



Wagerup 2009 Air Quality Study



May 2011



Department of
Environment and Conservation

Our environment, our future



Department of Environment and Conservation

168 St Georges Terrace

Perth WA 6000

Tel: +61-8-6467 5000

Fax: +61-8-6467 5562

www.dec.wa.gov.au

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Questions regarding the use of this material should be directed to:

Manager Air Quality Management Branch

Department of Environment and Conservation

Locked Bag 104

Bentley Delivery Centre

Western Australia 6983

Executive summary

The focus of the Wagerup 2009 air quality study was to investigate odour events associated with episodes of poor air quality that occur in the vicinity of the Alcoa Wagerup refinery. The monitoring program was undertaken from 1 May 2009 to 2 October 2009.

Continuous monitoring was undertaken for a range of air quality parameters at sites in Yarloop, Cookernup and adjacent to the refinery. A wide range of air quality parameters were monitored including volatile organic compounds (VOCs), particles, heavy metals, oxides of nitrogen (NO_x), sulfur dioxide (SO₂), carbon monoxide (CO), wind speed, wind direction and relative humidity.

Community members played an important role in notifying Department of Environment and Conservation (DEC) staff of odour events. Community observations were also used to target days for further analysis of continuous data from the monitoring stations in Yarloop and Cookernup. A Proton Transfer Reaction Mass Spectrometer (PTRMS) was used to monitor VOCs at Yarloop. The PTRMS data was analysed for days where multiple complaints were received in order to identify whether the presence of certain VOCs could be linked to odour events identified by community members and DEC staff. Two days where multiple observations were reported were selected for further analysis. These days were 3 and 12 June 2009.

VOCs detected by PTRMS are identified by association of the detected ion mass-to-charge ratio (m/z) with VOCs that are known, or expected to be present in the ambient air. The concentrations of VOCs corresponding to m/z 33 (methanol) and m/z 59 (acetone) detected by the PTRMS, increased above background levels during the time of the community complaints on 3 and 12 June 2009. There was also a corresponding increase in NO_x concentrations measured at monitoring stations in both Yarloop and Cookernup. At the time of these community complaints, the wind direction was from the sector which included the Wagerup refinery. As NO_x, acetone and methanol are known refinery emissions, these findings suggest that the Wagerup refinery was a likely source of these compounds, however the concentrations of VOCs detected were low. In general, for 64 per cent of the days where there were two or more community observations during the study period, there was an increase in concentration of m/z 33 (methanol) and m/z 59 (acetone) detected by the PTRMS between 6:00am and 11:00am, corresponding with the times of community complaints.

Canister samples taken by community members were analysed at the PTRMS in Yarloop. Canister samples were also taken by DEC staff during the intensive observation periods (IOPs) and analysed by the PTRMS. The PTRMS detected a wide suite of VOCs, some of which were tentatively identified and were not previously detected in canister samples taken in 2006 that were analysed by US-EPA methods. Many of these compounds identified are related to odours and were present at very low concentrations (i.e. low parts per billion (ppb) range).

A number of canister samples were sent to an independent laboratory for analysis via USEPA method TO-15. The levels of VOCs detected in the canisters analysed via USEPA method TO-15 were below their respective odour thresholds. However, acetone, formaldehyde, acetaldehyde and toluene were all detected in the canisters and are known refinery emissions (NPI 2009) with methanol being previously identified in refinery stack samples (Galbally et al

2008). As these compounds have been linked to refinery odour in this and previous studies, the combination and concentration ratio of these VOCs in combination with other air quality measurements (such as NO_x, CO, particles etc.) may be used as an indicator of refinery emissions even though single VOCs may be below the odour threshold for that compound.

Measurements of VOCs were taken in parallel with the PTRMS using traditional sampling methods such as adsorbent tubes and canisters to support the quantification and allow for positive identification of compounds detected by the PTRMS. Adsorbent tube and canister samples taken in parallel with the PTRMS measurements confirm that VOCs detected by the PTRMS were in the low ppb range.

Heavy metals were measured in the TSP samples collected at the Bancell Road monitoring site using a High Volume Air Sampler (HiVol). HiVol filter papers were collected every three days from 23 June 2009 to 2 October 2009, giving a three day average concentration for the heavy metals. Except for phosphorus, all three day averaged concentrations were below the annual guideline. It is important to note that even though one three day averaged phosphorus concentration was above the annual guideline, this does not necessarily mean that the annual guideline was exceeded due to different averaging times. An annual average allows for short term fluctuations in pollutant concentrations—i.e. concentrations of pollutants might be very low for the majority of the year but be elevated for a short period of time leading to very low concentrations on average over the year. When all of the samples taken during the study period are averaged, the phosphorus concentration is below the annual ambient guideline.

The 24 hour averaged particle (PM_{2.5}) concentrations measured at both Yarloop and Cookernup were below the NEPM Advisory Reporting Standard of 25µg/m³ for the majority of the study period. There was one day during the study period when the 24 hour averaged PM_{2.5} concentration measured in both Yarloop and Cookernup exceeded 25µg/m³ (16 May 2009). NO_x levels measured in both Yarloop and Cookernup displayed a similar trend to the particles spikes measured on 16 May. Particle levels (PM_{2.5} and PM₁₀) measured in Bunbury were also elevated and showed a very similar trend to the particles measured in Yarloop and Cookernup on this day. Analysis of the PM_{2.5} to PM₁₀ ratio measured at Bunbury indicates that the source of the elevated particle levels on 16 May 2009 was likely to be from wood smoke possibly caused by bushfires or controlled burns in the area. NO₂, CO and SO₂ concentrations did not exceed their respective NEPM standards over the study period.

Concentrations of air pollutants detected during the study were low, the exception to this being the particle levels measured on 16 May 2009. There are a number of sources of the compounds measured during this study including wood smoke, motor vehicles, vegetation and the Alcoa Wagerup refinery; with evidence of each of these sources contributing to the data. There were some short term spikes in concentration of acetone, methanol and NO_x that may be attributable to the Alcoa Wagerup refinery however the concentration measured during these spikes was low.

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Acknowledgments

Department of Environment and Conservation—Air Quality Management Branch

Jodi Ariti	Project manager/ report writing / data analysis
Philippe Najean	Technical and field support
Arthur Grieco	Technical support and advice / data analysis
Peter Rye	Technical support and advice / data processing
Adrian Blockley	Technical support and advice
Murray Cox	Technical and field support
Jason Wooster	Technical and field support
Chris Chambers	Technical and field support
Nigel Howard	Technical and field support
Peter Mountford	Technical and field support
Steve Price	Technical and field support
Vahid Rostampour	Technical and field support

University of Western Australia

Erika Zardin	PTRMS operation, field support and data analysis
Dr Sam Saunders	Technical advice and field support

CSIRO Marine and Atmospheric Research

Dr Ian Galbally	Technical advice
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1. Introduction

The focus of the Wagerup 2009 air quality study was to investigate odour events associated with episodes of poor air quality that occur in the vicinity of the Alcoa Wagerup refinery. The findings of the DEC winter 2006 study (Winter 2006 Study: Intensive Air Quality Investigations at Wagerup, DEC 2008) provided a greater understanding of the complex meteorological mechanisms that lead to odour events of concern to the community. In 2009 a targeted approach was taken, in which meteorological forecasts were used to predict days where forecasted weather conditions were likely to be conducive to the development of poor air quality. On these predicted poor air quality days, DEC staff were deployed in the area to take air samples for chemical analysis during odour events. The monitoring program was undertaken from 1 May to 2 October 2009.

DEC staff were deployed in the field for Intensive Observation Periods (IOPs) on 14 and 29 July 2009 and 2 October 2009 to assess odours from the refinery, take canister samples and undertake field odour surveys.

In addition to the IOPs when DEC staff were in the field undertaking odour surveys and actively taking samples, continuous monitoring was undertaken for a range of air quality parameters at sites in Yarloop, Cookernup and next to the Wagerup refinery. A wide range of air quality parameters were monitored including VOCs, particles, heavy metals, NO_x, SO₂, CO, and meteorological parameters such as wind speed, wind direction and relative humidity.

Community members played an important role in notifying DEC staff of odour events. Community observations were also used to target days for further analysis of continuous data from the monitoring stations in Yarloop and Cookernup. Community members were provided with an observation logbook and air sampling canisters and asked to notify DEC staff when an air sample was taken. Canister samples were then analysed by the PTRMS in Yarloop.

2. Monitoring sites

The location of the DEC monitoring stations and Alcoa meteorological stations used during this study are shown in Figure 2.1.

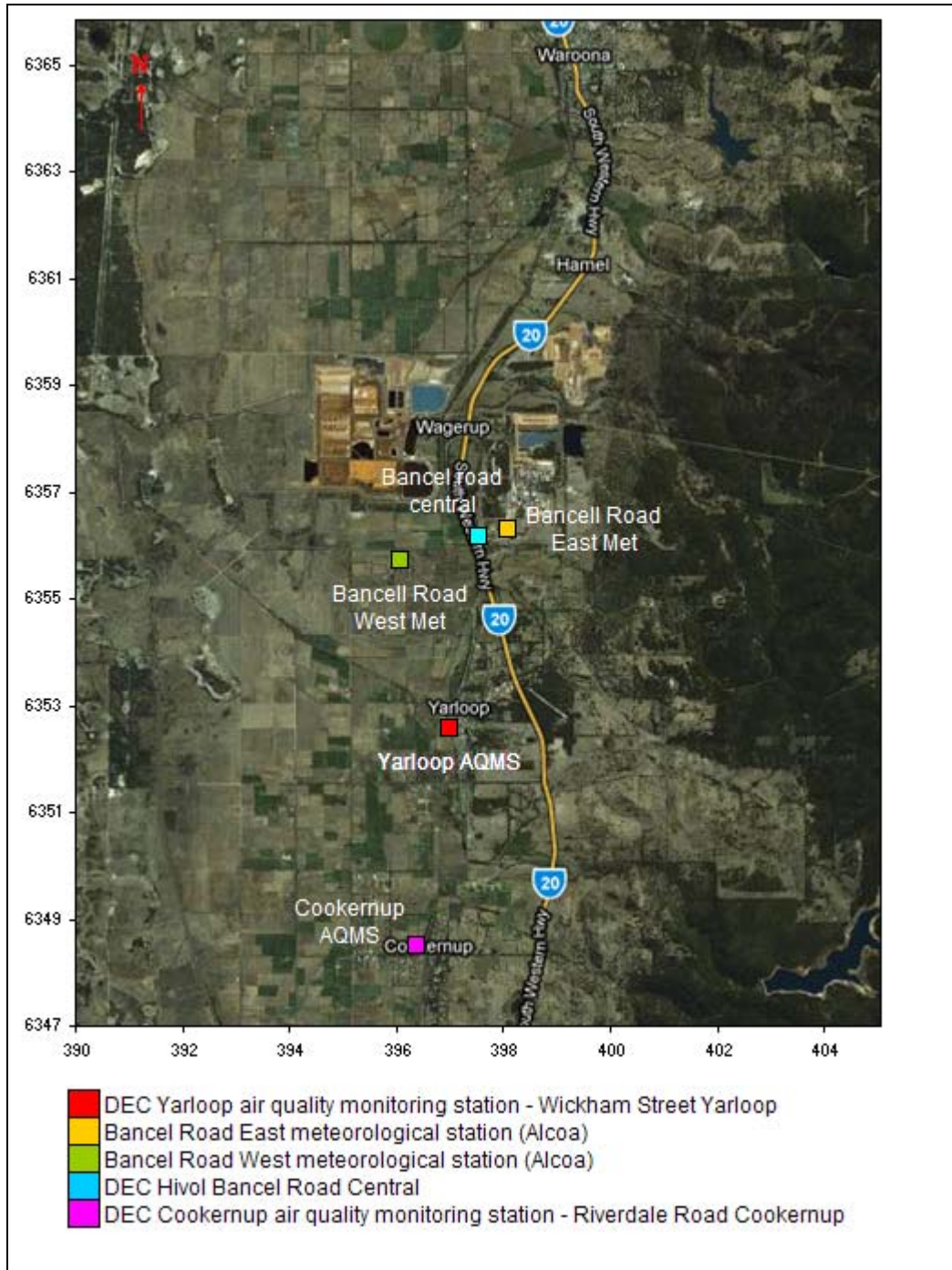


Figure 2.1 – Location of monitoring stations

3. Overview of measurement program and analysis

DEC used specialised instruments and systematic field observations to collect data between 1 May and 2 October 2009. These field experiments included the following measurements and equipment.

3.1. DEC air quality monitoring stations

Table 3.1.1 shows the air quality parameters measured at each DEC monitoring location. Alcoa monitoring stations are shown in addition to the DEC monitoring stations as meteorological data from permanent Alcoa monitoring stations were used to aid in the interpretation of results obtained.

Table 3.1.1 Parameters measured at each monitoring station

	Monitoring location				
	Yarloop (DEC)	Cookernup (DEC)	Bancell Rd Central (DEC)	Bancell Rd West (Alcoa)	Bancell Rd East (Alcoa)
VOCs	✓				
NO _x	✓	✓			
SO ₂	✓				
CO	✓	✓			
PM _{2.5}	✓	✓			
Heavy Metals			✓		
Meteorological measurements	✓	✓		✓	✓

3.2. Air quality parameters

3.2.1. Particles

Airborne particles are commonly classified by their size as total suspended particles, visibility-reducing particles (PM₂), and inhalable particles (coarse fraction PM₁₀ and fine fraction PM_{2.5}). Particles as PM_{2.5} were measured continuously via a Tapered Element Oscillating Microbalance (TEOM) at monitoring stations in Yarloop from 1 May 2009 to 2 October 2009 and Cookernup from 8 May 2009 to 2 October 2009.

3.2.2. Nitrogen dioxide (NO₂)

NO₂ is a precursor of photochemical smog. The majority of anthropogenic air emissions are in the form of nitric oxide (NO), that can be transformed to NO₂. At high temperatures, atmospheric nitrogen combines with oxygen to form a mixture of NO and NO₂ referred to as oxides of nitrogen (NO_x). Both gases are emitted by motor vehicle engines, industrial and commercial boilers, in power generation and from the Wagerup refinery (NPI 2009). In urban areas motor vehicle emissions are a major source of NO₂. Indoor sources of NO₂ include unflued gas appliances and other combustion devices. Natural sources of NO₂ are lightning and the atmospheric oxidation of ammonia. NO₂ was measured continuously via a chemiluminescence NO-NO₂-NO_x analyser (Thermo Electron Corporation, Model 42i) at monitoring stations in Yarloop from 1 May 2009 to 2 October 2009 and Cookernup from 20 May 2009 to 2 October 2009.

3.2.3. Sulfur dioxide (SO₂)

SO₂ is a colourless gas with a sharp irritating odour. It is produced in the combustion of coal and oil, and in the smelting of metallic sulfide ores. SO₂ was measured continuously in Yarloop via an ultraviolet (UV) fluorescent SO₂ analyser (Thermo Environmental Instruments Inc. Model 43i) from 1 May 2009 to 2 October 2009.

3.2.4. Carbon monoxide (CO)

CO is a colourless and odourless gas produced by the incomplete combustion of any carbon-based fuel (e.g. petrol, diesel, oil, gas, wood or coal). In urban areas, motor vehicles are the principal source of CO. In Perth, up to 80 per cent of all CO emissions are a result of motor vehicle exhaust (Australian Academy of Technological Sciences and Engineering, 1997). Power generation, domestic solid fuel heaters and burning vegetation are other significant sources. CO is a refinery emission (NPI 2009) and may also be formed in the atmosphere by the oxidation of methane. A Gas Filter Correlation (GFC) CO Analyser (Thermo Electron Corporation model 48i) was used to measure CO at the Yarloop monitoring station continuously from 1 May 2009 to 2 October 2009.

3.2.5. VOCs measured by Proton Transfer Reaction Mass Spectrometer (PTRMS)

A high sensitivity PTRMS (Ionicon Analytik, Innsbruck, Austria) was installed in Yarloop to continuously monitor volatile organic compounds in the ambient air from 1 May 2009 to 2 October 2009. The PTRMS is an extremely sensitive and advanced instrument for monitoring VOCs at ppb levels (Lindinger et al 1999). It is an on-line chemical ionization mass spectrometer, measuring the molecular mass of compounds present in whole air samples with a resolution of one atomic mass unit. As there are some compounds commonly present in ambient air that have the same molecular mass but different chemical composition, the PTRMS cannot differentiate between them, however compounds detected by the PTRMS are tentatively identified by association of the detected ion mass-to-charge ratio (m/z) with VOCs that are known, or expected to be present in the ambient air (de Gouw and Warneke, 2007). These VOCs can be identified by other discontinuous analytical techniques such as those listed in the

USEPA Compendium of Air Toxic methods. When available, such detailed chemical information can complement and support the tentative identification of VOCs detected by PTRMS. For the purpose of allowing positive identification of compounds, additional measurements of VOCs were taken in parallel with the PTRMS using traditional sampling methods followed by laboratory analysis with common analytical techniques (US-EPA). The information from these methods was particularly useful to facilitate the identification where more than one compound corresponded to a single mass (m/z) detected by the PTRMS. The advantage of using PTRMS is that a wide range of VOCs can be monitored simultaneously with a greater time resolution than traditional analysis techniques. In this study the PTRMS was capable of monitoring 179 masses (corresponding to over 179 possible compounds in air) every 90 seconds over the entire study period.

3.2.6. Heavy metals

Heavy metals occur naturally within the crust of the Earth. They mainly exist as solid metal particles or metals attached to the surface of other particles. Heavy metals are elements and therefore cannot be destroyed, nor can their properties be easily altered. Heavy metals enter our bodies through food, drinking water and air. Minute levels of some heavy metals are essential to human health, however high concentrations may be harmful. Heavy metals were monitored using a High Volume air sampler (HiVol) at Bancell Road from 23 June 2009 to 2 October 2009.

3.2.7. Intensive observation periods (IOPs)

DEC staff were deployed in the field for IOPs to assess odours from the refinery and to take canister samples. The canisters enable short term air samples to be collected and have a non reactive lining to allow laboratory analysis of VOCs. DEC staff were in the field taking measurements and conducting odour surveys as part of the IOPs on the 14 and 29 July 2009 and 2 October 2009.

3.2.8. Community sampling program

A community canister sampling program was also undertaken from 1 May 2009 to 2 October 2009. The community used logbooks to record observations on perceived air quality events corresponding with canister samples. An example of a community logbook is provided in Appendix 1. Many of the canisters that were taken by the community were analysed by the PTRMS in Yarloop. Canisters offer a simple and robust method of collecting air samples over short time periods.

4. Results

4.1. Continuous PTRMS data and community observations

Community observations were used to target days for detailed analysis of continuous data from the PTRMS. Observations were compiled from observation logbooks and complaints logged by Alcoa or DEC. The PTRMS time-series was analysed for days in which there were multiple complaints in order to identify whether the presence of certain VOCs could be linked to odour events identified by community members and DEC staff. Two days in which multiple observations were reported were selected for further analysis. These days were 3 June 2009 and 12 June 2009.

4.2. Continuous PTRMS data and community observations – 3 June

On 3 June 2009, four community reports of odour were recorded. The time and location of these reported odours were at 9am Yarloop, 9am South Western Highway Yarloop, 9:11am Yarloop and 9:20am Cookernup. These odours were described as ‘very strong caustic smell’, ‘caustic odour’ and ‘wet cement smell’.

The results of the Wagerup 2006 study (DEC 2008) demonstrated the meteorology near the Wagerup refinery is complex due to the influence of the Darling Scarp. Under certain conditions, there can be significant horizontal variation, in wind speed and direction, measured at different locations in the area. This horizontal variation in winds is evident in surface winds and also winds measured at different heights. Due to the variability of the winds in the area, a number of trajectories were calculated, using wind data from the available monitoring stations at Yarloop (10m), Bancell Road East (10m), Bancell Road East (30m), and Bancell Road West (10m).

Figure 4.2.1 shows a number of back trajectories, each ending at the DEC monitoring station in Yarloop (location of the PTRMS) at 9:20am on 3 June 2009. A trajectory is the path a parcel of air takes as it responds to changes in winds at different locations and times. A back trajectory indicates the recent history of a parcel of air before a given time. The locations of the monitoring stations are labelled on the map. The white triangles represent the location of the community complaints received on the day. Trajectories calculated using wind data from Yarloop (10m), Bancell Road East (10m), Bancell Road East (30m) and Bancell Road West (10m) are displayed in red, yellow, blue and green respectively.

It is evident in Figure 4.2.1 that there is variability in the winds used to calculate back trajectories from the different monitoring stations, consistent with the findings of the 2006 study, however as a general trend, it is apparent that the air sampled at the Yarloop monitoring station at the time of community complaints travelled over the refinery area before reaching Yarloop.

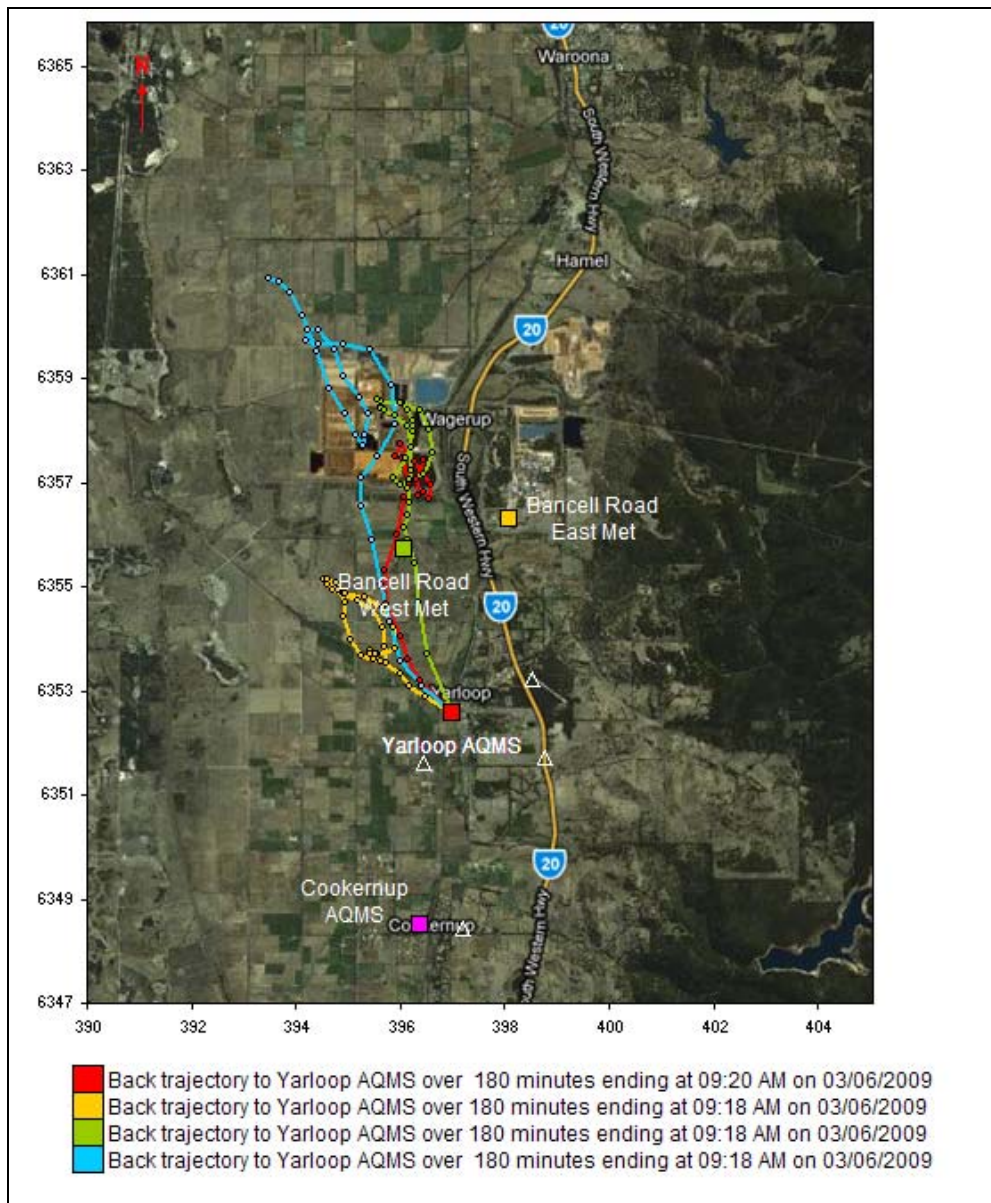


Figure 4.2.1 – Back trajectories to the DEC Yarloop monitoring station 3 June 2009

Figure 4.2.2 shows measurements of VOCs and NO_x, taken on 3 June 2009. The concentration of VOCs are displayed on the left hand axis and NO_x concentration is displayed on the right hand axis.

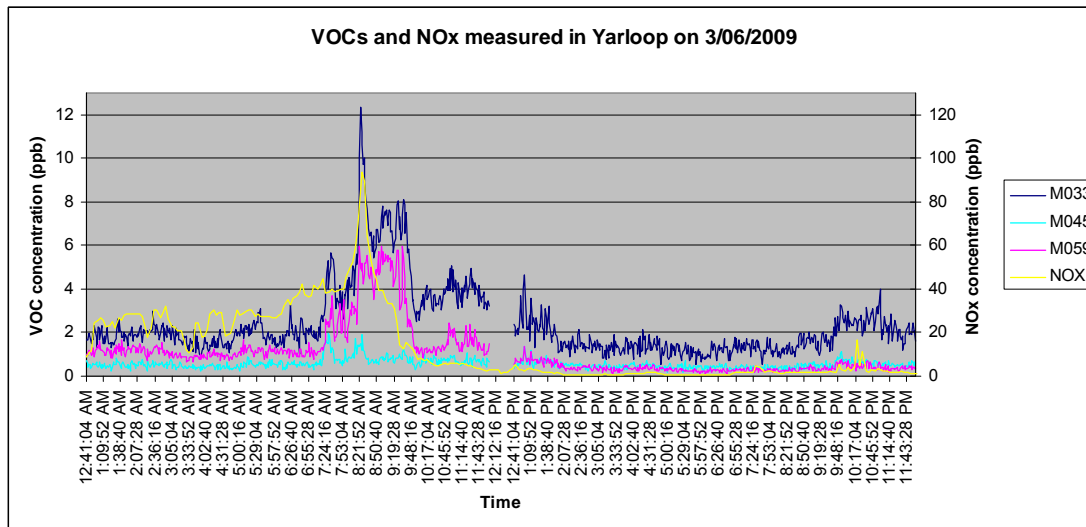


Figure 4.2.2 VOCs measured by PTRMS ($m/z33$, $m/z45$ and $m/z59$) and NO_x measured by chemiluminescence, 3 June 2009 in Yarloop.

Figure 4.2.2 shows the concentration of VOCs corresponding to masses (i.e. compounds with a mass to charge ratio m/z of 33 and 59) detected by the PTRMS in Yarloop appears to significantly increase (4–6 ppb above background levels) at the time of the community observations of ‘very strong caustic smell’ and ‘caustic odour’ at 9am and ‘wet cement’ at 9:20am. There is also a corresponding increase in NO_x concentration measured at monitoring stations in both Yarloop and Cookernup during this time period. CSIRO, (Galbally et al 2008) has identified the most likely candidates for m/z 33 and m/z 59 in the Wagerup area to be methanol and acetone respectively. Furthermore, studies (de Gouw and Warneke 2007) using Gas Chromatography coupled with PTRMS have not identified the presence of other compounds at m/z 33 other than methanol. Acetone and propanal are both detected at m/z 59 but multiple studies have confirmed that propanal only contributes a small proportion (0 -10 per cent) and for practical purposes the concentration at m/z 59 can be attributed to acetone (de Gouw and Warneke 2007).

Canister sampling undertaken by DEC during times when a ‘wet cement’ odour was present in the area has previously confirmed the presence of low levels of methanol and acetone in samples. The terms ‘wet cement’ and ‘caustic odour’ are the terms most commonly used by community members when describing Alcoa refinery odour. Acetone is a known refinery emission and odour bag analyses by PTRMS (Galbally et al, 2008) has previously identified methanol (m/z 33) in Refinery emissions. It is likely that the Wagerup refinery is the source of some of the NO_x , acetone and methanol detected during the time of complaints as these compounds are known to be emissions from the refinery, and because winds observed at Yarloop at that time had previously passed over the refinery area (Figure 4.2.1). This finding is further supported by the CSIRO study (Galbally et al 2008), in which observations of a ‘wet cement’ odour were linked to elevated concentrations of NO_x and acetone when wind direction was from the refinery sector. Further interpretation and analysis of the CSIRO data was performed by DEC and this is summarised in Appendix 2

4.3. Continuous PTRMS data and community observations— 12 June

On 12 June 2009, four community observations (concerning odour and health effects perceived to be from the refinery) were received. The time and location of these observations were at 7:45am to 8:15am Yarloop, 9:20am Yarloop, 10:30am Cookernup and 2:40pm Yarloop.

Figure 4.3.1 shows a number of back trajectories, each ending at the DEC monitoring station in Yarloop (location of PTRMS) at 9am 12 June 2009. The location of the monitoring stations are labelled on the map. The white triangles represent the location of the community complaints received on the day.

Trajectories calculated using wind data from Yarloop (10m), Bancell Road East (10m), Bancell Road East (30m), and Bancell Road West (10m) are displayed in red, yellow, blue and green respectively. It is evident in Figure 4.3.1 that there is horizontal variability in the winds used to calculate back trajectories from the different monitoring stations, however as a general trend, it is apparent that the air sampled at the Yarloop monitoring station at the time of community complaints travelled over the refinery area before reaching Yarloop.

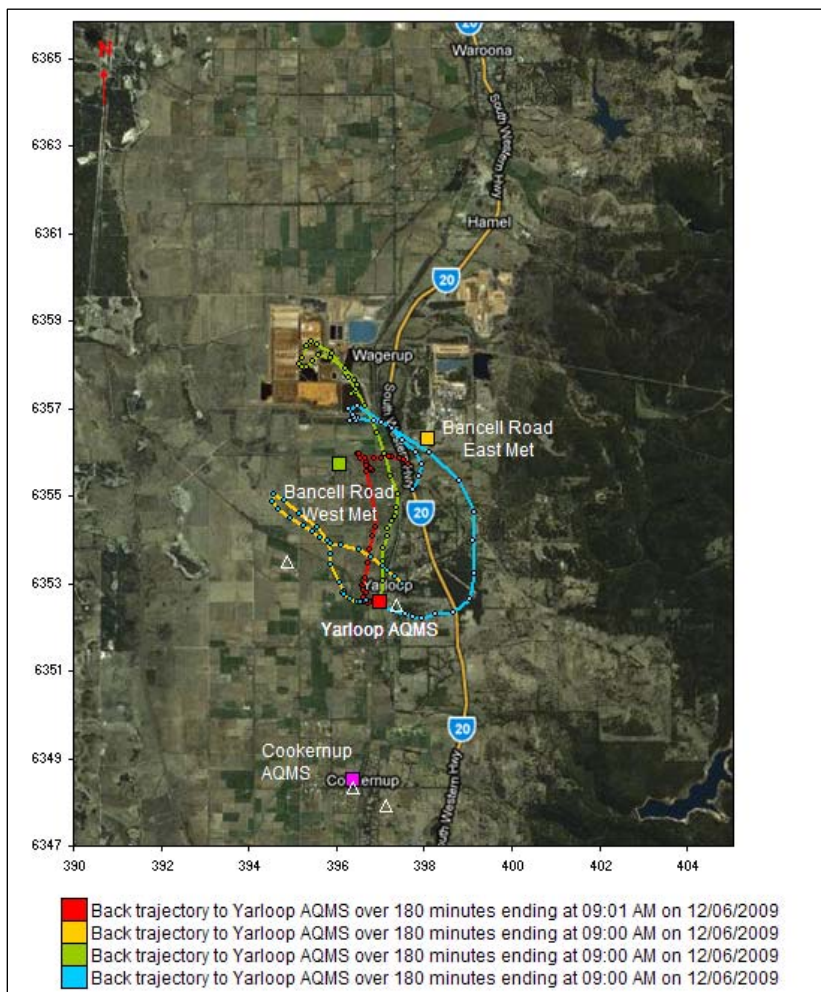


Figure 4.3.1 – Back trajectories to the DEC Yarloop monitoring station on 12 June 2009

Figure 4.3.2 shows measurements of VOCs and NO_x taken on 12 June 2009. The PTRMS detected increases in m/z 33 (methanol), m/z 45 (acetaldehyde) and m/z 59 (acetone), with the concentrations displayed on the left hand axis. The NO_x concentration for the same period is displayed on the right hand axis.

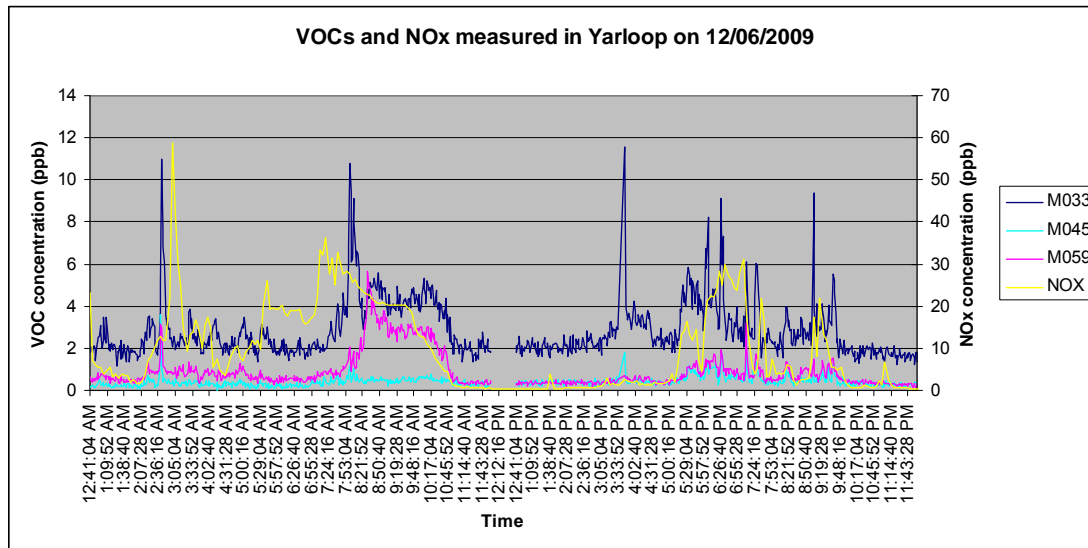


Figure 4.3.2 VOCs measured by PTRMS (m/z33, m/z45 and m/z59) and NO_x measured by chemiluminescence on 12 June 2009 in Yarloop.

There is an increase in the concentration of m/z 33 (methanol), m/z 59 (acetone) and NO_x from 7:40am to 10:50am (Figure 4.3.2) under a predominately northerly wind direction. This increase corresponds with three out of four of the community complaints and odour observations received. These odours were described as ‘worst ever refinery event—smell so strong we could not catch our breath’ at 7:45am to 8:15am, ‘strong wet cement smell’ at 9 am.

The 7:45am to 8:15am observation was from a location within approximately 250 meters of the PTRMS and corresponds with the sharp peak in m/z 33 (methanol) concentration detected by the PTRMS between 8:00am and 8:15am. It is likely, that over the 30 minute period that the odour was observed and the spike in concentration was detected by the PTRMS, that emissions from the refinery impacted both sites given the short distance between the PTRMS and the point where the odour was observed.

As three out of four of the community observations appear to be related to an increase in m/z 33 (methanol) and m/z 59 (acetone) concentrations and the winds that reached the Yarloop monitoring station at the time of the complaints had passed over the refinery area (Figure 4.3.1) and are known refinery emissions, the Wagerup refinery is a likely source of the observed odour.

Figure 4.3.2 also shows spikes in the concentration of m/z 33 (methanol) and m/z 59 (acetone) in the evening between 5:30pm and 10:00pm, however these spikes in concentration are generally of short duration. The evening spikes of m/z 33 (methanol) and m/z 59 (acetone) appear to be of a different origin as they are also accompanied by m/z 45 (acetaldehyde) and m/z 42 (acetonitrile, a biomass burning indicator) and occur under a predominately south

easterly wind direction. Acetaldehyde has a number of sources in the Wagerup area. It is a known refinery emission (NPI 2009) and also has sources in biomass burning, vehicle emissions and is emitted by vegetation. The presence of m/z 42 (acetonitrile) in combination with m/z 45 (acetaldehyde and other compounds) suggests that the source of the afternoon VOC spikes on 12 June 2009 may be due to the PTRMS detecting smoke from biomass burning.

Emission factors for a wide range of VOCs emitted by biomass burning (extra tropical forest) are presented by Andreae and Merlet (2001). Selected VOC emissions rates for the Wagerup refinery are also available (Alcoa 2005). These emission factors were used to calculate an acetone to acetaldehyde emission ratio for biomass burning and refinery emissions. The emission factors used and resulting ratios are summarised in Table 4.3.1. A comparison of the ratio of acetone to acetaldehyde concentration on the days where there were multiple community complaints provides an indication of whether the spike in concentration is likely to be influenced by refinery emissions or biomass burning. The average concentration ratio of acetone with respect to acetaldehyde on 12 June 2009 for the period 7:40am to 10:50am (corresponding to three out of four complaints) is 5.1 indicating that the refinery is a likely source of the broad peak of acetone and methanol detected in the morning. The afternoon VOC spikes have an acetone to acetaldehyde ratio of approximately 1:1 providing further evidence that the source of these spikes may be due to biomass burning.

Table 4.3.1 Acetone and acetaldehyde emissions from biomass burning and the Wagerup refinery.

	Acetone	Acetaldehyde	Calculated acetone/acetaldehyde molar ratio
Biomass burning (extra tropical forest fires)	0.52-0.59 g/kg (Andreae and Merlet 2001)	0.48-0.52 g/kg (Andreae and Merlet 2001)	0.84
Wagerup Refinery Emissions	4.96 g/s (peak) 1.43 g/s (average) (Alcoa 2005)	0.806 g/s (peak) 0.426 g/s (average) (Alcoa 2005)	4.67 (peak) 2.54 (average)

4.4. General trend for VOCs measured continuously by PTRMS with complaints data

In general, for 64 per cent of days where there were two or more community observations during the study, there was an increase in m/z 33 (methanol) and m/z 59 (acetone) detected by the PTRMS between 6am and 11am. On these days the community observations occur during this time. This increase in concentration (of approximately 5ppb to 8ppb above background) is evident by a broad peak in the PTRMS data indicating that these events develop over a time period of hours. On these days there are often short-term spikes in the concentration of m/z 33, m/z 59 and m/z 45 in the evening. These evening spikes are different to the broad peaks that occur in the morning as they show a different VOC signature (i.e. m/z 45 is also present), are of a much shorter duration and occur under varying wind directions. These afternoon spikes were not attributed to refinery odour by community reports during this study period.

For the remaining times where multiple community reports were received, no corresponding rise was registered at the PTRMS. Since reports of odours were obtained from a wide range of locations—from next to the refinery to Yarloop and Cookernup, it is highly likely that the refinery plume may be moving over parts of Yarloop and Cookernup but missing the PTRMS inlet at the monitoring station.

On days when multiple community observations were received, over 60 per cent of these corresponded with an increase in m/z 33 (methanol) and m/z 59 (acetone) at the PTRMS. Such a high percentage is surprising given that community observers were spread over a large area and provides further evidence that these compounds may be used, in combination with other air quality measurements as indicators of the refinery plume.

4.5. IOPs and canister samples analysed via PTRMS

A wide range of air quality measurements were taken from 1 May 2009 to 2 October 2009. This program included three Intensive Observation Periods (IOPs), targeting specific weather conditions conducive to the development of poor air quality. The days selected for the IOPs were determined using meteorological data and forecasts obtained from the Bureau of Meteorology. DEC staff were in the field taking measurements and conducting odour surveys as part of the IOPs on 14 and 29 July 2009 and 2 October 2009.

Canister samples collected by DEC staff during the IOPs were analysed by the PTRMS. These canister samples were taken when there was a wet cement odour or a wood smoke odour. Background samples were also taken when there was no odour for comparison to odour samples. There were no canister samples taken by community members during the IOPs, however community samples were taken during the study period at times when a refinery odour was present. Canister samples taken by community members were also analysed by the PTRMS. A small subset of DEC IOP and community canisters (9) were also sent to an accredited overseas laboratory for analysis by USEPA method TO-15 for quality assurance.

It is important to note that analysis of canisters via PTRMS has not previously been attempted. The results of the canister samples analysed by the PTRMS are not quantitative and only broad conclusions can be drawn from the results. Further samples need to be taken in order to verify the method used for analysis of canisters via PTRMS.

The PTRMS detected a wider suite of compounds not previously detected in canister samples taken in 2006 and analysed using USEPA method TO-15. Many of these compounds (tentatively identified in the PTRMS measurements) are odorous and were present at very low concentrations (i.e. in the low ppb range). The highest concentrations of VOCs detected by the PTRMS in DEC IOP canisters taken when a refinery odour (described as wet cement or caustic) was present correspond to m/z 33 (methanol), m/z 59 (acetone), m/z 61 (acetic acid, multiple compounds), m/z 43 (multiple compounds including isopropanol), m/z 45 (acetaldehyde), m/z 93 (toluene) m/z 47 (ethanol, formic acid and multiple compounds) and m/z 107 (xylenes, benzaldehyde and multiple compounds). The highest concentration VOCs detected in community canisters were m/z 33 (methanol), m/z 43 (multiple compounds including isopropanol), m/z 59 (acetone) and m/z 61 (acetic acid, multiple compounds).

There are multiple sources of these VOCs in the Wagerup region. Sources of anthropogenic emissions in the area include refinery emissions, vehicle exhaust and emissions from domestic, commercial, industrial and agricultural activities. A brief description of possible sources of these VOCs in the area follows. Methanol (m/z 33) has a large natural source from vegetation (Galbally and Kirstine, 2002) and has also been identified in refinery emissions (Galbally et al 2008). Acetone (m/z 59) is present in refinery emissions and emissions from biomass burning and also has sources in atmospheric chemistry and vegetation. Acetaldehyde (m/z 45) is present in refinery emissions, emissions from biomass burning, vehicle emissions and is emitted by vegetation. Toluene (m/z 93) has sources including the refinery, vehicle emissions and biomass burning. The PTRMS can detect multiple compounds at m/z 107, including ethylbenzene, benzaldehyde and xylenes. Sources of these compounds include the refinery, motor vehicles and biomass burning. Acetic acid (m/z 61) has sources in biomass burning (e.g. from bushfires, controlled burns, wood heaters) and atmospheric chemistry (Chebbi and Carlier, 1996). Isopropanol (m/z 43) is a common solvent. The PTRMS can detect multiple compounds at m/z 47 including ethanol and formic acid. Sources of atmospheric ethanol include domestic and industrial activities as well as production from waterlogged vegetation (Galbally et al 2008). Sources of formic acid include biomass burning and atmospheric photochemistry.

Alcoa undertook a study using Gas Chromatography-Mass Spectrometry-Olfactometry (GC-MS-O) with the aim of increasing understanding of Alumina refinery odour (Coffey et al 2009). A number of compounds including benzaldehyde, acetaldehyde, acetone and toluene were identified by GC-MS-O as contributing to refinery odour. Galbally et al (2008) have previously observed sources of m/z 59 (acetone), m/z 45 (acetaldehyde), m/z 33 (methanol) and m/z 43 (multiple compounds) as well as NO_x in the direction of the Wagerup refinery, which is consistent with known refinery emissions. As many of these VOCs have been identified in canister samples analysed by the PTRMS when an odour was present, in odour samples by Alcoa and have been previously linked to the refinery by wind direction, the combination and

concentration ratio of these VOCs in combination with other air quality measurements (such as NO_x, CO, particles) may be used as indicators of refinery influence.

Many of the VOCs (masses) detected in the canisters taken by DEC staff as part of the IOPs when a wet cement odour was present and by community members were also present in background canisters. Concentrations of VOCs detected were in the low ppb range. The PTRMS detected more compounds from canisters taken when a wood smoke odour was present than in the canisters taken when a wet cement odour was present. The masses detected in the DEC IOP wet cement and community samples were also detected in the wood smoke canisters.

A number of canister samples taken during odour events by either DEC staff or community members were sent to an independent laboratory for analysis via USEPA method TO-15. A total of nine canister samples were sent to the laboratory for analysis. VOCs detected in two or more of these canisters and their respective average concentrations are displayed in Table 4.5.1.

Table 4.5.1 Average concentration of VOCs detected in two or more canisters analysed by USEPA method TO-15

Compound	Number of canisters (%) in which compound was detected	Concentration detected above LOD in ppb average (maximum, minimum)	Limit of detection (LOD) ppb
Acetone	7 (78%)	4.1 (10, 2.4)	2.0
Formaldehyde	9 (100%)	8.3 (12, 5.2)	2.0
Acetaldehyde	8 (89%)	5.7 (9.2, 3.0)	2.0
Methanol	9 (100%)	12.4 (48, 5.0)	2.0
Ethanol	6 (67%)	1.7 (4.4, 1.0)	1.0
Toluene	2 (22%)	3.7 (30, 0.5)	0.5
Chloromethane	8 (89%)	0.7 (1.1, 0.5)	0.5

Methanol and formaldehyde were identified in all nine community and DEC IOP canisters analysed using USEPA method TO-15. Acetaldehyde and chloromethane were present in eight out of nine, acetone was present in seven out of nine and ethanol was present in six out of nine canisters.

The levels of VOCs detected in the canisters analysed via USEPA method TO-15 were below their respective odour thresholds however, acetaldehyde has a relatively low odour threshold and the concentration detected in some canisters was close to the lower limit of acetaldehyde odour thresholds reported in the literature. Acetone, formaldehyde, acetaldehyde and toluene are known refinery emissions and methanol has been previously identified in refinery stack samples (Galbally et al 2008). Furthermore, acetone, formaldehyde, acetaldehyde and toluene have been linked to refinery odour (Coffey et al 2009). Acetone has also been linked to refinery odour (Galbally et al 2008) however it was noted that the acetone concentrations detected were below the odour threshold. As these compounds have been linked to refinery odour in this and previous studies the combination and concentration ratio of these VOCs in combination with other air quality measurements (such as NO_x, CO, particles etc) may be used as an indicator of refinery emissions even though single VOCs may be below the odour threshold for that compound.

In one community canister sample taken on 14 June 2009 and analysed via USEPA method TO-15 a number of VOCs were detected, that weren't detected above the limit of detection in other canister samples analysed via USEPA method TO-15. The canister sample was taken when the community member noted an odour described as a 'strong caustic smell'. The results of this canister analysis are displayed in Table 4.5.2.

Table 4.5.2 VOCs detected in canister taken on 14 June 2009 (continued over page)

Compound	Concentration ppb	Limit of detection ppb
Acetone	3.8	2
Formaldehyde	11	2
Acetaldehyde	4.9	2
Methanol	14	2
Ethanol	3.3	1
Toluene	31	0.5
Chloromethane	0.6	0.5
Hexane	3	0.5
Benzene	4.1	0.5
Cyclohexane	1.9	0.5
2,2,4-Trimethylpentane	3.3	0.5
Heptane	1.6	0.5

Toluene	31	0.5
Ethylbenzene	2.4	0.5
m,p-Xylene	9.3	0.5
o-Xylene	2.9	0.5
1,2,4-Trimethylbenzene	1.1	0.5

Figure 4.5.1 shows a number of back trajectories, each ending at the location of where the canister sample was taken at 10:20am on 14 June 2009. The locations of the monitoring stations are labelled on the map.

Trajectories calculated using wind data from Yarloop (10m), Bancell Road East (10m), Bancell Road East (30m), and Bancell Road West (10m) are displayed in red, yellow, blue and green respectively.

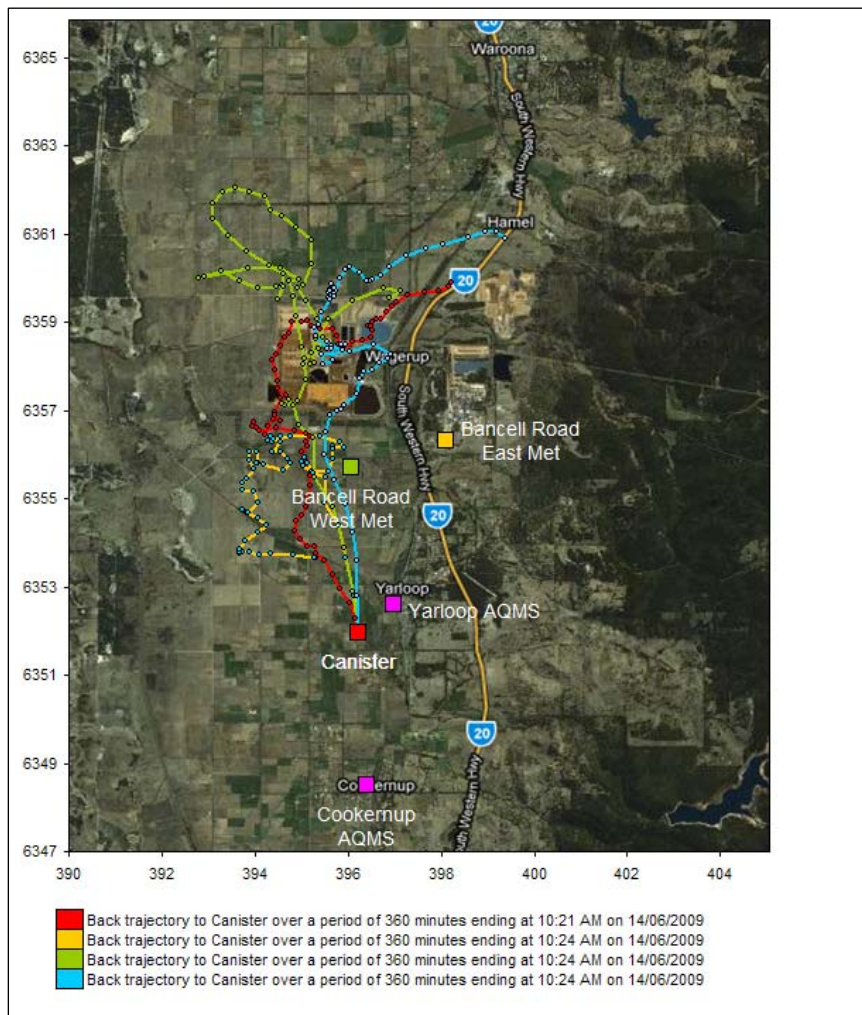


Figure 4.5.1 Back trajectories ending at the location of canister sample taken on 14 June 2009.

It is evident in Figure 4.5.1 that there is variability in the winds used to calculate back trajectories from the different monitoring stations, however as a general trend, it is highly likely that the air travelled over the refinery area before the 'strong caustic' odour was noted and the canister sample was taken.

All of the VOCs detected in other canisters analysed by USEPA method TO-15 (Table 4.5.1) were also detected in the canister collected on 14 June 2009. In addition to this a number of other VOCs that are common in vehicle emissions were also detected. Benzene, toluene, ethylbenzenes and xylenes are present in both motor vehicle and refinery emissions and 2,2,4-trimethylpentane (iso octane) is a common additive to petrol. One possible explanation for the VOCs detected in this canister is that refinery operations may have included using vehicles or petrol powered machinery (e.g. Refinery operations could have included dozing the RDAs at the time. This may be the reason for the extra compounds detected).

There are no Australian National Ambient Standards for the compounds measured from the canisters. However for formaldehyde, benzene, toluene and xylene there are Monitoring Investigation Levels (MILs) that have been developed by the National Environment Protection Council (NEPC). These MILs are provided in Appendix 3. Selected international ambient air quality guidelines for VOCs that do not have a corresponding NEPM MIL are also provided in Appendix 3 for reference.

The monitoring investigation levels are 'levels of air pollution below which lifetime exposure, or exposure for a given averaging time, does not constitute a significant health risk' (NEPC 2004). If these MILs are exceeded in the short-term it does not mean that adverse health effects will occur.

When comparing the MILs and guideline values in Appendix 3 to the results from the canisters analysed via USEPA method TO-15, it must be taken into account that the results provided in this study have been compiled using different averaging periods. If you wish to compare the data with the relevant guidelines, the averaging period for the guideline used must be obtained using the same averaging period.

The canisters used during this study capture an instant air sample over a period of time (typically one minute) and provide a snapshot of what the air was like at the time the canister sample was taken. It must be noted that it is not strictly valid to compare one minute average concentrations against a 24 hour or annual mean criteria. An annual average allows for short term fluctuations in pollutant concentrations, i.e. concentrations of pollutants might be very low for the majority of the year but be elevated for a short period of time leading to very low concentrations on average over the year.

The one minute averaged concentrations of VOCs detected in the canisters analysed by USEPA method TO-15 are all below the relevant 24 hour or annual MIL except for one canister taken on 14 June 2009. All VOCs detected in this canister were below the relevant MIL except for benzene. The one minute averaged benzene concentration from the canister was 4.1ppb compared to the annual average MIL of 3ppb. It is important to note that even though the one minute average canister concentration was above the annual MIL this does not necessarily mean that the annual guideline was exceeded due to different averaging times.

4.6. PTRMS ancillary measurements

To facilitate positive identification of compounds detected by the PTRMS and to reconfirm the quantitation, measurements of VOCs were taken in parallel using traditional sampling methods (adsorbent tubes and canisters) followed by laboratory analysis by common analytical techniques (USEPA methods).

On the days selected for the IOPs, VOCs were sampled using VOC adsorbent tubes (Tenax and DNPH tubes) in parallel with the continuous PTRMS measurements. These tubes allow the detection and quantification of a number of VOCs. The tubes contain a substance that absorbs VOCs when air is passed through the tube. A pump is used to obtain a known rate of air flowing through the tube. Once the sampling is completed, the tubes are analysed at a laboratory with USEPA method TO-11A and TO-17. The concentration of VOCs in the air is calculated using the quantity of each VOC trapped by the adsorbent in the tube and the volume of air that was sampled.

During the IOPs, sampling apparatus was configured so that six, one hour samples were taken consecutively using each of the adsorbent tubes from 6am to 12pm. This morning period corresponds to the time of day when most complaints have historically been received. This time period also corresponds with the time of day in which most odour impacts were observed during this study period. The analytical suite of VOCs analysed using the adsorbent tubes is provided in Appendix 4. The concentrations of VOCs detected by the adsorbent tubes were very low (i.e. below 10 ppb). Adsorbent tube and canister samples taken in parallel with the PTRMS measurements confirm that VOCs detected by the PTRMS were in the low ppb range.

4.7. Heavy metals

Heavy metals were measured at the Bancell Road Central monitoring site (Figure 2.1) using a HiVol. HiVol filter papers were run continuously over three days and collected every third day from 23 June 2009 to 2 October 2009, giving a three day averaged heavy metals concentration.

Figure 4.7.1 shows the results of the three day averaged heavy metal concentrations measured at Bancell Road. A total of 32 three day averaged samples were taken. The green diamonds and blue squares represent the average (of 32 three day averaged concentrations) and maximum (three day averaged) concentration for each element monitored respectively. The yellow crosses represent heavy metal concentrations measured in the Perth Background Air Quality Study at a site in the Perth CBD and are included for comparison to the levels measured at Bancell Road. The levels measured at Perth CBD are 24 hour average concentrations. The pink lines represent an ambient air guideline or standard for that element from one of the following jurisdictions:

- National Environment Protection Council (NEPC)
- World Health Organisation (WHO)
- Texas Commission on Environmental Quality (TCEQ).

All of the guidelines are annual averages except for zinc and vanadium which are a 24 hour average. Ambient guidelines could not be found for thorium, antimony, calcium, sodium and gallium.

It must be taken into account that the results provided in this study have been compiled using different averaging periods. If you wish to compare the data with the relevant guidelines, the averaging period for the guideline used must be obtained using the same averaging period.

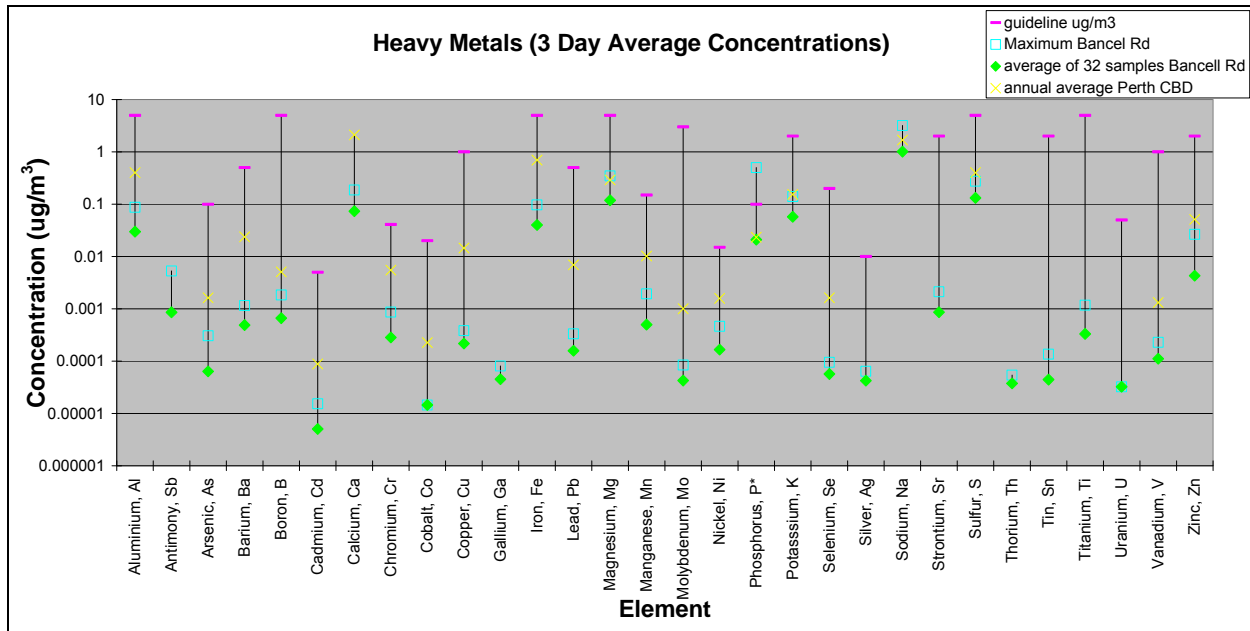


Figure 4.7.1—Maximum and average heavy metals concentrations measured at Bancell Road (Heavy metals concentrations measured in Perth CBD are also included for comparison)

Except for phosphorus, all three day averaged concentrations were below the annual guideline. It is important to note that even though one three day average phosphorus concentration was above the annual guideline this does not necessarily mean that the annual guideline was exceeded due to different averaging times. An annual average allows for short term fluctuations in pollutant concentrations, i.e. concentrations of pollutants might be very low for the majority of the year but be elevated for a short period of time leading to very low concentrations on average over the year. When all of the samples taken during the study period are averaged, the phosphorus concentration is below the annual ambient guideline. Heavy metals concentrations (24 hour averages) measured in the Perth CBD as part of the DEC Background Air Quality Study have been included in Figure 4.7.1 for reference. Caution needs to be taken when comparing concentrations measured in Perth CBD with those measured at Bancell Road due to different averaging times, however the average concentrations (32 samples) of all heavy metals measured at Bancell Road are lower (often by an order of magnitude) than the average concentrations of those measured in the Perth CBD as part of the Perth Background Air Quality Study.

4.8. Particles as PM_{2.5}

Particles as PM_{2.5} were measured continuously via a Tapered Element Oscillating Microbalance (TEOM) at monitoring stations during 2009 in Yarloop from 1 May to 2 October and Cookernup from 8 May to 2 October. A measurement was taken by the TEOMs located in Yarloop and Cookernup every five minutes. These data were then averaged to obtain a 24 hour average to allow comparison with the National Environment Protection Measure (NEPM) 24 hour ambient air quality Advisory Reporting Standard for PM_{2.5}. An Advisory Reporting Standard is a health-based standard used to assess the results of monitoring for particles as PM_{2.5}. The Variation to the National Environment Protection (Ambient Air Quality) Measure states that 'Establishing Advisory Reporting Standards and a protocol setting out monitoring and reporting requirements for PM_{2.5} will provide a tool for communicating information to the community on air quality related to PM_{2.5}, and enable the effectiveness of air quality management programs that are designed to manage PM_{2.5} emissions to be assessed.'

Figures 4.8.1 and 4.8.2 display the 24 hour averaged PM_{2.5} concentration measured at the Yarloop and Cookernup monitoring stations respectively during the study period. The red line indicates the NEPM PM_{2.5} advisory reporting standard of 25µg/m³. The 24 hour averaged PM_{2.5} concentrations measured at both Yarloop and Cookernup were below the advisory reporting standard of 25µg/m³ for the majority of the study period. There was one day (16 May 2009) during the study period when 24 hour averaged PM_{2.5} concentration measured in both Yarloop and Cookernup exceeded 25µg/m³. NO_x levels measured in both Yarloop and Cookernup displayed a similar trend to the particles spikes measured on 16 May.

Particle levels (PM_{2.5} and PM₁₀) measured in Bunbury were also elevated and showed a very similar trend to the particles measured in Yarloop and Cookernup on 16 May 2009. Analysis of the PM_{2.5} to PM₁₀ ratio measured at Bunbury indicates that the source to be wood smoke possibly caused by bushfires, or controlled burns in the area.

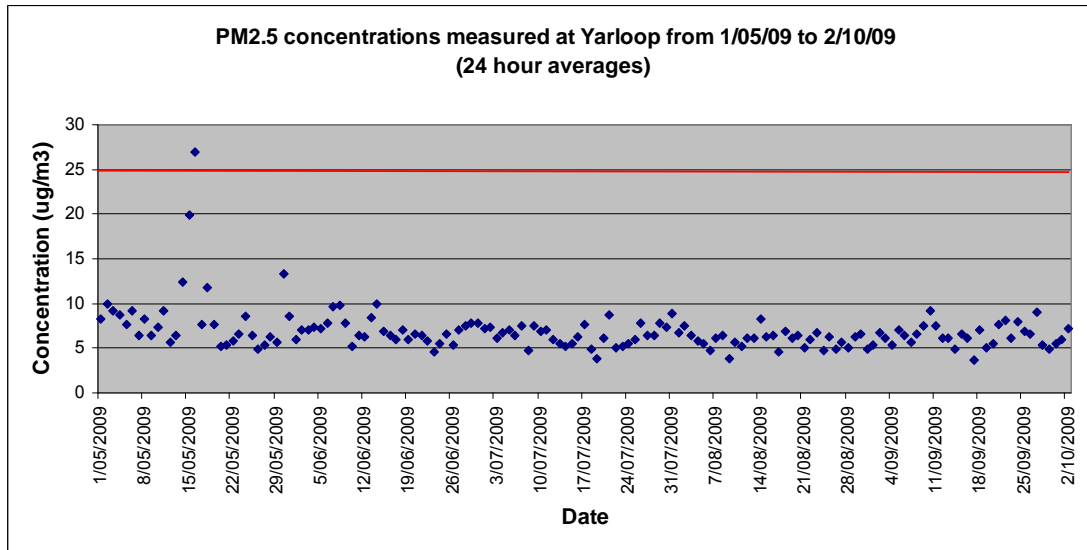


Figure 4.8.1–24 averaged PM2.5 concentrations measured at Yarloop from 1 May 2009 to 2 October 2009 and NEPM ambient guideline of 25 ug/m³

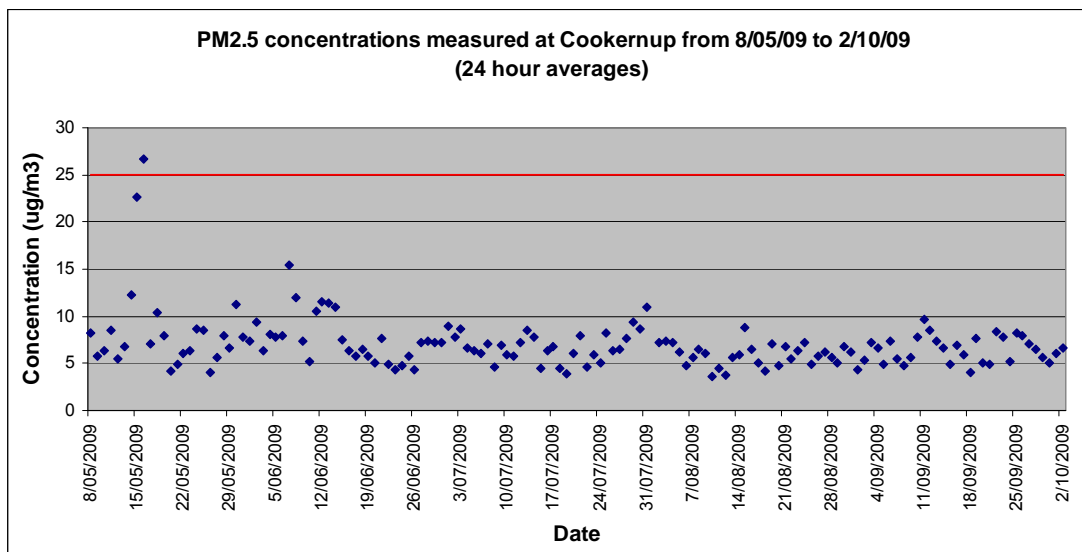


Figure 4.8.2–24 Hour averaged PM2.5 concentrations measured at Cookernup from 8 May 2009 to 2 October 2009 and NEPM ambient guideline of 25 ug/m³

4.9. Nitrogen dioxide (NO₂)

NO₂ was measured continuously at monitoring stations in Yarloop from 1 May 2009 to 2 October 2009 and Cookernup from 20 May 2009 to 2 October 2009. Figures 4.9.1 and 4.9.2 display the daily maximum (one hour averaged) NO₂ concentration measured at the Yarloop and Cookernup monitoring stations during the study period. The red line indicates the NEPM NO₂ standard of 0.12ppm (120ppb). The one hour averaged NO₂ concentrations measured at both Yarloop and Cookernup were below the standard of 0.12ppm (120ppb) over the entire study period. The highest one hour average measured at Yarloop of 17.2ppb occurred on 15 May 2009 and represents 14 per cent of the NEPM standard. The highest one hour average

measured at Cookernup of 14.9ppb occurred on 14 October 2009 and represents 12 per cent of the NEPM standard.

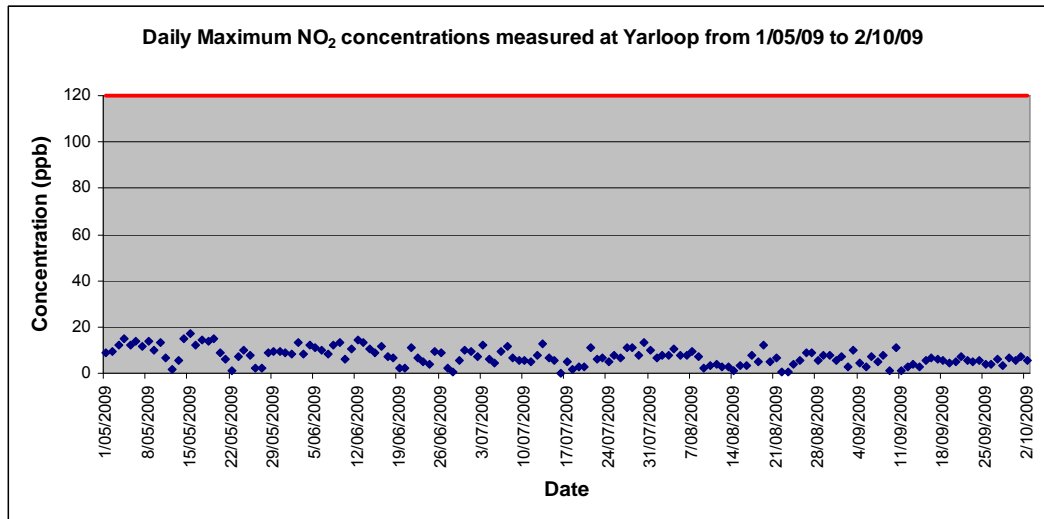


Figure 4.9.1—Daily maximum NO₂ concentrations measured at Yarloop from 1 May 2009 to 2 October 2009 (one hour averages) and NEPM ambient standard of 120ppb.

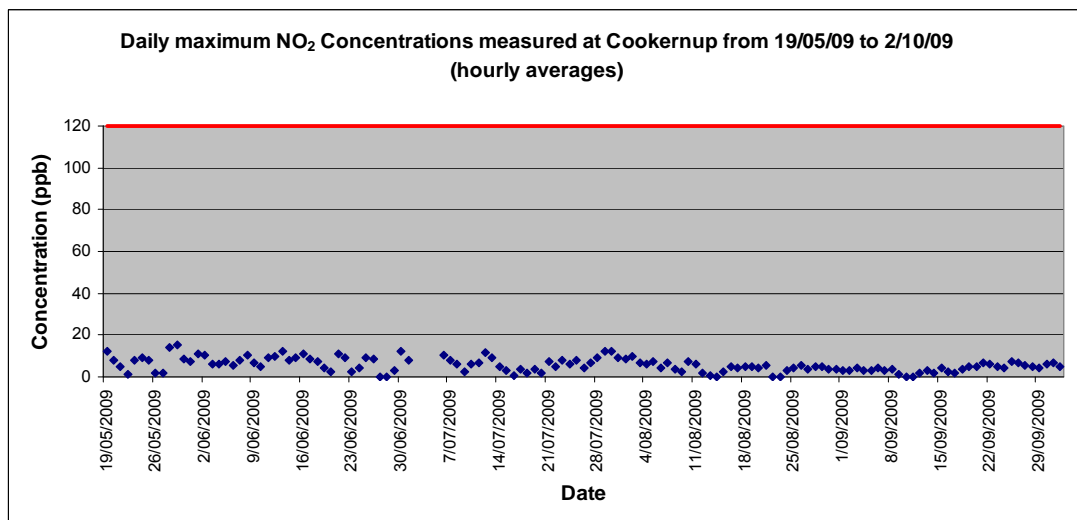


Figure 4.9.2—Daily maximum NO₂ concentrations measured at Cookernup from 19 May 2009 to 2 October 2009 (one hour averages) and NEPM ambient standard of 120ppb.

4.10. Carbon monoxide (CO)

Carbon monoxide was measured continuously at the Yarloop monitoring station from 1 May 2009 to 2 October 2009. Figure 4.10.1 displays the eight hour averaged CO concentration measured during the study period. The red line indicates the NEPM CO standard of 9ppm (9000ppb) averaged over eight hours. The eight hour averaged CO concentrations measured at Yarloop did not exceed the standard of 9ppm over the study period. The highest eight hour

average of 0.63ppm (630ppb) occurred on 27 July 2009 and represents 7 per cent of the NEPM standard.

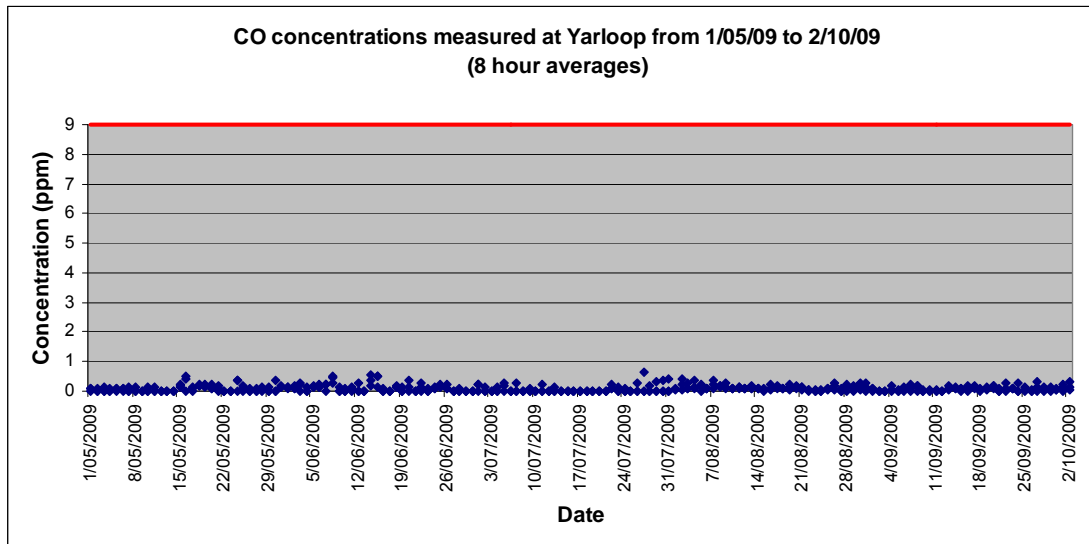


Figure 4.10.1– 8 Hour averaged CO concentrations measured at Yarloop from 1 May 2009 to 2 October 2009 and NEPM ambient standard of 9ppm.

4.11. Sulfur dioxide (SO₂)

Sulfur dioxide was measured continuously at the Yarloop monitoring station from 1 May 2009 to 2 October 2009. Figure 4.11.1 shows the daily maximum (one hour averaged) SO₂ concentration measured during the study period. The red line indicates the NEPM SO₂ standard of 0.2ppm (200ppb). The one hour averaged SO₂ levels measured at Yarloop did not exceed the standard of 0.2ppm over the study period. The highest one hour average of 0.014 ppm (14 ppb) occurred on 30 September 2009 and represents 7 per cent of the NEPM standard.

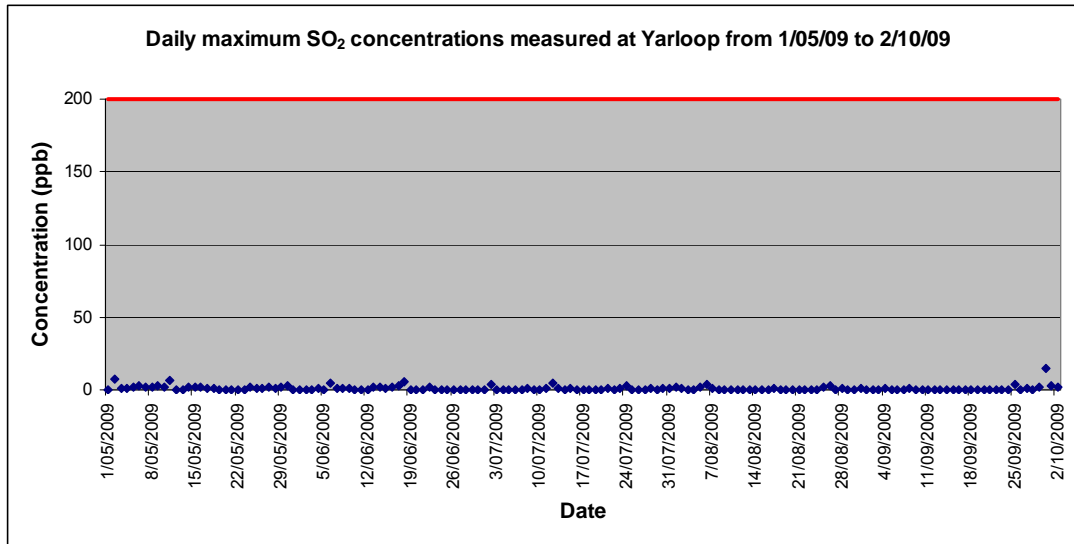


Figure 4.11.1—Daily maximum SO₂ concentrations measured at Yarloop from 1 May 2009 to 2 October 2009 (hourly averages) and NEPM ambient standard of 200ppb.

5. Conclusions

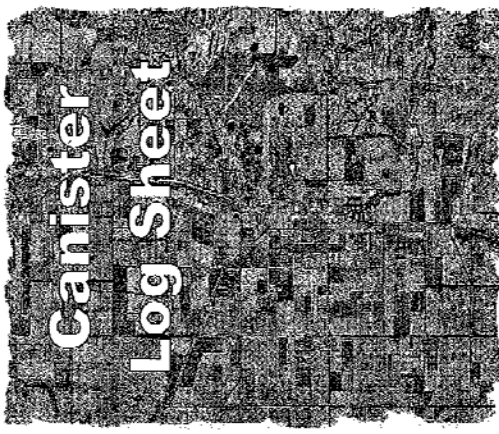
As part of the Wagerup 2009 air quality study, a wide range of air quality parameters were monitored at monitoring stations in Yarloop, Cookernup and Bancell Road from 1 May 2009 to 2 October 2009.

The air pollutant concentrations measured during the study were low, the exception to this being the particle levels measured on 16 May. There are a number of known emissions sources that are likely to have contributed to the levels measured, including wood smoke, motor vehicles, vegetation and the refinery. Evidence of each of these sources was observed in the data. There were some short term spikes in concentration of acetone, methanol and NO_x that may be attributable to refinery sources however the concentration of acetone and methanol measured during these spikes was low.

Appendices

Appendix 1: Example DEC community observation and canister sampling logbook

**Wagerup Community
Air Sampling Program**



**Canister
Log Sheet**

**Department of
Environment and Conservation**
Air Quality Management Branch

Postal Address: Locked Bag 104 Bentley Delivery Centre, WA 6008
Phone: (08) 9 333 7459
Facsimile: (08) 9333 7450
email: airquality@dec.wa.gov.au

Please complete this canister log sheet when a sample is taken and place it together with the Silco canister in the box provided.

Operators Name _____ (optional)
 Operators Contact Phone Number _____ (optional)
 Date _____
 Event Start Time _____ End Time _____
 Canister Sampling Time _____
 Location _____
 Canister serial number: # _____
 Canister pressure reading before taking sample _____ psi
 Do you want a replacement canister? Yes No

Intensity of the event (please circle one number - see chart on the bottom of page 3)

<input type="checkbox"/> Health Effected	0	1	2	3	4	5	6
--	---	---	---	---	---	---	---

Details (optional): _____

Odour _____
 Details (optional): _____

Visual _____
 Details (optional): _____

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Page 2 of 4 Pages

Appendix 2: VOCs measured by the CSIRO PTRMS on 27 August 2006

As part of the findings from the Wagerup 2006 study, DEC identified 27 August 2006 as being a day with significant refinery impacts on the surrounding area. Multiple community complaints were received across a broad area of Yarloop. Descriptions of the event included: '*worst smell that has been detected in a long time*', '*rated the odour as being 6/6*', and '*worst pollution event for years*'. Most complaints occurred between 9am and 10am. From 9am onwards, refinery odours were detected across a wide area to the south of the refinery as the layer of emissions was mixed to ground level in post-stable conditions with shallow convective mixing. Further information is available in the report 'Winter 2006 Study: Intensive Air Quality Investigations at Wagerup, DEC 2008.'

As part of the Wagerup 2006 air quality measurements, CSIRO was contracted by Alcoa to undertake an air quality monitoring study using PTRMS. The CSIRO PTRMS was located at Boundary Road, south of the Wagerup refinery and measurements were undertaken from 10 August to 7 October 2006. The results of the CSIRO study are available in the report 'A Study of VOCs during Winter 2006 at Wagerup, Western Australia, CSIRO 2008.' The PTRMS data obtained as part of the 2006 CSIRO PTRMS study was provided to DEC by Alcoa in October 2008. Figure 1 below shows VOCs corresponding to a mass to charge ratio of m/z 33 (methanol), m/z 59 (acetone) and m/z 45 (acetaldehyde and other compounds) detected by the CSIRO PTRMS on 27 August 2006. The time period in which most community complaints were received is circled on the graph (9am to 10 am).

The CSIRO PTRMS measured zero air for 30 minutes commencing at each of the following times all sampling days during the study period: 00:45 h, 04:45 h, 08:45 h, 12:45 h, 16:45h, and 20:45 h. The CSIRO PTRMS was therefore not measuring ambient air at the above times.

It is evident in Figure 1 that the concentration of VOCs corresponding to masses (i.e. compounds with a mass to charge ratio m/z of 33 and 59) detected by the CSIRO PTRMS on 27 August 2006 appears to significantly increase (4–6ppb above background levels) at the time in which most community complaints were received. There is a gap in the ambient measurements from 8:45am to 9:15am due to the PTRMS measuring zero air at this time, however the acetone and methanol concentration begins to increase before the zero air sequence starts at 8:45am and a peak in concentration is evident at 9:24am after the completion of the zero air sequence. This increase in acetone and methanol concentration detected by the CSIRO PTRMS on the 27 August 2006 corresponding with the time of community complaints is consistent with the 2009 DEC PTRMS results obtained by the at times when odour complaints were received by the community (e.g. 3 June and 12 of June 2009). This provides further evidence that methanol and acetone detected by PTRMS, in combination with other air quality measurements or community reports of odour may be used as indicators of the refinery plume.

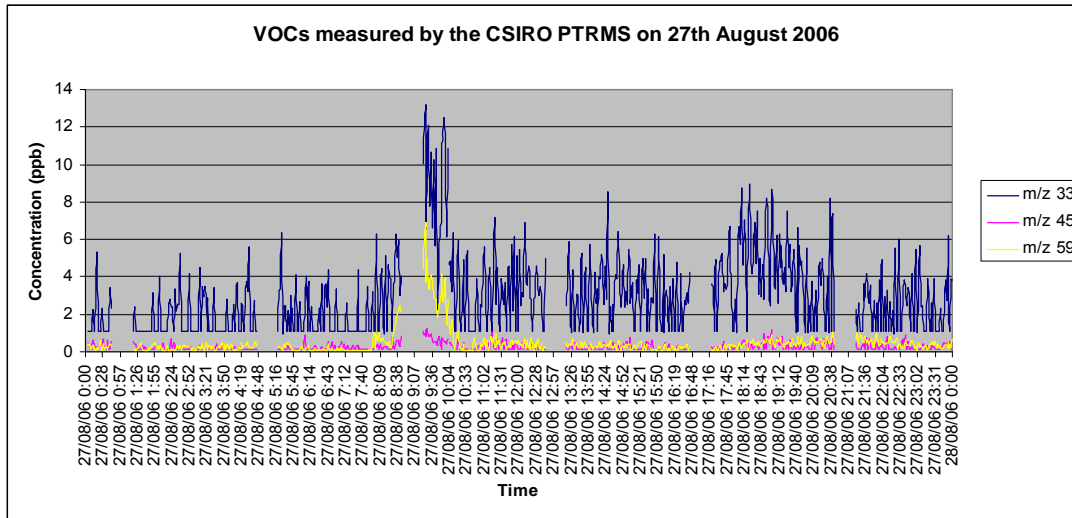


Figure 1 VOCs measured by the CSIRO PTRMS on 27 August 2006 as part of the Wagerup 2006 air quality measurements

Appendix 3: VOCs detected in canister samples analysed via USEPA method TO-15 and ambient air quality guidelines

Compound	Guideline, ESL or NEPM monitoring investigation level ppb	Averaging period	Jurisdiction
Hexane	1,500	1 hour (Short term ESL)	TCEQ
Benzene	3	Annual average	NEPC
Cyclohexane	1,000	1 hour (Short term ESL)	TCEQ
2,2,4-Trimethylpentane	750	1 hour (Short term ESL)	TCEQ
Heptane	850	1 hour (Short term ESL)	TCEQ
Toluene	1,000	24 hours	NEPC
Ethylbenzene	5070	Annual average	WHO
m,p-Xylene	250 (xylenes)*	24 hours	NEPC
o-Xylene	250 (xylenes)*	24 hours	NEPC
1,2,4-Trimethylbenzene	45	24 hours	OAQC
Acetone	2500	1 hour (Short term ESL)	TCEQ
Formaldehyde	40	24 hours	NEPC
Acetaldehyde	275	30 minutes	OAQC
Ethanol	-	-	-
Methanol	-	-	-

* NEPM Monitoring Investigation Level is for m, p and o-xylene

When comparing the guideline values in Appendix 3 to the results from the canisters analysed via USEPA method TO-15, it must be taken into account that the results provided in this study have been compiled using different averaging periods. If you wish to compare the data with the relevant guidelines, the averaging period for the guideline used must be obtained using the same averaging period.

NEPC – National Environment Protection Council
 NEPM – National Environment Protection measure
 MIL – Monitoring Investigation Level
 WHO – World Health Organisation

TCEQ - Texas Commission on Environmental Quality
 ESL – TCEQ Effects Screening Level
 OAQC – Ontario Ministry of the Environment Ambient Air Quality Criteria

TCEQ ESLs are not ambient air standards, however if predicted or measured airborne levels of a constituent do not exceed the screening level, adverse health or welfare would not be expected to result. Short Term ESLs indicate a one hour averaging period.

MILs indicate the concentration of an Air Toxic which if exceeded requires an appropriate form of further investigation and evaluation. Note: The monitoring investigation level values are levels of air pollution below which lifetime exposure, or exposure for a given averaging time, does not constitute a significant health risk. If these limits are exceeded in the short-term it does not mean that adverse health effects automatically occur.

Appendix 4: List of VOCs analysed for in method USEPA method TO-15, USEPA method TO-11A and USEPA method TO-17

Table 1. USEPA method TO-15 compound list (continued over page)

Analyte	MRL	Analyte	MRL
Propene	0.5	1,4-Dioxane	0.5
Dichlorodifluoromethane	0.5	Bromodichloromethane	0.5
Chloromethane	0.5	cis-1,3-Dichloropropene	0.5
Dichlorotetrafluoroethane	0.5	4-Methyl-2-pentanone	0.5
Vinyl chloride	0.5	trans-1,3-Dichloropropene	0.5
1,3-Butadiene	0.5	Toluene	0.5
Bromomethane	0.5	1,1,2-Trichloroethane	0.5
Chloroethane	0.5	2-Hexanone	0.5
Bromoethene	0.5	Dibromochloromethane	0.5
Trichlorofluoromethane	0.5	Tetrachloroethene	0.5
Acetone	2.0	1,2-Dibromoethane	0.5
Isopropyl Alcohol	2.0	Chlorobenzene	0.5
1,1-Dichloroethene	0.5	Ethylbenzene	0.5
1,1,2-Trichloro-1,2,2-Trifluoroethane	0.5	m,p-Xylenes	0.5
Allyl Chloride	0.5	o-Xylene	0.5
Methylene Chloride	1.0	Styrene	0.5
Carbon Disulfide	0.5	Bromoform	0.5
trans-1,2-Dichloroethene	0.5	1,1,2,2-Tetrachloroethane	0.5
Methyl tert-Butyl Ether	0.5	4-Ethyltoluene	0.5

Analyte	MRL	Analyte	MRL
Vinyl Acetate	0.5	1,3,5-Trimethylbenzene	0.5
1,1-Dichloroethane	0.5	1,2,4-Trimethylbenzene	0.5
2-Butanone	2.0	1,3-Dichlorobenzene	0.5
Hexane	0.5	Benzyl Chloride	0.5
cis-1,2-Dichloroethene	0.5	1,4-Dichlorobenzene	0.5
Ethyl Acetate	0.5	1,2-Dichlorobenzene	0.5
Chloroform	0.5	1,2,4-Trichlorobenzene	0.5
Tetrahydrofuran	0.5	Hexachlorobutadiene	0.5
1,1,1-Trichloroethane	0.5	Formaldehyde	2.0
1,2-Dichloroethane	0.5	Acetaldehyde	2.0
Benzene	0.5	Propanal	2.0
Carbon Tetrachloride	0.5	Methanol	2.0
Cyclohexane	0.5	Ethanol	1.0
2,2,4-Trimethylpentane	0.5	Acrolein	1.0
Heptane	0.5	Acetonitrile	1.0
Trichloroethene	0.5	Isoprene	1.0
1,2-Dichloropropane	0.5	Crotonaldehyde	1.0

Table 2

USEPA TO-11A compound list

Analyte	<u>PQL (ppb)</u>
Formaldehyde	0.23
Acetaldehyde	0.15
Acetone & acrolein	0.12
Propanal	0.12
2-butanone	0.09
Iso-butanal	0.09
Benzaldehyde	0.06
2-Pentanone	0.08
n-Pentanal	0.08
p-Tolualdehyde	0.06
2-Hexanone	0.07
Hexanal	0.07

Table 3

USEPA TO-17 compound list

Analyte	
Acetate, 2-ethoxyethyl-	Heptane
Acetate, 2-methoxyethyl-	Hexan-1-ol, 2-ethyl-
Benzene	Hexane
Benzene, 1,2,4-trimethyle-	Isopropyl acetate
Benzene, 1,4-dichloro-	Limonene
Butylacetate	Meth-1-oxy, 2-propanol-
Decane	Methyl tert-butylether
Disulfide, dimethyl-	Nonane
Ethane, 1,1,1-trichloro-	Octane
Ethanol, 2-butoxy-	Pinene, à-
Ethanol, 2-ethoxy-	Styrene
Ethanol, 2-methoxy-	Toluene
Ethene, tetrachloro-	Undecane
Ethyl tert-butylether	Xylene, m- & p
Ethylene, trichloro-	Xylene, o-

Glossary of terms and abbreviations

Adsorbent tubes	Adsorbent tubes are commonly used collection media for sampling of gases in air. Adsorbent tubes are usually made of glass or metal and contain various types of adsorbent material. Adsorbent tubes used in this study include DNPH and Tenax tubes.
Aerodynamic diameter	Also known as aerodynamic equivalent diameter (AED) is the diameter of a sphere of unit density (1g per cm ³) which has the same settling velocity in the same gas as the particle being measured. Particles with the same AED are dynamically identical.
Aerosol	A suspension of solid and liquid particles in air.
Air toxic	A pollutant selected for assessment and listed in Schedule 1 of the National Environment Protection (Air Toxics) Measure.
amu	Atomic mass unit
Back trajectory	A trajectory is the path of a parcel of air takes as it responds to changes in winds at different locations and times, ignoring the complexity of dispersion processes. A back trajectory indicates the recent history of a parcel of air before a given time.
Biomass burning	Burning of vegetation (e.g. from wildfires, domestic wood heaters and other sources).
Canisters	Specially prepared air sampling canisters with a non reactive lining to allow the capture of VOCs for subsequent analysis at a laboratory.
CO	Carbon monoxide
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DEC	Western Australian Department of Environment and Conservation

DNPH	2,4-Dinitrophenylhydrazine: a sorbent used for sampling of carbonyl compounds in air.
ESL	Effects Screening Level— ESLs are not ambient air standards, however if predicted or measured airborne levels of a compound do not exceed the screening level, adverse health or welfare would not be expected to result.
HiVol	High Volume Air Sampler: A device used to measure airborne particle matter.
IOP	Intensive Observation Period
Mass	The term mass has been used in this report to represent the protonated mass of the compound (ion) detected by the PTRMS in atomic mass units (amu).
MIL	Monitoring Investigation Level—The concentration of an Air Toxic which if exceeded requires an appropriate form of further investigation and evaluation.
MRL	Method Reporting Limit is the lowest amount of a substance that can be differentiated from the absence of that substance.
m/z	Mass to charge ratio
NEPC	National Environment Protection Council
NEPM	National Environment Protection Measure
NOx	Oxides of nitrogen
OAQC	Ontario Ministry of the Environment Ambient Air Quality Criteria
Odour threshold	The lowest concentration at which an odour is detectable by 50 per cent of the population.

PM _{2.5}	Particle matter with an equivalent aerodynamic diameter of 2.5 micrometres or less.
PM ₁₀	Particle matter with an equivalent Aerodynamic diameter of 10 micrometres or less.
ppb	Parts per billion (by volume)
ppm	Parts per million (by volume)
PTRMS	Proton Transfer Reaction Mass Spectrometer: an instrument used to measure volatile organic compounds in air.
PQL	Practical Quantitation Limit is the minimum concentration of a substance that can be measured with a high degree of confidence that the substance is present at or above that concentration.
Relative concentration	The concentration attributed to a mass number calculated from the PTRMS software
SO ₂	Sulfur dioxide
TCEQ	Texas Commission on Environmental Quality
Tenax TA	A sorbent used for sampling of VOCs in air.
TEOM	Tapered Element Oscillating Microbalance. An instrument for measuring the mass concentration of aerosol in air.
TO-11A	US EPA Compendium Method TO-11A. Determination of formaldehyde in ambient air using adsorbent cartridge followed by High Performance Liquid Chromatography (HPLC)
TO-15	US EPA Compendium Method TO-15 Determination of Volatile Organic Compounds (VOCs) in air collected In

	pecially prepared canisters and analysed by Gas Chromatography/ Mass Spectrometry (GC/MS)
TO-17	US EPA Compendium Method TO-17. Determination of Volatile Organic Compounds in ambient air using active sampling onto sorbent tubes
TSP	Total Suspended Particles: A mixture airborne solid and liquid particles (aerosol) having particle sizes from below 0.01 to 100 µm and larger.
µg/m ³	Micrograms per cubic metre: a unit for the concentration of a gas or particle matter in the atmosphere. (mass per unit volume of air).
US EPA	United States Environmental Protection Agency (http://www.epa.gov)
UKEA	United Kingdom Environment Agency
VOC	Volatile Organic Compounds (VOCs) are compounds with boiling points between 50 and 260 degrees that readily evaporate and remain in the air as gases at normal ambient temperatures. This group includes a very large group of compounds that have carbon atoms as a primary component.
Wet cement	Most common term used by the community to describe refinery odour.
WHO	World Health Organisation