Atmospheric Pollution Research

Composition and source contributions of air particulate matter pollution in a New Zealand suburban town

Perry K. Davy [1], Travis Ancelet [1,2], William J. Trompetter [1], Andreas Markwitz [1], David C. Weatherburn [2]

[1] *GNS Science, 30 Gracefield Road, PO Box 31312, Lower Hutt, New Zealand*
[2] *School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington, New Zealand*

ABSTRACT

Wainuiomata, a suburban town located at the southern end of the North Island of New Zealand, is subject to air particulate matter pollution episodes during the winter. The results of fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particulate matter monitoring in Wainuiomata from July 2006–September 2008 are presented. Receptor modeling was used to determine the sources contributing to particulate matter pollution and mass contributions to ambient particle concentrations from emission sources were estimated. PM_{10} concentrations displayed a seasonal pattern, with peak concentrations occurring during the winter. The results demonstrate that marine aerosol and crustal matter sources were the primary contributors to the coarse particle fraction, while the fine particle fraction was dominated by biomass burning with smaller contributions from marine aerosol and secondary sulfate particles. Arsenic was found to be present in the fine particle fraction and was associated with biomass burning, suggesting the use of copper chrome arsenate treated timber for domestic heating. Analysis of seasonal differences revealed that biomass burning was largely responsible for fine particle pollution episodes during the winter. Marine aerosol featured significantly as a PM_{10} source all year due to New Zealand's remote oceanic location.

1. Introduction

Particulate Matter (PM) has adverse effects on human health (Nel, 2005; Russell and Brunekreef, 2009). The health risk posed by PM is due to a number of factors, namely, particle size, surface area and chemical composition (Hannigan et al., 2005; Staniswalis et al., 2005). It has been well–established that the composition and size of PM tends to be dictated by its source. Therefore source identification of size–segregated PM is crucial in establishing source–specific health risks for an exposed population and for informing policy makers so that they may develop suitable legislation to better manage air quality within an airshed.

Wainuiomata is a suburban town with a population of approx–imately 16 000 located 15 km to the northeast of Wellington, the capital city of New Zealand (Figure 1). Wainuiomata is located in a valley basin with the south end of the town narrowing to a constricted valley that runs down to the ocean. While the air quality in Wainuiomata is generally good, the local topography makes the town susceptible to strong inversion conditions in the winter that significantly increases daily average PM_{10} concen–trations. These conditions can cause PM_{10} concentrations to exceed the New Zealand National Environmental Standard (NES) for PM_{10} of 50 µg m^{-3} (24–hour average), which has important implications for local policy makers. Little is known of the specific sources of size–resolved PM in Wainuiomata, and New Zealand in general, highlighting the importance of undertaking a source apportionment on size–resolved PM samples.

Positive matrix factorization (PMF) is a powerful and commonly used multivariate method capable of resolving factors contributing to PM samples without prior source knowledge. 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). Two receptor models are available to perform PMF, PMF2 (Paatero, 1997) and EPA PMF (USEPA, 2008). EPA PMF adopts a bilinear model which is solved by the Multilinear Engine (Paatero, 1999) and incorporates a graphical user interface. When compared with PMF2, EPA PMF has been shown to provide similar results with some minor differences in the final solutions (Kim and Hopke, 2007).

In this study, PMF2 was used to identify the major fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particle sources in Wainuiomata for samples collected from July 2006 to September 2008. Source contributions of size–resolved samples were evaluated over the entire sampling period and seasonal variation in the PM sources were also investigated.

2. Methodology

2.1. Sample collection

Air particulate matter samples were collected at an ambient air quality monitoring station located within the grounds of the Wainuiomata Bowling Club, a largely residential area located south of the town center (latitude −41.2681 degrees, longitude 174.9534 degrees). Wainuiomata is surrounded by hills 200 m high to the north and west and hills rising to a mountain range 800 m

Figure 1. *Location of the Wainuiomata monitoring site (★).*

high to the east. $PM_{2.5}$ and $PM_{10-2.5}$ samples were collected on a one–day–in–three basis (midday to midday) from July 2006 to September 2008, resulting in a total of 230 samples each for $PM_{2.5}$ and $PM_{10-2.5}$. Ambient PM samples were collected using a Gent sampler employing a stacked filter unit (SFU) (Maenhaut et al., 1994). The SFU contained coarse ($PM_{2.5-10}$) Nucleopore polycarbonate membrane filters and fine ($PM_{2.5}$) Teflon filters. Mass concentrations of the fine and coarse fractions were determined gravimetrically.

2.2. Elemental analysis

Ion Beam Analysis (IBA) was used to measure the concen–trations of elements with atomic number above neon in the particulate matter collected. IBA measurements for this study were carried out at the New Zealand Ion Beam Analysis Facility operated by the Institute of Geological and Nuclear Sciences (GNS) in Gracefield, Lower Hutt (Trompetter et al., 2005). The full suite of analyses included Particle–Induced X–ray Emission (PIXE), Particle–Induced Gamma–Ray Emission (PIGE), Rutherford Backscattering (RBS) and Particle Elastic Scattering Analysis (PESA).Black carbon (BC) was measured using a M43D Digital Smoke Stain Reflecto–meter. The determination of BC concentrations from the reflecto–meter measurements has been reported previously (Ancelet et al., 2011a).

2.3. Receptor modeling

Receptor modeling and apportionment of PM mass by PMF was performed using the PMF2 program (Paatero, 1997). With PMF, sources are constrained to have non–negative species concentrations, no sample can have a negative source contribution and error estimates for each observed point are used as point–by–point weights. This is a distinct advantage of PMF, since it can accommodate missing or below detection limit data that is a common feature of environmental monitoring (Song et al., 2001). Since the signal–to–noise ratio for an individual element can have a significant influence on a receptor model, it has been strongly suggested to down–weight or discard noisy variables (Paatero and Hopke, 2003). Therefore, the data in this study were screened by their signal–to–noise ratios(S/N). Variables with very low S/N (≤0.2) were excluded from the analysis, while weak variables

(0.2≤S/N≤2.0) were down–weighted. Rotational freedom in solutions were explored and controlled using FPEAK (Paatero et al., 2002) and observing the effect on the Q values (chi squared), G–vector plots and residual plots (Paatero et al., 2005). Q values obtained from the PMF analyses were in good agreement with the expected Q values of the data sets, for example, $Q_{expected}PM_{2.5} = 1\,998$ and $Q_{PMF}PM_{2.5} = 1\,307$. Only those solutions that could be related to physical sources were considered acceptable.

3. Results and Discussion

3.1. Sources of ambient $PM_{2.5}$

A summary of the $PM_{2.5}$ elemental analysis and signal–to–noise (S/N) ratios is presented in Table S1 in the Supporting Material (SM). Five primary source contributors were determined from the PMF analysis of ambient $PM_{2.5}$ elemental compositions in Wainuiomata. The elemental composition of the source profiles and average contributions from each source to overall $PM_{2.5}$ concentrations are presented in Table 1. The source contributors presented in Table 1 were found to explain 96 % of the $PM_{2.5}$ mass determined gravimetrically on average.

Factor one made up 48% of the $PM_{2.5}$ mass and was characterized to be biomass burning due to high loading values for BC, H and K. Potassium is typically used alongside BC as a marker for biomass burning and wood combustion in particular (Fine et al., 2002; Khalil and Rasmussen, 2003). A small amount of iron is also present in the biomass burning source, likely a result of the composition of home heating appliances (cast iron/steel) rather than the composition of the wood (Ancelet et al., 2011b). The biomass burning source was also found to have arsenic associated with it, suggesting that at least some homes were using copper chrome arsenate (CCA) treated timber for heating purposes. While the average concentration of arsenic over the entire study period was 9 ng m^{-3}, larger concentrations, as high as 91 ng m^{-3}, were observed. Arsenic concentrations displayed a distinct seasonality, with the highest concentrations occurring in the winter, supporting the conclusion that local residents are burning CCA treated timber. Figure S1 (see the SM) presents a plot of arsenic concentrations over the entire sampling period.

Table 1. *Elemental composition of source profiles and contribution to PM$_{2.5}$ (with associated standard deviations determined from bootstrapping in parentheses) in Wainuiomata*

Species	Factor 1 Biomass burning (ng m^{-3})	Factor 2 Motor vehicles (ng m^{-3})	Factor 3 Sulfate (ng m^{-3})	Factor 4 Marine aerosol (ng m^{-3})	Factor 5 Soil (ng m^{-3})
H	76 (20)	22 (14)	0 (12)	3 (7)	22 (8)
BC	846 (45)	172 (6)	0 (<0.1)	6 (9)	0 (4)
Na	9 (5)	0 (12)	34 (14)	379 (33)	0 (10)
Mg	2 (1)	1 (2)	5 (1)	28 (3)	3 (2)
Al	1 (0.8)	2 (7)	3 (0.9)	3 (2)	10 (3)
Si	4 (2)	9 (17)	11 (3)	6 (3)	23 (7)
S	17 (12)	14 (34)	127 (17)	42 (23)	14 (11)
Cl	0 (10)	44 (28)	26 (6)	451 (48)	7 (13)
K	35 (6)	2 (2)	5 (2)	12 (1)	3 (3)
Ca	1 (0.4)	4 (2)	3 (0.6)	10 (1)	2 (1)
Fe	2 (0.8)	4 (4)	2 (0.8)	0 (0.4)	3 (1)
Zn	3 (0.4)	1 (0.8)	2 (0.6)	1 (0.6)	1 (0.5)
As	5 (1)	1 (28)	3 (9)	2 (12)	3 (14)
PM$_{2.5}$	2 938 (0.2)	453 (0.4)	1 222 (0.3)	1 296 (0.3)	231 (0.3)

Factor two made up 7% of the PM$_{2.5}$ mass and represents motor vehicles due to the presence of BC, H, Ca and Fe. The third factor made up 20% of the PM$_{2.5}$ mass and was dominated by S. This factor was therefore considered to represent secondary sulfate. Because the conversion of SO$_2$ to sulfate is generally slow (Wojcik and Chang, 1997), this source is most likely the result of long–range transport, as opposed to a local source.

Factor four made up 21% of the PM$_{2.5}$ mass and was consid–ered to be marine aerosol due to the presence of Na and Cl, with minor contributions from Mg, S, K, and Ca. This source is not surprising due to Wainuiomata's proximity to the Pacific Ocean. Factor five contains Al, Si, S, K, Ca and Fe and made up 4% of the PM$_{2.5}$ mass. This factor was considered to be a crustal matter source.

A temporal analysis of the data was undertaken in order to better understand seasonality in the source contributions. Figure 2 presents a plot of source contributions by season and Figure S2 in the Supplementary material presents the contributions from each source over the entire sampling period (July 2006– September 2008). The biomass burning source shows a clear seasonal trend, with large contributions during the cool autumn and winter seasons and almost no contribution in the summer. The sulfate source also displayed seasonality, with concentrations peaking in the summer, indicating that the source activity (emission of precursor gases) or reactivity to form secondary sulfate is highest during the summer. Precursor gas sources could include marine phytoplankton activity (Buergermeister et al., 1990) and emissions of SO$_2$ gas from the Central Plateau volcanic zone of New Zealand. The motor vehicle, marine aerosol and crustal matter sources showed no distinct seasonality. The average mass contributions of each source were also divided into weekday (153 samples) and weekend (69 samples) categories to examine any differences that may occur due to anthropogenic activities. Figure S3 (see the SM) presents a plot of weekday and weekend mass contributions for each category. No statistically significant differences (Kruskal–Wallis test for non–normally distributed data) were observed between the source contributions on weekdays versus weekends. This is likely a result of the role that local meteorology plays in PM pollution events. High pressure systems and inversion conditions that bring meteorological conditions conducive to high PM pollution occur irrespective of the day of the week.
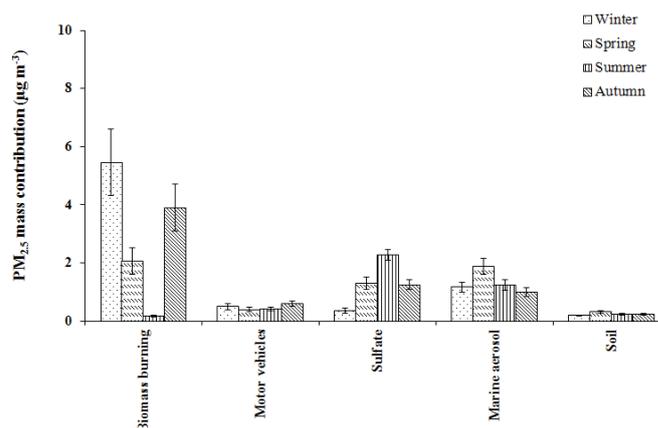

Figure 2. *Seasonal variations in PM$_{2.5}$ source contributions.*

3.2. Sources of ambient PM$_{2.5–10}$

Table S2 (see the SM) presents a summary of the elemental analysis and S/N ratios for PM$_{2.5–10}$ in Wainuiomata. Three primary source contributors were determined from the PMF analysis of ambient PM$_{2.5–10}$ elemental compositions. The elemental compo–sition of the source profiles and average contributions from each source to overall PM$_{2.5–10}$ concentrations is presented in Table 2. The source contributors presented in Table 2 were found to explain 94% of the PM$_{2.5–10}$ gravimetric mass on average.

Table 2. *Elemental composition of source profiles and contribution to PM$_{2.5–10}$ (with associated standard deviations from bootstrapping in parentheses) in Wainuiomata*

Species	Factor 1 Marine aerosol (ng m^{-3})	Factor 2 Road dust (ng m^{-3})	Factor 3 Soil (ng m^{-3})
BC	0 (2)	159 (23)	0 (2)
Na	1 221 (13)	0 (2)	17 (8)
Mg	102 (1)	13 (0.9)	15 (1)
Al	8 (0.6)	12 (0.5)	52 (0.6)
Si	11 (0.5)	33 (0.5)	135 (0.8)
S	140 (0.9)	23 (0.6)	18 (0.5)
Cl	1 975 (5)	32 (1)	2 (2)
K	39 (0.4)	13 (0.3)	17 (0.3)
Ca	46 (0.4)	20 (0.4)	14 (0.4)
Ti	0 (0.2)	1 (0.2)	2 (0.2)
Fe	0 (0.2)	17 (0.3)	25 (0.3)
Cu	1 (0.5)	1 (0.5)	0 (0.5)
Zn	0 (0.5)	2 (0.6)	1 (0.5)
PM$_{2.5–10}$	4 670 (0.1)	1 250 (0.1)	960 (0.1)

Factor one made up 68% of the coarse particle mass and was considered to be marine aerosol due to high concentrations of Na and Cl, along with Mg, S, K and Ca. Given the proximity of Wainuiomata to the Pacific Ocean, it is not surprising that marine aerosol dominates the coarse particle mass.

Factor two was considered to be a road dust source and made up 18% of the coarse particle mass. Road dust is generated by the turbulent passage of motor vehicles over local roads and the source profile features crustal elements (Al and Si) enriched with BC, Ca, Fe along with some Cu and Zn. Similar source profiles for road dust have been reported (Garg et al., 2000; Schauer et al., 2006). Black carbon in the profile is associated with deposited tailpipe emissions and the abrasion of tar sealed surfaces, while Zn is present in tailpipe emissions and tire wear dust (Thorpe and Harrison, 2008). Copper and iron are typically present in brake wear dust (Thorpe and Harrison, 2008).

Factor three made up 14% of the coarse particle mass and was considered to be a soil or crustal matter source due to the presence of Al, Si, K, Ca, Ti and Fe in the source profile.

A seasonal analysis of the source contributions is presented in Figure 3 while Figure S4 (see the SM) presents the contributions from each source over the entire sampling period. The marine aerosol contribution was highest during the spring and summer and the soil contribution was highest during the summer. The higher marine aerosol contributions during the spring and summer reflect the combination of increased wind speeds during these months and the increased evaporation potential for the generation and conversion of seawater droplets to marine aerosol particles (Fitzgerald, 1991). The road dust source showed little seasonal variability. Dividing the average mass contributions from each source into weekday (153 samples) and weekend (65 samples) categories shows no significant variation in the source contri–butions (see the SM, Figure S5). Similarly to the $PM_{2.5}$ sources, it is likely that meteorological factors play a more significant role in the mass contribution from each source as opposed to anthropogenic activities, like construction.
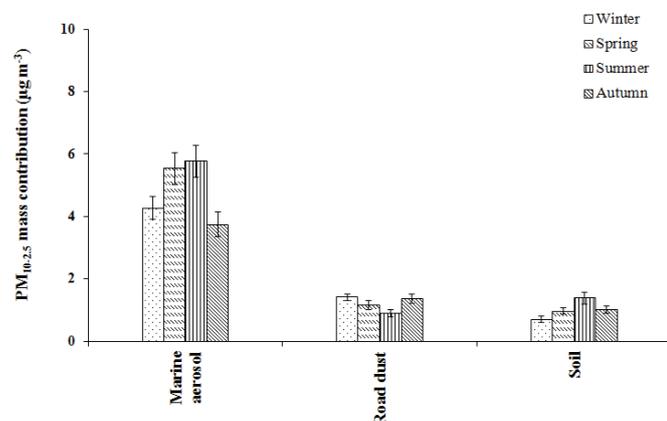

Figure 3. *Seasonal variations in $PM_{2.5–10}$ source contributions.*

4. Conclusions

This study aimed to characterize the elemental composition and identify the major fine and coarse particle sources using PMF in Wainuiomata, a suburban town located 15 km northeast of Wellington, New Zealand. The sampling campaign ran from July 2006–September 2008, over which time 230 samples each of size fraction were collected. PMF analysis of the fine particle fraction revealed five sources: biomass burning, motor vehicles, marine aerosol, sulfate and soil or crustal matter. Biomass burning was found to dominate the fine fraction with, contributing on average 48% of $PM_{2.5}$ mass. Surprisingly, arsenic in the samples was found to be associated with biomass burning, suggesting that residents are using CCA treated timber for domestic heating. More evidence supporting this assumption comes from the temporal analysis of arsenic concentrations, which peaked during high pollu–tion days. Marine aerosol and sulfate sources were also found to contribute significantly to $PM_{2.5}$ mass. Seasonal analysis of the source contributions revealed that biomass burning is dominant during autumn and winter. The sulfate source also demonstrated seasonality, with the largest contribution during the summer.

Source apportionment of the coarse fraction revealed three sources: marine aerosol, road dust and soil or crustal matter. Marine aerosol was found to dominate the coarse size fraction, contributing 68% of the coarse particle mass. Seasonal variations in the marine aerosol and soil sources were apparent in the coarse fraction.

Supporting Material Available

Elemental analysis results for $PM_{2.5}$ in Wainuiomata (Table S1), Elemental analysis results for $PM_{2.5–10}$ in Wainuiomata (Table S2), Time series plot for arsenic in $PM_{2.5}$ (Figure S1), Temporal variation in relative source contributions to $PM_{2.5}$ mass (Figure S2), Weekday/weekend variations in $PM_{2.5}$ source contributions (Figure S3), Temporal variation in relative source contributions to $PM_{2.5–10}$ mass (Figure S4), Weekday/weekend variations in $PM_{2.5–10}$ source contributions (Figure S5). This information is available free of charge via the Internet at http://www.atmospolres.com.

References

Ancelet, T., Davy, P.K., Trompetter, W.J., Markwitz, A., Weatherburn, D.C., 2011a. Carbonaceous aerosols in an urban tunnel. *Atmospheric Environment* 45, 4463-4469.

Ancelet, T., Davy, P., K., Trompetter, W.J., Markwitz, A., Weatherburn, D.C., 2011b. Characterisation of particulate matter emissions from a modern wood burner under varying burner conditions. *Air Quality and Climate Change* 45, 21-27.

Burgermeister, S., Zimmermann, R.L., Georgii, H.W., Bingemer, H.G., Kirst, G.O., Janssen, M., Ernst, W., 1990. On the biogenic origin of dimethylsulfide: relation between chlorophyll, ATP, organismic DMSP, phytoplankton species, and DMS distribution in Atlantic surface water and atmosphere. *Journal of Geophysical Research-Atmospheres* 95, 20607-20615.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2002. Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the southern United States. *Environmental Science and Technology* 36, 1442-1451.

Fitzgerald, J.W., 1991. Marine aerosols: a review. *Atmospheric Environment Part A-General Topics* 25, 533-545.

Garg, B.D., Cadle, S.H., Mulawa, P.A., Groblicki, P.J., Laroo, C., Parr, G.A., 2000. Brake wear particulate matter emissions. *Environmental Science and Technology* 34, 4463-4469.

Hannigan, M.P., Busby, W.F., Cass, G.R., 2005. Source contributions to the mutagenicity of urban particulate air pollution. *Journal of the Air and Waste Management Association* 55, 399-410.

Khalil, M.A.K., Rasmussen, R.A., 2003. Tracers of wood smoke. *Atmospheric Environment* 37, 1211-1222.

Kim, E., Hopke, P.K., 2007. Source identifications of airborne fine particles using positive matrix factorization and US environmental protection agency positive matrix factorization. *Journal of the Air and Waste Management Association* 57, 811-819.

Meanhaut, W., Francois, F., Cafmeyer, J., 1994. The Gent Stacked Filter Unit (SFU) Sampler for the Collection of Atmospheric Aerosols in Two Size Fractions. Description and Instruction for Installation and Use. Report NAHRES–19, IAEA, Vienna, pp 249–263.

Nel, A., 2005. Air pollution-related illness: effects of particles. *Science* 308, 804-806.

Paatero, P., Hopke, P.K., Begum, B.A., Biswas, S.K., 2005. A graphical diagnostic method for assessing the rotation in factor analytical models of atmospheric pollution. *Atmospheric Environment* 39, 193-201.

Paatero, P., Hopke, P.K., 2003. Discarding or downweighting high-noise variables in factor analytic models. *Analytica Chimica Acta* 490, 277-289.

Paatero, P., Hopke, P.K., Song, X.H., Ramadan, Z., 2002. Understanding and controlling rotations in factor analytic models. *Chemometrics and Intelligent Laboratory Systems* 60, 253-264.

Paatero, P., 1999. The multilinear engine - a table-driven, least squares program for solving multilinear problems, including the n-way parallel factor analysis model. *Journal of Computational and Graphical Statistics* 8, 854-888.

Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis. *Chemometrics and Intelligent Laboratory Systems* 37, 23-35.

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.

Russell, A.G., Brunekreef, B., 2009. A focus on particulate matter and health. *Environmental Science and Technology* 43, 4620-4625.

Schauer, J.J., Lough, G.C., Shafer, M.M., Christensen, W.F., Arndt, M.F., Deminter, J.T., Park, J.-S., 2006. Characterisation Of Metals Emitted From Motor Vehicles. Research Report 133. Health Effects Institute, Boston.

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

Staniswalis, J.G., Parks, N.J., Maldonado, Y.M., 2005. Temporal analysis of airborne particulate matter reveals a dose-rate effect on mortality in El Paso: indications of differential toxicity for different particle mixtures. *Journal of the Air and Waste Management Association* 55, 893-902.

Thorpe, A., Harrison, R.M., 2008. Sources and properties of non-exhaust particulate matter from road traffic: a review. *Science of the Total Environment* 400, 270-282.

Trompetter, W.J., Markwitz, A., Davy, P., 2005. Air particulate research capability at the New Zealand ion beam analysis facility using PIXE and IBA techniques. *International Journal of PIXE* 15**,** 249-255.

USEPA, 2008. EPA positive matrix factorization (PMF) 3.0 fundamentals and user guide. National Exposure Research Laboratory, Research Triangle Park, NC.

Wojcik, G.S., Chang, J.S., 1997. A re-evaluation of sulfur budgets, lifetimes, and scavenging ratios for eastern North America. *Journal of Atmospheric Chemistry* 26, 109-145.