CHARACTERISATION AND IDENTIFICATION OF SOURCES OF VOLATILE ORGANIC COMPOUNDS IN AN INDUSTRIAL AREA IN BRISBANE

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Summary

VOC samples (24-hour) were collected during June 2001 at Eagle Farm (a light industrial area in Brisbane) on sorbent tubes with TenaxTA/CarbosieveSIII packing and analysed by GC-MS. Concurrent sampling of carbonyls was also conducted using DNPH cartridges with analysis by HPLC. A total of 40 VOCs (36 VOCs by GC-MS and 4 (carbonyl containing) by derivitisation followed by HPLC analysis) were quantified in the samples. On average, n-alkanes and cyclic and branched alkanes account for 84.3 % of the total concentration of quantified VOCs, aromatic VOCs 12.3 %, chlorinated VOCs as well as carbonyls 1.5 %, while biogenic VOCs contributed less than 1 %. The most abundant individual compounds were n-pentane, 2,3-dimethylbutane, n-hexane and toluene. The concentrations of VOCs did not exceed the existing Queensland EPA and WHO air quality standards and guidelines. The absence of weekday/weekend trends was attributed to the industrial emissions in this area. The levels of VOCs measured at Eagle Farm were comparable to those from VOC studies in industrial areas in Sydney and Melbourne. Industrial and, to a lesser extent, motor vehicle exhaust emissions were identified as the major sources of VOCs. Evaporative emissions of petrochemicals contributed substantially to VOC concentrations.

Keywords: VOCs, sorbent tubes, GC-MS, HPLC, composition, sources

1. Introduction

VOCs are defined as organic compounds with boiling points (1 atm) below 260°C (De Nevers, 2000). VOCs include many compounds with different physical and chemical properties that posses a range of environmental and health-related impacts and can be emitted from both anthropogenic (eg. industrial processes and motor vehicle exhaust) and biogenic sources.

VOCs that can cause both acute and chronic adverse health impacts are included in the group of pollutants often referred to as air toxics or hazardous air pollutants (HAPs) (Kelly, 1990). Apart from adverse health impacts, VOCs are also precursors for a number of secondary pollutants such as ozone, aldehydes, peroxyacetyl nitrates (PANs) and secondary organic aerosols (Kalabokas et al., 2001).

The development of effective strategies for controlling VOCs relies on quantifying the ambient concentrations and the identification of emission sources of these pollutants. However, information on the ambient concentrations and the composition of VOCs in Australian cities is still limited (Environment Australia, 2000). The aim of this study was to investigate the ambient concentrations, composition and sources of emission of VOCs (including carbonyls) in ambient air of an industrial area in Brisbane.

2. Sampling and Analytical Methods

2.1. Sampling site and procedure

The sampling site chosen was the Queensland Environmental Protection Agency’s monitoring station at Eagle Farm. The area is characterised as light industrial with intensive movement of traffic especially heavy trucks. Industrial point sources in the area include fertiliser, chemical, paper, and food manufacturing, metal processing as well as petroleum related (refining and wholesaling). Sources situated within close proximity (300m) to the site are involved in petroleum wholesaling and dry-cleaning. The major roadways in the area carrying large traffic volumes include Kingsford Smith Drive (500 m) and the Gateway Motorway (1 km). Brisbane airport is located 7 km to the north-east from the monitoring site.
Daily (7am - 7am) VOC and carbonyl samples were collected from 2 June 2001 to 30 June 2001, resulting in a total of 28 VOC samples and 28 carbonyl samples. Volatile organic compounds (excluding carbonyls), were sampled onto sorbent tubes with TenaxTA/CarbosieveSIII dual packing (supplier: Supelco, 2000) using a SKC personal sampling pump according to the USEPA Method TO-17 (Woolfenden, 1997, USEPA, 1999b). The pump was modified to work on the permanent electricity supply and was also programmed to facilitate 24-hour sampling and to avoid a breakthrough problem. The flow rate was 100 mL/min and a total of 12 L of air was collected for each sample.

Carbonyl compounds were sampled on 2,4-dinitrophenylhydrazine-coated (DNPH) silica cartridges (supplier: Supelco, 2001) according to the USEPA Method TO-11A (USEPA, 1999a) with the same type of sampling pump as used for VOC sampling. The sampling flow rate for carbonyls was 1 L/min and a total of 280 L of air was collected for each sample.

2.2. Analytical techniques

The non-carbonyl VOCs were thermally desorbed from the sorbent tubes by a Perkin-Elmer ATD 400 Automated Thermal Desorption unit and then analysed using a Varian Air Saturn 2000 Gas chromatograph – mass spectrometer (GC-MS) (USEPA, 1999b, Woolfenden, 1997) at Queensland Health Scientific Services.

The carbonyl samples were eluted with 5 mL of acetonitrile and then analysed by High Performance Liquid Chromatography (HPLC) (Shimadzu Class-VP) (USEPA, 1999a) at Queensland Health Scientific Services.

3. Characterisation of VOCs

3.1. Composition of VOC samples

The quantified VOCs were separated into chemical families according to their chemical structure. A special group of biogenic VOCs was identified because these compounds have mostly natural origin. In contrast, some other quantified VOCs could be either of biogenic and anthropogenic origin (e.g., n-hexane, n-octane, acetaldehyde, acetone). A total of 40 compounds present in the Eagle Farm samples were quantified including 6 biogenic VOCs, 9 aromatic or alkyl benzene VOCs, the 6 C₅-C₁₀ n-alkanes, 9 cyclic and branched alkanes, 6 chlorinated VOCs and 4 carbonyls. The average concentration and composition of the VOC samples are presented in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mean (max)</th>
<th>Compound</th>
<th>Mean (max)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Biogenic VOCs</strong></td>
<td></td>
<td><strong>Cyclic and branched alkanes</strong></td>
<td></td>
</tr>
<tr>
<td>Isoprene</td>
<td>0.25 (1.9)</td>
<td>2,3-Dimethylbutane</td>
<td>60.2 (187)</td>
</tr>
<tr>
<td>α-Pinene</td>
<td>0.36 (1.9)</td>
<td>2-Methylpentane</td>
<td>3.81 (48)</td>
</tr>
<tr>
<td>β-Pinene</td>
<td>0.28 (1.1)</td>
<td>3-Methylpentane</td>
<td>2.02 (12)</td>
</tr>
<tr>
<td>Cymene</td>
<td>0.07 (0.3)</td>
<td>Methyl cyclopentane</td>
<td>1.45 (9.7)</td>
</tr>
<tr>
<td>Cineole (Eucalyptol)</td>
<td>0.11 (0.3)</td>
<td>2,4-Dimethylpentane</td>
<td>3.91 (27)</td>
</tr>
<tr>
<td>Terpinen-4-ol</td>
<td>0.01 (0.2)</td>
<td>Cyclohexane</td>
<td>0.66 (3.9)</td>
</tr>
<tr>
<td>Total biogenic VOCs</td>
<td>1.1 (3.7)</td>
<td>2-Methylhexane</td>
<td>7.44 (49)</td>
</tr>
<tr>
<td></td>
<td>(0.5 %)</td>
<td>3-Methylhexane</td>
<td>8.11 (62)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methyl cyclohexane</td>
<td>1.41 (5.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total cyclic and branched alkanes</td>
<td>89.0 (218)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chlorinated VOCs</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>3.29 (10)</td>
<td>1,1,1-Trichloroethane</td>
<td>0.15 (0.4)</td>
</tr>
<tr>
<td>Toluene</td>
<td>10.6 (83)</td>
<td>Carbon tetrachloride</td>
<td>0.40 (0.7)</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>1.36 (9.3)</td>
<td>Trichloroethylene</td>
<td>0.04 (0.1)</td>
</tr>
<tr>
<td>m- &amp; p-Xylene</td>
<td>4.89 (28)</td>
<td>Tetrachloroethylene</td>
<td>2.26 (12.5)</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>1.91 (12)</td>
<td>Chlorobenzene</td>
<td>0.05 (0.2)</td>
</tr>
<tr>
<td>Styrene</td>
<td>4.82 (22)</td>
<td>p-Dichlorobenzene</td>
<td>0.50 (2.2)</td>
</tr>
<tr>
<td>n-Propylenbenzene</td>
<td>0.11 (0.3)</td>
<td>Total chlorinated</td>
<td>3.4 (15.2)</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>0.26 (0.7)</td>
<td>Carbon</td>
<td>1.44 (2.3)</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>0.87 (2.6)</td>
<td>Formaldehyde</td>
<td>1.64 (2.2)</td>
</tr>
<tr>
<td>Total aromatics</td>
<td>28.1 (49)</td>
<td>Acetaldehyde</td>
<td>0.23 (0.9)</td>
</tr>
<tr>
<td></td>
<td>(12.3 %)</td>
<td>Acetone</td>
<td>0.14 (0.2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Propionaldehyde</td>
<td>3.5 (4.6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total carbonyls</td>
<td>(1.5 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total VOCs quantified</td>
<td>228 (100 %)</td>
</tr>
</tbody>
</table>

Table 1. The average concentrations and composition of VOC samples (in ppbv).
The highest average concentrations were observed for the members of n-alkane and cyclic and branched alkane families. Specifically, the highest average concentration (72.5 ppbv) among all quantified compounds was found for n-pentane, followed by 2,3-dimethylbutane (60 ppbv) and n-hexane (19 ppbv). Average concentrations of all other quantified n-alkanes ranged from 1 ppbv to 7 ppbv while those of cyclic and branched alkanes ranged from 0.6 ppbv to 8 ppbv. The average concentrations of the aromatic compounds were between from 0.1 ppbv to 10.6 ppbv. Toluene was the fourth most abundant VOC in this study with an average concentration of 10.6 ppbv.

The average concentration of benzene was 3.29 ppbv and varied significantly with maximum concentration reaching 10.3 ppbv. Concentrations of chlorinated VOCs ranged from 0.04 to 2 ppbv. A similar range of average concentrations was observed for carbonyls. The average concentrations of all biogenic VOCs were below 1 ppbv.

n-Alkanes accounted for 45.3 % (103.4 ppbv) of the average mass of the measured VOCs, while cyclic and branched alkanes accounted for 39 % (89 ppbv). Aromatic VOCs contributed approximately 12.3 % (28.1 ppbv), while the contribution of chlorinated VOCs as well as carbonyls was 1.5 % (3.4 and 3.5 ppbv, respectively). Biogenic VOCs, however, only contributed about 0.5 % (1.1 ppbv) to the average composition of quantified VOCs.

During the sampling period, the observed average and maximum concentrations of formaldehyde, toluene, styrene, trichloroethylene, tetrachloroethylene and xylenes did not exceed the Queensland EPP (Air) 1997 24-hour air quality standard for formaldehyde (70 ppbv), toluene (2000 ppbv), styrene (200 ppbv) and trichloroethylene (200 ppbv) and the WHO 24-hour air quality guidelines for tetrachloroethylene (33.8 ppbv) and xylenes (1013 ppbv).

3.2. Comparison of results with those from other Australian studies

The concentrations of BTX (benzene, toluene and m- & p-xylene) were nearly the same at Eagle Farm and in Melbourne, while those in Perth were lower (Figure 1). The concentrations m,p-xylene were the highest in Sydney.

In comparison to the annual averages for benzene, toluene and p-xylene in the Brisbane CBD, the concentrations of these compounds were 2 to 3 times higher at Eagle Farm. While benzene/toluene ratios were the same at Eagle Farm and in Melbourne (0.31) and similar in Sydney (0.4) this ratio was only 0.2 in Brisbane CBD and much higher (0.6) in Perth.

![Levels of BTX in some Australian cities](image-url)
The observed variations between data from different cities may be due to different sampling location, sampling techniques, meteorological parameters, sampling seasons of the year and averaging times. Apart from these differences, industrial emissions and their composition as well as seasonal variation in emissions may also contribute to observed variations between levels of VOCs in various cities (Na and Kim, 2001).

3.3. Weekday trends
The concentrations of the quantified VOCs were investigated for weekend/weekday trends. Statistical analysis did not show a significant difference between the weekday concentrations and the weekend concentrations. This finding is in contrast to those reported in a number of other studies, which found that VOC concentrations follow a distinctive weekday/weekend trend (Thijsse et al., 2000, Sharma et al., 2001). However, these studies also identified motor vehicles as the main source of VOC emissions with traffic volume following a weekday/weekend trend. The absence of the weekday/weekend trend in this study is probably due to the abundant contribution from industrial emissions including evaporative emissions, which are rather uniform throughout the week. The South-East Queensland Air Emission Inventory (SEQAEI) also estimated that total emissions from industrial sources are similar on a typical weekday and weekend (35 t/day vs. 28 t/day respectively) (Queensland DEH, 1995).

4. Identification of VOC emission sources

4.1. Major emission sources according to the SEQAEI
SEQAEI reports VOC emissions from motor vehicles and industry in the area of study (Queensland DEH, 1995, Table 2). The spatial distribution of industrial VOC emissions reported in the SEQAEI also shows that the highest values are observed in the Brisbane river mouth, including the Eagle Farm area in which the sampling site was located. On the other hand, the emission of VOCs from motor vehicles is much lower in Eagle Farm when comparing with that in the CBD.

Table 2 A comparison of VOC emissions from industry and motor vehicles (source: SEQAEI (Queensland DEH, 1995)).

<table>
<thead>
<tr>
<th></th>
<th>VOC emission from industry (tonnes/grid cell/year)</th>
<th>VOC emissions from motor vehicles (tonnes/grid cell/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brisbane CBD</td>
<td>1-10</td>
<td>2.8</td>
</tr>
<tr>
<td>Eagle Farm</td>
<td>&lt;300</td>
<td>0.7</td>
</tr>
</tbody>
</table>

4.2. Industrial vs motor vehicle sources
VOC sources were identified using tracers from the literature and correlation analysis (analysis Spearman coefficient, r). Correlation between atmospheric pollutant concentrations may indicate common sources and provide further information of any relationships between pollutants (Morawska et al., 1998). The concentrations of inorganic gaseous pollutants (NO_x, ozone, SO_2) were used in correlation analysis. This data was obtained from the Queensland EPA’s routine air quality monitoring at the Eagle Farm site.

The ratios of sum of measured aromatic, n-alkanes and cyclic and branched alkane concentrations were compared with data on non-methane hydrocarbon emissions from Australian vehicles reported in Duffy et al. (1999) to determine the contribution of motor vehicle exhaust to VOC levels at Eagle Farm (Table 3).

Table 3 Ratios of selected hydrocarbons measured in this study and in motor vehicle exhaust emissions reported in Duffy et al. (1999).

<table>
<thead>
<tr>
<th></th>
<th>This study</th>
<th>Exhaust emissions (Duffy et al., 1999)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics/Alkanes</td>
<td>0.13</td>
<td>4.8</td>
</tr>
<tr>
<td>Aromatics/Cyclic &amp; Branched Alkanes</td>
<td>0.14</td>
<td>3.6</td>
</tr>
<tr>
<td>Benzene/toluene</td>
<td>0.34</td>
<td>0.6</td>
</tr>
<tr>
<td>Benzene/pentane</td>
<td>0.03</td>
<td>1.9</td>
</tr>
<tr>
<td>Benzene/2,3-dymethylbutane</td>
<td>0.03</td>
<td>13.4</td>
</tr>
</tbody>
</table>

The above ratios clearly indicate that sources other than motor vehicle exhaust emissions influence the n-alkane and cyclic and branched alkane concentrations at Eagle Farm. As shown in 4.1 it is likely to be industrial point sources situated in the area of study.

It is also reported in the literature that n-alkanes have higher concentrations in industrial areas in comparison to urban city centres (Na et al., 2001). As was shown in Table 1, n-alkanes contributed 45.3 % to the average concentration of VOCs in the air at Eagle Farm, while concentrations of aromatics contributed only 12.3 %. This is consistent with an industrial area where industrial sources of VOCs dominate motor vehicle exhaust, which would be the main source in urban city centres (Thijsse et al., 1999, Sharma et al., 2000). The lack of correlation between concentrations of n-alkanes and cyclic and branched alkanes with levels of NOx also supports the fact that motor vehicles are not the major source. However, n-alkanes concentrations also showed a high correlation with benzene levels (all correlation coefficients were above 0.6 with highest for n-nonane, 0.74 and n-octane, 0.71). Benzene is used as a tracer for motor vehicle emissions, which suggests that motor vehicle exhaust emissions contributed to the levels of n-alkanes sampled at Eagle Farm. It is also possible that these
highly correlated compounds respond in similar ways to changing meteorological conditions. Similarly cyclic and branched alkanes levels were found to be significantly correlated with benzene concentrations ($r=0.66$) indicating vehicle exhaust as a likely emission source.

The strongest correlations between concentrations of aromatic compounds were observed between toluene, ethylbenzene and the xylenes. This indicates that these compounds are emitted by a common source. It is likely to be motor vehicle exhaust emissions since the concentrations of all the aromatics exhibited a strong correlation with NOx (all coefficients above 0.6) levels often used as tracers for motor vehicle exhaust emissions (Morawska et al., 1998). The literature suggests that these compounds can also originate from use of solvents and evaporative losses of fuel (Rappengluck and Fabian, 1999). Because of the lower correlation coefficients of toluene, ethylbenzene and the xylenes levels with benzene concentrations, these compounds may have emissions sources other than motor vehicles, such as losses from industrial solvent usage which also reported in the SEQAEI (Queensland DEH, 1995).

Concentrations of formaldehyde were significantly correlated with toluene, n-nonane, n-decane, o-xylene and benzene ($r>0.6$). Since these compounds are also emitted from motor vehicle exhaust, it therefore indicates that formaldehyde in Eagle Farm VOC samples was mainly from primary emissions originating from motor vehicle exhaust. Primary emissions of formaldehyde by industrial point sources have also been reported in the area of study (Environment Australia, 2001). Acetaldehyde and acetone can be emitted by vegetation and also can be produced as a result of photochemical oxidation of VOCs. Insignificant correlations of acetaldehyde and acetone levels with biogenic VOCs levels suggest that a secondary origin of these compounds is more likely. Primary emissions of acetone are reported by waste disposal facilities in the study area in the amount of 177 kilograms per year (Environment Australia, 2001).

### 4.3. Photochemical destruction of VOCs

A total of 24 out of the 40 VOCs showed a negative correlation with ozone. Once formed, ozone may react with some of these compounds – primarily those that are unsaturated or with aromatic rings. Aromatics, biogenics, trichloroethene and formaldehyde exhibited significant negative correlation coefficients below -0.5. A negative correlation with ozone concentrations is used as an indicator of photochemical destruction of VOCs (Tran et al., 2000). Therefore, a negative correlation of concentrations of listed compounds with ozone levels indicates that reaction with ozone may be an important sink for these compounds at Eagle Farm.

### 4.4. Biogenic sources

The SEQAEI reported that 64 % of the total VOC emissions in the area are biogenic (QLD DEH, 1995). These emissions were estimated for the entire south-east Queensland airshed, while measurements in this study were taken only in particular area that would not be representative of the whole airshed.

Among biogenic VOCs $\alpha$-pinene, $\beta$-pinene, cymene and cineole exhibited the strongest correlation ($r > 0.7$, $p=0.05$) and can be expected to have a common source. Since these compounds are regarded as biogenic (Guenther et al., 2000) it is likely that they were emitted by vegetation from surrounding areas.

It is of interest that isoprene, the most abundant biogenic compound (Guenther et al., 2000), did not show a significant correlation with any of these compounds and, therefore, is expected to come from a different source. Isoprene has been reported in motor vehicle exhaust emissions (Christensen et al., 1999, Sharma et al., 2000).

### 4.5. Evaporative sources

n-Pentane is a relatively volatile hydrocarbon and has been used as an indicator of evaporative losses of VOCs from petrochemicals (Derwent et al., 1995) when a correlation with ambient temperature is present. In this study, the correlation coefficient of n-pentane with ambient temperature was found to be 0.44 suggesting that at this site the evaporation of petrochemicals including solvent use, service stations and refineries is also a source of VOCs. A significant correlation with ambient temperature was also observed for n-heptane ($r=0.42$). The relatively low correlation coefficients, however, suggest the importance of other sources of n-alkanes sampled at Eagle Farm apart from evaporative losses.

A correlation coefficient of 0.38 between concentrations of cyclic and branched alkanes as a family and ambient temperature and a high correlation with n-alkanes and TEX (toluene, ethylbenzene and xylenes) levels may indicate that evaporative petrochemical emissions of these compounds significantly contribute to their ambient concentrations observed at Eagle Farm.

Tetrachloroethylene is often used as a tracer of emissions from dry-cleaning processes and is also an important industrial solvent (Vega et al., 2001). This compound contributed about 77 % to the average concentration of chlorinated VOCs in Eagle Farm. The high positive correlation ($r=0.62$) of this compound concentrations with ambient temperature also suggests evaporative emissions from solvent usage.

Chlorobenzene and p-dichlorobenzene also showed a significant positive correlation with ambient temperature suggesting that evaporative processes also affect ambient concentrations of these compounds.
4.6. Local vs regional sources
The relationship of VOC concentrations with meteorological parameters was also investigated. Altogether 26 out of 40 quantified VOCs as well as total VOC, biogenics, aromatics, cyclic and branched alkanes and chlorinated VOC as families exhibited a negative correlation with wind speed. This indicates that these VOCs more likely have been emitted by local industrial sources in the area of study.

5. Conclusions
A total of 40 VOCs were quantified in the Eagle Farm samples. n-Alkanes and cyclic and branched alkanes were the most abundant VOC families accounting for 84.3% of the total concentration of the quantified VOCs in the Eagle Farm samples. Aromatic VOCs accounted for 12.3%, chlorinated VOCs as well as carbonyls only accounted for 1.5% of the average composition of VOC samples, while biogenic VOCs accounted for less than 1%.

The concentrations of VOCs measured at Eagle Farm did not exceed the existing Queensland EPA and WHO air quality standards and guidelines.

There was no significant difference between the concentrations of VOCs collected at Eagle Farm on weekdays and on weekends, which was probably due to industrial emissions in the area.

Industrial and motor vehicle exhaust emissions were identified as the major sources of VOCs. Evaporative emissions of petrochemicals contributed substantially to VOC concentrations.

Areas for further research
Multivariate analysis techniques such as principal component analysis may provide more information on the identification and apportionment of sources of VOCs in this part of Brisbane airshed. This analysis is now in progress.

Acknowledgments
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References


