SOURCE APPORTIONMENT OF AMBIENT VOLATILE ORGANIC COMPOUNDS IN MAJOR CITIES IN AUSTRALIA BY POSITIVE MATRIX FACTORISATION

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Abstract

Source apportionment of the 6-daily, 24 h volatile organic compound (VOC) samples collected during 2003-2004 in Melbourne, Sydney and Brisbane was carried out using the Positive Matrix Factorisation software (PMF2). Fourteen C₄-C₁₀ VOCs were chosen for source apportionment. Biogenic emissions were not covered in this study because tracer VOCs such as isoprene were not measured. Five VOC source factors were identified, including the 'evaporative / fuel distribution' factor (contribute to 37% of the total mass of the 14 VOCs on average), the 'vehicle exhaust / petrochemical industry' factor (24%), the 'biomass burning' factor (13%), the 'architectural surface coatings' factor (5%) and the 'other sources' factor (14%). The relative contributions of the source factors to the ambient VOC concentration at the sampling sites were comparable to the relative emission loads of the local sources in Australian air emission inventories. The high contribution from evaporative emissions indicates that introduction of reduction measures for evaporative emissions could substantially reduce the VOC emissions in Australian cities. The total VOC mass and the contributions from vehicle related sources and biomass burning were higher in winter and autumn, while the contributions from surface coatings were higher in summer.

Keywords: VOC; source apportionment; positive matrix factorisation; TO-17; GC-MS; emission inventories

Introduction

Most of the population in Australia are confined to a small number of coastal cities including Melbourne (37°47′S 144°58′E), Sydney (34°0′S 151°0′E), Brisbane (27°29′S 153°8′E) and Adelaide (34°55′S 138°36′E). The climate of these cities ranges from typical subtropical climate with hot, humid summers and dry, mild winters (e.g. Brisbane), to temperate climate with hot, dry summers and cold, foggy winters (e.g. Melbourne). Apart from motor vehicles and industry as the common sources of air pollutants in these cities, domestic wood stoves are also commonly used in winter and autumn seasons in the cooler cities. Recirculation of air pollutants due to diurnal land breeze and sea breeze in these coastal cities, and the frequent temperature inversion phenomenon in winter, often increase the pollution levels in the cities (Tapper and Hurry 1996). Among the air pollution problems the elevated concentration of volatile organic compounds (VOCs) has been of concern due to their associated adverse health effects and smog formation potential (e.g. McLaren et al. 1996; Klimont et al. 2002). Therefore information on apportionment of the emission sources of VOCs is essential for developing effective control strategies for their associated problems.

This project aimed to provide information on the composition of airborne particles and VOCs in Melbourne, Sydney, Brisbane and Adelaide. The project collected concurrent 6-daily, 24 h (midnight to midnight) airborne particle and VOC samples from two sites in each city over 12 months during 2003 and 2004 (Table 1). The results on airborne particle sampling have been reported elsewhere (Hawas et al., 2003; Chan et al., 2008). The sampling and analysis of the VOC samples were according to US EPA TO-17 method (USEPA 1999). In total 468 days of VOC samples were collected and 25 C₄-C₁₀ VOCs were determined.

Various techniques have been used for source apportionment of atmospheric VOCs, including the chemical mass balance method (CMB; e.g. Fujita 2001; Hellen et al. 2003), factor analysis techniques such as UNMIX (e.g. Hellen et al. 2003; Jorquera and Rappengluck 2004), and principal component analysis techniques (PCA) such as PCA/APCS (e.g. Guo et al. 2004), PCA/MLR (e.g. Baldasano et al. 1998) and positive matrix factorisation (PMF; e.g. Kim et al. 2005; Brown et al. 2007). Four studies (Miller et al. 2002; Anderson et al. 2002; Hellen et al 2003; Jorquera and Rappengluck 2004) have compared 4 of these methods: CMB, PCA/APCS, UNMIX and PMF. Miller et al. (2002) found that PMF extracted factor profiles that most closely represented the major sources. Anderson et al. (2002) found the results from the methods agreed reasonably well for one city data set, but less consistent for another city data set. Hellen et al (2003) and Jorquera and

Rappengluck (2004) found the results from PMF method as comparable to those from the CMB method and the UNMIX method, respectively. Since the PMF technique takes into consideration the errors in the data and produces non-negative factor loadings and scores, therefore with careful selection of modelling parameters PMF has also been found to be better in the handling of missing data and resulting in better source profiles than the other methods (e.g. Huang et al. 1999; Hien et al. 2004; Jorquera and Rappengluck 2004).

This paper discusses the results of application of PMF analysis to the source apportionment of the VOC samples from the Australian cities.

Sampling and chemical analysis

Air samples were collected on dual-bed 'Air Toxics' sorbent tubes (Supelco #25086). The tubes were conditioned and spiked with deuterated internal standards covering a range of volatility before sampling. Brass swagelok end caps (with Teflon ferrules) were used to seal the tubes. At least one tube per fortnight was used as a field blank at the sites. Breakthrough tests were carried out at the beginning of the project to determine the sampling rate and volume. Samples were collected at a flow rate of around 17 mL min⁻¹ and a total volume of around 24 L. Flow rate differences between tubes were found to be insignificant at a relative standard deviation (RSD) of 0.8%. The average flow rate (between the initial setting and the final reading) of the sampling pumps was used to calculate the volume of air sampled. The maximum before/after sampling variation in flow rate of the pumps was found to be 17%.

The method of analysis was based on US EPA Method TO-17 (USEPA 1999). The sampled tubes were placed onto the automated thermal desorber (ATD 400 or Turbomatrix, Perkin Elmer) connected to a gas chromatograph-mass spectrometer (Air Saturn GC-MS, Varian). Calibration standards tubes were spiked with calibration standards and internal standards. Results were adjusted for internal standard recovery of sample compared to the calibration standards. The recovery % of internal standards was mostly within 80-120%. The minimum detection limit (MDL) of the analysis was 200 ng m⁻³. The Queensland Health Scientific Services laboratory performing the VOC analysis is accredited for this test by the Australian National Association of Testing Authorities (NATA). The laboratory has also achieved satisfactory results in international collaborative studies involving the determination of environmental levels of VOCs by US EPA Method TO-17.

Although 25 C₄-C₁₀ VOCs were measured, only the 14 VOCs which were detected in more than 30% of the samples were included in the PMF analysis, including methyl ethyl ketone, n-hexane, chloroform, benzene, trichloroethene, methyl isobutylketone, methyl cyclohexane, toluene, n-octane, ethyl benzene, total xylenes, n-nonane, total trimethyl benzenes and n-decane. The composition of the samples and percentage of samples above the MDL are listed in Table 2. Due to the lower emission load of VOCs in Adelaide than in the other cities (NEPC 2006), the VOC concentrations in the Adelaide samples were also lower than those in the samples from the other cities (Table 2). The number of Adelaide samples with sufficiently high VOC concentrations was insufficient for the PMF analysis and therefore the Adelaide data sets were excluded from the analysis.

Source apportionment by PMF

PMF principles

The 2-dimensional positive matrix factorisation model (PMF2) for source apportionment of VOC samples is (Paatero, 2004)

$$X = GF + E$$

where $X(n\times m)$ is the composition matrix of the collected samples, n and m are the number of samples and VOCs, respectively. $G(n\times p)$ is the source contribution matrix where p is the number of source factors extracted. $F(p\times m)$ is the source profile matrix (i.e. the composition of VOCs emitted from the sources). $E(n\times m)$ is the part of X which is not explained by the model. The elements in G and F are constrained to non-negative values only. The objective of PMF analysis is to minimise the goodness-of-fit indicator, Q, which is defined as

n m
$$Q = \sum \sum (e_{ij} / s_{ij})^{2}$$
 [2]
$$i=1 \ j=1$$

where e_{ij} 's are the elements in E and s_{ij} 's are the standard deviations (s.d.) of the measured concentrations. Q should be close to the degree of freedom of the analysis which equals to nm-pm-pn (Lee et al., 1999).

Two input files are needed for each run: a concentration matrix (X) and a standard deviation matrix (S). In this study, for measured concentrations above MDL the s.d.'s were estimated by (Xie and Berkowitz 2006):

s.d. =
$$MDL/3 + C \times Concentration$$
 [3]

where C is basically the coefficient of variation of the chemical analysis. The sources of error include both sampling error and analysis error. The coefficient of variation of VOC sampling and analysis has been reported as within 15% (Hellen et al. 2003) to 25% (Guo et al. 2004) and also has been found to be similar for the two main VOC sampling methods: sorbent tube method and canister method (Hellen et al. 2003). Since single tube sampling was used in this project rather than the distributed volume pairs method as recommended in US EPA TO-17 (i.e. concurrent sampling at various sampling rates; US EPA 1999), in this analysis the value of C for each site data set was experimented from 0.15 up to 0.30 by trial-and-error following Xie and Berkowitz (2006) (refer to the next section).

For measured concentrations below MDL, the concentrations were taken as half of the value of MDL and the s.d.'s were estimated by (Xie and Berkowitz 2006):

$$s.d. = MDL/3 + MDL/2$$

Choice of modelling parameters and number of factors

Experience from other researchers has shown that careful selection of modelling parameters and the number of factors is essential in getting sensible results from PMF analysis (e.g. Lee et al. 1999; Kim et al. 2005). For examples, at least 10 random starts for each run are needed to obtain the minimum Q value. The use of Robust mode in PMF also minimises the influence of outlier data (defined as concentration $> 4 \times s.d.$ of the VOC in this study). Another two parameters that need to be carefully chosen include the rotational freedom parameter (F_{peak}) and the number of source factors to be extracted.

The F_{peak} parameter controls if extreme values are to be assumed for the source profiles (by assigning positive F_{peak} values) or the source contributions (by assigning negative F_{peak} values). In this analysis, F_{peak} values from -0.2 to +0.9 were applied to each data set. The F_{peak} value before a sharp rise in Q occurs (i.e. before the goodness-of-fit deteriorates) in the Q against F_{peak} plot was

regarded as the appropriate F_{peak} value (Kim et al. 2005). This process results in source profiles with more extreme values for the tracer VOCs and so are easier to relate to physical sources of emission.

The selection of number of factors is based on the closeness of the Q value to the target Q value, and the scaled residual values (r_{ii} 's) in the scaled residual matrix (R) generated from the PMF run:

$$r_{ij} = e_{ij} / s_{ij}$$
 [5]

The number of factors that could be resolved from each site data set is indicated by (Lee et al., 1999):

- R₉₀ (the 90 percentile of the scaled residuals) is within ±2. That is, most of the residuals are within 2 times of the s.d.'s.
- A sharp drop in IM (the maximum value of the mean values of r_{ij}'s of each VOC) and/or IS (the
 maximum value of the s.d. values of r_{ij}'s of each VOC) in the IM or IS against number of factors
 plot. That is, further increase in number of factors does not result in a significant increase in data
 variance explained by the model.

The process to determine the number of factors and the appropriate C and F_{peak} values to use for each site data set, is as follows:

- Firstly, the PMF run is carried out on the data set using F_{peak} = 0 and C = 0.20 and number of factors from 3 to 8. A sharp drop in IM and/or IS, while still satisfying the criterion of R₉₀ within ±2, is used to indicate the number of factors.
- Secondly, if the Q value is found to be too small (Q <50% of the target Q value) for the chosen number of factors, the PMF run is rerun using the chosen number of factors but with a smaller value of C = 0.15. If the Q value is found to be too large (Q >150% of the target Q value), the PMF run is rerun using a larger value of C = 0.25 or C = 0.30. The choice of C value is based on the closeness of Q to the target Q value.
- Finally, using the chosen C value and the chosen number of factors, the PMF run is then
 repeated with F_{peak} values from -0.2 to +0.9. The F_{peak} value before a sharp rise in Q occurs is
 used in the final run.

In this study, the choice of 5 factors and C = 0.15 was found to fit most of the modelling criteria for the data sets. The F_{peak} values chosen for the site data sets were -0.1 (Alphington), 0 (Rocklea), +0.2 (Footscray) and +0.3 (Earlwood, Richmond and Springwood), respectively.

Identification of sources and estimation of source contributions

In source apportionment studies the derived source factors are usually related to the physical sources of emissions based on the closeness of the derived source profiles to those reported in the literature, and available information on local emission sources (e.g. Baldasano et al. 1998; Borbon et al. 2002).

In Australia, the National Pollutant Inventory database (NPI; NEPC 2006) provides updated information on the annual emission loads of major sources of emission of 90 air toxics, including some of the 14 VOCs in this study. Therefore the nationwide emission loads for the VOCs for the year 2003-2004 were used to indicate the major sources of emission. Since methyl cyclohexane, n-octane, n-nonane, total trimethyl benzenes and n-decane were not included in the NPI air toxics list, information on the possible sources of emission of these VOCs as reported in the literature was also utilised to supplement the NPI data. For example, methyl cyclohexane has been found to relate to vehicular emissions, n-octane are related to vehicular emissions and solvent use, while n-nonane, total trimethyl benzenes and n-decane are related to vehicular emissions, surface coatings and biomass burning (Vega et al. 2000, Jarquera and Rappengluck 2004, Xie and Berkowitz 2006, Fujita 2001 and Kim et al. 2005).

The emission load for motor vehicles in the NPI database includes both vehicular exhausts and evaporative emissions. Evaporative emissions include mainly running losses, followed by hot soak and diurnal losses (CARB 2005). The ratio of evaporative emissions to the total emissions from vehicle related sources has been reported to be from within 0.30-0.57 (e.g. in US and Australian cities; cited in Duffy et al. 1999) to 0.68 (e.g. for the South-east Queensland area in Australia; Queensland EPA 2003a). Although both vehicular exhausts and evaporative emissions contain mainly alkanes and aromatics, evaporative emissions are more abundant in alkanes with higher number of carbons, while vehicular emissions are more abundant in aromatics (Queensland DEH 1995). Therefore in this study, the abundance of higher carbon number alkanes comparing to those of aromatics in the source profiles were used to distinguish the vehicle exhaust factor from the evaporative emission factor.

Some VOC source apportionment studies have also reported separate source factors for petrol-fuelled vehicles and diesel-fuelled vehicles (e.g. Jorquera and Rappengluck 2004; Fujita 2001; based on that n-nonane, trimethyl benzenes and n-decane are more abundant in diesel exhaust than in petrol exhaust). In Australia, however, VOC emissions from motor vehicles are dominated by petrol-fuelled vehicles. For example, according to the Year 2000 South-east Queensland Air Emission Inventory, petrol-fuelled vehicles were responsible for 98% of the motor vehicle related VOC emissions (Queensland EPA 2003a). The PMF analysis in this study also did not reveal separate factors for the two fuel types.

Although biogenic emissions is also a major source of VOCs in Australian cities (e.g. Queensland EPA 2003a; NEPC 2006) and other cities (e.g. Hellen et al. 2003; Xie and Berkowitz 2006), the VOCs emitted from this source are mainly isoprene and monoterpenes (e.g. Jorquera and Rappengluck 2004). For example, the biogenic emission load in the South-east Queensland area has been estimated to be about 93% in isoprene and 5% in monoterpenes (Queensland EPA 2003b). Since both isoprene and monoterpenes were not measured in this study, the contribution from biogenic emissions cannot be estimated in this study.

Other major sources of VOCs which also cannot be identified in this study include emissions from the use of natural gas and liquid petroleum gas. This is because these sources are mainly associated with alkanes with less than 6 carbons (e.g. Guo et al. 2005), which were not measured in this study.

Results and discussions

Identified sources and source profiles

Five VOC source factors were identified from the PMF analysis for each site data set and were related to the possible sources of emission using the NPI data as a guide. The average composition of these source factors, together with the source profiles derived from the emission loads of similar sources in the NPI database, are shown in Figure 1. As shown in Figure 1, the source profiles from the PMF analysis are comparable to those derived from the NPI emission loads for the VOCs in common. Both the 'evaporative / fuel distribution' factor and the 'vehicle exhaust / petrochemical industry' factors are enriched with alkanes and aromatics (benzene, toluene and ethyl benzene). The 'evaporative / fuel distribution' factor is more abundant in higher carbon number alkanes (n-nonane and n-decane) but less abundant in aromatics than the 'vehicle exhaust / petrochemical industry' factor.

The 'architectural surface coatings' factor is associated with methyl ethyl ketone, methyl isobutyl ketone and n-hexane. This factor relates to solvents in paint, varnish and lacquer and solvents used as thinners and for cleanup (US EPA 1995). This factor could also be related to sources in relation to solvent use. The 'biomass burning' factor is associated with benzene, trichloroethene and methyl isobutyl ketone. This factor could also be related to domestic solid fuel burning, bush fires and controlled burning activities in Australia. The 'other sources' factor is associated with a wide range of VOCs including n-hexane, chloroform, benzene, methyl cyclohexane and n-octane. These VOCs could be related to various industrial activities in Australia.

It should be noted that the mass % of the VOCs in the same source factor extracted from different site data sets could vary substantially (e.g. Brown et al. 2007). For example, the mass % of total xylenes in the 'vehicle exhaust / petrochemical industry' factors varied substantially from 0.15 (Footscray, Melbourne samples) to 0.46 (Rocklea, Brisbane samples). The uncertainties of the VOC composition in the source profiles was $\pm 32\%$ on average and ranged from $\pm 10\%$ (for methyl ethyl ketone) to $\pm 55\%$ (for n-nonane).

Although in total these factors explained more than 81% of the variations in VOC concentrations, more than 30% of the variations in chloroform, trichloroethylene, methyl isobutyl ketone and methyl cyclohexane were not explained by these factors. These VOCs have large uncertainty in the measurement method and/or large number of samples which have concentrations below the MDL (Table 2).

Contribution of sources to the VOC mass of the samples

The average contribution of the source factors to the VOC mass of the samples collected from different sites are shown in Table 3. The uncertainties of the estimated source contributions was $\pm 56\%$ on average and ranged from $\pm 28\%$ (for 'evaporative / fuel distribution' contribution) to $\pm 84\%$ (for 'architectural surface coatings' contribution).

On average, the 5 source factors in total explained about 93% of the total mass of the 14 VOCs in the samples (Table 3). The average contributions of the factors in the samples were 'evaporative / fuel distribution' (37%), 'vehicle exhaust / petrochemical industry' (24%), 'architectural surface coatings' (5%), 'biomass burning' (13%) and 'other sources' (14%). Therefore on average sources in relation to motor vehicle and fuel use contributed about 61% of the mass of the VOCs.

The average contributions of the source factors to the total mass of the 14 VOCs in this study are compared with the emission loads of corresponding source types in the NPI database in Table 3. The average % contributions of the source factors to the VOC samples at the sites were comparable to the emission load % estimates (Table 3). The similar relative proportions of source emission loads and relative proportions of source contributions to ambient concentrations, also reflects the fact that the 14 VOCs in this study are mainly primary VOCs (Table 3). As shown in Table 1 and Table 3, the total ambient mass of the 14 VOCs was also roughly proportional to the emission load of total VOCs for the residential / industrial areas. But for the two suburban / semi-rural areas (Richmond and Springwood) the emission load to ambient concentration ratio was more than twice of those for the urban / industrial areas. This is probably because: (1) the area of the suburban areas defined by the government authorities is usually much larger than that of the urban areas. For example, the area of the suburban areas Richmond and Springwood are 180 km² and 40 km², respectively, while that of the urban areas Earlwood and Rocklea are only 9 km² and 12 km², respectively (NEPC 2006). That means, although the density of emission sources in the suburban areas is lower, their larger area could result in a similar number of emission sources in the whole suburb comparing to that in the urban areas. (2) The flatter terrain of the suburban areas could also enhance dispersion of air pollutants.

Table 3 also shows that the average contribution of evaporative emissions was about 61% of that of the total vehicle related emissions. This ratio is similar to the estimated ratio based on the emission load estimates in Australian emission inventories. For example, the average percentage of evaporative contribution is 63% of the total vehicle related contribution at the 2 Brisbane sites, while the percentage of evaporative emission load is estimated to be 68% of the total vehicle related emission load in the South East Queensland Air Emission Inventory (Queensland EPA 2003b).

The contribution of the source factors to VOC mass in the site samples basically reflects the emission source characteristics of the sites. As shown in Table 1 and Table 3, the VOC mass was higher at the sites with heavier traffic and/or industrial activities on average. The Richmond site (the Sydney residential / semi-rural area site) has the lowest VOC mass. This site is more than 50 km away from the Sydney city centre and is located within a university campus (Table 1). The average contribution of the sources (Table 3) is also consistent with the average concentration of the tracer VOCs for the sources (Table 1). For examples, the contribution of the vehicle related source factors and the concentration of ethyl benzene and total xylenes were both higher in the Melbourne and

Sydney samples, on average. The contribution of the 'architectural surface coatings' factor and the concentration of methyl ethyl ketone were both higher in the Melbourne samples. The contribution of the 'other sources' factor and the concentration of chloroform were both higher in the Sydney and Brisbane samples. On average, the Sydney Earlwood site samples have the highest contribution from vehicle related sources (23,800 ng m⁻³), while the Melbourne site samples on average have the highest contribution from biomass burning (3,200 ng m⁻³).

The ratio of average contribution of the 'evaporative / fuel distribution' factor to that of the 'vehicle exhaust / petrochemical industry' factor was very similar at all sites (about 0.61) except for the residential / semi-rural site, Richmond, Sydney (0.72). This is probably due to the higher proportion of evaporative contributions due to hot soak loss and diurnal loss from parked vehicles in the residential / semi-rural area (Queensland DEH 1995). The high contribution from evaporative emissions in the samples also indicates that introduction of reduction measures for evaporative emissions could substantially reduce the VOC emissions in Australian cities. For example, lowering the volatility of petrol has been found to reduce diurnal losses (EPA Victoria 1997), while repairing of the fuel system in cars has been found to reduce also hot soak and running losses (CARB 2005).

A compilation of VOC source apportionment results from this study and 11 other recent studies is shown in Table 4. This comparison has to use caution because of the samples being taken in different urban locations and from different time periods, and of the different number and type of VOCs measured in the studies. In general, Table 4 shows substantial variations in the number, types and contribution of source factors resolved from the studies. Motor vehicle related sources were the dominant sources in all the studies. In general, the relative contribution from motor vehicle related sources for the Australian cities was relatively lower than those observed in the other cities. As discussed in the previous section, sources in relation to biogenic emissions and use of natural gas and liquid petroleum gas could not be identified in this study. This study also did not resolve separate source factors for petrol and diesel-fuelled vehicles as in some of the other studies (e.g. Jorquera and Rappengluck 2004). The surface coatings factor was only also identified in the Los Angeles study. The biomass burning factor was not identified in the other studies. The other studies, however, identified sources of local industries.

Temporal variations in contribution of sources

The average contributions of the source factors to the VOC mass of the samples collected in different seasons are shown in Figure 2. The average total VOC mass was highest in winter and

lowest in summer. Further investigation into the city data sets (Table 2) shows that the seasonal variations in VOC mass was most significant in the Sydney samples, and was insignificant in the Melbourne samples. For example, the average ratio of total VOC mass in winter to that in summer was highest for Sydney (3.4), followed by Brisbane (2.5) and Melbourne (1.1) (Table 2). The difference in winter to summer VOC ratio in the cities reflects the difference in seasonal variations in temperature and humidity in the cities.

The average contributions of motor vehicle related sources and 'biomass burnings' were higher in the winter and autumn samples and lower in the summer samples. The average contribution of the 'surface coatings' factor was higher in summer. The average contribution of 'other sources' was lowest in summer, probably due to the more effective dispersion of pollutants from industrial activities and stacks in summer.

The average contributions of the source factors to the VOC mass of the samples collected on weekdays have also been compared to those collected on weekends. On average the total VOC mass was only slightly higher in the weekday samples than in the weekend samples. The contributions from the source factors in relation to motor vehicles were higher in the weekday samples than in the weekend samples, as expected. The average ratio of evaporative contribution to total vehicle contributions was rather uniform throughout the week. The contributions from the 'biomass burning', 'surface coatings' and 'other sources' factors were also rather uniform throughout the week.

Summary

Source apportionment was carried out for the VOC samples collected during 2003-2004 in Melbourne, Sydney and Brisbane by using the PMF2 software. On average, the 5 identified source factors explained approximately 93% of the total mass of the 14 C₄-C₁₀ VOCs chosen for the analysis. The average contributions of the factors to the VOC mass in the samples were 'evaporative / fuel distribution' (37%), 'vehicle exhaust / petrochemical industry' (24%), 'architectural surface coatings' (5%), 'biomass burning' (13%) and 'other sources' (14%). Therefore on average sources in relation to motor vehicle and fuel use contributed about 61% of the total mass of the VOCs. The relative contribution of the source factors to the ambient VOC concentration at the sampling sites were comparable to the relative emission load of the local sources in Australian air emission inventories.

The average ratio of evaporative contribution to total contributions of vehicle related sources was 0.61 which is similar to the ratio estimated in Australian emission inventories. Motor vehicle related sources were the dominant sources of VOCs in this study and in other cities. The high contribution from evaporative emissions also indicates that introduction of reduction measures for evaporative emissions could substantially reduce the VOC levels in Australian cities. While this study also identified biomass burning and surface coatings as the other main sources of VOCs, the other studies identified sources of local industry as the other main VOC sources instead.

The average VOC mass, the average contributions of motor vehicle related sources and the average contribution of 'biomass burnings' were higher in the winter and autumn samples and lower in the summer samples. The average contribution of the 'surface coatings' factor was higher in the summer samples.

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Captions

Table 1. Sampling sites and number of VOC samples (in bracket)

Table 2. Average and maximum VOC concentrations in the city samples (in ng m⁻³)

Table 3. Average contribution of source factors in the VOC samples estimated in this study and

average VOC emissions estimated in the National Pollutant Inventory (in % of total VOC mass)

Table 4. A comparison of the average results from recent source apportionment studies

Figure 1. VOC source profiles

Remarks: The white columns and the bars represent the values of average and standard deviation in source profiles derived from the 6 sample data sets. The white columns represent the source profiles derived from emission loads of similar sources in the 2004-2005 Australian NPI database. NPI does not include methyl cyclohexane, n-octane, n-nonane, total trimethyl benzenes and n-decane.

Figure 2. Seasonal trends of contribution of source factors in the VOC samples (in ng m⁻³)

Table 1. Sampling sites and number of VOC samples (in bracket)

City	Melbourne	Sydney	Brisbane	Adelaide
Site 1	Alphington (59)	Earlwood (61)	Rocklea (56)	Netley (60)
	Residential / light industrial area	Residential area	Residential / light industrial area	City / commercial area
	Next to a railway station; 7.1 km from the CBD	10.7 km from the CBD	~750 m from a minor road and ~1 km from a major road; former grazing paddock within an animal research farm; 7.6 km from the CBD	~500 m from a main road, and ~ 2 km from an aluminium foundry adjacent to airport; 7.1 km from the CBD
Site 2	Footscray (57)	Richmond (59)	Springwood (61)	Northfield (55)
	Residential / light industrial area	Residential / semi- rural area	Residential area	Residential area
	6.2 km from the	Inside a university	~1 km from a major road;	~200 m from a major
	CBD	campus; 51.1 km	inside a high school; 20.2	road; 7.6 km from the
		from the CBD	km from the CBD	CBD

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Table 2. Average and maximum VOC concentrations in the city samples (in ng m⁻³)

	Melbourne s	amples	Sydney san	mples	Brisbane sa	mples	Adelaide samples		
Number of samples	116		120		117		115		
	Ave (max)	% samples > MDL 1	Ave (max)	% samples > MDL	Ave (max)	% samples > MDL	Ave (max)	% samples > MDL	
Total mass of the 14									
VOCs									
All seasons	26180 (119620)		25230 (247660)		20340 (156320)		7270 (45760)		
2003 Autumn	27470 (91040)		13640 (32030)		33540 (62120)		4590 (6260)		
2003 Winter	26940 (80080)		41290 (247660)		28370 (156320)		9960 (45760)		
2003 Spring	27700 (63400)		21710 (122200)		18780 (39080)		7790 (21750)		
2003/2004 Summer	23590 (119240)		12120 (46890)		11430 (22080)		4690 (11760)		
2004 Autumn	25990 (119620)		28530 (104790)		17870 (50430)		6130 (22410)		
Methyl ethyl ketone	2540 (106870)	70	650 (4850)	63	490 (6530)	42	160 (1200)	19	
n-Hexane	1800 (20120)	78	2050 (40700)	53	1620 (11850)	65	370 (4620)	28	
Chloroform	170 (1280)	21	250 (1870)	38	220 (2300)	29	100 (430)	2	
Benzene	1830 (11040)	97	2190 (20280)	93	1770 (10590)	94	430 (3490)	44	
Trichloroethene	210 (1450)	34	520 (4070)	48	130 (430)	12	110 (380)	8	
Methyl isobutyl ketone	150 (830)	16	190 (1280)	24	290 (1980)	40	100 (100)	0	
Methyl cyclohexane	280 (2210)	29	430 (3910)	34	360 (3820)	35	140 (1010)	11	
Toluene	6610 (65110)	97	6320 (65990)	97	4920 (49190)	97	1780 (12250)	58	
n-Octane	270 (1530)	53	260 (2350)	33	270 (2240)	44	110 (330)	4	
Ethyl benzene	1600 (6210)	91	1030 (6530)	85	1420 (7330)	94	310 (1460)	44	
Total xylenes	5960 (24590)	97	5500 (69620)	97	4820 (41140)	100	1500 (14540)	58	
n-Nonane	380 (1410)	77	340 (3460)	50	390 (3240)	65	120 (500)	7	
Total trimethyl benzenes	2330 (8400)	97	2190 (24230)	92	2000 (18810)	92	740 (5730)	53	
n-Decane	440 (4070)	54	360 (4070)	38	330 (4310)	43	160 (1920)	14	

 $^{^{1}}$ MDL = 200 ng m⁻³

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Table 3. Average contribution of source factors in the VOC samples estimated in this study and average VOC emissions estimated in the National 6 Pollutant Inventory (in % of total VOC mass)

	Ave contributions to ambient VOC concentration estimated in this study								
	(Ave VOC emissions estimated in the National Pollutant Inventory ¹ in bracket)								
	Melbourne		Syc	lney	Brish	All sites			
	Alphington	Footscray	Earlwood	Richmond	Rocklea	Springwood	All sites		
Ave total mass of the 14 VOCs (ng m ⁻³)	24800	24300	36200	7900	22900	15400	21900		
Total VOC emission (tonnes/year) ¹	620	540	690	550	564	790	626		
Evaporative / fuel distribution ²	37 (6)	27 (5)	40 (5)	50 (6)	38 (15)	35 (7)	37		
Vehicle exhaust / petrochemical industry ²	27 (53)	21 (61)	26 (59)	20 (53)	25 (30)	18 (41)	24		
Vehicle related total	64 (59)	48 (66)	66 (64)	70 (59)	63 (45)	53 (48)	61		
Architectural surface coatings	6 (7)	7 (5)	3 (3)	9 (4)	4 (4)	4 (13)	5		
Biomass burning	10 (12)	16 (11)	11 (10)	11 (11)	9 (0.3)	23 (1)	13		
Other sources	12 (22)	11 (18)	15 (22)	6 (26)	20 (51 ³)	15 (38)	14		
Unexplained VOC mass	8 ()	18 ()	5 ()	4 ()	5 ()	6 ()	7		

¹ Compiled from the NPI 2003-2004 and 2004-2005 data (NEPC 2006), excluding emission from biogenic sources, for the suburbs in which the sites were located. 9

² Vehicle exhaust and evaporative emissions are estimated and combined together as 'motor vehicle emissions' in the National Pollutant Inventory. ³ 66% of the emissions are from 'printing and services to printing'.

Table 4. A comparison of the average results from recent source apportionment studies (averages in ng m⁻³) ¹

Study	Source apportionment method	No. of sources resolved	No. of VOCs measured	Ave VOC concentration	% Evaporative / fuel distribution	% Vehicle exhaust / petrochemical industry	% Architectural surface coatings	% Biomass burning	% Other sources	% Unexplained VOC mass
Melbourne, Sydney, Brisbane, 6 sites 2003-2004 (this study)	PMF	5	14	21900	36	22	6	13	16	7
Helsinki 2001 ²	CMB (C ₂ -C ₁₀)	8	45	34500	21.2	33.3			43.8 (gas, solvent, biogenic, distant sources)	
	CMB (C_6 - C_{10})				13	52			34 (distant sources)	
	UNMIX (C_6-C_{10})				23	53			25 (distant sources)	
Hong Kong, 2 sites 2001 ³	PCA/APCS	5	97	47800		43.5			56.5 (solvent, LPG, CNG)	
Santiago, 2 sites 1996 ⁴	PMF	6	47	66500	20.7	51.5			17.9 (LPG, biogenic)	9.9
	UNMIX				24.2	59.6			15.8 (biogenic, fugitive)	
Martonell, 2 sites 1992-1993 ⁵	PCA/MLR	4	29	71100		62.0			23.0 (industry)	
Berlin, 3 sites 1996 ⁶	CMB	3	100	98000	6.0	76.7			7.0 (natural gas)	-2.7
Los Angeles, 2 sites 2001-2003 ⁷	PMF	6	>30	98800	52.5	23.0	8.5		16.0 (CNG, industry, biogenic)	
Houston, 3 sites 2001 ⁸	PMF	7	40	185000		30.6			69.4 (flare, industry, solvent, CNG)	
Houston, 5 sites 2003 9	PMF	8	55	191000	37.4	32.2			30.4 (solvent, industry, biogenic)	
Taipei, 4 sites 1993 ¹⁰	CMB	5	8	230000	5.8	75.6				18.6
Mexico City, 3 sites 1997 11	CMB	5	49	1970000		58.7			48.2 (LPG, asphalt, paints, landfill)	-6.9
Mumbai, 12 sites 2001-2002 12	CMB	8	23	Not reported	70.4	13.3			14.2 (CNG, sludge, degreasing, oceanic, industry)	

¹⁴ the VOC concentration was reported in ppbC in the Los Angeles study (average of total VOC concentrations = 158 ppbC), the Houston 2001 study (296 ppbC),

the Houston 2003 study (305 ppbC) and the Mexico City study (3160 ppbC). Assuming each C atom as equivalent to one CH₂ unit and under 0 °C and 1 atm, the

ppbC value is converted to ng m⁻³ value for comparison by: ng m⁻³ = ppbC \times 14 \times 10³ / 22.4.

^{17 &}lt;sup>2</sup> compiled from Hellen et al. 2003

^{18 &}lt;sup>5</sup> compiled from Baldasano et al. 1998

^{19 8} compiled from Kim et al. 2005

^{20 11} compiled from Vega et al. 2000

³ compiled from Guo et al 2004

⁶ complied from Thijsse et al. 1999

⁹ compiled from Xie and Berkowitz 2006

¹² compiled from Srivastava 2004

⁴ compiled from Jorquera and Rappengluck 2004

⁷ compiled from Brown et al. 2007

¹⁰ compiled from Chan et al. 1996



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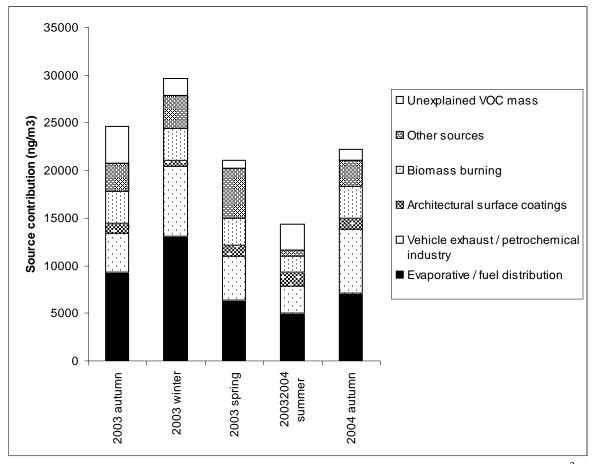
 

Figure 2. Seasonal trends of contribution of source factors in the VOC samples (in ng m⁻³)