Compositional analysis of airborne particulate matter samples associated with 6 December 2019 NESAQ PM_{10} exceedance

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On 6 December 2019, air quality monitoring stations across Auckland recorded elevated concentrations of airborne particulate matter, with three sites (Penrose, Papatoetoe and Patumahoe) exceeding the PM_{10} (24-hour average) National Environmental Standards for Air Quality (50 µg m^{-3}). The pan-Auckland impact suggested that this was a regional event and not due to local particulate emission sources, particularly considering that the rural background site at Patumahoe was similarly affected to the more urbanised monitoring stations. Monitoring data showed that PM_{10} concentrations were significantly higher than $PM_{2.5}$, indicating that the primary driver was likely to be a coarse particle ($PM_{10–2.5}$) source. The compositional analysis of filter-based samples of particulate matter collected at Penrose and Patumahoe immediately before, during and after the particulate matter event indicated that the particulate matter was largely composed (75%) of crustal material. This data, coupled with the colour of the samples (orange), analysis of meteorological and air mass transport mechanisms and reference to a previously recorded incursion, have led to the conclusion that the PM_{10} exceedances on 6 December 2019 at the Penrose, Patumahoe and Papatoetoe air quality monitoring sites was largely due to an Australian dust (crustal matter) event with some (lesser) impact also from Australian bushfire smoke.

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1.0 INTRODUCTION

On 6 December 2019, three Auckland Council air quality monitoring sites registered PM_{10} concentration (24-hour average) exceedances of the National Environmental Standards for Air Quality (NESAQ) of 50 µg m^{-3}. The elemental composition of airborne particulate matter samples collected onto filters from these sites has been analysed in order to determine the primary source(s) responsible for the high PM_{10} concentrations. In addition, the meteorological factors that may have contributed to the event have also been assessed. The following sections of this report present a description of the samples and sampling sites, the analytical methodology, and results, along with a conclusion of the source(s) contributing to the PM_{10} exceedance.

1.1 Auckland Council Air Quality Monitoring Sites and Particulate Matter Concentrations

The Auckland Council air quality monitoring network (Figure 1.1) consists of multiple sites located across the Auckland region. Particulate matter samples of $PM_{2.5}$ (includes all particles less than 2.5 micrometres in diameter) and PM_{10} (includes all particles less than 10 micrometres in diameter)[1] have been collected onto Teflon filters at a subset of the air quality monitoring sites for compositional analysis since mid-2004 (Davy and Trompetter 2019). The Auckland air quality monitoring network is operated for Auckland Council by Mote Limited as part of the Council's ambient air quality monitoring programme.

Figure 1.1 Auckland Council air particulate matter sampling sites (○) with PM_{10} NESAQ exceedances recorded at (●) (Map source: Auckland Council).

[1] By definition, $PM_{2.5}$ is a subset of PM_{10}.

Particulate matter concentrations measured at Auckland Council sites immediately before, during and after the PM_{10} exceedance event on 6 December 2019 show that PM_{10} and $PM_{2.5}$ concentrations (Figure 1.2) were highly correlated, including the background site at Patumahoe (near Pukekohe), 40 km southwest of the Auckland CBD. Only three of the Auckland Council sites (Penrose, Papatoetoe and Patumahoe) actually exceeded the PM_{10} (24-hour average) NESAQ (50 µm m^{-3}). However, the degree of correlation between sites suggests that particulate matter concentrations were reasonably homogeneous in the airmass across the entire region indicating that sources localised to each monitoring site were unlikely to be responsible, particularly since the Patumahoe site is classified as a rural background air quality monitoring station and is not subject the same PM source pressures (e.g. motor vehicle, domestic and industrial emissions) experienced by the more urban sites (Davy et al. 2012). It was notable that $PM_{2.5}$ concentrations only contributed about 30–35% of total PM_{10} mass at Penrose and Patumahoe for the exceedance day, as this suggests that a coarse particle ($PM_{10–2.5}$) source may have been primarily responsible for the high PM_{10} concentrations. This observation was consistent for all three sites where both $PM_{2.5}$ and PM_{10} were collected.

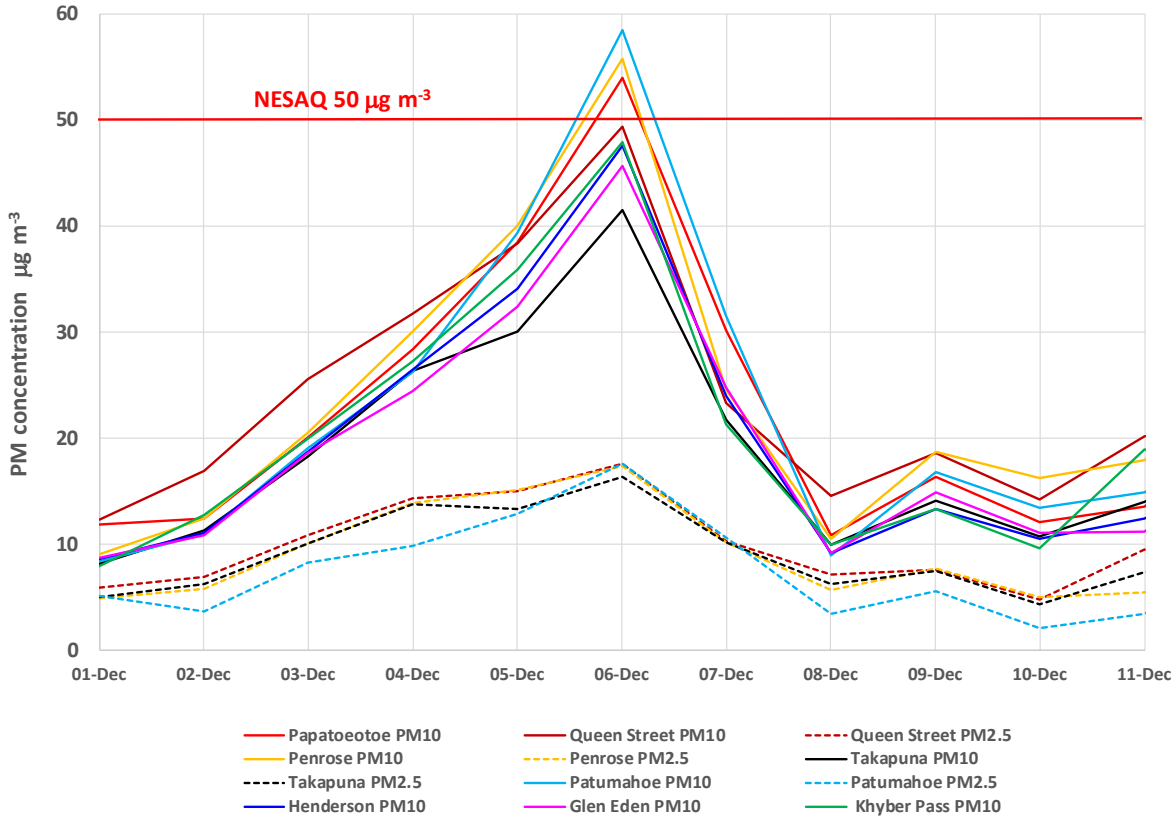

Figure 1.2 PM_{10} and $PM_{2.5}$ at Auckland Council air particulate matter sampling sites from 1 to 11 December 2019.

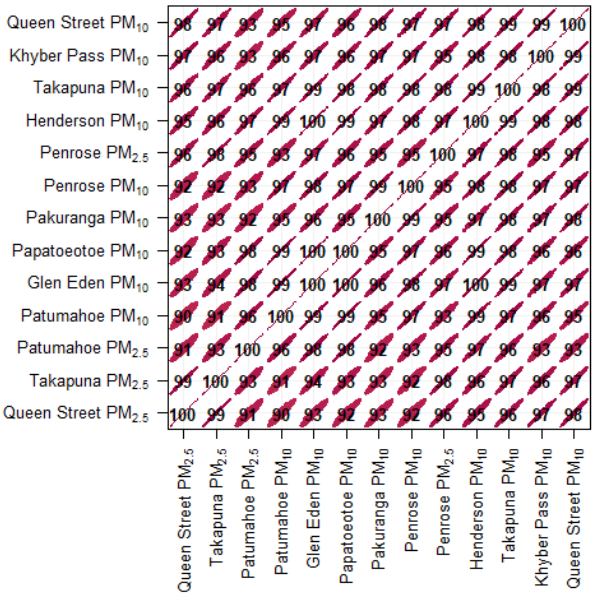

Figure 1.3 Highly correlated PM_{10} and $PM_{2.5}$ concentrations at Auckland Council air particulate matter monitoring sites from 1 to 11 December 2019.

1.2 Particulate Matter Samples Collected for Compositional Analysis

Compositional analysis of PM collected on filters provides information on the sources or source types contributing to total PM concentrations, a valuable tool for air quality management. Since there were no routine PM speciation samples collected during the PM_{10} exceedance event on 6 December, we have analysed the composition of PM collected onto the glass-fibre filter tapes used by the Beta Attenuation Monitor (BAM) systems for routine continuous PM monitoring at the Auckland Council air quality monitoring sites. Samples of BAM PM_{10} glass-fibre filter tape from the sites that exceeded the PM_{10} NESAQ were provided by Mote Limited; additionally, BAM $PM_{2.5}$ tape samples were also provided from the Penrose and Patumahoe sites. Table 1.1 presents the details for the samples that were analysed.

Table 1.1 Auckland air particulate matter sample details.

AQMS Site	Location	Sampling Dates	Sample Period	Sampler Type	PM Size Fraction	Filter Type
Penrose	Lat: -36.9021; Long: 174.8157	01 to 11 December 2019	24-hours	BAM	PM_{10}	Glass fibre (BAM tape)
		06 to 11 December 2019	8-hours	BAM	$PM_{2.5}$	Glass fibre (BAM tape)
Papatoetoe	Lat: -36.9691; Long: 174.8363	01 to 11 December 2019	24-hours	BAM	PM_{10}	Glass fibre (BAM tape)
Patumahoe	Lat: -37.2046; Long: 174.8638	01 to 11 December 2019	24-hours	BAM	PM_{10}	Glass fibre (BAM tape)
			8-hours	BAM	$PM_{2.5}$	Glass fibre (BAM tape)

2.0 ANALYTICAL METHODOLOGY AND RESULTS

Black carbon (BC) concentrations were measured in the particulate matter samples at GNS Science using the light reflectance method. X-ray fluorescence spectroscopy (XRF) was used to measure elemental concentrations in the particulate matter samples. XRF measurements in this study were carried out at the GNS Science XRF facility, and the spectrometer used was a PANalytical Epsilon 5 (PANalytical, the Netherlands). XRF is a non-destructive and relatively rapid method for the elemental analysis of particulate matter samples. For quality assurance purposes, elemental calibration standards were used for all reported elemental concentrations (Hyslop et al. 2019). Further details of the BC and XRF analytical methodologies are provided in Davy and Trompetter (2019). Tables 2.1 and 2.2 present the results for BC and elemental concentrations that were above the analytical limits of detection in the PM_{10} and $PM_{2.5}$ samples, respectively. Note that the elemental concentration data have been blank subtracted. A key limitation in the use of glass-fibre filter media for compositional analysis of collected PM is that the filters are relatively thick (200–500 µm) and have a high elemental background of silicon and alkali-earth metals (Na, Mg, Ca, K) and Zn, which precludes the extraction of any useful data for these elements. The thickness of the glass-fibre filter also results in attenuation (internal absorption) of X-rays, particularly those associated with the lighter elements. However, despite these limitations, useful PM compositional data has been extracted from glass-fibre filters in New Zealand studies (Davy and Ancelet 2014) and overseas (Watson et al. 2012; Raja et al. 2017).

Table 2.1 Concentrations of key elemental components of PM_{10} air particulate matter samples from Auckland Council air quality monitoring stations.

		Papatoetoe (11 Samples)			Patumahoe (11 Samples)			Penrose (11 Samples)		
	Unit	**Average**	**Max**	**# Samples>LOD**	**Average**	**Max**	**# Samples>LOD**	**Average**	**Max**	**# Samples>LOD**
PM_{10}	**µg m^{-3}**	20	54	-	22	58	-	23	56	-
BC	**ng m^{-3}**	641	1151	10	532	1157	11	761	1256	11
Na	**ng m^{-3}**	194	582	6	331	695	10	206	670	8
Mg	**ng m^{-3}**	52	103	11	70	99	11	56	81	11
S	**ng m^{-3}**	132	385	9	168	328	11	132	263	10
Cl	**ng m^{-3}**	1319	2891	11	1596	2976	11	1522	3211	11
Ti	**ng m^{-3}**	67	138	9	44	132	7	44	164	7
Fe	**ng m^{-3}**	306	1124	11	346	1159	11	379	1152	11

Table 2.2 Concentrations of key elemental components of $PM_{2.5}$ air particulate matter samples from Auckland Council air quality monitoring stations.

		Patumahoe (33 Samples)			Penrose (17 Samples)		
	Unit	**Average**	**Max**	**# Samples>LOD**	**Average**	**Max**	**# Samples>LOD**
$PM_{2.5}$	**µg m-3**	8	22	-	-	-	-
BC	**ng m-3**	584	1509	33	854	1796	17
Na	**ng m-3**	40	251	7	51	285	3
Mg	**ng m-3**	20	47	27	26	52	16
S	**ng m-3**	17	163	9	112	242	17
Cl	**ng m-3**	214	875	30	323	1133	16
Ti	**ng m-3**	34	293	7	69	201	8
Fe	**ng m-3**	42	231	14	105	301	16

In order to compare the relationship between the range of analytes measured in the PM and the total PM mass, a mass reconstruction approach was used based on geochemical principles (Cahill et al. 1989; Cohen 1999; Malm et al. 1994) with methodological details provided in Davy et al. (2017).

The key point for the mass comparison is that measured elemental mass should correlate with total PM mass to confirm that the measured components are sufficient to describe the system. Figure 2.1 presents the mass comparison between measured elemental mass and the PM_{10} mass at each of the Auckland Council sites that exceeded the NESAQ on 6 December 2019.

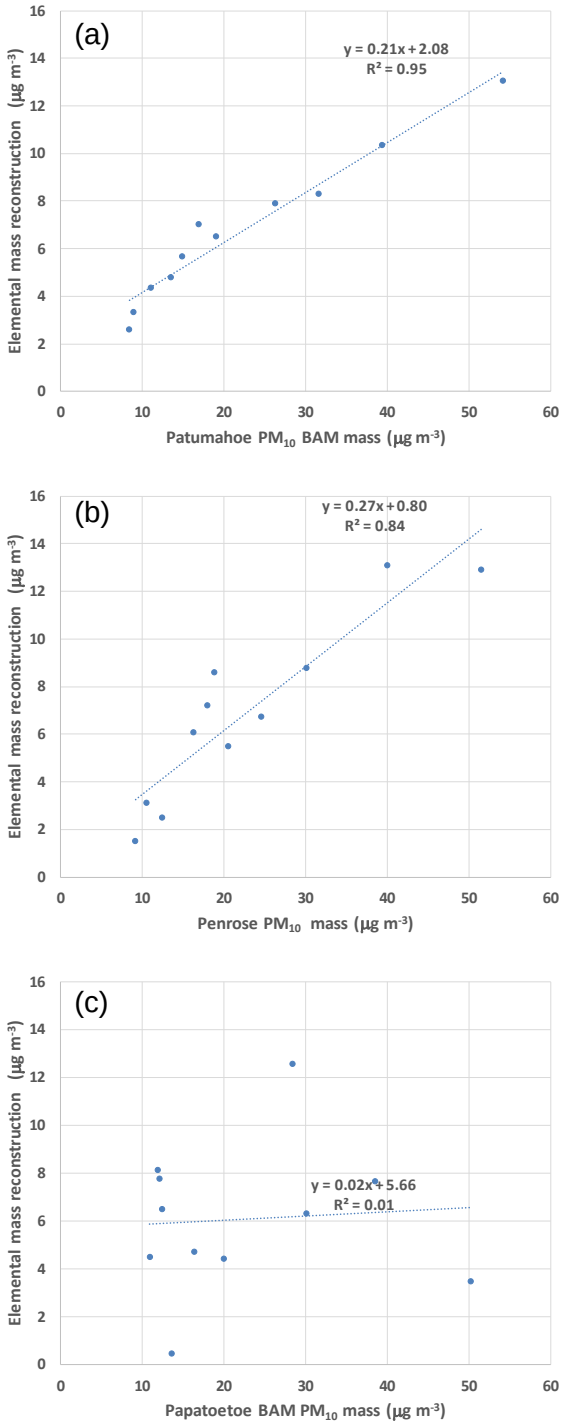

Figure 2.1 Elemental mass composition of air particulate matter samples compared to PM_{10} mass for (a) Patumahoe, (b) Penrose and (c) Papatoetoe.

Measured elemental mass and PM_{10} mass concentrations were found to be well correlated at Patumahoe and Penrose but not for Papatoetoe. Closer inspection of the data and visual appearance of the BAM tape samples (Figure 2.2) suggests that the Papatoetoe sample sequence did not correspond with those from Penrose and Patumahoe. In normal operation, the BAM tape advances once every 24 hours for PM_{10} mass concentration measurements (and once every 8 hours for $PM_{2.5}$). However, other factors, such as filter back-pressure, can result in tape advances at arbitrary times so that associating a date and time with a particular PM sample spot can easily get out of sequence (the BAM tape spots are not individually date/time-stamped by the instruments).

Another key feature of the visual appearance of the PM_{10} BAM tape samples was the orange colour around the PM_{10} exceedance date (Figure 2.2). The orange colouration was not particularly evident for the corresponding $PM_{2.5}$ BAM tape samples.

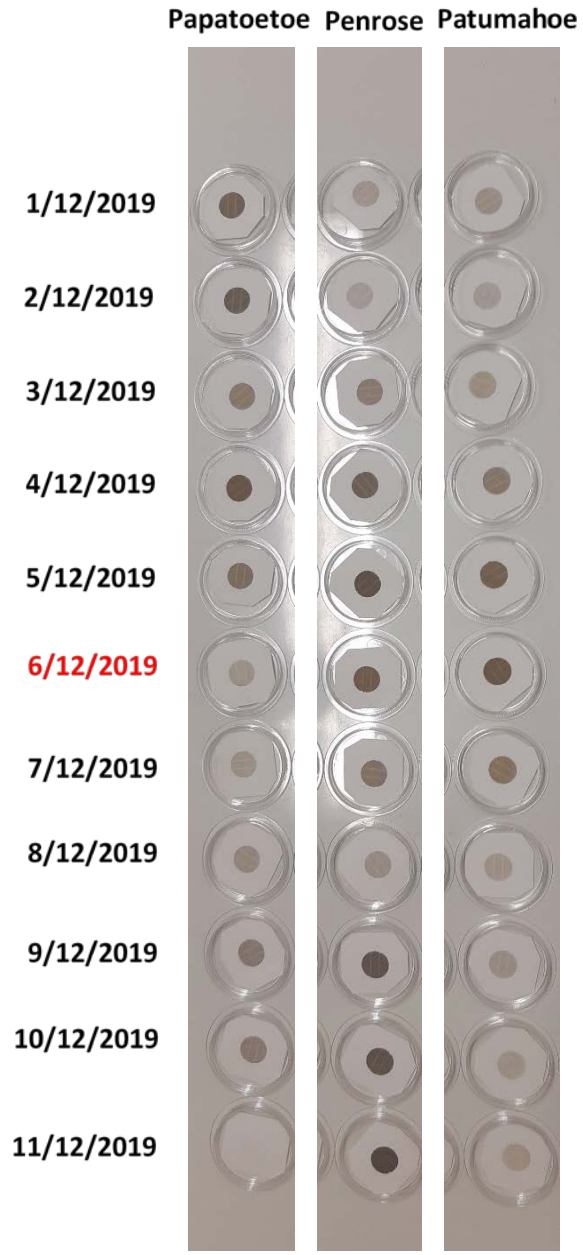

Figure 2.2 Visual appearance of PM_{10} BAM tape air particulate matter samples for (a) Patumahoe, (b) Penrose and (c) Papatoetoe.

When the elemental concentrations measured in the BAM tape samples were compared, it was found that individual elements were highly correlated between the sites and that two specific groupings were evident, as shown in the clustered correlation plot (Figure 2.3). Note that the Penrose $PM_{2.5}$ elemental concentrations have been excluded because the $PM_{2.5}$ BAM tape samples were only available for December 6 onwards (Table 1.1) and that Papatoetoe PM_{10} elemental concentrations were excluded due to the date sequencing disparity described above (the elemental associations were internally consistent within the Papatoetoe samples). The two groupings were the association of Na and Cl, representing a marine aerosol component (sea salt) and the other grouping of BC, PM, S, Fe and Ti concentrations representing combustion sources (BC) and crustal matter (Fe, Ti, S) and secondary sulphate aerosol (S). These source components and their origins are described in Davy et al. (2017).

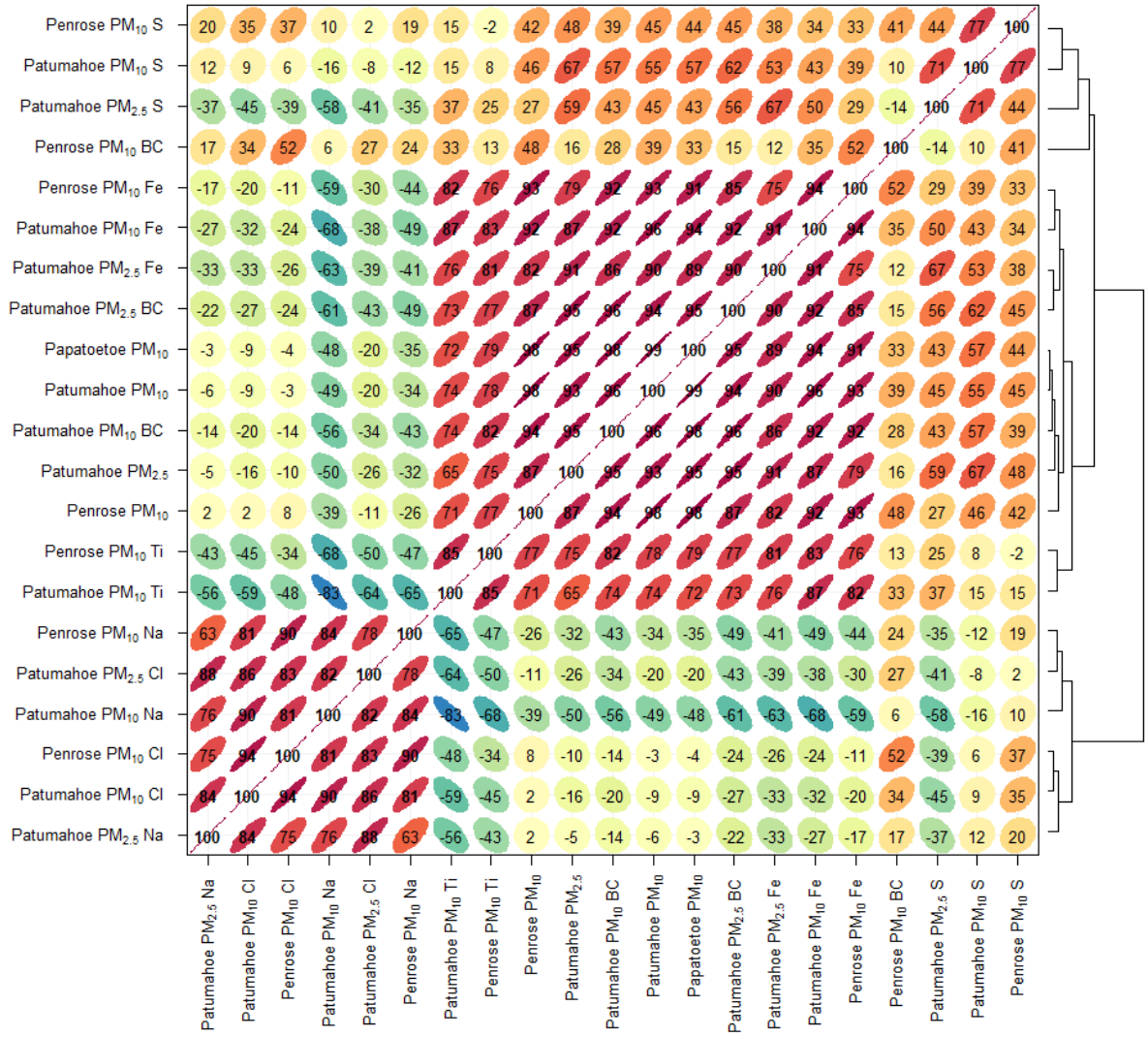

Figure 2.3 Clustered correlation plot for key components of PM_{10} and $PM_{2.5}$ BAM tape air particulate matter samples. The percentage correlation (r^2) is provided by the numerical values, while highly positively correlated variables are marked as red ellipsoids and strongly anti-correlated variables are highlighted as blue ellipsoids.

3.0 DISCUSSION

As shown in Figure 1.1, continuous $PM_{2.5}$ and PM_{10} monitoring data from the Auckland Council AQMS indicates that PM concentrations began rising on 2 December 2019 at all stations and culminated in peak concentrations on 6 December, with NESAQ PM_{10} exceedances at three sites (Papatoetoe, Penrose and Patumahoe) that decreased to what would be considered normal concentrations in the days thereafter. The elemental concentration (24-hour average) data for Penrose and Patumahoe, graphed alongside PM_{10} and $PM_{2.5}$ concentrations (Figure 3.1), shows how each of the components varied over time. Chlorine concentrations, (representing sea salt) peaked on 4 and 9 December at both sites, whereas Fe (representing crustal matter) and BC (representing combustion) increased from 2 December and peaked on 6 December at the same time as PM concentrations.

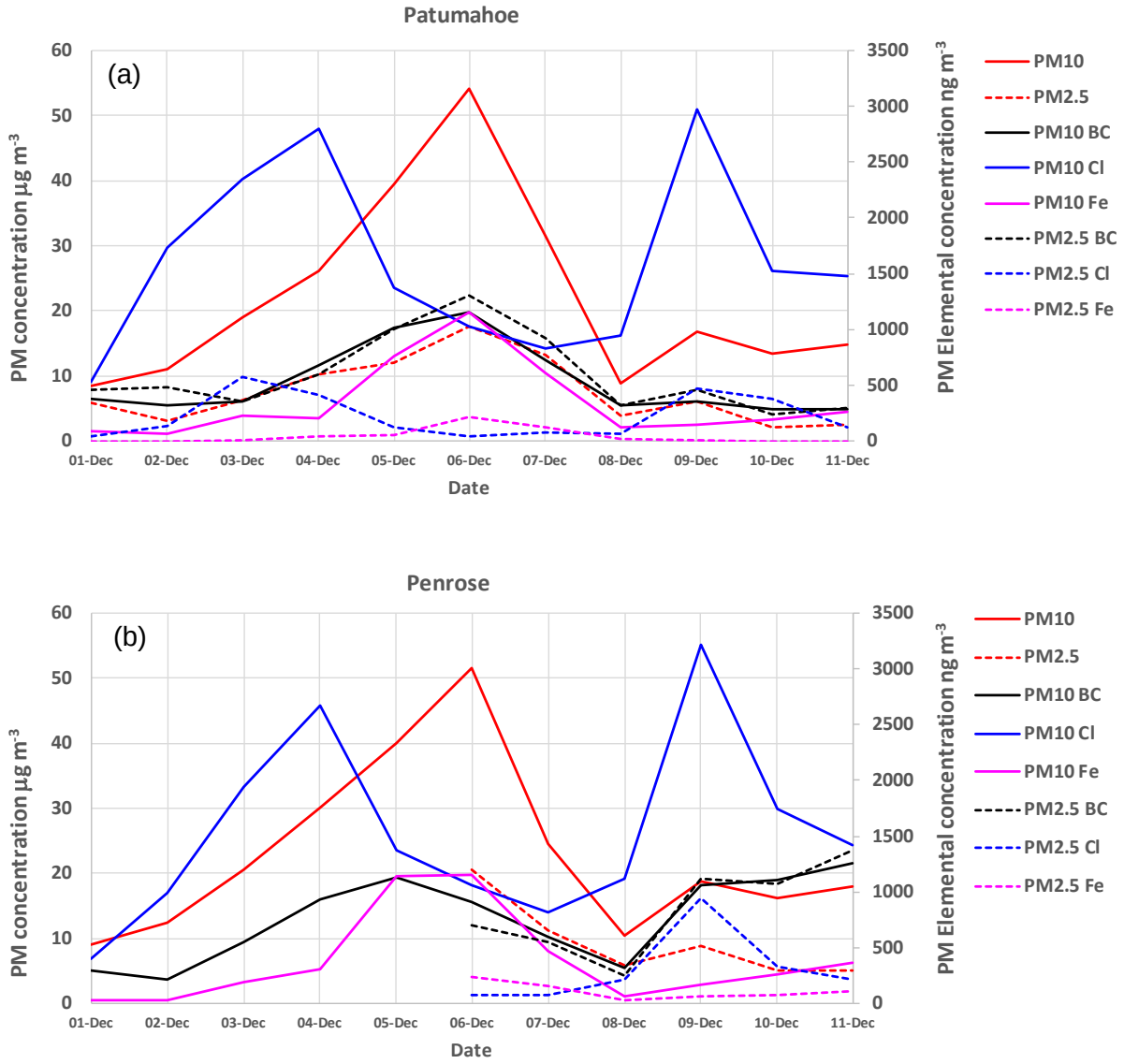

Figure 3.1 $PM_{2.5}$ and PM_{10} concentrations and key elemental components from the (a) Patumahoe and (b) Penrose monitoring sites.

Several features can be observed for the data:

1. BC concentrations are the same in PM_{10} as for $PM_{2.5}$ as BC is a sub-micron particulate matter component released during the combustion of fuels (Davy and Trompetter 2017).
2. Fe concentrations are much higher in PM_{10} than $PM_{2.5,}$ and this represents the crustal matter contribution (a predominantly coarse particle [$PM_{10–2.5}$] source).
3. Cl concentrations are also higher in PM_{10} than $PM_{2.5}$ and represents the marine aerosol (sea salt) contribution.

3.1 Meteorological Influences

Meteorological data for the Patumahoe, Penrose and Papatoetoe sites shows that local winds were light and blowing from the northeast to northwest sectors (likely to be influenced by topographical features) on 6 December 2019, as presented in Figure 3.2.

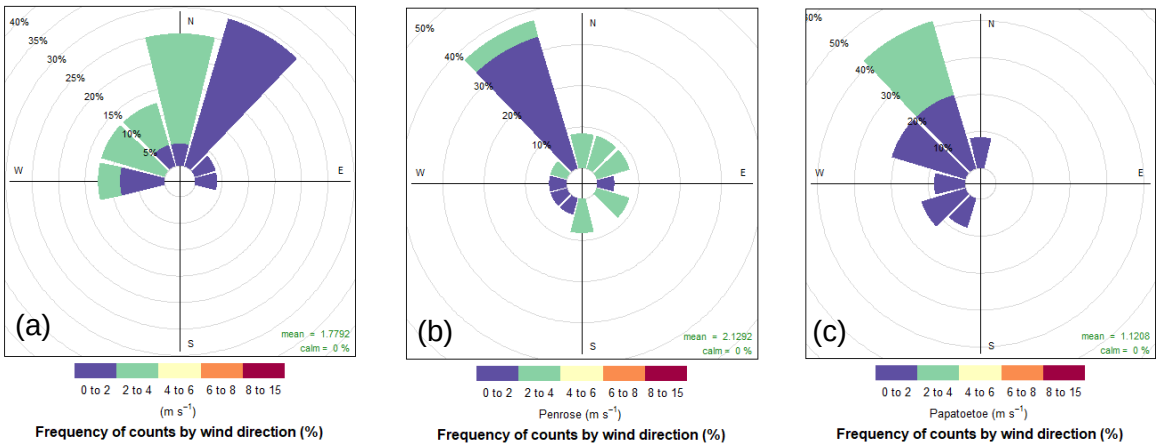

Figure 3.2 Wind roses showing wind speed and direction on 6 December for the (a) Patumahoe and (b) Penrose monitoring sites.

The synoptic mean sea-level pressure (MSLP) maps (Figure 3.3) over the period indicate a large area of low pressure beneath Tasmania and an area of high pressure to the northeast of New Zealand, with a ridge extending over Auckland. However, these two features were also directing a north-westerly outflow from Australia across the Tasman Sea.

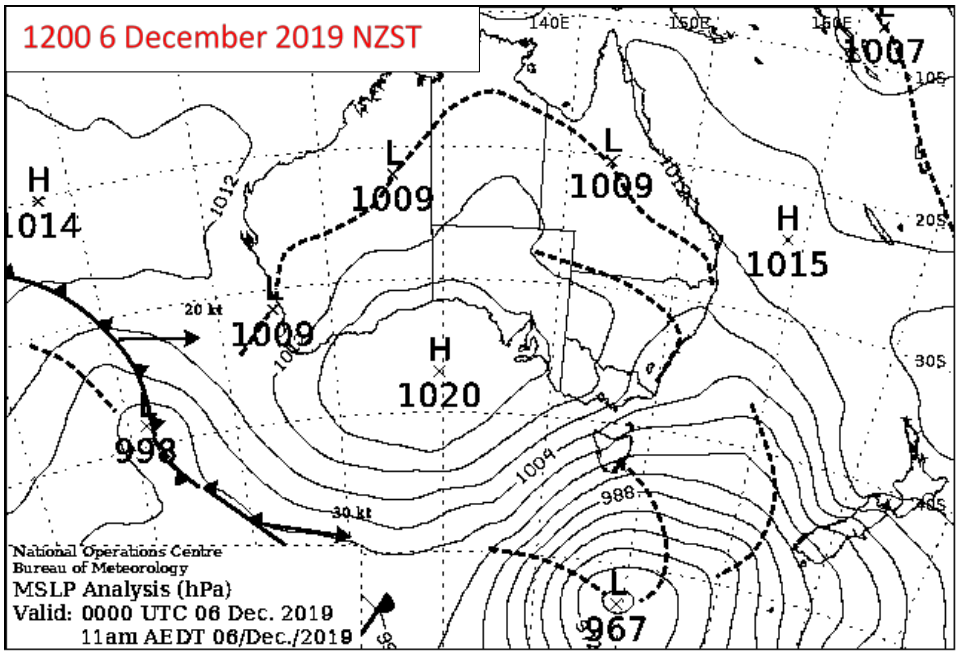

Figure 3.3 Synoptic MSLP map for midday (NZST) 6 December (Source: Australian Bureau of Meteorology).

Satellite imagery (Figure 3.4) also shows that smoke from the bushfires in New South Wales and Victoria was being carried over the Tasman sea in the north-westerly outflow.

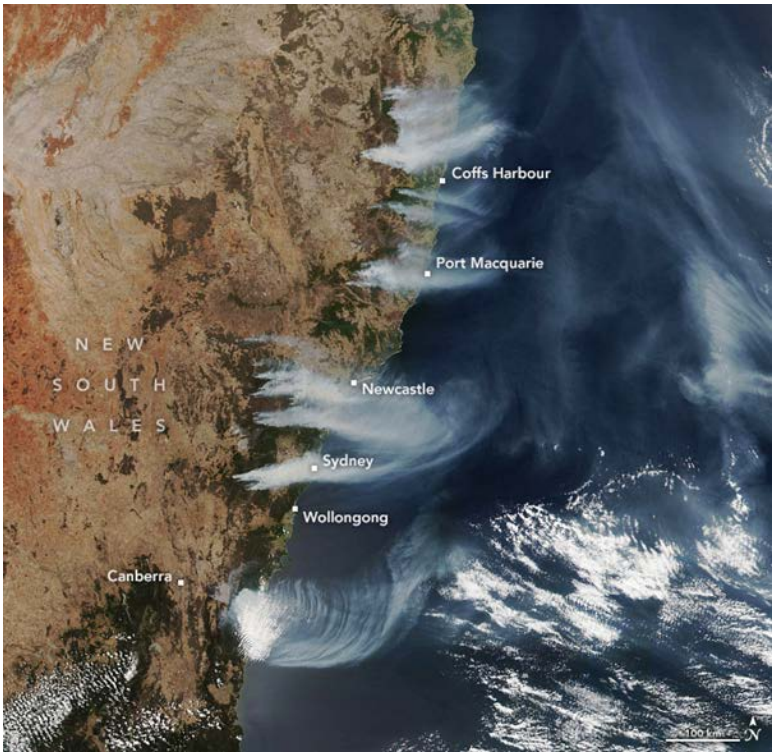

Figure 3.4 Satellite image 4 December 2019 (Source: NOAA MODIS).

When air mass back trajectories were calculated using HYSPLIT (https://www.ready.noaa.gov/HYSPLIT.php) they show that at ground level (10 m) on 6 December in Auckland the air mass was arriving out of the northerly sector (Figure 3.5) in line with the local wind data (Figure 3.2). However, at 2 km altitude above Auckland, the air mass was arriving out of the northwest (Figure 3.6) having passed over New South Wales, Australia.

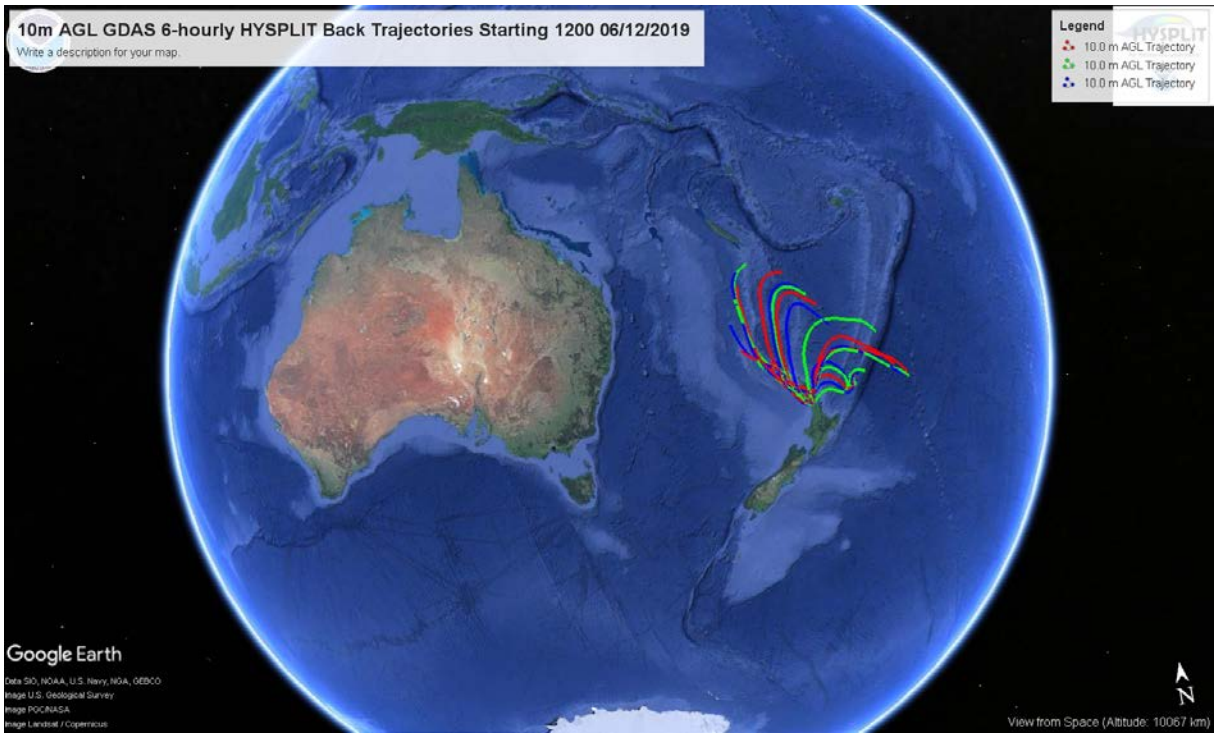

Figure 3.5 HYSPLIT air mass back trajectories starting at ground level (10 m) in Auckland at 12:00 on 6 December 2019. The trajectories run backwards for 96 hours (4 days) from the central Auckland starting point.

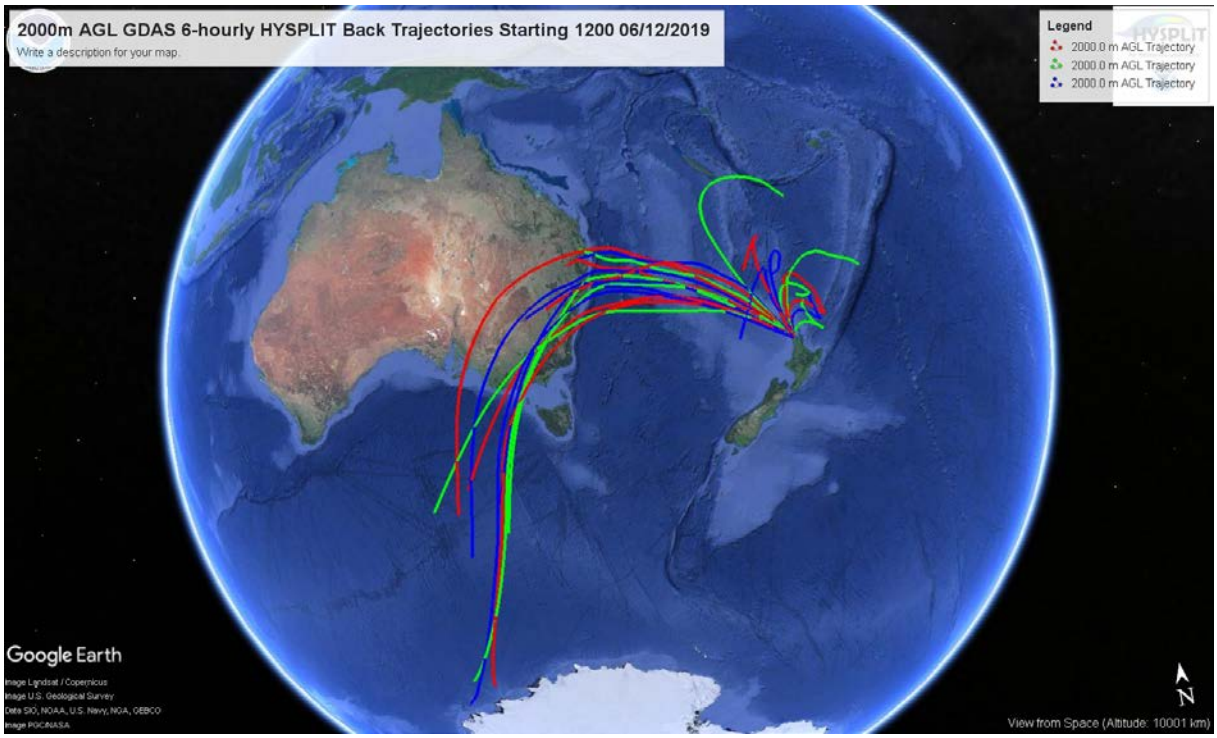

Figure 3.6 HYSPLIT air mass back trajectories starting 2 km above Auckland at 12:00 on 6 December 2019. The trajectories run backwards for 96 hours (4 days) from the central Auckland starting point.

3.2 Estimating Source Contributions to PM Concentrations on 6 December 2019

It is evident that the PM_{10} exceedance on 6 December 2019 at the Auckland Council air quality monitoring sites was likely caused by a regional transboundary particulate matter transport event. Satellite evidence shows smoke from Australian bushfires being carried out over the Tasman Sea and New Zealand. The bushfire smoke explains the regional rise in BC and $PM_{2.5,}$ as measured at the Auckland Council air quality monitoring sites, to peak on 6 December 2019 but not the predominance of the coarse fraction (70% of the PM_{10} exceedance). The key to this was the colour of the PM_{10} samples (orange) and the high crustal matter content as represented by Fe and Ti. By applying geochemical principles, the relative contribution of source types to PM_{10} concentrations on 6 December 2019 can be calculated. Figure 3.7 presents the relative source contributions to PM_{10} estimated for Patumahoe and Penrose. Note that the unquantified (remainder) amount of PM_{10} has been labelled as 'Other'. It is likely that this remaining PM_{10} was associated with the transboundary event (*cf* the correlation of the measured elemental mass with PM_{10} at Penrose and Patumahoe), most likely as combustion products (associated with the BC) such as organic and secondary organic carbonaceous species not measured by XRF.

A previous transboundary PM exceedance event for the Auckland region on 24 and 25 September 2009 (the filter samples were also orange) was shown to be the result of Australian crustal matter transported across the Tasman Sea after a large dust storm in the Lake Eyre region of central Australia (Davy et al. 2011). PM_{10} concentrations due to the soil component (≈ 40 μm^{-3}) for the 2009 event were very similar to those calculated here, as were the total iron concentrations measured in those 2009 samples.

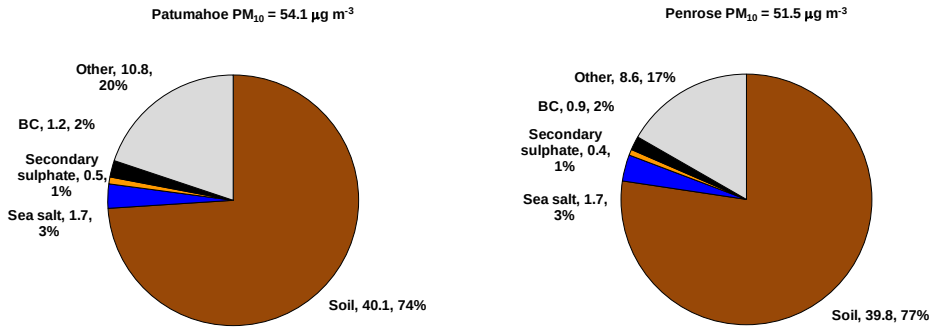

Figure 3.7 Estimated source contributions to PM_{10} at Patumahoe and Penrose on 6 December 2019.

The mechanism for the uplift of crustal matter along with the bushfire smoke has yet to be determined, but two scenarios are possible:

1. That the extremely large area of conflagration and resulting atmospheric turbulence also entrained crustal matter to be transported across the Tasman;
2. That particulate matter from an Australian dust storm has become mixed with the bushfire smoke and then transported across the Tasman.

There were a number of dust storms in the Australian desert around the same time as the bushfires, generated by the hot northwest winds that were fanning the flames of the bushfires. Figure 3.8 presents a satellite image for 2 December 2019 (UTC) showing a large area dust storm in northern New South Wales, while Figure 3.9 presents a satellite image for 6 December 2019 (UTC) showing this dust mixed with bushfire smoke being carried across the Tasman Sea to New Zealand.

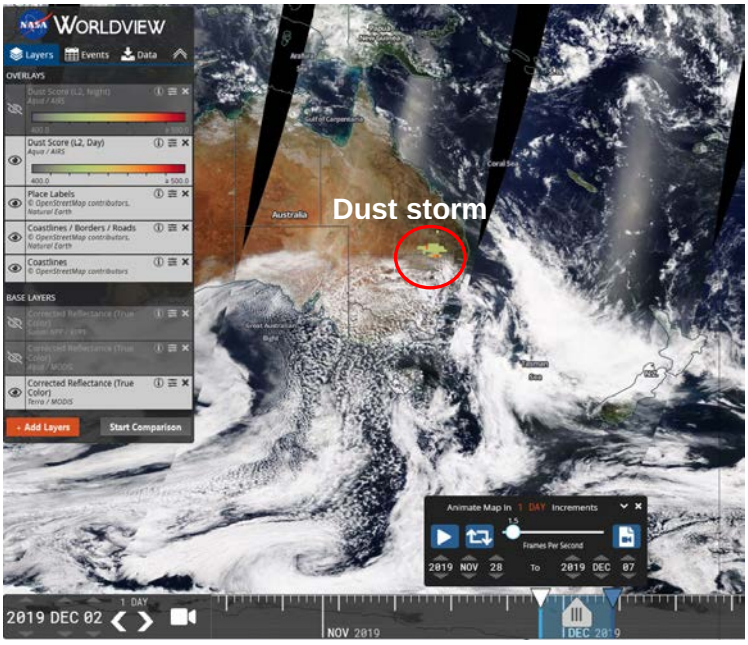

Figure 3.8 Satellite image for 2 December 2019 (UTC) showing a large area dust storm in northern New South Wales. Source https://worldview.earthdata.nasa.gov.

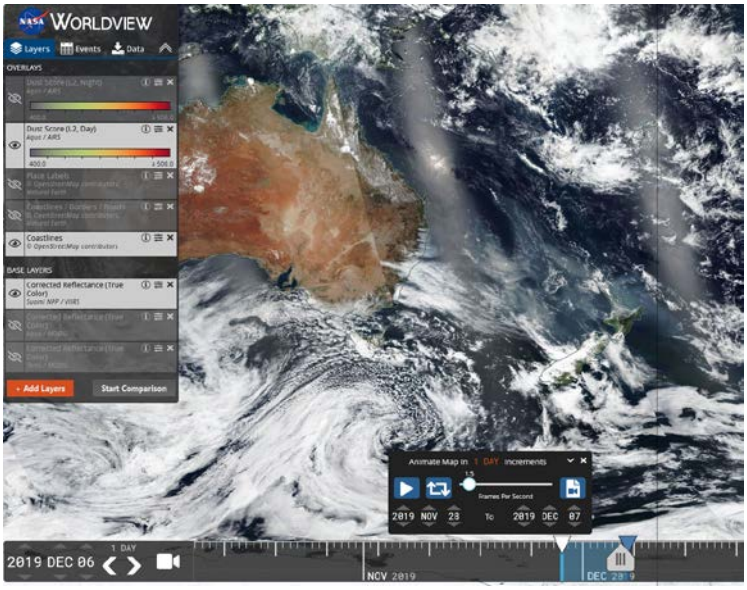

Figure 3.9 Satellite image for 6 December 2019 (UTC) showing dust mixed with bushfire smoke being carried across the Tasman Sea to New Zealand. Source https://worldview.earthdata.nasa.gov.

The relative difference between the coarse particle crustal matter and the fine bushfire particulate matter impact at ground level in Auckland can be explained by the preferential gravitational settling of the heavier crustal matter out of the atmosphere as the airmass passed over Auckland, while the finer particles remained suspended and were transported out over the Pacific Ocean.

4.0 CONCLUSION

On 6 December 2019 air quality monitoring stations across Auckland recorded elevated concentrations of airborne particulate matter, with three sites (Penrose, Papatoetoe and Patumahoe) exceeding the PM_{10} (24-hour average) NESAQ (50 µg m^{-3}). The pan-Auckland impact suggested that this was a regional event and not due to local particulate emission sources, particularly considering that the rural background site at Patumahoe was similarly affected to the more urbanised monitoring stations. Monitoring data showed that PM_{10} concentrations were significantly higher than $PM_{2.5}$, indicating that the primary driver was likely to be a coarse particle ($PM_{10–2.5}$) source. The compositional analysis of filter-based samples of particulate matter collected at Penrose and Patumahoe immediately before, during and after the particulate matter event indicated that the particulate matter was largely composed (75%) of crustal material. This data, coupled with the colour of the samples (orange), analysis of meteorological and air mass transport mechanisms and reference to a previously recorded incursion, have led to the conclusion that the PM_{10} exceedances on 6 December 2019 at the Penrose, Patumahoe and Papatoetoe air quality monitoring sites was largely due to an Australian dust (crustal matter) event with some (lesser) impact also from Australian bushfire smoke.

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