CSIRO

A Study of VOCs during Winter 2006 at Wagerup, Western Australia

2 June 2008

A report to

Alcoa World Alumina Australia

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Please cite as:

Galbally, I.E., Lawson, S.J., Hibberd, M.F., Bentley, S.T. Cheng, M., Weeks, I.A., Gillett, R.W., Selleck, P.W. and Dunne, E. (2008) *A Study of VOCs during Winter 2006 at Wagerup, Western Australia*. A report to Alcoa World Alumina Australia, CSIRO Marine and Atmospheric Research, Aspendale Australia.

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CONTENTS

EXECUTIVE SUMMARY

Background

This Study continues the work carried out by CSIRO for Alcoa World Alumina Australia to better understand air quality in the region around the Wagerup Alumina Refinery. In 2004, CSIRO was commissioned by Alcoa to produce the Wagerup Air Quality Review (CSIRO, 2004), to facilitate a common understanding of the current air quality information and knowledge concerning Wagerup and the surrounding area. As part of this Review, 18 Recommendations concerning further air quality studies in the Wagerup region were presented.

At the time of the review, CSIRO acknowledged that some of the recommended studies were difficult and at the forefront of current air quality measurement technology. Subsequently, at Alcoa's request, CSIRO Marine and Atmospheric Research conducted a Pilot Study to determine if the new technology, Proton Transfer Reaction Mass Spectrometry (PTR-MS) would provide the capability to detect and measure a broad range of volatile organic compounds (VOCs) on an essentially continuous basis at very low concentrations as would be required for such more detailed air quality studies. The Pilot Study was directed toward aspects of Recommendations 14 and 15 of the Review:

Recommendation 14: In future studies the suite of measurements should include respirable aerosol and its composition, those simple organic compounds that are or can be emitted by the refinery that have not been measured in previous ambient sampling (including polar compounds) and supporting measurements such as for chemical fingerprints of sources.

Recommendation 15: A key issue for Wagerup air quality studies is to measure the key pollutants with a response time of a few minutes to determine what pollutants, at what concentrations are contained in the air associated with short-term high concentration air quality events, and what are the sources of these events and what processes control when they occur in the surrounding district.

The Pilot Study (Galbally et al. 2006) successfully demonstrated the capability of PTRMS for the task of continuously monitoring of VOCs at very low concentrations in air. In addition, the Pilot Study demonstrated the technical capability to monitor the chemical characteristics of the air using several "on-line" instruments capable of collecting data at high time resolution.

This Winter Study was undertaken during winter, the time when community complaints regarding air quality have been most frequent. The Study monitoring location is between the Refinery and the town of Yarloop where many of the complaints have originated. This Study was commissioned as part of Alcoa's Environmental Review and Management Program, ERMP, for the Wagerup Unit 3 Expansion Project.

Objectives of the Winter 2006 Study

The objectives of the Winter Study were to identify substances above background (based on mass number) and to identify their most likely sources, both natural and man made, in the Wagerup area, based on measurements at a location south of the Wagerup Refinery. Measurements were made over 8 weeks in Winter 2006 using the PTR-MS and ancillary equipment.

This report presents an account of the work undertaken, a presentation of the data and an initial scrutiny of the data, suitable for a technical audience. The VOC concentration data from the Study have already been supplied to Alcoa.

Field Study

Measurements were made of volatile organic compounds, VOCs, by the PTR-MS and two independent compound specific VOC methods, along with other supporting air quality parameters, for 60 days between 10 August and 7 October 2006 at Wagerup, Western Australia. The Study site was located just north of Boundary Road and approximately 2km south of the main Wagerup Refinery 100 m stack. This site was chosen because it is roughly mid-way between the Refinery and Yarloop in a direct line, is far enough from the Refinery to be influenced by plume “grounding” from the tall stack, and close enough to be influenced by the lower level sources. In all, during this Study, 60 days of PTR-MS measurements were obtained; providing more than 9 million concentration measurements. Data processing techniques were developed to meet the specific needs of the project, namely, to interpret this large data set. During the Winter Study the Refinery was operating with a bauxite throughput typical of the whole year. The Refinery Liquor Burner was off line for most of the Study period. During this time a new Regenerative Thermal Oxidiser was being installed and commissioned to reduce the VOC emissions from the Liquor Burner. Consequently, any particular chemical characteristics of the Liquor Burner emissions will be diminished or absent in this data set.

Identification of Masses and Compounds

The mass spectrometer in the PTR-MS identifies chemical constituents by the mass to charge ratio of singly charged ions or that of their fragment or hydrated ions. In PTR-MS, only the masses of product ions are determined, which is a valuable but not unique indicator of the identity of the possible trace gases present. Likely candidate compounds must be assigned to detected masses. A total of 24 masses were detected at measurable concentrations in the PTR-MS data from Boundary Rd. Two independent techniques (DNPH cartridges and adsorbent tubes) for measuring specific VOCs in ambient air were compared against the PTR-MS measurements. Consequently, single candidate compounds were identified for 11 of the 24 protonated masses. The masses and their associated compounds are 33 (methanol), 42 (acetonitrile), 45 (acetaldehyde), 49 (methanethiol), 59 (acetone), 63 (dimethyl sulphide), 69 (isoprene), 73 (methyl ethyl ketone), 79 (benzene), 87 (2,3-butanedione), and 93 (toluene). The other 13 masses have been associated with multiple possible compounds. In addition to the 24 masses identified in measurable concentrations, there was also the detection of mass 31 by the

PTR-MS, which is indicative of formaldehyde, but the PTR-MS response to formaldehyde is widely recognized to be so poor, that the formaldehyde concentrations used in this Winter Study are those measured by the independent DNPH method. All VOCs identified by the two independent techniques were also observed by the PTR-MS.

There are 191 other masses which were not present in detectable concentrations in the data set from 60 days of monitoring. These masses correspond to a large number of chemical compounds that can be detected by the PTR-MS, and some by the independent techniques, but were not detected in this Winter Study in air from the Refinery nor from the surrounding region.

VOC Concentrations

The concentrations of VOCs in the ambient air at Wagerup were in the part per billion, ppb, to sub-ppb range. For 18 of the 24 masses detected by the PTR-MS, 99% of the concentrations were below 1 ppb. The median concentration of the Total VOCs (TVOC) in ambient air was 4.6 ppb. For the sum of the concentrations measured at the 24 masses detected by the PTR-MS, 99% of the concentrations were less than 21 ppb. Considering the whole data set of both PTR-MS and Carbonyl Samples, Mass 33, methanol, makes up 55% of the concentration of TVOC. Variations in mass 33 have a major influence on variations in TVOC. Formaldehyde contributes 9%, acetone 6.5%, and acetaldehyde 2.8% of the TVOC concentration. The median concentrations of the sum of the VOCs measured by the PTR-MS in this Winter Study are higher than those in the summer Pilot Study, but the peak concentrations in winter are around half of those observed during the summer Pilot Study. This difference comes about in part because a bushfire plume with high concentrations of several VOCs traversed the site on one occasion during the summer Study.

Comparison of the concentrations of VOCs observed at Wagerup with observations from other locations in Australia and overseas shows that the VOCs at Wagerup in this Winter Study are present in concentrations at the low end of what is measured in other rural environments. This is due to either the sources of these VOCs being less active at Wagerup in winter and /or the influence of oceanic air, which has extremely low concentrations of VOCs and is carried inland to Wagerup by westerly winds during wintertime.

Sources

All of the VOCs identified in this Winter Study have more than one possible source in the Wagerup region. The possible sources of these VOCs include industrial, domestic, biological, combustion and transport processes and production in the atmosphere from other organic compounds. Further, the analysis shows that the compounds and masses detected in this Winter Study occur in the air for all wind directions. When the hourly concentrations of the sum of the VOCs measured by the PTR-MS (PTR-MS - TVOC) are examined in relation to wind direction and the highest 10 to 20 concentrations (the top 1%) are examined there is no obvious preferential wind direction.

In the data from Boundary Rd it was possible (with a statistical technique) to identify (a) air from the Refinery direction whose CO_2:NO_x ratio lies in the range 1000 and 2500 consistent with Refinery plumes and (b) air from the South East to the West (Yarloop and surrounds) whose CO_2: NO_x ratio is in the range 0 – 1000 consistent with vehicle and residential emissions.

The analysis by wind direction provides evidence that a number of masses, mainly 59 (acetone), 45 (acetaldehyde), 33 (methanol) and 43 (multiple compounds) as well as NO_x have sources in the direction of the Refinery which is consistent with knowledge of Refinery emissions and Pilot Study results. The analysis by wind direction provides evidence that NO_x, CO_2 and mass 81 (fragment of monoterpenes) have sources that cause higher concentrations in directions other than that of the Refinery, which are consistent with the domestic, transport, vegetation and soil sources of these gases.

The daytime/night-time variation in trace gas concentrations can also provide some information about the sources. The diurnal (day-night) variation of CO_2 and mass 81 (fragmentation of monoterpenes) in the near surface air at Boundary Road shows behaviour consistent with known natural vegetation and soil sources of these gases and known boundary-layer processes. The diurnal variation of other gases, particularly acetone, acetaldehyde and methanol show broad daytime/nighttime differences that are understandable in terms of atmospheric mixing processes and sources including the Refinery. However acetone, acetaldehyde and methanol show concentrations in the early evening around 1900 to 2100 hours that are slightly elevated compared to the low levels observed at other times, and are currently unexplained.

From observations of vehicle numbers on the South Western Highway, atmospheric stability and the observed ratio of benzene to toluene concentrations (which has a distinct ratio for vehicle emissions compared to woodheater and agricultural burning), it is assessed that motor vehicle emissions make a minor but observable contribution to the TVOC concentrations at Boundary Rd during this Winter Study.

Odour

Two odour events were observed at Boundary Rd during this Winter Study by CSIRO staff. The odour events observed on the 18th of August and the 15th of September 2006 both occurred when air was coming to the Boundary Rd site from the direction of the Refinery and there were concurrent measurements of elevated concentrations of NO_x and acetone, known Refinery emissions. This is the first time that there has been an observation of a short-term odour at a point remote from the Refinery that is associated with the Refinery as determined by both wind direction and the chemical markers, NO_x and acetone, both known Refinery emissions. The only mass of the 24 masses detected from the PTR-MS measurements that appeared to vary in parallel with the odour variations on these two occasions was mass 59 (acetone). The TAPM modelled acetone concentrations, based on Refinery acetone emissions, for these odour events were within a factor of three in concentration of those measured with the PTR-MS.

The measured acetone concentrations were too low to be causing the odour, because they were below the odour detection threshold for acetone. It was not possible to identify the chemical(s) causing the odour. The possible reasons for this are:

- the PTR-MS does not respond to the odorous compound;
- the odorous compound can be smelled at concentrations lower than can be detected by the PTR-MS;
- the odorous compound has a molecular mass that corresponds with one of the identified PTR-MS masses and the contribution of the odorous compound to that mass has not yet been identified.

There is insufficient information to say which of these possibilities is the most likely.

In summary, the Winter Study has identified VOCs present in the air at Wagerup and identified their most likely sources in the Wagerup area, both natural and man made, based on measurements at a location south of the Wagerup Refinery made for 8 weeks between August and October 2006 using the PTR-MS and ancillary equipment.

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ACKNOWLEDGMENTS

We thank for their assistance with the project

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This work has been supported in part by the CSIRO Light Metals Flagship

GLOSSARY

Simple definitions of various technical terms are given here to assist the reader. If required, the reader should look to other sources for more formal and technical definitions.

ABL	Atmospheric Boundary Layer. The ABL is the lowest 100 to 3000 m of the atmosphere modified by the earth's surface. The ABL responds to surface forcings (i.e. heating, cooling, and roughness) with a time scale of about an hour or less, and its extent is deeper in the daytime and shallower in the nighttime. It is often turbulent and is capped by a temperature inversion (see definition below).
Aerosol	A suspension of fine solid, liquid or mixed-phase particles in air.
AGL	Height Above Ground Level
Ambient air quality	The prevailing quality of the air in a given area in terms of the types and amounts of various air pollutants present.
AQMS	Air Quality Monitoring System.
Background air	Background concentrations in this context refer to those concentrations observed in the air when the air is not under the direct influence of anthropogenic emissions. Background air contains concentrations of constituents that arise from natural sources, and from anthropogenic sources that are so distant that their contribution is already well mixed within the airmass by the time the air reaches the point of measurement.
Biomass Burning	Burning of vegetation in prescribed burns and wildfires
Carbonyls	The group of organic compounds that include the aldehydes and the ketones
CAS	The CAS Registry number is a unique substance identifier assigned by the American Chemical Society/Chemical Abstracts Service that is independent of any system of chemical nomenclature. CAS Registry numbers are internationally recognised. (http://www.cas.org/EO/regsys.html)

Chemical species	Chemical species is a common name for atoms, molecules, molecular fragments, free radicals and ions as entities being subjected to a chemical process or to a measurement.
Chemical transformation	Used in this review to describe the processes in the atmosphere where two or more chemical compounds react together producing new compounds.
CMAR	CSIRO Marine and Atmospheric Research (http://www.cmar.csiro.au).
CO	Carbon monoxide
Constitutional isomer	Compounds that have the same molecular formula but that differ in their connectivity (i.e. have their atoms connected in different ways).
Continuous monitoring	Ongoing, (unbroken in time except for standard instrument checks) measurements of the concentration of air pollutant(s) over a time which is typically any period between days and years. This monitoring is often undertaken to establish compliance with licence conditions.
CSIRO	Commonwealth Scientific and Industrial Research Organisation (http://www.csiro.au)
DEC	Department of Environment and Conservation (Western Australia) (http://www.dec.wa.gov.au)
Diffusion	In air pollution meteorology the words dispersion and diffusion are often used interchangeably. This is also the case in this report. However, strictly speaking the two words mean different things. Diffusion refers to dilution of pollutants by turbulent eddies in the atmosphere whose dimensions are smaller than that of a pollutant plume or a puff (see also Dispersion).
Dispersion	Dispersion refers to the movement or transport of pollutants horizontally or vertically by the wind field and their dilution by atmospheric turbulence. Dispersion includes both transport and diffusion of pollutants (see also Diffusion).
DNPH	2,4-Dinitrophenylhydrazine (used for trapping carbonyls)

DoE	Department of Environment (Western Australia), formerly the Department of Environmental Protection, now the Department of Environment and Conservation (http://www.dec.wa.gov.au)
Dwell time	The time taken by the mass spectrometer to measure the ion counts at a particular mass/charge ratio. In the PTR-MS this is the same as the time taken to make the concentration measurement for one mass. In this study the dwell time was typically 0.5 seconds.
Enhancement	This term is applied to the concentration of compounds during events and indicates the increase in concentration above background levels at some time during the event
Episodic monitoring	Measurements conducted for a limited period during particular conditions, such as when elevated pollutant levels are expected. It can be for a few hours, days or months (e.g. winter-time monitoring).
GASP	Global AnalySis and Prediction. A meteorological modelling system currently used by the Australian Bureau of Meteorology that can provide the large-scale (synoptic) meteorological input needed in the models TAPM and CALMET.
glc	Ground level concentration
h	Hour of the day
Indicative concentration	The concentration attributed to a mass number calculated from first principles for the PTR-MS
Inversion	An atmospheric layer in which potential temperature increases with altitude (e.g. Nocturnal Inversion). These layers are stable and resistant to vertical mixing and hence may restrict the vertical dispersion of pollutants. Properly described as a temperature inversion. The term is often used to refer to the bottom of an inversion layer, i.e. the lowest altitude at which the potential temperature starts increasing.
LOD	Limit Of Detection. The smallest concentration detectable by a measurement system as the concentration of the substance being

	measured approaches zero.
MDL	Minimum Detectable Limit. The lowest measured concentration in a sample that can be regarded as statistically significant.
Mass	In this report the term mass applies to the mass of the ion detected in the PTR-MS and measured in atomic mass units (amu). Multiple chemical species can contribute to the signal detected at any one mass.
mg	Milligram (1 mg = 10^{-3} gram = 0.001 gram). One thousandth of a gram
mg m^{-3}	Milligram per cubic metre. 1 mg m^{-3} = 1000 µg m^{-3}
NATA	National Association of Testing Authorities
n/a	Not applicable
n/r	Not recorded
ng	Nanogram (1 ng = 10^{-9} gram = 0.000000001 gram). One billionth of a gram
ng m^{-3}	Nanogram per cubic metre. 1 ng m^{-3} = 0.001 µg m^{-3}
NBL	Neutral Boundary Layer. A type of atmospheric boundary layer (ABL) that forms when winds are strong and/or when there is negligible heating or cooling of the ground (e.g. overcast conditions). The turbulence responsible for pollutant mixing under these conditions is generated by wind shear.
Nm^3	Normal cubic metres. Volume of a gas sample in cubic metres expressed at 0 degrees Celsius and 1.0 atmosphere (101.325 kilopascals).
NO	Nitric oxide
Nocturnal Inversion	A layer of stable air (see Inversion) of the order of 10m to several 100m depth adjacent to the earth's surface that can form at night over land due to infrared radiative cooling of the surface particularly under the

	meteorological conditions of a cloudless sky and light winds, and typically erodes quickly after sunrise.
NO_x	Oxides of nitrogen (commonly $NO_x = NO + NO_2$)
NO_2	Nitrogen dioxide
NPI	National Pollutant Inventory (see http://www.npi.gov.au/)
Obukhov length	A length scale for turbulence in the atmospheric boundary layer defined by the ratio of the buoyancy flux to the mechanical shearing stress within the air. The length has a zero value for neutral stability, a negative value for unstable conditions and a positive value for stable conditions.
Odour Intensity (I)	The relative perceived strength of an odour above its threshold, (see Odour threshold)
Odour Detection Threshold	The lowest odorant concentration at which an odour is detectable by (normally) 50% of the population. This concentration is defined as 1 Odour Unit (OU). Sometimes called Odour Threshold.
OU	Odour Unit. The odour units are dimensionless and are effectively "dilutions to odour threshold." An odour present at a concentration of 1 OU will be discerned as odourless by approximately half the population. Ten odour units represents a mixture, which if diluted by a factor of 10 will then have an odour detected by 50% of the respondents and so forth.
Odour Threshold	See Odour Detection Threshold
Potential Temperature	Potential temperature is a useful measure of the stability of the atmosphere. The potential temperature of a parcel of air at pressure P is the temperature that the parcel would acquire if the parcel of air is brought to a standard reference pressure P_0, usually 1013 hPa adiabatically, that is without heat being either added to or taken from the parcel of air. Potential temperature accounts for the changes in air density due to pressure changes. If the potential temperature increases with height, vertical motions are suppressed and the atmosphere is said to be stably stratified. If the potential temperature decreases with height, a

	rising parcel of air will continue to rise, generating convective motion and mixing the atmosphere; it is said to be unstable. If the potential temperature remains constant with increasing height, the atmosphere is said to be neutrally stratified. The potential temperature is usually denoted by θ and defined as $\theta = T\left(P_0/P\right)^{0.286}$ where *T* is the temperature in degrees Kelvin of the air at pressure *P* and P_0 is a standard reference pressure (usually 1013 hPa).
ppb	Parts per billion (by volume): 1 ppb = 1/1000 ppm.
ppm	Parts per million (by volume): a unit for the concentration of a gas in the atmosphere based on the mixing ratio approach. A concentration of 1 ppm is equivalent to a volume of 1 cubic metre of pure undiluted gas in 1 million cubic metres of air. The expression ppm (or ppb) is without dimensions. The ppm (or ppb) unit is useful because its value is unaffected by changes in temperature and pressure, and also because many sampling techniques are based on volume concentrations. Concentrations of gaseous compounds can be converted from mixing ratio units, e.g. ppm units (volumetric), to density units, e.g. mg m-3 (mass/volume), using the following formula: $C(\text{mg m}^{-3}) = \dfrac{273.15 \times M_w \times C(\text{ppm})}{22.4136 \times (273.15 + T)}$, where C is the concentration, M_w is the molecular weight of the gas, and T is the ambient temperature in degrees Celsius. At a temperature of 0 degrees Celsius, the conversion factors from 1 ppm to mg m-3 are: benzene (C6H6) 3.490; carbon monoxide (CO) 1.250; formaldehyde (HCHO) 1.340; nitrogen dioxide (NO2) 2.050; nitric oxide (NO) 1.340; ozone (O3) 2.140; sulfur dioxide (SO2) 2.860; toluene (C7H8) 4.113; xylene (C8H10) 4.740.
ppt	Parts per trillion (by volume): 1 ppt = 1/1000 ppb.
Primary air pollutant	Pollutant entering the atmosphere directly from a source. A primary air pollutant may react to form a secondary air pollutant (see definition

	below).
PTR-MS	Proton Transfer Reaction Mass Spectrometer: an instrument used to measure those volatile organic compounds and other chemical species that have a proton affinity greater than water
PTRMS-TVOC	The sum of the concentrations of the 24 masses measured by the PTR-MS found to have significant concentrations in the Wagerup Winter 2006 VOC Study. The PTRMS-TVOC concentration is calculated for each occasion where each of the individual masses are measured, including each PTR-MS 2 minute cycle.
Quantiles	The fraction (or percent) of points below the given value. That is, the 0.3 (or 30%) quantile is the point at which 30% percent of the data fall below and 70% fall above that value. Certain quantiles have special names. The 0.25-, 0.50-, and 0.75-quantiles are called the first, second and third quartiles. The 0.01-, 0.02-, 0.03, … , 0.98-, 0.99-quantiles are called the first, second, third, … , ninety-eighth, and ninety-ninth percentiles.
RDA	Residue Disposal Area – the area where red mud from bauxite refining is disposed.
Safe Sampling Volume (SSV)	This is a measure applied to adsorbent tubes. It is usually calculated by halving the measured retention volume (indirect method) or taking two-thirds of the breakthrough volume determined by sampling with two tubes in series (direct method), although these two approaches do not necessarily give identical results. The latter definition is used in this document.
SBL	Stable Boundary Layer. A type of atmospheric boundary layer (ABL) that develops during the night when the ground is substantially cooler than the air above it, thus forming a stable temperature gradient with height in the air that opposes vertical motions of air and resulting in little ambient turbulence.
sccm	Standard cubic centimetres (of gas) per minute
Secondary air pollutant	Secondary pollutants are not directly emitted from a process. Rather,

	secondary air pollutants are formed by physical processes and/or chemical reactions of primary pollutants in the surrounding air. Ozone and many aerosols are usually secondary air pollutants.
Sequencer	The adsorbent tube VOC (ATD-VOC) and Carbonyl Sequencer is an automatic air sampler for sampling of VOCs and Carbonyls using tubes and cartridges simultaneously.
SO_x	Sulfur oxides, the sum of SO_2 and SO_3
SO_2	Sulfur dioxide
SVOCs	Semi-Volatile Organic Compounds These organic compounds co-exist in the gas and liquid or solid phase in the atmosphere under ambient atmospheric conditions. (see also VOCs).
Subsidence Inversion	A temperature inversion that develops aloft as a result of air gradually sinking over a wide area and being warmed by adiabatic compression, usually associated with subtropical high pressure areas.
SUMMA	Stainless steel SUMMA™ canisters are specially treated relatively inert gas sampling canisters that are better suited to collect air samples which contain very low concentrations of air toxics than untreated metal canisters. SUMMA canisters are also sturdy and will handle rough transport.
TAPM	The Air Pollution Model. A prognostic meteorological and air pollution dispersion model developed by CSIRO Atmospheric Research (http://www.dar.csiro.au/tapm). The meteorological component of TAPM predicts the local-scale flow, such as sea breezes and terrain-induced circulations, given the larger-scale synoptic meteorology. The air pollution component uses the model-predicted three-dimensional meteorology and turbulence, and consists of a set of chemical species conservation equations and an optional particle trajectory module.
Temperature inversion	see Inversion
TEOM	Tapered Element Oscillating Microbalance. A device for measuring the

	mass concentration of aerosol in the air. Aerosol is collected on a Teflon coated borosilicate glass filter vibrating on a hollow tapered element. As the mass collected on the vibrating filter increases the frequency decreases, and is measured and recorded by an electronic circuit. The mass concentration is determined from the relationship between particulate mass and the measured vibration frequency and reported in µg m^{-3} after correction for temperature and pressure. Size selective inlets are used to measure PM10, PM2.5 etc.
TVOC	Total VOCs. The sum of the concentrations of the 24 masses measured by the PTR-MS found to have significant concentrations in the Wagerup Winter 2006 VOC Study plus formaldehyde which is not taken from measurements by the PTR-MS but is measured as 8-hour integrated concentrations by DNPH method. The TVOC can only be calculated for 8-hour intervals.
TO-11A	US EPA Compendium Method TO-11A. Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]. (http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf)
TO-14A	US EPA Compendium Method TO-14A. Determination Of Volatile Organic Compounds (VOCs) In Ambient Air Using Specially Prepared Canisters With Subsequent Analysis By Gas Chromatography. (http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-14ar.pdf)
US EPA	United States Environmental Protection Agency (http://www.epa.gov)
VOCs	Volatile Organic Compounds. These organic compounds have relatively low boiling points and, therefore, readily evaporate into the atmosphere under conditions of normal temperature and pressure.
WA	Western Australia
WA EPA	West Australian Environment Protection Authority (http://www.epa.wa.gov.au).

µg	Microgram (1 µg = 10^{-6} gram = 0.000001 gram). One millionth of a gram
µm	Micrometre (1 µm = 10^{-6} metre = 0.000001 metre). One millionth of a metre
µg m^{-3}	Microgram per cubic metre: a unit for the concentration of a gas or particulate matter in the atmosphere based on the density approach (mass per unit volume of air). Concentrations of gaseous compounds can be converted from density units, e.g. mg m^{-3} (mass/volume), to mixing ratio units, e.g. ppm units (volumetric), using the following formula: $C(\text{ppm}) = \frac{22.4136 \times (273.15 + T) \times C(mg/m^3)}{273.15 \times M_w}$, where C is the concentration, M_w is the molecular weight of the gas, and T is the ambient temperature in degrees Celsius. At a temperature of 0 degrees Celsius, the conversion factors from 1 mg m^{-3} to ppm are: benzene (C_6H_6) 0.287; carbon monoxide (CO) 0.800; formaldehyde (HCHO) 0.746; nitrogen dioxide (NO_2) 0.488; nitric oxide (NO) 0.746; ozone (O_3) 0.467; sulfur dioxide (SO_2) 0.350; toluene (C_7H_8) 0.243; xylene (C_8H_{10}) 0.211.

1 INTRODUCTION

1.1 Background

The Wagerup bauxite Refinery of Alcoa World Alumina Australia in Western Australia extracts alumina from bauxite and has an output of 2.4 million tonnes of alumina per annum. The site is about 130 km south of Perth, 25 km inland from the coast, in the western foothills of the north-south Darling escarpment, and operates round-the-clock. There are local communities near the Refinery. Yarloop is a small town 15° west of south and 3 km away from the Refinery. Hamel and Waroona are two small towns approximately 5 km and 8 km north of the Refinery. See Figure 1.

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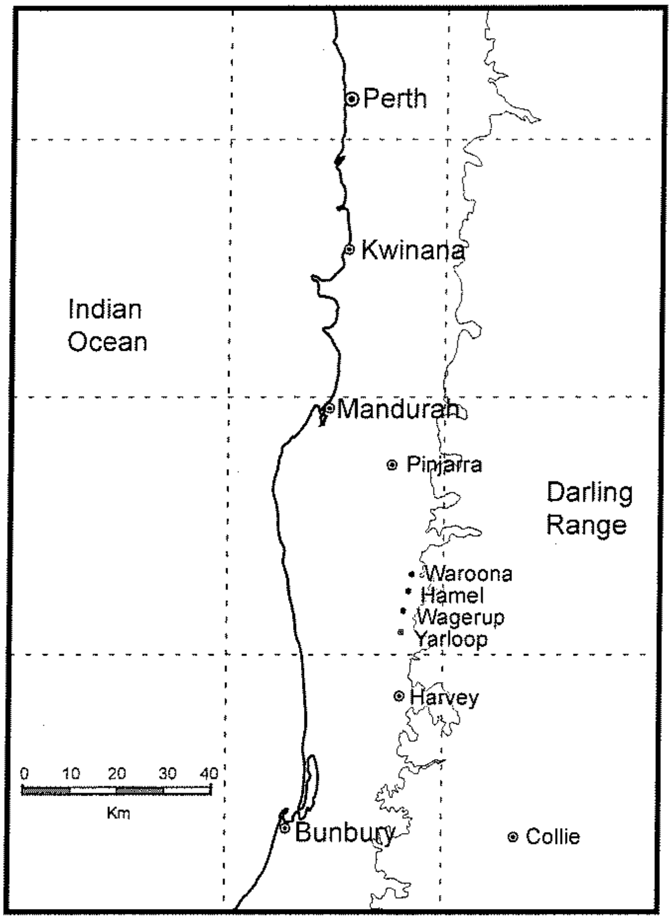

Figure 1. A schematic of the location of Wagerup which shows nearby towns and cities, the Indian Ocean and the edge of the escarpment and the Darling Range.

In 2004, CSIRO was commissioned by Alcoa to produce the Wagerup Air Quality Review, to facilitate a common understanding of the current air quality information and knowledge concerning Wagerup and the surrounding area. The Review presented 18 Recommendations concerning further air quality studies in the Wagerup region. Two of these Recommendations are:

Recommendation 14: In future studies the suite of measurements should include respirable aerosol and its composition, those simple organic compounds that are or can be emitted by the refinery that have not been measured in previous ambient sampling (including polar compounds) and supporting measurements such as for chemical fingerprints of sources.

Recommendation 15: A key issue for Wagerup air quality studies is to measure the key pollutants with a response time of a few minutes to determine what pollutants, at what concentrations are contained in the air associated with short-term high concentration air quality events, and what are the sources of these events and what processes control when they occur in the surrounding district.

At the time of the review, CSIRO acknowledged that some of the suggested studies, including those which might satisfy the above recommendations, were difficult and at the forefront of current air quality measurement technology. Subsequently, at Alcoa’s request, CSIRO Marine and Atmospheric Research conducted a Pilot Study at Wagerup to determine if the new technology, Proton Transfer Reaction Mass Spectrometry (PTR-MS) could provide the capability to detect and measure a broad range of volatile organic compounds (VOCs) on an essentially continuous basis at low concentrations as would be required for such more detailed air quality studies. The VOC emissions from alumina refining were incompletely characterized at the time of the Wagerup Air Quality Review. Hence there was interest in utilizing the broad detection capabilities of the PTR-MS for ambient measurements to ensure that no other major VOC (including polar compounds) was passing undetected. The Pilot Study (Galbally et al. 2006), successfully demonstrated the capability of PTRMS for the task of continuous monitoring VOCs at low concentrations in air. In addition, the Pilot Study demonstrated the technical capability to monitor the chemical characteristics of the air using several “on-line” instruments capable of collecting data at very high time resolution.

The Winter Study reported here follows from the technical evaluation Pilot Study and was commissioned as part of Alcoa’s Environmental Review and Management Plan (ERMP) for the Wagerup Unit 3 Expansion Project. The project addresses, in part, Recommendations 14 and 15, (above) with the provision that the focus is on “simple organic compounds” and not “respirable aerosol and its composition”. This Winter Study incorporates the use of other chemical techniques to measure VOCs (Appendix D) as well as the PTR-MS, and is intended to produce data to input into the ERMP, rather than being a technical evaluation of the PTR-MS, which was the purpose of the previous Study.

The combination of measurements of VOCs with (a) the continuous, sensitive and extensive PTR-MS technique and (b) independent techniques that identify specific VOCs, provided the best available technology in Australia for the continuous determination of the range and concentration of volatile organic pollutants occurring over an extended period of time in the atmosphere at Wagerup.

This Winter Study involves work in two rapidly developing areas of science. The PTR-MS is relatively new technology about which more is being learnt (de Gouw and Warnecke 2007) and atmospheric organic chemistry is an area where there are still considerable unknowns (Goldstein and Galbally 2007).

1.2 Objectives and Deliverables

The objective of the Winter Study was to use the PTR-MS at a location south of the Refinery, to identify substances above background (based on mass number) and to identify their most likely sources, both natural and man made, in the Wagerup area.

A list of the activities specified for the project are provided in Appendix A.

It was specified in the Study brief that the final report would include the following material:

1. A data set of hourly and peak two-minute concentrations of selected simple organic compounds, CO_2, CO, NO_x, $PM_{2.5}$ measurements and meteorological parameters from the measurements made.
2. Identification of between 15 and 25 mass numbers with concentrations above background.
3. Identification of the single most probable substance associated with each mass number, using integrated DNPH samples for carbonyl identification and adsorbent tubes for other VOC identification;
4. An analysis of the likely natural and man-made sources of the identified substances in the environment around Wagerup using:
    - NO_x/CO/CO_2 relationships to define the chemical signatures for known emission sources
    - Meteorology (wind speed and direction) and TAPM meteorological modelling
    - Previous CSIRO investigations

A report of no more than 50 pages is envisaged, accompanied by a CD with the data.

This report presents an account of the work undertaken, a presentation of the data and an initial scrutiny of the data, suitable for a technical audience. The data from the Study have already been supplied to Alcoa.

The experimental details of this Winter Study are presented in seven Appendices to this report

Appendix A	Work Carried Out Under the Proposal
Appendix B	The Air Quality Monitoring System and other Measurements
Appendix C	The PTR-MS
Appendix D	Other VOC Measurements
Appendix E	Concentrations and Identification of Observed Masses
Appendix F	Selected 8 hour Period During the Winter Study
Appendix G	Cooling Tower Bags

1.3 Winter Study Site

The location of the site for the PTR-MS and the associated measurements was off Boundary Rd, west of both the long term air quality monitoring site and the radiosonde launching site that are also on properties adjoining Boundary Rd. The Boundary Rd site was chosen because it is approximately half way and directly between the Refinery and the township of Yarloop (see below). The site is far enough from the Refinery to be subject to grounding of plumes from the tall stacks and close enough to the Refinery to be potentially influenced by the lower level sources. The AMG84 (Australian Map Grid) coordinates of the site are 397.820 km east and 6354.965 km north. Alternately the site location, as determined by GPS, is 32° 56.223' South, 115° 54.515' East, 45 m elevation (Ian Yull, Alcoa, personal communication). The bearing of the 100 m multiflue stack from the monitoring site was 10 degrees east of North and the range was 2066m. The site was about 40m north and 160 m east of the intersection of Boundary Road and South Western Highway

A photo of the site is shown in Figure 2 and an aerial photograph of the site and surrounding features in Figure 3.

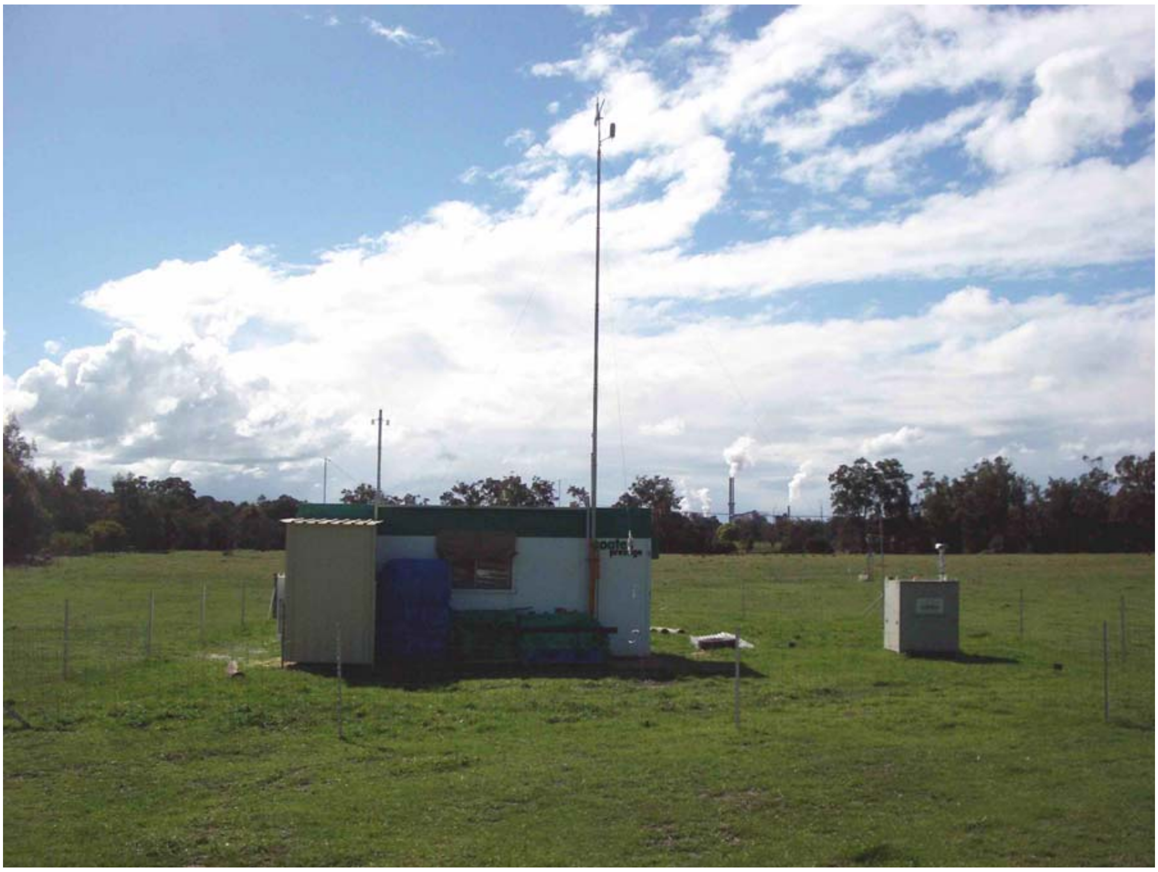

Figure 2. The site of the Wagerup Winter Study at Boundary Rd looking northwards towards the Refinery. The PTR-MS was housed in the demountable building shown in the foreground.

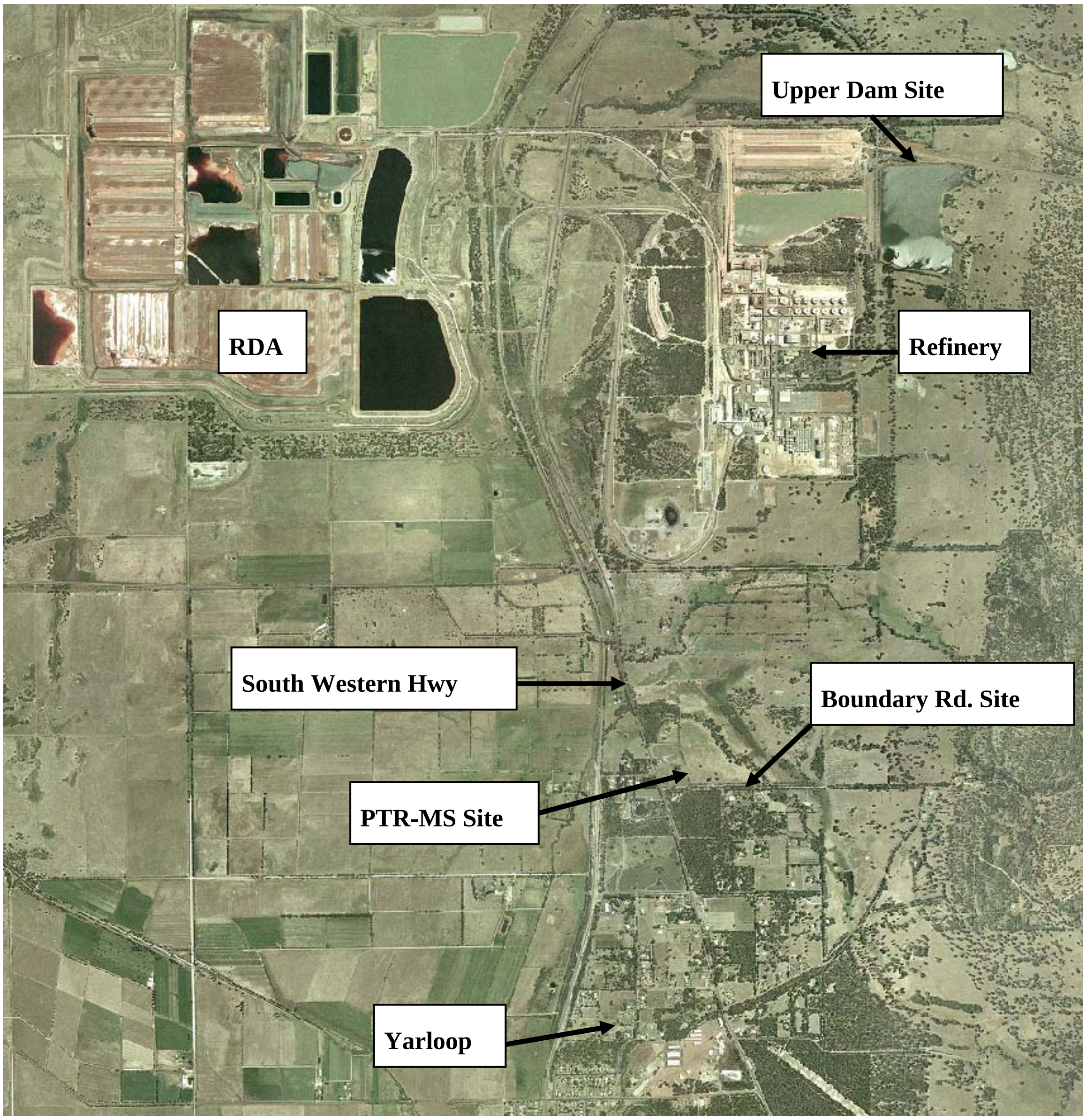

Figure 3. The Wagerup area showing the Alcoa Wagerup Refinery and the Boundary Rd site where the PTR-MS was located during the Wagerup Winter Study. The photograph is orientated so that the top is north.

1.4 Measurement Summary

The details of the measurements undertaken during this Winter Study are presented in Appendix B, C and D. The following is a brief summary of these and other measurements used in this report that were made around Wagerup during the Winter Study.

At the Boundary Road site the following measurements were carried out

CSIRO CMAR (Aspendale)

- PTR-MS scanning masses 21-231 every 2 minutes
- Carbonyls by DNPH cartridges and HPLC analysis (8 hour averages)
- VOCs by adsorbent tubes and GC-FID-MS analysis (8 hour averages)

CSIRO CMAR (Black Mountain)

- 2.8m Wind Speed and Direction, Temperature, Relative Humidity, Net Radiation, Ground Heat Flux
- Computed- Sensible Heat Flux, Latent Heat Flux, Friction Velocity, Monin-Obhukov Length.

Ecotech

- 10 m Wind Speed and Direction
- Temperature, Relative Humidity (RH)
- Carbon Monoxide (CO), Oxides of Nitrogen (NO_x), Carbon Dioxide (CO_2), Particulate matter with diameter 2.5 micrometers or less (PM2.5)

DEC

- 30 to 400 m wind speed and direction by acoustic sounding
- Ceilometer (cloud height).

At the Bancell Road site (approximately in line between the Boundary Rd site and the Refinery) the following measurements were carried out

Alcoa

- 10 m and 30 m Wind Speed and Direction
- Temperature, RH
- Solar Radiation

For details of the other meteorological sites see Air Assessments (2007).

2 THE VOLATILE ORGANIC COMPOUNDS OBSERVED IN THE AIR AT THE BOUNDARY ROAD SITE, WAGERUP

The full details of the work undertaken, the chemical analyses and the identification of chemical compounds observed in the air at Wagerup can be found in the seven appendices to this report. The reader unfamiliar with the nature of PTR-MS measurements is referred to Appendix C for background information. The details of the VOC PTR-MS measurements, the measurements of VOCs by two independent techniques (VOCs by adsorbent tubes described as AT-VOCs, and carbonyls, a class of VOCs, by DNPH cartridges) and the identification of the VOC composition of the PTR-MS masses are presented primarily in Appendices D and E. This section reports the key mass numbers (frequently abbreviated to masses) observed by the PTR-MS in the air at Boundary Road, the related compounds, their concentrations, their sources in the atmosphere and their concentrations observed elsewhere. The following Section 3 discusses detailed analyses including the contribution from the Refinery.

2.1 Observed compounds and their concentrations

There were 24 protonated masses detected in the air at Wagerup by the PTR-MS during this Study. Eleven of these have been identified with single candidate VOCs. The masses and their associated compounds are 33 (methanol), 42 (acetonitrile) 45 (acetaldehyde), 49 (methanethiol), 59 (acetone), 63 (dimethyl sulphide), 69 (isoprene), 73 (methyl ethyl ketone), 79 (benzene), 87 (2,3-butanedione), and 93 (toluene). The other 13 protonated masses have been associated with multiple VOCs.

There was also the detection of mass 31, formaldehyde by the PTR-MS, (as well as the 24 masses discussed above), but the PTR-MS response to formaldehyde is so poor (de Gouw and Warnecke, 2007), that the formaldehyde concentrations used in this Study are those measured by the independent DNPH method. The DNPH method is an 8-hour integrated method whereas the PTR-MS scans each mass every 2 minutes. Thus for 8-hour samples a total VOCs, TVOC, can be calculated using the 24 masses from the PTR-MS and formaldehyde from the DNPH method. In some cases there is need for shorter term integrated VOC measurements for the subsequent analyses and PTRMS-TVOC is used which is the sum of the concentrations of the 24 masses from the PTR-MS alone, omitting formaldehyde.

The reason for there being only 11 masses identified with single candidate compounds in this data set is that the concentrations of VOCs in the ambient air at Wagerup were low. For 18 of the 24 masses detected by the PTR-MS, 99% of the time concentrations were below 1 ppb. For many of the candidate compounds the concentrations in the air at Wagerup were below the detection limits of the two independent techniques (adsorbent tubes and DNPH cartridges) that were used to identify the compounds This is in spite of the sub-ppb limits of detection of VOCs by these two methods (Appendix D). Had there been significant concentrations of the candidate compounds present, the compounds would have been detected and identified by either the GC-MS-FID or DNPH-HPLC systems and thus would have moved from not measured to a measured status.

There were 12 VOCs quantitatively detected at Wagerup by the two independent techniques (adsorbent tubes and DNPH cartridges). These VOCs were formaldehyde, acetaldehyde, propanal, hexanal, acetone, methyl ethyl ketone, glyoxal, methylglyoxal, 2-methyl -2-propanol, 1-butanol, benzene and toluene. All these VOCs have protonated parent ions or protonated fragments that correspond with the 24 protonated masses detected by the PTR-MS (plus mass 31, formaldehyde), as described above.

As well as the quantitative detections, there were 13 VOCs that were qualitatively detected by the AT-VOC system at Wagerup. All these VOCs either directly or through their fragmentation products correspond to masses detected by the PTR-MS, as described above.

Thus there is consistency between the PTR-MS and the two independent techniques with regard to the identities of VOCs detected in the air at Wagerup. There are inconsistencies in the concentrations of the VOCs measured by the different techniques, and this is frequently observed in comparisons of instruments operating at low concentrations such as were observed at Wagerup.

Table 1 shows the average concentration of the masses/compounds and the percentages that each compound made up of the TVOC present for fifteen 8-hour periods of VOCs analysed by both PTR-MS and the two sets of independent chemical measurements (The data comes from 15 8-hour periods during the study chosen to represent the periods of highest and lowest 8-hour concentrations of VOCs in the PTR-MS data set. See Appendix E). Methanol is the dominant VOC with 56.9% of TVOC. Mass 43 (multiple compounds including isopropanol) contributes 10.1%, formaldehyde 8.0% and acetone 7.2%. The other 21 VOCs varied from 0.1% to 3.2%.

Table 1 also shows the average concentration of the masses/compounds and the percentages that each compound made up of the TVOC present for the ninety one 8-hour periods of VOCs analysed by both PTR-MS and the carbonyl measurements of formaldehyde. This set is the most extensive complete set of VOC measurements from this study at Wagerup. As would be expected, concentrations are generally lower in the complete data set, than in the 15 period set that was selected to include some of the peak concentrations. The percentage composition of the two sets are similar. Methanol is the dominant VOC with 55.1% of TVOC. Mass 43 (multiple compounds including isopropanol) contributes 9.4%, formaldehyde 9.2% and acetone 6.5%. The other 21 VOCs varied from 0.1% to 3.5%.

In several cases there is the listing of “multiple compounds” and “other compounds” in Table 1. The details of what these multiple compounds might be are provided in the section, Appendix E.4.

In Table 2, and in the subsequent analysis, the focus is on 15 masses/compounds that were present in measurements at Boundary Road during the Wagerup Winter Study. These compounds are (a) those compounds associated with the 12 PTR-MS masses that had highest average concentrations, (b) benzene and toluene, and (c) formaldehyde, (measured by DNPH). The 15 selected compounds cover 95.4% of the concentration of TVOC listed in Table 1. The average concentrations of masses/compounds for each mass detected by PTR-MS, and formaldehyde measured by DNPH, and the percentages of TVOC for each mass/compound for the 15 and 91 8-hour VOC periods during the Wagerup Winter Study (see text and Appendix F) Note the columns do not necessarily add up to 100% and the concentrations and percentages do not necessarily exactly correspond due to the rounding of the calculations that are done at higher precision.. The statistics of concentrations observed at Wagerup by the PTR-MS, and formaldehyde by DNPH, are presented in Table 2. The other 10 masses were not included in the analyses because their concentrations were very low and near their limits of detection.

2.1.1 VOCs not detected by PTR-MS

There are four reasons why a VOC may not be detected by the PTR-MS. These are presented in Appendix C and summarised below.

Some of the VOCs have proton affinities less than water and hence are not detected. These VOCs include the alkanes methane to butane and cyclohexane, some halogen substituted organics, carbonyl sulfide and carbon disulfide.

Formaldehyde has a proton affinity slightly greater than water, and experiences a back reaction in the drift tube and so is poorly detected by the PTR-MS under the conditions at which the PTR-MS was operated at Wagerup, and is measured by DNPH tubes.

The PTR-MS does not provide a sensitive detection (a real ambient measurement) at certain masses due to instrument design characteristics and internal interferences, as discussed in Appendix C.1

The PTR-MS, as it was operated at Wagerup, is relatively insensitive to ethanol and is completely unresponsive to oxalic acid. This behaviour is not fully understood and is probably associated with the fragmentation patterns of the protonated molecules.

However, there is consistency with regard to the VOCs detected in the air at Wagerup between the PTR-MS and the two independent techniques that were also used for measuring VOCs.

There are some VOCs that would be expected to be in the air at Wagerup and were not observed by these measurement techniques because the techniques are not sensitive to these compounds. These include ethane, propane, butanes and pentanes, some halogen substituted organics, carbonyl sulfide and carbon disulfide, ethanol and oxalic acid. The techniques used in this Study focused on “*those simple organic compounds that are or can be emitted by the refinery* *that have not been measured in previous ambient sampling (including polar compounds).*" Recommendation 14, Wagerup Air Quality Review (CSIRO 2004). With the exception of ethanol (for which the PTR-MS has a poor response) and oxalic acid (for which the PTR-MS has no response), this objective has been achieved.

Table 1. The average concentrations of masses/compounds for each mass detected by PTR-MS, and formaldehyde measured by DNPH, and the percentages of TVOC for each mass/compound for the 15 and 91 8-hour VOC periods during the Wagerup Winter Study (see text and Appendix F) Note the columns do not necessarily add up to 100% and the concentrations and percentages do not necessarily exactly correspond due to the rounding of the calculations that are done at higher precision.

Primary Protonated Mass	Candidate compound	15 periods Mean (ppbv)	15 periods Percentage of TVOC (%)	91 periods Mean (ppbv)	91 periods Percentage of TVOC (%)
33	Methanol	6.14	56.9	2.91	55.1
43	Multiple compounds including Isopropanol	1.09	10.1	0.50	9.4
n/a	Formaldehyde	0.86	8.0	0.48	9.2
59	Acetone	0.78	7.2	0.35	6.5
41	Multiple compounds?	0.35	3.2	0.19	3.5
45	Acetaldehyde	0.30	2.8	0.15	2.8
69	Isoprene	0.23	2.1	0.12	2.3
47	Formic Acid, Ethanol and possibly other compounds	0.16	1.5	0.10	1.9
61	Acetic acid and possibly other compounds	0.14	1.3	0.07	1.3
81	Monoterpenes and possibly other compounds	0.13	1.2	0.09	1.6
71	Multiple compounds?	0.11	1.0	0.04	0.8
93	Toluene	0.10	0.9	0.06	1.0
73	Methyl ethyl ketone	0.09	0.8	0.04	0.8
42	Acetonitrile	0.05	0.5	0.04	0.7
60	Trimethylamine & ^{13}C of mass 59 compound	0.05	0.5	0.02	0.4
87	2, 3-Butanedione	0.03	0.3	0.02	0.3
57	Multiple compounds?	0.03	0.3	0.02	0.3
75	Multiple compounds?	0.03	0.3	0.01	0.3
79	Benzene	0.02	0.2	0.01	0.2
117	Multiple compounds?	0.02	0.2	0.03	0.5
49	Methanethiol	0.02	0.2	0.01	0.3
97	Multiple compounds?	0.01	0.1	0.01	0.2
101	Hexanal other compounds?	0.02	0.2	0.01	0.2
63	Dimethyl sulphide	0.02	0.2	0.02	0.4
83	Multiple compounds?	0.01	0. 1	0.01	0.1

Table 2. The observed concentration statistics (in ppb) of the 15 masses/compounds that were present in measurements at Boundary Road during the Wagerup Winter Study. Measurements were by the PTR-MS except for formaldehyde. The formaldehyde measurements consist of 91 8-hour integrated DNPH samples.

Primary Protonated Mass	**Candidate compound**	**Max**	**90th percentile**	**75th percentile**	**Median**	**25th percentile**	**10th percentile**	**Min**
n/a	Formaldehyde	1.72	0.90	0.65	0.39	0.27	0.21	0.14
33	Methanol	33.1	6.4	4.1	2.5	1.1	0.02	bdl
41	Multiple compounds	3.6	0.62	0.37	0.17	bdl	bdl	bdl
42	Acetonitrile	2.8	0.12	0.07	0.03	bdl	bdl	bdl
43(fragment)	Multiple compounds including Isopropanol	8.0	1.3	0.8	0.4	0.1	bdl	bdl
45	Acetaldehyde	2.2	0.5	0.3	0.1	0.01	bdl	bdl
47	Formic acid, Ethanol and possibly other compounds	3.3	0.4	0.2	0.09	bdl	bdl	bdl
59	Acetone	6.8	0.9	0.5	0.3	0.1	0.04	bdl

Table 2, ctd.

Primary Protonated Mass	**Candidate compound**	**Max**	**90th percentile**	**75th percentile**	**Median**	**25th percentile**	**10th percentile**	**Min**
61	Acetic Acid and possibly other compounds	1.3	0.2	0.1	0.05	bdl	bdl	bdl
69	Isoprene	4.9	0.7	0.4	0.09	bdl	bdl	bdl
71	Multiple compounds including MVK/MACR	1.1	0.2	0.1	0.03	bdl	bdl	bdl
73	MEK	1.1	0.2	0.1	0.03	bdl	bdl	bdl
79	Benzene	1.6	0.2	0.08	bdl	bdl	bdl	bdl
81	Monoterpenes and possibly other compounds	4.2	0.4	0.2	0.09	bdl	bdl	bdl
93	Toluene	6.9	0.4	0.2	0.02	bdl	bdl	bdl

bdl = below detection limit

2.2 Non-Refinery sources of VOCs

The VOCs observed in the air at Wagerup can have a variety of potential sources. There are many VOCs that occur in the atmosphere from a variety of sources (Goldstein and Galbally 2007). A list of possible non-Refinery sources of those VOCs identified during the sampling at Wagerup is presented in Table 3 along with estimates of the atmospheric lifetimes of these key VOCs within the air. The lifetimes of these compounds within the air are an important consideration for the subsequent analysis. The key distinction is between compounds where the lifetime is either comparable with or shorter than the time an air parcel spends in the region surrounding Wagerup compared to those with a longer lifetime.

Compounds with a lifetime of only a few hours can be rapidly formed and lost within the atmosphere. What will be seen in the observations for compounds with short lifetimes is a complex interplay of atmospheric chemistry, local sources and meteorology affecting the observations. However, when the air flows directly from the Refinery to the Boundary Road site at moderate wind speeds of 2-3 m s^{-1}, the transit time is only 10 to 20 minutes and the concentrations observed in the plumes even for these compounds should be relatively unchanged provided the chemical lifetime of the compound is an hour or longer.

For the purpose of this Study, compounds with lifetimes of a day or longer can be considered to travel through the air unchanged by chemical processes. In these cases the influence of sources in the regions more distant from Wagerup are potentially important, and a schematic of locations is shown in Figure 1. Winds with a westerly component can bring air from the Indian Ocean to the site and winds with an easterly component can bring inland rural air to the site. This will be examined in the subsequent analysis.

Table 3. Some Non Refinery Sources of VOCs in rural air, estimates of atmospheric lifetimes of these VOCs, and concentrations observed at Boundary Rd, Wagerup and elsewhere

Compound	Source	Atmospheric Lifetime h = hours d = days y = years	Protonated Mass	Wagerup 25-75 percentile (ppb)	Concentrations elsewhere, mean and/or range (ppb)	Location	Reference (listed at end of table)
Formaldehyde	Atmospheric photochemistry, motor vehicles, vegetation, biomass burning	4h *	n/a.	0.27 – 0.65	~9.3 ~3.4	Urban Turkey Forest USA	1, 2, 3, 19, 20
Methanol	Vegetation, biomass burning	15d	33	1.1 – 4.1	2 – 7 4 (Ave.) 1 – 22	Urban Germany, Japan Summary of Rural obs.	4,10,11
Acetonitrile	Biomass burning, motor vehicles	1.5y	42	0 – 0.07	0.082 0.10 – 0.15 0.02 – 8	Global average Background North Sea Troposphere	5, 13,14
Isopropanol	Solvents, other unknown sources	2.3d**	43 (fragment)	0.1 – 0.8	1.6 - 28.9 0.02-0.08	Urban Osaka High Alpine, Switzerland	16, 10, 24
Acetaldehyde	Atmospheric photochemistry, motor vehicles, vegetation, biomass burning	11h*	45	0.01 – 0.3	1.3 (Ave.) 0.1 – 5.5 0.6	Forest Germany Free troposphere	1,2,3,9

Formic Acid	atmospheric photochemistry, biomass burning formicine ants	<1d - >7d	47	0 – 0.2	0.1 - 15 0.07 – 1.7 0.1 – 5	Urban Marine air Rural	7
Ethanol	Waterlogged vegetation, domestic and industrial activities	4 - 7d	47	0 – 0.2	0.09 – 6.5 0.02-0.04	Summary of rural observations Free troposphere	3, 6, 4
Acetone	Vegetation, atmospheric photochemistry, biomass burning	15d	59	0.1 – 0.5	3 (Ave.) 1 - 9 0.2 – 3	Forest Germany Global background atmosphere	1, 2, 3, 9
Acetic acid	Biomass burning, atmospheric photochemistry	<1d - >7d	61	0 – 0.1	0.5 – 16 0.1 – 3.5 0.05 – 1.9	Urban Rural Marine air	7
Isoprene	Tree emissions, biomass burning	2h*	69	0 – 0.4	1.2 (0 – 2.4)	Average in rural forest canopies	1, 2, 3, 12
Methyl vinyl ketone (MVK) & Methacrolein (MACR)	Atmospheric photochemistry, particularly isoprene oxidation	Several hours*	71	0 – 0.1	MVK ~0.2 -1.8 MACR ~0.1-1.0 MVK 0 - 0.5 MACR 0 - 0.4	Urban LA Forest Finland	1, 2, 3, 17, 18
Methyl ethyl ketone	Plant emissions, atmospheric photochemistry, biomass burning	13d	73	0 – 0.1	~0.2 0.6 (Ave.) 0.1 – 1.8	Urban Switzerland Forest Germany	1, 2, 3, 5,9

Benzene	Biomass burning, motor vehicles	12d	79	0 - 0.08	0.1 – 0.9	Aspendale VIC	1, 2, 3,8
Monoterpenes	Tree emissions	0.02 – 0.19d	81 (fragment)	0 – 0.2	0.04 – 0.74	Semi-urban	3, 22
					0.09 (Median)	Forest Germany	21
					0 – 3.0	Background	23
Toluene	Biomass burning, motor vehicles	2.4 - 3.6d	93	0 – 0. 2	0.2 - 2.2	Aspendale VIC	1, 3,8

*in sunlight. ; ** calculated assuming Temperature =298°K and a concentration of OH radicals of 1×10^{6} molecules cm^{-3}

References: 1. Seinfeld and Pandis (1998), 2. Scholes et.al. (2003), 3. Warneck (2000), 4. Galbally and Kirstine (2002), 5. Galbally et.al. (2007) 6. Singh et al. (1995) 7. Chebbi and Carlier (1996), 8. Lawson et al. (2005), 9. Muller et al., (2006), 10. Nguyen et al. (2001), 11. Leibrock and Slemr (1997), 12. Greenberg and Zimmerman (1984), 13. Bange and Williams (2000), 14. Hamm and Warneck (1990), 15. Jacob et al. (2002), 16. Legreid et al (2007), 17. Hakola et al.(2003), 18. Reissel et al.(2003), 19. Fierro et al. (2004), 20. Obadasi et al. (2005), 21. Amman et al. (2004), 22. Navazo et al. (2008), 23. Fillela and Penuelas (2006), 24. Legreid et al.(2007a).

2.3 Comparison of VOC concentrations observed at Boundary Rd and elsewhere

An aspect of this Study is to provide a perspective on how the concentrations of the VOCs observed at Wagerup compare with concentrations of these compounds observed in air elsewhere. In comparing atmospheric concentration data from different sites, the variability in the data and the averaging times must be considered. This presumes that even if there are differences in the measurement techniques used, and differences in sources of calibration material, that the measurements from different sources are comparable. For VOC data the available measurements are often limited, and may consist of a few weeks of observations. Depending on the location, the time of observations and the averaging period for an individual sample or data point, maximum and minimum concentrations can fluctuate widely. It was considered that for this initial comparison a robust measure would be to compare the 25th to 75th percentile range of hourly concentrations observed at Wagerup with concentration data available from elsewhere. The concentration data selected for locations “elsewhere” are those readily found by the authors, consistent with an initial scrutiny of the data. Observations elsewhere are described primarily by the names of chemical compounds, whereas observations at Wagerup are described by the mass first and the compound following, in keeping with the nature of the compound identification. Note both formic acid and ethanol are considered for mass 47. No analysis is made for mass 41 because there is no information to rank the multiple compounds contributing to that mass.

Table 3 presents the 25th to 75th percentile range of concentrations of the fifteen gases (see Section 2.1) measured at Boundary Rd and concentrations of these compounds in either urban, rural, forest or global background locations elsewhere.

Formaldehyde, a compound readily produced in atmospheric organic photochemistry, is present at Wagerup in concentrations of 0.27-0.65 ppb compared with average concentrations of 3.4 ppb in a forest in the USA and 9.3 ppb in Izmir, Turkey.

Methanol is the simplest alcohol and has a large natural source from vegetation (Galbally and Kirstine, 2002). Methanol has a 2 ppb to 7 ppb range for urban locations (Nguyen et al., 2001; Leibrock and Slemr, 1997) and a range of concentrations in rural environments of 1 to 22 ppb (Galbally and Kirstine, 2002). Mass 33 (methanol) had concentrations of 1 ppb to 4 ppb at Wagerup.

Acetonitrile has an atmospheric source which is almost exclusively from biomass burning. Acetonitrile has a long lifetime in the atmosphere of the order of a year, so the concentrations are not highly variable, unless sampling is carried out in biomass burning plumes or near other acetonitrile sources. The global average concentration is 0.082 ppb (Hamm and Warneck, 1990). In the lower atmosphere concentrations can range from 0.02 ppb far way from biomass burning sources to 8 ppb when sampling occurs in plumes from biomass burning episodes (Bange and Williams, 2000). Mass 42 (acetonitrile) concentrations of 0 to 0.071 ppb were measured at Wagerup, which are consistent with concentrations elsewhere.

Isopropanol, a three carbon alcohol, is used as a solvent and is also associated with emissions from use of ethanol based fuels (Nguyen et al., 2001). Concentrations of isopropanol from a high alpine site in Switzerland were 0.02-0.08 ppb (Legreid et al., 2007a). In urban Osaka isopropanol concentrations range from 1.6 – 28.9 ppb. The concentrations of mass 43 (isopropanol) observed at Wagerup of 0.1 – 0.8 ppb are below the urban concentrations observed in Osaka, Japan.

Acetaldehyde has atmospheric sources in photochemistry, motor vehicle emissions, vegetation and biomass burning. Acetaldehyde concentrations observed over a forest in Germany were 0.1 – 5.5 ppb (Muller et al., 2006). Mass 45 (acetaldehyde) ranged from 0.01 ppb to 0.3 ppb in concentration during the Wagerup Winter campaign which is at the lower end of the concentrations observed over a forested area in Germany.

Formic acid, the simplest of the organic acids, is produced by atmospheric photochemistry, biomass burning and biological processes including formicine ants (Chebbi and Carlier, 1996). Concentrations vary from 0.07 to 1.7 ppb in the background oceanic atmosphere, to 0.1 to 5 ppb in the rural atmosphere to 0.1 to 15 ppb in urban atmospheres (Chebbi and Carlier, 1996). The concentrations of mass 47 observed at Wagerup of 0 – 0.2 ppb lie at the low end of the range of rural concentrations of formic acid observed elsewhere.

Ethanol, the two carbon alcohol, is emitted from water logged plants, baking, industrial uses and from use as a fuel. The concentrations in the free troposphere in the northern hemisphere are 0.02 to 0.04 ppb and in a range of rural atmospheres of 0.1 – 6.5 ppb (Kirstine and Galbally, 2000). The concentrations of mass 47 observed at Wagerup of 0 – 0.2 ppb lie within the range of rural concentrations of ethanol observed elsewhere if allowance is made for the poor response to ethanol of the PTR-MS.

Acetone has atmospheric sources in vegetation, atmospheric chemistry and biomass burning (Seinfeld and Pandis, 1998). Mass 59 (acetone) concentrations measured during the campaign of 0.1 – 0.5 ppb, were comparable to the acetone global background concentrations of 0.2 to 3 ppb (Jacob et al. 2002) and lower than the range of 0.1 to 9.1 ppb observed over a forest in Bavaria Germany (Muller et al., 2006).

Acetic acid is produced by biomass burning and atmospheric photochemistry (Chebbi and Carlier, 1996). Concentrations of acetic acid in marine air (Pacific Ocean) are 0.05 – 1.9 ppb. Rural acetic acid concentrations are 0.1 – 3.5 ppb. Urban concentrations of acetic acid are 0.6 – 16 ppb (Chebbi and Carlier, 1996). The concentrations of mass 61 (acetic acid) observed at Wagerup during the Winter campaign of 0 – 0.12 ppb lie within the range of concentrations observed in marine and rural environments elsewhere.

The atmospheric source of isoprene is largely from biomass emissions and typically concentrations result from emissions from forest canopies. Anthropogenic emissions of isoprene are insignificant compared to natural sources. Average mixing ratios of isoprene in the continental boundary layer at 7 rural sites within forest canopies are summarised by Warneck (1988) with a median value of 1.2 ppb and a range of concentrations of trace to 2.4 ppb. An average isoprene concentration of 2.3 ppb was observed in a forest canopy (Bange and Williams 2000). Mass 69 (isoprene) ranged from 0 - 0.38 ppb in concentration during the Wagerup campaign.

Methyl vinyl ketone and methacrolein (MVK and MACR) have sources in atmospheric chemistry, in particular, oxidation of isoprene (Seinfeld and Pandis, 1998). MVK and MACR concentrations in a boreal forest in Finland were 0 - 0.5 ppb and 0 - 0.4 ppb respectively (Hakola et al., 2003). MVK and MACR concentrations in an urban area of Los Angeles were ~ 0.2 – 1.8 ppb and ~ 0.1 – 1.0 ppb respectively (Reissell et al., 2003). The combined mass 71 (MVK + MACR) concentrations observed at Wagerup of 0 – 0.1 ppb lie within the range of concentrations observed at the forested site in Finland.

Methyl ethyl ketone (MEK) has atmospheric sources in solvents, plant emissions, atmospheric photochemistry and biomass burning (Singh et al., 2004). Mass 73 (MEK) had a concentration range of 0 to 0.12 ppb at Wagerup, during the Winter campaign, and this is lower than the range of 0.1 to 1.8 ppb observed for MEK over a forest in Bavaria Germany (Muller et al., 2006).

Mass 79 *(*benzene) concentrations ranged from zero to 0.08 ppb during the Wagerup Winter Study. These are low concentrations compared with benzene observations at Aspendale, an urban location in Melbourne (Lawson et al., 2005) that ranged from 0.1 ppb to 0.9 ppb over a period of 10 months during 2003/2004.

Monoterpenes are emitted from plants, primarily trees (Guenther et al., 1995). Monoterpene concentrations in a rural background site in Iberia were 0 – 3.0 ppb (Navazo et al., 2008). A median of 0.09 ppb was observed at a forested site in Germany (Amman et al., 2004). Monoterpene concentrations in a semi-urban site near Barcelona were 0.04 – 0.74 ppb. Mass 81 (a fragment of monoterpenes) concentrations observed at Wagerup of 0 – 0.24 ppb lie within the range of background, rural and urban concentrations observed elsewhere.

Mass 93 (toluene) concentrations ranged from zero to 0.2 ppb during the Wagerup Winter Study. These are low concentrations compared with toluene observations at Aspendale, an urban location in Melbourne (Lawson et al., 2005) that ranged from 0.2 ppb to 2.2 ppb over a period of 10 months during 2003/2004.

With the exception of methanol which is produced mainly by vegetation, the concentrations of the other 14 masses (VOCs) observed during the Winter Study at Wagerup are on the whole lower than concentrations of the same gases observed in rural and urban air elsewhere. The reason for this may be either that the sources of these VOCs are lower in winter in the region surrounding Wagerup than elsewhere, or that the oceanic air that has extremely low concentrations of VOCs (Galbally et al. 2007), and that is carried inland to Wagerup by westerly winds, dominates other influences on VOC concentrations at Wagerup during wintertime.

3 ANALYSIS OF CONCENTRATIONS AND SOURCES, INCLUDING THE REFINERY

The objective of the Study was to identify substances present above background concentrations (based on mass number) and identify their most likely sources in the Wagerup area, both natural and man made, based on measurements at a location south of the Wagerup Refinery between the Refinery and Yarloop.

Background concentrations in this context refer to those concentrations observed in the air when the air is not under the direct influence of anthropogenic emissions. Anthropogenic emissions in this region include Refinery emissions, vehicle exhaust, emissions from domestic, commercial, industrial and agricultural activities (including burning) nearby or from more distant intense sources. Background air contains concentrations of constituents that arise from natural sources and from anthropogenic sources that are so distant that their contribution is already well mixed within the airmass by the time the air reaches the point of measurement.

Analyses have been undertaken on the data sets of two-minute average, hourly average and 8-hourly average concentrations of the mass numbers (from the PTR-MS), formaldehyde from the DNPH cartridges (only 8-hour data), CO_2, CO, NO_x , $PM_{2.5}$ measurements and meteorological parameters. The mass numbers used and associated compounds are: 33 (methanol), 41 (multiple compounds), 42 (acetonitrile), 43 (multiple compounds including isopropanol), 45 (acetaldehyde), 47 (formic acid), (ethanol and other compounds), 59 (acetone), 61 (acetic acid and possibly other compounds), 69 (isoprene), 71 (multiple compounds), 73 (methyl ethyl ketone), 79 (benzene), 81 (monoterpenes and possibly other compounds) and 93 (toluene). The analyses include masses 79 benzene, and 93 toluene because of their role as indicators of vehicle exhaust and biomass burning.

The analyses (as per the project brief) involved the examination of the data via:

time series,
variation in wind direction,
diurnal variations,
variation with highway vehicle traffic,
comparison with observed odour,
according to the highest TVOC concentrations ,
according to the lowest TVOC concentrations,
on days specified by Alcoa and
comparison with concentrations observed elsewhere (presented in Section 2).

These analyses are supplemented with other approaches including:

CO_2 /NO_x relationships for chemical signatures,
meteorology (wind speed and direction) and TAPM meteorological modeling, and

results of previous CSIRO investigations.

Some of the analyses conducted specifically search for the influence of the Refinery (e.g. concentration variation with wind direction) while others look at what are well established patterns of variation (e.g. diurnal concentration variation) to see whether any anomalous behavior (compared with that expected from current understanding) is observed.

3.1 Refinery emissions and source signatures

In alumina refining gaseous emissions can come from a variety of sources involved in the refining process. At Wagerup these sources include the generation of electricity and heat on site, transport of the alumina and other chemicals, milling and digestion of the bauxite, precipitation and purification of the alumina, cooling of the processes, calcining the alumina, and burning the excess organic material in the Bayer liquor.

Some information is presented here on the operation of the Refinery. Table 4 presents the bauxite throughput and natural gas consumption of the Refinery during the Winter Study and for the rest of 2006 (excluding the Study period) for reference, provided by Alcoa (file Wagerup_Emissions_CSIRO Data Request.xls, email from Kellie Rinaldi of Sinclair Knight Merz at Alcoa, 4 July 2007 and further information provided by Patrick Coffey of Alcoa in email dated 15 January 2008). It appears that the bauxite throughput, the Gas Turbine, HRSG, Boilers 1, 2 and 3, and Calciners 1, 2, 3, and 4 operated at normal capacity during the Winter Study compared with the rest of 2006.

The Liquor Burner was off line for most of the period of the Study. The Liquor Burner has historically been associated with complaints at Wagerup (CSIRO 2004). The following information has been provided by Alcoa and its consultants. “The Liquor Burner was off line between August and October 2006 for the installation of improved emissions control equipment. This was a major engineering upgrade project in which the existing Catalytic Thermal Oxidizer was replaced with a state of the art Regenerative Thermal Oxidizer for improved VOC destruction efficiency and reliability. The timing of the LB outage was set by the needs of the upgrade project. The Winter Monitoring Study was commenced as early in the winter period as was possible, but measurements did not commence until 10 August due to various technical and logistical complexities of the project. This meant that there was an unavoidable co-incidence of the LB being off-line for most of the period of the Study.” (Dr Greg Power, Arriba Consulting Pty Ltd, email dated 22 January 2008). A subsequent Study of Liquor Burner emissions indicates that this change has led to a 93.0% reduction in the projected annual Aggregate Priority VOC emissions from the Liquor Burner following the installation of the RTO (Alcoa 2006).

Alcoa’s emissions monitoring has identified many VOCs emitted from the Refinery (CSIRO

2004). Odour bag analyses by PTR-MS (Galbally et al, 2007) has identified three other masses, 33, (methanol), 42, (acetonitrile), and 51, (1,3 butadiyne) in Refinery emissions.

The VOC emissions to the atmosphere from the Refinery during the Study period have been calculated using the available quantitative emission rate data. These are both the ERMP Emission data (Alcoa 2005) and the latest results of VOC emission testing through to 2007 provided by Alcoa (file Emissions_WGVOCs Full HRA draft 5_may29.xls). The result of the Liquor Burner being off line during the Study period is estimated to reduce the VOC emissions from the Refinery by 5%, to 95% of the previous emissions, assuming the ERMP or VOC emission rates prior to the Winter Study. The change also means that any particular chemical or odour characteristics of the Liquor Burner emissions will be diminished or absent in the Winter Study ambient VOC data set.

The estimated emissions of VOCs from the various Refinery sources during the Study period are summarised in Table 5. It is observed, based on the VOCs analysed in stack sampling, that these Refinery VOC emissions consist of 56% acetone, 18% acetaldehyde, 14% formaldehyde, 9% 2-Butanone, 2% toluene, 1% benzene, and 1% xylenes plus some minor constituents.

Methanol is not listed as an emission from the Refinery (CSIRO 2004; Alcoa 2005; NPI 2006). However the Pilot Study (Galbally et al., 2006) presented evidence of a source of mass 33 (methanol) in the Refinery plumes. Exploratory studies (Galbally et al., 2007, Appendix G) indicate that methanol is in the Refinery emissions. Also methanol is a product of the alkaline digestion of plant (vegetation) material (Yoon et al. 2003; Zhu et al. 1999). As long as the organic matter within the bauxite has methoxy groups, such as those on either soil humic material or lignins, alkaline hydrolysis at elevated temperatures as happens in bauxite digestion, is expected to release methanol.

At Wagerup different parts of the Refinery have clusters of adjacent stacks. The composition of the emissions from each individual stack can be quite different. Information on source emission ratios from some Wagerup stacks is provided in the Pilot Study (Galbally et al. 2006). Of the groups of sources in the Refinery, the Boilerhouse Multiflue and Gas Turbine emit significant amounts of CO_2 and NO_x but very low VOCs. The 100m Multiflue and Calciner 4 emit a mixture of CO_2, NO_x and VOCs (the Liquor Burner emissions occur through the 100 m Multiflue stack). The Milling and Digestion and other non-combustion sources (including the Cooling Towers, and Calciner 4 Vacuum Pump and Dorrco) emit VOCs with little CO_2 or NO_x. Thus a plume from the Refinery can have a very variable source signature depending on whether there is a single dominant source emission or mix of source emissions present in the plume.

There is a 3-dimensional separation of the emissions that occurs because of the spatial distribution of the stacks and the vertical distribution of stack heights and plume rise effects. Table 5 provides individual VOC emissions from the major point sources at Wagerup. Almost all of the formaldehyde and approximately 55% of the acetaldehyde emissions come from elevated sources (high stacks), and around 70% of acetone emissions come from low level sources (low stacks and diffuse sources).

Table 4. The bauxite throughput and natural gas consumption of the Wagerup Refinery during the Winter Study and for the rest of 2006 excluding the Study period

Process	**Units** Bauxite & Natural Gas	**10 August to 7 October 2006**		**Rest of 2006 excluding the Study period**	
		Mean	**Median**	**Mean**	**Median**
Milling & Digestion Bauxite Throughput	tph	779	799	743	758
Powerhouse GT & HRSG	m^3/h	15780	16260	14379	15019
BOILER 1	m^3/h	16462	16438	15368	15701
BOILER 2	m^3/h	8950	9830	9915	10131
BOILER 3	m^3/h	10345	10333	9711	9959
Calciner 1	m^3/h	5198	5206	5182	5634
Calciner 2	m^3/h	5109	5179	5224	5535
Calciner 3	m^3/h	4637	4802	4015	4708
Calciner 4	m^3/h	7656	7352	7567	7315
Liquor Burner	m^3/h	105	6	1044	1182

Table 5. VOC estimated emission rates from stacks at the Wagerup Refinery (from file Emissions_WGVOCs Full HRA draft 5_may29.xls) for the Study period. The 100 m Multiflue includes the vents of Calciners 1 – 3, and some other sources and excludes the Liquor Burner emissions in this case. The CO_2/NO_x ratios are from the Pilot Study period (Galbally et al., 2006).

Source	**Source height (m)**	**CO_2/NO_x Emission ratio (v/v)**	**TVOC emission rate (g s^{-1})**	**Acetone emission rate (g s^{-1})**	**Acetaldehyde emission rate (g s^{-1})**	**Formaldehyde emission rate (g s^{-1})**	**2-Butanone emission rate (g s^{-1})**
100 m Multiflue (excluding the Liquor Burner)	100	1320	1.25	0.39	0.30	0.42	0.07
Boilerhouse Multiflue	65	1280	0.22	0.11	0.00	0.03	0.05
Gas Turbine (GT-HRSG)	40	2490	0.00	0.00	0.00	0.00	0.00
Calciner 4	49	2440	0.37	0.09	0.13	0.12	0.03
Milling and Digestion Vents	12	nil	1.34	0.89	0.31	0.00	0.11
Other non-combustion sources (see text)	4 - 20	nil	0.90	0.80	0.00	0.00	0.09
Total Emission rate	n/a	1500	4.1	2.28	0.74	0.57	0.35

3.2 PTRMS-TVOC Time Series and related processes

An examination of the time series of concentrations of VOCs measured during this Study at Wagerup provides a first overview of the data. The time series of hourly average PTRMS-TVOC and NO_x concentrations during the 8 weeks of the experiment are shown in Figure 4 and Figure 5, respectively.

There is no apparent strong association between the VOCs and NO_x in these time series, and this is borne out by the linear correlation between PTRMS-TVOC and NO_x being $r < 0.1$. This is consistent with the data in Table 5, where approximately one third of the VOC emissions are associated with combustion sources and NO_x emissions, and two thirds of VOC emissions are not associated with combustion and NO_x sources.

A time series of the 8 hour average Carbonyl data based on measurements by DNPH-HPLC are presented in Figure 6. Also presented in Figure 6 are the PTRMS-TVOC concentrations minus the Methanol concentrations averaged over the same 8 hour periods as the Carbonyls. (PTRMS-TVOC minus Methanol was chosen as a suitable parameter to represent VOCs). The Methanol concentrations and fluctuations dominate the variance in the data and methanol has a large background concentration. The removal of the Methanol concentration allows the analysis to explore the variance in concentration associated and the other 23 masses detected at Wagerup. There are major peaks and troughs in the PTRMS-TVOC minus Methanol and Carbonyl concentrations shown in Figure 6. These PTRMS-TVOC minus Methanol and the Carbonyl concentrations have correlated fluctuations over the observing period. This correlation arises in part because acetone and acetaldehyde are measured as part of both suites of measurements, and also because there are probably underlying correlations between other compounds occurring in TVOCs and the Carbonyls in the air at Wagerup. This correlation is also an indication of the consistency between the two independent measurement techniques.

In Figure 7 the hourly PTRMS-TVOC concentrations are plotted against run of the wind in the westerly direction (this being the virtual east-west distance travelled by an air parcel during the hour of the measurement plus the previous hour based on the local wind vector) measured by the sodar at 100 m height at Boundary Rd. What is observed is that in strong westerly winds (approximately 6 ms^{-1} and greater) when the two hour run of the wind is greater than about 40 km (comparable to the distance to the coast from Wagerup) the PTRMS-TVOC concentration drops to a level around 1 to 2 ppb, consistent with low VOC concentrations over the Southern Ocean (Galbally et al., 2007). In strong easterly winds with a run greater than about 40 km, the PTRMS-TVOC concentrations in inland rural air vary around 4 to 12 ppb. The highest TVOC concentrations occur when the net air travel during the previous 2 hours has been confined to 20 km east or west of Wagerup, see Figure 7.

A summary of 'peak' PTRMS-TVOC periods where the hourly PTRMS-TVOC value exceeded

20 ppb is shown in Table 6, along with the corresponding NO_x concentration, wind direction and wind speed for each of these periods. There are 11 hours of 20 ppb or above of PTRMS-TVOC. An examination of the wind directions at the time of the peaks reveals a complex picture. The largest NO_x concentration that occurs with these highest PTRMS-TVOC is 7.7 ppb. This NO_x concentration is quite low compared with the maximum hourly NO_x concentration observed during the Winter Study of 100 ppb. This is consistent with the low PTRMS-TVOC to NO_x correlation reported above. This indicates that these PTRMS-TVOC peaks are not associated with NO_x rich sources which would primarily be combustion sources.

The events (recorded in Table 6) on 29/8, 9/9, 15/9 have a northerly component to the wind, and on 14/9 and 29/9 there is a southerly and westerly component to the winds during the PTRMS-TVOC peak. When the hourly PTRMS-TVOC concentrations are examined in relation to wind direction, and the top 10 to 20 concentrations of PTRMS-TVOC (the top 1%) are considered there is no obvious preferential wind direction, see Table 6.

Table 7 presents a summary of low PTRMS-TVOC periods, where the hourly PTRMS-TVOC was below 5 ppb for >24 hours, along with the corresponding wind direction and NO_x data. The three periods of low PTRMS-TVOC correspond to south east, through south to westerly winds (clean air) coming from directions that generally do not include the Refinery. The low PTRMS-TVOC air has low NO_x concentrations also. An examination of the two lowest PTRMS-TVOC minus Methanol concentrations in Table 7 reveal that they occurred in winds from the westerly quadrant with wind speeds of 4 and 5 ms^{-1}. A logical explanation of the pattern is that the low concentration periods coincide with winds from the ocean where there are few PTRMS-TVOC sources as was shown in the run of the wind analysis above.

Mass 33 (methanol) makes up typically around 60% of the Total VOCs, see Section 2.1. The time series of mass 33 (methanol) dominates the variability in the TVOC time series, and the peak events in TVOCs are driven by variations in sources of mass 33 methanol. This is confirmed by the very strong correlation of hourly concentrations of PTRMS-TVOCs and mass 33, with a correlation coefficient of $r = +0.98$. The correlations of mass 33 (methanol), with the following mass numbers all have correlation coefficients >0.5.: 41 (multiple compounds), 42 (acetonitrile), 43 (multiple compounds including isopropanol), 45 (acetaldehyde), 47 (formic acid, ethanol and other compounds), 57, (multiple compounds), 59 (acetone), 60 (trimethylamine and ^{13}C of acetone), 61 (acetic acid and other compounds), 71 (multiple compounds), and 73 (methyl ethyl ketone) and 87 (2,3-butanedione), The largest correlation of mass 33 (methanol) with these masses was with 43 (multiple compounds including isopropanol), with a coefficient of 0.86. Mass 33 methanol has sources both from vegetation and from the Refinery (Galbally and Kirstine 2002, Galbally et al., 2006, Galbally et al., 2007). The conclusion from these correlations is that methanol has two or more sets of sources in the Wagerup region, one group being associated with emissions of these other VOCs and perhaps another set being independent of these other VOCs.

A major point of reference for this Wagerup Winter Study data is the VOC data set from Wagerup from the Pilot Study (Galbally et al. 2006). The statistics of this PTRMS-TVOC data are compared with those from the Pilot Study held in December 2005 to February 2006 in Table 8. While the median PTRMS-TVOC concentration is higher in winter than in summer (after calibration of both records), the peak concentrations in winter are about half of those in summer. This indicates that there is less variability in the VOC concentrations during this winter compared with the previous summer, and so there are fewer distinct peaks to interpret in the present Study. This comes about in part because a bushfire plume with high concentrations of several VOCs traversed the site on one occasion during the summer Study.

Table 6. Summary of hourly periods where the PTRMS-TVOC concentration was >20 ppb. Also shown is the corresponding NO_x concentration and wind direction, WD, during the hour of high PTRMS-TVOCs and the wind direction during the hour prior to the peak.

Time/Date start	Time/Date end	PTRMS-TVOCs (ppb)	NOx (ppb)	WD during peak hour (deg.)	WD prior to peak hour (deg.)	Wind Speed during peak hour ($m\ s^{-1}$)
28/08/06 18:00	28/08/06 19:00	25.0	7.3	151.8	59.4	7.10
9/09/06 16:00	9/09/06 17:00	20.5	2.6	3.0	6.1	2.40
9/09/06 17:00	9/09/06 18:00	21.0	2.4	131.7	3.0	2.12
9/09/06 18:00	9/09/06 19:00	24.6	2.4	122.3	131.7	2.23
14/09/06 19:00	14/09/06 20:00	23.6	7.7	177.0	203.4	2.00
15/09/06 12:00	15/09/06 13:00	20.8	3.1	339.5	344.8	4.05
15/09/06 13:00	15/09/06 14:00	21.2	5.7	350.3	339.5	3.84
15/09/06 14:00	15/09/06 15:00	21.4	6.4	338.1	350.3	4.19
29/09/06 11:00	29/09/06 12:00	20.2	2.9	259.7	255.5	3.42
29/09/06 15:00	29/09/06 16:00	20.0	3.6	332.8	303.3	3.57
5/10/06 19:00	5/10/06 20:00	23.0	2.0	144.7	182.3	1.04

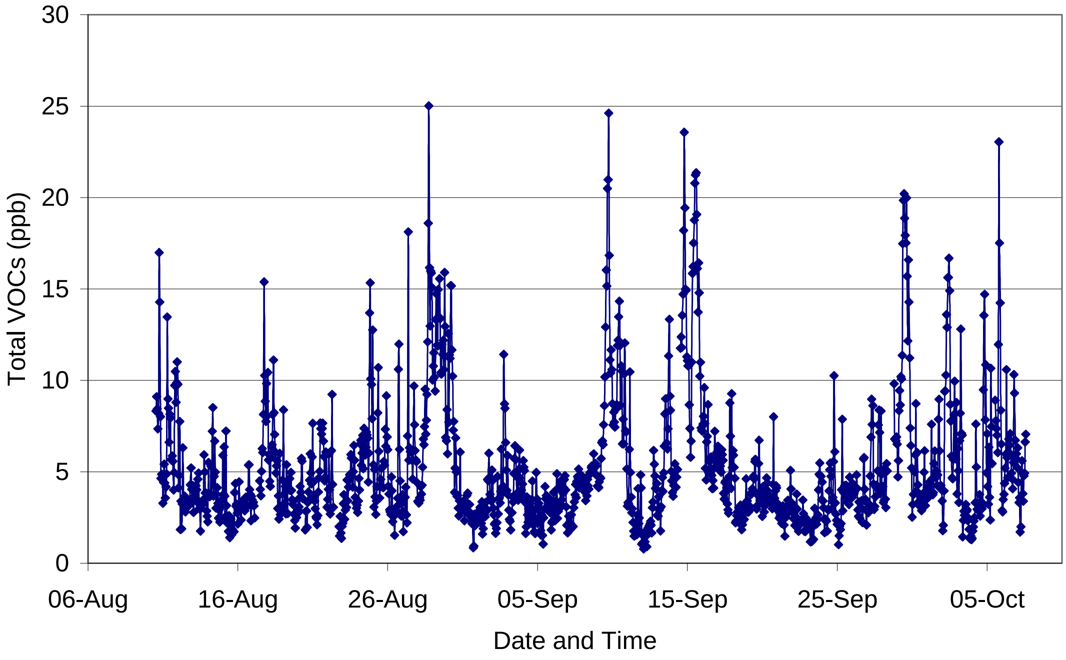

Figure 4. The time series of hourly average Total VOCs (PTRMS-TVOC) measured during the Wagerup Winter Study 2006

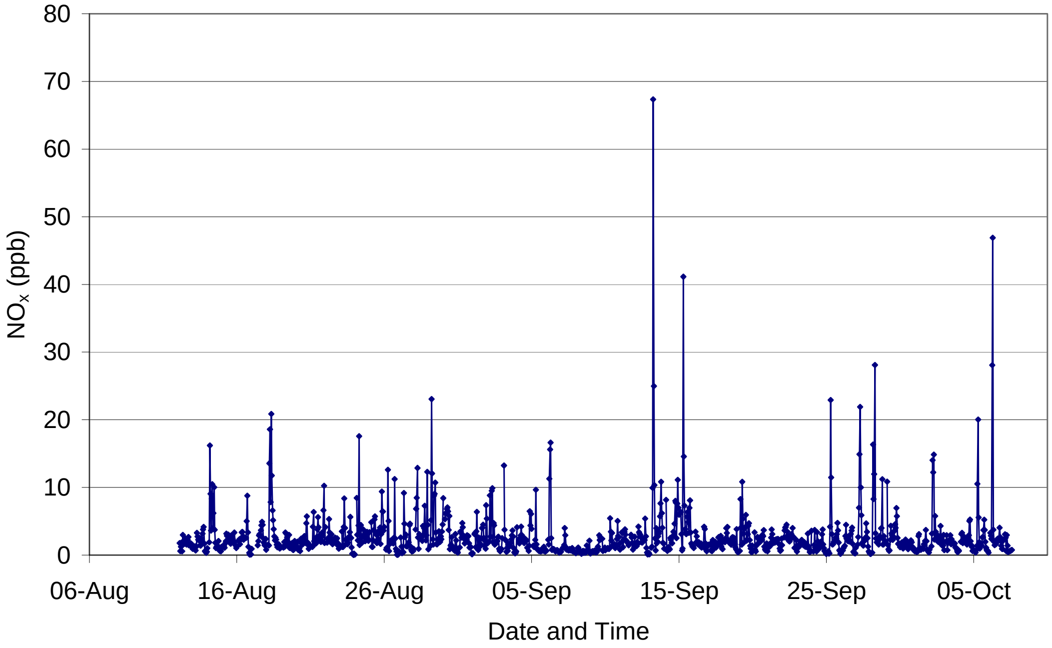

Figure 5. The time series of hourly NO$_x$ concentrations measured during the Wagerup Winter Study 2006

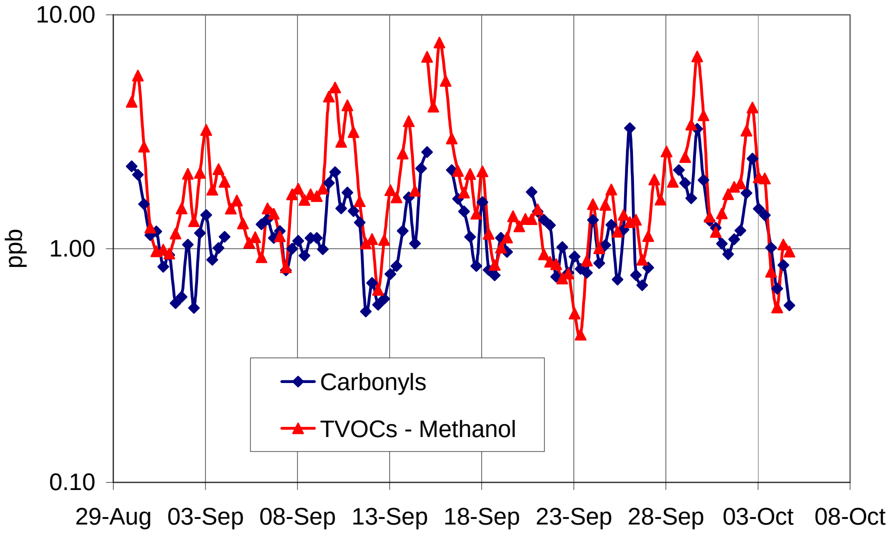

Figure 6. The time series of 8-hour average PTRMS-TVOC minus Methanol measured by PTR-MS and 8 hour average Total Carbonyls measured by DNPH-HPLC during the Wagerup Winter Study 2006

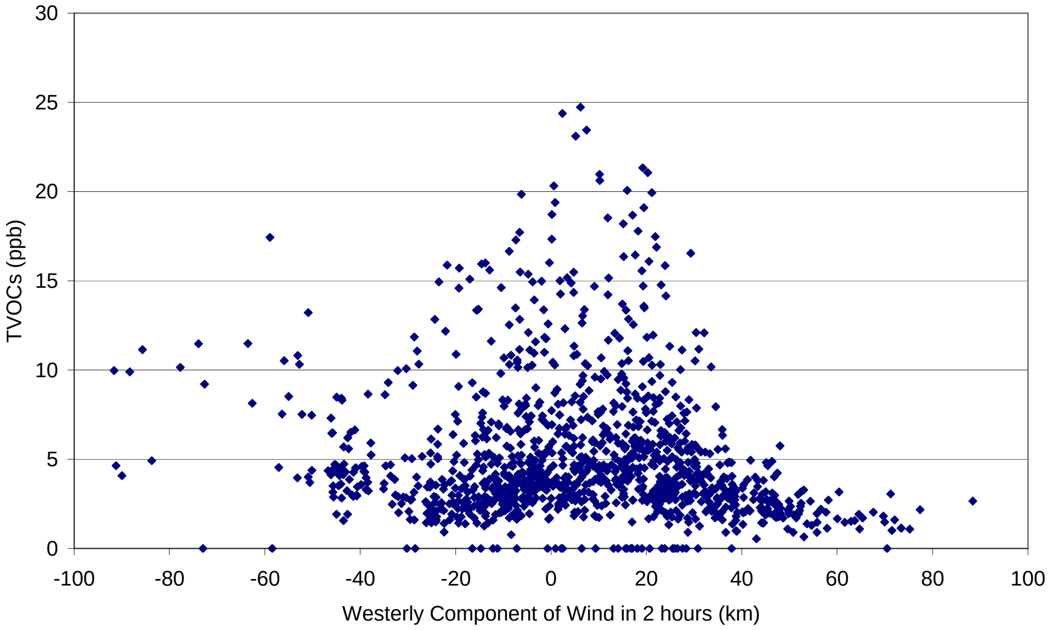

Figure 7. The PTRMS-TVOC concentrations observed at Boundary Rd vs the run of the westerly component of the 100m sodar wind observed in the hour of the measurement plus the previous hour.

Table 7. Summary of periods when the hourly PTRMS-TVOC concentration was <5 ppb for an extended period (>24 hours). Also shown is the mean NO_x value during each period of low TVOCs, and the range and average wind direction during the period.

Time/date start	Time/date end	PTRMS-TVOC (ppb)	Ave. NO_x (ppb)	Ave. Wind Direction (deg)	Range of Wind Direction (deg)
4/09/06 4:00	7/09/06 17:00	3.0	2.1	165.0	101-238
21/09/06 0:00	24/09/06 11:00	2.7	2.0	249.6	62-357
15/08/06 6:00	17/08/06 2:00	3.0	2.3	210.6	117-321

Table 8. Statistics of PTRMS-TVOC concentrations in ppb at Wagerup from the summer 2005/06 Pilot Study and the Winter 2006 Study.

Statistic	Winter 2006	Summer 2005/06
Median	4.16	3.70
Upper 25 percentile	6.57	8.05
Upper 10 Percentile	10.5	14.9
Upper 5 Percentile	13.7	21.0
Upper 1 Percentile	20.3	38.9
Maximum	51.3	113.3

3.3 Detection of Refinery plumes using relationships between NO_x and CO_2

One key way of detecting plumes from combustion sources and distinguishing them from other combustion and non-combustion sources is to examine the ratio of enhancement (above background) of CO_2 and NO_x concentrations in these plumes. Vehicle exhaust, biomass burning and industrial combustion sources can have quite different CO_2/NO_x emission ratios. Examples of these ratios are calculated from information in the National Greenhouse Gas Inventory (AGO 2008), for Wagerup (Galbally et al., 2006), for wildfires and agricultural burning (Scholes et al., 2003) and for residential wood heating (Scholes et al., 2003; Gras et al. 2002). The resulting ratios expressed as CO_2/NO_x volumetric or molar ratios are: stationary energy generation using natural gas 216; petrol fuelled road transportation 240; Wagerup Refinery combined 1500 (1280

– 2490), wildfires and agricultural burning 418-627; and residential wood heating 474-3373.

When an exhaust gas stream is emitted into the atmosphere from a source, the emission ratio from the source defines the ratio of the concentration enhancements of the two pollutants in the plume downwind of the source. This ratio is conserved while the level of these pollutants can be distinguished with precision from the concentrations of these pollutants in the background air. Ambient concentration measurements of those pollutants that are emitted from nearby sources, can be analysed to reveal whether the ambient measurements reveal enhanced concentration ratios that correspond with the emission ratios of the nearby sources.

An example of this type of analysis was presented in the Wagerup Pilot Study Report (Galbally et al., 2006). Figure 5.1.1.2 of the Pilot Study Report (Galbally et al., 2006), shows a scatterplot of CO_2 vs NO_x for 4-minute averaged data from the Upper Dam site during several periods when short term peaks of NO_x and CO_2 were coincident in time and when the wind was from the direction of the Wagerup Refinery. The Figure is reproduced here as Figure 8. The (NO_x, CO_2) points in the plot exhibit a tight linear relationship between NO_x and CO_2. Such a relationship is characteristic of emissions from a source of NO_x and CO_2 being diluted by mixing into background air containing much lower concentrations of NO_x and CO_2, with (NO_x, CO_2) points far from the origin of the plot corresponding to measurements of emissions that are less diluted than points nearer to the origin. This assumes the source strength is not varying; if this is not the case, then this will cause additional variability in the position of measurements along the "line of dilution". The slope of such a line provides an estimate of the CO_2:NO_x ratio. For the above mentioned figure from the Pilot Study (Galbally et al. 2006), the slope implies a volumetric CO_2:NO_x ratio of approximately 1600:1. As indicated in the Pilot Study (Galbally et al., 2006), this ratio is characteristic of the Wagerup Refinery combined emissions of NO_x and CO_2. This approach was useful also in distinguishing another source of NO_x rich combustion emissions of diesel exhaust near the northern end of the Refinery during the Pilot Study. Therefore the technique is examined here in relation to the Winter Study.

When a single well defined source of pollution does not dominate the signal, i.e. the background air into which the source emissions are diluted is affected by emissions from a number of sources, a CO_2 vs NO_x scatterplot will show a "cloud" of (NO_x, CO_2) points rather than a tight linear grouping. Even if this is the case, it still can be possible to determine an estimate of the CO_2:NO_x ratio for the source of interest. A technique to do this was developed by Bentley (2004) and further detail about the underlying method is included in that paper. This technique has been used here with the Wagerup Winter Study CO_2 and NO_x data from Boundary Rd.

The procedure used is to examine a plot of the one-minute NO_x and CO_2 data for short-term linear patterns within the overall "cloud" of points using the technique developed by Bentley (2004). This was done by dividing the (NO_x, CO_2) data points into groups of three consecutive points. A regression line was fitted to each individual group of three consecutive points, and the slopes for those groups whose regression r^2 exceeded 0.9 were accumulated into groups of the slope values that were used to produce histograms or other statistical analyses. Figure 9 shows a histogram of these high r^2 slopes, where the value within each histogram bin has been calculated as the sum of the r^2 values for the groups whose slopes lie within the bin. The use of r^2 values, rather than unity, reduces the influence of the less accurate slope values. Negative slopes, which cannot correspond to emission sources of NO_x and CO_2, as well as a small number of slopes above 10000, have been omitted from the plot. Figure 9 shows two distinct modal peaks, one centred at a CO_2:NO_x ratio of approximately 400, and the other of approximately between 1600. The key physical question is: what sources are identified by these CO_2:NO_x ratios observed at Boundary Rd, based on both prior knowledge of source signatures and the association of these source signatures with wind directions at Boundary Rd?

A further analysis of the groups (of slope values) with high r^2s (those contained in Figure 9) was performed to see whether the CO_2:NO_x ratio depended on wind direction. The slope data points within the high r^2 group (those with slopes lying between 0 and 10000) were partitioned into three subsets, depending on whether the slope lay between 0 and 1000, 1000 and 2500, or 2500 and 10000. The first two subsets of slope ranges each contain one of the two modes in Figure 9, the third subset contains what appear to be random fluctuations. For each of these subsets, a histogram of frequency of occurrence of a slope value in the subset range versus the wind directions at the time of the measurement of that slope were plotted (Figure 10, Figure 11, Figure 12).

Figure 10 shows that for the smaller slope mode where the CO_2:NO_x ratio lay between 0 and 1000, the bulk of the observations correspond to winds from the South East through South to the North West. When the wind is from the South East through South to the North-West (Yarloop and surrounds) the observed ratios are consistent with the sources from residential, commercial, vehicular, wildfires and agricultural burning and either or both of residential wood burning and Refinery emissions contributing to pollutants in the air.

Figure 11 shows that for the medium slope mode where the CO_2:NO_x ratio lay between 1000 and 2500, winds from just East of North (i.e. the direction of the Refinery) markedly influence the histogram as well as observations corresponding to winds from the South East through South to the North West. When the winds are from the North to East the observed ratios are consistent with either or both of Refinery plumes and residential wood burning contributing to pollutants in the air with little contribution from the other sources (residential, commercial., vehicular etc). Unfortunately the woodheater and Refinery influences cannot be distinguished because of the limited CO monitoring data available (Appendix B).

Figure 12 shows the largest slope mode where the CO_2:NO_x ratio lay between 2500 and 10000. Based on many other analyses of this type (Bentley 2004), and the minor role of this range as shown in Figure 9, it is assessed that there is little conclusive information in this plot.

Analyses were performed for the available data for CO and CO_2, and for CO and NO_x, but no fully defensible evidence of characteristic signatures could be derived from the corresponding histogram plots of the fitted slopes.

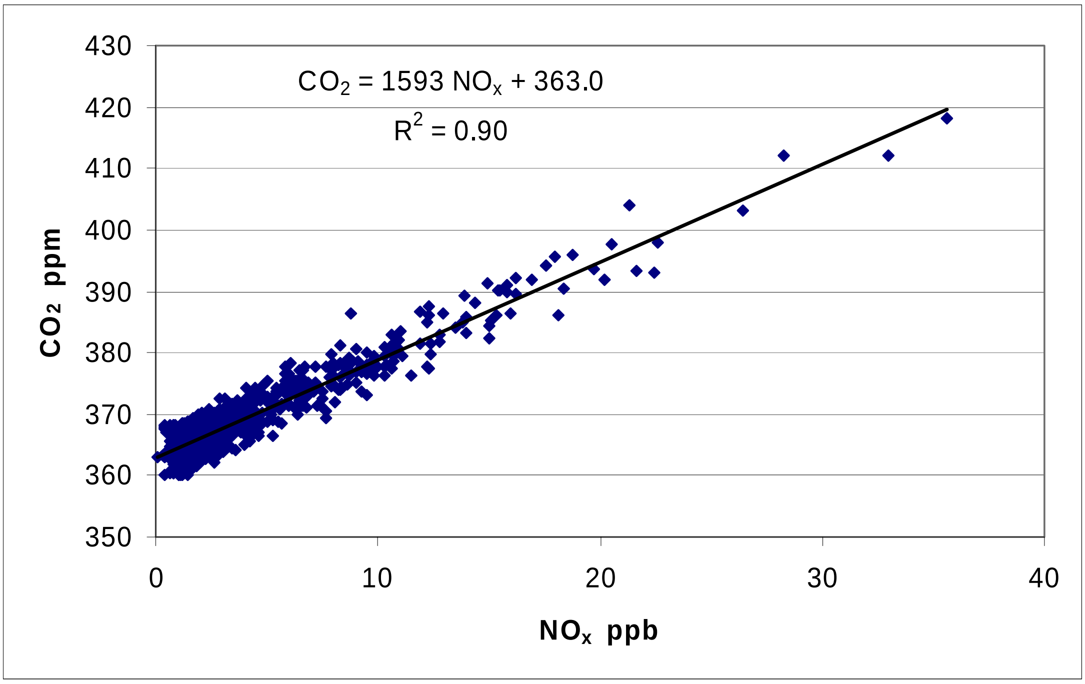

Figure 8. Scatterplot of CO_2 vs NO_x for 4-minute averaged data from the Upper Dam site during the Wagerup Pilot Study in 2005 (Galbally et al., 2006). .

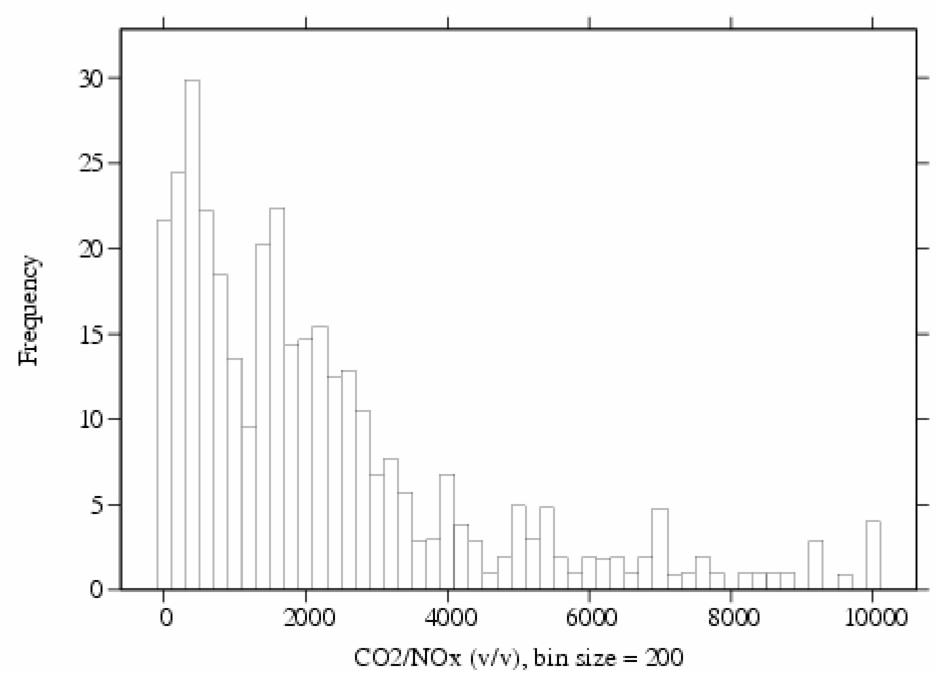

Figure 9. Histogram of slopes of three minute CO_2 vs NO_x regression lines. Each bin total is the sum of the r^2 values for the lines whose slopes lie within the bin.

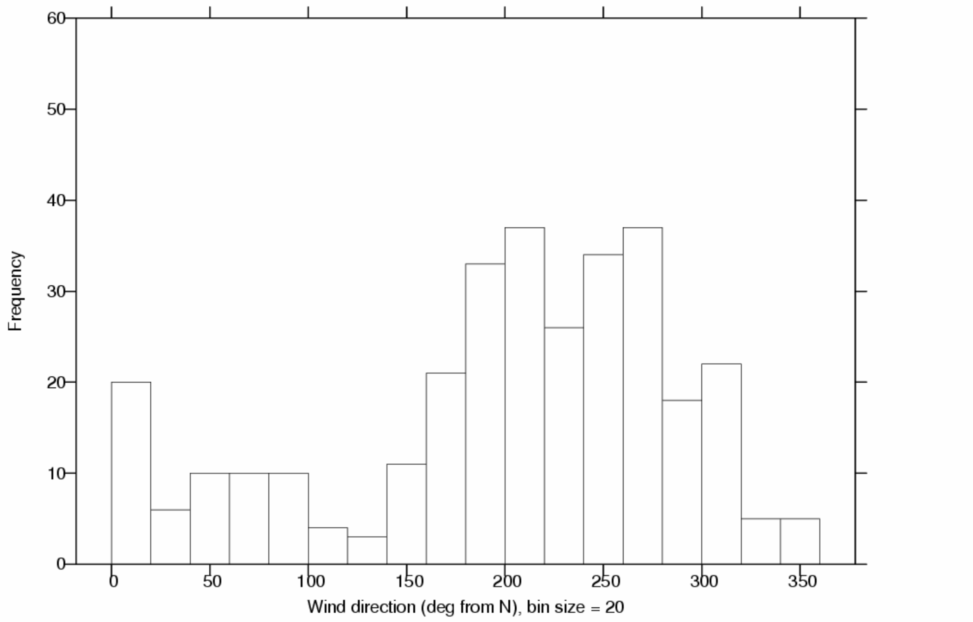

Figure 10. Histogram of wind direction corresponding to the points that were used to calculate the three minute CO_2 vs NO_x regression lines, and whose CO_2:NO_x slopes lie between 0 and 1000. This range of slopes includes the left-most modal peak in Figure 9.

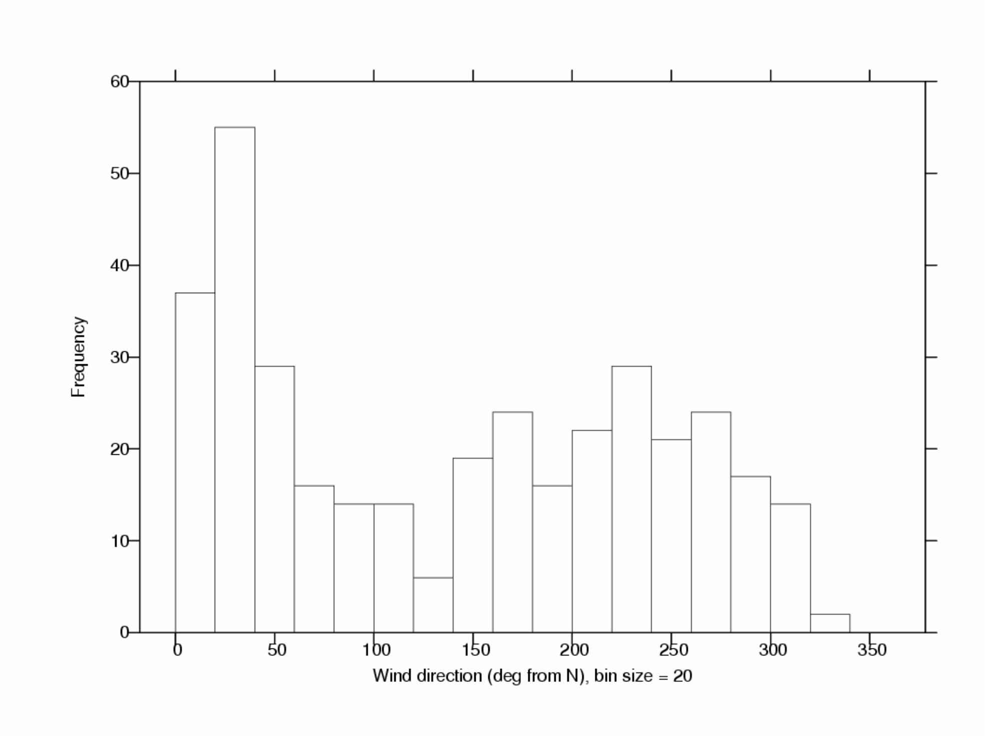

Figure 11. Histogram of wind direction corresponding to the points that were used to calculate the three minute CO_2 vs NO_x regression lines, and whose CO_2:NO_x slopes lie between 1000 and 2500. This range of slopes includes the modal peak that is second from the left in Figure 9.

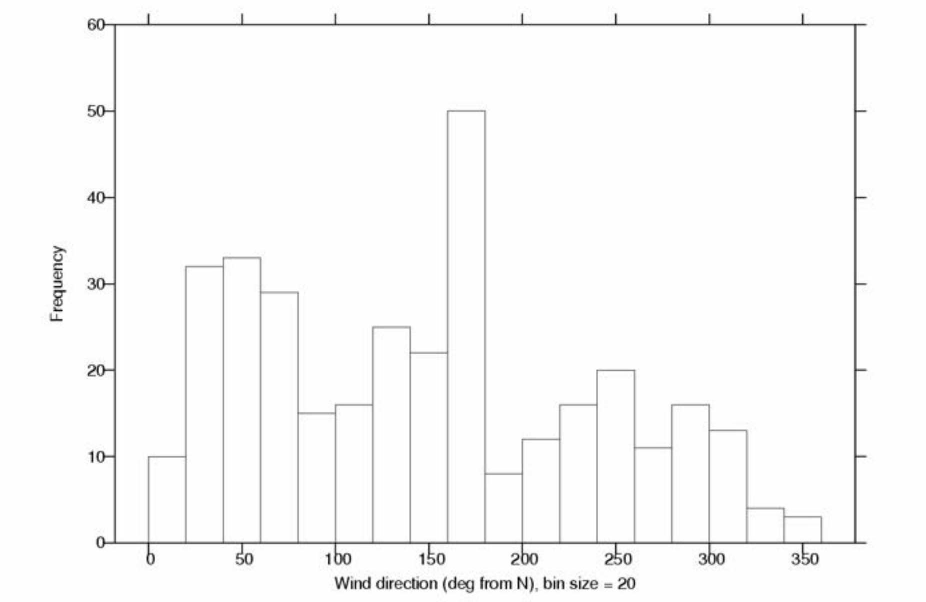

Figure 12. Histogram of wind direction corresponding to the points that were used to calculate the three minute CO_2 vs NO_x regression lines, and whose CO_2:NO_x slopes lie between 2500 and 10000

3.4 Concentration and Wind direction

The variation of concentrations of compounds in the air with wind direction can give an indication of nearby sources, as was shown in the Wagerup Pilot Study (Galbally et al., 2006) and has been discussed in previous sections of this report.

In the subsequent analysis the data are analysed both by wind direction and time of day. Wind direction and time of day are not two independent variables. At the Boundary Road site the dominant wind direction during the day is from the westerly sector (200^o to 300^o) and at night from the broad south easterly sector (60^o to 200^o). Winds from the Refinery direction $0\text{-}60^o$ occur throughout the 24 hours, with slightly increased frequency at 0700-1000 hrs in the morning. Winds from the direction of the Residue Disposal Area, RDA, and highway (300^o to 360^o) occur more frequently during the daytime than at night. These changes of the frequency of wind directions with time of day must be borne in mind in the separate analyses of VOC statistics with wind direction and with time of day that are presented in this and the following section.

A systematic study was made of the variation with wind direction (observed at Boundary Rd) of all compounds measured during this Study[1] and the key outcomes are presented here. For the 24 masses that have detectable concentrations within the air, there were detectable concentrations under all wind directions. This is consistent with there being widespread sources of the associated compounds in the environment as was presented in Section 2. There were also variations of concentrations with wind directions that indicated a source for some of these compounds in the direction of the Refinery. For the masses corresponding to acetone (59) and acetaldehyde (45), known to be emissions from the Refinery (Alcoa 2002, 2005), there are distinct variations of concentrations above background with wind direction revealing higher concentrations in the air when the wind blows from the Refinery to Boundary Road, that is a direction of 10 degrees east of North. The statistics of mass 59 (acetone) concentrations and mass 45 (acetaldehyde) concentrations observed within 10 degree wind direction bins for all data are shown in Figure 13 and Figure 14. There are similar behaviours with peaks either slightly east or west of North for masses 33, and 43 as well as smaller peaks for masses 42, 47, 60, 61 and 73.

For mass 33 (methanol) the direction from which the peak concentrations come is broader than for masses 59 and 45 (see Figure 15). This indicates that the sources for mass 33 in the Refinery

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[1] Subsequent to the completion of the analyses in this report, it was discovered that a systematic analysis indicated that the wind directions at Boundary Rd used here were offset by approximately +20 degrees (Air Assessments January 2007). Thus wind directions at Boundary Rd shown in this report should be rotated anticlockwise by 20 degrees. This correction improves the agreement between the wind direction at the time of the VOC peaks in the Figures 13 to 16 and the direction of the Refinery.

could be more extensive and may encompass the eastern part of the RDA as well as the Refinery plant. The solubility of methanol in liquid could explain its transfer to the RDA from the main part of the Refinery because the residue is pumped to the RDA along with water that ends up in several dams in the RDA.. There is no other obvious source of methanol in the direction west of north from Boundary Rd.

For NO_x there is evidence of a source in the Refinery direction, East of North, consistent with the Refinery as a known source see Figure 16, There is also a NO_x source in the direction of Yarloop, south to south west of the Boundary Road site,. This is consistent with there being NO_x emissions from residential, light commercial and vehicular transport activities.

The variations of CO_2 and mass 81 (a fragment formed from monoterpenes) with wind direction show highest concentrations in easterly flow, see Figure 17 and Figure 18. We attribute this to CO_2 and terpenes both being emitted at night from vegetation and also to CO_2 being emitted from the soil, and these emissions being trapped in the stable night time boundary layer and bought to the Boundary Road site in the night time easterlies from the escarpment. This attribution is consistent with the subsequent analyses of diurnal variations in the next sub-section of this report.

The median concentrations of $CO_{2,}$ which include the daytime influence, show a broad peak in the North-Easterly direction that may reflect the Refinery CO_2 emissions. However the biogenic influences on CO_2 are much larger than the Refinery plumes, which can be deduced by scaling the CO_2 to the observed NO_x that occurs in winds from the Refinery. The NO_x increases in the Refinery direction are between 3 and 10 ppb, Figure 16. If these are scaled to CO_2 concentrations by the ratio of 1500, see Section 3.3, they correspond to Refinery plumes with CO_2 enhancements of 5 to 15 ppm CO_2. These enhancements are small compared with much of the variation in Figure 17. Thus in the air at Wagerup variations in CO_2 due to biogenic processes are evident, and the influence of the Refinery on CO_2 concentrations is minor.

The analysis shows that the compounds and masses detected in this Study occur in the air for all wind directions. The analysis by wind direction provides evidence that a number of masses, mainly 59, 45, 33 and 43 as well as NO_x have sources in the direction of the Refinery, consistent with the Refinery being a known source of VOCs and NO_x, as well as identifying NO_x, CO_2 and mass 81 (a fragment of monoterpenes) as having distinct sources in other directions.

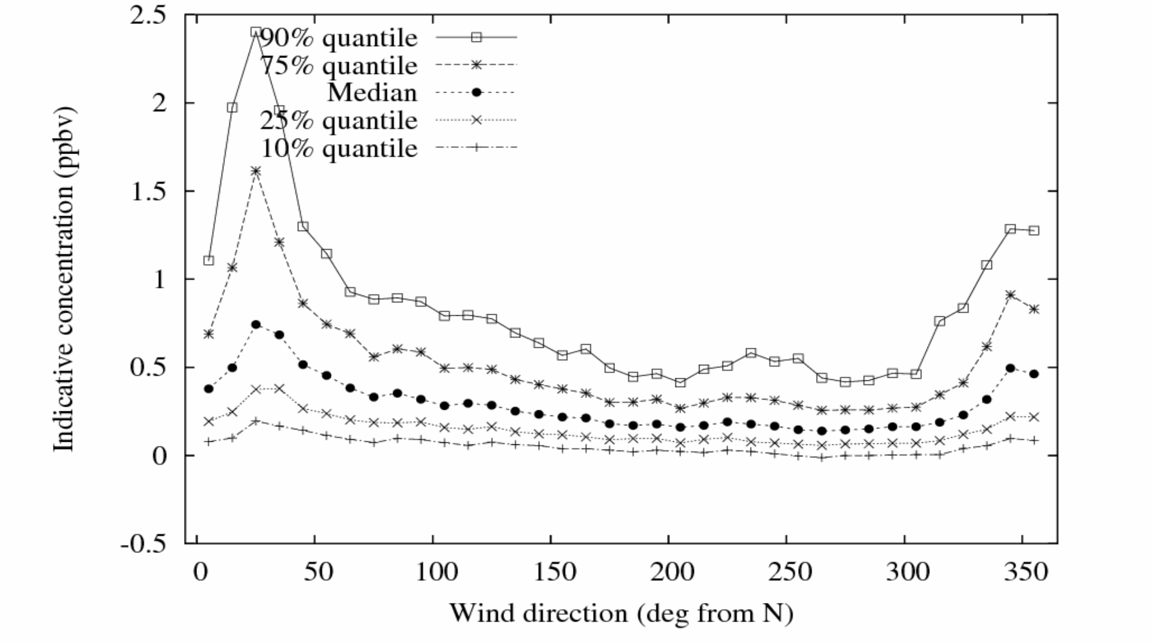

Figure 13. The statistics of mass 59 (acetone) concentrations observed within 10 degree wind direction bins for all data, Wagerup Winter Study 2006.

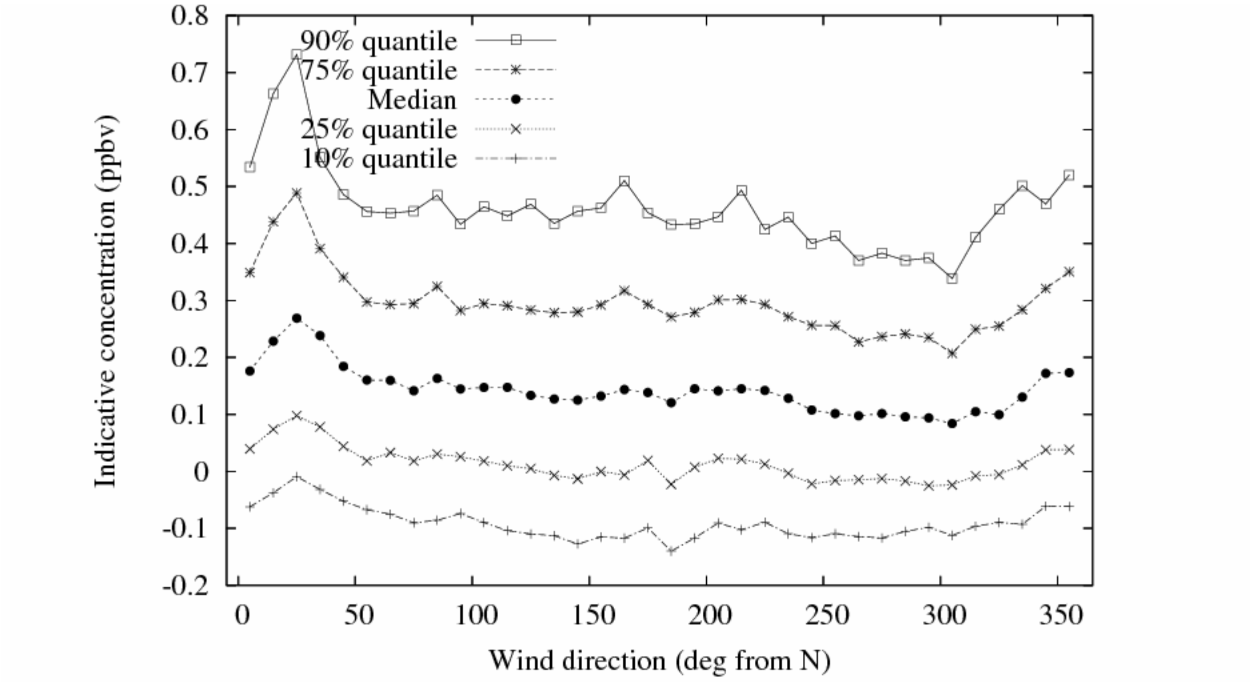

Figure 14. The statistics of mass 45 (acetaldehyde) concentrations observed within 10 degree wind direction bins for all data, Wagerup Winter Study 2006.

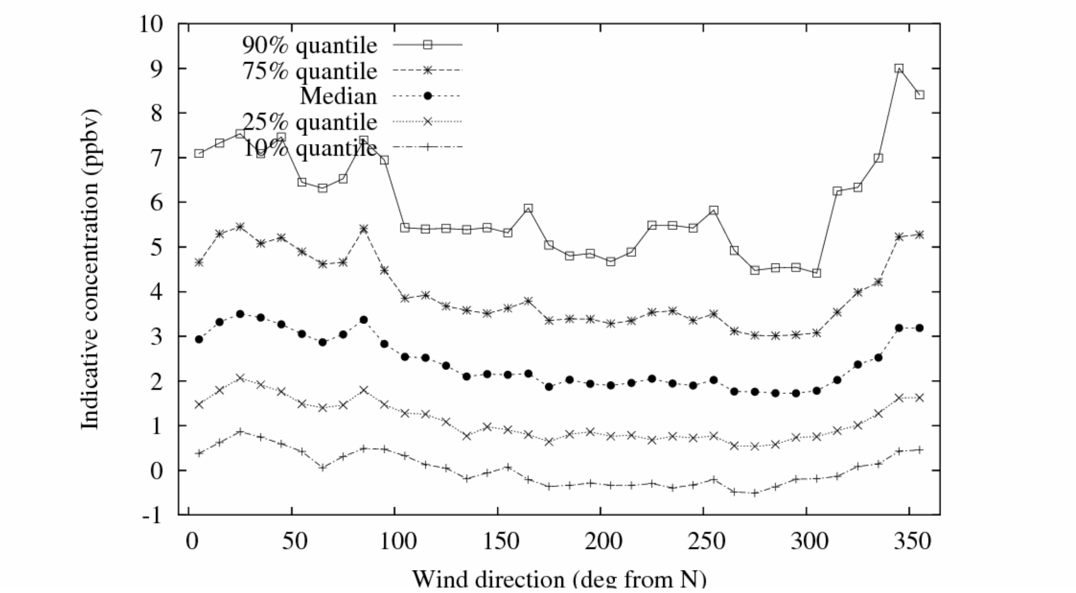

Figure 15. The statistics of mass 33 (methanol) concentrations observed within 10 degree wind direction bins for all data, Wagerup Winter Study 2006.

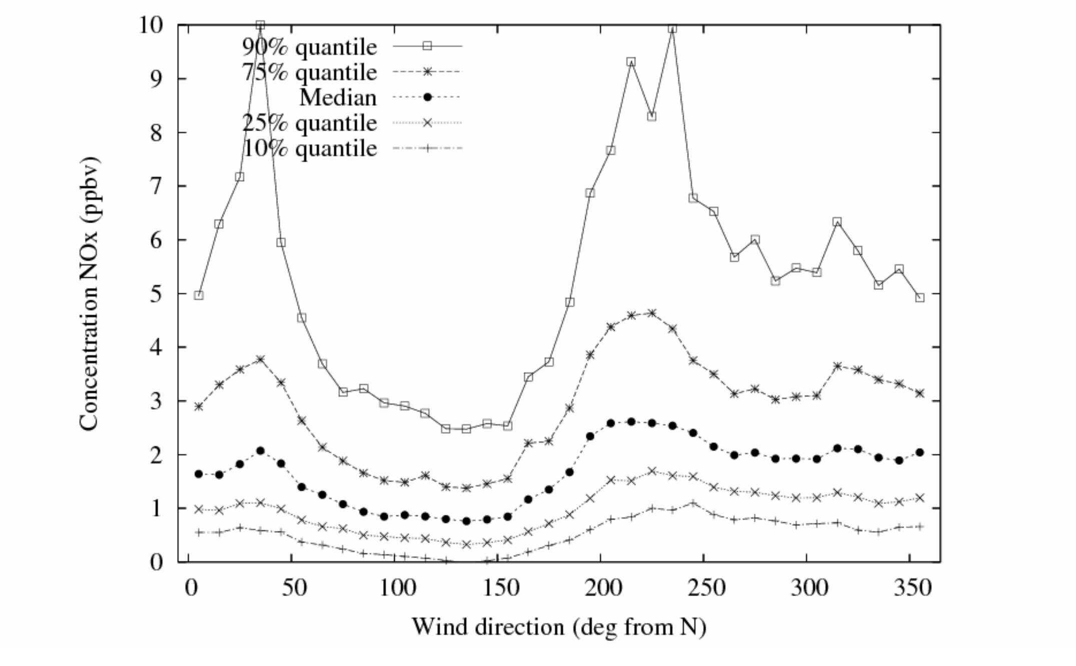

Figure 16. The statistics of NO_x concentrations observed within 10 degree wind direction bins for all data, Wagerup Winter Study 2006.

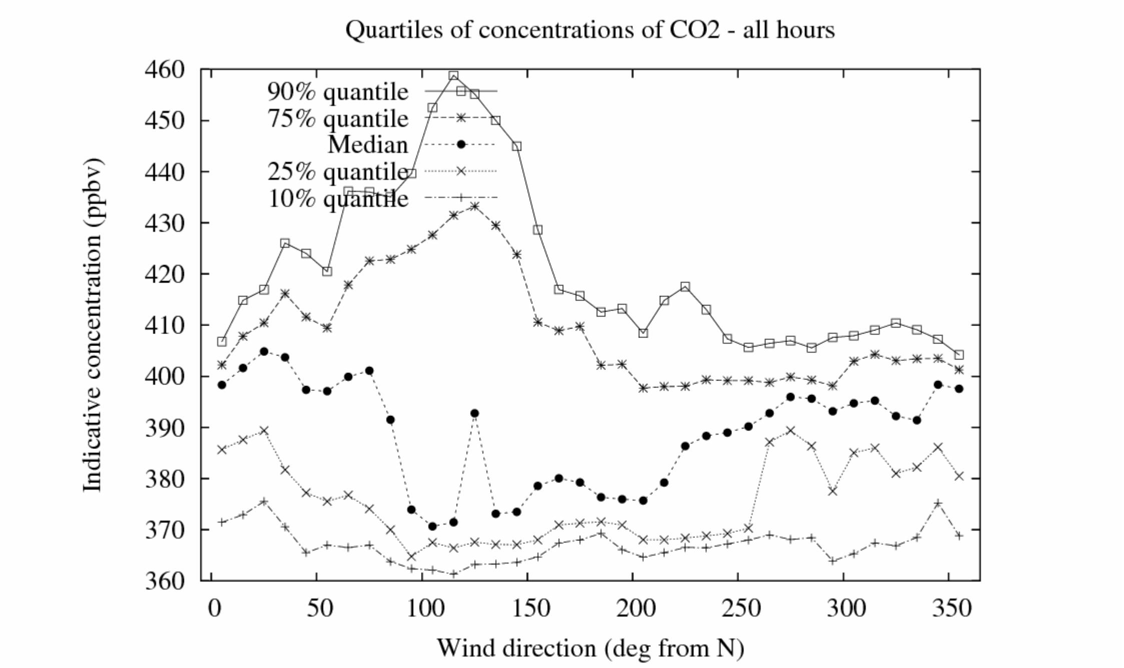

Figure 17. The statistics of mass carbon dioxide concentrations observed within 10 degree wind direction bins for all data, Wagerup Winter Study 2006.

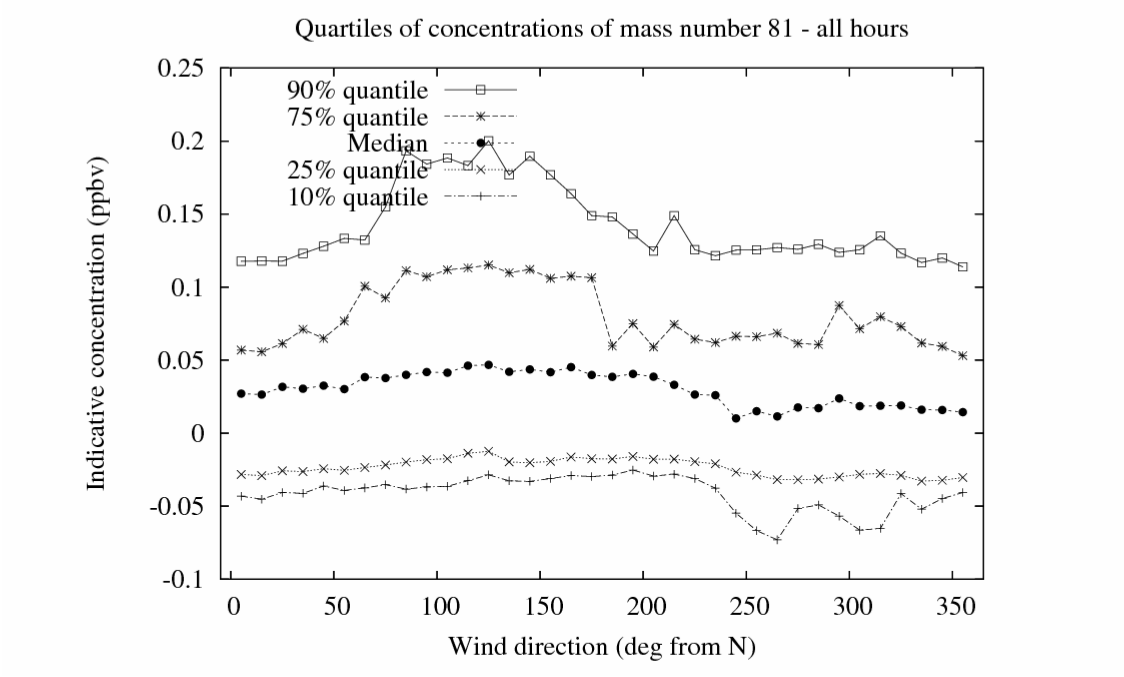

Figure 18 The statistics of mass 81 (fragmentation of monoterpenes) concentrations observed within 10 degree wind direction bins for all data, Wagerup Winter Study 2006.

3.5 Diurnal variation of concentration

The diurnal variation (day/night) variation in concentration of trace gases can provide information about the sources and sinks (removal) of trace gases in the atmosphere. The diurnal variation in the concentration of trace gases in near surface air (1 to 5m height), the height of the atmospheric composition measurements in this Study and also the height that people experience the air, depends on the balance of source, sink and transport processes during day and night. The three key processes are: (a) emissions (and at what height in the atmosphere these emissions occur) and/or production within the air; (b) local removal by either surfaces such as soil and plants or by chemical reactions within the air, and (c) transport particularly air mixing between the surface and the air layers overhead. Thus diurnal variations in trace species contain information about their sources and removal processes. What follows is a simplified explanation of these processes used to elicit information about sources, removal processes and atmospheric exchange happening at Wagerup. The explanations and diagrams include key features to show why diurnal variations occur, they do not include many of the complexities of the real atmosphere. In particular the complexities of topography and drainage flows are neglected and horizontal uniformity of the surface is assumed in this schematic whose purpose is illustrative. (Drainage flows are taken into account in the modelling and analyses presented in this report.) The schematic of these processes is presented in Figure 19 a-c.

At night solar radiation ceases heating the earth’s surface and the surface cools due to outgoing infrared radiation. The air immediately above the surface transfers heat to the surface and is thereby cooled. Two situations can occur. At night in light to moderate winds there is a shallow mixed layer near the earth’s surface where the mixing is driven by wind shear and this is represented by the circles in Figure 19. At night in clear skies in very light winds this layer does not develop. Above this mixed layer at night, or above the surface in very light winds, a stable layer of air, of up to 100m or more depth, with little or no vertical mixing, called a nocturnal or radiative inversion forms due to the ongoing cooling at the surface. Above the nocturnal inversion the air is not directly cooled by the surface.

During the daytime there are usually turbulent air motions that mix the air vertically. This vertical mixing during the daytime is due to a combination of turbulence produced by the wind and convective mixing which is driven by the sun heating of the earth’s surface and this is shown by the ellipses in Figure 19. This convective mixing can rise to heights between 500m and 3 km and in anticyclonic (or high pressure) weather the mixed layer is overlain by a subsidence inversion.

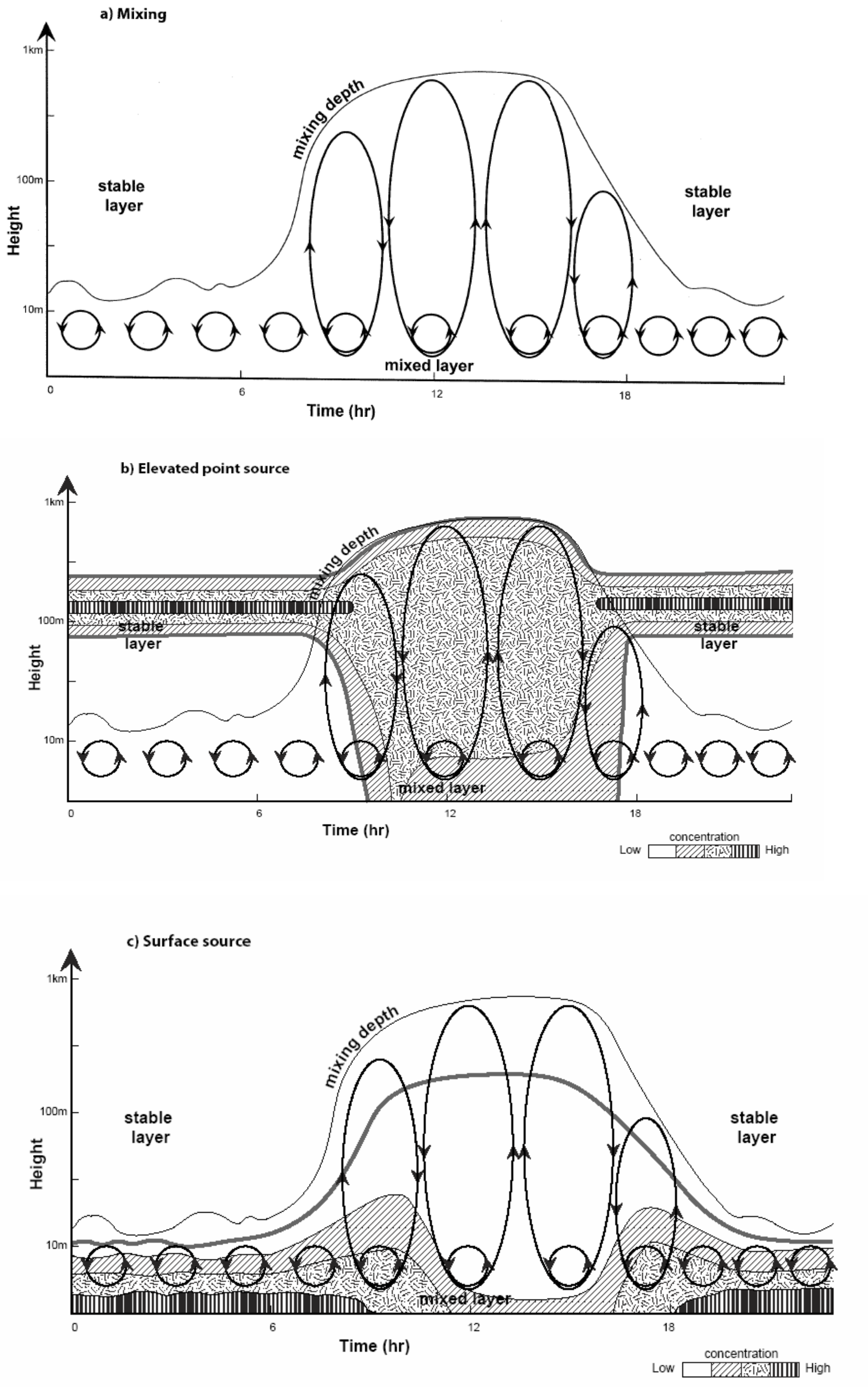

Figure 19. A schematic of the diurnal variation of mixing in the atmospheric boundary layer and the day/night variation of concentration of compounds emitted from an elevated and surface source. This figure includes key features to show why diurnal variations occur; it does not include many of the complexities of the real atmosphere.

Based on these ideas we can give a simplified explanation for the observed diurnal variation in concentrations. For gases that are emitted from elevated sources into the stable air, the gases will usually not be observed or be present at low concentrations in surface air at night because of the lack of vertical mixing to bring them to the surface, see Figure 19b. After sunrise, as the mixed layer grows, when it incorporates the air layer containing the emitted gases, but before the mixed layer has grown deeper, higher concentrations of the gases can be bought down to the near surface air.

This process is called fumigation (CSIRO 2004a-c), CSIRO 2005a-b). Then during the rest of the day, depending on whether either wind driven turbulence or convective mixing dominates, lower concentrations or comparable concentrations will occur in near surface air compared with those observed at fumigation. In the same way, daytime mixing brings compounds that have their sources via chemical production, either in the free atmosphere or higher within the atmospheric boundary layer, down to the near surface air, enhancing the daytime concentrations of these compounds in near surface air compared with at night.

For gases that are emitted into near surface air both day and night, there will be an increase in concentration of these gases in the near surface air overnight, because the nocturnal inversion traps the gases near the earth's surface. During the daytime the vertical mixing reduces the concentrations of these compounds in near surface air by providing the diluting mechanism of vertical mixing through the atmospheric boundary layer. This is shown in Figure 19c. The Monin-Obukhov atmospheric stability parameter measured at Boundary Rd indicated that unstable (well mixed) conditions occurred at Boundary Rd on average between 0800 and 1600 h.

A major driver of diurnal variations in trace gas concentrations is the presence of sunlight during the daytime and its absence at night. The solar radiation activates plant processes that affect emission and uptake of trace gases by plants. Solar radiation also drives photochemical processes that both produce and destroy compounds in the atmosphere during the daytime but not at night.

An example of these processes is provided by carbon dioxide which is taken up by plants during the day, in the presence of sunlight, and released by plants and soil, day and night. The concentration of CO_2 in near surface air rises at night due to the ongoing emissions of CO_2 that are trapped within the nocturnal inversion and CO_2 decreases during the day time due to both plant uptake and mixing of the surface air with the deeper atmospheric boundary layer. This diurnal variation in CO_2 concentration is shown in Figure 20.

Monoterpenes are detected as a fragment at mass 81, and as shown in Figure 21, there are higher concentrations at night and lower concentrations during the daytime. The monoterpenes are emitted from trees both day and night. During the daytime those monoterpenes react with hydroxyl radicals and ozone and are destroyed within the air, but at night these chemical removal processes are reduced in rate and the monoterpenes increase in concentration. Thus the diurnal variation of CO_2 and mass 81 in the near surface air at Boundary Road show behaviour consistent with known natural sources and known boundary-layer processes.

Compounds from the Refinery are released into either (a) air close to the earth's surface from low level stacks or area sources such as the Redisue Disposal Area (RDA) that have emissions near ambient temperatures, or (b) higher levels in the atmosphere boundary layer from the taller stacks including those with hotter emissions. The compounds released from the taller stacks will be more readily transported into the near surface air during the daytime than at night when a nocturnal inversion is present. However in the observations of such compounds, the relationships are made more complex by the fact that all of the compounds observed in this Study have sources other than the Refinery in rural air, see Table 3.

In Figure 22 the diurnal variation of mass 59 (acetone) is presented. The diurnal variation of mass 59 (acetone) shows a daytime minimum. This indicates that mass 59 (acetone) emissions observed in near surface air are probably from the near surface sources which include emissions from vegetation and could include emissions from lower level stacks and vents. The Refinery emission data, Section 3.1, indicate that 70% of the acetone emissions are from low level sources which is consistent with the daytime minimum in acetone. Acetone has (as do several other compounds) a daily maximum concentration, particularly marked in the 90th percentile, shortly after sunset at 1900 to 2100 h. The cause of this maximum is not immediately evident and it will be discussed later.

The diurnal variation of mass 45 (acetaldehyde) is more complex to interpret. Figure 23 shows that mass 45 has its lowest concentrations around dawn and dusk, with higher concentrations during the daytime and early in the evening. Acetaldehyde is emitted by the Refinery both by low level and by elevated sources. Acetaldehyde may be emitted by vegetation and also formed from the atmospheric oxidation of ethane and propene (which are generally present throughout the atmosphere (Kivlighon et al 2000)) as well as other hydrocarbons, a process that would occur during the daytime. These sources may explain the daytime maximum of acetaldehyde. Early in the evening at around 1900 to 2100 hours there is a maximum in the concentrations represented by the 25th to the 90th percentiles, Figure 23. The sources described above do not explain the occurrence of this maximum observed in the early evening around 1900 to 2100 h, and the causes will be discussed later.

Mass 33 (methanol), seen in Figure 24, shows a similar chemical behaviour of a slight daytime maximum, a night time minimum, and a most pronounced maximum just after dusk. There may be two contributing sources of methanol. Vegetation emits methanol during the daytime (Galbally and Kirstine 2002). The Refinery appears to emit methanol, as was indicated in Section 7.5 and also in the Pilot Study Report (Galbally et al. 2006). These sources may explain the daytime maximum of methanol, but fail to explain the maximum observed in the early evening around 1800 to 2100 h.

Nitrogen oxides, NO_x, have a diurnal variation shown in Figure 25, with a maximum at around 0700 to 0800 h and a smaller peak at 1700 to 1900 h. These peaks may correspond to a combination of vehicles and residential activity, combined with the nocturnal inversion. Any morning fumigation of NO_x in elevated Refinery plumes may be contained in the 0800 h to 1100 h wing of the morning peak. Any daytime plume groundings of NO_x in elevated Refinery plumes must be of lesser concentration than the peaks caused by these other processes.

The diurnal variation of acetone, acetaldehyde and methanol all show maxima in concentration in the early evening around 1900 to 2000 h. Three possible causes of these early evening increases are explored.

The increase could be due to the presence of woodfires or biomass burning in the early evening. The afternoon to evening increase of mass 42 (acetonitrile), a marker of biomass burning, is 0.02 ppb between 1300 and 2000 h (not shown). This increase is sufficiently small that the increases in methanol, acetone and acetaldehyde cannot be explained by woodfires or biomass burning.

Alternately, some compounds that have their sources primarily during daytime in surface air may continue to be produced for a short period after the onset of the nocturnal inversion so that a peak in concentration in surface air occurs after sunset which is subsequently dissipated after the source ceases emitting. This model is challenged by the facts that the 1900 – 2100 h peaks of acetone and acetaldehyde are not consistent with the diurnal variations of CO_2, NO_x, and mass 81, although they appear consistent with benzene and toluene, shown in Figure 27, (Section 3.6), all of which have surface sources.

The final possible explanation involves consideration of air trajectories. It was discussed in Section 3.4 that the winds at Boundary Road tend to be from the westerly quadrant during the day and turn around to somewhere in the southerly and easterly quadrants on average around 1900 h. The wind data from the district for the daytime and evenings of 13th and 15th September in Figure 26 and Figure 30 (Section 3.7) show a northerly wind earlier in the day followed by a rotation through the westerly and southerly quadrants sometimes as far as the easterly quadrant and with quite a narrow distribution of wind directions at any time. These early evening peaks may be the result of re-circulation of air within the district and possibly drainage flows, which may or may not involve Refinery emissions. Three dimensional wind fields would be required to clarify whether such a circulation exists.

The evening pattern of concentration increases for selected compounds would appear to remain unexplained at this stage. An unexplained early evening event was observed and discussed in the summer Pilot Study (Galbally et al., 2006).

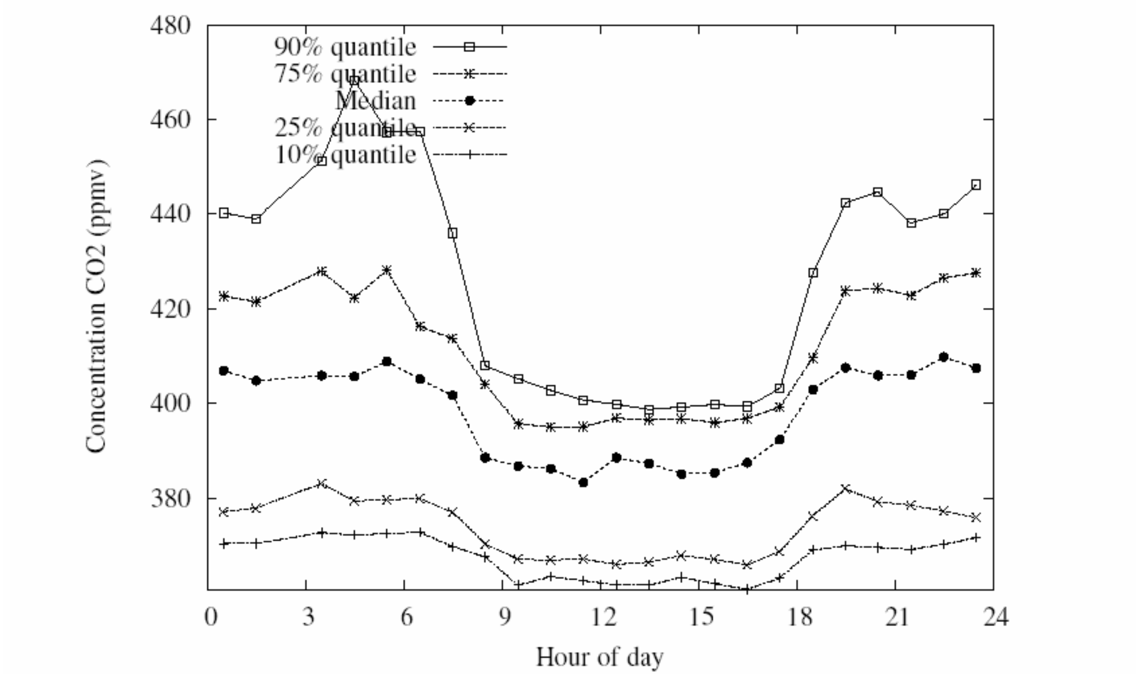

Figure 20. The statistics of concentrations of CO_2 within 1 hour wide bins for all data, Wagerup Winter Study 2006

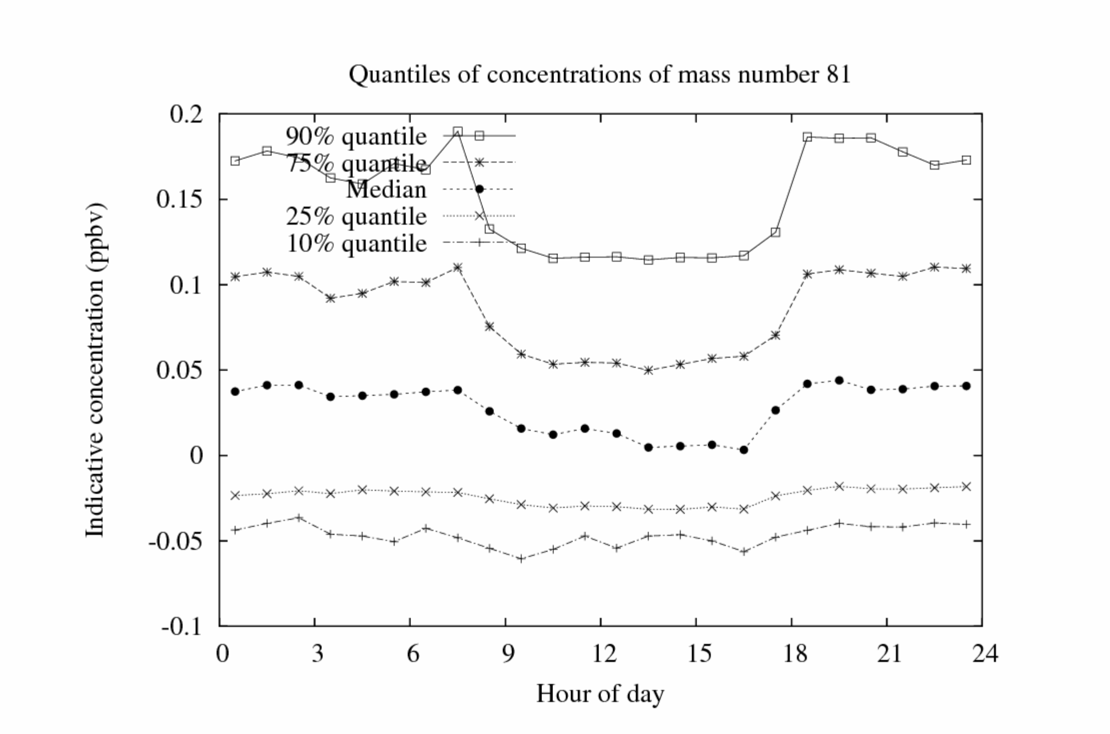

Figure 21. The statistics of concentrations of mass 81 (fragmentation of monoterpenes) within 1 hour wide bins for all data, Wagerup Winter Study 2006

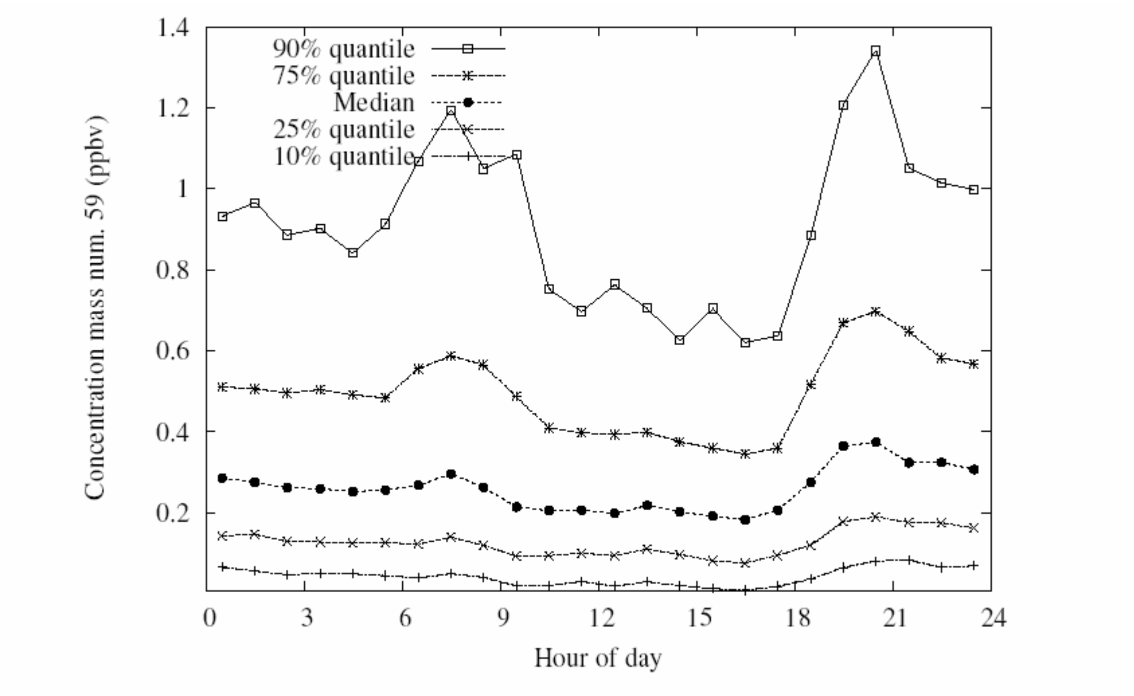

Figure 22.The statistics of concentrations of mass 59 (acetone) within 1 hour wide bins for all data, Wagerup Winter Study 2006

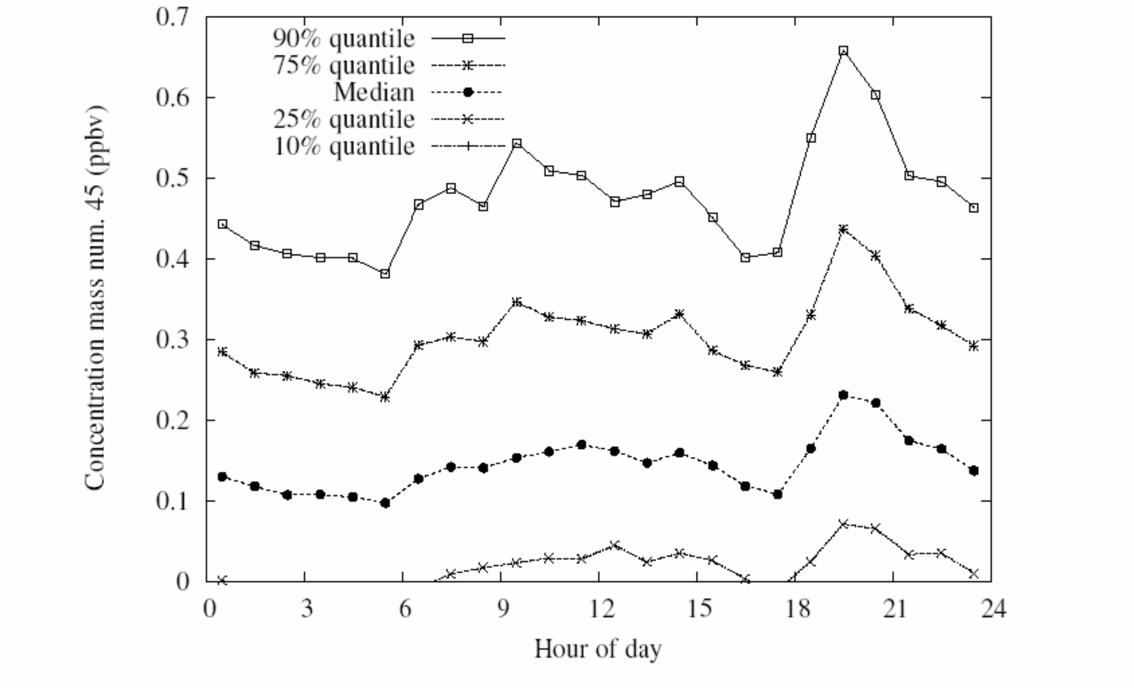

Figure 23. The statistics of concentrations of mass 45 (acetaldehyde) within 1 hour wide bins for all data, Wagerup Winter Study 2006

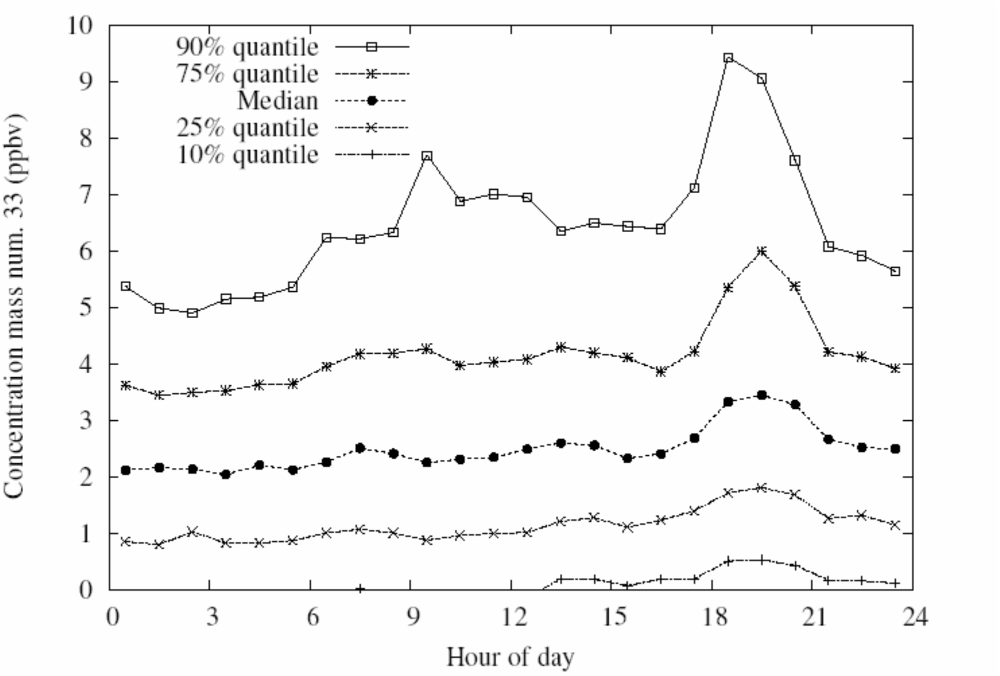

Figure 24. The statistics of concentrations of mass 33 (methanol) within 1 hour wide bins for all data, Wagerup Winter Study 2006

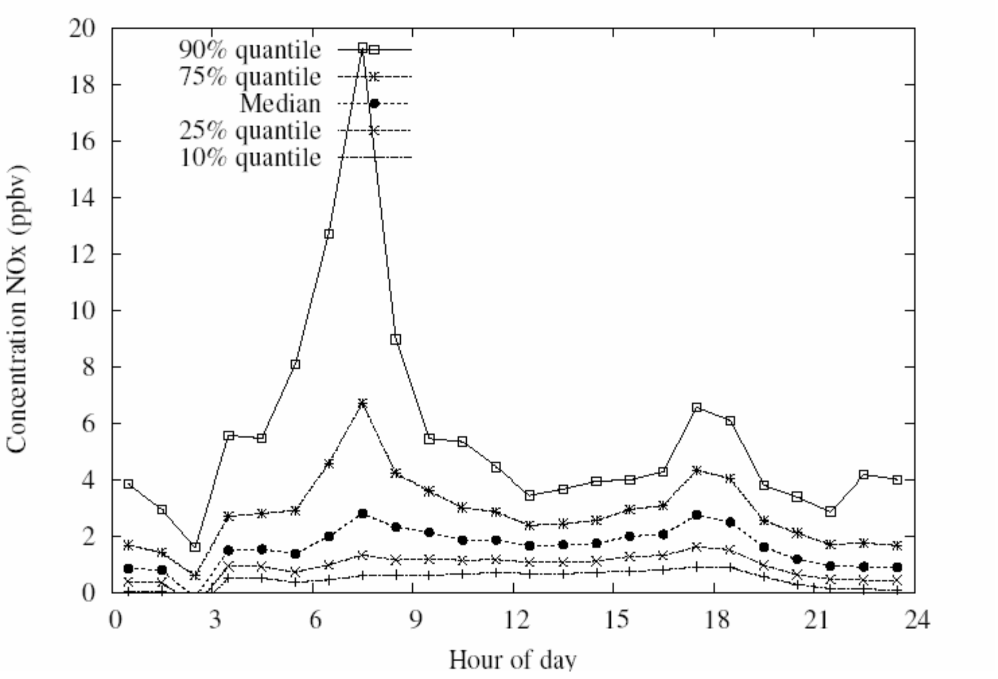

Figure 25. The statistics of concentrations of NO_x within 1 hour wide bins for all data, Wagerup Winter Study 2006

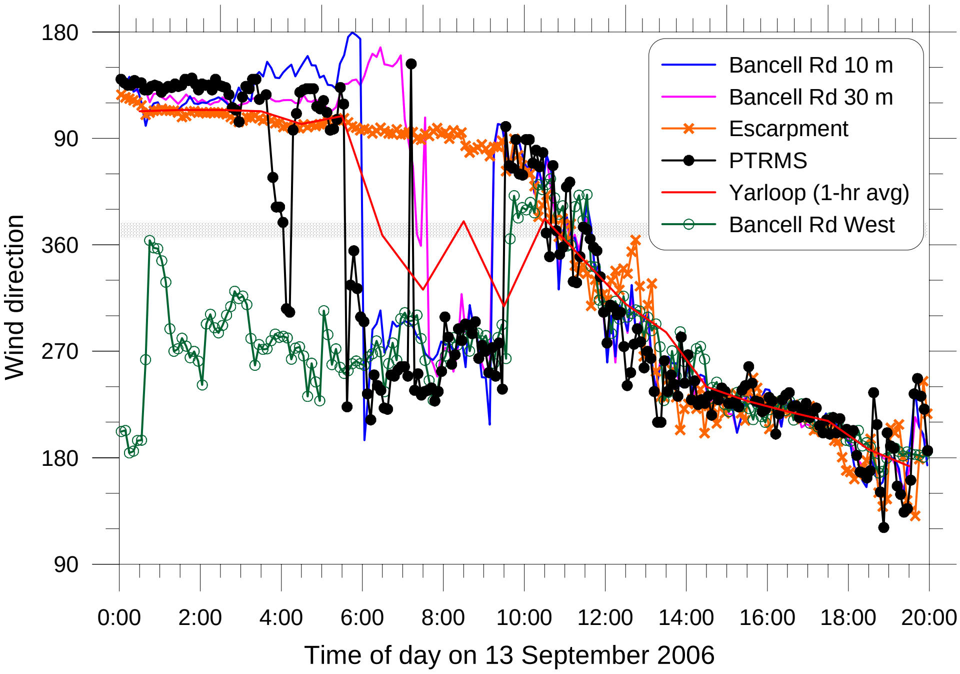

Figure 26. The wind direction for the district for the meteorological network on 13 September 2006.

3.6 Influence of South Western Highway

There are emissions of CO_2, CO, VOCs and NO_x from motor vehicle traffic on the South Western Highway approximately 160 m west of the Boundary Road site that could influence concentrations measured at the Boundary Rd site. Motor vehicle count rate was measured, as an hourly average, on the South Western Highway near the junction with Boundary Road during the Study. The South Western Highway is the nearest major traffic source to the Boundary Road Site.

The indicators available in this data set most characteristic of vehicle exhaust are benzene and toluene. The diurnal variation of vehicle count rate (vehicles per hour on the SW Highway), along with the diurnal variation of mass 79 (benzene) and mass 93 (toluene) two compounds associated with vehicle exhaust emissions (Duffey et al., 1999) are shown in Figure 27. The vehicle count rate reaches a maximum during the daytime as expected. There are peak concentrations in the early morning and early evening while stable atmospheric conditions prevail and lower concentrations when atmospheric mixing is more vigorous during the daytime. The Monin-Obukhov atmospheric stability parameter measured at Boundary Rd indicated that unstable (well mixed) conditions occurred at Boundary Rd on average between 0800 and 1600 h, consistent with the concentration variation in Figure 27. The diurnal variations of mass 79 and 93 are consistent with a surface source or sources that persists overnight.

There are other sources of benzene (mass 79) and toluene (mass 93) in the rural air at Wagerup.

Benzene and toluene are emitted from biomass burning including wildfires and woodheater burning. These biomass burning emissions contain more benzene than toluene (Scholes et al., 2002). The Refinery emissions inventory indicates that benzene and toluene are emitted at equal mass rates. Vehicle exhaust contains substantially more toluene than benzene (Duffey et al., 1998). The observed concentrations at Boundary Rd, Figure 27, show more toluene than benzene and therefore are most likely dominated by vehicle exhaust.

Benzene and toluene (masses 79 and 93) at Boundary Rd, on average make up 1.1% of the Total VOCs (TVOCs). Thus motor vehicle emissions make a minor but observable contribution to the TVOC concentrations observed at Boundary Rd.

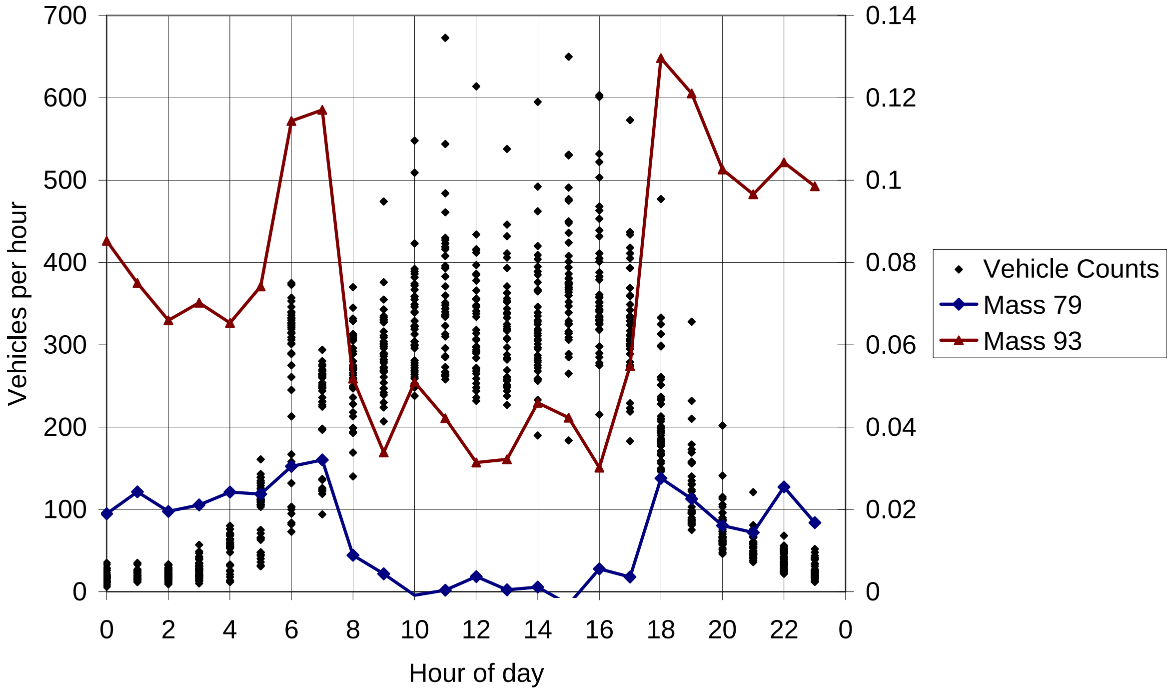

Figure 27. The diurnal variation of hourly vehicle count rate and the PTR-MS concentrations in ppb for mass 79 (benzene) and 93 (toluene) during the Wagerup Winter Study 2006.

3.7 Two odour events

Odour has been the cause of complaints in the Wagerup area as is summarised in CSIRO (2004). These odour complaints have been associated with the Refinery by wind direction (CSIRO 2004).

Two odour events observed at Boundary Road during the Winter Study are discussed in this section. The odour events analysed occurred on 18th August and 15th September 2006, and were selected because in both cases CSIRO personnel, and in the second case an independent observer at the site made and recorded several odour observations. The observations recorded were as follows. These observations are as written in the CSIRO station log. There was not a convention for recording odour observations at the site.

18 August 2007

“9:40 Wet cement smell

9:51 Odour distinct wet cement, slightly more acetone

10:02 Odour still distinct

10.05 Odour still distinct but weaker

10:18 Odour faint

10:26 Odour faint but discernable and identifiable”

15 September 2007

“9:15 Cement smell quite strong. David Pitt taking sample and notes. Odour 2.5-3 on a scale with a maximum of 6.

9:30 Smell is low

9:47 No smell

10:04 Whiffs of smell

11:16 No smell”

These two occasions are analysed in detail here. On each occasion there were no odour observations taken by CSIRO staff prior to the indicated times. For each of these odour days, wind direction and wind speed data from different sites were analysed according to time of day[2]. Figure 28 shows wind direction data from 18th August between 8:00-12:00 at the Escarpment, Bancell Rd at two heights (10 and 30m), Bancell Rd West and at the Boundary

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[2] This wind direction data was drawn from a database that had already been corrected for a 20° rotation offset of the Boundary Rd data, described in Section 3.

Road sites. The shaded area of the plot represents the direction of the 100 m multiflue stack from the PTR-MS at Boundary Rd. During the time the observed odour was strongest (approximately 9:40-10:05), the wind direction at the Escarpment and the Bancell Road sites overlaps with the shaded Refinery stack direction shown on the plot. The wind direction at Boundary Road at this time is further to the west, between 350-360 deg. The wind speed data from 18th August is shown from 0:00-12:00 in Figure 29, and the wind speed varies between 3 and 6 m/sec during this first odour period.

Figure 30 shows the wind direction data from 15th September between 0:00-20:00 at the Escarpment, Bancell Rd at two heights (10m and 30m), Bancell Rd West and at the Boundary Road sites. The increase in wind speed and alignment of all wind directions between 8:00 and 9:00 provides evidence of the breakdown of the nocturnal surface inversion at this time. At the time the odour was observed to be the strongest (09:15), the wind direction data from all sites corresponds very well with the shaded area of the plot which represents the direction of the Refinery stacks. As the observed intensity of odour decreases from 9:30 onwards, the wind direction moves further west, away from the Refinery. The wind speeds at different sites during this second odour period vary between 3-6 m/sec (Figure 31).

The relationship between observed odour at the Boundary Rd site and enhanced concentrations of chemical species was then investigated. Figure 32 shows mass 59 (acetone) and NO_x concentrations measured at Boundary Road on Odour day 1, 18th August. The time period where odour was observed at the site is highlighted in grey. The observation of odour coincides with elevated levels of mass 59 (acetone), with the strongest odour observations occurring between 09:40-10:02 then decreasing over time, which corresponds with the acetone concentrations which decrease alongside the odour. Unfortunately it was not possible to confirm the presence of odour prior to 09:40 when the acetone concentration was at its peak, as there were no personnel at the site at this time. The peak of NO_x at 09:28 appears to correspond with the acetone peak indicating that both species may have originated from the same source or at least on the same bearing from the Boundary Road site. No other increases in the detected PTR-MS masses or AQMS species were seen during the observed odour. Acetone increased later in the day around 1500 hrs. There was heavy rain at the site around this time and no odour observations were made.

Figure 33 shows mass 59 (acetone), NO_x and delta CO_2 during the second odour event on 15th September. Again the period where odour was observed is highlighted in grey. As with the previous figure, an increase in mass 59 (acetone) corresponds with the strongest observation of odour. There is also a peak in NO_x and delta CO_2 10 minutes prior to the observation of odour and the corresponding peak in mass 59. However as the NO_x / CO_2 and mass 59 peaks are offset from one another it is unlikely that they are from the same source. The ratio of the short term enhancements of CO_2 to NO_x in this peak are approximately 2000, consistent with Refinery emissions.

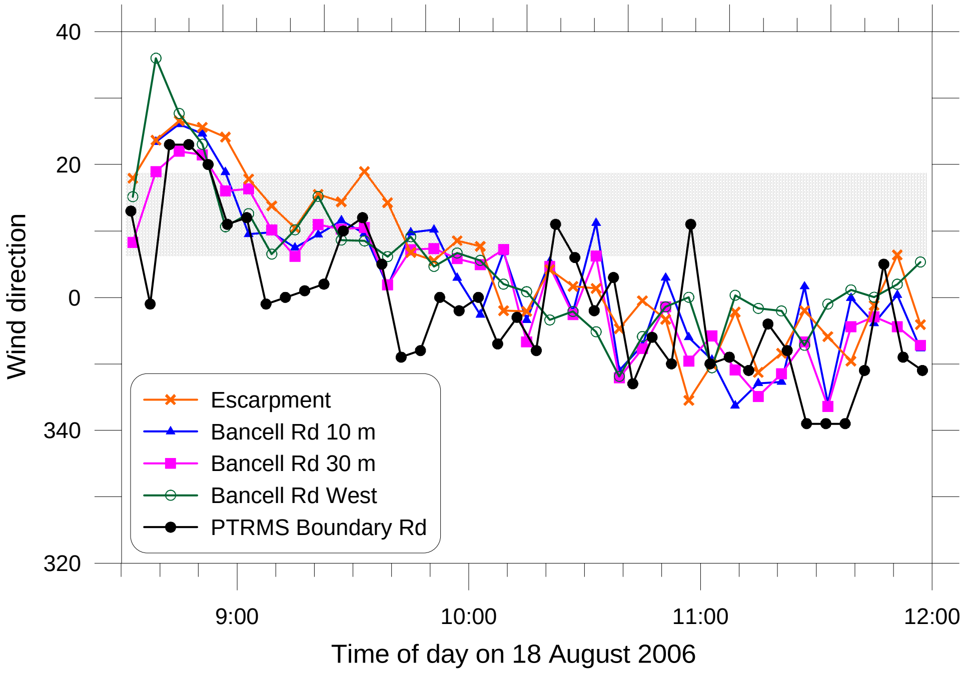

Figure 28. Wind direction measurements versus time of day on first Odour day, 18 August 2006. Shown are wind direction measurements for the PTR-MS site and several sites nearby.

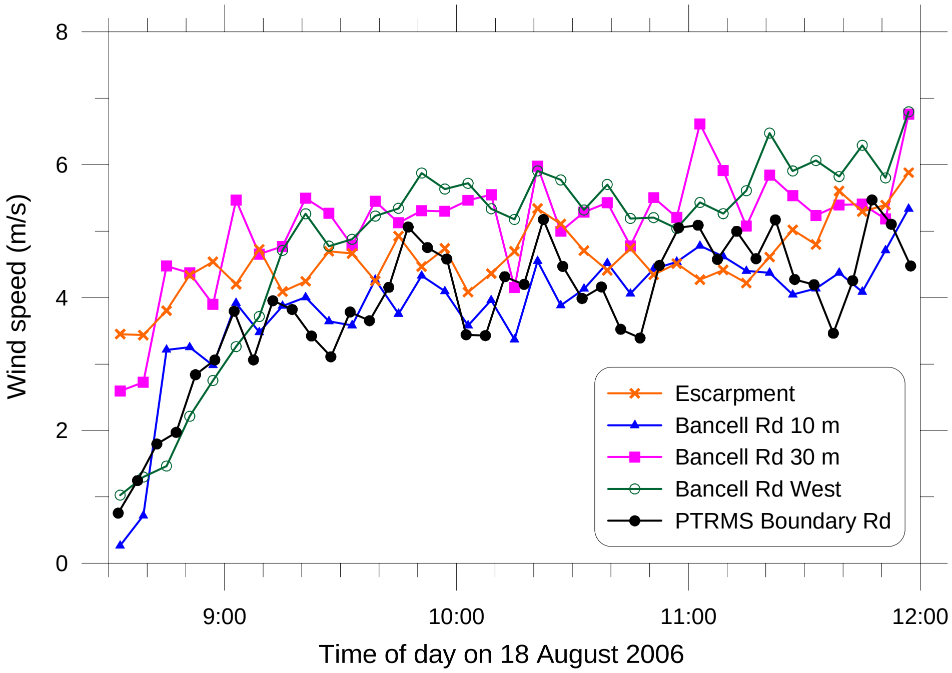

Figure 29. Wind speed measurements versus time of day on first Odour day, 18 August 2006. Shown are wind speed measurements for the PTR-MS site and several sites nearby.

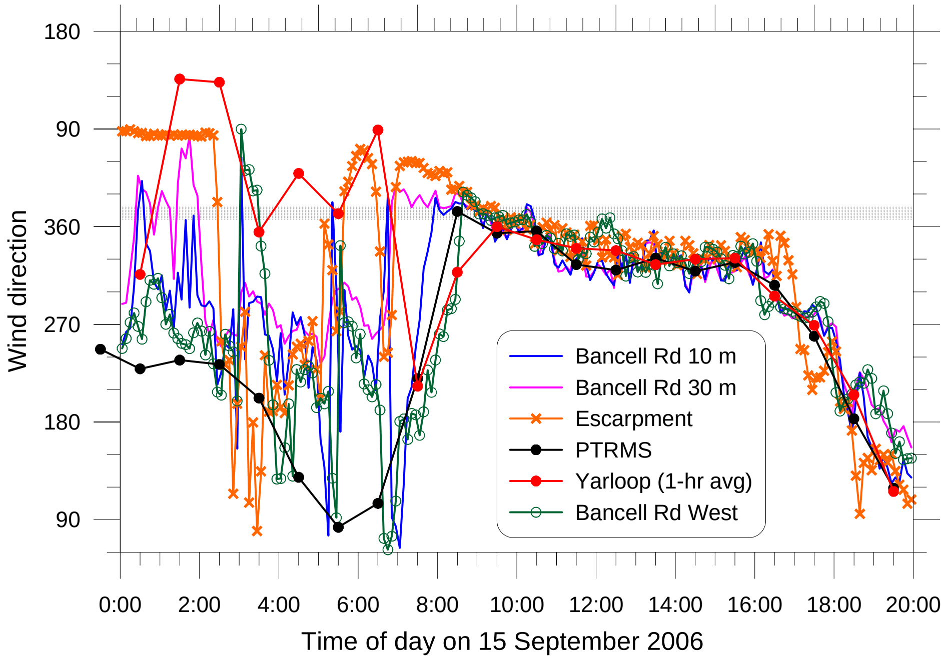

Figure 30. Wind direction measurements versus time of day on second Odour day, 15 September 2006. Shown are wind direction measurements for the PTR-MS site, and several sites nearby.

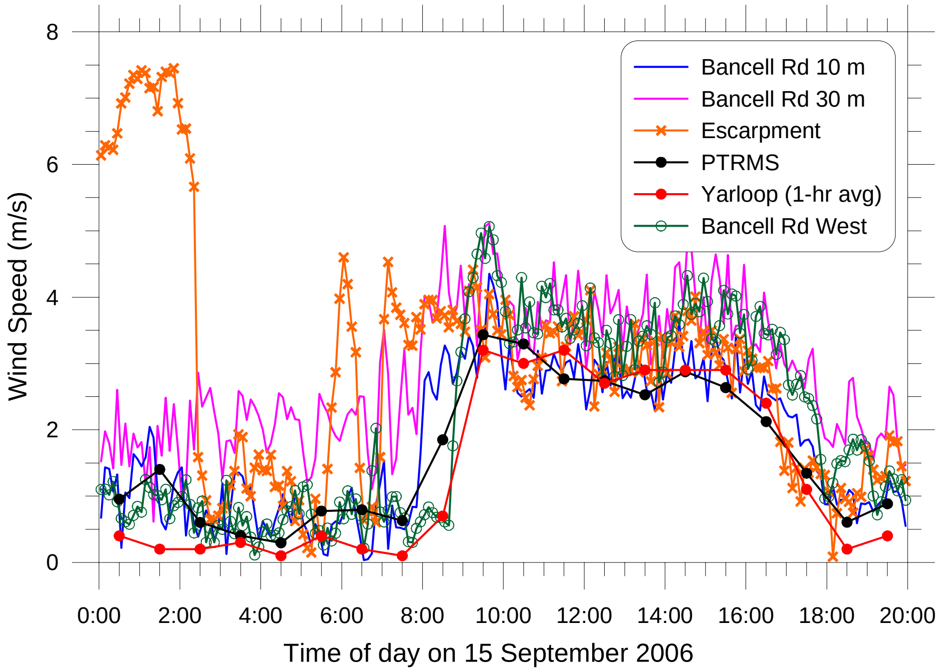

Figure 31. Wind speed measurements versus time of day on second Odour day, 15 September 2006. Shown are wind speed measurements for the PTR-MS site, and several sites nearby.

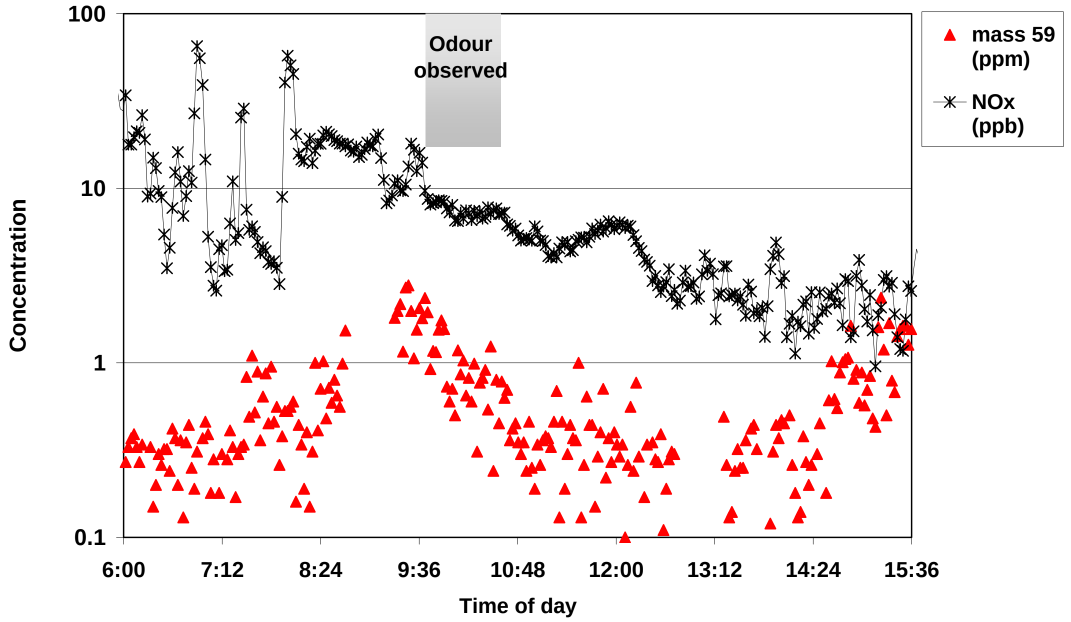

Figure 32. Concentration of NOx and mass 59 (acetone) versus time of day at Boundary Road on Odour day 1, 18th August. The time period where odour was observed at Boundary Road is highlighted in grey.

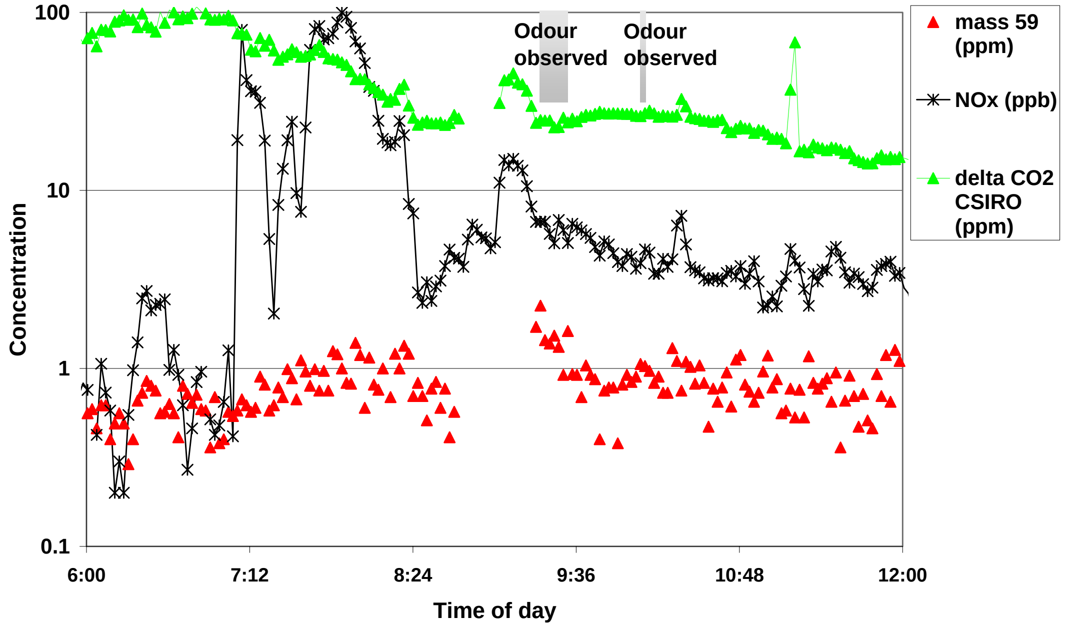

Figure 33. Concentration of NOx and mass 59 (acetone) versus time of day at Boundary Road on Odour day 2, 15th September. The time period where odour was observed at Boundary Road is highlighted in grey.

To understand these two odour events better the air quality model TAPM was used for modelling of the 18 August and 15 September 2006. The TAPM modelling was undertaken using the same meteorological grids as those used in the CSIRO modelling for the Wagerup ERMP in 2005. Four nested domains of 31 × 31 horizontal grid points were used with resolutions of 20-km, 7-km, 2-km and 0.5-km. The grids are all centred on the location 115°54′ E, 32°54.5′ S (AGD84 geodetic system), which is equivalent to 397.272 km east and 6358.475 km north in the MGA94 (Map Grid of Australia 1994) coordinate system. The lowest ten of the 25 vertical levels were 10, 25, 50, 100, 150, 200, 250, 300, 400 and 500 m, with the highest model level at 8000 m. Nested pollution grids of 53 x 53 grid points were used at double the resolution of the meteorological grids, i.e. the resolution of the innermost grid was 250 m. The building file used in the ERMP modelled (with coordinates adjusted to MGA94) was used. The Lagrangian mode was used for the innermost grid. The default databases of topography and deep soil parameters (with a deep-soil moisture content of 0.15) were used. Modelling used TAPM Version 3.07 with the new 2007 Wagerup land use file as developed by Environ (WG3 Land Use Classification, 27 March 2007, [Wag_luse.dat, 8701 bytes, 26/03/2007]).

The average and peak odour emission rates from the Wagerup Refinery (Alcoa 2005, EPA 2006) are given in Table 9. The average emission rates were used in the TAPM modelling.

Table 9. Odour emission rates from the Wagerup Refinery (Alcoa 2005, EPA 2006).

Source	Odour emission rate ERMP Current Refinery	
	Average (OU/s)	Peak (OU/s)
Cooling Pond	650,000	650,000
RDA	400,000	400,000
25A vents	329,000	344,000
45K Cooling Towers 2 & 3	251,000	691,000
45K Cooling Tower 1	173,000	474,000
100 m Multiflue (Calciner 1-3)	223,000	379,000
Calciner 4	80,000	113,000
Boiler Multiflue	27,000	33,000
50CT Cooling Towers	24,000	106,000

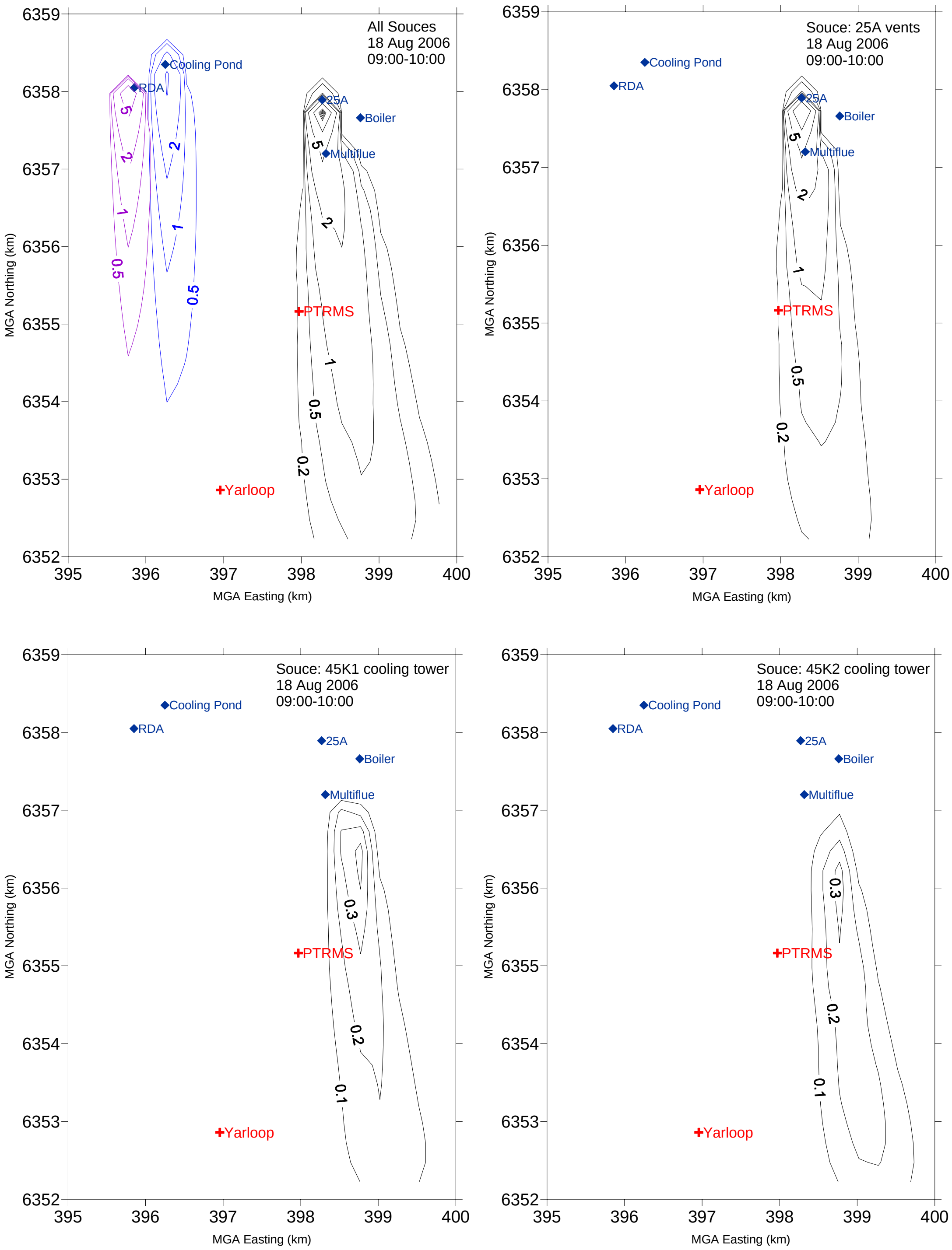

Figure 34. Modelled ground-level odour concentrations in odour units on 18 August for the indicated hours for the sources with the largest impact on ground level concentrations.

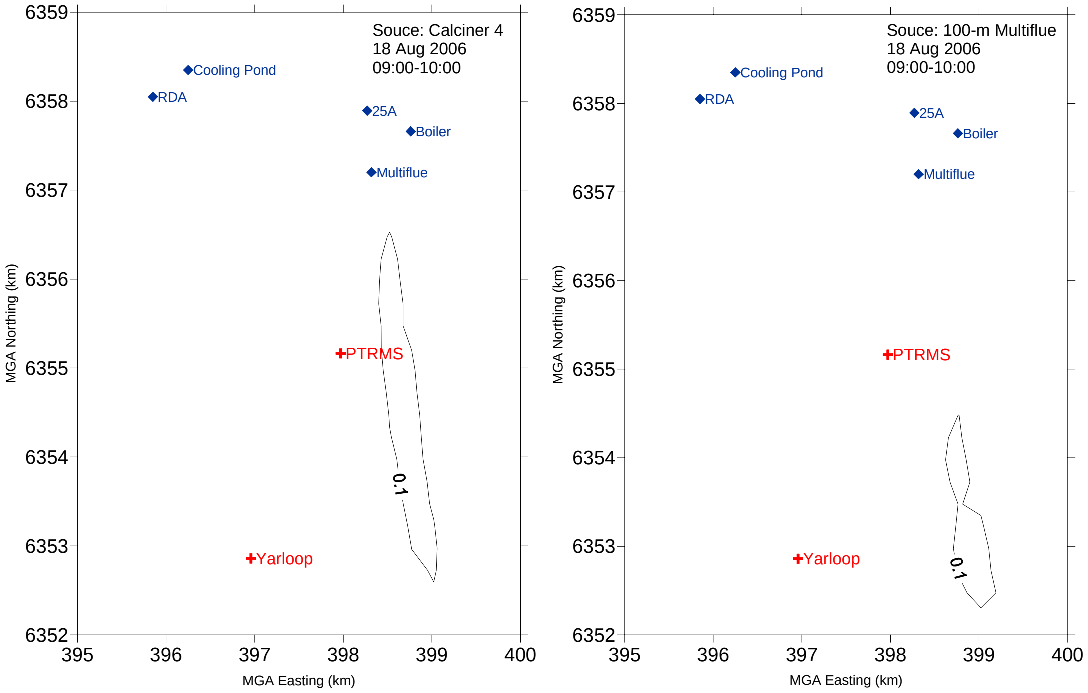

Figure 34 ctd. Modelled ground-level odour concentrations in odour units on 18 August for the indicated hours for the sources with the largest impact on ground level concentrations.

The modelled hourly average ground-level odour concentrations due to odour emissions from several sources are shown in the multi panel Figure 34 for the 18 August with the sources identified in the legends. The panels of Figure 34 show that a range of sources could be responsible for the observed odours. It should be noted that the timing of wind shifts is not always accurately predicted by the modelling.

The TAPM modelling presented in Figure 34 indicates that that the main Refinery area rather than the RDA or Cooling Pond contributed the odour at 0900 to 1000 h on 18th August. The source of the odour is identified from the panels in Figure 34 as most probably the 25A Vents. The Cooling Towers, Calciner 4 and the multi-flue 100m Stack do not contribute odour at the PTR-MS site at this time according to the modelling. The modelling output covers 0900 to 1000, the period in which the odour was detected.

TAPM modelling of the ground-level acetone concentrations on 18 August is shown in Figure 35. The sources included were the 100 m Multiflue, Calciner 4, Boilerhouse Multiflue, 45K Cooling Tower 2 and 3, 25A, RDA, and Cooling Pond. The emission rates were those summarised in Table 5 from the file Emissions_WGVOCs_Full_HRA_draft_5_may29.xls. Because of minor differences between the modelled and observed wind directions and the rate at which the wind direction is changing, the results are shown along an east-west transect through the PTR-MS site (the AMG Easting axis is parallel to Boundary Road). The y-axis shows the time of day from 06:00 to 11:00 (end of modelled hour) and the height is the modelled acetone concentration. The maximum modelled concentration at the PTR-MS site is 3.5 ppb due to 25A emissions between 06:00 and 08:00, and 1 ppb due to emissions from 25A and 45K2 later in the morning. These 1-hour average peaks are within a factor of two of the PTRMS measurements in Figure 32, which show an increase from approximately 0.3 to 1.5 ppb between 07:00 and 10:00. The location of the PTR-MS site is at an AMG Easting of 398 km, but given the uncertainty in modelled wind direction, the measured acetone could be from either of the peaks, i.e. from the 25A Vent or the Cooling Towers.

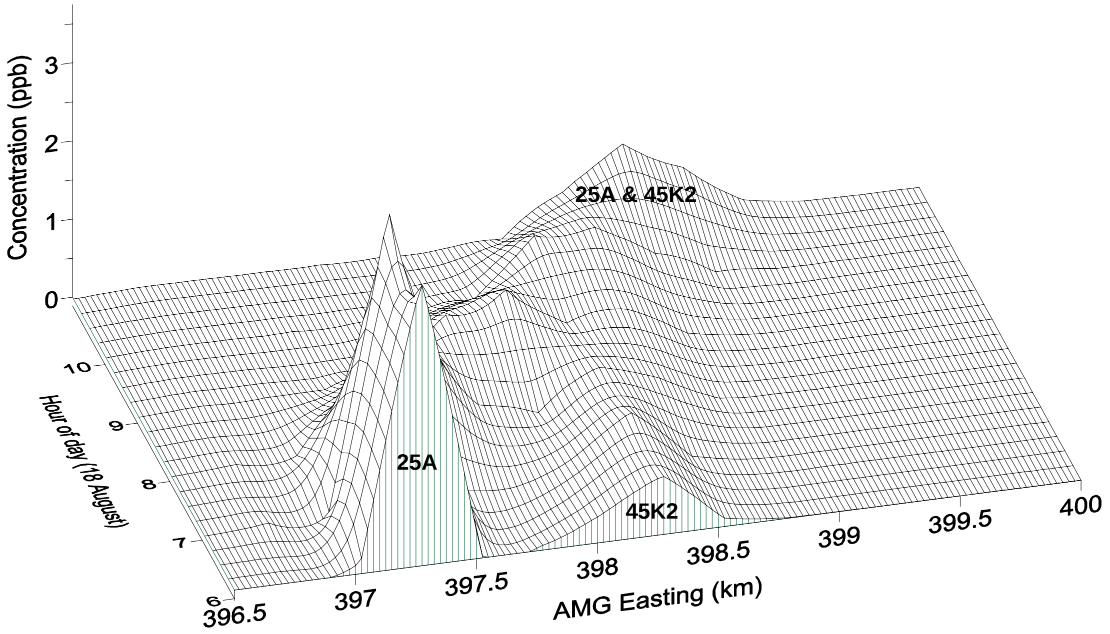

Figure 35. Modelled ground-level acetone concentrations on 18 August east-west along Boundary Road for the hours from 06:00 to 11:00. The results are plotted in this form because of uncertainty in the timing of the modelled wind direction changes.

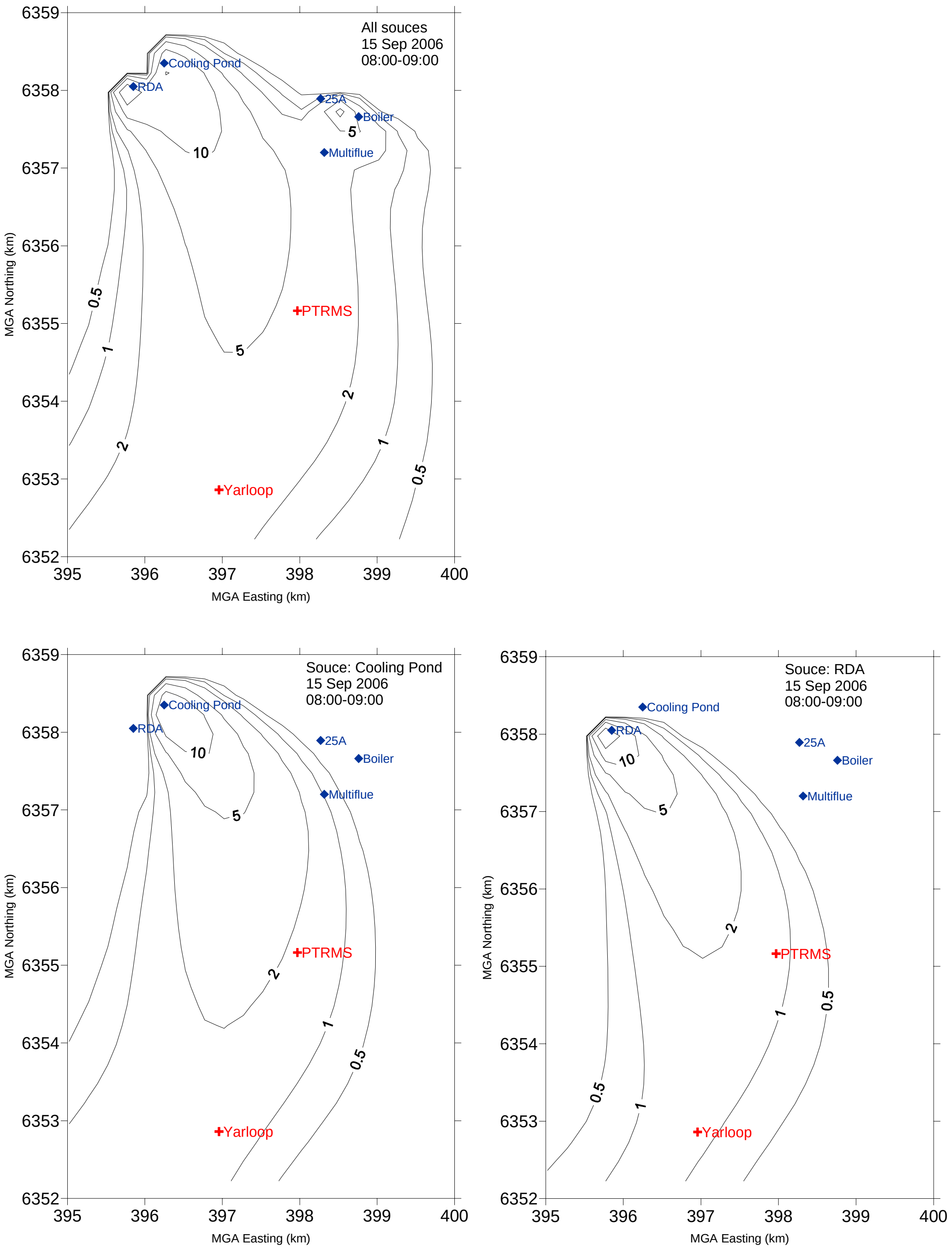

Figure 36. Modelled ground-level odour concentrations in odour units on 15 September for 0800 to 0900 h for the sources with the largest impact on ground level concentrations.

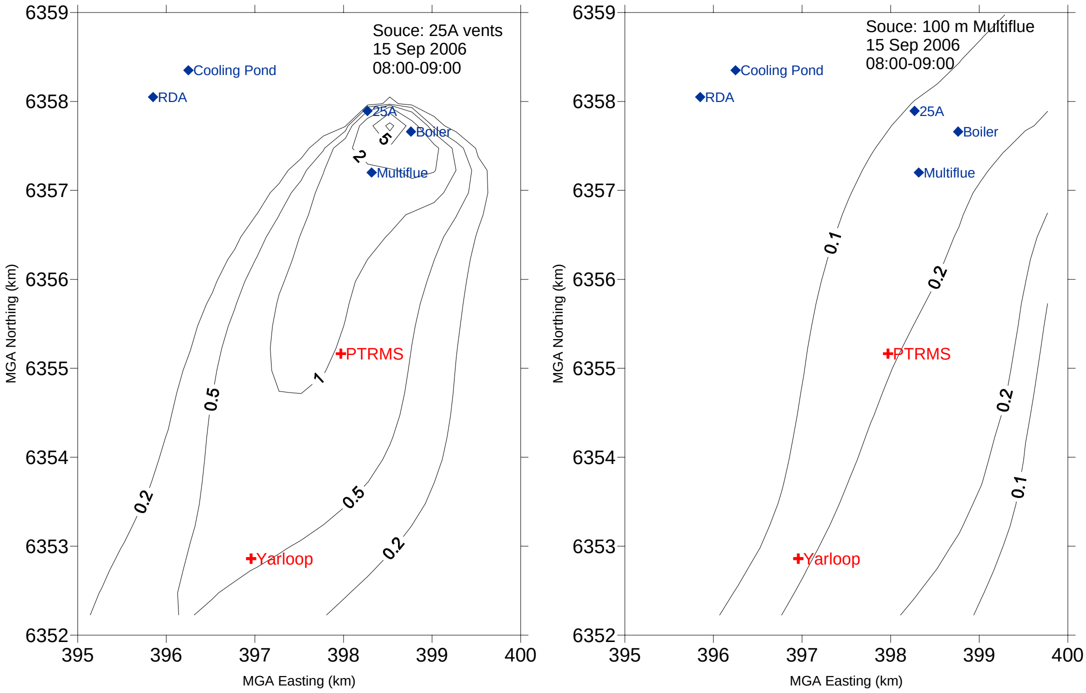

Figure 35 ctd. Modelled ground-level odour concentrations in odour units on 15 September for 0800 to 0900 h for the sources with the largest impact on ground level concentrations.

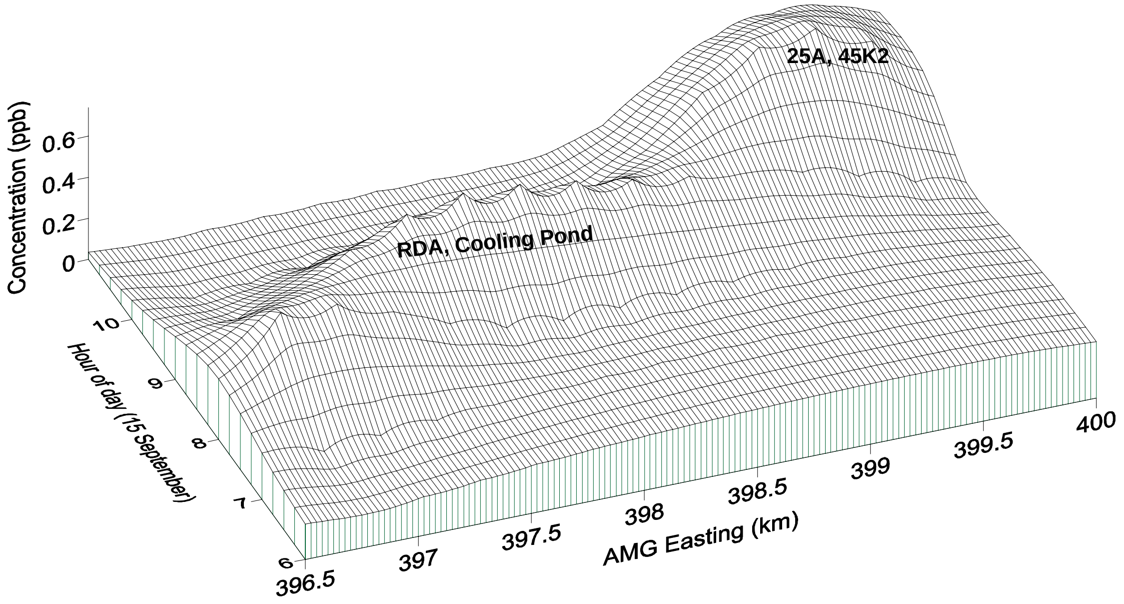

Figure 37. Modelled ground-level acetone concentrations on 15 September east-west along Boundary Road for the hours from 06:00 to 11:00.

The TAPM modelling presented in Figure 36 is for 0800 to 0900 h on 15 September as there is evidence that what was observed at 0915 h onwards was the end of an odour event. The modelling indicates that at this time all parts of the Refinery could contribute to the odour detected at the PTR-MS site. On this occasion there is wind shear with height.The modelling indicates that the Cooling Pond and the RDA and the 25A Vents clearly contribute to the odour at the PTR-MS site. The 100 m multiflue Stack makes a minor contribution to at the PTR-MS site at this time according to the modelling.

TAPM modelling of the ground-level acetone concentrations on 15 September is shown in Figure 37. In contrast to 18 August, the modelled acetone concentrations are lower with a maximum 1-hour average concentration of 0.7 ppb. These are due to the Cooling Towers and 25A vents and occur later in the morning. The peaks due to the RDA and Cooling Pond emissions are about 0.3 ppb. There is a gap in the PTR-MS acetone data before 09:15, so it is not possible to determine whether the actual acetone concentration on this day was higher than on 18 August.

The modelling shows a base concentration of about 0.1 ppb most of the morning on the 15 September and 0 ppb on the 18th September. These modelled concentrations are lower than those observed most probably due to the absence of other non-Refinery sources of acetone in the model.

Finally an investigation was carried out to look for differences between the composition of the air sampled by the PTR-MS during these two odour events, and the composition of air sampled in background conditions. Background conditions were defined as TVOC < 5 ppb for a day or more. Three such background periods were selected for this analysis:

15 August 6:00 – 17 August 2:00; 4 September 4:00 – 7 September 17:00; and 21 September 0:00 – 24 September 11:00.

Hourly PTR-MS data were taken for each of these background periods, and for the Odour periods on the 18 August and the 15 September. The average TVOC concentration during each of these 5 periods was calculated, and the contribution of each mass to the TVOC was determined, expressed as a percentage of the TVOC. It was found that mass 33 (methanol) made up between 30-60% of the TVOC concentration, in both the background and odour events. Its significant presence in background air is probably due to its biogenic sources. To look for differences between background and odour event air in less dominant and possibly more source-specific masses, methanol was excluded from the TVOC calculation. Figure 38 shows in the upper panel the percent contribution of each mass to the TVOC (excluding methanol) for the two odour events (left to right columns 1 and 2) and the three background events (columns 3, 4, and 5), and in the lower panel the same information in absolute concentration units. The average TVOC (excluding methanol) for the odour events on the 18th August and the 15th September were 4.7 ppb and 6.5 ppb respectively, while the average TVOC (excluding methanol) for the background events on the 15 August, 4 September and the 21 September were 1.7, 1.3 and 1.2 ppb respectively.

There are some apparent differences in composition between the air sampled during odour periods and background periods. In the odour periods, there appears to be a higher proportion of mass 59 (acetone) present than for the background periods, particularly for the odour event on the 18th August. This increase in mass 59 during odour periods agrees with the apparent relationship seen between mass 59 and odour in Figure 32 and Figure 33. There are several masses that are more prominent in the background air periods, when compared with the odour periods. Masses showing a greater contribution to the TVOC in background air include mass 69 (isoprene), 75 (multiple compounds), 81 (monoterpenes), 93 (toluene) and 107 (ethylbenzene and the xylenes).

The odour events observed on the 18th of August and the 15th of September 2006 both occurred when air was coming to the Boundary Rd site from the Refinery and were associated with NO_x and acetone, known Refinery emissions. Prior to this, the associations between the Refinery and odour have been based on wind direction alone. This is the first time that there has been an observation of a short-term odour at a point remote from the Refinery that is associated with the Refinery by both winds and the chemical markers, NO_x and acetone, both known Refinery emissions. Such observations are expected to be infrequent in time at a single fixed location downwind of the Refinery because of the continuously changing wind direction and atmospheric dispersion conditions. Their occurrence (with accompanying NO_x concentrations 8 ppb or greater) was estimated to be around 5 events per 2 months for a fixed location in the vicinity of Yarloop (CSIRO 2004).

The only VOC that appeared to vary in parallel with the odour variations on these two occasions that was evident from the PTR-MS measurements was acetone. The only masses that were evident from the PTR-MS measurements during these odour events were those already discussed in Section 2 and within this section.

The acetone concentrations were too low to be causing the odour, because they were below the odour detection threshold for acetone (e.g. Ruth 1986, Nagata 2003). It was not possible to identify the chemical(s) causing the odour. The possible reasons for this are:

- the PTR-MS does not respond to the odorous compound;
- the odorous compound can be smelled at concentrations lower than can be detected by the PTR-MS;
- the odorous compound has a molecular mass that corresponds with one of the identified PTR-MS masses and the contribution of the odorous compound to that mass has not yet been identified.

There is insufficient information to say which of these possibilities is the most likely.

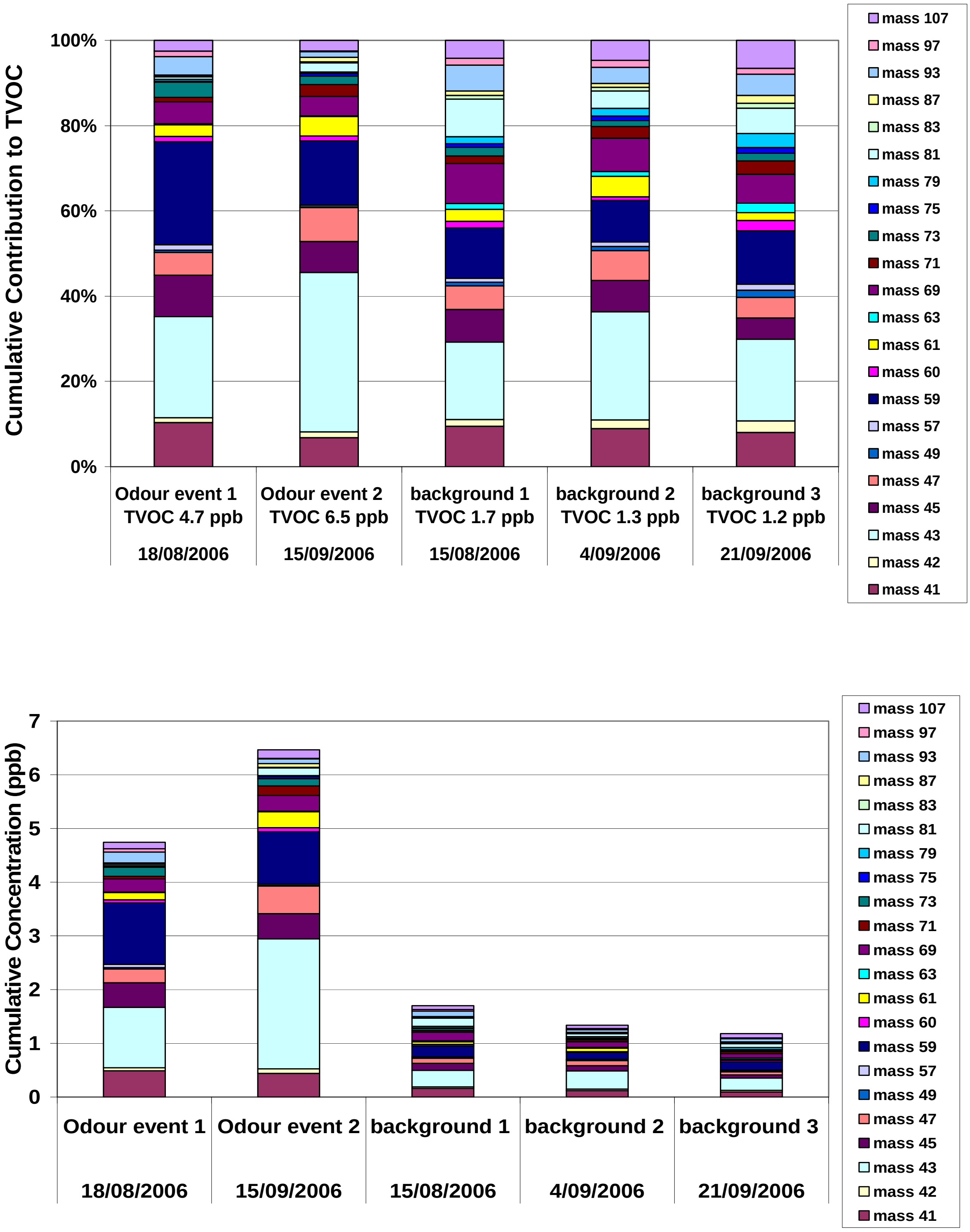

Figure 38. Comparison of composition of air sampled by the PTR-MS during two odour events on the 18 August 2006 and 18 September 2006, with the composition of background events (see text for definition) on the 15 August, the 4 September and 21 September 2006. The contribution of each mass to the TVOC (excluding methanol) is shown in the upper panel, expressed as a percentage of the TVOC (excluding methanol) and absolute concentrations in the lower panel.

3.8 $PM_{2.5}$ and VOCs on 29 September 2006

An initial analysis was undertaken to examine whether there are any associations between particles measured at the site and TVOCs. The PTRMS-TVOC and $PM_{2.5}$ concentrations in time series shown in Figure 39. show that 29th September was different to other high PTRMS-TVOC peaks in that it was accompanied by the highest $PM_{2.5}$ concentration during the Study and so this day was chosen for further analysis. A similar event occurred on the 2nd/3rd October, but with lower peaks, Figure 39. .

A further interest in this day was generated because Alcoa (Alexis Davie private communication 29 May 2007) provided photos of black smoke taken just south of the South Western Highway and the Refinery access road intersection (NW of the PTRMS monitoring site at Boundary Rd) at approximately 15:40 on 29/09/06. The smoke was observed and photographed by Anita Logiudice who attributed it to burning off vegetation and a tyre. Therefore the analysis focussed on whether the peaks in $PM_{2.5}$ and PTRMS-TVOC concentrations on this day at Boundary Rd were associated with the smoke from the vegetation and tyre burning.

The measurements for the day, Figure 40. , do not show a good correlation between hourly concentrations of $PM_{2.5}$ and PTRMS-TVOC. The $PM_{2.5}$ peaks at 0300, 1000 and 1900, and the PTR-MS-TVOC peak between 1000 and 1500. This is an indication that the peaks in $PM_{2.5}$ and PTRMS-TVOC concentrations on this day are often not related or are related in a non linear manner.

The location of the tyre burning would be at a range of approximately 3.5 km on a bearing 340 degrees from the Boundary Rd site. The wind directions and wind speeds for 1000 h to 1800 h this day from the meteorological network around Wagerup are shown in Figure 41. and Figure 42 The local winds did have a bearing of approximately 340 degrees, the direction of the burning, between 1500 and 1600 h, but not so for the rest of the day. The time sequence of $PM_{2.5}$ and PTRMS-TVOCs in Figure 40. shows that the $PM_{2.5}$ and PTRMS-TVOC at Boundary Rd have peaks before the burning was observed, and when the wind is blowing to Boundary Rd from another direction. Furthermore $PM_{2.5}$ concentration is low at the time the burning was observed. All this indicates that there was no consistent major influence of this burning event on the $PM_{2.5}$ and PTRMS-TVOC measurements throughout the day at Boundary Rd.

The PTRMS-TVOCs maximum is more associated with winds from a westerly quadrant. The $PM_{2.5}$ maxima do not have any ready explanation from the wind fields. Figure 41. does show some of the complexity of wind fields around Wagerup on this day. There are extremely light winds at all sites on four occasions during the day. At around 1300 and 1500 h for brief periods the wind direction at the Escarpment site becomes nearly opposite to the wind direction at Bancell Road. Tracing the transport of air parcels under these conditions is extremely difficult.

The composition of VOCs on this day and on background days are shown in Figure 43. The PTRMS-TVOC concentrations shown in each of these samples are 17.1 ppb for 10 hours of data on 29th September, 3.0 ppb for 42 hours of data from 15 to 17 August, 3.0 ppb for 86 hours of data from 4th to 7th September and 2.7 ppb for 84 hours of data from 21st to 24th September respectively. The proportions of PTRMS-TVOC in Figure 43. show that methanol was enhanced during the TVOC maximum.

An analysis of the absolute concentration data shows methanol is higher by 9 ppb, mass 43 (multiple compounds including isopropanol) is higher by 2 ppb, and acetone by 0.5 ppb. Given the complex changes in wind direction and speed shown in Figure 41. and Figure 42 the trajectories of the air on this occasion could possibly be resolved only from 3 dimensional wind fields, and even that might be difficult. The source of these peaks in $PM_{2.5}$ and PTRMS-TVOC concentrations on this day are not identified. An inspection of the hourly concentrations of individual VOCs from the PTR-MS does not indicate any unusual combination of VOCs such as benzene, and styrene that could be a signature of tyre burning.

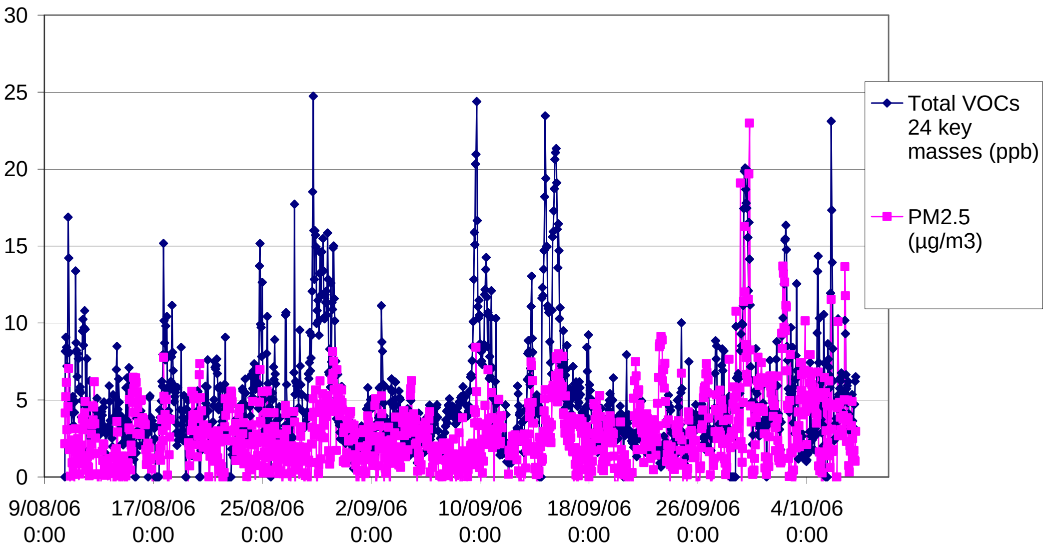

Figure 39. Time series of hourly $PM_{2.5}$ and hourly total VOCs (24 key species) Wagerup Winter Study 2006

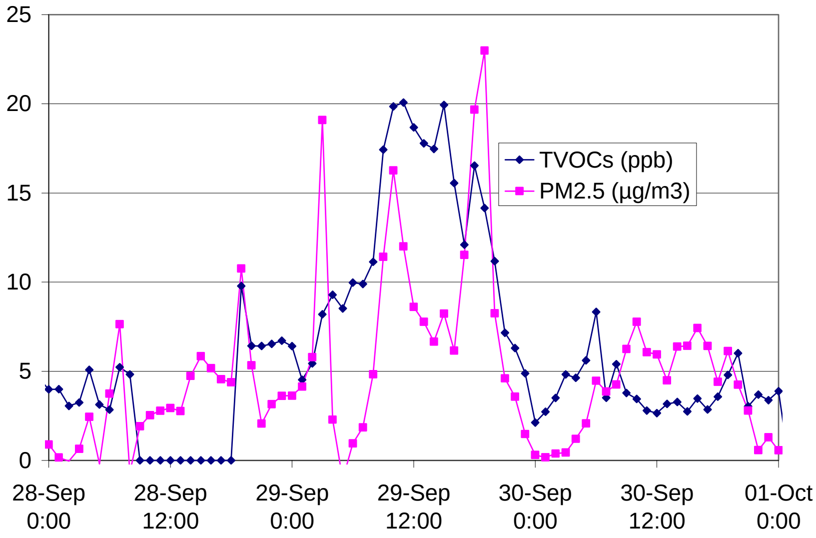

Figure 40. Time series of hourly $PM_{2.5}$ and hourly total VOCs (24 key species) for 28th, 29th and 30th September 2006 at Boundary Rd.

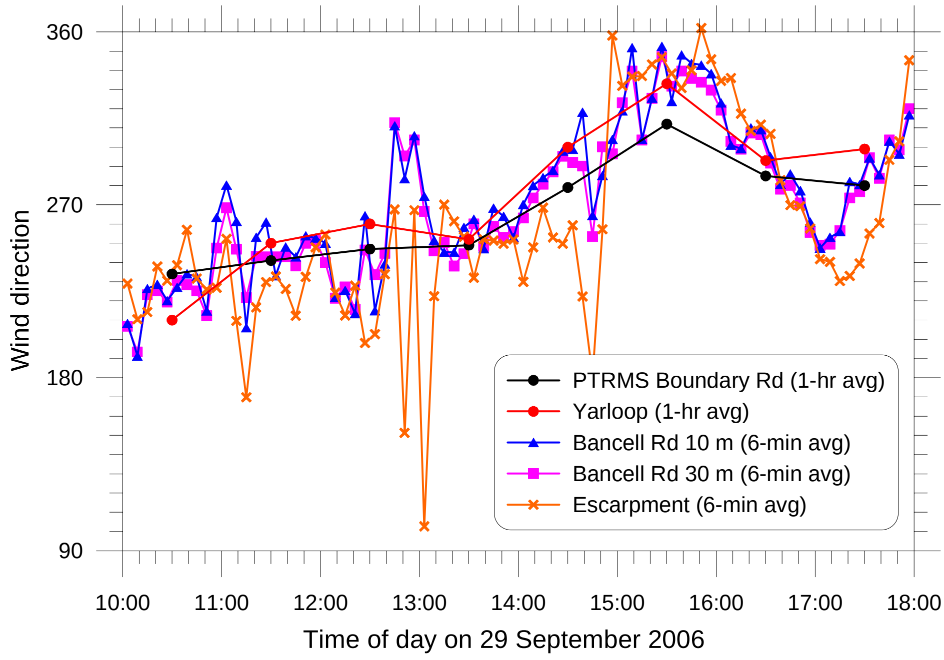

Figure 41. Time series of wind direction for the network of observations at Wagerup on 29th September 2006

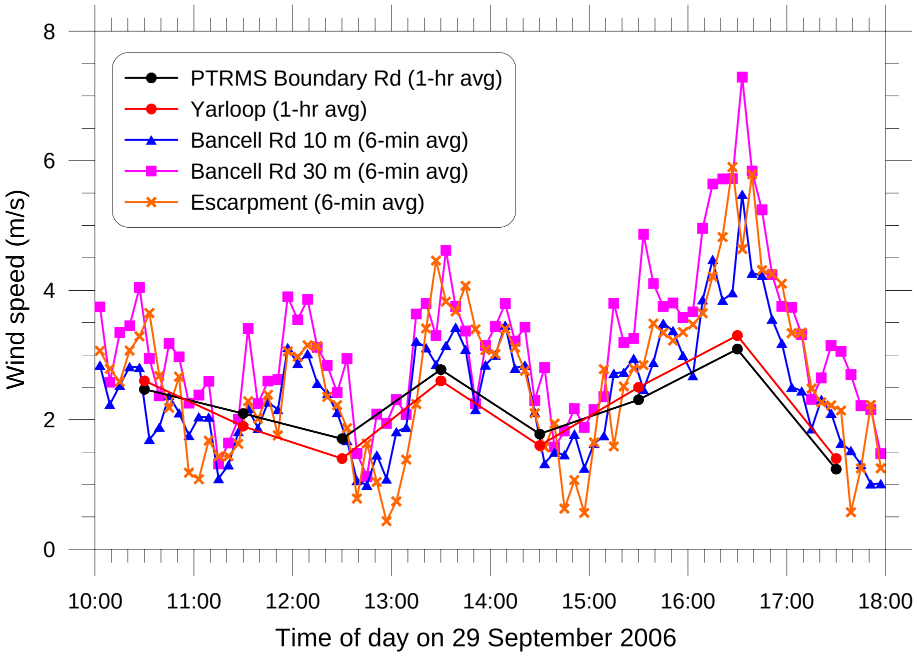

Figure 42 Time series of wind speed for the network of observations at Wagerup on 29th September 2006

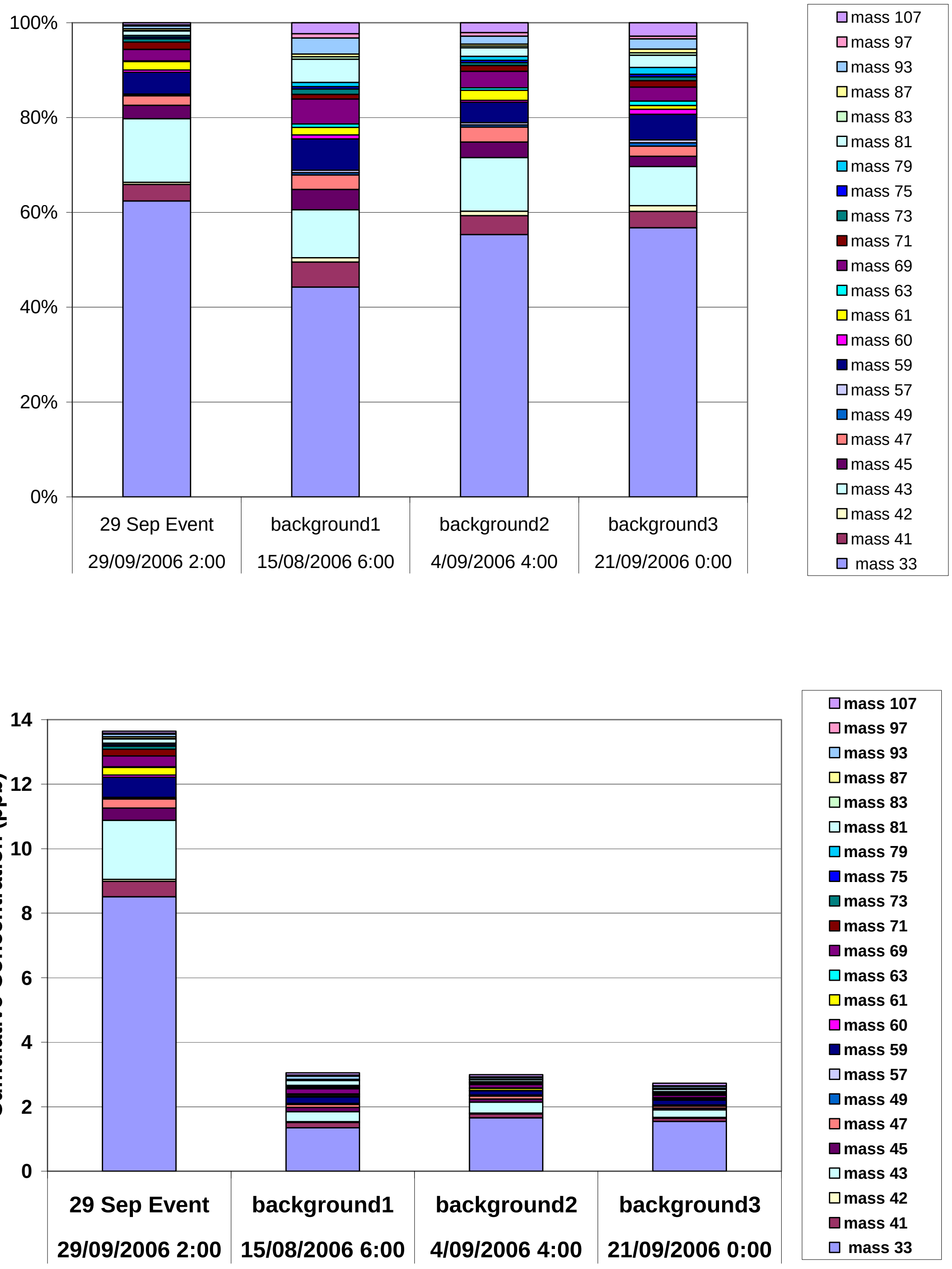

Figure 43. Total VOCs (24 key masses) in Event 29th September versus 3 background periods as proportions in the upper panel and absolute concentrations in the lower panel.

4 CONCLUSIONS

A total of 24 masses were detected at measurable concentrations in the PTR-MS data from Boundary Rd between August and October 2006 in the Wagerup Winter Study. Two independent techniques for measuring specific VOCs in ambient air were compared against the PTR-MS measurements. All VOCs identified by the two independent techniques were also observed by the PTR-MS. Eleven of the 24 protonated masses detected by the PTR-MS have been identified with single candidate compounds. The masses and their associated compounds are 33 (methanol), 42 (acetonitrile), 45 (acetaldehyde), 49 (methanethiol), 59 (acetone), 63 (dimethyl sulphide), 69 (isoprene), 73 (methyl ethyl ketone), 79 (benzene), 87 (2,3-butanedione), and 93 (toluene). The other 13 masses have been associated with multiple possible VOCs. There was also the detection of mass 31, formaldehyde by the PTR-MS (as well as the 24 masses listed above), but the PTR-MS response to formaldehyde is widely recognized to be so poor that the formaldehyde concentrations used in this Study are those measured by the independent DNPH method.

There are 191 other masses which were not present in detectable concentrations in the data set from 60 days of monitoring. These masses correspond to a large number of chemical compounds that can be detected by the PTR-MS, and some by the independent techniques, but were not detected in this Study in air either from the Refinery or from the surrounding region.

The concentrations of VOCs in the ambient air at Wagerup are in the parts per billion, ppb, to sub-ppb range. The median concentration of the Total VOCs (TVOCs) in ambient air was 4.6 ppb and 99% of the concentrations were less than 21 ppb. Considering the whole data set of both PTR-MS and carbonyl samples, Mass 33, (methanol) makes up 55%, formaldehyde is 9%, acetone 6.5%, and acetaldehyde 2.8% of the concentration of the TVOC in ambient air.

Comparison of the concentrations of VOCs observed at Wagerup with observations from other locations in Australia and overseas shows that the VOCs at Wagerup in this Winter Study are present in concentrations at the low end of what has been measured elsewhere in a rural environment. The reason for this is either the sources of these VOCs were lower at Wagerup in winter, or the influence of oceanic air which has extremely low concentrations of VOCs and which is carried inland to Wagerup by westerly winds during wintertime.

All of the VOCs identified in this Study have more than one possible source in the Wagerup region. The possible sources of these VOCs include industrial, domestic, biological, combustion and transport processes and production in the atmosphere from other organic compounds. Further, the analysis shows that the compounds and masses detected in this Study occur in the air for all wind directions. When the hourly TVOC concentrations are plotted versus wind direction and the highest 10 to 20 concentrations of TVOCs (the top 1%) are examined there is no obvious preferential wind direction.

In the data from Boundary Rd it was possible (with a statistical technique) to identify (a) emissions from the Refinery whose CO_2:NO_x ratio lies in the range 1000 and 2500 which is consistent with Refinery plumes and (b) emissions from the South East to the West (Yarloop and surrounds) whose CO_2: NO_x ratio is in the range 0 – 1000 which is consistent with vehicle and residential emissions.

The analysis by wind direction provides evidence that a number of masses, mainly 59 (acetone), 45 (acetaldehyde), 33 (methanol) and 43 (multiple compounds) as well as NO_x have sources in the direction of the Refinery which is consistent with knowledge of Refinery emissions and Pilot Study results. During the Winter Study the Refinery was operating with a bauxite throughput typical of the whole year. Refinery Liquor Burner was off line for most of the Study period. During this time a new Regenerative Thermal Oxidiser was being installed and commissioned to reduce the VOC emissions from the Liquor Burner. Any particular chemical characteristics of the Liquor Burner emissions will be diminished or absent in this data set. The analysis by wind direction also provides evidence of NO_x, CO_2 and mass 81 (fragment of monoterpenes) as having sources that cause high concentrations in directions other than that of the Refinery, which are consistent with the domestic, transport, vegetation and soil sources of these gases. Analysis of the day/night cycles of these trace gases indicated behaviors generally consistent with the sources described above.

From observations of vehicle numbers on the South Western Highway, atmospheric stability and the observed ratio of benzene and toluene concentrations (which has a distinct ratio for vehicle emissions compared to woodheater and agricultural burning), it is assessed that motor vehicle emissions made a minor but observable contribution to the TVOC concentrations at Boundary Rd during this Study.

Two odour events were observed at Boundary Rd during this Study by CSIRO staff. The odour events observed on the 18th of August and the 15th of September 2006 both occurred when air was coming to the Boundary Rd site from the direction of the Refinery and were associated with elevated NO_x and acetone concentrations, known Refinery emissions. The only mass of the 24 masses detected from the PTR-MS measurements that appeared to vary in parallel with the odour variations on these two occasions was mass 59 (acetone). The TAPM modelled acetone concentrations, based on Refinery acetone emissions, for these odour events, were within a factor of three in concentration of those measured with the PTR-MS. This is the first time that there has been an observation of a short-term odour at a point remote from the Refinery that is associated with the Refinery by both winds and the chemical markers, NO_x and acetone, both known Refinery emissions.

The acetone concentrations were too low to be causing the odour, because they were below the odour detection threshold for acetone. It was not possible to identify the chemical(s) causing the odour. The possible reasons for this are:

- the PTR-MS does not respond to the odorous compound;
- the odorous compound can be smelled at concentrations lower than can be detected by the PTR-MS;
- the odorous compound has a molecular mass that corresponds with one of the identified PTR-MS masses and the contribution of the odorous compound to that mass has not yet been identified

There is insufficient information to say which of these possibilities is the most likely.

In summary, the Study has identified VOCs present in the air at Wagerup and identified their most likely sources in the Wagerup area, both natural and man made, based on measurements at a location south of the Wagerup Refinery made for 8 weeks between August and October 2006 using the PTR-MS and ancillary equipment.

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APPENDIX A: WORK CARRIED OUT UNDER PROPOSAL

A.1 Activities

Activities identified in the project work proposal included:

- Locate and set up the PTR-MS south of the Refinery at a location agreed by Alcoa and CSIRO.
- Manage and calibrate the PTR-MS
- Process the data collected by the PTR-MS and determine background levels
- Identify mass numbers above background, looking at a total of between 15 and 25 relevant mass numbers
- Identify the single most probable substance associated with each mass number, using integrated DNPH samples for carbonyl identification and adsorbent tubes for other VOC identification
- Identify (for the Wagerup environment) the likely sources of the identified substances, given the wide range of natural and man-made sources in the area using
    - NOx/CO/CO_2 relationships
    - Meteorology (wind speed and direction) including TAPM meteorological modelling
    - Previous CSIRO investigations including the Pilot Study (Galbally et al., 2006) and the study “Meteorological and Dispersion Modelling Using TAPM for Wagerup”.

In addition to the above it was planned to make analysis of bag samples (taken by consultants from Refinery sources for odour analyses), during the winter campaign, to add to the information already obtained and provide further insights into identification of sources/substances. This work is presented in Appendix G.

A.2 Time line

The following is a timeline of the field component of the Study:

7 August 2006 CSIRO Team arrive on site at Wagerup

10 August 2006 PTRMS Ambient measurements commence

18 August 2006 Ambient adsorbent tube VOC measurements with the Sequencer commence

22 August 2006 Ambient carbonyl measurements with the Sequencer commence

7 October 2006 PTRMS Ambient measurements cease

7-9 October 2006 PTRMS and Sequencer measurements inside demountable

9-10 October 2006 Odour Bag Measurements

12 October 2006 CSIRO Team depart from site at Wagerup

A.3 Data collected

A copy of the data obtained during this trial from both the PTR-MS and the AQMS are presented in a .csv file (suitable for import into MS-Excel) on an accompanying compact disk. Two data files are provided, one where ‘nd’ is inserted when the concentration is below the minimum detectable limit, and the other where the value of half the minimum detectable limit is inserted where the concentration is below the minimum detectable limit.

APPENDIX B: THE AIR QUALITY MONITORING SYSTEM AND OTHER MEASUREMENTS

As with the Pilot Study (Galbally et al., 2006), other air quality measurements were made alongside the PTR-MS to aid in the interpretation of the data. The air quality measurements were carried out by Ecotech Pty Ltd (a consultant engaged by Alcoa) using Ecotech's AQMS (Air Quality Monitoring System). The following parameters were measured and the following instruments used:

- Oxides of Nitrogen ($NO/NO_2/NO_x$) with an Ecotech model Trace-9841 Chemiluminescence NO_x analyser
- Carbon monoxide (CO) with an Ecotech model Trace-9830 nondispersive infrared photometer
- Carbon dioxide (CO_2) with an Ecotech model 9820 nondispersive infrared photometer
- Wind Speed and Wind Direction with a MetOne Ultrasonic anemometer
- Temperature and Relative Humidity
- PM2.5 with a TEOM monitor.

The outputs from the above instruments were recorded by an Ecotech model 9400 Data Logger running WINAQMS acquisition software. The AQMS software was set up to initiate and control the automatic daily calibration checks of the gaseous analysers, which were performed at approximately midnight. This automatic process utilised the Station Calibration System, consisting of an Ecotech model GasCal 1000 gas dilution calibrator connected to an Ecotech Clean Air Generator, and an appropriate Calibration Gas Standard cylinder. The CSIRO and Ecotech AQMS data acquisition and control computers were time synchronised to ensure that the resulting data collected could be reliably merged.

The validated AQMS data were supplied by Alcoa, either directly or from their consultants Ecotech Pty Ltd, to CSIRO both as 1-minute averaged and hourly averaged data. The 1-minute data were averaged by CSIRO to 2-minute data that correspond with the PTR-MS analysis cycle timing. These measurements were made by Ecotech Pty Ltd who is accredited by NATA and the data were supplied to CSIRO as validated measurements.

During the period of the Study, 10 August to 7 October 2006, the AQMS data acquisition rates (not counting zeros and calibration) based on the data supplied to CSIRO were CO 31%, CO_2 40%, NO_x 92%, wind speed and direction 98%, temperature and relative humidity 100%.

The meteorological data provided to CSIRO included 1 minute and hourly data summaries. The hourly wind speed and wind direction data utilized in this report were calculated by CSIRO as vector average speeds and vector average directions from the 1 minute data. Boundary Rd does not satisfy the requirements for a Class 1 meteorological site as specified in AS2923-1987. The wind speeds will be reduced due to nearby vegetation for some wind directions. However for the purposes of this Study the key requirement is not the precise measurement of wind speed and direction but the composition of the air, and the site was good for that purpose[3].

Hourly vehicle count rates were measured for vehicles travelling on the South Western Highway at a location near the Boundary Rd junction during the Study.

A part of the source signature analysis that was intended for this report is absent due to the limited availability of ambient CO concentration data from Boundary Rd. One intended purpose of CO data was to distinguish between the Boilerhouse emissions and those of the 100m multiflue, the GT/HRSG and Calciner 4 (see Galbally et al., 2006).

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[3] Subsequent to the completion of this report, it was discovered that the wind directions at Boundary Rd were offset by approximately +20 degrees (Air Assessments January 2007). Thus wind directions at Boundary Rd shown in this report should be rotated anticlockwise by 20 degrees. Where necessary this is discussed, and allowed for, in the body of the report.

APPENDIX C: THE PTR-MS

Proton transfer reaction mass spectrometry, PTR-MS, was developed in the late 1990s by Professor Werner Lindinger and co-workers at the University of Innsbruck, Austria, and is a recent development in the application of chemical ionisation mass spectrometry to air analyses (Lindinger et al., 1998). PTR-MS instruments are manufactured and supplied by Ionicon Analytik of Innsbruck, Austria. The theory and practice of application of PTR-MS to atmospheric composition studies is still being developed.

The PTR-MS measures the presence and concentration of chemical species in the air that have a proton affinity greater than water. Measurements with PTR-MS allow real-time monitoring of a wide range of organic compounds and a few other chemical species in air. The permanent constituents of air, oxygen, nitrogen, etc. have a proton affinity less than H_2O and so are not detected by the PTR-MS. Organic compounds containing oxygen, nitrogen and sulfur, aromatic hydrocarbons and some alkenes and alkynes generally have proton affinities greater than H_2O and so are measured by the PTR-MS. Alkanes generally are not detected by the PTR-MS.

The PTR-MS measures these chemical species according to their mass as a singly charged ion. The mass recorded usually is the mass of the chemical species (in atomic mass units, amu) plus 1, the additional mass being due to the proton attached to the chemical species. In some cases the chemical species fragments following the proton addition, in which case the mass recorded is that of the charged fragment.

The pattern of the fragmentation is that charge is conserved and the protonated parent ion is replaced by a protonated fragment. Under these circumstances, the primary effect of a failure to recognise that a fragmentation has taken place, is a mis-identification of the compound, rather than a loss of observed VOC concentration (PTRMS-TVOC). Tables of the fragmentation patterns (where fragmentation occurs) of many chemical species are available (Ionicon, 2007 unpublished; Warneke et al., 2003; Buhr et al., 2002), although these tables do not cover all of the multitude of volatile and semi-volatile organic compounds that are known to exist nor do they cover the full range of PTR-MS operating conditions. Fragmentation patterns are dependent on conditions set within the PTR-MS drift tube.

The minimum detectable limits of the PTR-MS for many compounds are around 100 ppt (0.1 ppb, or 1 in 10^{10}) for a dwell time of 1 second. The detection limit decreases (sensitivity increases) for longer dwell times (measurement periods).

The PTR-MS has greater sensitivity and better temporal resolution than other generally available techniques. In measuring gaseous organic compounds the PTR-MS has the limitation that it cannot distinguish between two or more chemical species that have the same molecular mass and also undergo proton addition in the PTR-MS.

PTR-MS is a new technology that is being rapidly developed and taken up throughout the world in a wide variety of applications in environmental monitoring, food technology, and health sciences (Lindinger et al., 1998). CSIRO Marine and Atmospheric Research purchased a High Sensitivity model PTR-MS from Ionicon in mid-2005 (see Figure 4.1), and are utilising the instrument for atmospheric composition studies in a range of situations. This was the first PTR-MS in Australia and the 68th in the world. The application of the PTR-MS technology to air analyses is a relatively new technique and is subject to ongoing research.

The main technical specifications of the High Sensitivity PTRMS are given in Table C.1.

Table C.1 Main technical specifications of the PTR-MS from Ionicon Analytik GmbH.

PTR-MS Parameter	Specification
Mass range	1-512 amu (up to 2048 amu on request)
Resolution	< 1 amu
Response time	100 ms
Measuring (dwell) time	2 ms/amu - 60 s/amu
Detection threshold	5 pptv
Linearity range	5 pptv - 10 ppmv
Adjustable flow	50 - 500 sccm
Inlet system heating range	up to 150°C
Reaction chamber heating range	40 - 120°C
Power supply	100-230 V, max 750 W
Dimensions	78x86x55 cm (w x h x d)
Weight	135 kg
Interface	Ethernet 10/100MBit RJ45 (TCP/IP)

C.1 Instrumentation

The PTR-MS operates with the aid of auxiliary equipment (designed and constructed by CSIRO), see Figure C.1, which regulates the flow of air in the sample inlet and controls whether the PTR-MS is sampling ambient air, zero air or calibration gas.

Zero readings were made by diverting the ambient air being sampled through a zero furnace that destroys VOCs in the air before it enters the PTR-MS. Zero measurements were made for 30 minutes commencing at each of the following times on every sampling day: 00:45 h, 04:45 h, 08:45 h, 12:45 h, 16:45h, and 20:45 h.

As with almost all other systems used to measure trace gas concentrations, the PTR-MS records a non-zero value when measuring "zero" air that has passed through the zero furnace. For the PTRMS, this value is always positive. The zero value at a particular time is estimated by linearly interpolating between the measured zero values averaged in the 30 minute periods listed above, and subtracting the interpolated average zero value from the apparent PTR-MS reading to provide a zero-corrected reading. Due to this subtraction process and the underlying measurement noise in the instrument, measurements of ambient air that has, for a particular VOC, zero concentration, will lead to the detection of a scatter of concentrations with in most cases small negative and positive deviations from zero. This “noise” is used to determine the minimum detection limit of the measurement of that VOC (see next section).

Figure C.1 The PTR-MS (left) and the associated zero and calibration gas dilution system (to the right) at the Boundary Rd site during the Wagerup Winter Study.

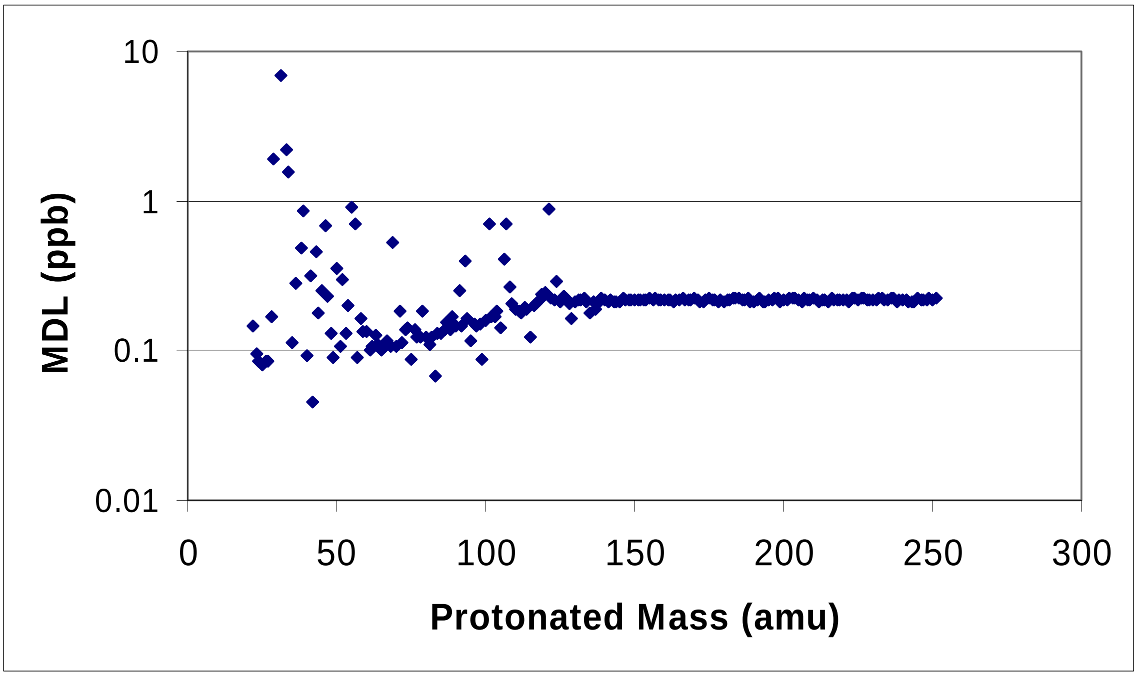

Figure C.2. Minimum detection limit (ppb) for each mass for a 0.5 second dwell time measurement, determined from field data from the PTR-MS during the Wagerup Winter Study.

C.2 PTR-MS operation, data processing, edits and quality

The PTR-MS instrument was operated at Wagerup in a scanning mode sequentially measuring each mass, at 1 amu intervals, between masses 21 and 251 and then commencing again at mass 21. This range is chosen to cover the molecular masses of most VOCs that potentially could occur in the atmosphere. Data were obtained from 10 August to 7 October 2006. The dwell time for a single mass measurement was 0.5 second. For each of the 231 masses there is a 0.5 second measurement every 2 minutes. In all, during this Study, 60 days of PTR-MS measurements were obtained, providing more than 9 million measurements made up of, in most cases, 40583 measurements of each individual mass (of the 231 masses measured) of which 34813 measurements were of the ambient concentration of each mass. Hourly concentrations were calculated when there was PTR-MS data for two-thirds of the hour or greater. During the period of the Study, 10 August to 7 October 2006, the data acquisition rate (not counting zeros and calibration) was 85% for the PTR-MS.

The principles underlying the operation of the PTR-MS are described by Lindinger et al. (1998). In principle the concentration of a chemical species being measured by the instrument can be calculated from the basic chemical properties of the species and the physical characteristics of the instrument. These concentrations are described as indicative concentrations. Alternately, concentrations can be calculated based on the instruments response to calibrated gas mixtures presented to the PTR-MS. There have been differences observed by a number of researchers between the PTR-MS indicative concentrations and the concentrations resulting from use of the PTR-MS response to standard gas mixtures (Warneke et al., 2003), although the data is often presented in terms of PTR-MS sensitivity (Warneke et al., 2003). In this Study the PTR-MS response is defined by the ratio of the indicative PTR-MS concentration (ppb) to the concentration derived from the calibration gases (ppb). The calibration factor is defined as the inverse of the PTR-MS response. The concentration measurements derived from calibration gases are used in preference to indicative concentrations.

The raw data files from the PTR-MS are processed with proprietary software developed by CSIRO that takes the ion counts and an array of other instrument information, makes corrections for zeros and calculates either indicative concentrations, or (for those species present in the calibration gases) calibrated concentrations. The algorithm used in this software is based on the physical principles underlying the design of the PTR-MS as outlined in Lindinger et al. (1998) and other documents.

Assumptions used in formulating the algorithm for calculating the indicative concentrations include that: the chemical species has a typical proton exchange rate with H_3O^+, the chemical species does not fragment following the proton addition, and the chemical species passes into the PTR-MS instrument un-attenuated. These assumptions have been demonstrated to hold for a number of the simple organic molecules that do not fragment and are being studied here. If the fragmentation pattern is well known then this approach can be modified to allow the calculation of the concentrations of some simple molecules that do fragment. As mentioned earlier, the primary effect of a failure to recognise that a fragmentation has taken place is a mis-identification of the compound, rather than a loss of observed VOC concentration (PTRMS-TVOC).

The minimum detectable level (MDL) applicable for a single measurement of each mass is determined from the scatter in the individual zero measurements observed over the course of the Study using the principles of ISO6879 (ISO, 1995). These minimum detectable limits are shown in Figure C.2, and vary from a maximum value of more than 6 ppb for formaldehyde which had a significant instrument zero signal, to of-the-order-of 0.2 ppb for many of the masses. The MDLs for the specific masses that had detectable concentrations are provided in Section 6 of this Report. For the average of a set of multiple measurements, a lower MDL is applicable.

Some masses are not recorded in the final data tables because the PTR-MS does not provide a real ambient measurement at this mass due to instrument design characteristics and internal interferences. These masses are: 21, 25, 30, 32, 37, 38, 39, 52, 55, 56, 106, 108, 120, 124 and 126. The specific reasons are that masses 21, 30, 32, 37, 38, 39 and 55 are ions associated with the ion source, including protonated water vapour, dimers, a trimer and their isotopes (e.g. mass 32 = O_2^+). Mass 25 has no known chemical source and is therefore the background noise contributing to the ion reading. The remaining masses are due to interferences from the materials that make up the PTR-MS. For further discussion of the implications of the above, see Section C.4.

C.3 PTR-MS Calibrations

A series of calibrations against certified gas standards were performed on the PTR-MS for this Study. The certified gas standards contained several carbonyls, several alcohols and a range of hydrocarbon compounds. Varying concentrations were obtained by diluting the gas standard mix with zero air using a pair of mass flow controllers. As with the Pilot Study (Galbally et al., 2006), linear responses versus concentration were obtained. These calibrations were conducted manually by a skilled technician or scientist because at that stage automatic equipment for span or calibration checks had not been developed by CSIRO. Subsequently such technology was developed, and over a 4 week study in October and November 2007 in which the PTR-MS was unattended at a site remote from CSIRO Aspendale, automatic calibrations were carried out daily. The PTR-MS calibration response through the Study varied with a relative standard deviation of ± 4% for methanol up to ±13% for MEK. This stability of calibration is illustrated also in de Gouw and Warnecke (2007).

Table C.2 presents the compounds for which the PTR-MS at Wagerup was calibrated, including the protonated mass utilized in the PTR-MS calibration and a calibration factor that converts the indicative concentration into a calibrated concentration, provided that the signal for the mass corresponds to the compound used in the calibration. These calibration factors have been applied to these mass numbers. The calibration factors for each compound were calculated by averaging several PTR-MS response values measured throughout the Study, then taking an inverse of this average response. In the case of masses 41 and 43, the PTR-MS response was based on the results of a calibration with an alcohol mix that displayed fragmentation to these masses. For mass 43 an additional response of propene was included. In the case of the monoterpenes which are measured as a fragment at mass 81, a calibration gas was not available. As the PTR-MS response to a compound has a component of mass dependence, with compounds of similar molecular weight and structure generally having similar response, the calibration factor of benzene (mass 79) was taken for monoterpenes and doubled to account for the approximate 50% of the monoterpene concentration measured as a fragment at mass 81 (Tani et al 2003). The set of 4 carbonyl calibrations showed standard deviations varying from 12 to 27% for the calibration factors for these compounds. All of these calibration factors in Table C.2 are greater than 1, which suggests a systematic difference between the calibrated concentrations obtained using standard gas mixtures and the calculated indicative concentrations.

The calibration factors cover the 12 masses determined to have the highest concentrations in the air at Wagerup, see Section 2, with the exception of masses 47 and 61. The concentrations of these two masses make up less than 3% of the total VOCs detected by the PTR-MS , see Table

1. The average concentrations of masses/compounds for each mass detected by PTR-MS, and formaldehyde measured by DNPH, and the percentages of TVOC for each mass/compound for the 15 and 91 8-hour VOC periods during the Wagerup Winter Study (see text and Appendix F) Note the columns do not necessarily add up to 100% and the concentrations and percentages do not necessarily exactly correspond due to the rounding of the calculations that are done at higher precision.. The concentrations of these two masses may be underestimated because the concentrations used are indicative concentrations rather than calibrated concentrations. This is not expected to impact on the conclusions of the Study as is discussed below.

If the indicative concentrations of these two masses 61 and 47 were multiplied by a factor of five, which is greater than all of the calibration factors in Table C.2, the outcome would be a 11% increase in TVOC concentration (Table 1) from 4.6 to 5.1 ppb. This calibration would not change in any way the patterns of behaviour of the compounds associated with mass 47 and mass 61, nor their potential association both with the Refinery and with other sources. This extreme “calibration” would cause the average concentrations of mass 47, formic acid, ethanol plus possibly other compounds to be 0.8 ppb and that of mass 61, acetic acid plus possible other compounds to be 0.7 ppb, values still within the range observed elsewhere.

C.4 VOCs not measured by the PTR-MS

There are four reasons why a VOC may not be measured by the PTR-MS. These are presented as dot points and discussed below.

- The VOC has a proton affinity less than water and therefore does not undergo a proton addition reaction required for its detection.
- The VOC has a proton affinity near that of water and as well as proton addition, there is a back reaction where the proton passes back to a subsequent water molecule that the protonated molecule encounters.
- The VOC undergoes proton addition and its protonated ion has a mass that is not sensitively detected by the PTR-MS due to interferences at that mass.
- The VOC undergoes proton addition and subsequently fragments and its sole protonated fragment ion has a mass that is not sensitively detected by the PTR-MS due to interferences at that mass .

Some of the VOCs that have proton affinities less than water include the alkanes methane to butane and cyclohexane, some halogen substituted organics, carbonyl sulfide and carbon disulfide. Formaldehyde has a proton affinity slightly greater than water, and experiences a back reaction in the drift tube and so is poorly detected by the PTR-MS under the conditions at which the PTR-MS was operated at Wagerup.

The PTR-MS does not provide a sensitive detection (a real ambient measurement), at masses 21, 25, 30, 32, 37, 38, 39, 52, 55, 56, 106, 108, 120, 124 and 126, due to instrument design characteristics and internal interferences, as discussed in Section C.1 Less than 60 organic compounds, many of them isomers, known to have primary protonated ions corresponding to these masses (Hunter and Lias 2003).

The PTR-MS, as it was operated at Wagerup, is relatively insensitive to ethanol and is completely unresponsive to oxalic acid. This behaviour is not fully understood and is probably associated with the fragmentation patterns of the protonated molecules.

The two independent techniques (Carbonyls by DNPH and AT-VOCs) detected a number of VOCs at Wagerup, and for all these compounds detected, there were corresponding masses detected by the PTR-MS in the air at Wagerup.

There are some VOCs that would be expected to be in the air at Wagerup and were not observed by these measurement techniques because the techniques are not sensitive to these compounds. These include ethane, propane, butanes and pentanes, some halogen substituted organics, carbonyl sulfide and carbon disulfide, ethanol and oxalic acid. The techniques used in this Study focused on "*those simple organic compounds that are or can be emitted by the Refinery that have not been measured in previous ambient sampling (including polar compounds).*" Recommendation 14, Wagerup Air Quality Review (CSIRO 2004).

Table C.2 Compounds and calibration information averaged over all applicable calibrations for the PTR-MS at Wagerup in Winter 2006

Compound	Primary Protonated Mass	PTR-MS response	Calibration factor
Methanol	33	0.34	2.90
Multiple compounds	41	0.39	2.54
Acetonitrile	42	0.64	1.56
Mixed	43	n/a	2.52
Acetaldehyde	45	0.64	1.56
1,3 butadiene	55	0.41	2.41
Acetone	59	0.58	1.73
Isoprene	69	0.24	4.13
Methacrolein/MVK	71	0.65	1.55
MEK	73	0.48	2.08
Benzene	79	0.71	1.40
Monoterpenes (fragment)	81	n/a	2.80
Toluene	93	0.32	3.08
Ethylbenzene and Xylenes	107	0.22	4.50
Tri methyl benzenes	121	0.22	4.55

APPENDIX D: OTHER VOC MEASUREMENTS

Supporting VOC measurements were made during the Wagerup Winter 2006 Study to provide specific identification of some of the chemical species observed as mass numbers with the PTR-MS. For the duration of the Study a two channel automatic sampler was used to take 8 hour integrated samples for carbonyls on DNPH cartridges and for selected VOCs on adsorbent tubes. The DNPH cartridges and VOC adsorbent tubes were analysed at the CSIRO Marine and Atmospheric Research laboratories at Aspendale Victoria. VOC and US EPA Method TO15 analyses have been undertaken in the past in the CMAR the laboratory and published in the international scientific literature (Duffy et al. 1999, Hinwood et al, 2006).

D.1 Sequencer

The adsorbent tube VOC (AT-VOC) and Carbonyl Sequencer developed by CSIRO is an automatic air sampler for sampling of VOCs and Carbonyls using tubes and cartridges simultaneously. It has two channels: one for VOC and the other one for Carbonyl. Each channel contains a sample inlet, 9 sampling ports individually selectable via 18 solenoid valves (9 inlets and 9 outlets), a sampling pump and an electronic flowmeter. The sequencer is shown in Figure D.1.

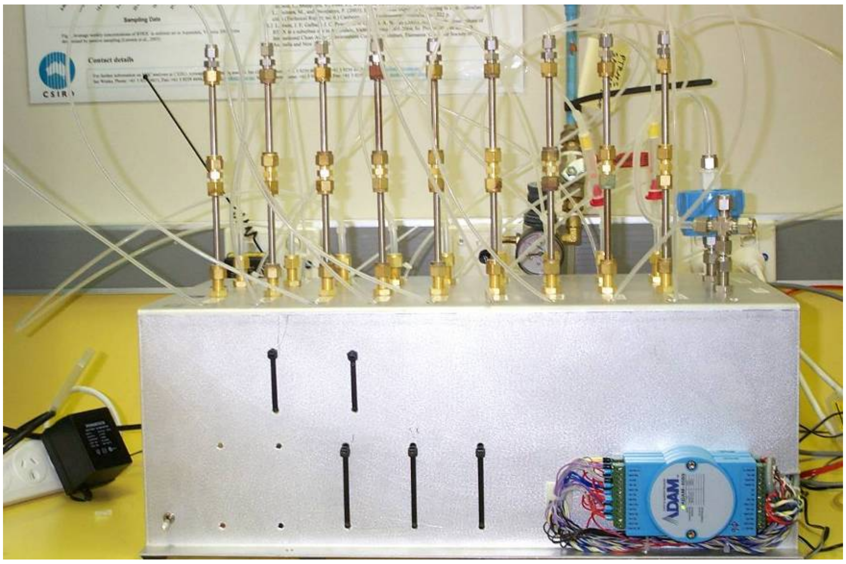

Figure D.1. The front view of the sequencer.

A computer based software system controls and logs the activities of the sequencer via hardware interfaces. The Sequencer utilises the manifold valves to select 1 of 9 sampler pairs for each of the VOC and carbonyl sampling. The sequencer is set up to run on a three day cycle.

D.2 Carbonyls

The measurement of carbonyls in ambient air in this Study via use of DNPH tubes was based on EPA Method TO11A. The main variation to that method as undertaken in the CSIRO laboratory was that spiked samples to check for complete recovery were done only intermittently, rather than with every analytical run. The recoveries obtained were 100%. A 13 carbonyl pure standard mixture from Supelco was used on every analytical run. Subsequently some additional standards were prepared in the CSIRO laboratory and glyoxal and methylglyoxal were identified in the samples.

Samples were collected on Supelco LpDNPH S10 air monitoring cartridges. Carbonyls are trapped on the LpDNPH cartridge, which is packed with high purity silica adsorbent coated with 2,4-dinitrophenylhydrazine (2,4-DNPH), where the carbonyls are converted to hydrazone derivatives. The samples are collected with an air sampling pump at a flow rate between 1.4 to 2.0 L/min over an 8 hour period giving a typical sample volume of 800L. An ozone scrubber was placed in front of the LpDNPH cartridge. The cartridges are analysed at the CSIRO Aspendale laboratory, where the derivatives are eluted from the cartridge in 2.5ml of acetonitrile.

The High Performance Liquid Chromatography (HPLC) system employed in this work consisted of a Dionex GP40 gradient pump, a Waters 717 autosampler, a Shimadzu System controller SCL-10A VP, a Shimadzu diode array detector SPD-M10A VP, a Shimadzu Column Oven CTO-10AS VP and Shimadzu CLASS-VP chromatography software. The compound separation was performed with a Supelco Supelcsil LC-18 column, 5 µm, 4.6 mm ID x 250 mm in length, Part No 58298. The chromatographic conditions employed in this Study included a flow rate of 2.0 ml min^{-1} and an injection volume of 20 µl, and detector wavelength of 360 nm. The peaks were separated by gradient elution with a mobile phase of 60% acetonitrile and 40% Milli-Q water initial conditions to 100% acetonitrile at 17 min, and column temperature of 30ºC. Standard solutions were prepared from Supelco Carb Method 1004 DNPH Mix 2, and the HPLC grade acetonitrile was purchased from Merck. The water used for analysis was 18.2 mΩ.cm grade produced from a Millipore Milli-Q Advantage 10 system.

Thirteen carbonyl compounds are measured, and calibrated with the 2-4-DNPH derivatives of the carbonyls which are commercially available, in the analysis of the Wagerup samples. Standards were prepared in the CSIRO laboratory to identify glyoxal, methyl glyoxal which are not available commercially in the 2-4-DNPH derivative form. The information on these 15 analysed compounds and their detection limits are presented in Table D.1. Of these 15 compounds analysed for, 8 compounds were detected in the air at Wagerup.

Table D.1 The carbonyl compounds analysed for by DNPH-HPLC, and their detection limits by this method, at Wagerup Winter 2006. D = detected in the air at Wagerup, ND = not detected.

Name	Formula	Molecular Weight	CAS No	Limit of Detection (ppb)	Detection at Wagerup
Formaldehyde	CH_2O	30.03	50-00-0	0.022	D
Acetaldehyde	C_2H_4O	44.05	75-07-0	0.029	D
Acrolein	C_3H_4O	56.06	107-02-8	0.000	ND
Glyoxal	$C_2H_2O_2$	58.04	107-22-2	0.000	D
Acetone	C_3H_6O	58.08	67-64-1	0.089	D
Propanal	C_3H_6O	58.08	123-38-6	0.004	D
2-Butenal	C_4H_6O	70.09	4170-30-3	0.000	ND
Methacrolein	C_4H_6O	70.09	78-85-3	0.000	ND
Methyl glyoxal	$C_3H_4O_2$	72.07	78-98-8	0.022	D
Methyl ethyl ketone	C_4H_8O	72.10	78-93-3	0.000	D
Butanal	C_4H_8O	72.10	123-72-8	0.000	ND
Pentanal	$C_5H_{10}O$	86.13	110-62-3	0.000	ND
Hexanal	$C_6H_{12}O$	100.16	66-25-1	0.000	D
Benzaldehyde	C_7H_6O	106.12	100-52-7	0.000	ND
m-Tolualdehyde	C_8H_8O	120.14	620-23-5	0.011	ND

D.3 AT-VOCs by GC-MS-FID

The measurement of VOCs in ambient air was carried out by actively trapping the VOCs on an adsorbent tube and then subsequently releasing these VOCs by thermal desorption and analysis of the VOCs by gas chromatography with flame ionisation (FID) and mass spectrometric detection (MSD). The method of AT-VOC analysis in this Study is a CSIRO method compatible with ISO16017-1:2000 (ISO 2000). Sampling and sorbent tube desorption was conducted according to USEPA Compendium method TO-17 (USEPA TO-17).

Compounds were identified by mass spectrometry and quantified by flame ionization detection. Calibration of the VOCs was carried out using a BTEX standard gas mixture (Scott Specialty Gases, San Bernadino, CA, USA) and using the empirical relationships involving effective carbon number (ECN) to apply these calibrations to other organic compounds (Jorgensen et al., 1990). Additional analytical checks of retention times and mass spectral identifications were performed with other standard gas mixtures containing in total, 42 hydrocarbons, 4 halocarbons, 11 oxygenated VOCs and one nitrile.

Air samples were collected onto PerkinElmer's Chromosorb^{TM} 106 sorbent tubes using constant-flow air sampling pumps (SKC Model 222) at 20 mL/min over an 8 hour period, giving a typical volume of 9.6 L. The tubes were analysed by using a PerkinElmer ATD 400 Automated Thermal Desorber and a Hewlett Packard 6890A gas chromatograph (GC), equipped with a Flame Ionization Detector and a Mass Selective Detector.

Tubes were cleaned prior to shipping to the field site by heating the tubes while purging them with helium (ultra high purity grade) for 20 mins at 210^{o}C and 15mins at 180^{o}C consecutively. The cleaned tubes were capped with a Swagelok fitting with PTFE ferrules and then stored in sealed containers. Fourteen tubes were shipped to the field site and returned unused. These were field blanks and are used to determine the blank levels and detection limits of the compounds for this method (AT-VOCs by GC-MS-FID). The blank level was taken as the mean of the field blank measurements of a compound. Because there were only 14 field blanks, the minimum detection level was taken as the blank corrected concentration of the largest concentration of a compound measured in the field blanks. 70 laboratory blanks were analysed. These laboratory blanks showed lower concentrations than the field blanks.

The Automated Thermal Desorber/GC procedure was as follows: The tube was thermally desorbed at 180°C for 2 minutes while back-flushed into the GC-MS-FID. Analysis was carried out on an Alltech AT-1 capillary column (60 m × 0.32 mm internal diameter x 1.0 μm film thickness) using a GC program from 35–240°C.

The quantification of these compounds in the air by AT-VOC and GC-MS-FID at Wagerup requires that (a) the compounds be trapped and subsequently thermally desorbed from the adsorbent tubes with an efficiency approximating 100%, (b) there be a satisfactory separation of the compound on the column and satisfactory identification free from interferences and (c) there be a quantitative response from the detector.

Compounds meet requirement (a) when the sampling volume used at Wagerup, 9.6 L, is less than the "Safe Sampling Volume" for that compound for the amount and type of adsorbent used (Chromosorb 106). If the volume sampled is greater than the Safe Sampling Volume then there will be some breakthrough of the material being sampled and only a qualitative measurement will be obtained. A set of "Safe Sampling Volumes" for Chromosorb 106 has been published (MDHS 72, 1993). The available results indicate that for (a) alkanes of the size of hexane and above, (b) benzene and higher aromatics, (c) alcohols butanol and above, (d) carbonyls methyl ethyl ketone and above and (e) esters ethyl acetate and above, the "Safe Sampling Volumes" are greater than 10L. Thus these chemicals meet criteria (a). The abbreviations used in the following Tables for comparison of the sampled volume with the Safe Sampling Volume for the compound and adsorbent used (Chromosorb 106), are: OK = volume sampled is less than the Safe Sampling Volume. Exceeded = volume sampled is greater than the Safe Sampling Volume, u/k = the Safe Sampling Volume is unknown. In many cases where the Safe Sampling Volume is unknown, we can infer, from the chemical properties of the compound and those of related compounds where the Safe Sampling Volume is known, that the unknown Safe Sampling Volume is most likely greater than 10 L. In these cases we have calculated a detection limit based on the assumption that the ratio of volume sampled to Safe Sampling Volume is OK.

In Table D.2 is a list of five compounds quantified in the Wagerup AT-VOC samples and their detection limits. These are methyl ethyl ketone, 2-methyl 2-propanol, 1-butanol, benzene and toluene.

In Table D.3 there is a group of 13 compounds that were explicitly identified in the Wagerup AT-VOC samples but not quantitatively determined because either the Safe Sampling Volume was exceeded or was unknown for these compounds. These compounds are: methanol, ethanol, 2-methyl-propene, acetone, acetic acid, isopropanol, isoprene, 2,3-butanedione, hexanal, octanal, alpha-pinene, nonanal and eucalyptol. In some of these cases where the Safe Sampling Volume is near or expected to be near 10 L, we have calculated a detection limit based on the assumption that the ratio of volume sampled to Safe Sampling Volume may be satisfactory, as discussed previously.

The available information about these quantified and qualitatively detected compounds is taken into account in the analysis of the Wagerup VOC data.

In Table D.4 there is a further group of compounds that were explicitly analysed for and might be expected to occur in the air at Wagerup, but were not detected in the AT-VOC samples. In some of these cases we have calculated a detection limit based on the assumption that the ratio of volume sampled to Safe Sampling Volume may be satisfactory, as discussed previously.

This analysis focused on all major peaks (VOCs) that were evident in the gas chromatograph analyses. As can be seen from Tables D.2, D.3 and D.4, this extends down to detection limits of 0.01 ppb. (The larger detection limits generally are associated with field blank contributions to that VOC analysis.) No peaks in the chromatograms that were comparable in size with the major peaks have been left un-analysed. There are other VOCs that, if present in the air at Wagerup, would have been trapped on the absorbent tubes, separated on the column used, and detected by the MS analysis. The absence of detection in this method is confirmation of the absence of those compounds (to the applicable level of detection). Examples of such compounds are the xylenes, ethyl benzene and the isomers of tri methyl benzene.

Table D.2 VOCs quantified in the AT-VOC samples of Wagerup Winter 2006 and the detection limits by the AT-VOC system. The abbreviations are for comparison of the sampled volume with the Safe Sampling Volume for the compound and adsorbent used (Chromosorb 106). They are: OK = volume sampled is less than the Safe Sampling Volume. Exceeded = volume sampled is greater than the Safe Sampling Volume., u/k = the Safe Sampling Volume is unknown.

Name	Formula	Molecular Weight	CAS Number	Sample Volume: Safe Sampling Volume	Detection Limit (ppbv)
Methyl ethyl ketone	C_4H_8O	72	78-93-3	OK	0.07
2-Methyl 2-propanol	$C_4H_{10}O$	74	75-65-0	OK	0.11
1-Butanol	$C_4H_{10}O$	74	71-36-3	OK	0.01
Benzene	C_6H_6	78	71-43-2	OK	0.06
Toluene	C_7H_8	92	108-88-3	OK	0.02

Table D.3 VOCs qualitatively identified in the AT-VOC samples of Wagerup Winter 2006. The abbreviations are for comparison of the sampled volume with the Safe Sampling Volume for the compound and adsorbent used (Chromosorb 106). They are: OK = volume sampled is less than the Safe Sampling Volume. Exceeded = volume sampled is greater than the Safe Sampling Volume., u/k = the Safe Sampling Volume is unknown.

Name	Formula	Molecular Weight	CAS Number	Sample Volume: Safe Sampling Volume	Detection Limit (ppbv)
Methanol	CH_4O	32	67-56-1	Exceeded	-
Ethanol	C_2H_6O	46	64-17-5	Exceeded	-
2-methyl-propene	C_4H_8	56	115-11-7	u/k	-
Acetone	C_3H_6O	58	67-64-1	Exceeded	-
Acetic acid	$C_2H_4O_2$	60	64-19-7	u/k	-
Isopropanol	C_3H_8O	60	67-63-0	Exceeded	-
Isoprene	C_5H_8	68	78-79-5	u/k	-
2,3-Butanedione	$C_4H_6O_2$	86	431-03-8	u/k	0.03
Hexanal	$C_6H_{12}O$	100	66-25-1	u/k	0.02
Octanal	$C_8H_{16}O$	128	124-13-0	u/k	0.02
α-Pinene	$C_{10}H_{16}$	136	80-56-8	u/k	0.01
Nonanal	$C_9H_{18}O$	142	124-19-6	u/k	0.07
Eucalyptol	$C_{10}H_{18}O$	154	470-82-6	u/k	0.01

Table D.4 Compounds analysed for but not detected in the Wagerup AT-VOC samples. The abbreviations are for comparison of the sampled volume with the Safe Sampling Volume for the compound and adsorbent used (Chromosorb 106). They are: OK = volume sampled is less than the Safe Sampling Volume. Exceeded = volume sampled is greater than the Safe Sampling Volume., u/k = the Safe Sampling Volume is unknown.

Name	Formula	Molecular Weight	CAS Number	Sample Volume: Safe Sampling Volume	Detection Limit (ppbv)
Acetonitrile	C_2H_3N	41	75-05-8	u/k	-
Acetaldehyde	C_2H_4O	44	75-07-0	Exceeded	-
Methanethiol	CH_4S	48	74-93-1	u/k	-
Acrolein	C_3H_4O	56	107-02-8	Exceeded	-
Trimethylamine	C_3H_9N	59	75-50-3	u/k	-
Dimethylsulfide	C_2H_6S	62	75-18-3	u/k	-
Furan	C_4H_4O	68	110-00-9	u/k	0.03
Methyl vinyl ketone	C_4H_6O	70	78-94-4	OK	0.03
Cycloheptene	C_7H_{12}	96	628-92-2	u/k	0.01
Benzaldehyde	C_7H_6O	106	100-52-7	u/k	0.08
Ethanol, 2-butoxy-	$C_6H_{14}O_2$	118	111-76-2	OK	0.02
Decanal	$C_{10}H_{20}O$	156	112-31-2	u/k	0.08

APPENDIX E: CONCENTRATIONS AND IDENTIFICATION OF OBSERVED MASSES

E.1 The approach adopted concerning compound identification

A fundamental aspect of this Study is the identification of substances at concentrations that, judging from earlier studies, might possibly occur only just above the resolving power of the PTR-MS. In performing such identifications in this Study we do not explicitly undertake hypothesis testing by statistical methods. However we do draw upon some knowledge from that science, concerning the Type 1 and Type 2 errors also known as rejection and acceptance errors (Keeping, 1995) as outlined below.

The overall approach of our analysis of the PTR-MS data is to minimize the probability of failing to identify the presence of a substance in the air at Wagerup when it is indeed present (a Type 1 error), rather than to minimize the probability of concluding that a substance is in the air at Wagerup when it is not actually present (a Type 2 error).

E.2 Significant masses observed with the PTR-MS at Wagerup

Because of the large number of ambient concentration measurements in the PTR-MS data set, special data analysis techniques were utilized to interpret the large PTR-MS data set. These were first presented in the Pilot Study (Galbally et al., 2006). Two bulk properties of the data set, described as measures, were examined to help focus the subsequent analysis.

The first data measure is the fraction of occasions throughout the total data set for a given mass where the reading for that particular mass was above the minimum detection limit (MDL) for that mass. This measure is expressed as a dimensionless fraction represented by F {previously represented as T>MDL in Galbally et al., (2006)}. This first measure is essentially "for a particular mass, during what portion of the measurements is a signal being detected?"

The second data measure is designed to identify significant peaks in the concentration data. The 99th percentile of concentration readings, P, represents the 348 highest concentrations in this data set for an individual mass (34813 measurements per mass each of 0.5 seconds duration, see Appendices A, B and C) and as such represents a concentration that is not often reached or exceeded in the data set. The second measure is the ratio for each mass of the 99 percentile of concentration readings, P, to the MDL. This measure is expressed as a dimensionless fraction represented by P/MDL. The second measure is essentially "how large are the peak concentrations compared with the MDL?"

In Table E.1 information is presented on those masses that have the highest values of these measures: essentially those masses that were unequivocally detected at the Study site. The data show 40 masses with periods above the MDL of greater than 0.07, and 31 masses with peak values (defined as the 99 percentile) that are greater than or equal to 2 MDLs, P/MDL>2.

Overall, 24 masses meet these two criteria. The 24 masses listed in Table E.1 are used in the subsequent analysis. The masses in Table E.1 are ordered according to the observed dimensionless peak concentration, P/MDL.

(It should be noted that this analysis of which masses are detected and which not, is independent of whether indicative or calibrated concentrations are used, because both the numerator and the denominator are scaled by the calibration factor when it is used.)

There are 191 other masses which do not have compounds present in detectable concentrations in the PTR-MS data set from 60 days of monitoring. These masses correspond to a large number of chemical compounds (which are mainly volatile organic compounds), that can be detected by the PTR-MS, but were not detected in this Study in air either from the Refinery or from the surrounding region. There are some VOCs that would be expected to be in the air at Wagerup and were not observed by these measurement techniques because the techniques are not sensitive to these compounds. These include ethane, propane, butanes and pentanes, some halogen substituted organics, carbonyl sulfide and carbon disulfide, ethanol and oxalic acid. The techniques used in this Study focused on "*those simple organic compounds that are or can be emitted by the refinery that have not been measured in previous ambient sampling (including polar compounds)*." Recommendation 14, Wagerup Air Quality Review (CSIRO 2004). All VOCs identified by the two independent techniques (see following sections) were also observed by the PTR-MS.

Most of the VOCs detected have protonated molecular masses of less than 100. This probably arises because of two reasons. Firstly the vapour pressure of compounds decreases with increasing molecular mass (see Goldstein and Galbally 2007), and this means that the mixing ratio in the atmosphere away from sources is likely to be lower for compounds of higher molecular mass. Secondly, monoterpenes, that have a parent ion protonated mass of 137, are known to fragment to mass 81, and indeed are detected at that mass. Compounds with protonated masses of 101 and 117 are detected.

Table E.1. The 24 PTR-MS protonated masses detected and used in the subsequent analyses of the Wagerup Winter Study measurements. See the text for definitions of MDL, F, P, and P/MDL. N is the number of ambient measurements of each individual mass, each measurement being of 0.5 second duration.

Mass (amu)	MDL (ppbv)	F	Peak (ppbv)	P (ppbv)	P/MDL	N
59	0.13	0.73	6.83	2.44	18.36	34813
43	0.45	0.44	8.03	3.04	6.69	34813
33	2.19	0.55	33.11	12.68	5.78	34813
61	0.10	0.30	1.29	0.49	4.80	34813
41	0.32	0.31	3.61	1.25	3.94	34813
45	0.25	0.32	2.16	0.88	3.51	34813
73	0.14	0.19	1.11	0.43	3.10	34813
42	0.05	0.25	1.81	0.14	3.04	34813
81	0.11	0.20	1.49	0.32	2.88	34813
71	0.18	0.16	1.13	0.52	2.85	34813
47	0.23	0.22	3.32	0.64	2.72	34813
69	0.53	0.16	4.87	1.41	2.68	34813
93	0.40	0.13	6.86	0.98	2.45	34813
75	0.09	0.13	0.61	0.20	2.34	34813
97	0.15	0.11	1.51	0.34	2.33	34813
57	0.09	0.12	0.88	0.21	2.26	34813
83	0.07	0.12	0.33	0.15	2.22	34813
60	0.13	0.11	0.74	0.29	2.17	34813
79	0.18	0.09	1.55	0.40	2.17	34813
87	0.16	0.10	0.76	0.33	2.11	34813
117	0.21	0.12	0.82	0.43	2.05	34813
49	0.09	0.11	0.41	0.18	2.05	34813
101	0.71	0.10	3.67	1.45	2.05	34813
63	0.13	0.11	0.78	0.26	2.04	34813

E.3 The Search for Candidate Compounds

There have been a number of studies published in the scientific literature that relate measurements of specific masses made by PTR-MS to specific compounds via simultaneous chemical composition measurements made by other techniques. Summaries of identifications that have been made under varying atmospheric environments are presented in de Gouw and

Warnecke (2007), Karl et al., (2007), and Ionicon (2007). Depending on the chemical processes and emissions in the surrounding environment, a particular mass measured by the PTR-MS may have different chemical compositions. Unfortunately there are not standard methodologies to identify the composition of these PTR-MS observed masses.

E.3.1 The Procedure for the Search for Candidate Compounds

The following approach, for the identification of chemical compounds that are contributing to observed PTR-MS masses, has been developed for this Study.

The examination of the possible chemical composition of the observed PTR-MS masses involves the application of following steps, carried out in a sequential manner, to the analysis of the PTR-MS record:

1. sorting all the mass data from the PTR-MS to identify those masses that have sufficient concentration to facilitate identification;
2. examination of the known chemical species that are detected by the PTR-MS at those masses either directly or as primary fragments to determine an initial list of candidate compounds;
3. exclusion from the list of candidate compounds of species that have secondary fragments or isotope patterns (at two or more masses) that are inconsistent with the observations and then preparation of a reduced list of candidate compounds;
4. examination of the simultaneous measurements of compound concentrations made by independent analytical techniques, to determine the contribution of candidate compounds to the concentration of the observed PTR-MS masses.

E.3.2 Masses that have sufficient concentration to facilitate identification

There are 24 mass numbers that have discernable non-zero measurements in the PTR-MS data set as listed in Table E.1. These mass numbers listed in order of decreasing P/MDL are 59, 43, 33, 61, 41, 45, 73, 42, 81, 71, 47, 69, 93, 75, 97, 57, 83, 60, 79, 87, 117, 49, 101, and 63.

E.3.3 Preparation of an initial list and its refinement to a reduced list of candidate compounds

In selecting the candidate compounds for the 24 masses, there has been a review of 265 chemical species that have a proton affinity greater than water and have these protonated masses (Hunter and Lias 2003). There has been a review of the fragmentation patterns of 141 compounds that could contribute charged fragments at these masses using a table of fragmentation patterns provided by Ionicon Analytik (2005). Because of the pattern of low and comparable concentrations across the mass range, only fragmentations that contributed more than 20% of the total mass to the fragment ion were thoroughly considered. Radicals or other chemicals that would not be expected to be produced in either the atmosphere or an alumina Refinery, or survive in the atmosphere were rejected from consideration. We have weighted our choice of possible compounds towards those that have already been positively identified by PTR-MS in the ambient atmosphere (deGouw and Warnecke 2007; Karl et al. 2007). The interim list of candidate compounds consists of 150 compounds that can directly contribute to these masses plus another 32 compounds that can contribute to the masses via fragmentation.

Ion fragmentation patterns in the PTR-MS provide information important for the confirmation of the identities of the compounds. For example in the case of mass 33, the protonated chemical species can be either methanol or a fragment of methyl formate. Methanol does not fragment and its protonated signal is all at mass 33. Methyl formate does fragment and has peaks at mass 61 and mass 33, with 97% of the signal being in mass 61(Ionicon Analytik 2005). In the case that the 33 mass concentration was solely due to methyl formate, the peak at mass 61 should be 30 times larger than that at 33 amu. In a data set where mass 61 is generally smaller in concentration than mass 33, and mass 61 can be contributed to by other compounds that do not fragment to mass 33, at most only 3% of mass 33 can be due to methyl formate. Therefore the most appropriate identification of more than 97% of the mass 33 concentration is methanol.

A consideration of isotopes has a role in either identifying or excluding possible compounds contributing to a PTR-MS measured mass. This feature is well known in mass spectrometry. Carbon is made up of 98.89% ^{12}C and 1.11% ^{13}C isotopes. Any carbon compound with a natural mixture of carbon, that has n carbon atoms in the molecule will have a primary molecular mass that has a contribution of n times ^{12}C. A small percentage of the molecules of the compound will have a molecular mass of the normal compound mass plus 1, a contribution due to the occurrence of the isotope ^{13}C in the molecule. The fraction of molecules that have this extra mass unit is n times 1.11%. In the PTR-MS signals, the primary ion will occur at the protonated mass and there will be a signal at the mass number of the primary ion plus 1, of magnitude n times 1.1%of the primary ion signal. This occurs because ^{13}C makes up 1.11% of naturally occurring carbon. Similarly an oxygenated compound with a single oxygen atom will have at the mass number of its protonated compound mass plus 2, a contribution of 0.2% of the primary ion signal due to the isotope O^{18} that makes up 0.2% of the naturally occurring oxygen. Other examples of this isotope effect also occur. This isotope effect is visible in Table E.1. Mass 59 is identified as protonated acetone (3 x ^{12}C), and the ^{13}C of protonated acetone will give a signal at mass 60 of roughly 3% of that at mass 59. When the ion counts are examined in detail, the values of mass 60 corresponding to the highest mass 59 counts are approximately 7% of the mass 59 readings, indicating that under these conditions of high mass 59 (acetone) concentrations, up to a half of the mass 60 reading is due to the isotopic effect of $^{13}C/^{12}C$.

Reduced lists of candidate compounds were prepared for the primary and secondary masses. These are presented in the following two sub-sections of the report.

E.4 Comparison of Concentrations for Protonated Masses measured by PTR-MS, with compounds measured by the ATD-VOC and Carbonyl Techniques

The next step in the identification process involves the use of independent analytical techniques to determine the contribution to the concentration of the observed masses by the final candidate compounds. The independent analytical techniques that have been utilized in this Study to provide specific chemical species identification are DNPH sampling and HPLC analyses for carbonyls, and adsorbent tube sampling and AT-GC-MS-FID for VOC analyses. With each of these techniques the search is limited by the detection efficiency and calibration standards utilized. Therefore not every possible candidate compound is measured.

A comparison is made of concentrations measured by the PTR-MS for 12 detected protonated masses, and the concentrations measured by independent techniques of compounds that correspond to these masses and could be measured at these concentrations. The data comes from 15 8-hour periods during the Study chosen to represent the periods of highest and lowest 8-hour concentrations of VOCs in the PTR-MS data set. AT-VOC samples and carbonyl samples were processed for these periods. The 15 8-hour periods and the Total VOC concentrations for 24 protonated masses measured by PTR-MS for this Study are listed in Table E.2.

E.4.1 Comparison of Concentrations for the initial 12 Primary Protonated Masses

The 12 initial mass numbers (from the top of Table E1) and their possible candidate compounds are listed in Table E.3. Table E.3 also lists whether the candidate compound was sought for, or observed, with the AT-VOC and Carbonyl measurements or whether the candidate compound was not measured by the 2 independent techniques utilized. These 12 mass numbers are considered first because they have the greatest fraction of data above the detection limit, and the highest peaks relative to the detection limit.

The mean concentrations and standard error (se) of the possible compounds measured by PTR-MS and the two independent techniques for the 15 8-hour period in the Wagerup Winter Study are listed in Table E.4. It can be seen in Table E.4 that the mean concentrations of these VOCs are in general quite low from 0.05 to 1.1 ppb, with the exception of methanol of 6 ppb.

Table E.4 compares the concentrations determined by the PTR-MS with those observed by the two independent techniques to examine the issue of identification. A match between a particular mass and a candidate compound (or set of compounds) is considered satisfactory when, after the above processes have been carried out, either: (1) there is only one possible compound for the PTR-MS mass, or (2) within the accuracy and precision of the measurements there is agreement between the concentration determined by the PTR-MS and the sum of one or more compounds contributing to that PTR-MS mass, as determined by independent analytical techniques.

It may be anticipated that on some occasions the concentration(s) of the contributing compounds may be less than the concentration at a specific mass observed by the PTR-MS. In this case the remaining fraction (PTR-MS concentration minus identified contributing concentrations) will be classified as an unknown compound.

The basis of the identifications will be indicated by the following letters: S = single suitable candidate, I = independent measurement, T = tentative identification based on indirect evidence and other studies.

Table E.2 The Total VOC concentrations from PTR-MS measurements for the 15 8 hour periods.

No. of Event	Start time	End time	Total VOC concentration (24 masses) (ppbv)
1	29/08/2006 16:00	30/08/2006 00:00	10.48
2	30/08/2006 00:00	30/08/2006 08:00	11.21
3	9/09/2006 09:00	9/09/2006 17:00	12.06
4	9/09/2006 17:00	10/09/2006 01:00	14.49
5	14/09/2006 17:00	15/09/2006 01:00	16.13
6	17/09/2006 17:00	18/09/2006 01:00	5.35
7	25/09/2006 17:00	26/09/2006 01:00	3.64
8	28/09/2006 17:00	29/09/2006 01:00	7.33
9	29/09/2006 01:00	29/09/2006 09:00	8.37
10	29/09/2006 09:00	29/09/2006 17:00	18.54
11	29/09/2006 17:00	30/09/2006 01:00	9.41
12	2/10/2006 01:00	2/10/2006 09:00	7.65
13	2/10/2006 09:00	2/10/2006 17:00	11.03
14	2/10/2006 17:00	3/10/2006 01:00	6.36
15	3/10/2006 01:00	3/10/2006 09:00	6.74

Table E.3 Possible identities of the 12 initial protonated masses measured with the PTR-MS in the Wagerup Winter Study, and the measurement of these compounds by the independent techniques described in the text. The abbreviations are for analyses by the independent techniques. They are: Qual = qualitative detection, D = quantitative detection, ND = not detected in concentration above the detection limit, NM = not measured by the technique.

Protonated Mass (amu)	Candidate Compounds	CAS Number	ATD-VOC Measurement	Carbonyl Measurement
33	Methanol	67-56-1	Qual	NM
41	Propyne 1,2-Propadiene Cyclopropene	74-99-7 463-49-0 2781-85-3	NM NM NM	NM NM NM
42	Acetonitrile	75-05-8	ND	NM
43	Cyclopropane Propene Ketene n-Propanol Isopropanol	75-19-4 115-07-1 463-51-4 71-23-8 67-63-0	NM NM NM NM Qual	NM NM NM NM NM
45	Acetaldehyde Ethylene oxide 1,2-Ethanediol	75-07-0 75-21-8 107-21-1	ND NM NM	D NM NM
47	Formic acid Ethanol Dimethyl ether Thioformaldehyde	64-18-6 64-17-5 115-10-6 865-36-1	NM Qual NM NM	NM NM NM NM
59	Acetone Propanal Ethene, methoxy- 1,3-Propanediol Glyoxal	67-64-1 123-38-6 107-25-5 504-63-2 107-22-2	D NM NM NM NM	D D NM NM D
61	Methyl formate Acetic acid Ethane, methoxy Hexyl acetate Ethyl acetate Propyl acetate	107-31-3 64-19-7 540-67-0 142-92-7 141-78-6 109-60-4	NM Qual NM NM NM NM	NM NM NM NM NM NM

Table E.3 ctd. Possible identities of the 12 initial protonated masses measured with the PTR-MS in the Wagerup Winter Study, and the measurement of these compounds by the independent techniques described in the text. The abbreviations are for analyses by the independent techniques. They are: Qual = qualitative detection, D = quantitative detection, ND = not detected in concentration above the detection limit, NM = not measured by the technique.

Protonated Mass (amu)	Candidate Compounds	CAS Number	ATD-VOC Measurement	Carbonyl Measurement
69	Isoprene	78-79-5	Qual	NM
	Furan	110-00-9	ND	NM
	3-Methyl butanal	590-86-3	NM	NM
	Pentanal	110-62-3	NM	ND
	Octanal	124-13-0	Qual	NM
	Nonanal	124-19-6	Qual	NM
71	Methyl vinyl ketone	78-94-4	ND	ND
	Methacrolein	78-85-3	NM	ND
	2-Butenal	4170-30-3	NM	ND
	Furan, 2,5-dihydro-	1708-29-8	NM	NM
	2-Butene, 2-methyl-	513-35-9	NM	NM
	3-Methyl, 1-butanol	123-51-3	NM	NM
	2-Ethyl-1-hexanol	104-76-7	NM	NM
73	Methyl-ethyl-ketone	78-93-3	D	ND
	Furan, tetrahydro-	109-99-9	NM	NM
	Methyl glyoxal	78-98-8	NM	D
81	Cyclohexadiene	592-57-4	NM	NM
	α-Pinene	80-56-8	D	NM
	Furfural alcohol	98-00-0	NM	NM
	(E)-3-Hexenal	6789-80-6	NM	NM
	Eucalyptol	470-82-6	D	NM

Table E.4 Mean Concentrations and standard error (se) of the possible compounds measured by PTR-MS and the two independent techniques for the 15 8-hour periods in the Wagerup Winter Study

Primary Protonated Mass	PTR-MS Mean (se) (ppbv)	Possible Compound	CAS No	AT-VOC Mean (se) (ppbv)	Carbonyl Mean (se) (ppbv)
33	6.14 (0.67)	Methanol	67-56-1	Qual > 0.63	NM
41	0.35 (0.05)	Multiple compounds?		NM	NM
42	0.05 (0.01)	Acetonitrile	75-05-8	ND <0.07	NM
43	1.09 (0.17)	Isopropanol and other compounds	67-63-0	Qual >0.20	NM
45	0.30 (0.03)	Acetaldehyde	75-07-0	ND <3.01	0.36 (0.07)
47	0.16 (0.03)	Formic acid Ethanol and other compounds	64-18-6 64-17-5	NM Qual >0.74	NM NM
59	0.78 (0.11)	Acetone Propanal Glyoxal	67-64-1 123-38-6 107-22-2	1.55 (0.21) NM NM	0.24 (0.03) 0.05 (0.01) 0.03 (0.004)
61	0.14 (0.03)	Acetic acid and other compounds	64-19-7	Qual 2.77	NM
69	0.23 (0.05)	Isoprene Furan Pentanal other compounds	78-79-5 110-00-9 110-62-3	Qual >0.02 ND <0.03 NM	NM NM ND < 0.00
71	0.11 (0.02)	Methyl vinyl ketone Methacrolein 2-Butenal other compounds	78-94-4 78-85-3 4170-30-3	ND <0.03 NM NM	ND ND <0.01 ND
73	0.09 (0.02)	Methyl ethyl ketone Butanal Methyl glyoxal	78-93-3 123-72-8 78-98-8	0.14 (0.01) NM NM	0.53 (0.03) ND <0.00 0.10 (0.02)
81	0.12 (0.03)	α-Pinene Eucalyptol other compounds	80-56-8 470-82-6	0.03 (0.01) 0.02 (0.01)	NM NM

Of the 12 PTR-MS masses considered, 4 masses (33, 42, and 45) have only one candidate compound that contributes to that mass and therefore their identifications are already determined, and the identification is indicated by S in Table E.5.

The PTR-MS concentration of mass 45 and the concentration of acetaldehyde determined by DNPH-HPLC agree to within the standard errors of the mean mass and therefore are considered to be identified. For mass 59 acetone, the independent techniques straddle the PTR-MS results, indicating that the most likely compound is acetone. This identification for acetaldehyde and acetone is indicated by I.

For the two PTR-MS masses (47 and 61), there has been identification of one contributing compound in each case. In the cases of PTR-MS masses 47, and 61, the concentrations indicated by the AT-VOC measurement are larger than the concentrations indicated by the PTR-MS. This may occur in part because the PTR-MS has a low sensitivity to ethanol (CSIRO unpublished) and acetic acid (de Gouw and Warnecke 2007) and in part due to other compounds contributing. For the two PTR-MS masses (43, and 81), there has been identification of one or more contributing compounds. But these are inadequate in concentration to explain the full concentration from the PTR-MS. In all 4 of these cases the identification is indicated by I, but the compound description has qualifying words concerning other compounds.

The PTR-MS concentration of mass 69 cannot be explained by either furan or pentanal. For AT-VOC, there is qualitative identification of isoprene, but not quantitative. However there is indirect evidence from the scientific literature to add to these observations (de Gouw and Warnecke 2007; Karl et al. 2007) to indicate that the identification is isoprene. The identification is indicated by T.

The two masses (41 and 71) have no candidate compound that could be detected by the independent techniques utilized here. Mass 71 had three candidate compounds measured but none provided an explanation of the PTR-MS concentration. Therefore the chemical identities of these masses are unidentified.

These identities are summarized in Table E.5.

Table E.5 Suggested identities of the 12 initial protonated masses measured with the PTR-MS in the Wagerup Winter Study, and the basis of the identification, S = single suitable candidate, I = independent measurement, T = tentative identification based on indirect evidence and other studies.

Protonated Mass (amu)	Candidate Compounds	CAS Number	Basis of Identification
33	Methanol	67-56-1	S
41	Multiple compounds?	-	-
42	Acetonitrile	75-05-8	S
43	Multiple compounds including Isopropanol		I
45	Acetaldehyde	75-07-0	I
47	Formic acid, Ethanol and possibly other compounds	-	T & I
59	Acetone Glyoxal	67-64-1 177-22-2	I
61	Acetic acid and possibly other compounds	-	I
69	Isoprene	78-79-5	T
71	Multiple compounds?	-	-
73	Methyl ethyl ketone Methyl Glyoxal	78-93-3 78-98-8	I
81	Mono terpenes and possibly other compounds	-	I

E.4.2 Identification of the 12 other Protonated Masses

The 12 other masses (that occurred in the lower half of Table E1) and possible candidate compounds are listed in Table E.6. These 12 mass numbers are considered second because they have a lesser fraction of time above the detection limit and lesser peaks relative to the minimum detection limit compared, with the initial 12 mass numbers. For these 12 masses, the probable and possible candidate compounds are identified, from the AT-VOC and carbonyl analyses done here and from the PTR-MS atmospheric chemistry literature (de Gouw and Warnecke, 2007; Karl et al. 2007). The suggested identities of the 12 secondary protonated masses are presented in Table E.7. No further analysis is made to determine the chemical identity of these masses. This is because of the difficulty or impossibility of identification where the concentration signals are approaching the detection limits of the instruments.

Table E.6. Possible identities of the 12 other protonated masses measured with the PTR-MS in the Wagerup Winter Study; 1 This Study and associated work; 2 de Gouw and Warnecke (2007); 3 Karl et al. (2007);4 Mayr et al.(2003); 5 NIST(2005) Chemistry Webbook, 6 Boschetti et al.(1999); 7 Buhr et al (2002).

Protonated Mass (amu)	Probable Compounds	Other Possible Compounds	CAS Number	Reference
49	Methanethiol	-	74-93-1	4
57	Acrolein		107-02-8	3
	2-Butene, (E)-		624-64-6	3
	1-Propene, 2-methyl-		115-11-7	1,3
	1-Butanol		71-36-3	3
	1-Propanol, 2-methyl-		78-83-1	1
60	^{13}C of acetone (contributor)		60-35-5	1
	Trimethylamine & other amines		75-50-3	5
63	Dimethyl sulphide		75-18-3	2
		1,2-Ethanediol	107-21-1	5
75	Hydroxyacetone		116-09-6	2, 3
	Methyl acetate		79-20-9	3
79	Benzene		71-43-2	1, 2, 3
	Ethylbenzene		100-41-4	3
83	Furan, 3-methyl-		930-27-8	2, 3
	Furan, 2-methyl-		534-22-5	2, 3
	Hexenol-		928-96-1	2
	Hexanal		66-25-1	2, 3
	Hexenyl acetate		3681-82-1	2
		Isoprene hydroxy carbonyls		2

87	2, 3-Butanedione 2-Pentanone Pentanal	Methacrylic acid 2-Methyl-3-butene-2-ol	431-03-8 107-87-9 110-62-3 54193-36-1 115-18-4	1, 3 2, 3 1, 3 2 2
93	Toluene		108-88-3	1, 2, 3
97	Furans Furaldehydes	Cycloheptene Cyclopentene, 1,2-dimethyl- Methane sulfonic acid Heptanal	e.g. 3710-43-8 628-92-2 765-47-9 75-75-2 111-71-7	3 3 5 5 7
101	Hexanal Isoprene hydroperoxides	Multiple chemical species	66-25-1 -	1 2
117		Multiple chemical species	-	6,7

Table E.7. Suggested identities of the 12 other protonated masses measured with the PTR-MS in the Wagerup Winter Study, and the basis of the identification, S = single suitable candidate, I = independent measurement, T = tentative identification based on indirect evidence and other studies.

Protonated Mass (amu)	Candidate Compounds	CAS Number	Basis of Identification
49	Methanethiol	74-93-1	S
57	Multiple compounds?	-	-
60	Trimethylamine & ^{13}C of acetone	75-50-3 -	T
63	Dimethyl sulphide	75-18-3	T
75	Multiple compounds?	-	-
79	Benzene	71-43-2	T
83	Multiple compounds?	-	-
87	2, 3-Butanedione	431-03-8	I
93	Toluene	108-88-3	S&I
97	Multiple compounds?	-	-
101	Hexanal other compounds?	66-25-1	I&T
117	Multiple compounds?	-	-

E.4.3 Multiple and Other Compounds

In a number of cases in the tables in the previous sub-section there has been the listing of multiple compounds or other compounds against mass numbers. This arises because where several organic compounds have the same molecular mass, technically described in the mass spectrometry literature as Isobars, and also all have proton affinities greater than water, then the PTR-MS will be sensitive to these several compounds and will sum the response to all of them under the one mass. For most of these masses, a number of the possible compounds are listed in the first tables in sections E4.1 and E.4.2. In some cases this is not done, and the following is a selection of some of the possible compounds and fragments of compounds contributing to these masses.

Mass 41: Propyne (Warneke et al. 2003), 1,2 propadiene, cyclopropane, (NIST , 2005 Chemistry webbook); C_4 – C_9 alcohols (Buhr et al. 2002); propylene glycol (Ionicon 2007); Propanoic acid, 2-methyl, 2-methylpropyl ester, 2-methyl propanoic acid (Ezra et al., 2004); 2-methyl butyric acid, methacrylic acid, (Ionicon, 2007); butyl formate, octyl acetate, methyl decanoate (Aprea et al. 2007); hexyl acetate (Fall et al. 1999); ethyl acetate, butyl isobutyrate, isobutyl isobutyrate, ethyl butyrate (Buhr et al. 2002); Acetaldehyde (Blake et al. 2006), propanal, pentanal, octanal, nonanal (Buhr et al. 2002) 2-methyl butanal, 3-methyl butanal (Ionicon 2007); hexanal, methacrolein (Blake et al., 2006); Alkyl nitrates (Aoki et al., 2007); p-cymene (Tani et al., 2003).

Mass 43:, 1-propanol, isopropanol, 1-hexanol, 2-hexanol, 2-pentanol, 3 methyl-1-butanol (Buhr et al., 2002); Acetic acid (Maleknia, et al., 2007); Propylene (Christian et al., 2004); Propene (Lindinger et al., 1998); Cyclopropane (Warneke et al., 2003); 1-butanol, 3-methyl, acetate (Ezra et al., 2004) Alkyl nitrates (Aoki et al., 2007).

Mass 75: Methyl acetate (Boschetti at al., 1999), butyl propanoate, propyl propanoate (Aprea et al., 2007), propionic acid (von Hartungen et al., 2004), ethyl propanoate (Buhr et al., 2002), acetol (Christian et al. 2004).

Mass 101: Hexanal (Mayr et al., 2003), 2-hexanone (Buhr et al. 2002), isoprenic hydroperoxides (Crutzen et al., 2000), acetyl acetone (Maleknia et al., 2007).

Mass 117: Butyl acetate, ethyl butanoate, propyl propanoate, methyl-2-methylbutanoate, methyl-3-methylbutanoate (Boschetti et al. 1999), caproic acid (von Hartungen et al., 2004), propanoic acid, 2-methyl, ethyl ester (Ezra et al., 2004).

APPENDIX F: SELECTED 8-HOUR PERIODS DURING THE STUDY

The PTR-MS and AQMS observations from Boundary Rd were averaged over 8 hours to match the periods when carbonyls were sampled for 8 hours. Twenty two of these occasions were examined in detail. The reasons for selecting these periods were that either a high concentration was observed by PTR-MS, Carbonyl-DNPH or NO_x measurements or there was an odour event, or Alcoa requested the data. The dates and times of these periods, the observed TVOC, carbonyl, CO, $CO_{2,}$ NO_x, concentrations, meteorological parameters and the reason for the selection are recorded in Table F.1.

Any information derived from analyses of these occasions are included in the body of the report.

Table F.1 The 8 hour periods selected and corresponding data from the Wagerup Winter Study.

Date & Start Time (8-hour)	PTR-MS TVOC ppb	Carbonyl Total ppb	CO (ppm)	CO_2 (ppm)	NO_x (ppb)	WS (m/s)	WD (deg)	Reason*
24/08/2006 16:00	9.26	n/a	n/a	406	2.7	1.7	65	MOA
29/08/2006 16:00	10.48	2.25	n/a	n/a	2.9	2.5	17	MCNOA
30/08/2006 0:00	11.21	2.07	n/a	n/a	6.2	4.1	24	MC
09/09/2006 9:00	12.06	1.91	0.07	360	1.4	3.6	56	MC
09/09/2006 17:00	14.49	2.12	0.07	373	1.4	3.2	83	MCN
10/09/2006 09:00	11.12	1.74	0.1	370	1.9	1.8	66	MA
13/09/2006 17:00	7.75	1.66	n/a	n/a	4.8	2.0	169	MOA
14/09/2006 17:00	16.13	2.59	n/a	n/a	6.9	1.7	202	MC
15/09/2006 1:00	9.51	n/a	n/a	n/a	10.2	0.8	178	MCNA
15/09/2006 9:00	18.82	n/a	n/a	n/a	4.7	1.5	330	MCNOA
15/09/2006 17:00	11.01	n/a	n/a	n/a	3.1	1.5	134	MCA
17/09/2006 17:00	5.35	1.58	n/a	n/a	1.9	1.4	23	C
24/09/2006 17:00	4.42	1.26	n/a	n/a	1.4	1.8	164	MOA
25/09/2006 17:00	3.64	3.28	n/a	n/a	1.9	1.3	173	C
28/09/2006 17:00	7.33	1.91	n/a	n/a	3.6	2.2	187	MC
29/09/2006 1:00	8.37	1.64	n/a	n/a	2.6	3.2	93	MC
29/09/2006 9:00	18.54	3.25	n/a	n/a	3.2	3.3	277	MC
29/09/2006 17:00	9.41	1.96	n/a	n/a	3.1	1.3	48	MC
02/10/2006 1:00	7.65	1.73	n/a	n/a	7.1	0.8	195	MC
02/10/2006 9:00	11.03	2.43	n/a	n/a	2.9	3.0	262	MC
02/10/2006 17:00	6.36	1.48	n/a	n/a	2.2	0.6	337	C
03/10/2006 1:00	6.74	1.39	n/a	n/a	1.7	2.1	352	C

*M-PTRMS high, C-Carbonyl high, N- NO_x high, O-Odour event, A-Alcoa requested

APPENDIX G: COOLING TOWER BAGS

This work is a continuation of the exploratory Study of PTR-MS response and odour commenced after the Pilot Study (Galbally et al. 2007). At the end of the Winter Study, stack sampling was conducted by consultants for odours from the cooling towers at the Refinery. Four of these cooling tower bags along with 4 N_2 blank bags were supplied to the CSIRO team by Alcoa Wagerup on 9th and 10th of October 2006. The details of bags and sampling information are presented in Table G.1.

Table G.1. Description of cooling tower bags and sampling information

Date Supplied	Bag No	Description	PTRMS	AT-VOC	Carbonyls
10/10/2006	1	N_2 blank bag	sampled	sampled	
10/10/2006	2	N_2 blank bag	sampled	sampled	sampled
10/10/2006	3	N_2 blank bag	sampled		sampled
10/10/2006	4	N_2 blank bag	sampled		
9/10/2006	1	Cooling Tower #2 Alcoa WG Ro6410	sampled		sampled
9/10/2006	2	Cooling Tower #2 Alcoa WG Ro6410	sampled	sampled	
10/10/2006	3	Cooling Tower Alcoa WG Ro6410	sampled		sampled
10/10/2006	4	Cooling Tower Alcoa WG Ro6410	sampled	sampled	

The samples contained cooling tower air diluted in nitrogen by a factor of 19 (to ensure that there would be no condensation of water after the sample was taken). Concentrations of compounds in the cooling tower air were determined from:

Concentration = (conc. in Cooling Tower bag minus conc.in N_2 blank bag) x 19

The results of the N_2 blank bags analysed in this set showed contamination of the bags particularly with respect to acetaldehyde. The previous Study (Galbally et al. 2007) indicated that the blank samples had concentrations of some VOCs within them that were comparable with sample concentrations.

The results of the measurements by PTRMS of the cooling tower bags showed that there were two masses that were unequivocally measured in the four cooling tower bags; mass 33 (methanol) with an average concentration of 341 ppb, and mass 59 (acetone) with an average concentration of 116 ppb. Interpretation of the PTR-MS measurements for other masses was difficult due to contamination of the blank nitrogen bags. A further complexity was the difference in humidity between the cooling tower bags and the blank nitrogen bags, which meant that artefacts were present due to variations in water vapour between the cooling tower bags and the blank nitrogen bags.

The concentrations of VOCs detected by AT-VOC and Carbonyls detected by DNPH showed differences between the sample and blank bags that were scattered and provided no additional information.