



## Elemental Composition of Ambient Fine Particles in Urban Schools: Sources of Children's Exposure

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### ABSTRACT

Currently, there is a limited understanding of the sources of ambient fine particles that contribute to the exposure of children at urban schools. Since the size and chemical composition of airborne particle are key parameters for determining the source as well as toxicity, PM<sub>1</sub> particles (mass concentration of particles with an aerodynamic diameter less than 1 µm) were collected at 24 urban schools in Brisbane, Australia and their elemental compositions determined. Based on the elemental compositions four main sources were identified; secondary sulphates, biomass burning, vehicle and industrial emissions. While secondary sulphates were likely to be a large contributing source by mass, industrial emissions accounted for the most variation in trace metals in the PM<sub>1</sub> that children were exposed to at the schools. PM<sub>1</sub> concentrations at the schools were compared to the elemental composition of the PM<sub>2.5</sub> particles (mass concentration of particles with an aerodynamic diameter less than 2.5 µm) from a previous study conducted at a suburban and roadside site in Brisbane. This comparison suggested that the more toxic heavy metals (V, Cr, Ni, Cu, Zn and Pb), mostly from vehicle and industrial emissions, were predominantly in the PM<sub>1</sub> fraction. Thus, the results from this study points to PM<sub>1</sub> as a potentially good particle size fraction for investigating the health effects of airborne particles. Further work is required to confirm this hypothesis.

**Keywords:** Industrial emissions; Vehicle emissions; PM<sub>1</sub> composition; Health effects.

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### INTRODUCTION

Long-term exposure to airborne particles in adults has been associated with a number of harmful effects to cardiovascular (Brook *et al.*, 2010) and respiratory systems (Pope *et al.*, 2002). Due to their immature immune systems and faster breathing rates, children are more susceptible to these detrimental health effects (Zhang and Zhu, 2010; R ckerl *et al.*, 2011). In an urban environment vehicle emissions are one of the main sources of airborne particles (Morawska *et al.*, 2008) and children's exposure to vehicle emissions has therefore been associated with a number of

long-term negative health effects, including increased wheezing (Ryan *et al.*, 2009) and the development of asthma (Gehring *et al.*, 2010).

The size and chemical composition of ambient particles are important parameters in determining their toxicity (Heal *et al.*, 2012). A clear relationship has been established between exposure to PM<sub>2.5</sub> (mass concentration of particles with an aerodynamic diameter less than 2.5 µm) and adverse cardiovascular effects (Brook *et al.*, 2010) and increased levels of lung cancer (Pope *et al.*, 2002). Thus many epidemiological studies have focused on PM<sub>2.5</sub> when investigating the health effects of air pollution (Heal *et al.*, 2012). The chemical composition of airborne particles is also thought to affect the toxicity as airborne particles contain toxic and carcinogenic compounds, such as polycyclic aromatic hydrocarbons and heavy metals (Harrison *et al.*, 2004). In urban environments it has been observed that the majority of the toxic metals, such as V, Ni, Cu, As, Cd and Pb are in the PM<sub>1</sub> fraction (Cheng *et al.*, 2009; Moreno *et al.*, 2011).

Trace metals can be used as surrogates for determining the influences of various sources (such as traffic, industrial

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and ship emissions), to the overall composition of the airborne particles (Moreno *et al.*, 2006; Arhami *et al.*, 2009). Children spend a large portion of their day at school and traffic emissions have been shown to be a prominent source at schools in urban areas, primarily due to the influence of school buses (Hochstetler *et al.*, 2011). However, not all schools are serviced by school buses. Instead, many schools are more influenced by local and school-related traffic (such as drop-off and pick up times) or other urban sources nearby. Therefore, the relative contribution of different sources at urban schools may differ from other urban environments. Overall, to date, there is limited information on the contributing sources of ambient fine particles that children are exposed to at urban schools (Mejía *et al.*, 2011).

The current study aimed to address the aforementioned gaps in knowledge in the sources of trace elements that contribute to children's exposure at schools by analysing the elemental composition of PM<sub>1</sub> samples obtained from various schools. To determine the size fraction of the detected elements, particularly the heavy metals, concentrations from the present study were compared to previous work on PM<sub>2.5</sub> composition in Brisbane. The sources of the trace elements that children were exposed to at schools, with a focus on toxic heavy metals, were identified using principal component analysis (PCA). In addition, we sought to determine the more relevant size fraction (PM<sub>1</sub> versus PM<sub>2.5</sub>) for exposure assessment based upon their elemental composition.

## METHOD

### *Sampling Sites and Instrumentation*

The PM<sub>1</sub> sampling was conducted from October 2010 till August 2012 as part of a larger project known as UPTECH ([www.ilqhqut.edu.au/Misc/UPTECH%20Home.htm](http://www.ilqhqut.edu.au/Misc/UPTECH%20Home.htm)) which was designed to study the effect of ultrafine particles from traffic emissions on children's health. Twenty five randomly selected schools within the Brisbane Metropolitan Area participated in this study and are referred to as S01 to S25. At each school a centrally located site, which was assumed to give the best overall exposure, was chosen to conduct the measurements. Schematic diagrams of the sampling locations within the schools (referred to as Site B in Salimi *et al.*, 2013) and surrounding roads can be found in Salimi *et al.* (2013). Inlets for the sampling were placed approximately 3m off the ground and on the top of a monitoring trailer, which served to house a TSI DustTrak DRX (model 8534) and a Monitor Sensors  $\mu$ Smart Series weather station. The DustTrak DRX is an optical instrument that simultaneously measures the mass concentration of ambient particles across the PM<sub>1</sub>, PM<sub>2.5</sub>, PM<sub>10</sub> and total PM fractions. Optically measured particle mass concentrations are not equivalent to gravimetric results however they are useful in this study to examine the relative contributions of PM<sub>1</sub> to PM<sub>2.5</sub> concentrations. Particle mass concentrations for each of these size fractions were recorded and averaged every 30s by the DustTrak DRX.

Data from nearby weather stations was also obtained from the Bureau of Meteorology (BOM) and Queensland Department of Science, Information Technology, Innovation

and the Arts (DSITIA) as the collected data at some of the schools would have been affected by local winds due to schools buildings. Traffic counts were taken on the busiest road in the school's proximity, referred to as the main road throughout. In the traffic count, cars, motorbikes and scooters were classified as light-duty vehicles. Light trucks with 2, 3 and 4 axels were classified as medium vehicle and long articulated trucks classified as heavy vehicles.

### *Sampling Methodology*

The PM<sub>1</sub> particles were collected on 47 mm, 0.2  $\mu$ m pore size Teflon filters (Whatman) with the filter area reduced to 25 mm to concentrate the particles, using cyclone type sampler with a flow rate of 16.7 litres per minute (L/min), maintained with critical orifices. For each sampling period two samples were collected with the flow rate split across the filters at 5.8 L/min, however only one sample was used for PIXE analysis and the other sample analyzed by aerosol mass spectrometry (see Crilley *et al.*, 2013). The sampling period was 24 hours, from 08:00 until 08:00 the next day, Monday to Friday for one week to give a total of four samples at each school. No PM<sub>1</sub> samples were collected at S11 due to instrument malfunction. This sampling regime typically gave sampling volumes of 8.2 m<sup>3</sup>. After sampling, each filter was placed in a Petri dish and then sealed in a ziplock bag. Gravimetric analysis of sample filters as well as blank filters was performed pre and post sample collection on a 5 point Mettler Toledo micro balance in the Chemistry laboratories at Queensland University of Technology. Prior to weighing, all filters were preconditioned at a constant temperature and humidity (25°C and 40%) for at least 24 hours.

### *Elemental Analysis*

Elemental analysis was performed using ion beam analysis at the Australian Nuclear Science and Technology Organisation (ANSTO) in Sydney, Australia on a STAR accelerator (2.0-MV HVEE tandetron, High Voltage Engineering Europa, Amersfoort, The Netherlands) (Cohen *et al.*, 2010) using particle induced gamma emissions (PIGE) spectroscopy and particle induced x-ray emission (PIXE) spectroscopy. These techniques can measure the following commonly occurring elements in PM<sub>1</sub> particles: Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Sr, Cd and Pb and have been described in details elsewhere (Cohen *et al.*, 1996; Cohen, 1998; Cohen *et al.*, 2004). Na was analysed by PIGE and the remaining 20 elements by PIXE.

### *Quality Control*

**Flow rate for the PM<sub>1</sub> cyclone:** this was checked at the beginning of each sample and always set to within  $\pm 0.1$  L/min of the desired flow rate.

**Gravimetric analysis:** a test filter that was given the same preconditioning treatment as the sample filters, was weighed repeatedly over the project. The standard deviation of the mean weight (90.15 mg) was 10  $\mu$ g, indicating high stability of the balance.

**Ion beam analysis:** The average minimum detection limit

(MDL) ranged from 3.3 to 40.8 ng/m<sup>3</sup> as summarised in Table S1 (Supporting Information) for the PIXE elements. For Na, the PIGE analysis program could not calculate the MDL, as Na was not detected in any sample. However, previous work by Friend *et al.* (2011a) found an average MDL of 35.5 and a range of 20 to 60 ng/m<sup>3</sup> for PM<sub>2.5</sub> sampled in Brisbane.

#### **Data Analysis**

Principal component analysis (PCA) and ANOVA were performed using SPSS v19. For the PCA, missing values were replaced by the mean and Varimax rotation was applied to the loadings. Only factors that had an eigenvalue above one were considered. Rose plots of wind direction and speed were calculated using IGOR Pro v6.22.

## **RESULTS AND DISCUSSION**

#### **Meteorological Characteristics during Sampling**

The project was conducted over nearly two years with sampling covering all of the seasons, as reflected in the range of meteorological conditions recorded at the schools and listed in Table 1. Brisbane is a subtropical city with a low level of variation between the average daily temperatures and an average temperature ranging from 13 to 24°C across all the schools (Table 1). May until October is the cooler, drier period with generally more stable weather and is referred to as winter. November to April is the summer and it is warmer, with higher humidity and rainfall. These weather conditions were observed throughout the project, as shown in Table 1. Wind rose plots were used to determine the wind direction during the sampling period, and these are given in the Supporting Information Fig. S1 and summarised in Table 1.

#### **Traffic Characteristics of the Schools**

The majority of the schools was in residential areas and had mostly light vehicles passing the schools, though schools such as S04, S06, S08, S23 and S25 were beside roads that service industrial/commercial areas and had higher levels of medium and heavy vehicles. Some schools such as S07, S09, S19 and S20 were located on busy arterial roads and others such as S01, S16 and S18 were beside quiet residential streets, as indicated by the traffic volume passing the schools.

#### **Gravimetric Analysis**

The average mass of PM<sub>1</sub> measured on the filters across the 24 schools was 90 ± 60 µg and this equated to an average concentration of 11 ± 7 µg/m<sup>3</sup>. Though the DustTrak is an optical instrument and thus the concentrations are not directly comparable to the gravimetric results, the ratios of PM<sub>1</sub> to PM<sub>2.5</sub> are expected to be the same for DustTrak and gravimetric analysis. On average, the PM<sub>1</sub> made up 83 ± 17% of the PM<sub>2.5</sub> fraction by mass, as determined by the DustTrak. Therefore the PM<sub>1</sub> fraction made up the majority of the PM<sub>2.5</sub> that children were exposed to at the schools.

#### **Average Elemental Composition**

The average concentrations and summary statistics for each

element across all of the schools are presented in Table 2. The most abundant element at the schools was generally S. The largest source of S in Brisbane is secondary sulphates (Friend *et al.*, 2011a). The next most abundant elements on average from Table 2 were Si, Ca and Fe, which along with the other elements known to be of a crustal origin such as K, Mn and Ti (Friend *et al.*, 2011a; Radhi *et al.*, 2011) made a significant component of the total trace element concentration of the PM<sub>1</sub> at the schools. Cl was also abundant at the schools and as Brisbane is a coastal city this may be due to the influence of sea salt particles. However, Na was below the detection limit for all samples possibly due in part to the higher MDL of PIGE technique compared to PIXE (Cohen, 1998) and this is discussed further in a later section. The remaining elements, P, V, Cr, Co, Ni, Cu, Zn, Br, Cd and Pb, are related to anthropogenic sources, such as vehicle, ship and industrial emissions (Moreno *et al.*, 2006; Arhami *et al.*, 2009; Friend *et al.*, 2011a; Pant and Harrison, 2013) and the contributing sources are investigated further in a later section.

#### **School-based PM<sub>1</sub> Elemental Composition**

The concentrations of the elements were compared between the schools in order to investigate the driving factors of the concentrations of heavy metals that children are exposed to at school. The average PM<sub>1</sub> concentration of selected elements (S, V, Fe, Ni, Zn and Pb) are given in Fig. 1, with that of Si, Cr, Cu and Br given in Fig. S2 (Supporting Information). From Fig. 1, except for Fe and Zn, S02 clearly had the relatively highest concentrations of all of these elements and this was likely due to the combined influence of two sources: industrial/shipping and traffic emissions. Along with the six elements from Fig. 1, S02 also had elevated concentrations of elements such as Cr, Cu and Br (Fig. S2) compared to the other 23 schools. The predominant wind direction at S02 was from the east (Table 1) and both the Port of Brisbane (approximately 10 km) and a main road (which recorded comparatively high traffic counts) lie in this direction. It is noteworthy that elements with elevated concentrations at S02 have previously been associated with industrial (e.g. (Moreno *et al.*, 2006), shipping (Arhami *et al.*, 2009; Moreno *et al.*, 2010), and traffic emissions (Lough *et al.*, 2005; Thorpe and Harrison, 2008b).

S02, S04 and S17 are within similar distance to the port and during sampling the main wind direction was from the port area. These three schools recorded comparatively high concentrations of S and V (Fig. 1), elements previously associated with shipping emissions (Arhami *et al.*, 2009), which suggests emissions from the port affected the schools. Also from Fig. 1, the schools that recorded some of the highest concentrations of Fe, Zn and Pb (S02, S10, S19 and S20) were schools beside some of the more heavily trafficked roads (Table 1) implicating traffic emissions (Lough *et al.*, 2005; Thorpe and Harrison 2008). However S07 and S09 had equally high traffic counts and yet recorded relatively low concentrations of these elements, which was likely due to the fact that the main wind direction was not from the main road at these schools (Table 1).

**Table 1.** Average traffic and meteorological conditions at the schools during the sampling. Note the date indicates that sampling start date.

School	Date	Temp (°C)	RH (%)	Wind speed (m/s)	Prominent wind direction	Frequency of wind from main road (%)	Direction of main road	Local traffic (veh/h)	% Light	% Med	% Heavy
S01	Nov-10	23	65	4.90	East	16	South	158	95.6	3.8	0.6
S02	Oct-10	22	76	3.31	East	35	East	859	95.2	4.6	0.3
S03	Nov-10	23	71	2.81	Northeast	0	Southwest	312	98.3	1.6	0.1
S04	Mar-11	23	60	1.63	East	5	West	806	87.0	7.9	2.2
S05	Mar-11	22	80	1.22	South	26	South	616	96.5	3.0	0.4
S06	May-11	15	73	3.78	West	2	East	268	87.8	8.2	2.9
S07	Jun-11	17	65	0.72	South	0	Northeast	1019	95.3	3.5	0.6
S08	Jun-11	13	69	1.11	West	19	Northwest	565	86.0	13.4	0.7
S09	Jul-11	13	65	1.91	W/SW	0	North	1164	90.7	3.6	1.8
S10	Aug-11	14	73	2.1	South	7	West	893	95.1	3.3	0.7
S12	Aug-11	15	75	0.75	West	2	South	176	97.3	2.5	0.2
S13	Oct-11	21	66	1.31	South	4	West	655	95.6	3.6	0.5
S14	Oct-11	22	74	1.09	Southeast	4	East	173	95.7	3.8	0.5
S15	Nov-11	24	65	4.13	Northeast	12	West	858	92.1	5.9	0.9
S16	Nov-11	25	75	0.96	North	40	North	46	97.8	1.6	0.4
S17	Dec-11	24	71	0.91	Southeast	15	East	757	95.3	3.0	0.6
S18	Mar-12	22	71	1.00	S/SE	0	West	35	97.9	2.1	0
S19	Mar-12	23	79	3.27	South	31	South	1093	89.9	3.2	2.0
S20	Apr-12	20	63	0.68	West	17	East	1121	96.2	2.5	0.8
S21	Jun-12	14	58	0.78	West	31	West	151	97.4	2.1	0.4
S22	Jun-12	14	66	0.64	West	1	Northwest	469	96.8	2.5	0.6
S23	Jul-12	15	60	0.66	South	40	S/SE	657	71.1	28	0.6
S24	Aug-12	15	40	2.99	West	3	North	160	97.1	2.4	0.5
S25	Aug-12	15	68	3.53	North	31	S/SW	332	92.0	6.5	1.2

**Table 2.** Summary statistics for the PM<sub>1</sub> concentration of the elements at all schools (ng/m<sup>3</sup>). < MDL indicates that the concentration was below the minimum detection limit.

	Average	Standard deviation	Min.	Max.	Median	% Detected
Na	< MDL	< MDL	< MDL	< MDL	< MDL	0
Al	1.6	6.1	0.0	50.9	0.0	22
Si	75.8	69.2	17.9	401.4	65.7	100
P	6.3	7.1	0.0	45.6	4.4	97
S	177.9	130.1	63.5	760.1	154.1	100
Cl	21.2	28.8	0.0	166.5	11.5	99
K	8.9	9.2	0.0	51.2	6.2	98
Ca	28.9	25.5	5.0	133.9	24.7	100
Ti	2.0	2.2	0.0	13.0	1.4	84
V	0.6	1.4	0.0	10.7	0.0	33
Cr	2.8	7.0	0.0	53.1	1.0	85
Mn	4.4	6.5	0.0	55.8	2.4	97
Fe	19.1	18.3	0.0	83.9	12.4	98
Co	0.3	0.9	0.0	6.5	0.0	22
Ni	0.9	2.9	0.0	25.3	0.2	55
Cu	3.0	6.9	0.0	43.9	1.4	81
Zn	5.9	7.1	0.0	34.0	2.9	90
Br	5.6	11.6	0.0	59.5	2.8	68
Sr	10.3	27.3	0.0	191.1	3.3	61
Cd	5.5	19.1	0.0	123.8	0.0	22
Pb	10.3	27.9	0.0	238.0	3.0	68

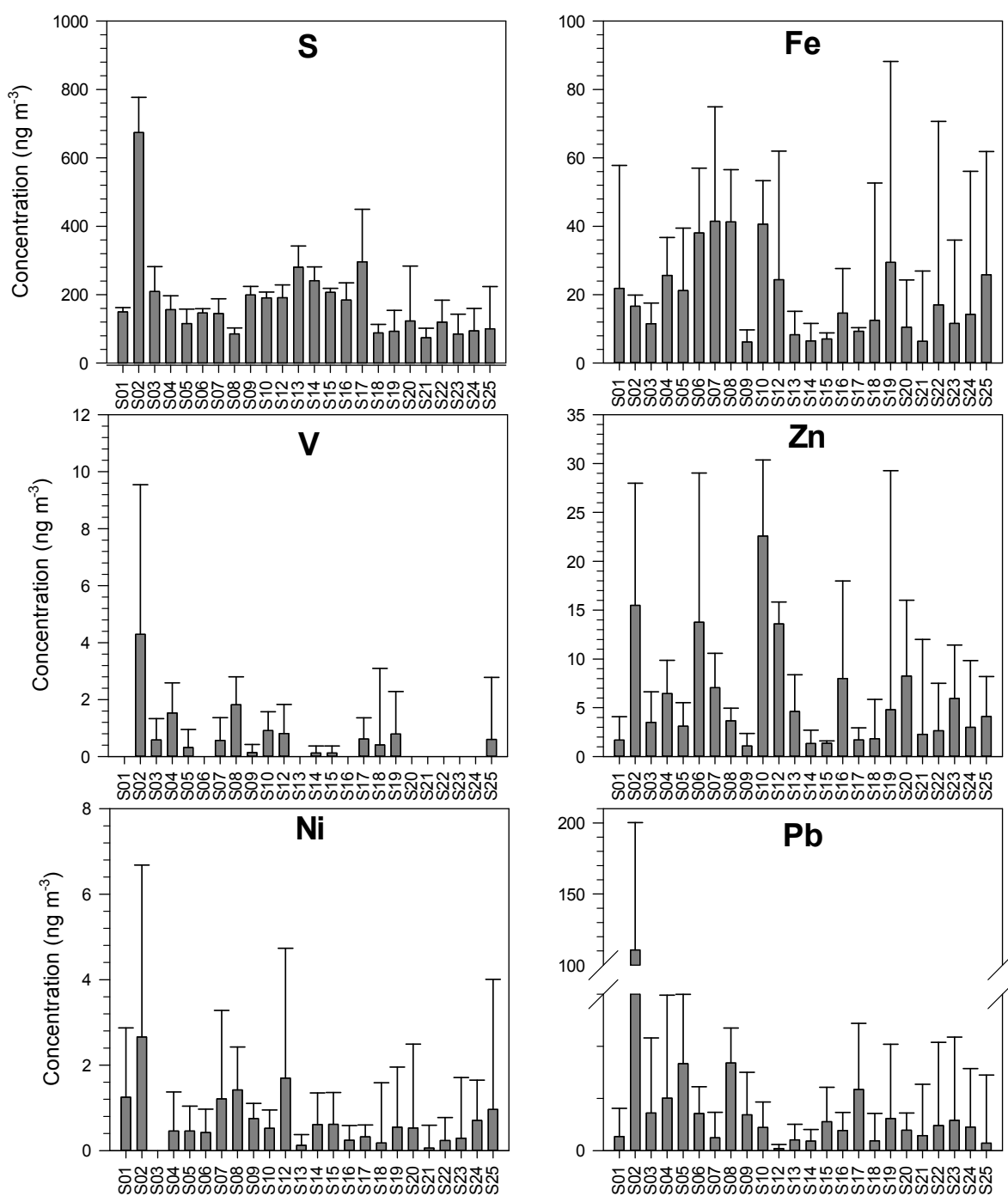
### Source Identification across Brisbane Metropolitan Area Using PCA

Overall, the PM<sub>1</sub> elemental concentrations at the schools indicate an array of contributing sources to the elemental composition, especially for the anthropogenic elements at the schools. Therefore PCA was applied to the average PM<sub>1</sub> elemental concentrations of the detected elements at each school in order to determine the contributing sources and their relative importance. With all of the schools included, the number of components identified was only three and all of the elements except for Al, Fe and Zn have high loadings in the first component (See Table S3, Supporting Information). These three elements were the only elements that were not elevated at S02 compared to the rest of the schools (Figs. 1 and S2), and this shows that S02 was an outlier. Therefore PCA was applied to the data without S02 and the number of components increased to seven, explaining a total of 81% of the variance. The results of this PCA are shown in Table 3, along with the proposed source identity for each component.

Table 3 shows that most of the sources of the PM<sub>1</sub> identified at the schools were anthropogenic in origin. Component 1 was characterised by highest loadings of S and also high loadings of Si, P, Cl and Ca and was attributed to secondary sulphates (Friend *et al.*, 2011a, b). Previous work with an aerosol mass spectrometry found that at selected schools secondary sources rather than primary emissions were the largest source of non-refractory PM<sub>1</sub> (Crilley *et al.*, 2014a), in agreement with the results from the current work. This component explained the most variance and was thus a significant source of the PM<sub>1</sub>. Two oil refineries present in Brisbane emit a combined  $6.7 \times 10^6$  kg of SO<sub>2</sub> into the atmosphere per annum (NPI, 2013) and may be

contributing to the high concentrations of secondary sulphates in Brisbane (Friend *et al.*, 2011a).

A vehicle emission source was identified in the PCA, which was characterised by Ti, Mn, Br and Pb (Component 2); these elements have been associated with vehicle emissions (Lin *et al.*, 2005 and references therein). Though leaded petrol was banned in 2001 in Queensland, Pb and Br are still associated with vehicle emissions in Brisbane (Friend *et al.*, 2011a, b) and in other studies around the world (Lin *et al.*, 2005; Lough *et al.*, 2005). From Fig. 1, schools with high concentrations of Pb (e.g., S15, S17 and S19) were also found to have high concentrations of hopanes that were attributed primarily to vehicle emissions in our previous work (Crilley *et al.*, 2014b). However the correlations were poor between Pb, Br and these hopanes, which may be due to differing traffic composition between the schools (Table 1) as gasoline and diesel vehicles have been observed to have varying emission rates of Pb, Br and hopanes (Rogge *et al.*, 1993; Lin *et al.*, 2005; Phuleria *et al.*, 2006; Cheng *et al.*, 2010). Furthermore, elements which have previously been assigned to vehicle wear emissions (e.g., Fe, Cu and Zn) (Thorpe and Harrison, 2008; Gietl *et al.*, 2010; Harrison *et al.*, 2012b) did not have high loadings in this component, suggesting that there was limited input from non-exhaust emissions in this factor, possibly as these particles are present more in the coarse particle fraction (Iijima *et al.*, 2007; Bukowiecki *et al.*, 2009). In addition, Mn and Ti have also previously been associated vehicle exhaust emissions (Wang *et al.*, 2003) and this suggests that the source of the component is vehicle exhaust emissions. This component accounted for the second highest amount of variance and this evidence points to vehicle emissions as an important anthropogenic source at the schools.



**Fig. 1.** Average PM<sub>1</sub> concentrations at each school for selected elements. Error bars represent 1 standard deviation.

Component 3 was attributed primarily to ship emissions due to the high loadings of Ni and V, which have previously been associated with oil combustion/shipping emissions (Arhami *et al.*, 2009; Moreno *et al.*, 2010). Cr and Sr also recorded high loadings in component 3 and have previously been associated with petrochemical (Singh *et al.*, 2002) and cement works (Widory *et al.*, 2010), industries that are present around the Port of Brisbane.

Along with high loadings of Fe and Zn, K had the highest loading in component 4. As K is a well-known tracer for biomass burning (See e.g., Richard *et al.*, 2011; Harrison *et*

*al.*, 2012a), component 4 was attributed to biomass burning. K was found to be well correlated ( $r^2$  of 0.6) with the concentration of levoglucosan, another established marker for biomass burning (Crilley *et al.*, 2014b) further pointing to biomass burning as the source. Zn and Fe have also previously been found in the emissions from biomass combustion (Friend *et al.*, 2011a, b) and as elements in the PM<sub>1</sub> fraction are generally related more to combustion processes than to crustal material or vehicle wear emissions (Minguillón *et al.*, 2012), this observation further point to biomass burning as the source.

**Table 3.** PCA results for the schools excluding S02.

	Component						
	1	2	3	4	5	6	7
Si	<b>0.83</b>	0.31	0.04	0.32	0.12	0.23	-0.04
P	<b>0.87</b>	0.18	0.13	-0.26	-0.06	-0.07	-0.08
S	<b>0.94</b>	-0.10	-0.02	0.12	-0.17	0.05	0.10
Cl	<b>0.58</b>	0.46	0.12	-0.26	0.33	-0.19	0.10
K	0.28	-0.03	-0.04	<b>0.73</b>	-0.28	0.07	0.15
Ca	<b>0.82</b>	0.20	-0.06	0.37	-0.04	0.21	-0.01
Ti	0.29	<b>0.85</b>	0.02	0.09	0.12	-0.06	0.04
Cr	0.25	0.10	<b>0.87</b>	0.07	-0.05	-0.10	0.03
Mn	0.24	<b>0.65</b>	0.03	0.34	0.48	-0.07	0.09
Fe	-0.27	0.33	0.52	<b>0.62</b>	0.16	0.04	-0.20
Ni	-0.12	-0.05	<b>0.83</b>	0.10	0.14	-0.02	0.16
Cu	0.22	0.06	-0.02	-0.03	0.05	<b>0.90</b>	0.02
Zn	0.07	-0.13	0.31	<b>0.68</b>	0.25	-0.11	-0.23
Br	0.31	<b>0.54</b>	0.22	-0.23	0.24	-0.40	0.01
Sr	0.13	0.19	<b>0.60</b>	0.03	<b>0.61</b>	0.14	-0.06
Pb	-0.05	<b>0.80</b>	0.14	-0.14	-0.11	0.34	0.01
Al	0.22	-0.09	0.02	-0.08	-0.66	-0.17	0.11
V	-0.03	0.47	<b>0.62</b>	0.06	-0.23	0.04	-0.45
Co	0.00	0.08	0.08	-0.05	0.00	0.01	<b>0.91</b>
Cd	0.05	0.00	0.06	-0.17	<b>0.68</b>	-0.37	0.24
Variance (%)	19.6	14.4	13.3	10.1	10.0	7.3	6.4
Eigenvalue	3.93	2.88	2.67	2.02	1.99	1.46	1.28
Source	Secondary Sulphate	Vehicle emission	Ship/Port	Biomass burning	Industry	Industry	Industry

Components 5 to 7 were also attributed to emissions from industry. Pollution from industrial activities can be highly specific chemically (Moreno *et al.*, 2006) and this explains why a number of components related to industrial sources are observed in the PCA results. Cd and Sr recorded high loadings in component 5 while component 7 was characterised by high loadings of Co; all of these elements have been previously shown to be from industrial sources (Moreno *et al.*, 2006; Widory *et al.*, 2010). Co in particular has been previously been attributed to industrial sources in Brisbane (Lim *et al.*, 2005). The main industrial areas of Brisbane are in the southwest and northeast parts and the major wind direction at schools that recorded high concentrations of Co and Cd (S03, S05, S20 and S23) was from these areas (Fig. S1). The short sampling times at each school made identifying individual industrial sources difficult, however likely industrial sources include various metallurgical and cement plants (Moreno *et al.*, 2006; Widory *et al.*, 2010), all of which are present in Brisbane.

Copper, the characteristic element of component 6, has been proposed as a tracer for brake wear emissions (Thorpe and Harrison, 2008a); however the lack of other metals with high loadings, such as Fe, which are also known to be from brake wear (Gietl *et al.*, 2010; Harrison *et al.*, 2012b) suggests that the source may not be related to vehicle movement. In addition, brake wear particles are expected to be in the larger size fractions (Iijima *et al.*, 2007; Bukowiecki *et al.*, 2009; Pant and Harrison, 2013) while emissions from anthropogenic combustion processes, as opposed to mechanical processes, are found more in smaller sizes

(Minguillón *et al.*, 2012). Therefore the source of the Cu in the PM<sub>1</sub> was assigned to industrial emissions, which has been observed before for fine particles in Brisbane (Lim *et al.*, 2005) and elsewhere (Moreno *et al.*, 2006; Viana *et al.*, 2008).

With sulphur generally being the most abundant element at each school, secondary sulphates were likely a significant source in this study. However from the PCA, all of the industrial sources (Components 3, 5–7) combined explained more variance than the vehicle emissions component, indicating that for the anthropogenic sources, industrial emissions had most variation between the schools. Thus industrial emissions accounted for the variation of trace elements in the PM<sub>1</sub> fraction that children were exposed at school.

#### Comparison to a Previous Brisbane Study

In Table 4, the PM<sub>1</sub> element concentrations from the schools were compared to a similar study by Friend *et al.* (2011a) on the PM<sub>2.5</sub> composition at a suburban and roadside site in Brisbane. The sampling by Friend *et al.* (2011a) encompassed three years and one year of sampling for the suburban and roadside site, respectively. Therefore they are considered to be representative of the typical ambient concentrations for these types of sites in Brisbane.

Sodium was detected in the previous study (Table 4), as sea salt particles are generally in the larger particles; however in the present study the sampled particles were in the PM<sub>1</sub> fraction. As outlined in a previous section, Na had a high MDL. To assess whether Na was below the MDL, the expected Na concentrations were calculated based on the

**Table 4.** Comparison of the average PM<sub>1</sub> elemental concentrations (ng/m<sup>3</sup>) at the schools (current study) to PM<sub>2.5</sub> elemental concentrations (ng/m<sup>3</sup>) at a suburban and roadside site in Brisbane (Friend *et al.*, 2011a). < MDL indicates that the concentration was below the minimum detection limit.

Site	Suburban		Roadside		Schools	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
Na	330.8	237.0	332.1	181.8	< MDL	< MDL
Al	41.6	236.5	104.2	474.6	1.6	6.1
Si	133.4	698.1	324.7	1428.4	75.8	69.2
P	2.9	3.1	1.9	2.1	6.3	7.1
S	282.4	159.4	291.9	156.2	177.9	130.1
Cl	231.5	300.9	246.9	294.0	21.2	28.8
K	54.7	83.9	81.8	177.1	8.9	9.2
Ca	25.0	46.1	50.2	104.0	28.9	25.5
Ti	7.2	39.2	20.7	87.3	2.0	2.2
V	0.8	1.0	1.3	2.3	0.6	1.4
Cr	0.7	1.3	0.8	0.9	2.8	7.0
Mn	5.3	9.4	4.9	14.3	4.4	6.5
Fe	85.4	329.5	241.9	761.2	19.1	18.3
Co	0.7	2.3	1.3	5.2	0.3	0.9
Ni	0.5	0.6	0.4	0.3	0.9	2.9
Cu	2.0	1.9	9.9	7.7	3.0	6.9
Zn	15.5	39.5	14.2	13.1	5.9	7.1
Br	3.0	2.4	3.8	2.2	5.6	11.6
Pb	5.0	4.2	5.6	3.8	10.3	27.9

determined Cl concentrations. Assuming the only source of Na was sea salt particles and a ratio of 1:1 for fresh sea salt particles, based on the average and maximum concentrations for Cl at the schools (Table 2), the expected average and maximum concentrations of Na were calculated to be 14 and 75 ng/m<sup>3</sup>, respectively. Compared to the average MDL for Na 35.5 ng/m<sup>3</sup> (range of 20–60 ng/m<sup>3</sup>) from previous work (Friend *et al.*, 2011a), the calculated concentrations for Na generally fall below the MDL, and thus would explain why there was no Na detected in the current work despite the likely presence of sea salt particles in Brisbane. That the maximum calculated Na concentration was above the MDL may indicate that there were additional sources of Cl at the schools (Friend *et al.*, 2011a, b).

Crustal elements (Al, Si, K, Ti and Fe) had lower concentrations in the PM<sub>1</sub> fraction compared to the PM<sub>2.5</sub> (Table 4). One-way ANOVA analysis of these concentrations found that compared to the PM<sub>2.5</sub> concentrations at the suburban site (Friend *et al.*, 2011a), Al, Si, Ti and Fe had statistically significant lower concentrations at the schools. Crustal elements are generally found preferentially in the larger size fractions and this would explain the lower concentrations observed at the schools (Richard *et al.*, 2011; Theodosi *et al.*, 2011; Minguillón *et al.*, 2012). The smaller size fraction collected at the schools, combined with the Fe rich nature of Australian soils (Radhi *et al.*, 2011) would partly explain why Al was not detected in every sample at the schools (Table 2).

On average, the concentrations of P, Cr, Ni, Br and Pb in the PM<sub>1</sub> at the schools were found to be higher than those found at the roadside and suburban sites (Table 4) (Friend *et al.*, 2011a). Vehicle emissions are one of the primary sources of Ni, Br and Pb in urban environments

(Moreno *et al.*, 2006) and thus the higher concentrations at the schools points to a contribution from school-related traffic. However, analysis by ANOVA found that none of the higher average concentrations at the schools compared to the other sites were statistically significant ( $p > 0.05$ ).

The observation that the PM<sub>1</sub> concentrations of V, Cr, Ni, Cu, Br and Pb in the current work were not statistically different to the suburban and roadside PM<sub>2.5</sub> concentrations (Table 4), suggests that these elements were predominantly in the PM<sub>1</sub> fraction. Richard *et al.* (2011) showed that the PM<sub>1-2.5</sub> fraction is the crossover between the coarse crustal material and particles associated with anthropogenic sources, in agreement with the results from this study.

#### **Implications for Investigating Health Effects of Airborne Particles**

In the current study, measurements with a DustTrak determined that the majority of the PM<sub>2.5</sub> (82%) by mass, was actually in the PM<sub>1</sub> fraction where unlike crustal related elements (e.g., Al, Si and Ti) heavy metals such as V, Ni, Zn and Pb were likely preferentially found. Thus the difference observed between the size fractions suggests that the PM<sub>1</sub> did not include appreciable levels of crustal material, which were instead likely in the PM<sub>1-2.5</sub>, as has been observed elsewhere (e.g., Richard *et al.*, 2011; Theodosi *et al.*, 2011; Minguillón *et al.*, 2012;). The presence of heavy metals (V, Ni, Zn and Pb) in airborne particles have been associated with detrimental health effects in a number of studies (e.g., Chen and Lippmann, 2009; Kelly and Fussell, 2012; Reche *et al.*, 2012; Xiao *et al.*, 2013) and are therefore thought to be contributing to the observed health effects related to airborne particles. Previous results have shown that variations in the concentrations of Ni and V, and to a lesser



extent Zn, Cu and Pb, were more strongly associated with variations in the PM<sub>10</sub> health risk estimates, compared to Al and Si (Kelly and Fussell, 2012 and references therein). Furthermore, smaller particles have been implicated as having greater toxicity compared to the larger particles (Donaldson *et al.*, 2002; Oberdörster *et al.*, 2005; Rückerl *et al.*, 2011; Kelly and Fussell, 2012). As the results from this study found that PM<sub>1</sub> contains notably fewer contributions from crustal material and with these metals (V, Ni, Zn and Pb) found to be preferentially in the PM<sub>1</sub> fraction, it suggests based on the size and chemical composition, the PM<sub>1</sub> fraction may have greater detrimental health effects compared to PM<sub>2.5</sub>. Currently the main metric for measuring the concentration of airborne particles is PM<sub>2.5</sub> in many epidemiological studies, as clear relationships have been established between PM<sub>2.5</sub> and harmful health effects (See e.g., Brook *et al.*, 2010). However, the results from this study suggest that the more appropriate size fraction to use when investigating the health effects of airborne particles may be PM<sub>1</sub>.

## CONCLUSIONS

The trace elemental composition of the PM<sub>1</sub> was analysed at 24 urban schools to determine the sources of airborne particles that children are exposed to at urban schools. The elemental composition varied from school to school as a result of differing source contributions. PCA was applied to identify these sources within Brisbane and found four types of emission sources: secondary sulphates, biomass burning, vehicle and industrial. The four sources classified as industrial were distinguished by different elements, notably a shipping/port emission source with high loadings of V, Cr, Ni and Sr. While industrial emissions accounted for the most variation in the PM<sub>1</sub> trace metals that children were exposed to at the schools, overall secondary sulphates were likely to be a large contributing source by mass.

Comparison of the elemental concentrations from this study to previous work on the PM<sub>2.5</sub> elemental composition studies conducted in Brisbane (Friend *et al.*, 2011a) revealed that the contribution of Pb, Br and Ni had concentrations were higher at the schools, pointing to an influence from school related traffic. However, analysis by ANOVA revealed that this difference was not statistically significant and generally elements from anthropogenic sources had similar concentrations. Therefore the anthropogenic elements, which are generally more toxic (e.g., V, Ni, Zn and Pb), were likely predominantly in the PM<sub>1</sub>. As the smaller particles are thought to have a greater detrimental health effect, the results from this study point to PM<sub>1</sub> being a potentially better metric to use when investigating the health effects of airborne particles. However, as this study was conducted in only one urban microenvironment (schools) and on a subset of the chemical composition of airborne particles (trace elements), further work which could include examining other classes of chemical species is required to confirm this hypothesis.

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## SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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## **Elemental composition of ambient fine particles in urban schools: sources of children's exposure**

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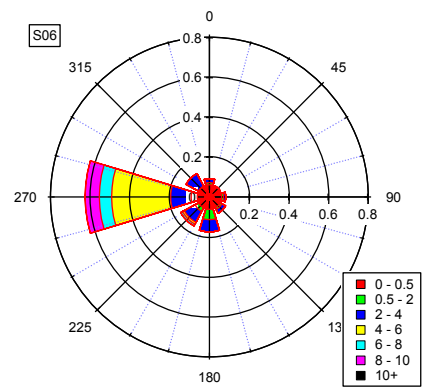
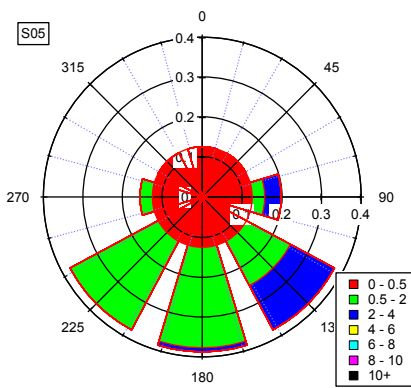
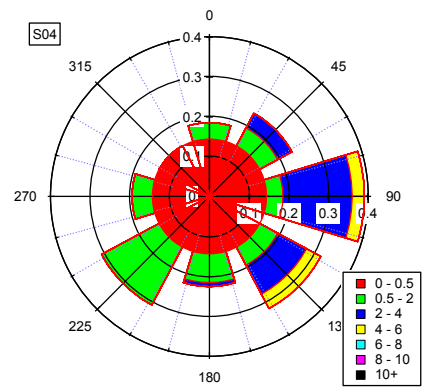
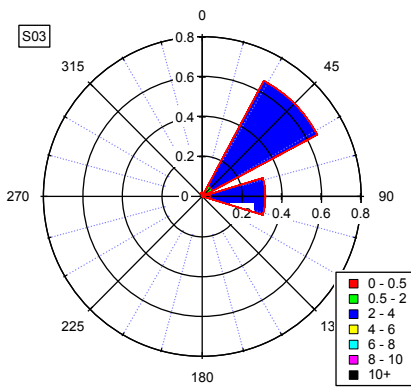
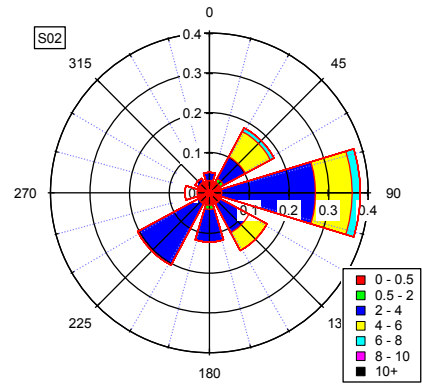
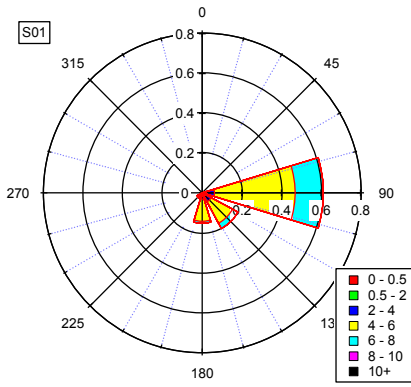
<sup>2</sup> Institute for Environmental Research, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW, 2232, Australia.

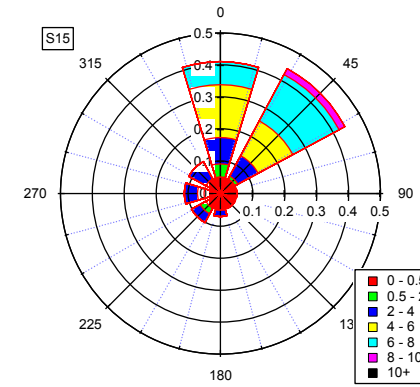
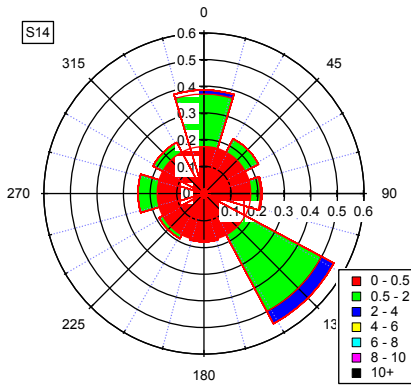
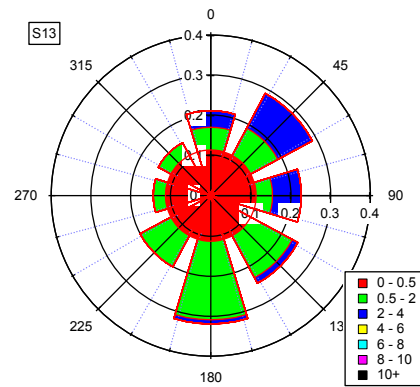
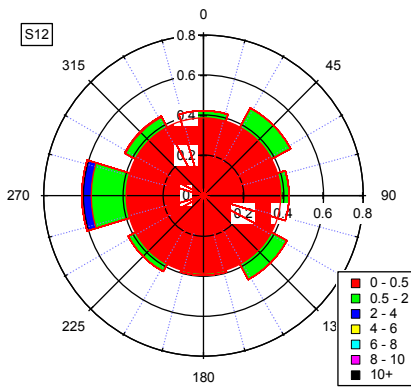
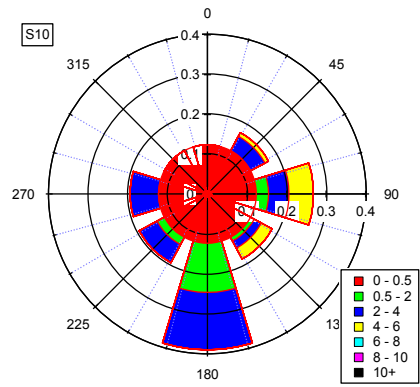
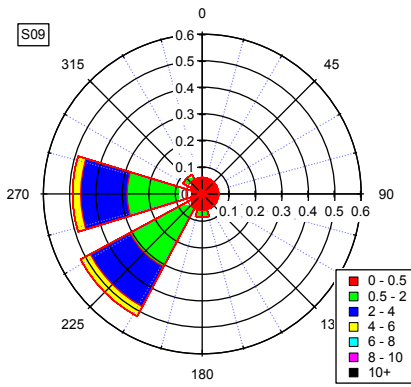
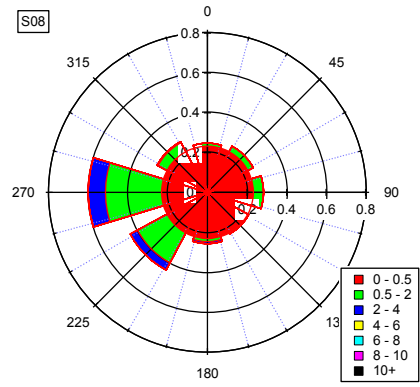
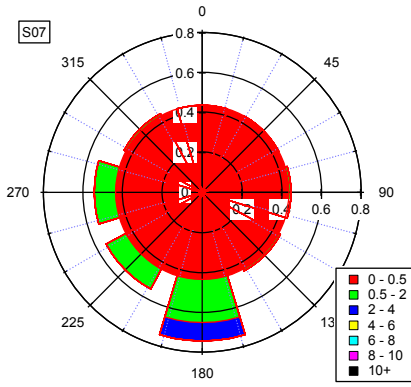
<sup>#</sup>Current Address: School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK.

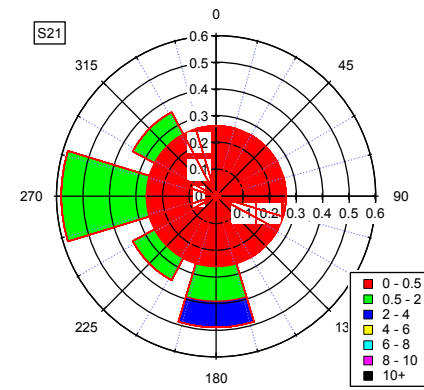
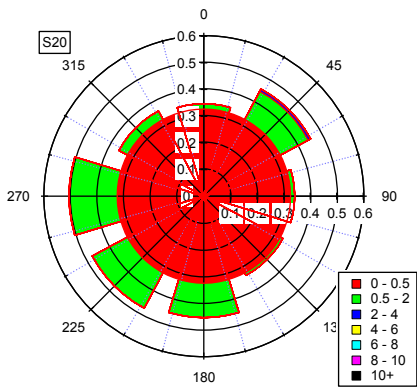
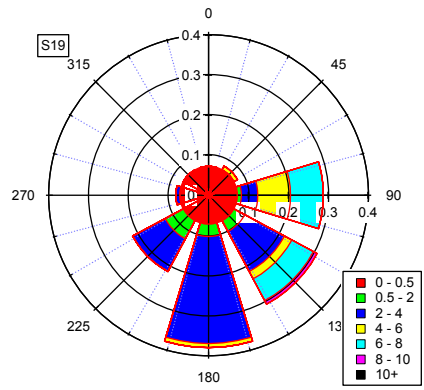
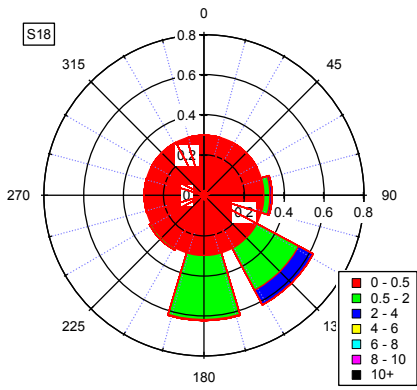
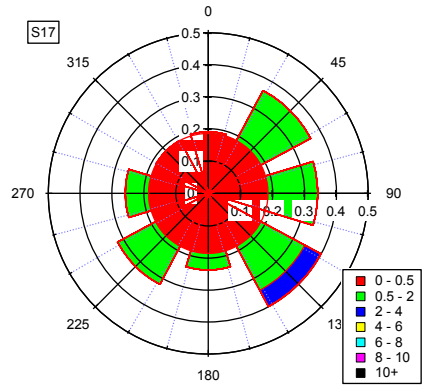
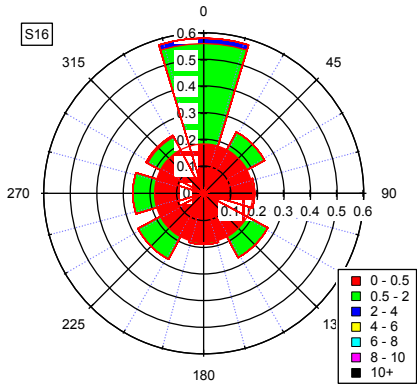
The Supporting Information contains 2 Figures and 2 Tables.

Table S1: Summary of the minimum detection limits (MDL) for each element in ng m<sup>-3</sup>. Note for Na the PIGE analysis program only calculates a MDL when Na is detected.

	<b>Average</b>	<b>Min</b>	<b>Max</b>
<b>Na</b>	N/A	N/A	N/A
<b>Al</b>	18.7	8.1	36.9
<b>Si</b>	11.5	5.1	23.0
<b>P</b>	10.3	4.7	20.6
<b>S</b>	9.6	4.4	19.1
<b>Cl</b>	10.0	4.7	19.7
<b>K</b>	9.1	4.2	17.5
<b>Ca</b>	8.5	3.9	16.3
<b>Ti</b>	6.9	3.0	13.0
<b>V</b>	5.8	2.5	10.7
<b>Cr</b>	4.6	1.9	8.2
<b>Mn</b>	3.8	1.6	6.8
<b>Fe</b>	3.5	1.4	6.5
<b>Co</b>	4.0	1.6	7.8
<b>Ni</b>	3.3	1.4	6.2
<b>Cu</b>	3.5	1.6	6.7
<b>Zn</b>	4.0	1.7	7.7
<b>Br</b>	12.7	5.8	25.5
<b>Sr</b>	32.4	15.2	70.0
<b>Cd</b>	40.8	0.0	648.7
<b>Pb</b>	20.3	9.4	40.7









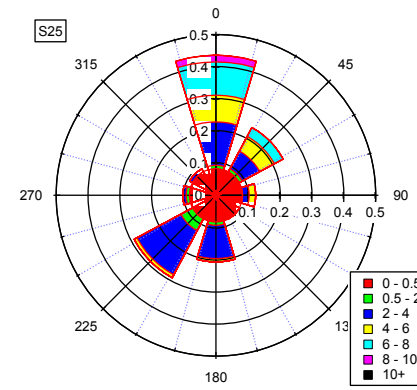
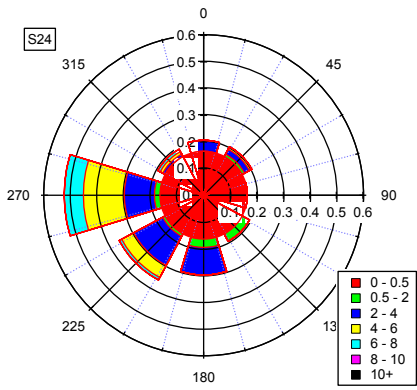
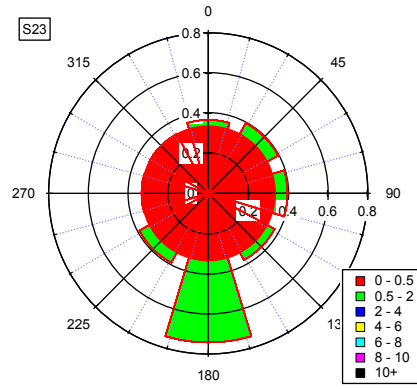
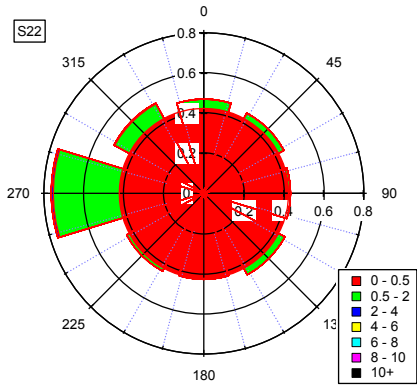


Figure S1: Wind rose plots of the sampling period at each school

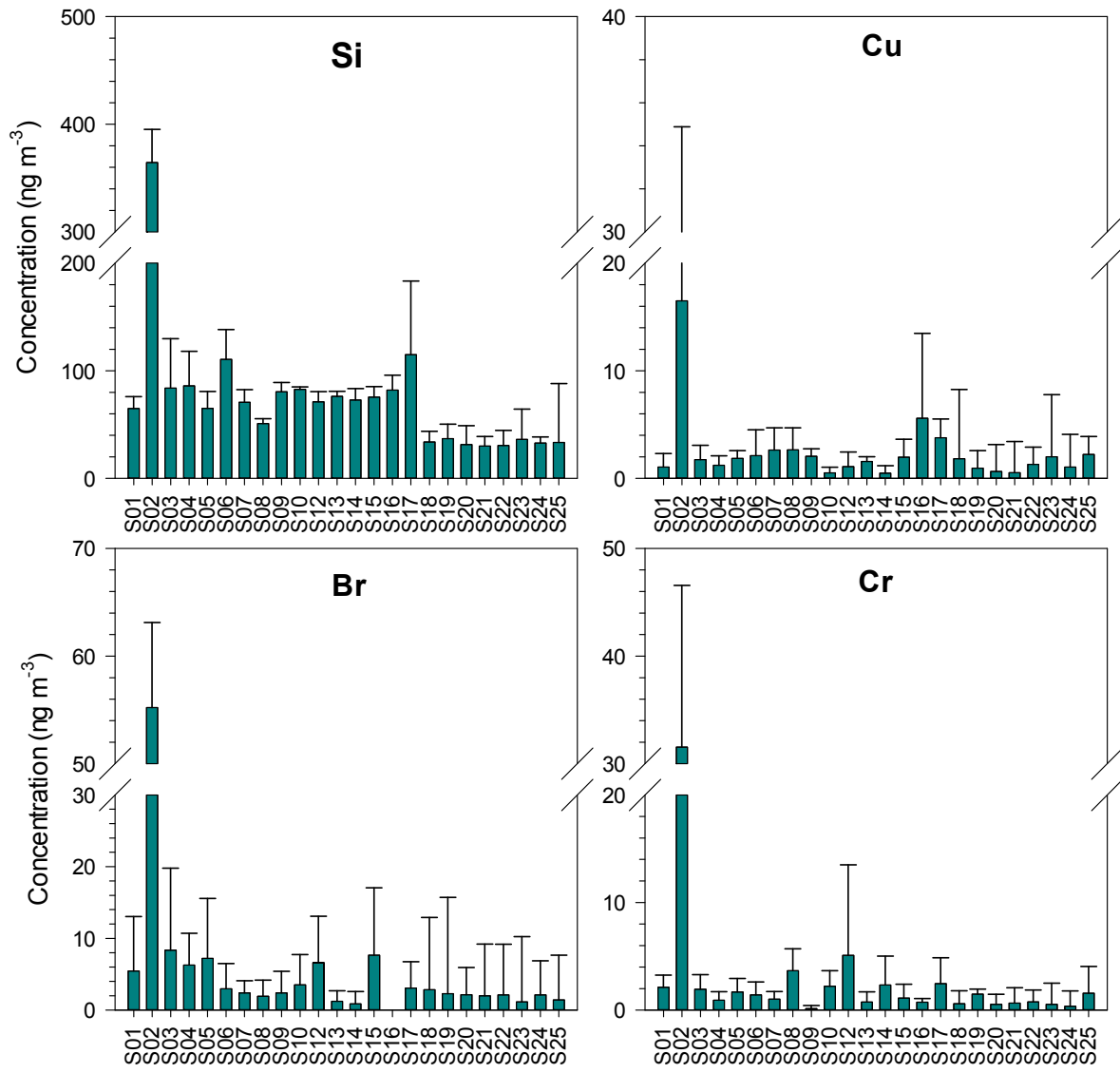


Figure S2: Average PM<sub>1</sub> concentrations of selected elements at all of the schools. Error bars represent 1 standard deviation.

Table S2: Principal Component Analysis for all of the schools.

	Component		
	1	2	3
Al	-0.12	-0.15	<b>0.80</b>
Si	<b>0.95</b>	0.19	0.14
P	<b>0.92</b>	-0.01	0.17
S	<b>0.91</b>	0.05	0.34
Cl	<b>0.90</b>	0.01	-0.04
K	0.43	0.46	0.49
Ca	<b>0.91</b>	0.19	0.22
Ti	<b>0.72</b>	0.19	-0.07
V	<b>0.82</b>	0.37	-0.08
Cr	<b>0.96</b>	0.19	0.02
Mn	<b>0.94</b>	0.23	-0.06
Fe	-0.14	<b>0.91</b>	-0.20
Ni	<b>0.67</b>	0.40	-0.20
Cu	<b>0.92</b>	0.10	0.04
Zn	0.28	<b>0.77</b>	0.06
Br	<b>0.97</b>	0.11	-0.03
Sr	<b>0.96</b>	0.19	-0.06
Pb	<b>0.96</b>	0.13	-0.02
Co	<b>0.85</b>	0.00	-0.01
Cd	<b>0.95</b>	0.10	-0.07
Variance (%)	66.1	77.3	83.3
Eigenvalue	13.22	2.24	1.19