

# Contributions of Different Sources to Primary and Secondary PM10 Aerosols in Brisbane, Australia

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## ABSTRACT

PM10 aerosol samples (particles with aerodynamic diameter  $<10\mu\text{m}$ ) were collected during 47 days from an industrial area in Brisbane from April to June 1999. The chemical composition of the samples was analysed by techniques including Ion Beam Analysis. Concurrent data on concentrations of  $\text{SO}_2$  and  $\text{NO}_x$  at the site were also collected by the State EPA. The chemical mass balance method (CMB) was used to estimate the contribution of different emission sources using source profiles developed from literature composition of particulate emissions from local sources. By assuming the unexplained mass of S, N and organic carbon (OC) as mainly originated from secondary formation, the primary and secondary contributions of these elements were determined. The results of secondary contribution of OC was also compared with those using another method in which primary OC is estimated from the minimum ratio of concentrations of OC to elemental carbon (EC) in the samples.

On average, 15% of the total mass, 73% of the S, 93% of the N and 57% of the OC elements in the PM10 samples were from secondary formation. Soil and roadside dust (32%), sea salt (27%), secondary formation (15%), unexplained sources of EC (12%), vehicular exhausts (9%) and biomass burning (9%) were the major sources of the PM10 aerosols. The percentage of secondary OC estimated from the CMB method (57%) is lower than that estimated from the minimum OC/EC ratio method (68%), probably due to the uncertainties in the concentrations of carbonaceous matter and Pb in the source profiles of vehicular exhausts and biomass burning. The relationship between ambient levels of  $\text{SO}_2$  and  $\text{NO}_x$  and the extent of formation of secondary sulphates and nitrates in the PM10 samples is also investigated in this study.

## Keywords:

PM10 aerosols; secondary formation; Ion Beam Analysis; source apportionment; chemical mass balance.

## 1. INTRODUCTION

PM10 aerosols can cause health problems (e.g. asthma; Anderson *et al.* 1992) and haze problems (e.g. visibility impairment; Pryor *et al.* 1997) in cities. Therefore information on the nature and contributions of sources of these particles is necessary for the development of effective control strategies.

During the last three decades different techniques have been developed for the source apportionment of airborne particles, including: the chemical mass balance method (CMB, e.g. Lowenthal *et al.* 1995), factor analysis techniques (e.g. Hopke, 1985), individual particle analysis techniques (e.g. Xhoffer *et al.* 1992) and the use of dispersion models such as box models (e.g. Simpson, 1990). Secondary contributions from gaseous pollutants sulphur dioxide ( $\text{SO}_2$ ), oxides of nitrogen ( $\text{NO}_x$ ) and volatile organic compounds (VOCs) are among the major sources of PM10 in urban environment (e.g. Turpin and Huntzicker, 1991). Various approaches have been taken to estimate the extent of secondary contributions. These approaches include: assuming that all the particulate sulphates and nitrates are produced from secondary formation (Okamoto *et al.* 1986), relating the results of source apportionment of sulphates and nitrates from factor analysis to the ambient concentrations of gaseous pollutants (Okamoto *et al.* 1990), relating the results of source apportionment to the sources of gaseous emissions and wind trajectories (Gao *et al.* 1994), and estimating the primary organic carbon (OC) from the minimum ratio of concentrations of OC to elemental carbon (EC) in the samples (Turpin and Huntzicker, 1991). These approaches have not, however, been able to accurately apportion sources of both primary and secondary aerosols. The aim of this study is to determine the primary and secondary contribution of emission sources to PM10 aerosols in Brisbane using the CMB method. The objectives of the present study are:

- to analyse PM10 samples collected in an industrial area in Brisbane;
- to determine the primary and secondary contributions of different emission sources using the CMB method and assuming the unexplained mass of S, N and OC as originated mainly from secondary formation;
- to compare the results of secondary contribution of OC by using the CMB method and the minimum OC/EC ratio method; and
- to investigate the relationship between ambient levels of  $\text{SO}_2$  and  $\text{NO}_x$  and the extent of secondary formation of particulate sulphates and nitrates.

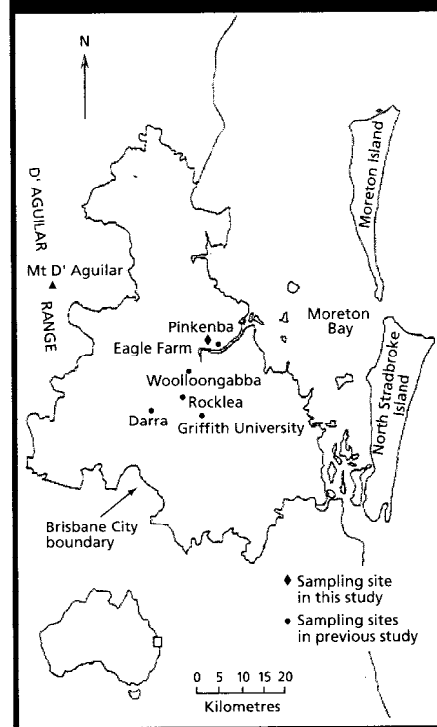
## 2. EXPERIMENTAL

### 2.1 Collection and chemical analysis of samples

Forty-seven sets of 24-hour PM10 aerosol samples were collected from a site in Eagle

Farm, Brisbane, a coastal city with a population of more than 1.6 million and also the fastest growing urban region in Australia (Figure 1) from April 1999 to June 1999. This site was chosen because it is within an industrial area with high emissions of  $\text{SO}_2$ ,  $\text{NO}_x$  and VOCs from industrial sources. Also, concurrent data on the ambient concentrations of  $\text{SO}_2$  and  $\text{NO}_x$  were available from the Queensland Environmental Protection Agency monitoring site at the same location. The PM10 samples were collected on glass-fibre filters at 1.2m above the ground with a high volume sampler and also with a PM10 dichotomous sampler on teflon filters.

Figure 1. Brisbane airshed and the sampling sites.



The teflon filters were analysed using Ion Beam Analysis (IBA) at Lucas Heights Research Laboratories in Sydney following the methodologies developed by Cohen *et al.* (1993). Elements with more than 40% of measured values below the detection limit were excluded (Chan, 1997). Thirteen elements were included, namely H, Al, Si, S, Cl, K, Ca, Ti, Mn, Fe, Zn, Br and Pb. Since IBA techniques are non-destructive, the teflon filters were also analysed by ion chromatography to determine the concentrations of soluble  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ .

# PM10 AEROSOLS IN BRISBANE

Elemental carbon and the OC content of the glass-fibre filters were determined using a modified Walkley-Black procedure developed by Chan *et al.* (1995).

A summary of the results of chemical composition in the samples for the sampling period is shown in Table 1. The precision of the results of chemical analyses was found to be  $\pm 20\%$  in general. All the results are expressed in  $\mu\text{g}/\text{m}^3$ .

**Table 1. Composition of the PM10 samples (in  $\mu\text{g}/\text{m}^3$ )<sup>a</sup>.**

Chemical species	Average concentration	Range
PM10	17.0	3.3-35.8
H	0.504	0.065-1.494
Al	0.274	0.012-0.869
Si	1.074	0.105-2.944
S	0.479	0.193-1.292
Cl	1.267	0.047-3.965
K	0.158	0.027-0.380
Ca	0.193	0.018-0.508
Ti	0.083	0.001-0.968
Mn	0.011	0.002-0.044
Fe	0.414	0.016-1.311
Zn	0.049	0.003-0.427
Br	0.026	0.000-0.073
Pb	0.062	0.011-0.173
EC <sup>b</sup>	2.367	0.000-10.400
OC <sup>c</sup>	2.646	0.449-5.831
NH <sub>4</sub> <sup>+</sup>	0.181	0.000-0.905
Na <sup>+</sup>	1.253	0.059-3.553
K <sup>+</sup>	0.105	0.027-0.199
Mg <sup>2+</sup>	0.157	0.011-0.502
Cl <sup>-</sup>	1.670	0.001-13.526
NO <sub>3</sub> <sup>-</sup>	0.471	0.059-2.338
SO <sub>4</sub> <sup>2-</sup>	0.798	0.167-2.357
SO <sub>2</sub>	7.38	0.78-20.93
NO	27.25	1.62-113.83
NO <sub>2</sub>	26.88	9.60-47.76

**Remarks:**

a 47 sampling days from April to June 1999 at the Eagle Farm site (Brisbane)

b Elemental carbon

c Organic carbon

## 2.2 Development of source profiles

Previous urban aerosol studies have identified the following sources: soil and roadside dust, sea salt, vehicular exhaust, biomass burning (mainly from domestic wood burning), cement dust, ilmenite dust (TiFeO<sub>3</sub>, from mineral processing industry), other industrial emissions, carbon dusts unexplained by the other sources (unexplained EC and OC) and secondary formation as the major sources of PM10 aerosols in Brisbane (e.g. Queensland DEH, 1995, Chan *et al.* 1999). In this study, the source profiles for the major emission sources in Brisbane were developed based on information from literature on the chemical composition of particulate emissions from local sources (e.g. USEPA, 1993, Chan *et al.* 1999).

Source profiles of particulate emissions from the major sources in Brisbane have been derived based on (Chan *et al.* 1999): results of analysis of source samples in Brisbane (including a dust sample collected during a dust storm event, roadside dust samples and surface sea water samples), data on similar sources in other cities (e.g. source profiles of industrial dusts, biomass burning and vehicular exhausts (modified according to the vehicle fleet composition in Brisbane) from the USEPA's SPECIATE database (Chan, 1997), and multivariate analysis of chemical composition of receptor samples (Chan *et al.* 1999). A compilation of these source profiles is shown in Table 2. Previous aerosol studies in Brisbane have also shown that these source profiles are applicable for source apportionment purposes (Chan *et al.* 1999).

## 2.3 Source apportionment by CMB

The contributions from the sources to the PM10 mass for each sampling day were estimated by regression of the PM10 mass with the source profiles. The regression is done by using the CMB7.0 software (USEPA, 1990). Better results were obtained by including 11 sources and 17 species in the regression. These sources include: soil and roadside dust, sea salt, vehicular exhausts, ilmenite dust, combined emissions from other industries, and unexplained sources of N, S (assumed to be in the form of NO<sub>3</sub><sup>-</sup> and

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) (e.g. Harrison, 1992, Okamoto *et al.* 1986), unexplained organics (assumed to be 63.9% in OC (Chan *et al.* 1995), based on the composition of organic material in aerosol samples collected from Southern California by Rogge *et al.* (1993)) and unexplained EC. The contributions from soil dust and roadside dust which have similar source profiles were estimated using a CMB procedure developed by Chan *et al.* (1999). The 17 species were namely Na<sup>+</sup>, Mg<sup>2+</sup>, Al, Si, Cl<sup>-</sup>, K, Ca, Ti, Mn, Fe, Zn, Br, Pb, OC, EC, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>. The CMB7.0 software provides several goodness-of-fit indicators of the model results. These indicators and their target values are (USEPA, 1990):

- t-statistics (source contribution/error of source contribution) > 2;
- Chi-square < 4;
- R<sup>2</sup> > 0.8;
- percentage of total pollutant mass explained by the sources between 80 and 120%;
- C/M ratio (ratio of calculated to measured concentrations of elements) close to one; and
- absolute value of R/U ratio (ratio of residual to uncertainty) < 2.

After the contribution of the sources to the PM10 mass had been estimated for each sampling day, the primary and secondary contributions of the sources to elements S, N and OC in the PM10 sample were estimated as follows. Using element S

**Table 2. A compilation of the source profiles of PM10 emissions from major sources in Brisbane (in %g/g)<sup>a</sup>.**

Elements	Roadside dust	Soil dust	Sea salt	Wood burning	Vehicular exhausts	Combined industrial dusts	Ilmenite dust
Na	0.82	0.66	31.8	0.02	0.00	1.75	0
Mg	0.76	0.00	2.42	0.02	0.35	0.25	0
Al	2.86	7.41	0.00	0.01	0.20	1.78	0
Si	24.8	18.1	0.00	0.00	0.50	3.57	0
S	0.32	0.30	1.75	0.50	0.36	4.37	0
Cl	0.06	0.34	31.8	0.33	0.08	2.76	0
K	0.94	0.99	1.49	2.62	0.02	2.18	0
Ca	2.20	2.08	1.52	0.02	0.08	2.77	0
Ti	0.58	0.50	0.00	0.00	0.02	0.08	31.6
Cr	0.02	0.01	0.00	0.00	0.02	0.18	0
Mn	0.05	0.06	0.00	0.00	0.14	0.67	0
Fe	4.54	3.57	0.01	0.00	0.53	3.09	36.8
Zn	0.20	0.40	0.00	0.01	0.07	3.32	0
Br	0.00	0.00	0.09	0.00	0.79	0.05	0
Pb	0.08	0.02	0.00	0.00	3.05	4.94	0
EC <sup>b</sup>	2.60	0.63	0.00	15.1	42.8	0.42	0
OC <sup>c</sup>	7.09	3.11	0.00	41.9	35.5	4.84	0
K <sup>+</sup>	0.01	0.02	0.54	0.00	0.00	0.00	0
Cl <sup>-</sup>	0.01	0.19	31.8	0.00	0.01	0.00	0
NO <sub>3</sub> <sup>-</sup>	0.01	0.00	0.80	0.00	0.01	0.21	0
SO <sub>4</sub> <sup>2-</sup>	0.10	0.12	5.25	0.07	0.14	9.05	0

**Remarks:**

a Compiled by Chan (1997). Also source profiles for unexplained sources of organics (assume 63.9% OC), N (assume as in the form of NO<sub>3</sub><sup>-</sup>), S (assume as in the form of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) and EC (assume 100% EC).

b Elemental carbon

c Organic carbon

as an example, the secondary contribution of the sources to element S in the PM10 sample was estimated by:

$$\begin{aligned} \text{Secondary contribution to PM10 S} \\ = \text{S in contribution from unexplained} \\ \text{S sources} \end{aligned} \quad [1]$$

while the primary contribution of the sources was estimated by:

$$\begin{aligned} \text{Primary contribution to PM10 S} \\ = \text{PM10 S} - \text{Secondary contribution} \\ \text{to PM10 S} \end{aligned} \quad [2]$$

The primary and secondary contributions of sources to PM10 N and OC were calculated similarly. Based on the results of primary and secondary contributions to PM10 S, N and OC, the primary and secondary contributions of the sources to PM10 mass were estimated by assuming  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NO}_3^-$  as the main form of sulphates and nitrates in PM10 aerosols (e.g. Harrison, 1992, Okamoto *et al.* 1986) and the organic matter comprising of 63.9% OC (Chan *et al.* 1995).

## 2.4 Estimation of secondary OC by the minimum OC/EC ratio method

Since EC is a primary pollutant, by assuming the ratio of primary OC to EC throughout the sampling period as constant the minimum ratio of OC to EC can be used to estimate concentration of primary OC in a sample (Turpin and Huntzicker, 1995, Offenberger and Baker, 2000):

$$\text{Primary OC} = \text{EC} \times (\text{OC/EC})_{\min} \quad [3]$$

Then the concentration of secondary OC can be estimated by:

$$\text{Secondary OC} = \text{OC} - \text{Primary OC} \quad [4]$$

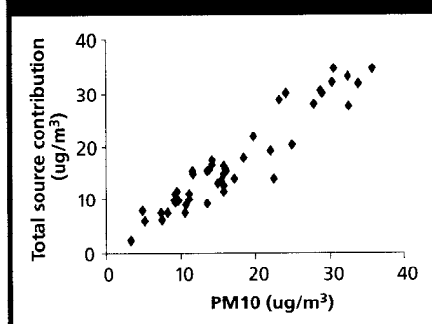
## 3. RESULTS AND DISCUSSION

### 3.1 Results of CMB

A summary of the results of source apportionment of the PM10 mass in the samples by CMB is listed in Table 3. The value of the above goodness-of-fit indicators in the CMB analysis comply with the criteria

stated in Section 2.3 for most of the samples. For example, the total contribution of sources explains 99% of the PM10 mass on average and is also highly correlated to the total pollutant mass ( $n=47$ ,  $r^2=0.99$ ) as shown in Figure 2. The average  $R^2$  value was 0.97. The t-statistic value was larger than 1.0 for most of the samples and the average Chi-square value was 2.5.

Figure 2. Total estimated contribution of sources against the PM10 mass ( $r^2=0.99$ ).



The main sources of error of the results from CMB are:

- the validity of the source profiles derived from previous studies (refer to Section 3.3 for further discussions);
- the assumption that the unexplained S was existing in the completely neutralised ammonium sulphate form;
- the assumption that the organic compound in PM10 aerosols consists of 63.9% OC; and
- the assumption that all the major local sources have been included.

### 3.2 Contribution of sources to PM10 aerosols in Brisbane

The results of contributions to ambient concentrations of PM10 in the Eagle Farm samples are listed in Table 3. On average,

soil and roadside dust (32%), sea salt (27%), secondary formation (15%), unexplained sources of EC (12%), vehicular exhausts (9%) and biomass burning (9%) were the major sources of the PM10 aerosols.

The results of source apportionment from the previous study of PM10 samples collected at five other sites (locations shown in Figure 1) in 1993 and 1994 in Brisbane using the CMB approach (Chan, 1997) are also included in Table 3 for comparison. The other five sites include the Griffith University campus (located within an urban conservation forest area which is surrounded by suburbia), the Rocklea site (within a mixed light industrial/residential area), the Pinkenba site (within a heavy industrial area), the Darra site (close to a cement plant and within a mixed industrial/residential area) and the Woolloongabba site (inner urban and adjacent to a road with high traffic density). Since the samples were collected from different time periods, the comparison is only indicative.

As shown in Table 3, the industrial contribution to PM10 mass was much higher for the Eagle Farm site and the Pinkenba site which are located within industrial areas. The previous studies also show various contributions from cement dust when Queensland Cement Limited was still operating in Brisbane. The contributions from natural and area sources (sea salt and wood burning) were rather uniform for the sites while the contributions from other sources basically reflect sources close to the sites (e.g. vehicular exhausts for the Woolloongabba site and ilmenite dust for the Pinkenba and Eagle Farm sites).

Table 3 also shows that all sites have considerable contributions from unexplained sources of EC and organics. The substantial contributions from carbonaceous matter unexplained by the source profiles, in particular the vehicular exhausts profile and the biomass burning profile since these sources are major contributors of carbonaceous matter, indicates

Table 3. Source apportionment of ambient PM10 at the Eagle Farm (this study) and other sites (previous study<sup>a</sup>) in Brisbane ( $\mu\text{g}/\text{m}^3$ ).

Average contribution	Eagle Farm (this study)	Pinkenba	Rocklea	Darra	Woolloongabba	Griffith University
	PM10	PM10	PM10	PM10	PM10	PM10
No. of samples	47	24	24	24	24	24
Total mass	17.0 (3.3-35.8)	22.0	24.3	38.0	29.6	18.8
Roadside dust	2.64 (0.00-6.34)	4.65	7.09	12.05	6.12	4.05
Soil dust	2.46 (0.00-10.96)	(crustal)	(crustal)	(crustal)	(crustal)	(crustal)
Sea salt	3.87 (0.00-11.08)	2.78	2.76	2.34	3.64	2.91
Wood burning	1.33 (0.00-7.39)	1.72	1.64	4.11	1.50	1.19
Vehicular exhausts	1.52 (0.00-4.15)	0.00	3.07	3.80	10.34	1.45
Industrial emissions	0.78 (0.02-4.85)	0.63	0.00	0.00	0.00	0.15
Ilmenite dust	0.31 (0.00-2.85)	0.92	0.25	0.32	0.29	0.16
Cement dust	—	0.42	0.19	13.64	0.24	1.05
Unexplained $\text{NO}_3^-$	0.10 (0.01-0.51)	—	—	—	—	—
Unexplained $(\text{NH}_4)_2\text{SO}_4$	0.35 (0.13-0.98)	0.45	1.06	0.27	0.43	0.36
Unexplained organics	2.04 (0.00-5.75)	1.61	1.33	0.00	0.00	1.78
Unexplained EC	1.48 (0.00-8.38)	1.60	2.06	0.00	0.32	0.94

#### Remarks:

a From Chan (1997). The samples were collected from September 1993 to August 1994. Nitrate on the samples was not analysed.

Also soil dust and roadside dust were not apportioned separately in the previous CMB procedure and were combined together as crustal matter.

that the source profiles derived from previous studies may not accurately characterise the sources in subsequent years (refer to Section 3.3 for further discussions).

## 3.3 Secondary contribution of S, N and OC elements

Following the procedures described in Sections 2.3 and 2.4, the secondary contribution of the sources of emission to the S, N and OC elements in the PM10 samples were estimated. The results of primary and secondary contributions from the sources are summarised in Table 4. As shown in Table 4, on average, the secondary contributions were 73%, 93% and 56% of the PM10 S, N and OC elements, respectively. These results are similar to those found from a previous Brisbane aerosol study in which the secondary contributions were found to be 70%, 78% and 65% of the S, N and OC elements, respectively (Chan *et al.* 1999).

The primary and secondary contributions of the sources to PM10 mass has also been estimated according to the procedures described in Section 2.3. As shown in Table 4, the total contribution of secondary sulphates, nitrates and OC to the PM10 mass was 15% on average.

A comparison of the estimated primary and secondary contributions of OC by the CMB method and the minimum OC/EC ratio method is also shown in Table 4. The average percentage of secondary OC estimated from the CMB method (57%) is lower than that estimated from the minimum OC/EC ratio method (68%), although the percentages estimated from the two methods are not significantly different from each other. One explanation for this difference is that the two methods are based on different assumptions: the CMB method assumes no changes in the chemical composition of particles during dispersion (e.g. no change in the primary OC content from the sources to the receptor), while the minimum OC/EC ratio method assumes the ratio of concentrations of primary OC to EC as constant throughout the sampling period.

The uncertainties in the concentrations of OC, EC and Pb in the source profiles may also be the cause of this difference. Organic carbon and EC are the most abundant elements in aerosols from vehicular exhausts and biomass burning. However, the concentrations of these two elements in literature source profiles also vary significantly (e.g. USEPA, 1993). This is due to the emission of these two elements being highly dependent on factors including the vehicle fleet composition and weather

conditions. For example, the source profile of vehicular exhausts used in this study was derived based on the average vehicle fleet composition in Brisbane (Chan, 1997).

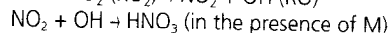
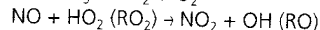
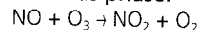
However, the proportion of diesel trucks may be higher in an industrial area such as Eagle Farm, leading to a relatively higher emission of soot particles. Actually this possibility is also supported by the low value of minimum OC/EC ratio found in this study (0.43), comparing with those found from the other aerosol studies (e.g. 1.4-2.4 for the Los Angeles Basin, Turpin and Huntzicker, 1991; 1.0-2.0 from both urban and rural areas, Castro *et al.* 1999). The fact that leaded petrol is phasing out in Australian cities also makes Pb no longer a reliable tracer element for vehicular exhausts and contributes to a higher uncertainty in the estimation of contribution from motor vehicles by CMB.

There is also a lack of information on the composition of emissions from biomass burning in Australia. The source profile of biomass burning used in this study was derived based on overseas literature data supplemented by the results of principal component analysis from a previous aerosol study in Brisbane (Chan *et al.* 1999).

## 3.4 Relationship between ambient concentrations of NOx and secondary formation of nitrates

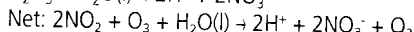
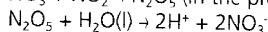
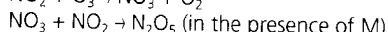
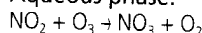
The concentration of secondary sulphates and nitrates has been found to be highly correlated with emissions and ambient concentrations of SO<sub>2</sub>, NOx and NH<sub>3</sub> (e.g. Gao *et al.* 1994). In this study the relationship between the ambient concentrations of NOx and SO<sub>2</sub> and the secondary formation of particulate nitrates and sulphates is also investigated. The reaction mechanisms of the oxidation of these gases in air have been studied thoroughly by other researchers (e.g. Harrison, 1992). The average residence time of NOx in the air is about one day (Brasser *et al.* 1999). The oxidation of NOx is mainly through a gaseous phase reaction mechanism followed by an aqueous phase reaction mechanism (taken from Schwartz, 1989, R represents an organic group and M represents any molecule):

### Gaseous phase:



followed by:

### Aqueous phase:



The nitrate ion such formed can then react with ammonia in air and/or with the chemical components in the particles to form the secondary nitrates. Solar radiation has also been found to play an important role in the reaction mechanisms (Brasser *et al.* 1999).

The amount of secondary contribution to PM10 N is plotted against the ambient concentrations of NOx to investigate the factors which may affect secondary formation of nitrates. The possible effects of meteorological factors including temperature (as a surrogate for solar radiation), humidity and wind speed are also investigated. There is a proportional trend between secondary N and ambient NO<sub>2</sub> (Figure 3). This trend is also observed for NO and NOx but less apparent than for NO<sub>2</sub>. This indicates that the conversion of NO to NO<sub>2</sub> is probably not the rate-determining step in the mechanisms. Since the reaction rate of NOx in air is relatively slow (residence time about one day), the daily ratio of secondary PM10-N to ambient NO<sub>2</sub>-N is expected to be mainly determined by kinetic factors. Therefore the ratio can be used to indicate the rate of conversion of NO<sub>2</sub>-N. As shown in Figure 3, the ratio of secondary N to NO<sub>2</sub>-N ranges from 0.1-3.7% (1.1% on average). The formation of secondary N is also found influenced by temperature and humidity (Figure 4). This result reflects the role of the aqueous phase mechanism and solar radiation in the oxidation of NOx.

Figure 3. Secondary formation of PM10-N against ambient concentration of NO<sub>2</sub>.

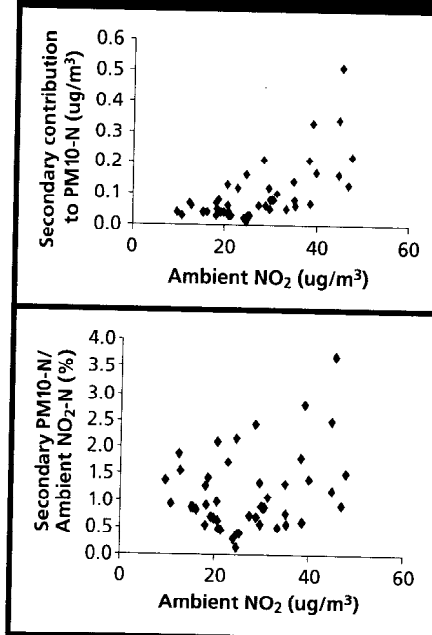


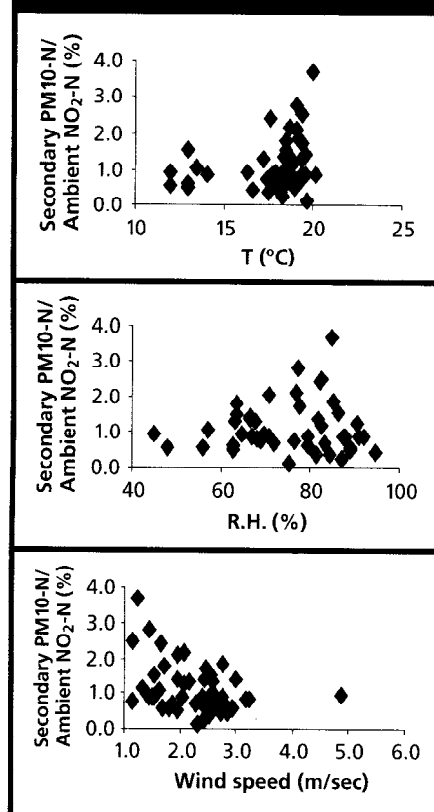
Table 4. Percentage of primary and secondary contributions of the sources to the PM10 aerosol samples in this study.

Contribution	S	N	OC by CMB method	OC by OC/EC ratio	PM10 mass <sup>a</sup>
Primary	27.1%	7.0%	43.4%	32.3%	84.6%
	(4-57.4%)	(0.8-35.3%)	(2.4-100%)	(13.7-100%)	(23.2-97.2%)
Secondary	72.9%	93.0%	56.6%	67.7%	15.4%
	(42.6-96.0%)	(64.7-99.2%)	(0-97.6%)	(0-86.7%)	(2.8-76.8%)

Remarks:

a Assume (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NO<sub>3</sub><sup>-</sup> as the main chemical form of PM10 S and N.

Figure 4. Secondary formation of PM10-N against temperature, humidity and wind speed.



On the other hand, there is an inversely proportional trend between secondary formation and wind speed (Figure 4), due to better dispersion of NOx in strong winds.

### 3.5 Relationship between ambient concentrations of SO<sub>2</sub> and secondary formation of sulphates

The average residence time of SO<sub>2</sub> in the air

Figure 5. Secondary formation of PM10-S against ambient concentration of SO<sub>2</sub>. '■' represents the days with higher ratios of secondary-S to SO<sub>2</sub>-S. '●' represents the days with lower ratios.

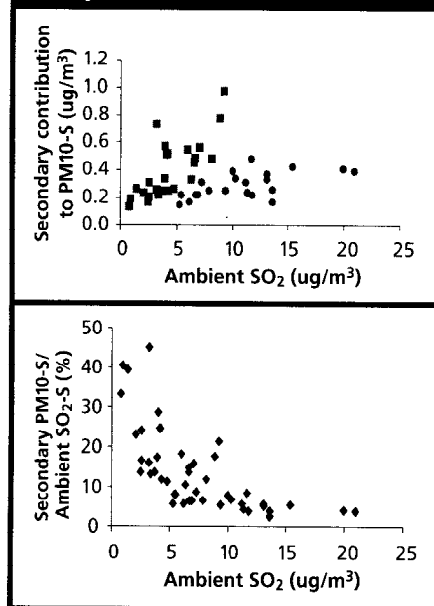
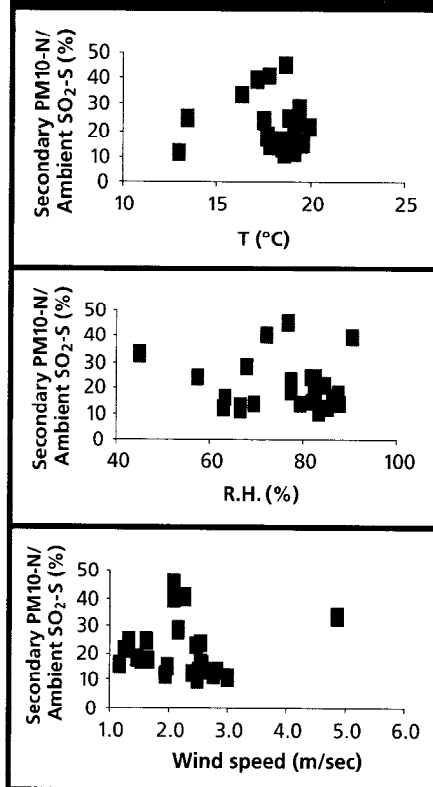
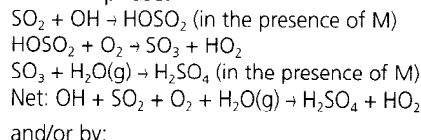


Figure 6. Secondary formation of PM10-N against temperature, humidity and wind speed (high secondary-S to SO<sub>2</sub>-S ratio group).



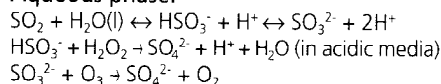
is about 10 days (Brasser *et al.* 1999). The oxidation of SO<sub>2</sub> can be through a gaseous phase reaction mechanism and/or an aqueous phase reaction mechanism (taken from Schwartz, 1989, M represents any molecule):

#### Gaseous phase:



and/or by:

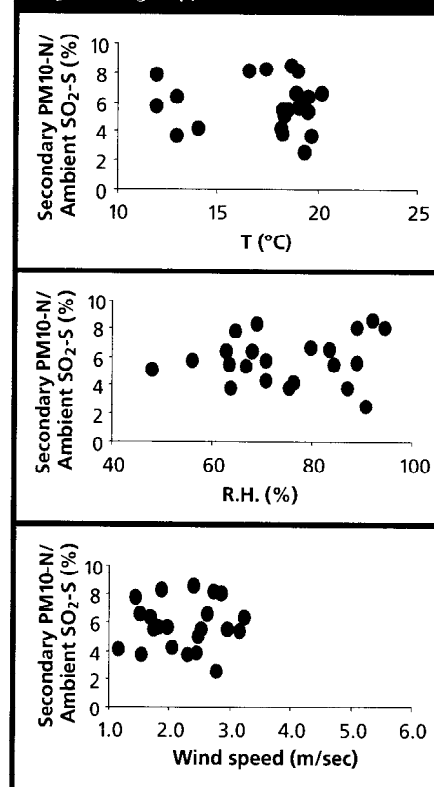
#### Aqueous phase:



The sulphate ions once formed can then react with ammonia in air and/or with the chemical components in the particles to form the secondary sulphates.

The plots of formation of secondary PM10-S in Figure 5 show that the overall average ratio of secondary S to SO<sub>2</sub>-S is 13.8% and the data points seem to fall into two groups. One with higher ratios (from 11.8-45.3%, represented by '■' in the figures, 25 data points) while the other group have lower ratios (from 2.5-8.2%, represented by '●' in the figures, 22 data points). The ratio also decreases with increase in concentration of ambient SO<sub>2</sub> (Figure 5). This is probably due to the longer residence time of SO<sub>2</sub> (slower reactions) which makes the supply of SO<sub>2</sub> unlikely to be a limiting factor. The influence of temperature, humidity and wind speed is less apparent for SO<sub>2</sub> than for NOx and shows up only in the group with a higher extent of conversion (Figure 6 and Figure 7). This is probably due to the slower

Figure 7. Secondary formation of PM10-N against temperature, humidity and wind speed (low secondary-S to SO<sub>2</sub>-S ratio group).



reactions of SO<sub>2</sub> and indicates the faster aqueous phase mechanism plays a more important role on sampling days with a higher rate of conversion of SO<sub>2</sub>.

## 4. CONCLUSION

This study investigates the contributions of different sources to primary and secondary PM10 aerosols in an industrial area in Brisbane. The CMB method was used to estimate the contributions of different emission sources. The secondary contributions of S, N and OC were determined by assuming the unexplained mass of S, N and OC as mainly originated from secondary formation. The results of secondary contribution of OC were also compared with those using the minimum OC/EC ratio method.

On average, soil and roadside dust (32%), sea salt (27%), secondary formation (15%), unexplained sources of EC (12%), vehicular exhausts (9%) and biomass burning (9%) were the major sources of the PM10 aerosols. Also 15% of the total mass, 73% of the S, 93% of the N and 57% of the OC elements in the PM10 samples were from secondary formation. The average percentage of secondary OC estimated from the CMB method (57%) is lower than that estimated from the minimum OC/EC ratio method (68%).

The formation of secondary nitrates and sulphates in the samples is found to be enhanced under high temperature, high humidity and/or low wind speed conditions. This finding is consistent with the role of aqueous phase reactions and solar radiation in the oxidation of NOx and SO<sub>2</sub> in air.

The influence of meteorological conditions is less apparent for SO<sub>2</sub> than for NO<sub>x</sub>, probably due to the relatively slower reaction rate of SO<sub>2</sub>. The formation of secondary sulphates in the samples reveals the possibility of two concurrent reaction mechanisms. The results also indicate that the aqueous phase mechanism plays a more important role on sampling days with higher formation of secondary sulphates.

This study also indicates that the source profile of vehicular exhausts needs to be updated frequently due to the change in vehicle fleet composition and the gradual phase out of leaded petrol in Australian cities. There is also a lack of information on composition of emissions from biomass burning in Australia.

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