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Dear Nick,

Compositional analysis of airborne particulate matter samples associated with the New Zealand International Convention Centre fire

As requested, we have analysed the elemental composition of airborne particulate matter samples collected onto filters at the Queen Street central Auckland air quality monitoring site. In addition, we have also analysed the composition of an airborne particulate matter sample collected by Dr Joel Rindelaub (Research Fellow at the School of Chemical Sciences, University of Auckland), adjacent to the Sky City complex overnight on 22–23 October 2019. We present a description of the samples and sampling sites, the analytical methodology and results, along with a brief contextual review in terms of other combustion sources and the contaminants produced therein.

1.0 SAMPLES AND SAMPLING SITES

The Auckland Council (AC) Queen Street air quality monitoring station is located on a veranda over the footpath 4 m above Queen Street and was established in 1995. Particulate matter samples (denoted as PM₁₀ and includes all particles less than 10 micrometres in diameter) have been collected at the site for compositional analysis since late 2005 (Davy and Trompetter 2019). The Queen Street site is currently operated by Mote Limited for AC as part of the AC ambient air quality monitoring programme. The Auckland University total suspended particulate matter sample (denoted as TSP and includes all airborne particles) was collected opportunistically in a carpark adjacent to the Sky City complex. Figure 1.1 shows a map of the central Auckland sampling locations in relation to the New Zealand International Convention Centre (NZICC).

Two 24-hour Queen Street PM_{10} samples (one collected on 22/10/2019 during the fire, and one from an earlier date for comparison) and a blank filter (Whatman PTFE Membrane Filter, 0.2 µm pore size, 46.2 mm diameter) along with the Auckland University TSP sample and

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blank (FluoroporeTM PTFE Membrane Filter, 0.2 µm pore size, 47 mm diameter) were received at the GNS Science National Isotope Centre by courier from Mote Limited on Monday 4 November. All samples were packaged in individual, labelled petri dishes. We note that the Auckland University sample was only half the filter, as the other half has been retained for additional analyses. The half-filter was sufficient for our analytical purposes. Table 1.1 presents the sampling details with further detail provided in Appendix 1.

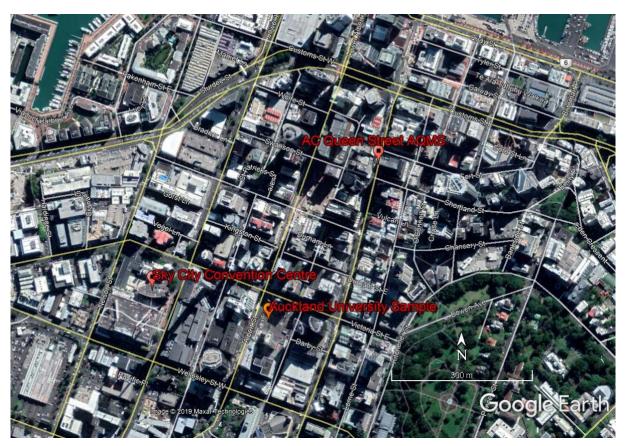


Figure 1.1 Central Auckland air particulate matter sampling sites during the NZICC fire (Map source: Google Earth).

Table 1.1 Central Auckland air particulate matter sampling details during the NZICC fire.

Site	Location	Sampling Date	Time Period	Sampler Type	Volume Sampled (m³)	PM Size Fraction
Queen Street AQMS	Lat: -36.8476; Long: 174.7655	30/09/2019	24-hours	Partisol	22.7	PM ₁₀
Queen Street AQMS	Lat: -36.8476; Long: 174.7655	22/10/2019	24-hours	Partisol	22.5	PM ₁₀
Auckland University SkyCity	Lat: -36.8491; Long: 174.7636	22/10/2019 20:20 to 23/10/2019 06:23	10 hours	SKC PCXR8	2.45	TSP

2.0 ANALYTICAL METHODOLOGY AND RESULTS

Black carbon (BC) concentrations were measured in the particulate matter samples at GNS Science using the light absorption method. X-ray fluorescence spectroscopy (XRF) was used to measure elemental concentrations in the particulate matter samples. Each sample was measured three times to provide a concentration analytical standard deviation. 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). Table 2.1 presents the results for black carbon and elemental concentrations in the central Auckland particulate matter samples that were above the analytical limits of detection. Note that the elemental concentration data have been blank subtracted. A table of the full analytical results is presented in Appendix 1.

Table 2.1 Elemental composition of air particulate matter samples from central Auckland.

	AC	_QueenStre	eet_30/09/20	019	AC	_QueenStr	eet_22/10/20	019	AU_SkyCity_22-23 Oct 2019				
Species	Conc. (ng m ⁻³)	StdDev. (ng m ⁻³)	Uncert. (ng m ⁻³)	LOD (ng m ⁻³)	Conc. (ng m ⁻³)	StdDev. (ng m ⁻³)	Uncert. (ng m ⁻³)	LOD (ng m ⁻³)	Conc. (ng m ⁻³)	StdDev. (ng m ⁻³)	Uncert. (ng m ⁻³)	LOD (ng m ⁻³)	
вс	1233	21	132	158	6498	477	388	159	75547	5482	4988	1463	
Na	1009	15	105	6	1018	19	106	6	3561	147	394	57	
Mg	121	3	17	7	141	10	19	7	821	50	125	64	
Al	126	9	19	10	165	7	23	10	757	58	183	91	
Si	124	10	15	4	169	4	20	4	459	16	73	41	
Р	0	0	1	2	0	0	1	2	88	33	20	16	
s	168	6	22	8	199	3	25	8	2654	192	316	75	
CI	2183	15	219	1	2321	17	233	1	13162	1133	1321	7	
K	72	0	8	2	95	2	11	2	1240	27	135	16	
Са	88	1	10	2	169	1	18	2	229	19	35	17	
Ti	9	1	2	2	8	1	2	2	0	45	10	15	
٧	1	1	0	0	0	0	0	0	33	4	6	3	
Cr	0	1	1	1	1	0	1	1	26	10	12	10	
Mn	4	1	2	2	3	1	2	2	20	8	17	19	
Fe	156	3	19	5	170	1	20	5	22	8	52	45	
Ni	0	1	1	1	0	1	0	1	23	4	6	6	
Cu	6	1	1	1	7	1	2	1	42	10	13	13	
Zn	17	1	2	1	94	1	10	1	4214	30	428	10	
As	0	0	1	1	41	1	5	1	893	13	98	14	

	AC	_QueenStre	eet_30/09/20)19	AC	_QueenStre	eet_22/10/20	019	AU_SkyCity_22-23 Oct 2019			
Species	Conc. (ng m ⁻³)	StdDev. (ng m ⁻³)	Uncert. (ng m ⁻³)	LOD (ng m ⁻³)	Conc. (ng m ⁻³)	StdDev. (ng m ⁻³)	Uncert. (ng m ⁻³)	LOD (ng m ⁻³)	Conc. (ng m ⁻³)	StdDev. (ng m ⁻³)	Uncert. (ng m ⁻³)	LOD (ng m ⁻³)
Br	4	1	1	0	12	2	1	0	1084	36	111	3
Sb	12	2	6	6	19	8	6	6	379	90	74	54
Pb	3	2	2	2	12	8	3	2	69	49	21	21

The Queen Street PM₁₀ sample collected on 30 September 2019 provides a useful comparison for identifying those elements that were significantly higher in the Queen Street sample collected during the fire. The data, as presented in Figure 2.1, shows that these include black carbon, zinc and arsenic. The Auckland University TSP sample, while not directly comparable to the Queen Street PM₁₀ samples as TSP includes all airborne particle size fractions, shows that most elemental concentrations were significantly higher (note the logarithmic scale) than the Queen Street samples.

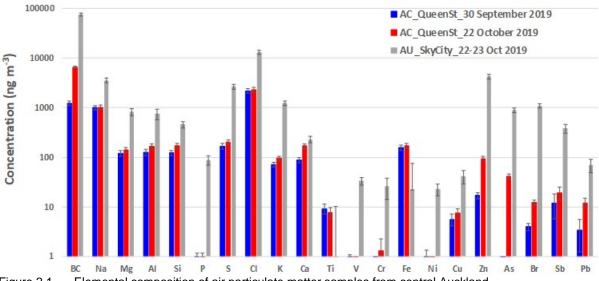


Figure 2.1 Elemental composition of air particulate matter samples from central Auckland

3.0 DISCUSSION

Fire broke out at approximately 13:15 pm on 22 October 2019 at the NZICC construction site in central Auckland. The fire was located in the roof space and quickly spread, involving the combustion of bituminous sealing material, straw used for insulation, wood, and other construction materials. Emissions to atmosphere from the combustion of materials (fuels) include particulate matter (smoke), gases and liquid droplets with the relative mix depending on the type of fuel, the nature of the combustion process and a range of other factors. The composition and size range of the particulate matter produced depends on composition of the material being burnt and the temperature that it burns at. The downwind concentrations of particulate matter emissions from a single large fire, such as the NZICC, depends on factors such as the height of smoke release, wind speed and direction, along with the location and height of a receptor site with respect to the fire.

Continuous $PM_{2.5}$ and PM_{10} monitoring data (Figure 3.1) from the AC Queen Street AQMS shows that there was some elevated but intermittent particulate matter PM_{10} concentrations primarily driven by the smaller $PM_{2.5}$ fraction at the site during the afternoon of 22 October, consistent with a wafting smoke plume. Winds were out of the west-southwest quarter, blowing the smoke from the fire toward the general direction of the lower Queen Street and Auckland downtown area, as shown in the webcam image (Figure 3.2) captured soon after the fire began. As shown in Figure 3.1, the highest PM_{10} concentrations measured at the

Queen Street AQMS occurred from the early hours of 23 October through to about midday of the same day, most likely a combination of peak fire emissions and higher wind speeds pushing the smoke lower to ground level as shown in the webcam image (Figure 3.3) taken just after 10:00 am on 23 October.

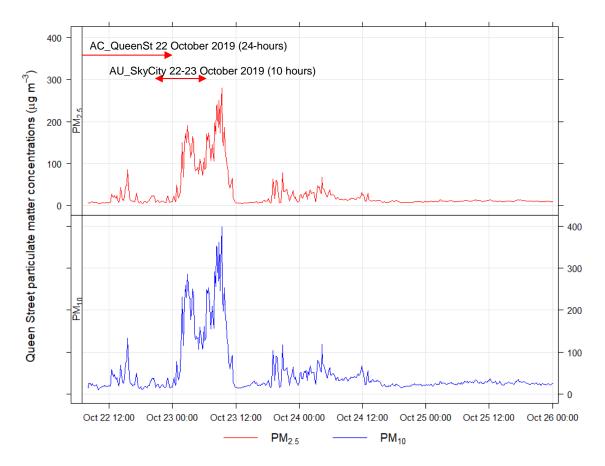


Figure 3.1 Continuous PM_{2.5} and PM₁₀ concentrations from the Queen Street monitoring site. The red arrows show the time period covered by the Auckland Council and Auckland University samples, respectively.



Figure 3.2 Webcam image looking east from the silo marina, captured at 1:17 pm 22 October 2019, showing smoke from the fire blowing across downtown Auckland. The base of the Sky Tower can be seen at top right. (Source: Snaplt webcam Silo Marina, Auckland.)

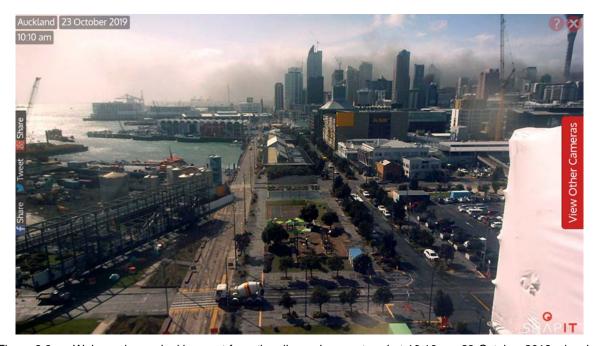


Figure 3.3 Webcam image looking east from the silo marina, captured at 10:10 am 23 October 2019, showing smoke from the fire blowing across downtown Auckland. The base of the Sky Tower can be seen at top right. (Source: Snaplt webcam Silo Marina, Auckland.)

The Queen Street PM_{10} speciation filter sample (22/10/2019), collected on the day that the fire started, would have only collected some of the earlier combustion products from the fire, as sampling stopped at midnight and did not capture those peak PM_{10} concentrations on 23 October. However, the elevated BC, Zn and As concentrations compared to the 30 September sample, shown in Table 2.1 and Figure 2.1, are indicative of combustion products from various materials. Black carbon is a product of incomplete combustion of all fuels (Davy and Trompetter 2017), zinc is associated with the combustion of wood and other fuels, while the arsenic is a key marker for air particulate matter associated with the combustion

of copper chrome arsenate (CCA)-treated timber (Cavanagh et al. 2012, Davy et al. 2014, Davy and Trompetter 2018).

The Auckland University TSP sample collected at a carpark nearer the SkyCity complex has clearly sampled higher concentrations of particulate matter from the fire, as evidenced by the measured elemental concentrations associated with combustion emissions. This sample shows very high concentrations of black carbon (an ultrafine sub-micron particle species), zinc and arsenic, along with other elements (P, V, Ni, Cr, Cu) that are likely to be associated with the combustion of construction materials and the capture of smoke and ash in the sample. The copper and chrome in treated timber are usually retained in the ash while arsenic, a much more volatile metal, is released to the atmosphere during combustion as particulate matter (Helsen and van den Bulck 2004, Helsen et al. 2003). The nickel and vanadium may be associated with the combustion of bituminous material, as both heavy metals are found in crude oils and oil refinery products (Moreno et al. 2010).

4.0 SUMMARY

The composition of two particulate matter samples collected during the NZICC construction site fire in central Auckland show the impact of the combustion products. The Auckland Council Queen Street monitoring site sample collected over 24 hours on the 22 October 2019 shows a lesser but distinct signature, primarily by the presence of elevated black carbon and arsenic, due to the amount of smoke impacting at that monitoring station during the sample period (ending at 23:59 on 22 October 2019). The continuous PM_{2.5} and PM₁₀ monitoring data reflect this with the major impact at the site occurring in the early hours of 23 October through to midday. The TSP sample collected near the SkyCity complex by Dr Joel Rindelaub (AU) from the evening of 22 October through to the morning of 23 October 2019 shows a more substantial impact of combustion emissions, with elevated concentrations of heavy metals such as arsenic, vanadium and nickel, along with other combustion products.

Yours sincerely

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APPENDIX 1: XRF Elemental Analytical Results for the Auckland Council Queen Street and Auckland University samples

	AC	_QueenStre	eet_30/09/20	019	AC	_QueenStre	eet_22/10/20)19	AU_SkyCity_22-23 Oct 2019				
Species	Conc. (ng m ⁻³)	Std Dev. (ng m ⁻³)	Uncert. (ng m ⁻³)	LOD (ng m ⁻³)	Conc. (ng m ⁻³)	Std Dev. (ng m ⁻³)	Uncert. (ng m ⁻³)	LOD (ng m ⁻³)	Conc. (ng m ⁻³)	Std Dev. (ng m ⁻³)	Uncert. (ng m ⁻³)	LOD (ng m ⁻³)	
вс	1233	21	132	158	6498	477	388	159	75547	5482	4988	1463	
Na	1009	15	105	6	1018	19	106	6	3561	147	394	57	
Mg	121	3	17	7	141	10	19	7	821	50	125	64	
AI	126	9	19	10	165	7	23	10	757	58	183	91	
Si	124	10	15	4	169	4	20	4	459	16	73	41	
Р	0	0	1	2	0	0	1	2	88	33	20	16	
S	168	6	22	8	199	3	25	8	2654	192	316	75	
CI	2183	15	219	1	2321	17	233	1	13162	1133	1321	7	
K	72	0	8	2	95	2	11	2	1240	27	135	16	
Ca	88	1	10	2	169	1	18	2	229	19	35	17	
Ti	9	1	2	2	8	1	2	2	0	45	10	15	
V	1	1	0	0	0	0	0	0	33	4	6	3	
Cr	0	1	1	1	1	0	1	1	26	10	12	10	
Mn	4	1	2	2	3	1	2	2	20	8	17	19	
Fe	156	3	19	5	170	1	20	5	22	8	52	45	
Ni	0	0	1	0	0	0	0	0	2	2	4	4	
Cu	0	1	1	1	0	1	0	1	23	4	6	6	
Zn	6	1	1	1	7	1	2	1	42	10	13	13	

	AC	_QueenStre	eet_30/09/20	019	AC	_QueenStre	eet_22/10/20	019	AU_SkyCity_22-23 Oct 2019				
Species	Conc. (ng m ⁻³)	Std Dev. (ng m ⁻³)	Uncert. (ng m ⁻³)	LOD (ng m ⁻³)	Conc. (ng m ⁻³)	Std Dev. (ng m ⁻³)	Uncert. (ng m ⁻³)	LOD (ng m ⁻³)	Conc. (ng m ⁻³)	Std Dev. (ng m ⁻³)	Uncert. (ng m ⁻³)	LOD (ng m ⁻³)	
As	17	1	2	1	94	1	10	1	4214	30	428	10	
Se	0	1	1	1	0	2	1	1	4	13	11	11	
Br	4	1	1	0	12	2	1	0	1084	36	111	3	
Sr	2	1	1	1	2	1	1	1	5	6	13	12	
Мо	0	4	1	2	0	4	1	2	0	10	11	16	
Cd	5	3	9	6	0	4	4	6	0	36	39	58	
Sn	15	3	5	5	10	3	5	5	0	29	29	43	
Sb	12	2	6	6	19	8	6	6	379	90	74	54	
Te	4	5	9	8	4	5	9	8	0	59	50	75	
Cs	0	3	7	11	4	1	11	11	0	83	67	100	
Ва	13	10	24	16	16	5	27	17	0	174	101	152	
La	17	9	11	11	8	11	15	11	110	115	88	99	
Се	0	81	111	167	0	88	112	169	0	1184	1033	1548	
Sm	51	175	123	108	152	79	103	109	0	266	665	997	
Pb	3	2	2	2	12	8	3	2	69	49	21	21	
Hg	0	0	0	1	0	1	0	1	0	0	4	6	
In	0	4	3	5	3	3	7	5	57	51	43	47	
w	0	44	45	67	0	39	45	68	0	1731	415	622	