

CHEMICAL CHARACTERISATION AND SOURCE APPORTIONMENT OF FINE PARTICLES IN CHRISTCHURCH, NEW ZEALAND: PART I - MODELLING BY POSITIVE MATRIX FACTORISATION

Angelique J Scott

University of Canterbury, Private Bag 4800, Christchurch, New Zealand

Environment Canterbury, PO Box 345, Christchurch, New Zealand

angie.scott@ecan.govt.nz

ABSTRACT

A source apportionment study was conducted in Christchurch, New Zealand during 2001 and 2002. The study provided source attribution information alternative to that supplied by emission inventories, and investigated a potential tool for measuring the effectiveness of air quality control strategies over time. Speciated fine particle measurements ($PM_{2.5}$) were collected during the summer of 2001/2002 and the winter of 2002. Major sources and their contributions to concentrations were determined using the Positive Matrix Factorisation (PMF) receptor modelling technique. Five sources were identified including motor vehicles, marine aerosol, wood combustion, secondary particulate and an unidentified sulphur source. Wood combustion (primarily residential heating) contributed 89% of average predicted $PM_{2.5}$ mass during the winter months.

INTRODUCTION

Christchurch is situated on the eastern coastline of the South Island of New Zealand (Figure 1). The metropolitan area extends from the Port Hills in the south to the gently sloping Canterbury Plains to the north. These topographical features, combined with the Southern Alps to the west and the coastline to the east, have significant impacts on meteorology. Temperature inversions occur frequently during the wintertime, trapping pollutants at the surface, resulting in elevated contaminant concentrations.

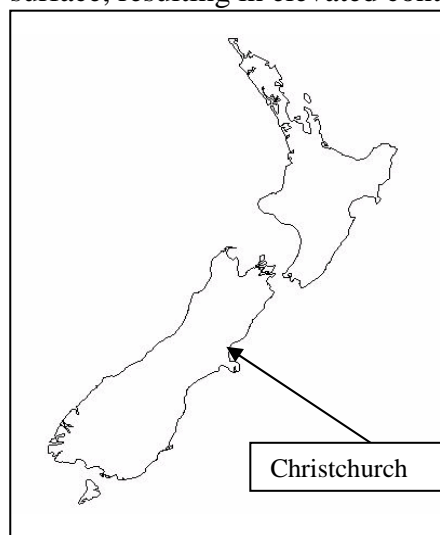


Figure 1 Location of Christchurch, New Zealand

Regular exceedences of the Ministry for the Environment's (MfE) guideline for particulate matter less than 10 microns in aerodynamic size (PM_{10} ; $50 \mu g/m^3$, 24-hour average) and the identification of residential heating as the primary source of wintertime PM_{10} emissions,^[1-3] led to the development of the Proposed Canterbury Natural Resources Regional Plan – Air Quality (Proposed NRRP). The ability of the proposed plan to improve air quality in Christchurch, however, is being questioned by some in the community who maintain that motor vehicles, not residential heaters, are the main source of particulates.

To address this issue, Environment Canterbury, the local government authority charged with managing air quality in the region, initiated the 2001/2002 source apportionment study. The chemical constituents present in fine particles ($PM_{2.5}$) were measured during the summer and winter months of 2001 and 2002. A multivariate receptor model known as Positive Matrix Factorisation (PMF) was applied to the speciated dataset to characterise key $PM_{2.5}$ sources, quantify source contributions to concentrations (rather than emissions as in the case of emission inventories), and thus evaluate whether receptor models could potentially be used to attribute longer-term

changes to particle concentrations on a source-by-source basis. This paper provides a brief overview and key findings of the study.

METHODOLOGY

A SuperSASS (Speciation Air Sampling System) filter-based sampler collected 24-hour PM_{2.5} samples for elemental and ionic analysis at Environment Canterbury's Coles Place monitoring site in the residential suburb of St Albans, Christchurch. Monitoring was conducted during the summer months (November 2001 to March 2002) and in winter (May to August 2002). Polycarbonate filters (47 mm diameter, 0.4 µm pore size) were used to collect PM_{2.5} mass for gravimetric analysis, and trace element determination (elements ranging from sodium to lead) by the Proton Induced X-ray Emission (PIXE) technique. Black carbon was measured using light reflection/transmission. Inorganic ions were collected, after passing through a magnesium oxide denuder, on Teflon (0.5 µm pore size) and nylon (0.45 µm pore size) filters. Ions, including nitrate, sulphate, chloride and ammonium, were analysed by ion chromatography. Organic and elemental carbon were measured using a Rupprecht and Patashnick Series 5400 Ambient Carbon Particulate Monitor. A temperature differential of 230°C was used to distinguish between organic and elemental carbon. Subsequent investigation has revealed that this may not be appropriate and further work is being conducted in 2004 to address this issue. Samples were also collected using MiniVol Portable Air Samplers to provide ambient elemental source profiles for source identification purposes.

The analytical data were transformed into concentrations (µg/m³), compiled into matrices of chemical species and observations, and quality assured. Chemical species with less than 70% of data above zero, and sulphate and elemental carbon were eliminated from the analysis (to prevent double counting with sulphur and black carbon). Organic carbon measurements were multiplied by 1.4^[4] to provide an estimate of total organic mass (OC_{adj}). An error matrix was compiled, as required for the PMF model, with no missing or zero data. Data substitution, where necessary, was based on the Polissar *et al.* (1998) approach where progressively higher uncertainties were allocated to below detection limit, zero and missing data.^[5]

A statistical analysis was conducted using Statistica 6.0 and the PMF multivariate receptor model applied to the data to characterise the key sources of PM_{2.5}. This model was preferred to other factor analytical techniques as the data are not normalised (factor scores and loadings are provided in real units) and measurement variations are taken into account. Essentially, the model conducts a least-squares analysis which incorporates a data point weighting system to account for errors associated with individual concentration observations.^[6] Unlike methods such as principal components analysis, the results may be used directly to assemble source profiles and quantify relative source contributions.

The model is operated by an initialisation file. Optimal operation of the model is achieved by adjusting various parameters in the file, including number of factors, until an acceptable Q-value, or goodness of model fit is achieved.^[7] Parameter adjustments detailed in the literature^[5,6,11,12] and multiple PMF run results (trial-and-error) were used to determine optimal operating parameters. Elemental profiles and a matrix of daily factor scores for a five-factor solution were output by the model. The scores were regressed against gravimetric mass to allow daily particle concentrations to be apportioned to each source.

RESULTS AND DISCUSSION

Fine particles and primary chemical constituents

Table 1 presents summary statistics for chemical species present in fine particles measured during the study. PM_{2.5} concentrations were seasonally distributed with the greatest concentrations occurring during the winter months (96.3 µg/m³ maximum) and lower concentrations during the summer (1.1 µg/m³ minimum). The 24-hour averaged data exceeded the USEPA fine particle standard of 65 µg/m³ on six days, the Environment Canada Standard of 30 µg/m³ on 34 days and the MfE monitoring standard of 25 µg/m³ on 44 days. Additional guideline exceedences would have been detected if filter blockages (due to high particulate loadings), invalidating at least nine days during the winter, had not occurred.

The major chemical constituents of PM_{2.5} were organic and elemental carbon, sulphate, sulphur, chlorine, sodium and nitrate. Elemental and organic carbon, nitrate, sulphate, ammonium and potassium were significantly higher during the winter months, whereas sodium and chlorine were more abundant at warmer times of the year.

Species	Minimum		Mean		Median		Maximum		25 th Percentile		75 th Percentile	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
Organic carbon	0.4	2.0	1.0	7.0	0.9	5.9	2.4	22.9	0.7	3.7	1.2	9.1
Sulphur	0.1	0.13	0.4	0.5	0.4	0.5	1.3	1.0	0.3	0.4	0.6	0.7
Chlorine	0.03	0.05	0.5	0.5	0.5	0.4	2.1	2.5	0.13	0.2	0.7	0.6
Silicon	0.05	0.06	0.11	0.14	0.10	0.14	0.2	0.3	0.09	0.12	0.13	0.2
Iron	0.012	0.02	0.03	0.06	0.03	0.05	0.06	0.2	0.02	0.04	0.03	0.07
Potassium	0.006	0.04	0.05	0.3	0.04	0.2	0.2	0.9	0.03	0.11	0.06	0.3
Magnesium	0.02	0.04	0.11	0.14	0.10	0.13	0.2	0.3	0.08	0.10	0.13	0.2
Black carbon	0.2	0.8	1.1	7.1	0.9	5.5	3.4	22.7	0.6	3.2	1.3	9.8
Sodium	0.08	0.013	0.8	0.6	0.8	0.5	2.0	2.4	0.5	0.3	1.1	0.7
Calcium	0.003	0.005	0.04	0.04	0.04	0.04	0.09	0.09	0.03	0.03	0.05	0.05
Zinc	0.001	0.002	0.009	0.04	0.006	0.03	0.06	0.2	0.003	0.012	0.011	0.05
Chromium	0.001	0.001	0.006	0.011	0.006	0.011	0.02	0.03	0.003	0.007	0.008	0.014
Nickel	0.001	0.001	0.004	0.005	0.003	0.005	0.01	0.02	0.003	0.003	0.004	0.007
Aluminium	0.001	0.0003	0.02	0.03	0.03	0.03	0.05	0.2	0.02	0.02	0.03	0.04
Ammonium	0.005	0.005	0.12	0.4	0.07	0.3	0.9	1.2	0.01	0.2	0.2	0.6
Nitrate	0.12	0.12	0.3	0.8	0.13	0.7	1.3	2.3	0.12	0.5	0.4	1.0
Sulphate	0.11	0.4	0.8	1.3	0.8	1.2	2.3	2.7	0.5	1.0	1.0	1.6
Fine particles	1.1	2.2	6.5	27.7	5.5	20.9	28.3	96.3	3.4	11.9	7.6	37.5

Table 1 Major chemical constituents of fine particles in Christchurch 2001/2002 (µg/m³)

Key sources and contributions to PM_{2.5}

The PMF receptor model was applied to the total dataset and a five-factor solution derived. The Q-value obtained, 2138, corresponded closely to the theoretical Q-value, 2544. Chemical profiles were derived directly from the F-Factor matrix (factor loading matrix) as data were provided in µg/m³. The G-Factor matrix (daily factor score matrix) was regressed against gravimetric PM_{2.5} measurements using Multiple Linear Regression. The regression coefficients were multiplied by the daily factor scores to determine daily source contributions to predicted PM_{2.5} mass. A comparison of measured PM_{2.5} mass with predicted PMF mass indicated a good relationship with an r² coefficient of determination of 0.91. The five sources resolved by PMF were identified as motor vehicles, marine aerosol, wood combustion, secondary particulate and a sulphur source (Figure 2). Daily source contributions from each of these sources are indicated in Figure 3.

The motor vehicle profile was characterised by the presence of combustion related species (organic and elemental carbon), secondary particulate (nitrate), soil related compounds (silicon, iron, calcium and aluminium), and metals (zinc, nickel and chromium). These species are commonly found in emissions generated by engine combustion, wear-and-tear of brake pads and resuspended in road dust. Although source profiles between countries are expected to vary (due to different fuels and motor vehicle technologies), this profile was

similar to those identified by other studies.^[5,6,8-11] The greatest motor vehicle contributions occurred during the winter months (Figures 3 and 4). Restricted dispersion conditions conducive to contaminant buildup and increases in motor vehicle use are likely at that time of the year. Motor vehicles were more significant, however, on a relative percentage basis during the summer (19.3% of average predicted PM_{2.5}) with a lower contribution during the winter (6.9%).

The marine aerosol profile was characterised by chemical species found in sea water, including chlorine, potassium, magnesium, sodium and calcium. Sulphur was absent from the profile, suggesting it may have been transformed through photochemical processes to form sulphate, and was therefore associated with the secondary particulate or sulphur source profiles. Combustion related species were also evident in small quantities. These substances may be derived from local sea-side combustion sources and transported in the easterly sea breeze, along with marine aerosol, to the receptor site at Coles Place. Nevertheless, the profile was similar to those identified elsewhere.^[5,6,8,9,11,12] Daily marine aerosol contributions were greatest outside the winter months (Figures 4 and 5). Marine aerosol, on a relative percentage basis, was more significant during the summer (28.4% of average predicted PM_{2.5}) than in the winter (3.1%). Meteorological conditions most conducive to marine aerosol formation and transportation predominantly occur at this time.

The wood combustion profile was characterised by organic and elemental carbon, potassium and small quantities of chlorine and nitrate. Potassium is a marker for wood smoke,^[5,8,12,13] and organic and elemental carbon are commonly detected in wood combustion discharges. The profile corresponded closely with those labelled variously in the literature as wood smoke, biomass burning, vegetation burning and forest fires.^[5,6,8,12] Contributions from wood combustion sources were greatest during the winter months of the year (Figures 3 and 4). This corresponds with emission inventory data which consistently identified residential heating (predominantly wood combustion) as the main particulate source in Christchurch.^[1-3] There are 53 000 wood burning appliances used in Christchurch during the winter, many of which are operated during the evening hours when dispersion is most limited. On a relative percentage basis, wood combustion contributed 47.9% to average predicted PM_{2.5} during the summer and 89.2% during the winter. Although residential heaters are unlikely to be used during the summer months, outdoor burning of green waste occurs at that time in and around the Christchurch metropolitan area.

The secondary particulate profile was characterised by secondary species (ammonium and nitrate), sulphur (as sulphate) and secondary organic carbon. Profiles in the literature vary as individual secondary species may be separated out into independent source profiles. Key characteristics, however, are the dominance of one or more secondary particulate species. Chemical species found in soil (silicon and iron), marine aerosol (sodium and chlorine) and industrial and motor vehicle emissions (metals such as iron and zinc) were also evident in this profile. The nature of this source therefore is ambiguous and associated with a reasonably high degree of uncertainty. While the greatest contributions occurred during the winter, peaks were also evident in the summer (Figure 3). On a relative percentage basis, the secondary particulate source constituted only 0.2% of average predicted PM_{2.5} during the winter and 0.4% in the summer. It is clearly insignificant when compared to wood combustion, motor vehicles and marine aerosol.

The sulphur source was characterised by a high sulphur component, and the presence of silicon, potassium, magnesium, elemental carbon, sodium, calcium, aluminium and nitrate.

The abundance of sulphur and sodium strongly suggests a photochemical source comprising sodium sulphate compounds. Similar profiles have been identified elsewhere as aged marine aerosol.^[5,6] Unlike the other sources identified by this study, a seasonal trend in contributions was not demonstrated (Figures 3 and 4). On a relative percentage basis, the sulphur source contributed to 4% of average predicted summertime PM_{2.5} with a substantially lower contribution of 0.6% in the winter. As this source made greater contributions than secondary particulate, it is likely that this is in fact an additional secondary particulate source.

The modelling did not separately resolve sources such as industry, coal burning and soil. These sources were most likely incorporated into the other source profiles. It is expected, however, that contributions to PM_{2.5} from these sources would be minor due to factors such as timing of emissions and size distribution of particles contained in the emissions.

CONCLUSIONS

Source apportionment of summer and wintertime PM_{2.5} data was conducted successfully using the PMF receptor modeling technique. Three significant sources were identified, including wood combustion, motor vehicles and marine aerosol. The profiles and trends in contributions from each source made good physical sense and the study verified that wood combustion (mainly residential heating) was the primary source of PM_{2.5} in Christchurch. Source apportionment using a receptor model is particularly useful as it provides measures of PM_{2.5} over time, attributes contributions directly to concentrations (rather than emissions), readily quantifies natural sources, and provides source contribution information on a daily basis thus indicating differences in source contributions over time. In this regard, this method would be a useful addition to the tools currently used by Environment Canterbury to monitor the effectiveness of control strategies for air quality.

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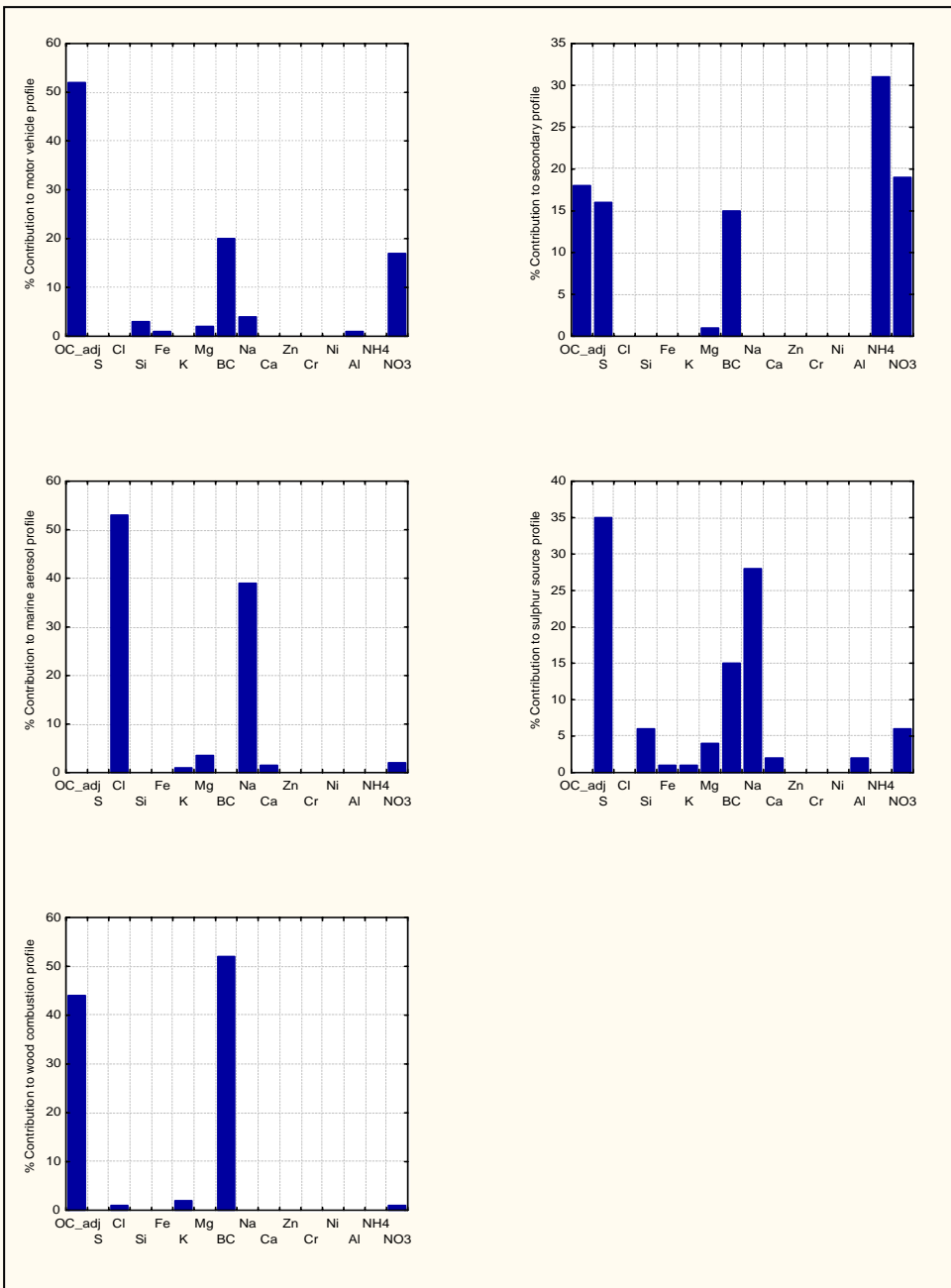


Figure 2 Chemical profiles for key PM_{2.5} sources in Christchurch

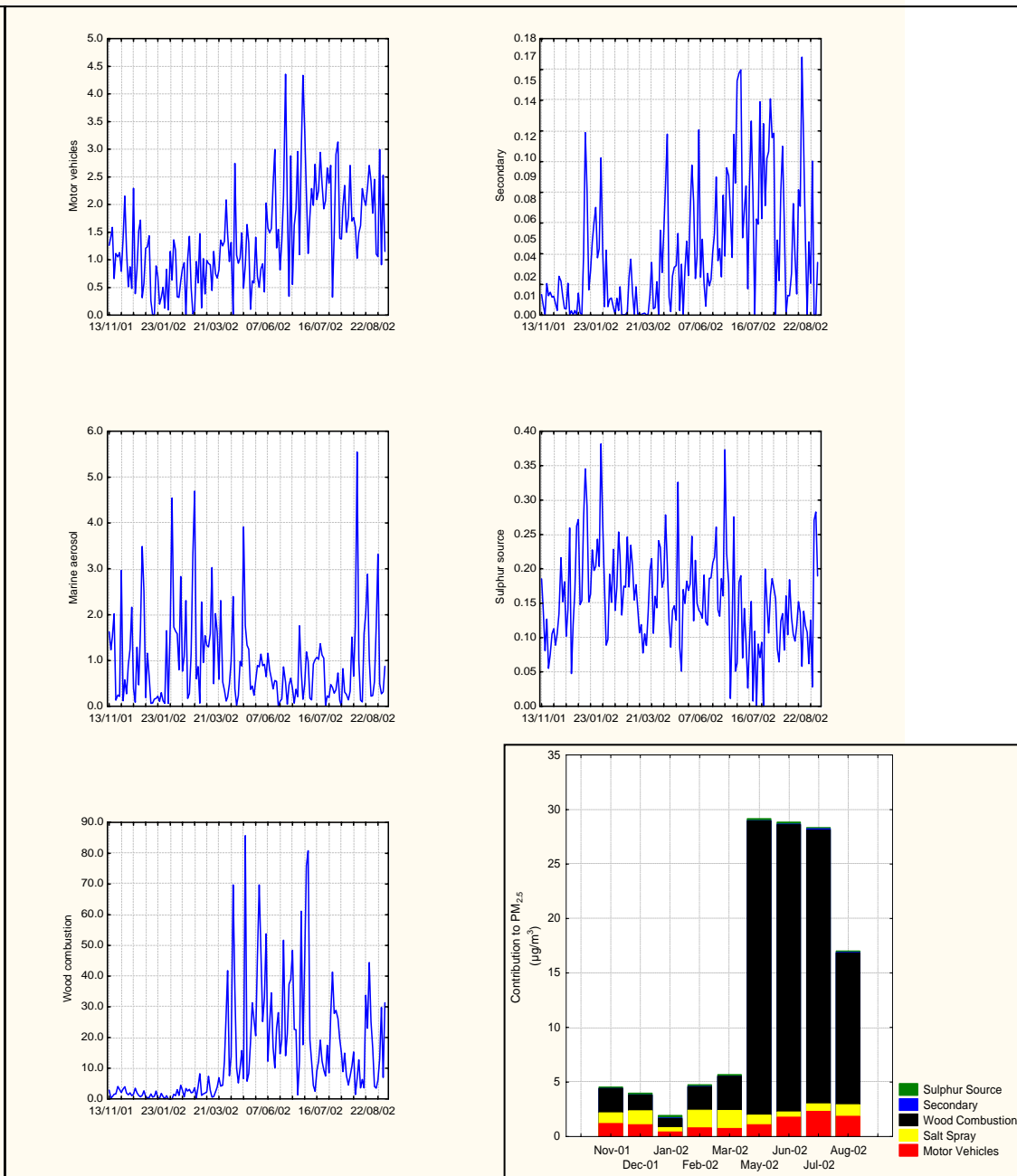


Figure 3 Daily source contributions to PM_{2.5}

Figure 4 Monthly average contributions to predicted PM_{2.5} mass