Identification and quantification of volatile organic compounds in the Cape Town brown haze

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Abstract

The formation of a brown haze due to urban pollution is a common phenomenon in many industrialised cities in the world. Cape Town in South Africa is renowned for its scenic beauty but this is marred by a brown haze layer that develops on certain days during inversion and windless conditions in the winter. In order to identify and quantify the temporal and spatial distribution of volatile organic compounds (VOC's) which are a contributing factor to this phenomenon, TO Canisters and Carbotrap^{TM} 300 tubes were used for this investigation. Samples were taken at six different sites in the Cape Metropolis area, at ground level and at 1000 and 1500 ft above sea level (ASL). In addition, 75 µm PDMS and Carboxen SPME fibres were also used. All samples collected were analysed by GC-MS and the different data sets were compared with each other. The daytime concentrations of the VOC's appeared to be significantly higher than the night time concentrations. Open-chain hydrocarbons and benzene related compounds were generally found at ground level, while at higher levels of 1000 and 1500 ft above sea level, alcohols and ketone-compounds were detected.

Keywords: brown haze, brown clouds, VOC, canisters, tubes, SPME, urban air, air pollution.

1 Introduction

The formation of a brown haze due to urban pollution is a common phenomenon in may industrialised cities in the world. The Cape Town brown haze develops from March to August during winter on certain windless days. The haze consists of a white to brown layer, which covers most of the Cape Peninsula and Cape

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Flats. The haze is usually most intense in the early mornings and then gradually disperses during the day [1]. A study using X-Ray Emission Spectroscopy (PIXE) was undertaken during the winter period 1992 in an attempt to determine the common pollutant elements in the brown haze [2]. During 1997 the CSIR undertook a project on behalf of the Department of Environmental Affairs to quantify atmospheric volatile organic compounds (VOC's) in the major metropolitan areas in South Africa using passive samplers. In this study it was found that the mean total volatile organic compounds (TVOC) concentrations in Cape Town was significantly higher than in Johannesburg and Durban [3]. In comparison to other pollutants, the monitoring of VOC's in South Africa is not yet well developed and there is no long term database of information. The new air quality legislation in South Africa requires the measurement and monitoring of ambient benzene levels since benzene is a well known human carcinogen. In this study we report the spatial and temporal distribution of all the VOC's that could be detected using the EPA TO-14A and TO-17 methodologies on a typical brown haze day in Cape Town. Sampling was carried out in collaboration with the Cape Town Metropolitan Council (CMC) air quality officers at existing monitoring sites of the CMC. These sites were selected based on information from different industrial and other activities impacting on the air quality of Cape Town.

2 Sampling procedures

2.1 Equipment and sampling sites

The sampling in Cape Town was done on 28 and 29 July 2003 over an eight-hour time interval. This represents a typical day and night conditions during the winter season and 29 July was characterised by a moderate brown haze cloud in the morning. Three different sampling techniques, solid phase micro extraction (SPME) fibres, Carbotrap^{TM} 300 tubes and 6 litre canisters were selected to determine the VOC concentrations. The brown haze forms in layers at different levels above ground level [1], so samples were also taken at 1000 and 1500 ft above sea level (ASL) using a fully equipped research aircraft (Aerocommander 690A), operated by the South African Weather Service.

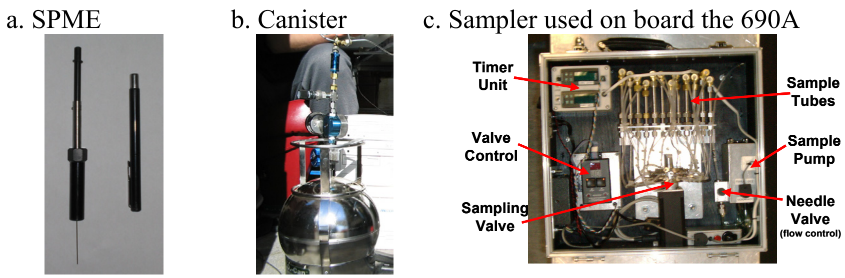
a. SPME
b. Canister
c. Sampler used on board the 690A

Figure 1: Sampling devices used.

The samples on board the Aerocommander were taken for shorter time intervals between 10 - 40 minutes using a specially designed continuous sequential tube sampler fitted with 12 standard Perkin Elmer adsorbent sampling tubes as well as 6 litre canisters fitted with a variable flow controller.

Samples were taken at five different sites during the night of 28 July and day of 29 July (see Figure 2):

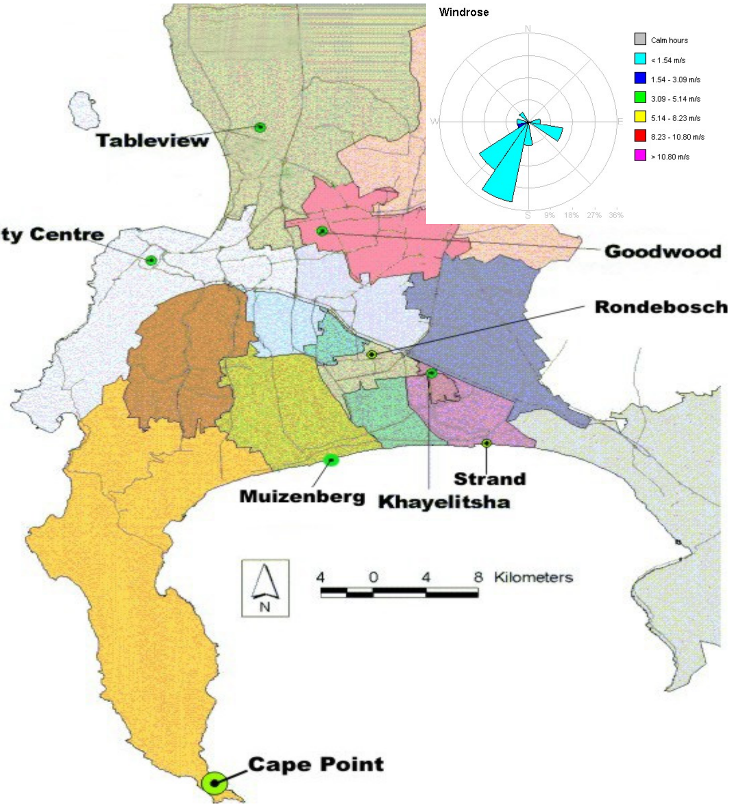

Figure 2: Map of Cape Town indicating the different air quality monitoring stations of the CMC as well as the windrose for the sampling periods. (VOC sampling was not carried out at (Rondebosch, Muizenberg and Strand). Residential areas: Goodwood and Tableview. Informal settlement: Khayelitcha. Central business district: City Centre Background: Global Atmospheric Watch (GAW) station at Cape Point.

2.2 Background samples and data comparisons and corrections

Cape Point (see Figure 2) is the most southern tip of Africa and the wind blows predominantly in a south-westerly direction towards South Africa. Thus we can assume that VOC's measured at Cape Point is coming from the Atlantic Ocean.

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We can further assume that this air should be relatively pollution free compared to air from the land. The air samples at Cape Point was characterised as clean background marine air in terms of the CO and Radon 222 levels measured on 28 and 29 June 2003 [4].

Background corrections were also carried out at the different sites by placing a sealed canister and sealed tube at these sites. During analysis of the different samples, the VOC concentration in the laboratory air was also analysed for background correction purposes. Duplicate tube samples were collected at the Goodwood site using different flow rates to check the impact thereof on the reported concentrations.

2.2.1 Samples taken at 1000 ft above sea level

Canister and tube samples were taken at 1000 ft above sea level (ASL) using the specially equipped Aerocommander from Rondebosch to Goodwood, Rondebosch to Muizenberg and Muizenberg to Rondebosch (see Figure 2).

2.2.2 Samples taken at 1500 ft above sea level

Samples were taken with the Aerocommander at 1500 ft ASL from Rondebosch to Goodwood, Rondeboch to Muizenberg, Muizenberg, and Malmesbury to Goodwood. The flight path also covered sections from Malmesbury to Muizenberg, Rondebosch and over Khayelitsha (see Figure 2).

2.3 Meteorological data

Meteorological data for Cape Town on 28 – 29 July 2003 was monitored and made available by the Cape Town metropolitan council.

Table 1: Meteorically conditions at Cape Town on 28 - 29 July 2003.

Date and time	Temperature/°C	General
28/07/2003 (18:00 - 02:00)	11.8 – 15.2 Average: 14.8	Wind: Light SW breeze (<1.5 m/s) O_3-levels: 1-10 ppb; Average: 3.5 ppb Relative humidity: 82-87; Average 84.8
29/07/2003 (06:00 - 14:00)	11.9 – 26.9 Average: 18.1	Wind: Light SW breeze (<1.5 m/s) O_3-levels: 2-35 ppb; Average: 17 ppb Relative humidity: 26 – 84; Average 58.8

2.4 Analysis of samples

Samples were analysed at the Potchefstroom University for CHE. A calibration standard obtained from Supelco (Cat no: 41900-U) containing 39 VOC's, (100 ppb) was used as an external standard. Samples were analysed by a Hewlett Packhard Agilent 6890 gas chromatograph (GC) and Micromass Autospec-TOF mass spectrometer (MS) according to the EPA TO-14a compendium method. The column used was a Perkin Elmer PE-1 60 m, 320 µm id, 1 µm film thickness. The samples were first concentrated on a Perkin-Elmer Turbo matrix thermal desorber. The detection limit of this method is about 100 ppt. Mass spectrometric analyses were run in magnetic scan mode according to the EPA TO-17 compendium method. The GC temperature oven program was started at -10°C (4 minutes hold) by using liquid carbon dioxide, the temperature was then increased at a rate of 7°C.min^{-1} to 250°C and held 10 minutes at this value. VOC's not present in the Supelco standard were identified using the MS data system library (NIST), that consist of a library of 35 000 compounds. Since the adsorption rate and stability of all the compounds on the SMPE fibres are unknown, it was only used as a quantitative comparison to the other techniques.

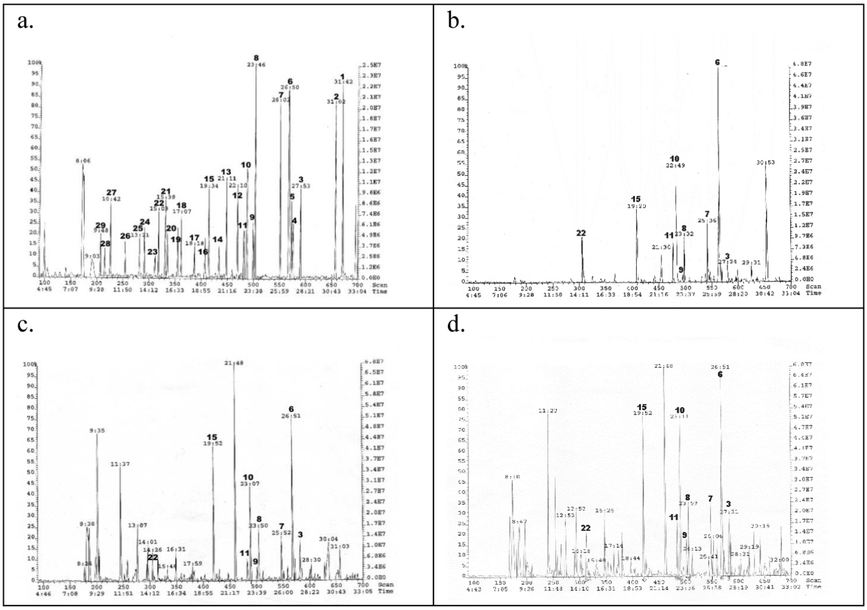

Figure 3: Comparison of the chromatograms of samples collected at Goodwood on 29 July 2003 (integrated 8 hour average, 06:00 – 14:00). a. Chromatogram of calibration standard consisting of 39 VOCs. Peaks of interest are benzene (22), toluene (15), ethylbenzene (11), p+m-xylene (9), styrene (10), o-xylene (8), 1,3,5-trimethylbenzene (7), 1,2,4-trimethylbenzene (6), 1,3,5-trimethylbenzene (3). b. Chromatogram of the Carboxen SPME fibre. c. Chromatogram of the Carbotrap^{TM} 300 adsorption tube operated at a flow rate of 4 cm^3.min^{-1}. d. Chromatogram of the Carbotrap^{TM} 300 adsorption tube operated at a flow rate of 16 cm^3.min^{-1}.

The VOC's found at Goodwood (see Table 2) are mostly associated with emissions from petrol and diesel combustion. The comparison between the tubes operated at different flow rates is acceptable. According to Woolfenden [5] pump flow rates above 5 - 10 $cm^3.min^{-1}$ should be used for tubes to minimize errors due to ingress of VOCs via diffusion. In this study, the tube samplers were connected to the manifold of a standard air quality monitoring station by a rather long and thin Teflon tube and any diffusion error can be excluded. The data in Table 2 indicates that the correlation between compounds detected by Carboxen SPME, the Carbotrap™ 300 tubes and the canisters was very good.

Table 2: Volatile organic compound concentrations at the Goodwood site on 29 July 2003 (06:00 – 14:00).

Compound	Tube 1/ppb (flow 16 $cm^3.min^{-1}$)	Tube 2/ppb (flow 4 $cm^3.min^{-1}$)	Carboxen SPME (Exposed for 8 h)
Benzene	2.25	3.21	Detected
Toluene	6.28	8.33	Detected
Ethyl benzene	3.03	4.12	Detected
p-Xylene	10.06	8.43	Detected
m-xylene	10.03	8.41	Detected
Styrene	1.29	1.58	Detected
o-xylene	0.34	0.35	Detected
1,1,2,2-Tetrachloroethane	0.34	0.35	Detected
1,3,5-Trimethylbenzene	0.36	0.43	Detected
1,2,4-Trimethylbenzene	3.83	6.88	ND
1,2-Dichlorobenzene	2.11	3.85	Detected

VOC’s not present in the Supelco standard were also detected in samples taken at Goodwood during the day (29 July 2003), however since no calibration standard for these compounds was available, these were not quantified. The following compounds not included in the Supelco standard were identified by using the MS NIST library data base: acetone, pentane, 1-pentene, 2-methylbutane, cyclopentane, methylcyclopentane, cyclohexane, cyclopentamine, heptane, 6-methyl-3-undecane, 4-methyl-3-penten-2-one, 1-octene, decane, octane, nonane, decane, propyl benzene, 1,4-diethylbenzene, 1,3-diethylbenzene, 1-ethyl-2,4-dimethylbenzene, 1,3,5-dimethyloctane, 1,4-dimethyl-2-ethylbenzene, 1-etyl-2,4-dimethylbenzene. A number of other compounds present in the GC chromatograms could not be identified conclusively. The SPME fibres also did not detect all the compounds detected by the tubes, this can possibly due to the fact that equilibrium has not been reached or differences in the adsorption characteristics.

The comparison between the concentrations measured by using Carbotrap™ 300 tubes and the canisters are good. By comparing the data in Table 3 with that in Table 2, it is evident that the concentrations of most of the VOC’s are lower during the evening than during the day at this site. This can be due to the fact that the traffic intensity decreases during the evening in a residential area. Varshney and Padhy [6] found that the TVOC (total volatile organic compounds) peaks at 9:00 am, which coincide with the peak hour traffic in Delhi.

Table 3: Volatile organic compound concentrations at the Goodwood site on 28 July 2003 (18:00 – 02:00).

Compounds	Tube/ppb ($16\ cm^3.min^{-1}$)	Canister/ppb ($12.6\ cm^3.min^{-1}$)
Benzene	0.43	0.19
Toluene	1.56	1.93
Ethyl benzene	1.03	1.06
p-Xylene	1.50	1.03
m-xylene	1.49	1.03
Styrene	0.18	0.38
1,2-Dichlorobenzene	2.07	2.75

VOC's detected, but not quantifiable in Goodwood during the night (28 July 2003), include: 2-methylbutane, pentane, 1-pentene, cyclohexane, cyclopentamine, heptane, nonane, 4-methyl-3-penten-2-one, octane, nonane, 1,3-hydroxethone, decane, dodecane, 1,4-diethylbenzene, 1,2-diethylbenzene, 1,3-diethylbenzene, 1-ethyl-2,4-dimethylbenzene, 1-methyl-2-(1-methylethyl)benzene, 1-ethyl-2,4-dimethylbenzene, 1,2,3,4-tetramethylbenzene, 1-amine-3,5-dimethylbenzene, 1,2,4-trichlorobenzene, dodecane, 1,4-dimethyl-2-ethylbenzene, 2-ethyl-1,4-dimethylbenzene, 1-chloro-8-heptadecene, and hexadecane. It appears that most of the VOC's found in these samples are associated with petrol and diesel and the combustion products of these fuels.

Table 4: VOC's concentrations (ppb) sampled by using Carbotrap™ 300 tubes at a flow rate of $0.23\ cm^3.min^{-1}$ and a sampling time of 10 minutes at different altitudes on flights from Rondebosch to Goodwood and on an approach flight from Malmesburg to Rondebosch.

	1000 ft ASL	1500 ft ASL	
Chloroform	0.64		
Benzene	(masked)	-	1.48
Toluene	43.08	3.18	3.21
1,2,4-Trimethylbenzene	9.23	0.64	0.52
1,3-Dichlorobenzene	0.17	0.18	

The VOC concentrations found at 1 000 ft ASL (Table 4) markedly differ from that observed at ground level. The 1-butanol peak in the Rondebosch to Goodwood flight at 1000 ft was so intense, it overlaps the benzene and carbon tetrachloride peaks in the GC trace in such a way that it masked the peaks of these compounds. In the same sample, the toluene concentration was abnormally high (43.08 ppb) probably indicating that this sample has been fouled by a strong individual source. No benzene was found at 1 500 ft in the flight from Rondebosch to Goodwood.

The concentration of toluene and 1,2,4-trimethylbenzene was found to be much higher at 1000 ft than at 1 500 ft ASL. The toluene levels at Malmesbury (a rural area 50 km to the north of Cape Town) correlate well with the toluene level found in the Rondebosch to Goodwood area. In the study by John [3] in 1998, toluene was found to have the highest concentration of all the VOCs measured in Cape Town. According to the study by John, industry contributes 66% of the total toluene concentration [3]. The levels of toluene and benzene are also much higher than found in similar studies that were done in United Kingdom [7].

In the study by John [3] 1,2,4-trimethylbenzene was found to be the compound with the second-highest index value (after toluene). This was linked mostly to industrial activities (73%) and the smallest contribution from townships [3].

The VOC's detected at 1000 ft that could not be quantified unambiguously include compounds such as acetone, pentane, 2-butanone, 1-butanol and dodecane. Samples taken at 1 500 ft include compounds such as: acetone, 2-methylbutanone, pentane, hexane, 2-butanone, 1-butanol, heptane, 1,2-dichloro-4-nitrobenzene, dodecane, 2-metylpiperazine. It was also found that compounds containing alcohol- and ketone-groups are found in higher concentrations at higher altitudes than found on ground level.

Benzene is the only VOC included as criteria pollutant to be monitored in the new South Africa air quality legislation. The spatial and temporal distribution of benzene during the sampling period is therefore of special interest and presented in Table 5.

Table 5: Spatial and temporal distribution of benzene (ppb) using TO canisters fitted with appropriate flow controllers resulting in an 8 hour integrated sampling period.

Site	Day time	Night time
Cape Point	0.00	0.00
Goodwood	3.21 (2.25*)	0.19 (0.43*)
Table View	0.00	0.24
City Hall	0.22	0.23
Khayelitscha	0.17	0.47

* Results from Carbotrap^{TM} 300 tubes

The benzene levels at the Goodwood site were much higher than found at any of the other sampling sites. This result can be partly explained by the prevailing meteorological conditions and geographical position of this site at the time of sampling. Although Goodwood is a residential area, it is also the only site down wind of the city centre during the sampling period. Two major motoring highways (the N7 and N1) and the R102 with a high traffic density, passes near the Goodwood site. The increased daytime benzene levels can thus probably be explained by traffic emissions. The reported daytime value at Goodwood exceed the annual average target value of 1.6 ppb (5 μg/m^3) set in the new South African ambient air quality guidelines. The daytime benzene levels at the Table View site (also a residential area but in close vicinity of petrol chemical storage tanks) were very low mainly due to the prevailing meteorological conditions at the time of sampling. The day and night time benzene levels at the City Centre is very similar during the day and night probably reflecting the active nightlife (constant traffic density) at the city centre. The higher than expected benzene levels in Khayelitscha (an informal settlement) during night time is most probably linked to the fact that the Cape Town international airport is about 8 km to the northwest of this site. Taking the prevailing wind direction at the time of sampling into account, the high levels may be due to emissions by aircraft taking off from Cape Town international.

The highest benzene level reported in this study (3.2 ppb) is higher than that reported [7] for Birmingham (1.02 ppb), Cardiff (1.21 ppb) and Leeds (1.94), very similar to that reported [8] for Baltimore (2.27 ppb) and lower than that reported [9] for Atlanta (7.66 and 4.00 ppb). It is slightly higher than the averaged values report for the period Oct 1994 to Sept 1995 of 1.62 ppb (5.39 μg/m^3) for Goodwood and 1.2 ppb (4.05 μg/m^3) for Table View [3].

It follows from the results reported in this study that VOC emissions in Cape Town will most definitely play a significant role in the brown haze formation but is probably also not the only contributing factor.

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