to PM ₁₀ at the Lyttelton monitoring site	iv
Figure 2.1	Lyttelton air quality speciation monitoring site location (●) (Source: Google Earth 2021).....	2
Figure 3.1	Particulate matter source chemical profiles derived from the receptor modeling at Lyttelton.....	9
Figure 3.2	Average source contributions to PM _{2.5} at the Lyttelton monitoring site.....	9
Figure 3.3	Average source contributions to PM ₁₀ at the Lyttelton monitoring site	10
Figure 3.4	Temporal variations in source contributions to PM _{2.5} mass at Lyttelton.....	11
Figure 3.5	Temporal variations in source contributions to PM ₁₀ mass at Lyttelton	11

TABLES

Table 3.1	Elemental concentrations in PM _{2.5} collected at Lyttelton (337 samples).....	5
Table 3.2	Elemental concentrations in PM _{10-2.5} collected at Lyttelton (337 samples).	6

APPENDICES

APPENDIX 1	ELEMENTAL CONCENTRATIONS BY ION BEAM ANALYSIS.....	21
	A1.1.1 Particle-Induced X-Ray Emission.....	22
	A1.1.2 Particle-Induced Gamma-Ray Emission	23
A1.2	XRF and IBA Data Reporting.....	23
	A1.2.1 Limits of detection and uncertainty reporting for elements	24
A1.3	Black Carbon Measurements.....	25
A1.4	Positive Matrix Factorization	26
	A1.4.1 PMF model outline	26
	A1.4.2 PMF model used	27
	A1.4.3 PMF model inputs	28
A1.5	Dataset Quality Assurance	30
	A1.5.1 Mass reconstruction and mass closure.....	30
	A1.5.2 Dataset preparation.....	31
APPENDIX 2	ELEMENTAL CORRELATION PLOTS.....	33
APPENDIX 3	PMF RECEPTOR MODELLING DIAGNOSTICS	34

APPENDIX FIGURES

Figure A1.3	Particulate matter analysis chamber with its associated detectors.....	21
Figure A1.4	Schematic of the typical IBA experimental setup at GNS Science.	22
Figure A1.5	Typical PIXE spectrum for an aerosol sample analysed by PIXE.....	22
Figure A1.6	Typical PIGE spectrum for an aerosol sample.	23
Figure A1.7	Elemental limits of detection for PIXE routinely achieved as the GNS IBA facility for air filters. .	25
Figure A2.1	Elemental correlation plot for PM _{10-2.5} and PM _{2.5} composition	33

APPENDIX TABLES

Table A3.1	Summary of EPA PMF settings for receptor modelling of Lyttelton PM _{2.5} .and PM _{10-2.5} elemental data	34
Table A3.2	Output diagnostics for receptor modelling Lyttelton PM _{2.5} .and PM _{10-2.5} elemental data.....	35

EXECUTIVE SUMMARY

This report presents the results of an analysis of particulate matter (PM₁₀ and PM_{2.5}) concentrations and chemical composition measured at a Lyttelton monitoring site in the Canterbury Region. The data have been used in a receptor modelling study to determine the emission sources contributing to particulate matter concentrations at the monitoring site and estimate their impact on total particulate matter concentrations.

The key results from the study were the identification of six sources contributing to the fine and coarse particulate matter collected at the monitoring site:

- **Motor vehicles** representing tailpipe emissions co-mingled with road dust
- **Soil** typical of a wind-blown crustal matter component.
- **Cement** which included Ca as a primary component typical of cement dusts (ordinary Portland cement is approximately 60 % CaO) likely associated with activities involving the transfer of bulk cement powders.
- **Ship emissions** from primary ship engine emissions with characteristic black carbon, sulphur, vanadium and nickel content reflective of the heavy fuel oil composition and their combustion products.
- **Marine aerosol** (or sea salt) which was found to be the predominant source at Lyttelton over the monitoring period. Marine aerosol is a natural long-range source generated in the oceanic regions around New Zealand.
- **Coal dust** that primarily contributed to coarse particle concentrations and likely to be the result of suspended dusts from the storage and bulk cargo handling of coal at Lyttelton Port. The coal dust was largely a coarse particle (PM_{10-2.5}) source that occurred intermittently throughout the monitoring campaign.

Figure ES1 and ES2 present the relative contributions of the identified sources to PM_{2.5} and PM₁₀ respectively.

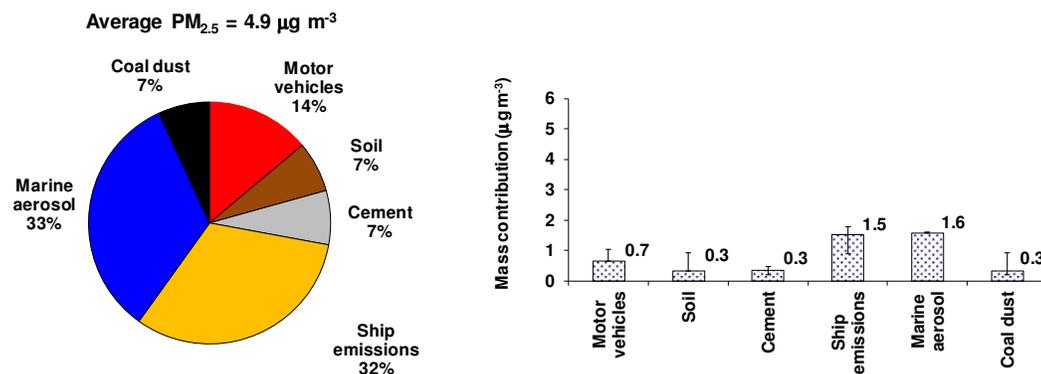


Figure ES1 Average source contributions to PM_{2.5} at the Lyttelton monitoring site

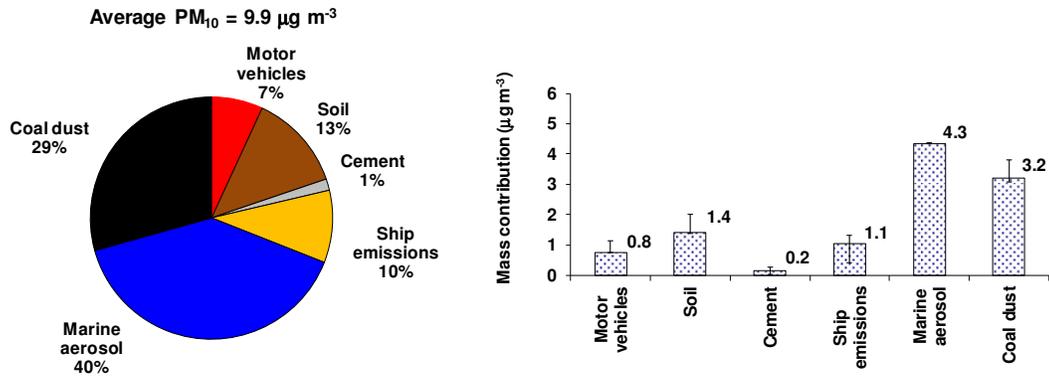


Figure ES2 Average source contributions to PM_{10} at the Lyttelton monitoring site

1.0 INTRODUCTION

Lyttelton Port Company (LPC) owns and operates a coal stockyard adjacent to the Lyttelton Port wharf and cargo handling facilities. Coal is handled and stored at the yard ready for export. LPC holds a resource consent to discharge coal dust into air from the coal stockyard operation. The discharge permit expires on 19 February 2022 and so a replacement consent must be secured if the coal stockyard is to continue to operate.

This report presents the results of an air particulate matter sampling and compositional analysis campaign at Lyttelton Port, Christchurch. Discharges of coal dust from the operation of the coal stockyard are likely to be contributors to emissions of PM₁₀ dust in the area. Accordingly, the Port seeks to understand the contributions of coal dust emissions to total ambient PM₁₀ concentrations.

1.1 Identifying the sources of airborne particle pollution

An evaluation of the contribution of coal dust to ambient particulate matter concentrations in the local airshed enables a better understanding of the effects of coal dust on the receiving environment.

Measuring the total mass concentration of particulate matter provides little or no information on the identities of the contributing sources, including coal dusts. Airborne particles are composed of many elements and compounds emitted from various sources. Receptor modeling allows the determination of relative mass contributions from sources (including the coal stockyard) impacting the total particulate matter mass of samples collected at a monitoring site located off Gilmour Terrace, Lyttelton.

In this study, samples of airborne coarse (PM_{10-2.5}) and fine (PM_{2.5}) particulate matter were collected at a monitoring site near the Port with subsequent compositional analysis of those samples in order to assist identification of the respective emission sources. Elemental concentrations in the samples were determined using ion beam analysis (IBA) techniques at the New Zealand IBA facility operated by GNS Science in Lower Hutt (Trompetter, Markwitz et al. 2005, Barry, Trompetter et al. 2012). IBA describes a range of mature analytical techniques that provide the non-destructive determination of multi-elemental concentrations in samples.

1.2 Report structure

This report is comprised of 4 main chapters broken down as follows:

1. Chapter 2 describes the Lyttelton ambient air quality monitoring site along with the methodology and analytical techniques used for the receptor modeling analysis.
2. Chapter 3 presents the receptor modeling results including the temporal variations in PM₁₀ and PM_{2.5} source contributions.
3. Chapter 4 provides a summary of the research findings.

2.0 SAMPLING AND ANALYSIS

2.1 Site location

Samples were collected between December 2020 and May 2021 at a monitoring site located on a hillside (Lat: -43.6061; Long: 172.7273) above Lyttelton Port as shown in Figure 2.1. The site was a temporary air quality monitoring station set up by Mote Limited who operated continuous particulate matter (PM₁₀, PM_{2.5}) monitoring systems at the site.



Figure 2.1 Lyttelton air quality speciation monitoring site location (●) (Source: Google Earth 2021)

2.2 Sampling of airborne particulate matter

The Lyttelton air quality monitoring site was equipped with a Streaker sampler (PIXE International Corporation, USA), in the same fashion as previously reported (Ancelet, Davy et al. 2012). The instrument consists of a pre-impactor that removes particles larger than PM₁₀ from the incoming air flow, a thin Kapton foil that collects coarse particles (PM_{10-2.5}) through impaction and a Nucleopore filter (0.4 µm pore size) that collects fine particles (PM_{2.5}) with discrete spacing between each deposit to ensure that each only consisted of particulate matter collected during the intended sample period (Prati, Zucchiatti et al. 1998). Initially 8-hourly time integrated samples were collected, but this was subsequently switched to six-hourly to increase the number of samples collected as some problems with sampler programming and power outages were experienced during the campaign. The high-resolution particulate matter monitoring program ran from 15 December 2020 to 27 April 2021 and samples were collected on each set of size-resolved (PM_{10-2.5} and PM_{2.5}) filter. Overall, 680 discrete samples of particulate matter (340 each of fine and coarse) were collected during the monitoring representing approximately 1700 hours of sampling time.

Because each discrete particulate matter sample was collected on a single filter, gravimetric determination of the particulate matter mass for each sample was not possible. Instead, the particulate matter data from the continuous samplers operated by Mote Ltd alongside was

used for the data analysis process and assignment of source mass contributions to ambient particulate matter concentrations.

2.3 Sample analysis

Ion beam analysis (IBA) was used to measure the concentrations of elements with atomic numbers above neon in the PM samples. The IBA was performed using a 3MeV accelerator proton beam with standards (SrF₂, NaCl, Cr, Ni, SiO, KCl, Al) run before and after each analytical cycle. Spectral X-ray peak deconvolution was performed using Gupix software (Maxwell, Teesdale et al. 1995). The number of pulses (counts) in each peak for a given element is used by the Gupix software to calculate the concentration of that element. The background and neighbouring elements determine the statistical error and the limit of detection. Note that Gupix provides a specific statistical error and limit of detection (LOD) for each element in each PM sample and these have been used to provide the uncertainty matrix used in the Positive Matrix Factorisation (PMF) analysis. IBA measurements were carried out at the New Zealand National Isotope Centre operated by the Institute of Geological and Nuclear Sciences (GNS Science) in Gracefield, Lower Hutt, New Zealand (Trompetter, Markwitz et al. 2005). Further details on the IBA techniques used, analytical uncertainties and limits of detection have been reported previously ((Zhou, Davy et al. 2016). Black carbon (BC) was measured using a M43D Digital Smoke Stain Reflectometer (Ancelet, Davy et al. 2011).

Prior to the PMF analyses, concentrations and uncertainty matrices were prepared in the same manner as previous studies (Polissar, Hopke et al. 1998, Song, Polissar et al. 2001) (see also Appendix 1 for details).

2.4 Conceptual model

An important part of the receptor modeling 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. The initial conceptual model includes local emission sources (point and line):

- Transport (motor vehicles and trains) – all roads in the area act as line sources, and roads with higher traffic densities and congestion will dominate.
- Biomass combustion, primarily from activities such as vegetation burnoffs, wild-fire or use of domestic solid fuel appliances for space heating. Since the monitoring was undertaken during summer and early autumn domestic solid fuel fire (wood burner) emissions may not significantly impact at the monitoring site;
- Potential industrial emissions from combustion processes (boilers) and particle generating activities.
- Local wind-blown soil or road dust sources, road works, unpaved yards and demolition/construction activities may contribute.
- Ship engine emissions in Lyttleton Port and other activities that may give rise to dusts such as bulk storage and associated loading and unloading of cargoes that contain dusts and powders.

Area sources that originate further from the monitoring site would also be expected to contribute to ambient particle loadings, and these include:

- Marine aerosol (sea salt);
- Secondary particulate matter resulting from atmospheric gas-to-particle conversion processes – includes sulphates, nitrates and organic species;

Another category of emission sources that may contribute are those considered to be 'one-off' emission source such as fireworks displays and other special events (e.g. Guy Fawkes day).

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

2.5 Receptor modeling

Receptor modeling and apportionment of PM mass by PMF was performed using the EPAPMF version 5.0.14 program in accordance with the User's Guide (USEPA, 2015). 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 point are used as point-by-point weights. This is a distinct advantage of PMF, since it can accommodate missing or below detection limit data that is a common feature of environmental monitoring (Song, Polissar et al. 2001). Another advantage of PMF is that PM mass concentrations can be included in the model as another variable and the results are directly interpretable as the covariant PM mass contributions associated with each factor (source). Prior to the PMF analyses, data and uncertainty matrices were prepared in the same manner as previous studies ((Polissar, Hopke et al. 1998, Song, Polissar et al. 2001). Data screening and the source apportionment were performed in accordance to the protocols and recommendations set out by (Paatero, Eberly et al. 2014, Brown, Eberly et al. 2015). Due to the effect that random analytical noise can have on the receptor modeling process, variables with low signal-to-noise ratios were examined by alternate inclusion and exclusion in a modelling run and only those variables that could be explained in association with source emissions were included in the final results (Paatero and Hopke 2003).

2.6 Data analysis and reporting

The data have been analysed to provide the following outputs:

- masses of elemental species apportioned to each source;
- source elemental profiles;
- average PM₁₀ and PM_{2.5}, mass apportioned to each source;
- temporal variations in source mass contributions (time series plots);
- analysis of source contributions to particulate matter concentrations on peak PM_{2.5} and PM₁₀ days.

The data analysis was conducted using version 4.0.2 of the R statistical software (Team 2011) and version 2.7-4 of the 'openair' package (Carlsaw and Ropkins 2012).

3.0 RESULTS AND DISCUSSION

3.1 Elemental concentrations in PM_{2.5} and PM_{10-2.5}

Elemental concentrations for PM_{10-2.5} and PM_{2.5} at Lyttelton are presented in Table 3.1 and Table 3.2 respectively. The data indicate that some measured species were close to or below the limits of detection (LOD) in each of the samples. Important elemental constituents of PM_{2.5} elemental mass concentrations included BC, Na, Si, S, Cl and Ca. Coarse BC with Na, Mg, Al Si, S, Cl, Ca and K were primary constituents of PM_{10-2.5}. This would indicate that combustion sources, marine aerosol, soil and secondary sulphate particles were important contributors to PM_{10-2.5} and PM_{2.5} at the monitoring site. An elemental correlation plot for PM_{10-2.5} and PM_{2.5} composition is provided as Figure A2.1 in Appendix 2.

Table 3.1 Elemental concentrations in PM_{2.5} collected at Lyttelton (337 samples).

	Units	Average	Maximum	Minimum	Median	Std.Dev	Avg. Uncert.	Avg. LOD	#>LOD
BC	ng m ⁻³	287	1669	0	224	271	88	175	233
Na	ng m ⁻³	68	386	0	51	72	83	292	18
Mg	ng m ⁻³	13	98	0	10	14	12	27	65
Al	ng m ⁻³	10	86	0	7	12	6	14	114
Si	ng m ⁻³	42	620	0	25	58	4	10	258
P	ng m ⁻³	0	12	0	0	1	7	8	2
S	ng m ⁻³	84	460	0	71	65	4	7	318
Cl	ng m ⁻³	185	1591	0	74	283	7	6	270
K	ng m ⁻³	14	142	0	10	16	3	6	241
Ca	ng m ⁻³	15	113	0	2	23	4	6	149
Sc	ng m ⁻³	1	22	0	0	3	4	7	24
Ti	ng m ⁻³	5	55	0	3	9	3	6	109
V	ng m ⁻³	1	16	0	0	2	4	6	32
Cr	ng m ⁻³	2	21	0	1	3	3	6	66
Mn	ng m ⁻³	1	19	0	0	2	5	7	11
Fe	ng m ⁻³	6	68	0	4	9	3	6	157
Co	ng m ⁻³	1	22	0	0	3	7	10	14
Ni	ng m ⁻³	2	27	0	0	4	7	11	25
Cu	ng m ⁻³	4	38	0	1	7	9	14	42
Zn	ng m ⁻³	9	80	0	6	11	8	15	103
Ga	ng m ⁻³	3	56	0	0	7	17	24	10
Ge	ng m ⁻³	5	52	0	0	9	25	32	19
As	ng m ⁻³	2	65	0	0	6	31	41	4
Se	ng m ⁻³	7	92	0	0	14	33	49	18
Br	ng m ⁻³	10	196	0	0	22	45	61	23
Rb	ng m ⁻³	12	356	0	0	33	67	96	15
Sr	ng m ⁻³	18	377	0	0	41	89	123	22
Mo	ng m ⁻³	67	925	0	0	123	212	298	36
I	ng m ⁻³	6	138	0	0	13	16	23	45
Ba	ng m ⁻³	3	43	0	0	7	16	24	12
Hg	ng m ⁻³	6	138	0	0	13	65	23	45
Pb	ng m ⁻³	3	43	0	0	7	84	24	12

Table 3.2 Elemental concentrations in PM_{10-2.5} collected at Lyttelton (337 samples).

	Units	Average	Maximum	Minimum	Median	Std.Dev	Avg. Uncert.	Avg. LOD	#>LOD
BC	ng m ⁻³	154	471	0	148	87	51	175	178
Na	ng m ⁻³	866	5364	0	664	790	11	292	283
Mg	ng m ⁻³	86	473	0	69	71	23	29	310
Al	ng m ⁻³	67	263	0	54	55	21	12	301
Si	ng m ⁻³	176	757	0	133	154	6	7	325
P	ng m ⁻³	0	0	0	0	0	33	6	1
S	ng m ⁻³	116	584	0	98	88	6	7	333
Cl	ng m ⁻³	1463	7191	0	1107	1300	2	3	337
K	ng m ⁻³	67	237	0	61	40	8	4	335
Ca	ng m ⁻³	101	612	0	88	70	5	4	336
Sc	ng m ⁻³	3	25	0	2	4	114	6	74
Ti	ng m ⁻³	4	37	0	2	5	69	6	131
V	ng m ⁻³	0	11	0	0	1	94	9	2
Cr	ng m ⁻³	1	17	0	0	1	77	8	15
Mn	ng m ⁻³	0	10	0	0	1	101	7	9
Fe	ng m ⁻³	46	178	0	35	38	15	5	308
Co	ng m ⁻³	0	18	0	0	1	79	10	4
Ni	ng m ⁻³	1	31	0	0	3	68	9	14
Cu	ng m ⁻³	2	26	0	0	3	87	11	17
Zn	ng m ⁻³	8	66	0	6	10	64	11	122
Ga	ng m ⁻³	2	59	0	0	5	61	18	12
Ge	ng m ⁻³	2	43	0	0	5	60	23	13
As	ng m ⁻³	2	71	0	0	7	52	30	9
Se	ng m ⁻³	5	61	0	0	10	52	35	23
Br	ng m ⁻³	3	59	0	0	8	68	43	11
Rb	ng m ⁻³	4	145	0	0	13	46	66	7
Sr	ng m ⁻³	10	225	0	0	25	52	80	15
Mo	ng m ⁻³	24	829	0	0	67	37	199	19
I	ng m ⁻³	8	108	0	0	13	13	22	66
Ba	ng m ⁻³	7	97	0	1	13	15	24	23
Hg	ng m ⁻³	8	108	0	0	13	104	22	66
Pb	ng m ⁻³	7	97	0	1	13	153	24	23

3.2 Receptor modeling analyses of particulate matter

3.2.1 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 (and the PM mass) attributed to that source. In this study the primary source contributors were determined using results from the PMF analysis of the particulate matter elemental composition. Model parameters, inputs and diagnostics are provided in Appendix 3.

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. The “best” solution (i.e., number of factors etc.) is generally determined by the practitioner after taking

into account the model diagnostics, the conceptual receptor model (see Section 2.4) 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:

- compositions of source emissions are constant over the period of ambient and source sampling;
- chemical species do not react with each other (i.e., they add linearly);
- all sources with a potential for contributing to the receptor have been identified and have had their emissions characterized;
- the number of sources or source categories is less than or equal to the number of species measured;
- the source profiles are linearly independent of each other; and
- 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, these are (Hopke 2003):

1. the model must explain the observations;
2. the predicted source compositions must be non-negative;
3. the predicted source contributions must be non-negative;
4. 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 since a receptor model is still an approximation of the real-world system. A number of factors also affect the nature of a sources' 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;
 - a. adsorption of other species onto particle surfaces;
 - b. gas to particle conversions forming secondary particulate matter, for example the conversion of SO_2 gas to SO_4^{2-} ;
 - c. volatilisation of particle components such as organic compounds or volatilisation of Cl through reaction with acidic species;

- d. 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 do not analyse for nitrate or organic matter so the missing mass that the analysis is not explaining is likely a combination of nitrate and organic matter. 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 its 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.

3.3 Source contributions to PM_{2.5} and PM₁₀ at the Lyttelton site

A source is identified by the specific grouping and relative concentration of elements in each fingerprint, by reference to known source compositions along with the analysis of temporal variations and variations by wind speed and direction. These data have been used to identify the likely origin of each source identified as presented in the following sections.

The **six** sources contributing to fine and coarse particulate matter identified were:

- The first factor was identified as a “**motor vehicles**” profile because of the significant contributions of BC, Zn, Mn, Ca and Fe to this source along with crustal matter components (Al, Si) representing tailpipe emissions co-mingled with road dust (Lough, Schauer et al. 2005, Cheung, Ntziachristos et al. 2010). Similar profiles have been separated for Auckland motor vehicle sources as part of a multi-year, multi-site receptor modelling study (Davy, Ancelet et al. 2014).
- The second factor was identified as “**soil**” and contains coarse particle Al, Si, S, K, Ca and Fe as primary species typical of a crustal matter component.
- The third factor labelled “**cement**” included Ca as a primary component typical of cement dusts (ordinary Portland cement is approximately 60 % CaO). Similar source profiles have been associated with activities involving the transfer of bulk cement powders (e.g. concrete batching plants).
- The fourth factor was identified as “**ship emissions**” source contribution is due to primary ship engine emissions with characteristic black carbon, sulphur, vanadium and nickel content reflective of the composition heavy fuel oils and their combustion products.
- The fifth factor was identified as a ‘**marine aerosol**’ (sea salt) source due to the predominance of Na and Cl in the profile.
- The sixth factor has been identified as a ‘**coal dust**’ source and contains a substantial proportion of black carbon along with crustal elements. Interestingly there appears to be a significant inclusion of coarse sea salt in the profile which may be covariant with coal dust by the windier conditions that are likely to give rise to airborne particles from bulk coal storage.

Figure 3.1 presents the source chemical profiles extracted from the PMF analyses of fine and coarse particulate matter. The graph shows the concentration (logarithmic scale) of species attributed to each source, while the red square represents the percentage of that species across all the source chemical profiles.

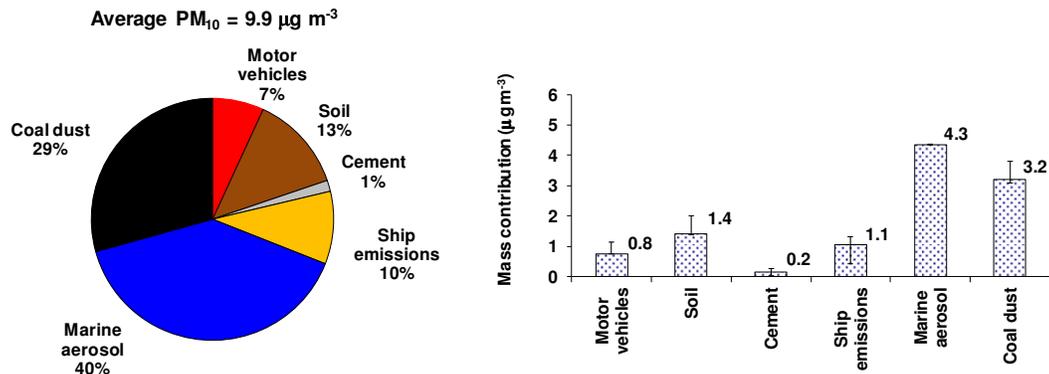


Figure 3.3 Average source contributions to PM_{10} at the Lyttelton monitoring site

Average $PM_{2.5}$ source contributions estimated by PMF indicate that marine aerosol and ship emissions were the largest contributors to $PM_{2.5}$ mass (33% and 32% respectively) with lesser contributions from motor vehicles (14%).

Marine aerosol was found to be the primary contributor to PM_{10} concentrations (40%), with coal dust (29%) as the second highest. Soil (13%), ship emissions (10%), motor vehicles (7%) and cement (1%) were the other contributing sources to PM_{10} mass.

3.3.2 Temporal variations in source contributions

Temporal variations in $PM_{2.5}$ and PM_{10} source contributions during the monitoring period are presented in Figures 3.4 and 3.5 respectively. Note that the gaps in the time-series are due to missed sample periods. In both the PM_{10} and $PM_{2.5}$ samples it is evident that peak particulate matter concentrations were generally dominated by the marine aerosol (sea salt) source during the monitoring period.

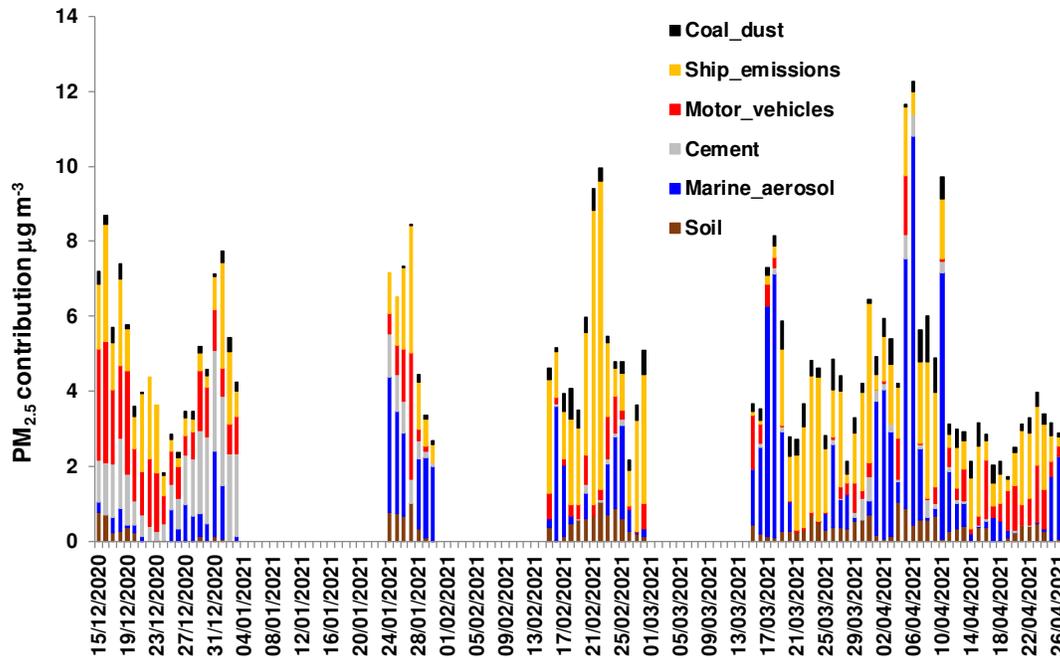


Figure 3.4 Temporal variations in source contributions to PM_{2.5} mass at Lyttelton

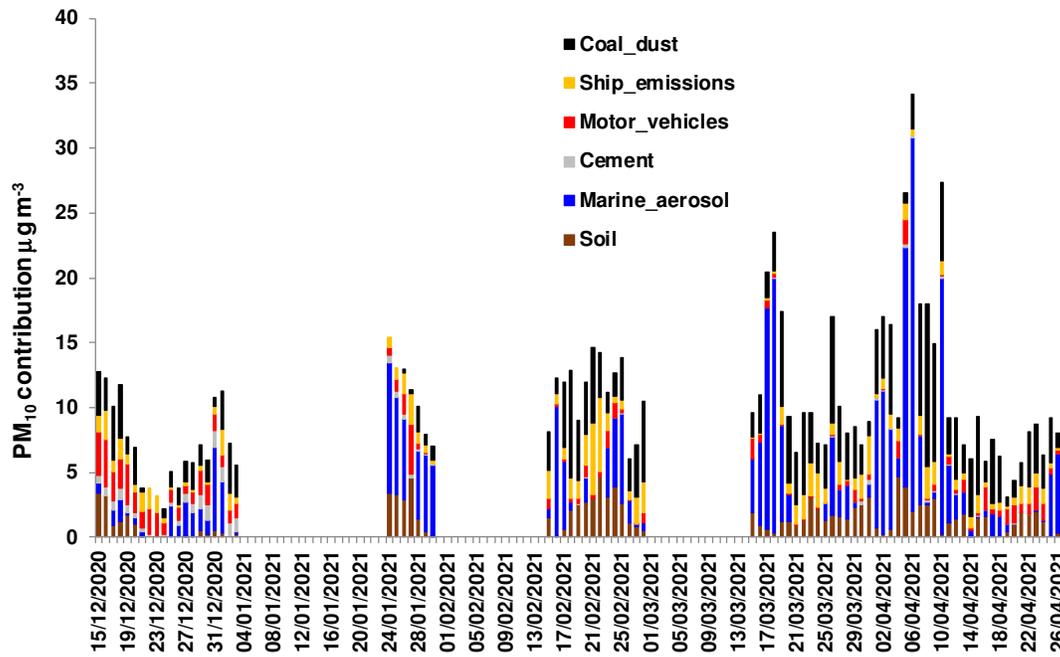


Figure 3.5 Temporal variations in source contributions to PM₁₀ mass at Lyttelton

4.0 SUMMARY OF THE LYTTELTON RECEPTOR MODELING RESULTS

Monitoring and compositional analysis of air particulate matter at Lyttelton showed that peak concentrations during the monitoring period occurred during higher wind speeds. Six source contributors to PM concentrations were identified from receptor modeling. The receptor modeling analysis showed that some source contributors had distinct periods or episodes of higher concentrations and that peak PM₁₀ concentrations were primarily influenced by marine aerosol.

4.1 Sources of Particulate Matter at the Lyttelton monitoring site

4.1.1 Motor vehicles

The motor vehicle source was identified as a minor contributor to both PM_{2.5} (14%) and PM₁₀ (7%). 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 soil generated by the turbulent passage of vehicles on local roads. For motor vehicle source contributions, peak concentrations are usually related to the direction of the busiest local road.

4.1.2 Soil

The soil source was likely to be the result of wind-blown crustal matter over the summer period.

4.1.3 Cement

The high calcium elemental content was used to identify the cement source and was found present as a minor and intermittent component of particulate matter collected at the monitoring site. The source was likely to originate during the bulk handling and transfer of cement cargoes.

4.1.4 Ship emissions

Emissions of combustion products from ships engines can impact on local air quality in port areas, regional air quality and global climate (Huebert 1999, Endresen, Sørgård et al. 2003, Ault, Moore et al. 2009, Eyring, Isaksen et al. 2010, Hellebust, Allanic et al. 2010, Matthias, Bewersdorff et al. 2010). Species emitted to atmosphere from ships engines include usual combustion products (CO_x, NO_x), gaseous sulphur oxides (SO_x) that relate to fuel composition, volatile organic compounds (VOCs) from incomplete fuel combustion and particulate matter which includes trace heavy metals (e.g. vanadium and nickel) (Agrawal, Malloy et al. 2008, Agrawal, Welch et al. 2008, Fridell, Steen et al. 2008, Healy, O'Connor et al. 2009). The receptor modelling analysis for the Lyttelton site has shown that the source contains sulphur along with BC, V and Ni as specific markers for particles emitted directly from the ship engine combustion processes (primary particulate matter emissions) (Fridell, Steen et al. 2008, Furuyama, Fujita et al. 2011). Due to the high sulphur content of ship engine fuels, acid gases and acid liquid droplet aerosol are also known to be associated with primary particle emissions from ships (Agrawal, Malloy et al. 2008, Lack, Corbett et al. 2009).

4.1.5 Marine Aerosol

Marine aerosol was found to be a significant contributor to both PM_{2.5} and PM₁₀ at Lyttelton and is generally a significant particle source in New Zealand airsheds. A receptor modelling study conducted in Christchurch during 2013-2015 found that marine aerosol contributed 1.7 µg m⁻³ to PM_{2.5} and 6-7 µg m⁻³ to PM₁₀ which was not dissimilar to that found in this study (Davy, Ancelet et al. 2016). The elemental composition for the marine aerosol source closely

resembled that of seawater and the source profile is dominated by chlorine and sodium. Analysis of temporal and seasonal variations in marine aerosol has shown higher concentrations during spring and summer (Davy and Trompetter 2018), but marine aerosol concentrations can also peak at other times since the generation of marine aerosol is dependent on meteorological factors, such as wind speeds across an oceanic fetch and evaporation potential.

4.1.6 Coal dust

The coal dust was largely a coarse particle ($PM_{10-2.5}$) source that occurred intermittently throughout the monitoring campaign. The chemical composition profile contained black carbon, sulphur and crustal matter species typical of the trace elements found in coal. Highest concentrations as measured at the monitoring site would be associated with winds blowing from the direction of the bulk storage and cargo transfer areas.

5.0 REFERENCES

- Agrawal, H., Q. G. J. Malloy, W. A. Welch, J. Wayne Miller and D. R. Cocker Iii (2008). "In-use gaseous and particulate matter emissions from a modern ocean going container vessel." Atmospheric Environment **42**(21): 5504-5510.
- Agrawal, H., W. A. Welch, J. W. Miller and D. R. Cocker (2008). "Emission measurements from a crude oil tanker at sea." Environmental Science and Technology **42**(19): 7098-7103.
- Ancelet, T., P. K. Davy, T. Mitchell, W. J. Trompetter, A. Markwitz and D. C. Weatherburn (2012). "Identification of particulate matter sources on an hourly time-scale in a wood burning community." Environmental Science and Technology **46**(9): 4767-4774.
- Ancelet, T., P. K. Davy and W. J. Trompetter (2015). "Particulate matter sources and long-term trends in a small New Zealand city." Atmospheric Pollution Research **6**(6): 1105-1112.
- Ancelet, T., P. K. Davy, W. J. Trompetter, A. Markwitz and D. C. Weatherburn (2011). "Carbonaceous aerosols in an urban tunnel." Atmospheric Environment **45**(26): 4463-4469.
- Ancelet, T., P. K. Davy, W. J. Trompetter, A. Markwitz and D. C. Weatherburn (2014). "Particulate matter sources on an hourly timescale in a rural community during the winter." Journal of the Air and Waste Management Association **64**(5): 501-508.
- Ancelet, T., P. K. Davy, W. J. Trompetter, A. Markwitz and D. C. Weatherburn (2014). "Sources and transport of particulate matter on an hourly time-scale during the winter in a New Zealand urban valley." Urban Climate.
- Ault, A. P., M. J. Moore, H. Furutani and K. A. Prather (2009). "Impact of emissions from the Los Angeles Port region on San Diego air quality during regional transport events." Environmental Science and Technology **43**(10): 3500-3506.
- Barry, B., W. J. Trompetter, P. K. Davy and A. Markwitz (2012). "Recent developments in the air particulate research capability at the New Zealand Ion Beam Analysis Facility." International Journal of PIXE **22**: 121-130.
- Begum, B. A., P. K. Hopke and W. X. Zhao (2005). "Source identification of fine particles in Washington, DC, by expanded factor analysis modeling." Environ. Sci. Technol. **39**(4): 1129-1137.
- Brimblecombe, P. (1986). Air: Composition and Chemistry.
- Brown, S. G., S. Eberly, P. Paatero and G. A. Norris (2015). "Methods for estimating uncertainty in PMF solutions: Examples with ambient air and water quality data and guidance on reporting PMF results." Science of the Total Environment **518-519**: 626-635.
- Brown, S. G. and H. R. Hafner (2005). Multivariate Receptor Modelling Workbook. Research Triangle Park, NC, USEPA.
- Cahill, T. A., R. A. Eldred, N. Motallebi and W. C. Malm (1989). "Indirect measurement of hydrocarbon aerosols across the United States by nonsulfate hydrogen-remaining gravimetric mass correlations." Aerosol Sci. Technol. **10**(2): 421-429.
- Carslaw, D. C. (2012). The openair manual - open-source tools for analysing air pollution data. Manual for version 0.7-0, King's College London.
- Carslaw, D. C. and K. Ropkins (2012). "openair - an R package for air quality data analysis." Environmental Modelling & Software **27-28**: 52-61.

Cheung, K. L., L. Ntziachristos, T. Tzamkiozis, J. J. Schauer, Z. Samaras, K. F. Moore and C. Sioutas (2010). "Emissions of particulate trace elements, metals and organic species from gasoline, diesel, and biodiesel passenger vehicles and their relation to oxidative potential." Aerosol Science and Technology **44**(7): 500-513.

Chueinta, W., P. K. Hopke and P. Paatero (2000). "Investigation of sources of atmospheric aerosol at urban and suburban residential areas in Thailand by positive matrix factorization." Atmos. Environ. **34**(20): 3319-3329.

Cohen, D., G. Taha, E. Stelcer, D. Garton and G. Box (2000). The measurement and sources of fine particle elemental carbon at several key sites in NSW over the past eight years. 15th Clean Air Conference, Sydney, Clean air Society of Australia and New Zealand.

Cohen, D. D. (1999). "Accelerator based ion beam techniques for trace element aerosol analysis." Advances in Environmental, Industrial and Process Control Technologies **1**(Elemental Analysis of Airborne Particles): 139-196.

Davy, P., K., T. Ancelet, W. Trompetter and A. Markwitz (2014). Source apportionment and trend analysis of air particulate matter in the Auckland Region, GNS Science Consultancy Report 2014/194.

Davy, P., K., T. Ancelet and W. J. Trompetter (2016). Source apportionment of PM_{2.5} and PM_{10-2.5} samples from St Albans, Christchurch, GNS Science Consultancy Report 2016/72.

Davy, P., K. and W. J. Trompetter (2017). Apportionment of PM_{2.5} and PM₁₀ sources in the Richmond airshed, Tasman District. GNS Science Consultancy Report 2017/86

Institute of Geological and Nuclear Sciences: 69 p.

Davy, P., K. and W. J. Trompetter (2017). Apportionment of PM₁₀ sources in the Tokoroa airshed, Waikato Region. GNS Science Consultancy Report 2017/75, Institute of Geological and Nuclear Sciences: 75 p.

Davy, P. K., T. Ancelet, W. J. Trompetter and A. Markwitz (2017). Source apportionment and trend analysis of air particulate matter in the Auckland region. GNS Science consultancy report 2014/194, Institute of Geological and Nuclear Sciences: 245 p.

Davy, P. K., G. Gunchin, A. Markwitz, W. J. Trompetter, B. J. Barry, D. Shagjjamba and S. Lodoysamba (2011). "Air particulate matter pollution in Ulaanbaatar, Mongolia: Determination of composition, source contributions and source locations." Atmospheric Pollution Research **2**(2): 126-137.

Eberly, S. (2005). EPA PMF 1.1 User's Guide, USEPA.

Endresen, Ø., E. Sørsgård, J. K. Sundet, S. B. Dalsøren, I. S. A. Isaksen, T. F. Berglen and G. Gravir (2003). "Emission from international sea transportation and environmental impact." Journal of Geophysical Research D: Atmospheres **108**(17): ACH 14-11 ACH 14-22.

Eyring, V., I. S. A. Isaksen, T. Berntsen, W. J. Collins, J. J. Corbett, O. Endresen, R. G. Grainger, J. Moldanova, H. Schlager and D. S. Stevenson (2010). "Transport impacts on atmosphere and climate: Shipping." Atmospheric Environment **44**(37): 4735-4771.

Fine, P. M., G. R. Cass and B. R. Simoneit (2001). "Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States." Environ. Sci. Technol. **35**(13): 2665-2675.

Fridell, E., E. Steen and K. Peterson (2008). "Primary particles in ship emissions." Atmospheric Environment **42**(5): 1160-1168.

- Furuyama, Y., H. Fujita, A. Taniike and A. Kitamura (2011). "Ion beam analyses of particulate matter in exhaust gas of a ship diesel engine." Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms.
- Healy, R. M., I. P. O'Connor, S. Hellebust, A. Allanic, J. R. Sodeau and J. C. Wenger (2009). "Characterisation of single particles from in-port ship emissions." Atmospheric Environment **43**(40): 6408-6414.
- Hellebust, S., A. Allanic, I. P. O'Connor, C. Jourdan, D. Healy and J. R. Sodeau (2010). "Sources of ambient concentrations and chemical composition of PM_{2.5-0.1} in Cork Harbour, Ireland." Atmospheric Research **95**(2-3): 136-149.
- Hopke, P., K. (1999). Quality assurance, quality control and data validation in environmental analysis of airborne particles. Elemental analysis of airborne particles. S. Landsberger and M. Creatchman. Amsterdam, Gordon and Breach Science Publishers. **1**: 235-254.
- Hopke, P. K. (1999). "An introduction to source receptor modeling." Adv. Environ. Indust. Process Control Technol. **1**(Elemental Analysis of Airborne Particles): 273-315.
- Hopke, P. K. (2003). "The evolution of chemometrics." Anal. Chim. Acta **500**(1-2): 365-377.
- Hopke, P. K., Y. L. Xie and P. Paatero (1999). "Mixed multiway analysis of airborne particle composition data." J. Chemomet. **13**(3-4): 343-352.
- Horvath, H. (1993). "Atmospheric Light Absorption - A Review." Atmos. Environ. **27A**: 293-317.
- Horvath, H. (1997). "Experimental calibration for aerosol light absorption measurements using the integrating plate method - Summary of the data." Aerosol Science **28**: 2885-2887.
- Huebert, B. J. (1999). "Sulphur emissions from ships." Nature **400**(6746): 713-714.
- Jacobson, M. C., H. C. Hansson, K. J. Noone and R. J. Charlson (2000). "Organic atmospheric aerosols: review and state of the science." Reviews of Geophysics **38**(2): 267-294.
- Jeong, C.-H., P. K. Hopke, E. Kim and D.-W. Lee (2004). "The comparison between thermal-optical transmittance elemental carbon and Aethalometer black carbon measured at multiple monitoring sites." Atmos. Environ. **38**(31): 5193.
- Kara, M., P. K. Hopke, Y. Dumanoglu, H. Altioek, T. Elbir, M. Odabasi and A. Bayram (2015). "Characterization of PM Using Multiple Site Data in a Heavily Industrialized Region of Turkey." Aerosol and Air Quality Research **15**(1): 11-+.
- Kim, E., P. K. Hopke and E. S. Edgerton (2003). "Source identification of Atlanta aerosol by positive matrix factorization." J. Air Waste Manage. Assoc. **53**(6): 731-739.
- Kim, E., P. K. Hopke, T. V. Larson, N. N. Maykut and J. Lewtas (2004). "Factor analysis of Seattle fine particles." Aerosol Sci. Technol. **38**(7): 724-738.
- Lack, D. A., J. J. Corbett, T. Onasch, B. Lerner, P. Massoli, P. K. Quinn, T. S. Bates, D. S. Covert, D. Coffman, B. Sierau, S. Herndon, J. Allan, T. Baynard, E. Lovejoy, A. R. Ravishankara and E. Williams (2009). "Particulate emissions from commercial shipping: Chemical, physical, and optical properties." Journal of Geophysical Research D: Atmospheres **114**(4).
- Lee, E., C. K. Chan and P. Paatero (1999). "Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong." Atmos. Environ. **33**(19): 3201-3212.

- Lee, J. H., Y. Yoshida, B. J. Turpin, P. K. Hopke, R. L. Poirot, P. J. Liroy and J. C. Oxley (2002). "Identification of sources contributing to Mid-Atlantic regional aerosol." J. Air Waste Manag. Assoc. **52**(10): 1186-1205.
- Li, J., G. Michalski, P. Davy, M. Harvey, T. Katzman and B. Wilkins (2018). "Investigating Source Contributions of Size-Aggregated Aerosols Collected in Southern Ocean and Baring Head, New Zealand Using Sulfur Isotopes." Geophysical Research Letters **45**(8): 3717-3727.
- Lough, G. C., J. J. Schauer, J. S. Park, M. M. Shafer, J. T. Deminter and J. P. Weinstein (2005). "Emissions of metals associated with motor vehicle roadways." Environmental Science and Technology **39**(3): 826-836.
- Malm, W. C., J. F. Sisler, D. Huffman, R. A. Eldred and T. A. Cahill (1994). "Spatial and seasonal trends in particle concentration and optical extinction in the United States." J. Geophys. Res. Atmos. **99**(D1): 1347-1370.
- Matthias, V., I. Bewersdorff, A. Aulinger and M. Quante (2010). "The contribution of ship emissions to air pollution in the North Sea regions." Environmental Pollution **158**(6): 2241-2250.
- Maxwell, J. A., W. J. Teesdale and J. L. Cambell (1995). "The Guelph PIXE software package II." Nucl. Instr. And Meth. B **95**: 407.
- Norris, G., R. Duvall, S. Brown and S. Bai (2014). EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide. USEPA.
- Paatero, P. (1997). "Least squares formulation of robust non-negative factor analysis." Chemom. Intell. Lab. Syst. **18**: 183-194.
- Paatero, P. (2000). PMF User's Guide. Helsinki, University of Helsinki.
- Paatero, P., S. Eberly, S. G. Brown and G. A. Norris (2014). "Methods for estimating uncertainty in factor analytic solutions." Atmos. Meas. Tech. **7**(3): 781-797.
- Paatero, P. and P. K. Hopke (2002). "Utilizing wind direction and wind speed as independent variables in multilinear receptor modeling studies." Chemometrics and Intelligent Laboratory Systems **60**(1-2): 25-41.
- Paatero, P. and P. K. Hopke (2003). "Discarding or downweighting high-noise variables in factor analytic models." Analytica Chimica Acta **490**(1-2): 277-289.
- Paatero, P., P. K. Hopke, B. A. Begum and S. K. Biswas (2005). "A graphical diagnostic method for assessing the rotation in factor analytical models of atmospheric pollution." Atmospheric Environment **39**(1): 193-201.
- Paatero, P., P. K. Hopke, X. H. Song and Z. Ramadan (2002). "Understanding and controlling rotations in factor analytic models." Chemometrics and Intelligent Laboratory Systems **60**(1-2): 253-264.
- Polissar, A. V., P. K. Hopke, W. C. Malm and J. F. Sisler (1998). "Atmospheric aerosol over Alaska 1. Spatial and seasonal variability." J. Geophys. Res. Atmos. **103**(D15): 19035-19044.
- Polissar, A. V., P. K. Hopke, P. Paatero, W. C. Malm and J. F. Sisler (1998). "Atmospheric aerosol over Alaska 2. Elemental composition and sources." J. Geophys. Res. Atmos. **103**(D15): 19045-19057.
- Prati, P., A. Zucchiatti, S. Tonus, F. Lucarelli, P. A. Mandò and V. Ariola (1998). "A testing technique of streaker aerosol samplers via PIXE analysis." Nuclear Instruments and Methods

in Physics Research, Section B: Beam Interactions with Materials and Atoms **136-138**: 986-989.

Ramadan, Z., B. Eickhout, X.-H. Song, L. M. C. Buydens and P. K. Hopke (2003). "Comparison of Positive Matrix Factorization and Multilinear Engine for the source apportionment of particulate pollutants." Chemomet. Intellig. Lab. Syst. **66**(1): 15-28.

Salma, I., X. Chi and W. Maenhaut (2004). "Elemental and organic carbon in urban canyon and background environments in Budapest, Hungary." Atmos. Environ. **38**(1): 27-36.

Seinfeld, J. H. and S. N. Pandis (2006). Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. New York, John Wiley & Sons, Inc.

Song, X. H., A. V. Polissar and P. K. Hopke (2001). "Sources of fine particle composition in the northeastern US." Atmospheric Environment **35**(31): 5277-5286.

Team, R. D. C. (2011). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria.

Trompetter, W., A. Markwitz and P. Davy, K. (2005). "Air particulate research capability at the New Zealand Ion Beam Analysis Facility using PIXE and IBA Techniques." International Journal of PIXE **15**(3&4): 249-255.

Trompetter, W. J. (2004). Ion Beam Analysis results of air particulate filters from the Wellington Regional Council. Wellington, Geological and Nuclear Sciences Limited.

Watson, J. G., T. Zhu, J. C. Chow, J. Engelbrecht, E. M. Fujita and W. E. Wilson (2002). "Receptor modeling application framework for particle source apportionment." Chemosphere **49**(9): 1093-1136.

Zhou, S., P. K. Davy, M. Huang, J. Duan, X. Wang, Q. Fan, M. Chang, Y. Liu, W. Chen, S. Xie, T. Ancelet and W. J. Trompetter (2018). "High-resolution sampling and analysis of ambient particulate matter in the Pearl River Delta region of southern China: Source apportionment and health risk implications." Atmospheric Chemistry and Physics **18**(3): 2049-2064.

Zhou, S., P. K. Davy, X. Wang, J. B. Cohen, J. Liang, M. Huang, Q. Fan, W. Chen, M. Chang, T. Ancelet and W. J. Trompetter (2016). "High time-resolved elemental components in fine and coarse particles in the Pearl River Delta region of Southern China: Dynamic variations and effects of meteorology." Science of the Total Environment **572**: 634-648.

This page left intentionally blank.

APPENDICES

APPENDIX 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 Lyttelton 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 A1.1 shows the PM analysis chamber with its associated X-ray, γ -ray and particle detectors for Proton-Induced X-ray Emission (PIXE), Proton-Induced Gamma-ray Emission (PIGE), Proton Elastic Scattering Analysis (PESA) and Rutherford Back Scattering (RBS) measurements.

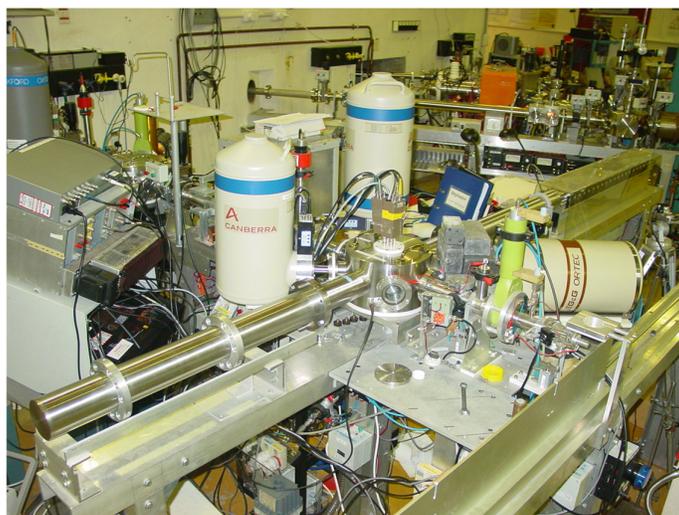


Figure A1.1 Particulate matter analysis chamber with its associated detectors.

The following sections provide a generalised overview of the IBA techniques used for elemental analysis and the analytical setup at GNS Science (Cohen 1998, Cohen et al. 1996, Trompetter 2004, Trompetter and Davy 2005). Figure A1.2 presents a schematic diagram of the typical experimental setup for IBA of air particulate filters at GNS Science.

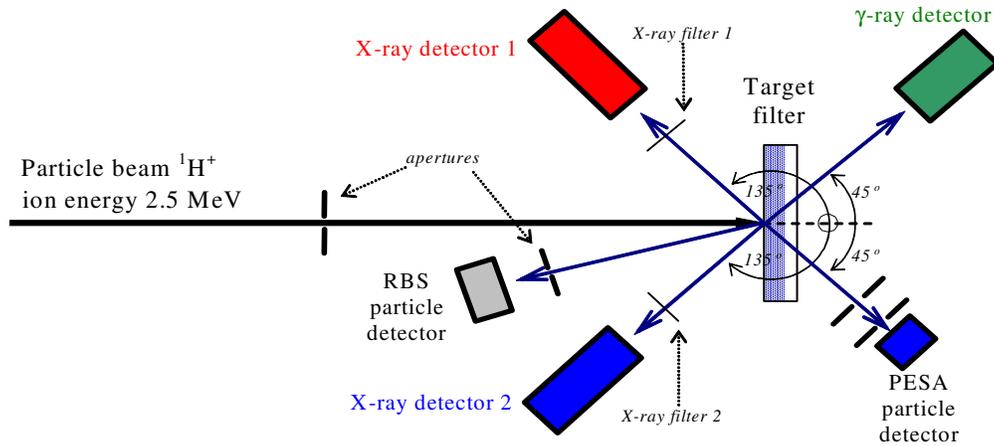


Figure A1.2 Schematic of the typical IBA experimental setup at GNS Science.

A1.1.1 Particle-Induced X-Ray Emission

Particle induced X-ray emission (PIXE), is used to determine elemental concentrations heavier than neon by exposing the filter samples to a proton beam accelerated to 2.5 million volts (MeV) by the GNS 3 MeV van-de-Graaff accelerator. When high energy protons interact with atoms in the sample, characteristic X-rays (from each element) are emitted by ion-electron processes. These X-rays are recorded in an energy spectrum. While all elements heavier than boron emit K X-rays, their production become too few to satisfactorily measure elements heavier than strontium. Elements heavier than strontium are detected via their lower energy L X-rays. The X-rays are detected using a Si(Li) detector and the pulses from the detector are amplified and recorded in a pulse height analyser. In practice, sensitivities are further improved for the lighter elements by using two X-ray detectors, one for light element X-rays and the other for heavier element X-rays, each with different filtering and collimation. Figure A1.3 shows an example of a PIXE spectrum for airborne particles collected on a filter and analysed at the GNS IBA facility.

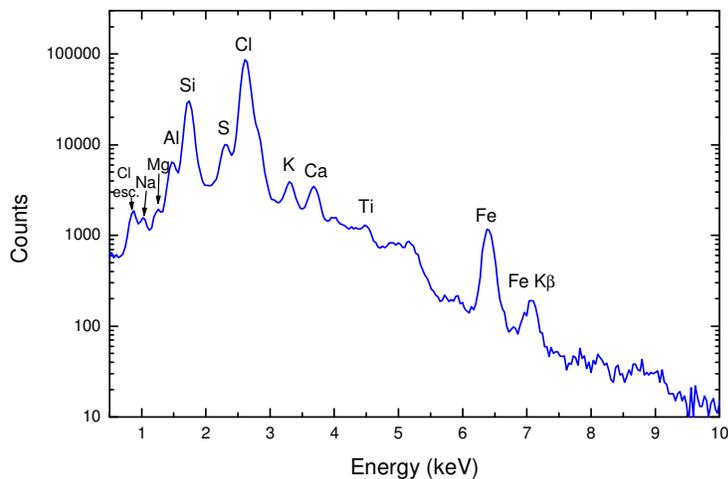


Figure A1.3 Typical PIXE spectrum for an aerosol sample analysed by PIXE.

As the PIXE spectrum consists of many peaks from different elements (and a Bremsstrahlung background), some of them overlapping, the spectrum is analysed with quantitative X-ray analysis software. In the case of this study, Gupix Software was used to perform the deconvolution with high accuracy (Maxwell et al. 1989, Maxwell et al. 1995). The number of

pulses (counts) in each peak for a given element is used by the Gupix software to calculate the concentration of that element. The background and neighbouring elements determine the statistical error and the limit of detection. Note, that Gupix provides a specific statistical error and limit of detection (LOD) for each element in any filter, which is essential for source apportionment studies.

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

A1.1.2 Particle-Induced Gamma-Ray Emission

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

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

Gamma rays are higher in energy than X-rays and are detected with a germanium detector. Measurements of a light element such as sodium can be measured more accurately using PIGE because the γ -rays are not attenuated to the same extent in the filter matrix or the detector material, a problem in the measurement of low energy X-rays of sodium. Figure A1.4 shows a typical PIGE spectrum.

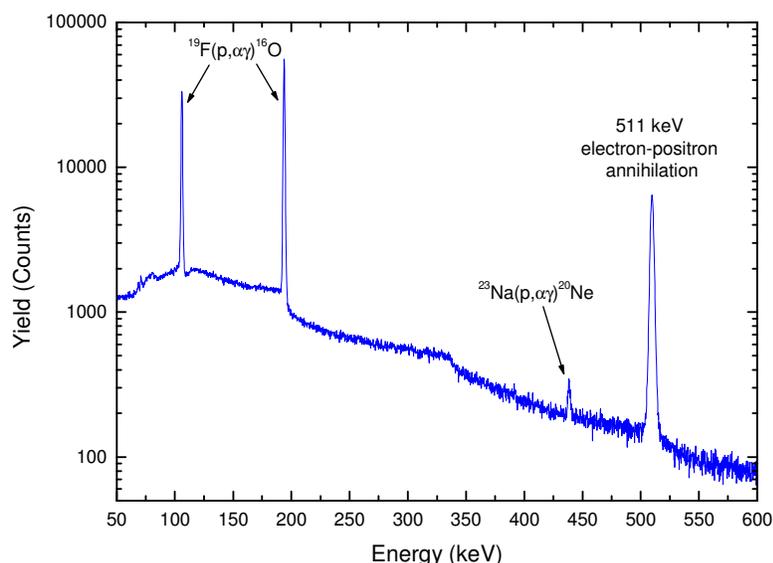


Figure A1.4 Typical PIGE spectrum for an aerosol sample.

A1.2 IBA Data Reporting

Most filters used to collect particulate matter samples for IBA analysis are sufficiently thin that the ion beam penetrates the entire depth producing a quantitative analysis of elements present. Because of the thin nature of the air particulate matter filters, the concentrations

reported from the analyses are therefore in aerial density units (ng cm^{-2}) and the total concentration of each element on the filters is calculated by multiplying with the exposed area of the filter. Typically, the exposed area is approximately 12 cm^2 for the sample deposit on the standard 47mm Teflon or polycarbonate filters used in most studies. For example, to convert from $\text{Cl} (\text{ng cm}^{-2})$ into $\text{Cl} (\text{ng m}^{-3})$ for filter samples, the equation is:

$$\text{Cl} (\text{ng m}^{-3}) = 11.95 (\text{cm}^2) \times \text{Cl} (\text{ng cm}^{-2}) / \text{Vol}(\text{m}^3) \quad \text{Equation 1.1}$$

A1.2.1 Limits of detection and uncertainty reporting for elements

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

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

Also, where an individual elemental concentration is reported as zero (0) means the measurement value (as derived from the spectral deconvolution) was zero but does not necessarily mean the element was not present but below the method limit of detection and indeterminate. Where this is the case then the corresponding uncertainty value (\pm) can be regarded as $5/6 \text{ LOD}$ (Kara et al. 2015):

For IBA, to determine the concentration of each element the background is subtracted, and peak areas fitted and calculated. The background occurs through energy loss, scattering and interactions of the ion beam as it passes through the filter material or from γ -rays produced in the target and scattered in the detector system (Cohen 1999). The peaks of elements in spectra that have interferences or backgrounds from other elements present in the air particulate matter, or filter matrix itself, will have higher limits of detection. The IBA was performed using a 3MeV accelerator proton beam with standards (SrF₂, NaCl, Cr, Ni, SiO₂, KCl, Al) run before and after each analytical cycle. Spectral X-ray peak deconvolution was performed using Gupix software (Maxwell et al. 1989, 1995). The number of pulses (counts) in each peak for a given element is used by the Gupix software to calculate the concentration of that element. The background and neighbouring elements determine the statistical error and the limit of detection. Note that Gupix provides a specific statistical error (uncertainty) and limit of detection (LOD) for each element in each PM sample. The statistical uncertainty is calculated from the X-ray peak fitting process (called the fit error) and is related to the square root of the peak area. The limit of detection for an element in each sample spectra is defined as three times the error (3σ) obtained for the background and overlap (but not the elements own area) in a 1 full-width-half-maximum region centred about the principal X-ray peak of the element. The summary statistics provided for elemental concentrations in each dataset are therefore averages of the individual uncertainty and LOD values.

Choice of filter material is an important consideration with respect to elements of interest as is avoiding sources of contamination. The GNS IBA laboratory routinely runs filter blanks to correct for filter derived analytical artefacts as part of their QA/QC procedures. Figure A1.5 shows the LODs typically achieved by PIXE for each element at the GNS IBA facility. All IBA elemental concentrations determined in this work were accompanied by their respective LODs. The use of elemental LODs is important in receptor modeling applications.

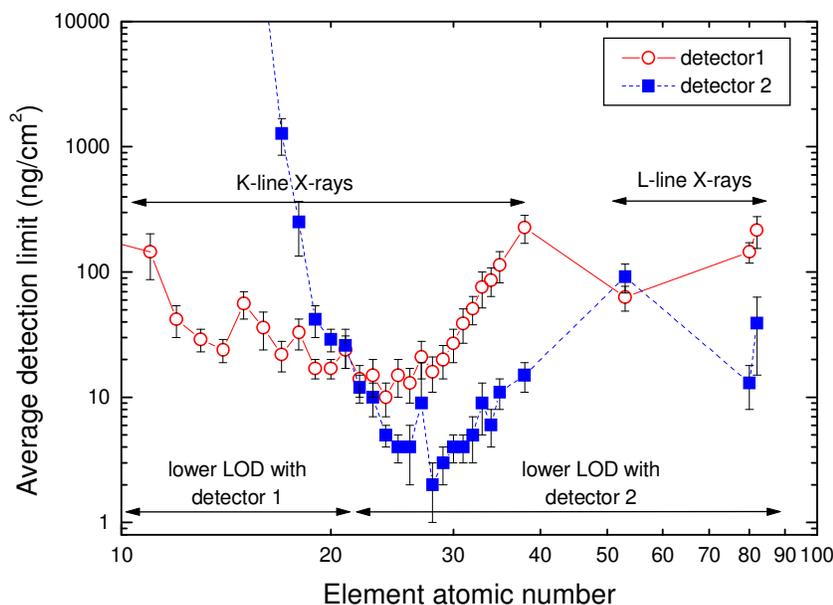


Figure A1.5 Elemental limits of detection for PIXE routinely achieved as the GNS IBA facility for air filters.

A1.3 Black Carbon Measurements

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

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

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

$$BC (\mu\text{g cm}^{-2}) = (100/2(F\epsilon)) \ln[R_0/R] \quad \text{Equation APPENDIX 1.2}$$

where:

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

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

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

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

$$\text{BC } (\mu\text{g cm}^{-2}) = [1000 \times \text{LOG}(R_{\text{blank}}/R_{\text{sample}}) + 2.39] / 45.8 \quad \text{Equation APPENDIX 1.3}$$

where:

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

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

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

A1.4 Positive Matrix Factorization

Positive matrix factorisation (PMF) is a linear least-squares approach to factor analysis and was designed to overcome the receptor modeling problems associated with techniques like principal components analysis (PCA) and the *a priori* knowledge required for chemical mass balance approaches (Paatero, Hopke 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 that is a common feature of environmental monitoring results (Song, Polissar 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 modeling results. For the weakest (closest to detection limit) species, the variance may be entirely from noise (Paatero and Hopke 2002). Paatero and Hopke 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 (Paatero and Hopke 2003). 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).

A1.4.1 PMF model outline

The mathematical basis for PMF is described in detail by Paatero (Paatero 1997, Paatero 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:

$$X = GF + E \quad \text{Equation APPENDIX 1.4}$$

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 :

$$e_{ij} = x_{ij} - y_{ij} = x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}$$

Equation APPENDIX 1.5

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:

$$Q(E) = \sum_{i=1}^n \sum_{j=1}^m (e_{ij} / \sigma_{ij})^2$$

Equation APPENDIX 1.6

where σ_{ij} 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 modeling studies in a number of countries around the world (Hopke, Xie et al. 1999, Lee, Chan et al. 1999, Chueinta, Hopke et al. 2000, Song, Polissar et al. 2001, Lee, Yoshida et al. 2002, Kim, Hopke et al. 2003, Jeong, Hopke et al. 2004, Kim, Hopke et al. 2004, Begum, Hopke et al. 2005) including New Zealand (Davy, Gunchin et al. 2011, Ancelet, Davy et al. 2012, Ancelet, Davy et al. 2014, Ancelet, Davy et al. 2014, Ancelet, Davy et al. 2015, Davy, Ancelet et al. 2016, Davy and Trompeter 2017, Davy and Trompeter 2017, Davy, Ancelet et al. 2017, Li, Michalski et al. 2018, Zhou, Davy et al. 2018).

A1.4.2 PMF model used

Two programs have been written to implement different algorithms for solving the least squares PMF problem, these are PMF2 and EPAPMF, which incorporates the Multilinear Engine (ME-

2) (Hopke, Xie et al. 1999, Ramadan, Eickhout 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 A1.5.2.

A1.4.3 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 APPENDIX 1.7:

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

Equation APPENDIX 1.7

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 “good” signal, though 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, Duvall 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 LOD (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 LOD (low signal to noise ratio); there is doubt about some of the measurements and/or the error estimates; or the elemental species is only detected some of the time. If ‘Weak’ is chosen EPA.PMF 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 3 times above the LOD, a 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 there was a lower level of confidence in their measurement. Mass concentration gravimetric measurements and BC were also down weighted as ‘Weak’ depending on the dataset because their concentrations are generally several orders of magnitude above other species, which can have the tendency to ‘pull’ the model. Paatero and Hopke recommend that such variables be down weighted and that it doesn’t particularly affect the model fitting if those variables are from real sources (Paatero and Hopke 2003). 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 had mostly zero values, or 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) should be approximately equal to the number of data points in the concentration data set (Eberly 2005):

$$\text{Theoretical } Q = \# \text{ samples } \times \# \text{ species measured} \quad \text{Equation APPENDIX 1.8}$$

However, a slightly different approach to calculating the Theoretical Q value was recommended (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:

$$Q_{th} = (\# \text{ samples } \times \# \text{ good species}) + [(\# \text{ samples } \times \# \text{ weak species}) / 3] - (\# \text{ samples } \times \text{ factors estimated}) \quad \text{Equation APPENDIX 1.9}$$

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 and co-workers (Paatero, Eberly et al. 2014, Brown, Eberly 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:

$$\text{The expected value of } Q \text{ is approximately } = (\text{number of non-weak data values in } X) - (\text{numbers of elements in } G \text{ and } F, \text{ taken together}). \quad \text{Equation APPENDIX 1.10}$$

A downweighted 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 ten 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 the 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 the 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, Hopke 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, Eldred et al. 1989, Malm, Sisler et al. 1994, Cohen 1999):

$$\text{Reconstructed mass} = [\text{Soil}] + [\text{OC}] + [\text{BC}] + [\text{Smoke}] + [\text{Sulphate}] + [\text{Seasalt}] \quad \text{Equation APPENDIX 1.11}$$

where:

$$[\text{Soil}] = 2.20[\text{Al}] + 2.49[\text{Si}] + 1.63[\text{Ca}] + 2.42[\text{Fe}] + 1.94[\text{Ti}]$$

$$[\text{OC}] = \Sigma[\text{Concentrations of organic compounds}]$$

$$[\text{BC}] = \text{Concentration of black carbon (soot)}$$

$$[\text{Smoke}] = [\text{K}] - 0.6[\text{Fe}]$$

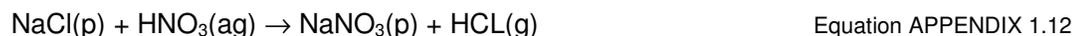
$$[\text{Seasalt}] = 2.54[\text{Na}]$$

$$[\text{Sulphate}] = 4.125[\text{S}]$$

The reconstructed mass (RCM) is based on the fact that the six composite variables or ‘pseudo’ sources given in Equation APPENDIX 1.11 are generally the major contributors to fine and coarse particle mass and are based on geochemical principles and constraints. The [Soil] factor contains elements predominantly found in crustal matter (Al, Si, Ca, Fe, Ti) 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.

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

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



Alternatively, where Cl 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 [Seasalt] = 1.65[Cl] can be substituted, particularly where Na concentrations are uncertain.

Most fine sulphate particles are the result of oxidation of SO₂ gas to sulphate particles in the atmosphere (Malm, Sisler 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 + (16x4)/32)).

Additionally, the sulphate component not associated with sea salt can be calculated from equation A1.14 (Cohen 1999):

$$\text{Non-sea salt sulphate (NSS-Sulphate)} = 4.125 ([S_{\text{tot}}] - 0.0543[\text{Cl}]) \quad \text{Equation APPENDIX 1.14}$$

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, Eldred *et al.* 1990; Malm, Sisler *et al.* 1994; Cohen 1999).

The RCM 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 OC, 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 modeling 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, Duvall et al. 2014). For this study, all data were checked for consistency with the following parameters:

1. Individual sample collection validation;
2. Gravimetric mass validation;
3. Analysis of RCM versus gravimetric mass to assess mass closure and linearity;

4. Identification of unusual values including noticeably extreme values and values that normally track with other species (e.g., Al and Si) 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;
5. Species were included in a dataset if at least 70% of data was above the LOD and signal-to-noise ratios were checked to ensure data had sufficient variability. Important tracers of a source where less than 70% of data was above the LOD were included but model runs with and without the data were used to assess the effect;

In practice during data analyses, the above steps were a reiterative 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 checked to ensure 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 that they must be carefully compiled. The effect of underestimating uncertainties can be severe, while overestimating 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, Hopke et al. 2015):

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

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

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

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

PM gravimetric mass: Uncertainty given as $4 \times$ mass value to down-weight the variable.

Reiterative 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 ELEMENTAL CORRELATION PLOTS

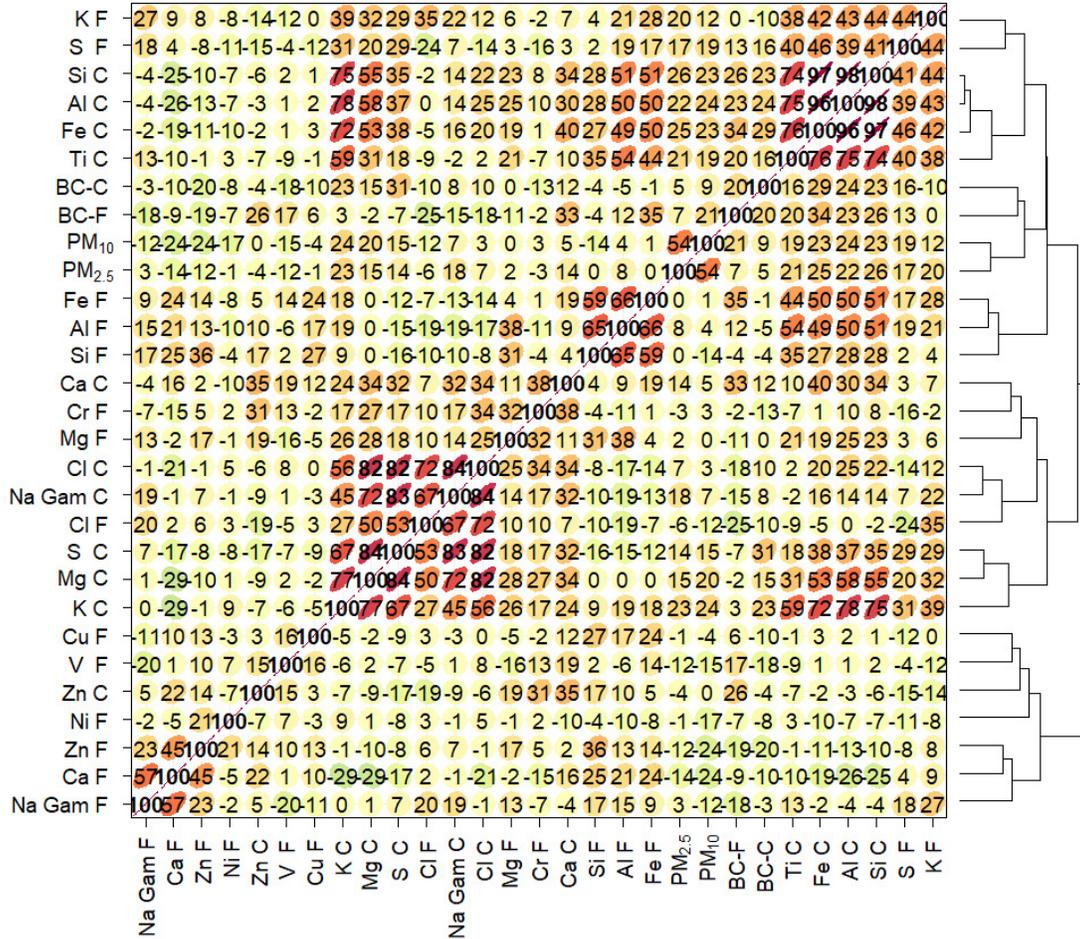


Figure A2.1 Elemental correlation plot for PM10.2.5 and PM2.5 composition

APPENDIX 3 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 and co-workers (Paatero et al., 2014, Brown et al., 2015) and should be read in conjunction with Section **Error! Reference source not found.** and **Error! Reference source not found.**

Table A3.1 Summary of EPA PMF settings for receptor modelling of Lyttelton PM_{2.5} and PM_{10-2.5} elemental data

Parameter	Setting
Data type; averaging timeframe	PM _{2.5} and PM _{10-2.5} 6-hourly
N samples	337
N factors	6
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 normalized factor contributions g _{ik}	-0.2
Robust mode	Yes
Constraints	None
Seed value	Random
N bootstraps in BS	200
r ² for BS	0.6
DISP dQ _{max}	4, 8, 16, 32
DISP active species	BC, S F, Cl F, K F, Ca F, Fe F, Al C, Si C, S C, Cl C, K C, Ca C, Fe C
N bootstraps; r ² for BS in BS-DISP	200; 0.6
BS-DISP active species	BC, S F, Cl F, K F, Ca F, Fe F, Al C, Si C, S C, Cl C, K C, Ca
BS-DISP dQ _{max}	0.5, 1, 2, 4
Extra modelling uncertainty	15%

Table A3.2 Output diagnostics for receptor modelling Lyttelton PM_{2.5} and PM_{10-2.5} elemental data.

Diagnostic	6 factors
Q _{Theoretical}	5954
Q _{Expected}	4929
Q _{true}	2065
Q _{robust}	2065
Q _{robust} /Q _{expected}	0.419
DISP Diagnostics	
Error code	0
Largest Decrease in Q:	-0.007
DISP % dQ	0
DISP swaps by factor	0
BS-DISP Diagnostics	
BS mapping (F _{peak} BS) - Unmapped	94.5% (97.8%) - 6
BS-DISP % cases accepted	94%
Largest Decrease in Q:	-28.8
BS-DISP % dQ	-1.84
# of Decreases in Q:	3
# of Swaps in Best Fit:	1
# of Swaps in DISP:	7
BS-DISP swaps by factor	2,0,0,1,1,0

This page left intentionally blank.



www.gns.cri.nz

Principal Location

1 Fairway Drive
Avalon
PO Box 30368
Lower Hutt
New Zealand
T +64-4-570 1444
F +64-4-570 4600

Other Locations

Dunedin Research Centre
764 Cumberland Street
Private Bag 1930
Dunedin
New Zealand
T +64-3-477 4050
F +64-3-477 5232

Wairakei Research Centre
114 Karetoto Road
Wairakei
Private Bag 2000, Taupo
New Zealand
T +64-7-374 8211
F +64-7-374 8199

National Isotope Centre
30 Gracefield Road
PO Box 31312
Lower Hutt
New Zealand
T +64-4-570 1444
F +64-4-570 4657