

# Multi-elemental analysis of PM<sub>10</sub> and apportionment of contributing sources – Tokoroa 2014

Prepared by:  
Travis Ancelet and Perry Davy  
Geological and Nuclear Sciences Ltd.  
(Introduction prepared by Jonathan Caldwell, Waikato Regional Council)

For:  
Waikato Regional Council  
Private Bag 3038  
Waikato Mail Centre  
HAMILTON 3240

June 2017

Document #: 4093981

Peer reviewed by:  
Jonathan Caldwell

Date July 2017

Approved for release by:  
Dominique Noiton

Date August 2017

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# Acknowledgement

The efforts of the Environmental Monitoring team, particularly Kane Lynn, are gratefully acknowledged for collection and management of the monitoring data, including partisol filters used in this report and servicing and maintenance of the monitoring station used. Ian Buchanan is also thanked for coordinating laboratory services.

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# Executive summary

Evidence for the main source of PM<sub>10</sub> (particulate matter 10 micrometres or less in diameter) in the Tokoroa airshed during the winter of 2014 has been obtained through a source apportionment study. Elemental analysis of PM<sub>10</sub> samples collected over the period May to October 2014 in Tokoroa were used along with black carbon concentrations and wind speed and wind direction data to perform receptor modelling using positive matrix factorisation. Essentially, a statistical modelling technique used to identify and apportion the sources of PM<sub>10</sub> on a particular day.

The five different emission sources identified were:

1. biomass combustion (woodburners)
2. marine aerosol (from seaspray)
3. secondary sulphate (typically from industry, shipping, volcanic/geothermal emissions)
4. secondary nitrate (typically from agricultural emissions)
5. lime dosing (very localised source from the addition of lime to treat the water at the Billah St water treatment plant)

The biomass combustion source arises from residential wood combustion for home heating and accounted for 73 % of the PM<sub>10</sub> mass on average for the full analysis period<sup>1</sup> and was by far the most dominant contributor and key source responsible for exceedances of the National Environmental Standards for Air Quality. Associated with the biomass combustion source profile were arsenic and lead, which suggests that residents are burning CCA-treated and lead-painted timber, respectively. This practice appears to be common throughout New Zealand, but likely poses a health risk to the exposed population.

Unfortunately, the composition of the filters used for PM<sub>10</sub> collection did not allow for the quantification of a number of important elements for characterising sources like soil and motor vehicles. Given that the sources identified in this work accounted for 96 % of the PM<sub>10</sub>, motor vehicles and soil are likely to be minor contributors at this location during winter. It is possible that motor vehicles and crustal matter would contribute to more PM<sub>10</sub> mass outside of winter.

It is recommended that with a longer-term study, new sources may be identified, using Teflon filters, that could lead to a greater understanding of the sources and factors that contribute to PM<sub>10</sub> pollution in Tokoroa.

The results of this study are consistent with the findings of source apportionment studies undertaken elsewhere around New Zealand and provides further evidence to support Waikato Regional Council's ongoing management focus on home heating.

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<sup>1</sup> The proportional contribution from biomass burning during the wintertime period of May to August is 78% (Personal communication from Travis Ancelet, GNS, 7 July 2015).



# 1 Introduction

Waikato Regional Council has monitored air quality in Tokoroa at the Billah Street monitoring station since 2001. The main air contaminant of concern is particles in the air which are routinely monitored as PM<sub>10</sub> (particles in the air less than 10 microns in diameter) but may also be represented by different size fractions including PM<sub>2.5</sub> (particles in the air less than 2.5 microns in diameter).

The National Environmental Standards for Air Quality (NESAQ) includes an ambient air quality standard for PM<sub>10</sub>. The standard for PM<sub>10</sub> is 50 micrograms per cubic metre of air (50 µg/m<sup>3</sup>) as a 24 hour average for the period midnight to midnight with one allowable exceedance per 12 month period within an airshed<sup>2</sup>. A breach of the standard within an airshed occurs when there has been two or more exceedances within a 12 month period, after which the airshed is classified as polluted until such time as it has been breach free for five years.

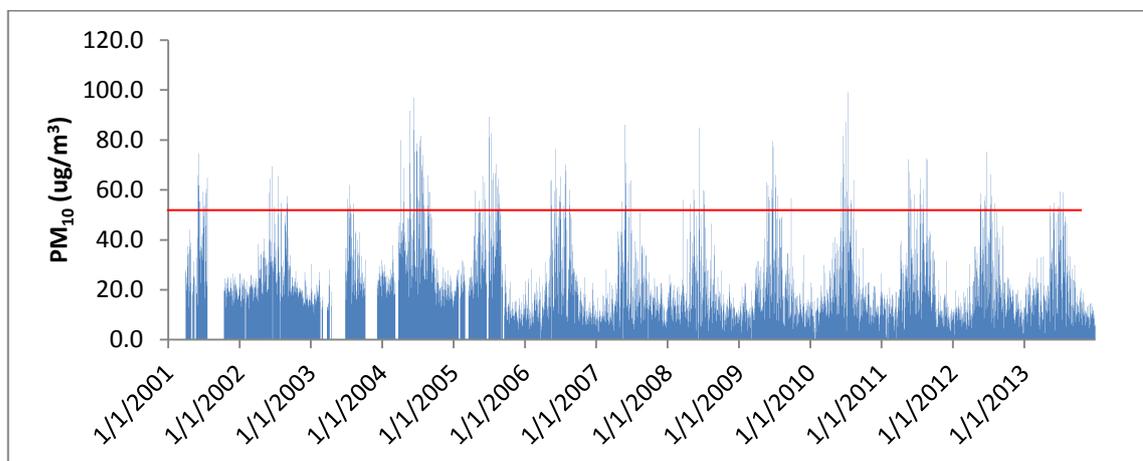
Tokoroa has on average had more than 10 exceedances per year and as such is classified as a polluted airshed. Under the NESAQ specifications, Tokoroa has to meet an interim target of no more than three exceedances of 50 µg/m<sup>3</sup> for PM<sub>10</sub> by September 2016 and no more than one exceedance by September 2020.

Understanding the various sources of emissions contributing to ambient PM<sub>10</sub> concentrations within an airshed is important in helping to manage the reduction of PM<sub>10</sub> concentrations within that airshed.

The evidence for the main source of PM<sub>10</sub> in Tokoroa comes from a number of lines of evidence including:

- an analysis of monitoring data from Tokoroa and in other urban areas around New Zealand;
- air emission inventories undertaken in both Tokoroa and in other urban areas around New Zealand; and
- source apportionment analyses undertaken in other urban areas around New Zealand.

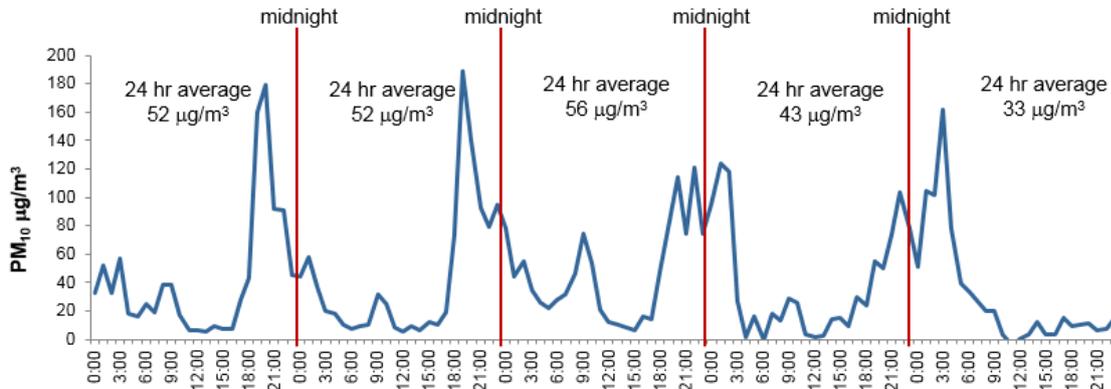
An analysis of the monitoring data for Tokoroa indicates that PM<sub>10</sub> exceedances occur during the winter months of May to August which is the period when wood burners are used for home heating (refer to Figure 1.1). Discharges from industry and transport do not typically change from season to season.



**Figure 1-1: Daily average PM<sub>10</sub> concentrations measured in Tokoroa airshed – 2001 to 2013.**

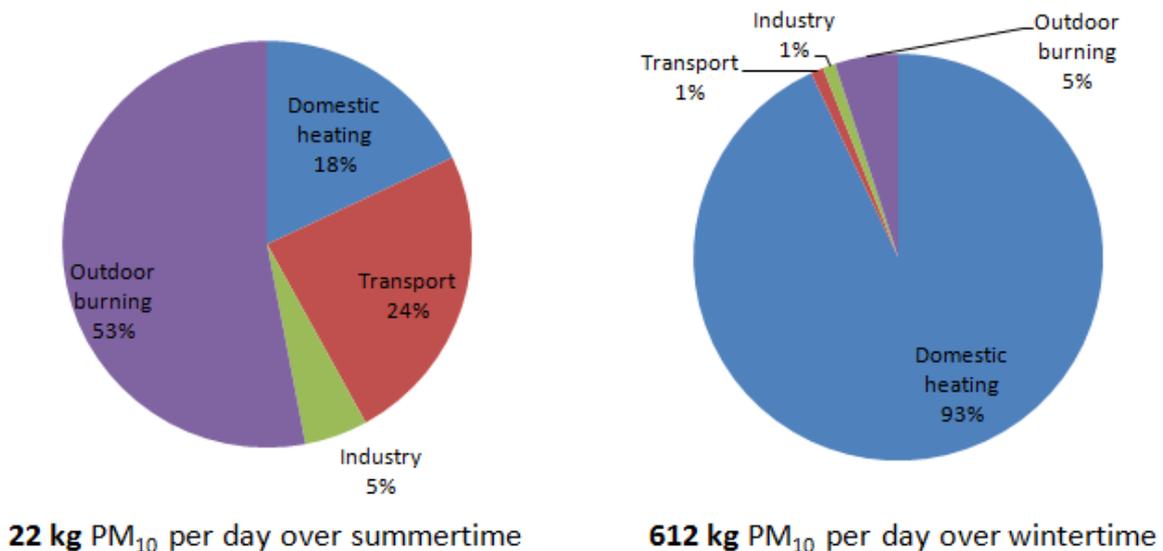
<sup>2</sup> An “airshed” is defined by the NESAQ regulations as an “air quality management area” that has been identified by Regional Councils and Unitary Authorities and made public.

Further evidence from monitoring is provided from an analysis of the hourly monitoring profiles for PM<sub>10</sub> during days when the daily average concentration is either elevated or there has been an exceedance of the standard. The profiles of five consecutive days in Tokoroa during winter presented in Figure 1.2 is typical of woodburner emissions and shows a peak in the evening with a gradual reduction overnight and a smaller secondary peak consistent with the use of the woodburner to heat up the house in the morning. This “diurnal” pattern is observed around the country in urban areas during winter when woodburner use is at a maximum.



**Figure 1-2: Typical hourly PM<sub>10</sub> profile during winter in Tokoroa.**

A comparison of summertime and wintertime emission source contributions as estimated by the Air Emission Inventory undertaken for Tokoroa in 2012 is presented in Figure 1.3. A comparison of summertime versus wintertime emission sources indicates clearly that over wintertime when PM<sub>10</sub> emissions are high, domestic home heating is the main contributing source. A reduction in daily winter PM<sub>10</sub> emissions of around 11% is estimated to have occurred in Tokoroa between 2007 to 2012 as a result of reductions in domestic heating emissions (Wilton, 2012).



**Figure 1-3: Comparison of summertime and wintertime emission source contributions (Air Emission Inventory – Tokoroa 2012).**

More direct evidence for the main source of PM<sub>10</sub> during the winter in urban areas of New Zealand is obtained from source apportionment analyses. Source apportionment typically involves the measurement of concentrations of trace elements and black carbon contained

within PM<sub>10</sub> (or PM<sub>2.5</sub>) that has been collected on a filter using standard gravimetric monitoring equipment (e.g. Sequential Partisol) and subsequent statistical analysis using Positive Matrix Factorisation.

A comparison of a number of source apportionment studies undertaken in wintertime around the country indicates that in both the North Island and the South Island, biomass burning (woodburners) are identified as the dominant wintertime source for PM<sub>10</sub> ranging from 50% in Auckland to 89% in Alexandra (refer to Figure 1.4).

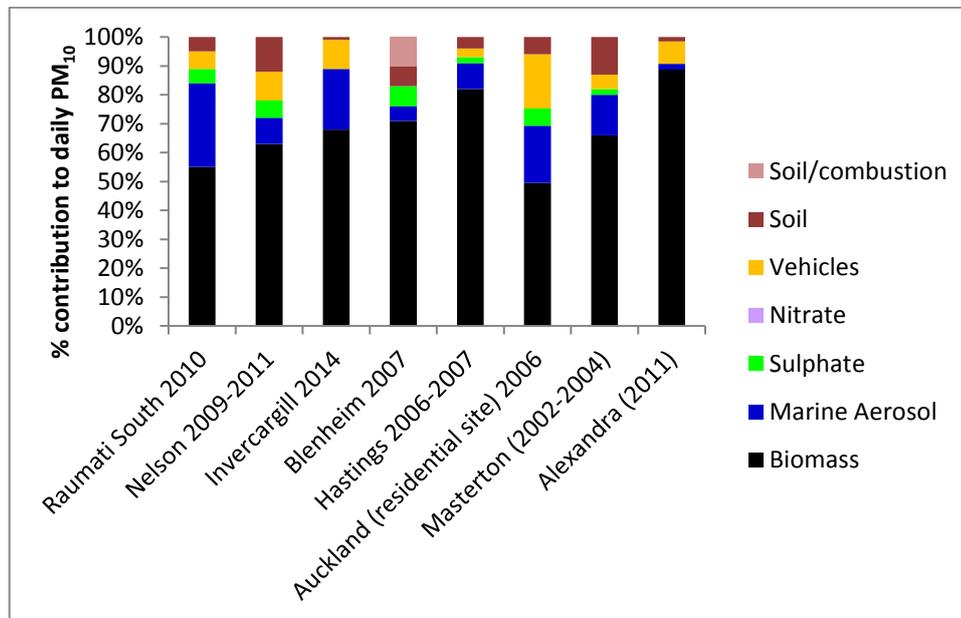


Figure 1-4: Comparison of source apportionment analyses from urban areas around New Zealand.

Over the period May to October 2014, PM<sub>10</sub> samples were collected on filters in Tokoroa by Waikato Regional Council using a Sequential Partisol. The filters were sent to Geonuclear Sciences Ltd (GNS) for source apportionment analysis.

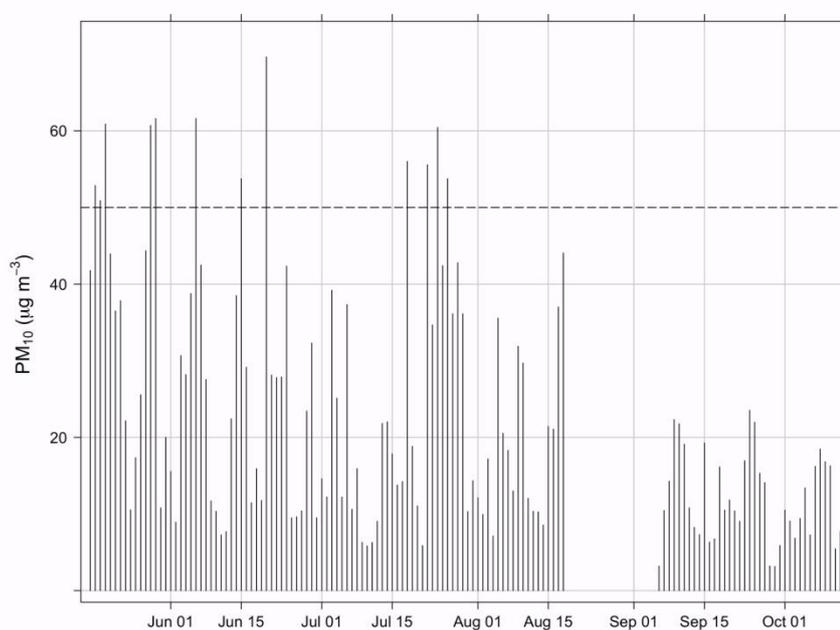
The five different emission sources identified by GNS in this particular source apportionment study were:

1. biomass combustion (woodburners);
2. marine aerosol (from seaspray);
3. secondary sulphate (typically from industry, shipping, volcanic/geothermal emissions);
4. secondary nitrate (typically from agricultural emissions); and
5. lime dosing (very localised source from the addition of lime to treat the water at the Billah St water treatment plant in Tokoroa).

In order to ensure consistency with the Waikato Regional Council Technical Report format, the following sections of this report have been extracted from the original letter-based report that was provided by GNS in 2015. A copy of the original letter-based report is included in the Appendix.

## 2 Site description and sampling

PM<sub>10</sub> sampling was undertaken by Waikato Regional Council at their air quality monitoring station at 80 Billah Street in Tokoroa (NZTM: N5765821; E1850246). The site is classified as residential and is located next to a large water reservoir. Continuous PM concentrations for compliance monitoring purposes are recorded at the site using an FH62 beta-attenuation monitor (Thermo-Fisher), and data on wind direction and speed (Vector A101M and W200P) and temperature (PT100) are also collected at the site. 24-hour PM<sub>10</sub> samples for analysis were collected onto borosilicate glass fibre filters (Pallflex, PALL) at the site using a sequential Partisol system (Thermo-Fisher 2025) from 16 May to 12 October 2014. A total of 132 samples were collected over this period. **Error! Reference source not found.** presents a time-series of PM<sub>10</sub> concentrations. It is apparent that PM<sub>10</sub> concentrations exceeded the National Environmental Standard for Air Quality (NESAQ) of 50 µg m<sup>-3</sup> twelve times during this study, although the actual number of exceedances reported may vary because the Partisol sampler was not used for compliance monitoring. The gap in the time-series is from missed sampling days.



**Figure 2-1: Time-series of PM<sub>10</sub> concentrations in 2014. The hashed line indicates the NESAQ (50 µg m<sup>-3</sup>).**

## 3 PM<sub>10</sub> analysis

The collected PM<sub>10</sub> samples were analysed for their elemental content using X-ray fluorescence spectroscopy (XRF) (Watson et al., 1999). Because the filters were composed of glass fibre, the elemental analysis was complicated by the introduction of large background silicon concentrations and a number of contaminants present in the filters that included potassium, iron and zinc. Overall, elemental information could not be used for Na, Mg, Al, Si, K, Fe and Zn. These elements are critical in the identification of some sources, including crustal matter and motor vehicle emissions, therefore additional analyses of PM<sub>10</sub> composition for water-soluble ions were quantified using ion chromatography (Dionex ICS-3000 reagent free ion chromatograph with conductivity detection) by CSIRO in Aspendale, Australia. This data, combined with black carbon (BC) concentrations determined using light reflection (Ancelet et al., 2011) provided sufficient information to perform receptor modeling using positive matrix

factorisation (PMF) (discussed in Section 4). **Error! Reference source not found.** presents a summary of the analytical data obtained in this study. It is important to note that not all of the species presented in **Error! Reference source not found.** were used for the source apportionment.

**Table 3-1: Statistical data from the PM<sub>10</sub> analyses. All values are in ng m<sup>-3</sup> except for PM<sub>10</sub> (µg m<sup>-3</sup>).**

	Average	Maximum	Minimum	Median	Standard Deviation	Average Uncert
PM <sub>10</sub> (µg m <sup>-3</sup> )	22	70	3	17	16	4
BC*	4776	11759	651	3771	3081	229
Mg	102	2296	0	82	196	15
S	96	581	0	72	97	25
Cl	824	3568	21	653	658	89
Ca	2310	10166	0	2386	2066	235
Ti	242	1578	0	0	362	92
V	9	150	0	0	24	2
Cu	7	36	0	6	5	1
As	8	34	0	4	8	3
Sn	4	27	0	0	6	5
Sb	8	41	0	5	8	6
Pb	39	218	0	31	36	7
Br	1	11	0	0	2	7
Na <sup>+</sup>	754	3575	0	659	659	346
NH <sub>4</sub> <sup>+</sup>	5	44	0	3	7	1
K <sup>+</sup>	84	533	0	0	122	103
Mg <sup>2+</sup>	72	378	0	56	70	9
Ca <sup>2+</sup>	342	5836	0	56	896	56
Cl <sup>-</sup>	1410	6253	42	1115	1111	148
NO <sub>2</sub> <sup>-</sup>	2	73	0	0	9	2
Br <sup>-</sup>	1	7	0	0	2	1
NO <sub>3</sub> <sup>-</sup>	302	1496	0	242	280	80
SO <sub>4</sub> <sup>2-</sup>	569	1484	108	486	320	90
oxalate	85	252	0	90	72	63
formate	117	1727	0	0	340	17
MSA**	14	124	0	10	17	2

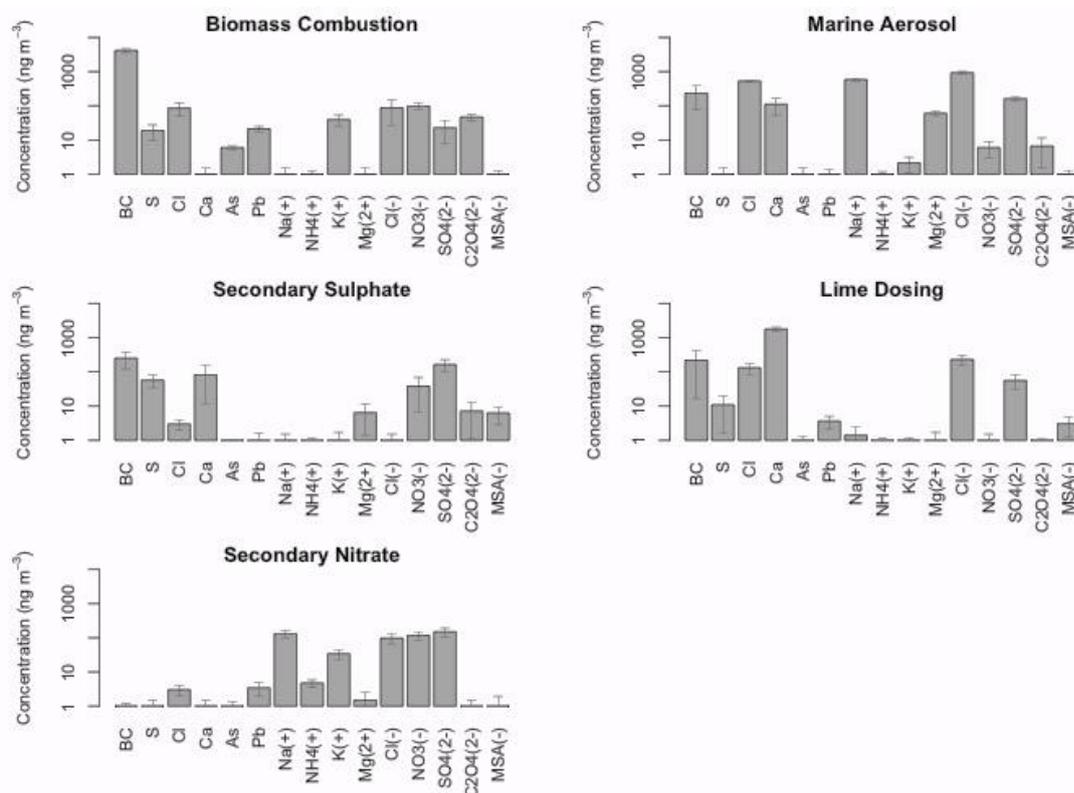
\* BC = black carbon

\*\* MSA = methanesulphonic acid

## 4 Receptor modelling using PMF

Positive matrix factorisation is a powerful and commonly used receptor model that is capable of resolving factors, or particulate matter (PM) sources, without prior source knowledge. It is

however, important to note that source-specific profiles (fingerprints) must be known to properly assign the PMF model outputs. PMF has a number of advantages over traditional factor analysis techniques including non-negativity constraints and the ability to accommodate missing or below detection limit data. The results of the analysis are directly interpretable as mass contributions from each factor (Paatero and Tapper, 1994; Paatero, 1997; Song et al., 2001). When PMF was applied to the compositional data we identified five PM<sub>10</sub> sources: biomass combustion, marine aerosol, secondary sulphate, secondary nitrate and lime dosing, accounting for 96 % of the PM<sub>10</sub> mass on average. The source profiles obtained are presented in **Error! Reference source not found.**



**Figure 4-1: PM<sub>10</sub> source profiles.**

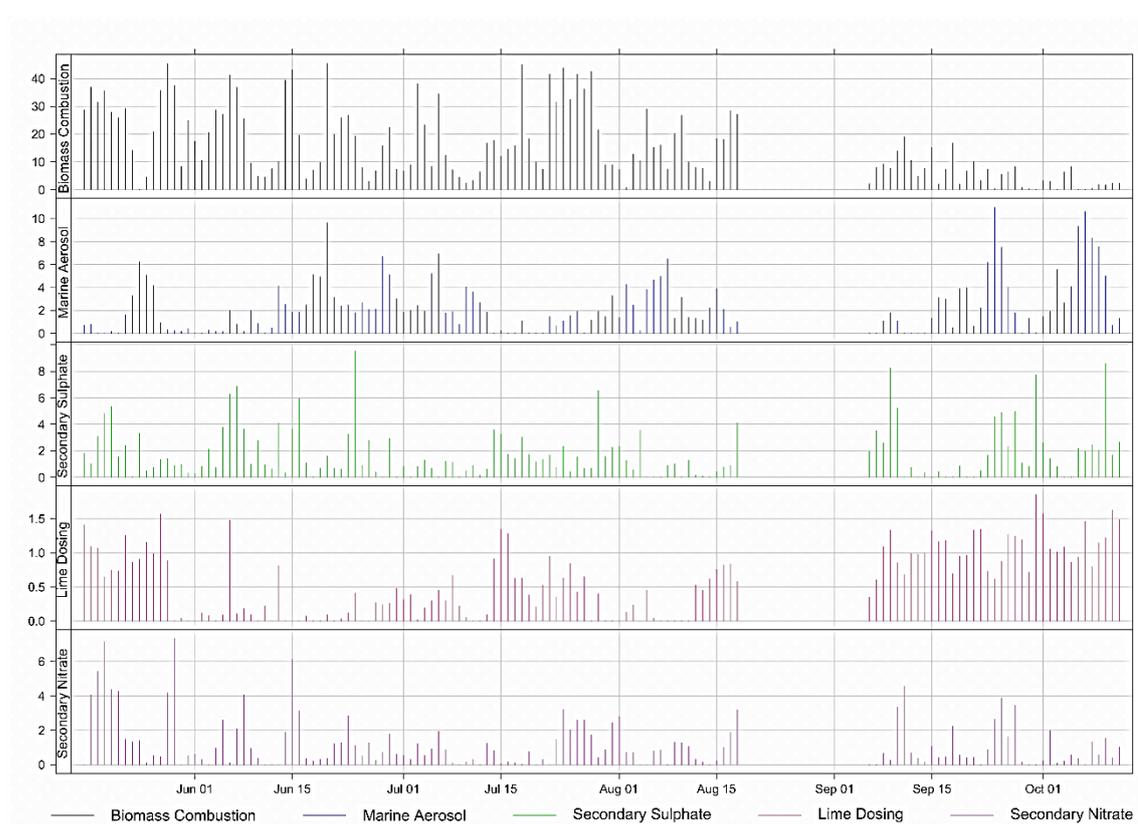
The biomass combustion source arises from the use of domestic wood fires for home heating and the profile features high concentrations of BC (a marker of incomplete combustion), K, oxalate, nitrate, As and Pb, which is consistent with previous studies (Khalil and Rasmussen, 2003; Davy et al., 2012). The biomass combustion source accounted for 73 % of the PM<sub>10</sub> mass on average. The As and Pb in the profile suggests that residents are burning copper chrome arsenate (CCA)-treated and lead-painted timber, respectively. This behavior appears to occur across New Zealand and could pose additional health problems for the exposed population (Ancelet et al., 2012; Davy et al., 2012).

The marine aerosol source features Na, Mg, Cl and Br as major species, consistent with the composition of seawater. The marine aerosol source accounted for 11 % of the PM<sub>10</sub> mass on average. The secondary sulphate source features high concentrations of S, sulphate and methanesulphonic acid (MSA) and is consistent with the process of secondary sulphate formation (Kolaitis et al., 1989). Secondary sulphate accounted for 8 % of PM<sub>10</sub> on average.

The secondary nitrate source features ammonium, potassium, nitrate and sulphate. The secondary nitrate source arises from atmospheric processing of precursor gases and the profile is consistent with those reported internationally. The secondary nitrate source accounted for 6 % of the PM<sub>10</sub> mass on average.

The lime dosing source accounted for 3 % of the PM<sub>10</sub> mass on average and featured Ca as the primary element in the source profile. The lime dosing source was only present when the activity was occurring at the reservoir and wind conditions were appropriate.

Time-series of the source contributions are presented in **Error! Reference source not found.** When analysing **Error! Reference source not found.** it is important to note that the scales on the y-axes are not the same. This has been done to more accurately depict how the source contributions varied over time. Biomass combustion contributions peaked during the heart of winter (June to August) and had decreased substantially by September and October. This pattern is consistent with domestic heating practices across the country.



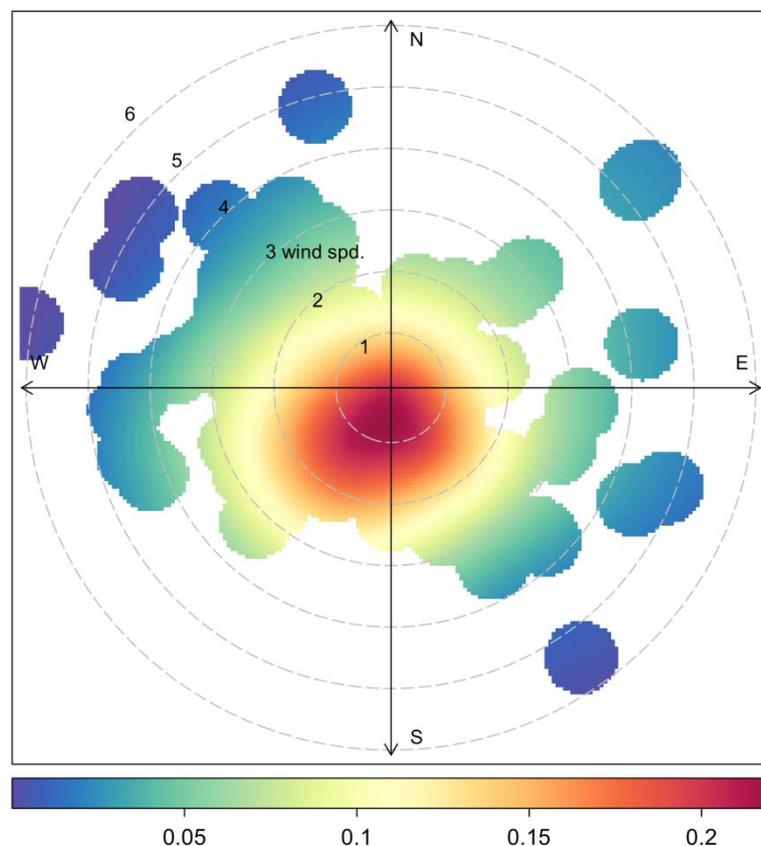
**Figure 4-2: Time-series of source contributions (in  $\mu\text{g m}^{-3}$ ).**

The contributions from other sources tended to increase under favourable meteorological conditions; for example, marine aerosol contributions peaked under moderate-to-high wind speeds. The lime dosing source peaked during days when lime dosing was reported to Waikato Regional Council and wind speeds were high. Peaks were not present for each day that lime dosing occurred and this is likely because elevated wind speeds were required to disperse the lime being used or winds were in the opposite direction. A more tailored study would be required to identify the key factors responsible for the elevated lime dosing contributions.

## 5 Source transport

To evaluate how source contributions are affected by wind speed and direction, bivariate polar plots were used (Carslaw and Ropkins, 2012). **Error! Reference source not found.** presents a polar plot of biomass combustion contributions. In Figure 5-1 the weighted mean statistic was used because it combines the concentration data with the frequency of occurrence to identify

which wind speeds/directions dominate the overall biomass combustion contributions. **Error! Reference source not found.** Figure 5-1 shows that biomass combustion contributions peaked under low wind speeds from the south, suggesting that elevated biomass combustion contributions occur under cold, calm katabatic drainage conditions (Ancelet et al., 2012).

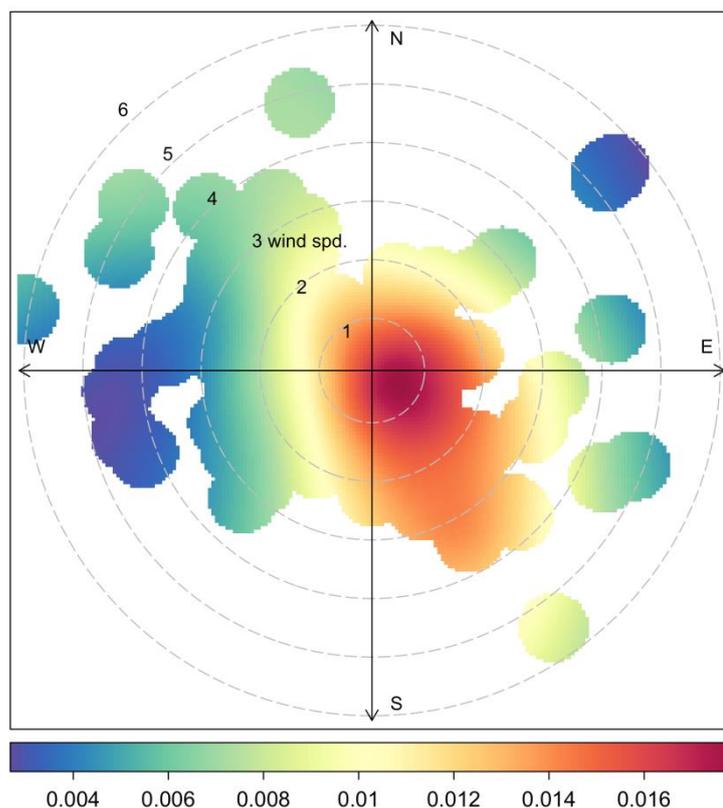


**Figure 5-1:** Polar plot of biomass combustion contributions. The radial dimensions indicate the wind speed in  $1 \text{ m s}^{-1}$  increments and the color contours indicate the average contribution to each wind direction/speed bin. The legend below the plot provides an indication of the concentration combined with the frequency of occurrence. The warmer colours indicate higher concentrations and frequencies.

Marine aerosol contributions peaked under moderate-to-high wind speeds from the west. This result is expected because of the proximity of Tokoroa to the west coast and the prevailing winds in Tokoroa (southeasterly and westerly). Other New Zealand inland locations, such as Alexandra, Masterton and Palmerston North, experience similar marine aerosol contributions. As discussed in Section 4, lime dosing contributions also occurred under moderate-to-high wind speeds.

Secondary sulphate contributions peaked under southeasterly winds (**Error! Reference source not found.**). This suggests that the source possibly originated in the Central Plateau region and/or from emissions associated with the Kinleith pulp and paper mill. Sulphate contributions in Tokoroa were similar to those measured in cities like Nelson and Auckland, where sulphate sources included marine-derived secondary sulphate and shipping emissions. This suggests that it is possible sulphate contributions in Tokoroa resulted from long-range transport because geothermal and industry sulphate emissions would be expected to be slightly higher. More work would be required to confirm the exact origin of the secondary sulphate in Tokoroa.

The secondary nitrate source contributions peaked under low wind speeds from the north. The exact origin of this source is unclear, but it is possible that agricultural emissions, associated with pasture and livestock, are responsible for elevated secondary nitrate contributions.



**Figure 5-2:** Polar plot of secondary sulphate contributions. The radial dimensions indicate the wind speed in  $1 \text{ m s}^{-1}$  increments and the color contours indicate the average contribution to each wind direction/speed bin. The legend below the plot provides an indication of the concentration combined with the frequency of occurrence. The warmer colours indicate higher concentrations and frequencies.

## 6 Contributions during peak days

For air quality compliance purposes it is extremely important to identify which source(s) contribute to PM concentrations on “peak” days. For the purposes of this investigation we have considered all days when  $\text{PM}_{10}$  concentrations were higher than  $33 \mu\text{g m}^{-3}$  (Ministry for the Environment “Alert” level). This analysis is presented in Figure 6-1. From Figure 6-1 it is clear that biomass combustion, or domestic wood burning, was the dominant contributor to  $\text{PM}_{10}$  concentrations, often contributing greater than  $33 \mu\text{g m}^{-3}$  on its own.

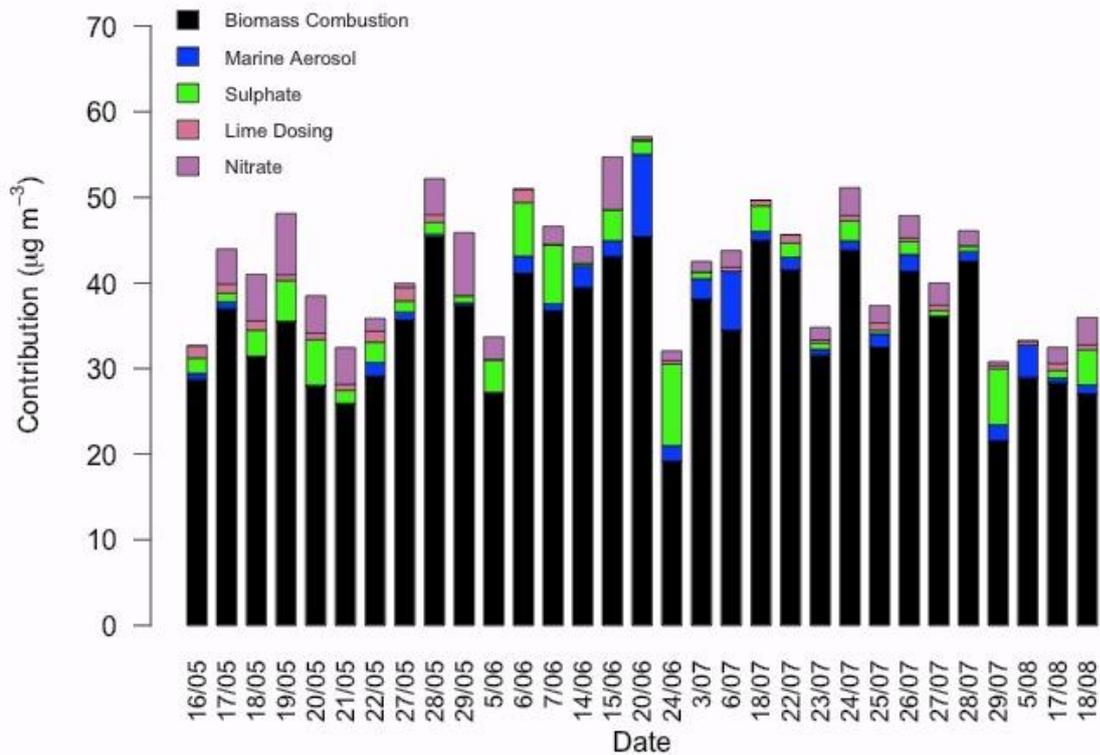


Figure 6-1: Barplot of source contributions on days (during 2014) when PM<sub>10</sub> concentrations exceeded the Ministry for the Environment “Alert” level (33 µg m<sup>-3</sup>).

## 7 Conclusions

PM<sub>10</sub> concentrations in Tokoroa are elevated during winter, exceeding the NESAQ a number of times each year. In this work, we analysed PM<sub>10</sub> samples collected from May to October 2014 for their black carbon, elemental and soluble ion concentrations. Using positive matrix factorisation we identified five PM<sub>10</sub> sources: biomass combustion, marine aerosol, secondary sulphate, lime dosing and secondary nitrate. The biomass combustion source arises from residential wood combustion for home heating and accounted for 73 % of the PM<sub>10</sub> mass on average. On days when PM<sub>10</sub> concentrations exceeded the Ministry for the Environment “Alert” level, biomass combustion was by far the most dominant contributor and key source responsible for exceedances of the NESAQ. Associated with the biomass combustion source profile were arsenic and lead, which suggests that residents are burning CCA-treated and lead-painted timber, respectively. This practice appears to be common throughout New Zealand, but likely poses a health risk to the exposed population. Because biomass combustion source contributions peak under low wind speeds during the winter, it would be possible to anticipate high pollution events in advance.

Unfortunately, the composition of the filters used for PM<sub>10</sub> collection did not allow for the quantification of a number of important elements for characterising sources like soil and motor vehicles. It is likely that, even though they were not identified in this work, these sources would contribute some quantity of PM<sub>10</sub>. Given that the sources identified in this work accounted for 96 % of the PM<sub>10</sub>, motor vehicles and soil are likely to be minor contributors at this location during winter. It is possible that motor vehicles and crustal matter would contribute to more PM<sub>10</sub> mass outside of winter.

## 8 Recommendations

The results of this study provide valuable information about the sources of PM<sub>10</sub> in Tokoroa. Based on these results, it is possible for Waikato Regional Council to evaluate options for improving local air quality by targeting a reduction in biomass combustion for home heating. It is possible that with a longer-term study, new sources may be identified that could lead to a greater understanding of the sources and factors that contribute to PM pollution in Tokoroa. It would be critical in this longer-term work that more appropriate filters, for example Teflon, are used.

The presence of arsenic and lead associated with domestic home heating is a cause for concern. These elements are well-known to be toxic and in addition to their presence in air, it is likely that ashes from fires contain even higher concentrations of these elements. Reducing these emissions, and those of particles in general, is critical for ensuring positive health outcomes for local residents.

The origins of the secondary sulphate and nitrate source could be investigated further to identify whether they are anthropogenic or natural in origin. If they are anthropogenic, it could be possible to manage them so that their effect on air quality in Tokoroa is minimised.

# References

- Ancelet, T., Davy, P.K., Trompetter, W.J., Markwitz, A., Weatherburn, D.C., 2011. Carbonaceous aerosols in an urban tunnel. *Atmospheric Environment* 45, 4463–4469. doi:10.1016/j.atmosenv.2011.05.032
- Ancelet, T., Davy, P.K., Mitchell, T., Trompetter, W.J., Markwitz, A., Weatherburn, D.C., 2012. Identification of Particulate Matter Sources on an Hourly Time-Scale in a Wood Burning Community. *Environmental Science & Technology* 46, 4767–4774. doi:10.1021/es203937y
- Carlaw, D.C., Ropkins, K., 2012. openair - An R package for air quality data analysis. *Environmental Modeling Software* 27-28, 52–61. doi:10.1016/j.envsoft.2011.09.008
- Davy, P.K., Ancelet, T., Trompetter, W.J., Markwitz, A., Weatherburn, D.C., 2012. Composition and source contributions of air particulate matter pollution in a New Zealand suburban town. *Atmospheric Pollution Research* 3, 143–147. doi:10.5094/APR.2012.014
- Khalil, M. A. K., Rasmussen, R. A., 2003. Tracers of wood smoke. *Atmospheric Environment* 37 (9–10), 1211–1222.
- Kolaitis, L.N., Bruynseels, F.J., Van Grieken, R.E., Andreae, M.O., 1989. Determination of methanesulfonic acid and non-sea-salt sulfate in single marine aerosol particles. *Environmental Science & Technology* 23, 236–240.
- Paatero, P., Tapper, U., 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* 5, 111–126.
- Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis. *Chemometrics and Intelligent Laboratory Systems* 37, 23–35.
- Song, X.-H., Polissar, A.V., Hopke, P.K., 2001. Sources of fine particle composition in the northeastern US. *Atmospheric Environment* 35, 5277–5286.
- Watson, J. G., Chow, J. C., Frazier, C. A., 1999. X-ray Fluorescence Analysis of Ambient Air Samples, in *Advances in Environmental, Industrial and Process Control Technologies* 1, 139–196.
- Wilton, E., 2012. Air Emission Inventory – Hamilton and Tokoroa 2012, *Waikato Regional Council Technical Report 2012/34*.

# **Appendix – Original letter-based report by GNS**

30 June 2015

Waikato Regional Council  
Private Bag 3038  
Hamilton 3240

Attention: Jonathan Caldwell

National Institute of  
30 Grafton Road  
Lower Hutt 5010  
PO Box 31312  
Lower Hutt 5040  
New Zealand  
T +64-4-370 1444  
F +64-4-370 4857  
www.gns.cri.nz

Dear Jonathan

## Multi-elemental analysis of PM<sub>10</sub> and apportionment of contributing sources

### 1.0 SUMMARY

This letter summarises the results of a study of particulate matter less than 10 µm in diameter (PM<sub>10</sub>) collected in Tokoroa from 18 May to 12 October 2014. The aim of this work was to analyse PM<sub>10</sub> samples collected on a 24-hour basis for their elemental content and to use the elemental concentrations obtained for identifying the particulate matter (PM) emission sources contributing to PM<sub>10</sub> in Tokoroa. This work was funded in full by Waikato Regional Council.

### 1.1 SITE DESCRIPTION AND SAMPLING

PM<sub>10</sub> sampling was undertaken by Waikato Regional Council at their air quality monitoring station at 80 Billah Street in Tokoroa (NZTM: N5765821; E1850246). The site is classified as residential and is located next to a large water reservoir. Continuous PM concentrations for compliance monitoring purposes are recorded at the site using an FH82 beta-attenuation monitor (Thermo-Fisher), and data on wind direction and speed (Vector A101M and W200P) and temperature (PT100) are also collected at the site. 24-hour PM<sub>10</sub> samples for analysis were collected onto borosilicate glass fibre filters (Pallflex, PALL) at the site using a sequential Partisol system (Thermo-Fisher 2025) from 18 May to 12 October 2014. A total of 132 samples were collected over this period. Figure 1.1 presents a time-series of PM<sub>10</sub> concentrations. It is apparent that PM<sub>10</sub> concentrations exceeded the National Environmental Standard for Air Quality (NESAQ) of 50 µg m<sup>-3</sup> twelve times during this study, although the actual number of exceedances reported may vary because the Partisol sampler was not used for compliance monitoring. The gap in the time-series is from missed sampling days.

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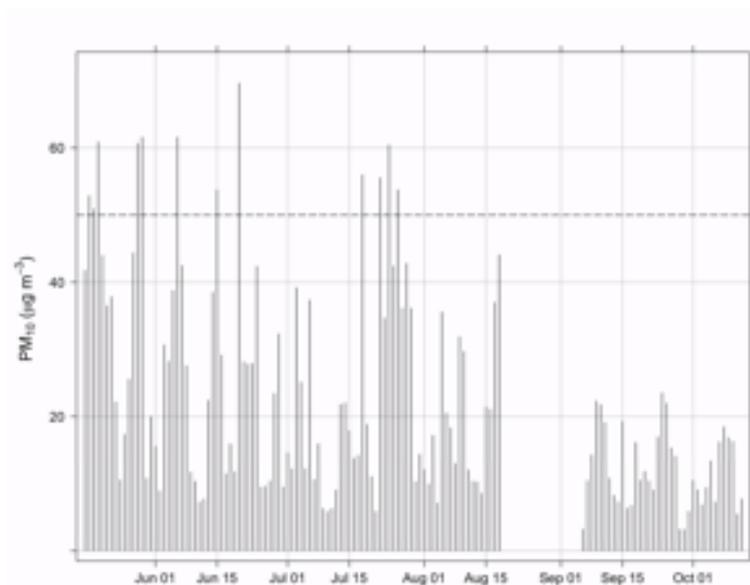


Figure 1.1 Time-series of  $PM_{10}$  concentrations in 2014. The hashed line indicates the NESAQ ( $50 \mu\text{g m}^{-3}$ ).

## 1.2 $PM_{10}$ ANALYSIS

The collected  $PM_{10}$  samples were analysed for their elemental content using X-ray fluorescence spectroscopy (XRF) (Watson et al., 1999). Because the filters were composed of glass fibre, the elemental analysis was complicated by the introduction of large background silicon concentrations and a number of contaminants present in the filters that included potassium, iron and zinc. Overall, elemental information could not be used for Na, Mg, Al, Si, K, Fe and Zn. These elements are critical in the identification of some sources, including crustal matter and motor vehicle emissions, therefore additional analyses of  $PM_{10}$  composition for water-soluble ions were quantified using ion chromatography (Dionex ICS-3000 reagent free ion chromatograph with conductivity detection) by CSIRO in Aspendale, Australia. This data, combined with black carbon (BC) concentrations determined using light reflection (Ancelet et al., 2011) provided sufficient information to perform receptor modeling using positive matrix factorisation (PMF) (discussed in Section 1.3). Table 1.1 presents a summary of the analytical data obtained in this study. It is important to note that not all of the species presented in Table 1.1 were used for the source apportionment.

Table 1.1 Statistical data from the PM<sub>10</sub> analyses. All values are in ng m<sup>-3</sup> except for PM<sub>10</sub> (µg m<sup>-3</sup>)

	Average	Maximum	Minimum	Median	Standard Deviation	Average Uncert
PM <sub>10</sub> (µg m <sup>-3</sup> )	22	70	3	17	16	4
BC <sup>*</sup>	4776	11759	651	3771	3081	229
Mg	102	2296	0	82	196	15
S	96	581	0	72	97	25
Cl	824	3568	21	653	658	89
Ca	2310	10166	0	2386	2066	235
Tl	242	1578	0	0	362	92
V	9	150	0	0	24	2
Cu	7	36	0	6	5	1
As	8	34	0	4	8	3
Sn	4	27	0	0	6	5
Sb	8	41	0	5	8	6
Pb	39	218	0	31	36	7
Br	1	11	0	0	2	7
Na <sup>+</sup>	754	3575	0	659	659	346
NH <sub>4</sub> <sup>+</sup>	5	44	0	3	7	1
K <sup>+</sup>	84	533	0	0	122	103
Mg <sup>2+</sup>	72	378	0	56	70	9
Ca <sup>2+</sup>	342	5836	0	56	896	56
Cl <sup>-</sup>	1410	6253	42	1115	1111	148
NO <sub>2</sub> <sup>-</sup>	2	73	0	0	9	2
Br <sup>-</sup>	1	7	0	0	2	1
NO <sub>3</sub> <sup>-</sup>	302	1496	0	242	280	80
SO <sub>4</sub> <sup>2-</sup>	569	1484	108	486	320	90
oxalate	85	252	0	90	72	63
formate	117	1727	0	0	340	17
MSA <sup>**</sup>	14	124	0	10	17	2

\* BC = black carbon

\*\* MSA = methanesulphonic acid

### 1.3 RECEPTOR MODELING USING PMF

Positive matrix factorisation is a powerful and commonly used receptor model that is capable of resolving factors, or particulate matter (PM) sources, without prior source knowledge. It is however, important to note that source-specific profiles (fingerprints) must be known to properly assign the PMF model outputs. PMF has a number of advantages over traditional factor analysis techniques including non-negativity constraints and the ability to accommodate missing or below detection limit data. The results of the analysis are directly interpretable as mass contributions from each factor (Paatero and Tapper, 1994; Paatero, 1997; Song et al., 2001). When PMF was applied to the compositional data we identified five PM<sub>10</sub> sources: biomass combustion, marine aerosol, secondary sulphate, secondary nitrate and lime dosing, accounting for 98 % of the PM<sub>10</sub> mass on average. The source profiles obtained are presented in Figure 1.2.

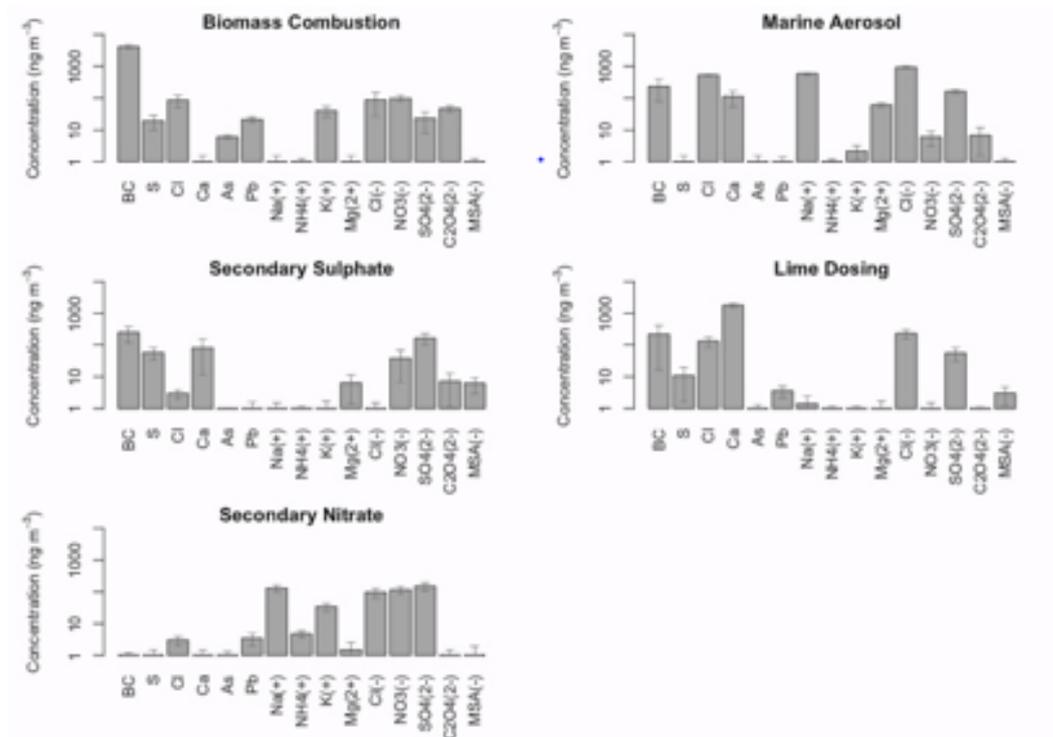


Figure 1.2 PM<sub>10</sub> source profiles.

The biomass combustion source arises from the use of domestic wood fires for home heating and the profile features high concentrations of BC (a marker of incomplete combustion), K, oxalate, nitrate, As and Pb, which is consistent with previous studies (Khalil and Rasmussen, 2003; Davy et al., 2012). The biomass combustion source accounted for 73 % of the PM<sub>10</sub> mass on average. The As and Pb in the profile suggests that residents are burning copper chrome arsenate (CCA)-treated and lead-painted timber, respectively. This behavior appears to occur across New Zealand and could pose additional health problems for the exposed population (Ancelet et al., 2012; Davy et al., 2012).

The marine aerosol source features Na, Mg, Cl and Br as major species, consistent with the composition of seawater. The marine aerosol source accounted for 11 % of the PM<sub>10</sub> mass on average. The secondary sulphate source features high concentrations of S, sulphate and methanesulphonic acid (MSA) and is consistent with the process of secondary sulphate formation (Kolaitis et al., 1989). Secondary sulphate accounted for 8 % of PM<sub>10</sub> on average.

The secondary nitrate source features ammonium, potassium, nitrate and sulphate. The secondary nitrate source arises from atmospheric processing of precursor gases and the profile is consistent with those reported internationally. The secondary nitrate source accounted for 6 % of the PM<sub>10</sub> mass on average.

The lime dosing source accounted for 3 % of the PM<sub>10</sub> mass on average and featured Ca as the primary element in the source profile. The lime dosing source was only present when the activity was occurring at the reservoir and wind conditions were appropriate.

Time-series of the source contributions are presented in Figure 1.3. When analysing Figure 1.3 it is important to note that the scales on the y-axes are not the same. This has been done to more accurately depict how the source contributions varied over time. Biomass combustion contributions peaked during the heart of winter (June to August) and had decreased substantially by September and October. This pattern is consistent with domestic heating practices across the country.

Figure 1.3 Time-series of source contributions (In  $\mu\text{g m}^{-2}$ ).

The contributions from other sources tended to increase under favourable meteorological conditions; for example, marine aerosol contributions peaked under moderate-to-high wind speeds. The lime dosing source peaked during days when lime dosing was reported to Waikato Regional Council and wind speeds were high. Peaks were not present for each day that lime dosing occurred and this is likely because elevated wind speeds were required to disperse the lime being used or winds were in the opposite direction. A more tailored study would be required to identify the key factors responsible for the elevated lime dosing contributions.

#### 1.4 SOURCE TRANSPORT

To evaluate how source contributions are affected by wind speed and direction, bivariate polar plots were used (Carslaw and Ropkins, 2012). Figure 1.4 presents a polar plot of biomass combustion contributions. In Figure 1.4 the weighted mean statistic was used because it combines the concentration data with the frequency of occurrence to identify which wind speeds/directions dominate the overall biomass combustion contributions. Figure 1.4 shows that biomass combustion contributions peaked under low wind speeds from the south, suggesting that elevated biomass combustion contributions occur under cold, calm katabatic drainage conditions (Ancelet et al., 2012).

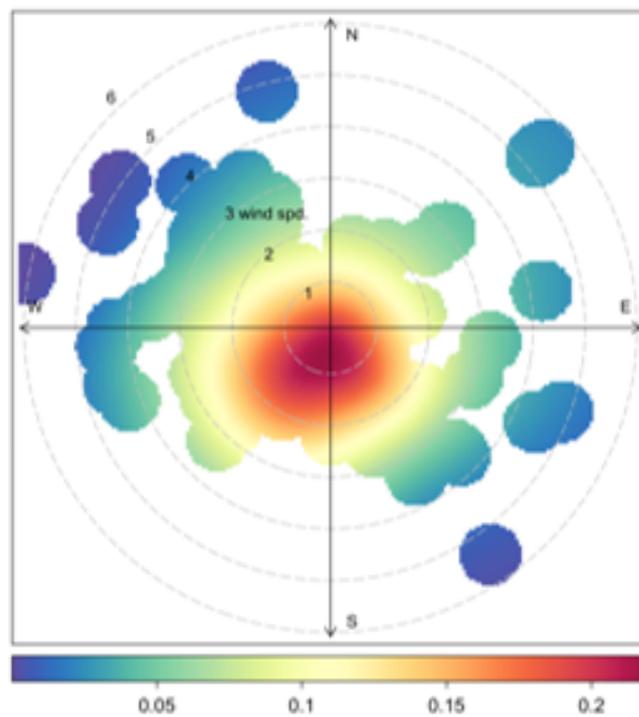


Figure 1.4 Polar plot of biomass combustion contributions. The radial dimensions indicate the wind speed in  $1 \text{ m s}^{-1}$  increments and the color contours indicate the average contribution to each wind direction/speed bin. The legend below the plot provides an indication of the concentration combined with the frequency of occurrence. The warmer colours indicate higher concentrations and frequencies.

Marine aerosol contributions peaked under moderate-to-high wind speeds from the west. This result is expected because of the proximity of Tokoroa to the west coast and the prevailing winds in Tokoroa (southeasterly and westerly). Other New Zealand inland locations, such as Alexandra, Masterton and Palmerston North, experience similar marine aerosol contributions. As discussed in Section 1.3, lime dosing contributions also occurred under moderate-to-high wind speeds.

Secondary sulphate contributions peaked under southeasterly winds (Figure 1.5). This suggests that the source possibly originated in the Central Plateau region and/or from emissions associated with the Kinleith pulp and paper mill. Sulphate contributions in Tokoroa were similar to those measured in cities like Nelson and Auckland, where sulphate sources included marine-derived secondary sulphate and shipping emissions. This suggests that it is possible sulphate contributions in Tokoroa resulted from long-range transport because geothermal and industry sulphate emissions would be expected to be slightly higher. More work would be required to confirm the exact origin of the secondary sulphate in Tokoroa.

The secondary nitrate source contributions peaked under low wind speeds from the north. The exact origin of this source is unclear, but it is possible that agricultural emissions, associated with pasture and livestock, are responsible for elevated secondary nitrate contributions.

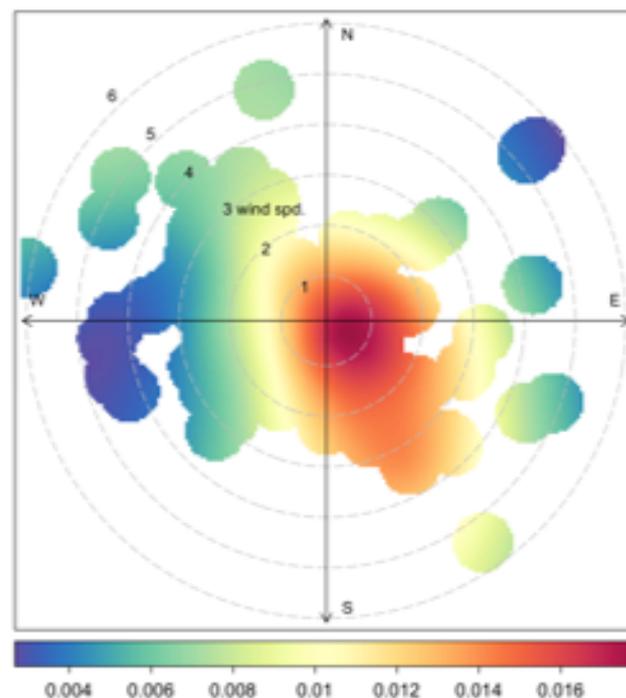


Figure 1.5 Polar plot of secondary sulphate contributions. The radial dimensions indicate the wind speed in  $1 \text{ m s}^{-1}$  increments and the color contours indicate the average contribution to each wind direction/speed bin. The legend below the plot provides an indication of the concentration combined with the frequency of occurrence. The warmer colors indicate higher concentrations and frequencies.

## 1.5 CONTRIBUTIONS DURING PEAK DAYS

For air quality compliance purposes it is extremely important to identify which source(s) contribute to PM concentrations on "peak" days. For the purposes of this investigation we have considered all days when PM<sub>10</sub> concentrations were higher than 33 µg m<sup>-3</sup> (Ministry for the Environment "Alert" level). This analysis is presented in Figure 1.6. From Figure 1.6 it is clear that biomass combustion, or domestic wood burning, was the dominant contributor to PM<sub>10</sub> concentrations, often contributing greater than 33 µg m<sup>-3</sup> on its own.

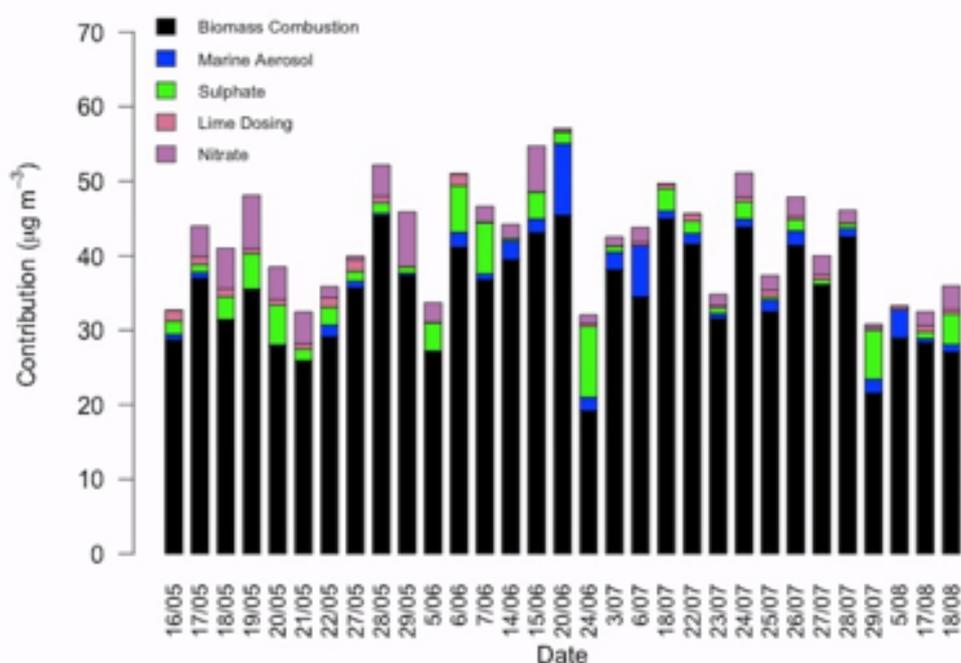


Figure 1.6 Barplot of source contributions on days (during 2014) when PM<sub>10</sub> concentrations exceeded the Ministry for the Environment "Alert" level (33 µg m<sup>-3</sup>).

## 2.0 CONCLUSIONS

PM<sub>10</sub> concentrations in Tokoroa are elevated during winter, exceeding the NESAQ a number of times each year. In this work, we analysed PM<sub>10</sub> samples collected from May to October 2014 for their black carbon, elemental and soluble ion concentrations. Using positive matrix factorisation we identified five PM<sub>10</sub> sources: biomass combustion, marine aerosol, secondary sulphate, lime dosing and secondary nitrate. The biomass combustion source arises from residential wood combustion for home heating and accounted for 73 % of the PM<sub>10</sub> mass on average. On days when PM<sub>10</sub> concentrations exceeded the Ministry for the Environment "Alert" level, biomass combustion was by far the most dominant contributor and key source responsible for exceedances of the NESAQ. Associated with the biomass combustion source profile were arsenic and lead, which suggests that residents are burning CCA-treated and lead-painted timber, respectively. This practice appears to be common

throughout New Zealand, but likely poses a health risk to the exposed population. Because biomass combustion source contributions peak under low wind speeds during the winter, it would be possible to anticipate high pollution events in advance.

Unfortunately, the composition of the filters used for PM<sub>10</sub> collection did not allow for the quantification of a number of important elements for characterising sources like soil and motor vehicles. It is likely that, even though they were not identified in this work, these sources would contribute some quantity of PM<sub>10</sub>. Given that the sources identified in this work accounted for 98 % of the PM<sub>10</sub>, motor vehicles and soil are likely to be minor contributors at this location during winter. It is possible that motor vehicles and crustal matter would contribute to more PM<sub>10</sub> mass outside of winter.

### 3.0 RECOMMENDATIONS

The results of this study provide valuable information about the sources of PM<sub>10</sub> in Tokoroa. Based on these results, it is possible for Waikato Regional Council to evaluate options for improving local air quality by targeting a reduction in biomass combustion for home heating. It is possible that with a longer-term study, new sources may be identified that could lead to a greater understanding of the sources and factors that contribute to PM pollution in Tokoroa. It would be critical in this longer-term work that more appropriate filters, for example Teflon, are used.

The presence of arsenic and lead associated with domestic home heating is a cause for concern. These elements are well-known to be toxic and in addition to their presence in air, it is likely that ashes from fires contain even higher concentrations of these elements. Reducing these emissions, and those of particles in general, is critical for ensuring positive health outcomes for local residents.

The origins of the secondary sulphate and nitrate source could be investigated further to identify whether they are anthropogenic or natural in origin. If they are anthropogenic, it could be possible to manage them so that their effect on air quality in Tokoroa is minimised.

Yours sincerely



Travis Ancelet  
Scientist



Perry Davy  
Senior Scientist

#### 4.0 REFERENCES

- Ancelet, T., Davy, P.K., Trompeter, W.J., Markwitz, A., Weatherburn, D.C., 2011. Carbonaceous aerosols in an urban tunnel. *Atmospheric Environment* 45, 4483–4489. doi:10.1016/j.atmosenv.2011.05.032
- Ancelet, T., Davy, P.K., Mitchell, T., Trompeter, W.J., Markwitz, A., Weatherburn, D.C., 2012. Identification of Particulate Matter Sources on an Hourly Time-Scale in a Wood Burning Community. *Environmental Science & Technology* 46, 4767–4774. doi:10.1021/es203937y
- Carlaw, D.C., Hopkins, K., 2012. *openair* - An R package for air quality data analysis. *Environmental Modeling Software* 27-28, 52–61. doi:10.1016/j.envsoft.2011.09.008
- Davy, P.K., Ancelet, T., Trompeter, W.J., Markwitz, A., Weatherburn, D.C., 2012. Composition and source contributions of air particulate matter pollution in a New Zealand suburban town. *Atmospheric Pollution Research* 3, 143–147. doi:10.5094/APR.2012.014
- Khalil, M. A. K., Rasmussen, R. A., 2003. Tracers of wood smoke. *Atmospheric Environment* 37 (9–10), 1211–1222.
- Kolaitis, L.N., Bruynseels, F.J., Van Grieken, R.E., Andreae, M.O., 1989. Determination of methanesulfonic acid and non-sea-salt sulfate in single marine aerosol particles. *Environmental Science & Technology* 23, 236–240.
- Paatero, P., Tapper, U., 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* 5, 111–126.
- Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis. *Chemometrics and Intelligent Laboratory Systems* 37, 23–35.
- Song, X.-H., Polissar, A.V., Hopke, P.K., 2001. Sources of fine particle composition in the northeastern US. *Atmospheric Environment* 35, 5277–5286.
- Watson, J. G., Chow, J. C., Frazier, C. A., 1999. X-ray Fluorescence Analysis of Ambient Air Samples, in *Advances in Environmental, Industrial and Process Control Technologies* 1, 139–196.