ENVIRON

Compound Selection Procedure

Wagerup Refinery Unit Three Expansion

for

Alcoa World Alumina Australia

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1.   INTRODUCTION

Alcoa World Alumina Australia (Alcoa) proposes to increase alumina production capacity of the Wagerup refinery (refinery) from 2.35 million tonnes per annum (Mtpa) to approximately 4.7 Mpta. Studies into the potential environmental impacts associated with the Project have been conducted, including the investigation of the potential air quality and health impacts arising from air emissions from the refinery. A critical component of both the air quality and health impact assessments is the definition of the atmospheric emissions arising from the baseline and expanded refinery scenarios.

This report documents the approach and methods used by Alcoa to identify and estimate the quantity of air emissions arising from Baseline and Expanded refinery scenarios, and comment on the approach and methods used. In developing a comprehensive list of compounds for the HRA, Alcoa has also taken into consideration the findings of the independent Environmental Audit of Alcoa's Wagerup refinery conducted between April 2002 and May 2003 that was commissioned by the Department of Environment (DoE). In addition, Alcoa has undertaken a review of emission monitoring data available for the Wagerup and Pinjarra refinery to characterise atmospheric emissions released from the existing refinery's operations, and to characterise emissions expected to be released from an expanded Wagerup refinery. Emissions have been quantified for 27 individual compounds or groups of compounds, comprising the following compound classes:

- particulates;
- products of combustion;
- metals;
- organic compounds (e.g. aldehydes, ketones and aromatics [including polycyclic aromatic hydrocarbons (PAHs); and
- ammonia.

2.　　APPROACH AND METHODOLOGY

The pollutants considered in the Quantitative Health Risk Assessment (QHRA) represent Alcoa's current best available knowledge of the nature of emissions released to air from the refinery. This knowledge has been gathered primarily from source emissions monitoring campaigns conducted at the refinery, supported by the findings of the comprehensive emissions monitoring program conducted for the *Wagerup Refinery Air Emissions Inventory* (Alcoa, 2002) program, and the air emission estimates reported to the NPI for the refinery.

The refinery emissions inventory program was a comprehensive program specifically designed to screen a wide range of compound classes to allow a broad understanding of the emissions composition. The findings from the study have therefore been used as the primary reference source to identify the classes of compounds expected to be present in emissions from the refinery. The subsequent emissions monitoring program conducted for the refinery was designed to target the key classes of compounds likely to be present in gaseous emissions.

The culmination of the findings from these studies, and the inclusion of the pollutants covered in the Ambient Air NEPM (NEPC, 1998) and the draft Ambient Air Toxics NEPM (NEPC, 2003) resulted in the development of the list of compounds considered in the QHRA.

The key processes (presented in Figure 1.0) undertaken to identify and prioritise compounds of interest included:

- Determination of major refinery emission scenarios and examination of all likely air emission scenarios to account for variances in emissions;
- Compound identification process that included completion of a comprehensive programme of workshops and external studies by national experts to identify all possible compounds likely to be emitted from the refinery;
- Completion of the Wagerup refinery air emission inventory that involved the sampling and analysis and review of a comprehensive list of compounds;
- Compound selection that included a two step screening process to identify those compounds most likely to contribute to potential health risk
- Air dispersion modelling to ascertain ground level concentration of the identified compounds;
- Health risk assessment of the identified compounds; and
- Expert review of the compound selection process.

Figure 1.0:   Compound Identification Process
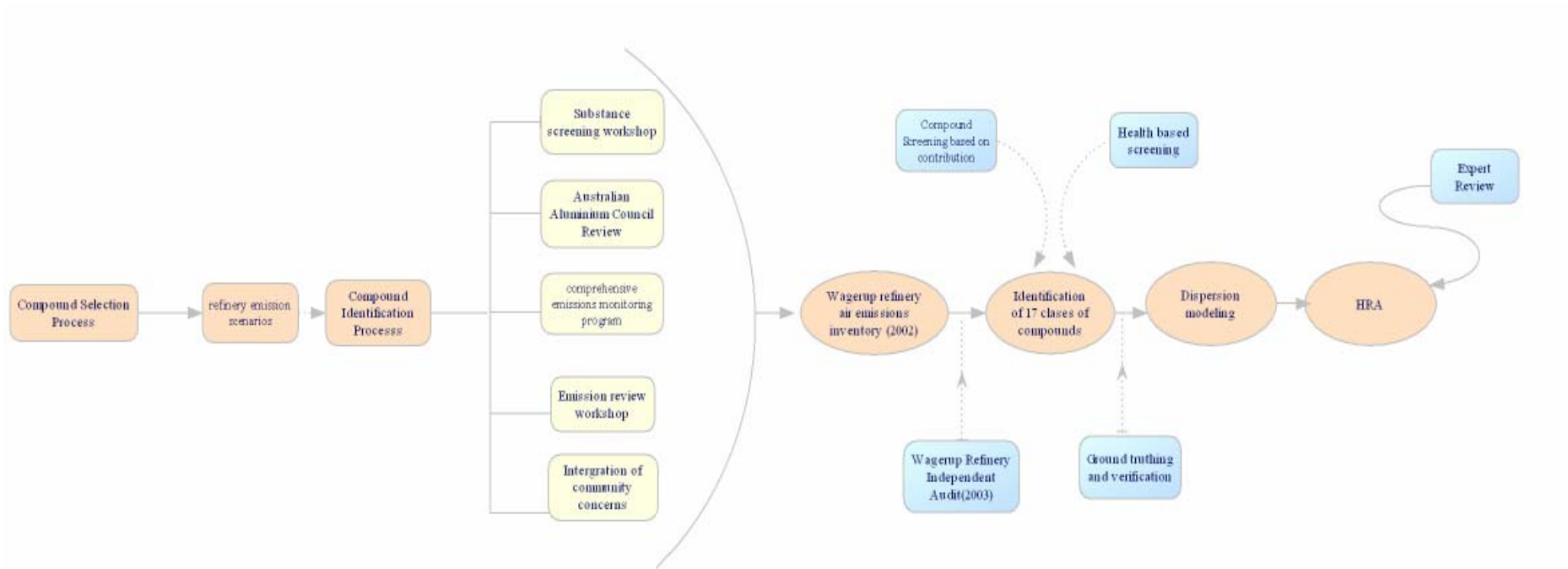
3. REFINERY EMISSION SCENARIOS – A SUMMARY

In-order to assess the air quality impacts associated with chronic (long-term) and acute (short-term) health impacts for the QHRA, emission representative of annual average and daily peak mass emissions were considered for the Baseline and Expansion scenarios using annual average and peak refinery production rates as an indicator of emission variability.

3.1 BASELINE SCENARIO

Emissions for the baseline emissions scenario have been derived by Alcoa based on various stack emission monitoring programs conducted at the Wagerup refinery, using results obtained between July 2002 and March 2004. Typically peak emissions have been defined using the maximum measured emission concentration over the defined monitoring period with average emissions defined by calculating the average of all measured emissions concentrations over the defined monitoring period. The subsequent mass emission rates were determined by using flowrates calculated for an average and peak refinery alumina production rate.

3.2 EXPANSION SCENARIO

Emissions for the expanded refinery emissions scenario have been derived by Alcoa based on a notional design for the expanded refinery, and using conservative estimates of pollution control efficiencies for those sources to be upgraded with new air pollution control equipment as part of the Wagerup refinery expansion. The Expansion scenario assumed an average refinery alumina production rate of 12,877 tpd and a peak production rate 13,699 tpd, which is based on the nominal design production rate and the maximum design production rate for the Expansion respectively. This also takes into consideration the expected reduction in emission associated with the installation of various air emission control equipment. As with the baseline peak production scenario, it should be noted that these assumptions are expected to result in an over-estimation of the actual peak emissions, since it is very unlikely that daily peak emissions for all refinery processes and sources would occur at the same time as is implicitly assumed.   The additional sources that are to be included in the expansion scenario include two calciners, the oxalate kiln and additional boilers or gas turbines.

For both the baseline and expanded refinery emission scenarios, "peak" and "average" emissions have been estimated and applied to the assessment of acute and chronic exposure respectively.

4. COMPOUND IDENTIFICATION

The pollutants considered in the QHRA were determined by undertaking a review and workshops to further understand the compounds likely to be emitted from the Bayer alumina refining process. Following the review extensive monitoring was undertaken to quantify the emissions identified to ascertain their contribution to the overall refinery emissions.

The external reviews and workshops undertaken to support the compound identification process initiated by Alcoa include the following:

- A substance Screening Workshop was held in December 1999 with broad Alcoa technical representation and specialist input from three university chemists representing inorganic and organic chemistry from Curtin University, the University of WA and the WA Chemistry Centre. The workshop developed a list of substances that should be included in any detailed inventory program, those that could be excluded based on present knowledge, and those that were highly unlikely to be present or problematic.

- A consultancy undertaken for the Australian Aluminium Council by Assoc. Professor David McConchie at Southern Cross University, NSW. The review examined the National Pollutant Inventory 90-substance list and identified (i) those substances definitely emitted from Australian alumina refineries, (ii) those that evidence exists to suggest that they may be emitted and (iii) those with negligible likelihood of existing or being emitted from Bayer process refineries in Australia. The review was used as a basis for supporting the exclusion from consideration for NPI reporting of the third group of substances by the Australian alumina refinery industry.

- An Emissions Review workshop held in December 2001 with broad specialist input from:
    - Curtin, Macquarie, and Murdoch Universities;
    - University of WA and University of Technology Sydney;
    - CSIRO Division of Atmospheric Research; and
    - WA Departments of Health, Environmental Protection and Minerals and Petroleum Resources.

    The workshop participants were presented with research and monitoring results and invited to review the proposed emissions inventory program and recommend any further parameters worthy of inclusion.

- Ongoing review by in-house and external specialists of the continually accruing data from routine and non-routine sampling conducted since the initial program was formulated.

- Review of information supplied by the community regarding parameters of concern, by way of complaints or input at community meetings. These were reviewed against the proposed monitoring plan to ensure the major areas of concern were adequately addressed, where appropriate. If chemicals have not been included, a clear explanation as to why, was included in the monitoring program report.

The knowledge gained from the various reviews and workshops outlined above were incorporated into the *Wagerup Refinery Air Emissions Inventory* (Alcoa, 2002) program, and the air emission estimates reported to the NPI for the refinery.

5. WAGERUP REFINERY AIR EMISSIONS INVENTORY

An examination of all known air emission compounds, their likely presence in the Bayer circuit and their potential significance was conducted to develop a list of relevant compounds to monitor. This determination was based on a current understanding of the Bayer process chemistry, external reviews and workshops and from monitoring performed by Alcoa and external specialist consultants.

The objective of the Wagerup refinery emissions inventory program was to survey the chemical composition of gaseous and particulate emissions to air from various parts of the Bayer refinery circuit. The program was therefore designed to screen as wide a range of compound classes as possible, in order to gain a broad understanding of the emissions composition.

The following groups of compounds were included in this screening process:

- all reportable air emissions under the NPI (including Tables 1 and 2) that are known or believed likely be emitted by the Bayer refining process;
- all of the target organic compounds regularly monitored in Alcoa's current and recent organic source monitoring programs;
- all of the eighty compounds included on the NEPC's preliminary list of Air Toxics that are known or believed likely to exist in the Bayer refining process; and
- any additional compounds that are unique to the Bayer process emissions but may not be included in any of the above lists as determined via the workshops and review process.

The culmination of these assessments resulted in the identification of the 17 classes of compounds included for the Wagerup refinery emissions inventory monitoring program, which included:

- VOC's

- SVOC's

- Aldehydes and ketones

- Carboxylic acids

- Other organics (methanol, ethanol, methane)

- Ammonia and amines

- Cyanide and compounds

- Halides and halogens

- Hydrogen sulphide and mercaptans

- Combustion products (i.e. CO, NO_2, SO_2)

- Metals

- Particulates

- Dioxins and furans

The refinery emissions inventory monitoring program involved the extensive analysis of some 15 emission sources for up to 17 classes of compounds, which allowed the analysis of approximately 600 individual compounds. To the best of Alcoa's knowledge the Wagerup refinery air emissions inventory program is the most comprehensive alumina refinery air emissions survey so far undertaken through the alumina industry.

The sampling and analytical components of the Wagerup refinery emissions inventory program were performed entirely by external specialist companies. Environmental Consultancy Services (ECS) conducted all sampling, and the analysis was carried out by ECS, The Chemistry Centre of WA, Geotechnical Services, Leeder Consulting and/or Severn Trent Laboratories (STL). Wherever possible United States Environmental Protection Agency (USEPA), American Society for Testing and Materials (ASTM), Victorian Environmental Protection Authority (VEPA), or otherwise recognised standard methods designed for the accurate quantification of the specified compound classes were used for the sampling and analyses. Further monitoring undertaken in 2003-2004 was used to validate and verify compounds identified in the emissions inventory.

5.1   WAGERUP REFINERY INDEPENDENT AUDIT

An independent Environmental Audit of Alcoa's Wagerup refinery was conducted in April 2002 –
May 2003, and was commissioned by the DoE (AWN, 2003). The scope of the audit included the
following programs related to quantification of air emissions from the Wagerup refinery:

- odour emissions quantification;

- VOC emissions monitoring;

- ambient monitoring;

- metals emissions monitoring; and

- emissions inventory.

Consideration has been given to the major findings of the audit of the Wagerup refinery, with a view
to ensuring that these are reflected in the air emissions monitoring programs conducted for the
refinery as far as reasonably practical.

5.1.1 Consideration of major audit outcomes

The independent auditor raised a number of issues in association with the difficulties of sampling
from sources with very high moisture content, particularly for those sources at temperatures near the
saturation point for the measured moisture content. Examples of these sources include the Slurry
Storage (25A) vents and Digestion Containment (Blow-off) vents. Alcoa is currently working with
specialist monitoring consultants to develop variations to standard sampling techniques to cope with
very high moisture sources. Some of these methods have not yet been fully developed and validated,
but it is Alcoa's intention to gain as wide a possible level of review for any variations that emerge,
with the wider Australian sampling and regulatory communities. Standard sampling techniques were
employed for such sources, but with particular attention paid to maximising dry gas sample volume to
obtain improved limits of detection within the constraints of the method and source characteristics. .
This has benefited the sampling of all compound groups from the affected sources, but in particular
has resulted in improved sampling certainty for polar and other water soluble compounds or
substances.

The independent auditor agreed with the overall conclusion from the Wagerup emissions inventory program that 'on the basis of the results of this program it would be most efficient, and in keeping with a risk based approach, to focus future emissions monitoring, both investigative and regulatory, on the sources and compound groups deemed most significant from this program.' He did however qualify this agreement with a call for follow up on specific areas of the emissions inventory program. Further investigation into acid gas emissions, long chain alcohols, attention to sampling plane issues and sampling from wet stacks, as discussed above were all mentioned as areas for follow-up. Alcoa Wagerup Refinery has completed some of these areas of further investigation while others are continuing. None of the results to-date indicates any additional emitted substances of significance or risk additive to those already tested for and included in this evaluation.

6.   COMPOUND SELECTION

A two step screening method was used to identify those compounds most likely to contribute to potential health risk, and therefore included in the suite of compounds to undergo air dispersion modelling.

The first stage of the compound screening identified the compounds that are estimated to be emitted in the largest quantities on an annual mass emission basis from the refinery. The second stage of the compound screening method used an approach endorsed by the USEPA, which involved using the ratio of the NPI emission estimate reported divided by the relevant acute (i.e. short-term) and chronic (i.e. long-term) health-based ambient air quality guidelines as an indicator of the relative significance of each of the pollutants. The ambient air quality guidelines used in the screening approach were the World Health Organisation (WHO), USEPA Integrated Risk Information System (IRIS), and the Californian Office of Environmental Health Hazard Assessment (OEHHA) /Air Resources Board (ARB) guidelines, and the pollutants considered were all those reported to the NPI for the refinery. A detailed description of the screening methodology is presented in Appendix B.

Based on the comprehensive list of methods detailed above, a concise list of compounds was determined based on their contribution to the total refinery emissions and their potential to contribute to health risk. A list of compounds initially considered for the screening method with those compounds chosen based on their contribution to potential health risk and to overall emissions are presented in Table 1.0.

Table 1.0: List of Compounds Considered in the HRA

Compound Name [1]	General Regulatory Information			Exposure Assessment	
	Criteria Pollutants (Air NEPM)	Covered by the Draft Air Toxics NEPM	Reported to the NPI	Compounds Selected	Compounds Not Included based on Contribution (to emissions)
Nitrogen dioxide	✓		✓ [6]	✓	
Carbon monoxide	✓		✓	✓	
Sulphur dioxide	✓		✓	✓	
Particulate matter (as PM10)	✓		✓	✓	
Acetone			✓	✓	
Acetaldehyde			✓	✓	
Formaldehyde		✓	✓	✓	
2-Butanone [2]			✓	✓	
Benzene		✓		✓	
Toluene		✓		✓	
Xylenes [3]		✓		✓	
PAHs [4]		✓	✓	✓	
Mercury			✓	✓	
Arsenic			✓	✓	
Selenium			✓	✓	
Dioxins and furans			✓		✓
Ammonia			✓	✓	
Manganese			✓	✓	
Cadmium			✓	✓	
Chromium			✓	✓	
Lead			✓		✓
Nickel			✓	✓	
Acrolein				✓	
Methylene chloride				✓	
Ethylbenzene				✓	
Styrene				✓	
Propanal					✓
2-Pentanone					✓
1,2,4-Trimethylbenzene				✓	
1,3,5-Trimethylbenzene				✓	
Butenal					✓
Dibromomethane					✓
2-Methylpropanal					✓
Tribromomethane					✓
Butanal					✓
Benzaldehyde					✓
1,3,5-Trimethylbenzene					✓
Isopropanol					✓
Methacrolein					✓
Hexane					✓
n-Propylbenzene					✓
2-Methylbutane					✓
Tolualdehyde					✓
Isopropylbenzene					✓
Methyl isobutyl ketone [5]					✓
Cyclopentadiene					✓
Iodomethane					✓
Pentanal					✓
Hexanal					✓
Dichloromethane					✓
2-Hexanone					✓
Dichlorodifluromethane					✓
3-Methylpentane					✓

Compound Name [1]	General Regulatory Information			Exposure Assessment	
	Criteria Pollutants (Air NEPM)	Covered by the Draft Air Toxics NEPM	Reported to the NPI	Compounds Selected	Compounds Not Included based on Contribution (to emissions)
Chlorodibromomethane					✓
sec-Butylbenzene					✓
Methylcyclohexane					✓
2,4-Dimethyl-3-pentanone					✓
Methylcyclopentane					✓
1,2,3-Trimethylcyclopentane					✓
Bromomethane					✓
3-Methyl-1-ethylbenzene					✓
Trimethyl-1,3-cyclopentadiene					✓
1,2-Dimethylcyclopentane					✓
1,2-Dichloroethene					✓
2-Methylpentane					✓
3-Methylcyclopentane					✓
Trimethylcyclopentadiene					✓
1,4-Dimethyl-2-ethylbenzene					✓
Cyclohexane					✓
Carbon Tetrachloride					✓
Ehylcyclohexane					✓
1,2-Dimethyl-1,3-cyclopentadiene					✓
1-Methyl-2-ethylbenzene					✓
Pentane					✓
3-Methylcyclohexane					✓
2,3,5-Trimethylfuran					✓
2-Methylnaphthalene					✓
1,2,3-Trimethylbenzene					✓
3,3-Dimethy-1,3-cyclopentadiene					✓
Diethylbenzene					✓
1-Ethyl-4-ethylbenzene					✓
1-Methylindan					✓
1,2,4-Trimethylpentane					✓
1,2-Dimethyl-3-ethylbenzene					✓
3,5-Dimethylcyclopentane					✓
Chloromethane					✓
Ethylcyclopentane					✓
1-Methyl-4-isopropylbenzene					✓
1,3-Dichlorobenzene					✓
Methyl cyclopentadiene					✓
Nonane					✓
Isopropyltoluene					✓
1,2-Dichlorobenzene					✓
2,2,4-Trimethylpentane					✓
n-Butylbenzene					✓
Carbon disulphide					✓
p-Propylbenzene					✓
Chloroethene [7]					✓
p-Isopropyltoluene					✓
Undecane					✓
1,1-Dimethylindan					✓
2-Methyl-1-propenylbenzene					✓
Bromochloromethane					✓
5-Methylindan					✓
Chlorobenzene					✓
1,2,3,4-Tetrahydro-5-methylnaphthalene					✓
Decane					✓
3-Hexanone					✓
2,2 Dichloropropane					✓
Chloroethane					✓

Compound Name [1]	General Regulatory Information			Exposure Assessment	
	Criteria Pollutants (Air NEPM)	Covered by the Draft Air Toxics NEPM	Reported to the NPI	Compounds Selected	Compounds Not Included based on Contribution (to emissions)
Dimethyl disulphide					✓
Trichlorofluromethane					✓

Notes:

1. 1 Includes metals in elemental form and as compounds.

2. 2 methyl ethyl ketone (MEK)

3. 3 Synonym: Xylenes include m,o & p xylene

4. Xylenes includes m,o & p xylenes

5. 4 polycyclic aromatic hydrocarbons (as BAP equivalents)

6. 5 Synonym: MIBK

7. 6 Reported to the NPI as Oxides of Nitrogen

6.1 PRODUCTS OF COMBUSTION

Combustion products from all combustion sources within the refinery were included with the major combustion products evaluated included carbon monoxide, oxides of nitrogen (as NO_2), sulphur dioxide and particulate matter (as PM_{10}) . The major sources within the facility that were identified to emit combustion products included the calciners, boilers, gas turbines and the liquor burner with the oxalate kiln stack, additional boilers and calciners being the additional combustion sources in the expansion scenario . The emission rates determined for both the base and Expansion scenarios are detailed in Table 2.

Table 2.0: Summary of emission rates for Products of Combustion

Analytes	Emission Rates - Base case		Emission Rates - Expansion Case	
	Average (kg/yr)	Peak (kg/yr)	Average (kg/yr)	Peak (kg/yr))
Oxides of Nitrogen	1.01E+06	2.37 E+06	1.26 E+06	2.26 E+06
Sulphur Dioxide	6.95 E+04	2.92 E+05	1.096 E+05	3.59 E+05
Carbon Monoxide	9.1 E+05	2.46 E+06	1.42 E+06	3.1 E+06
Dust (as PM_{10})	5.99 E+04	2.65 E+05	6.47 E+04	1.67 E+05

Notes:
1. Emissions reported to the nearest 100 kg/y.

6.2 VOLATILE ORGANIC COMPOUNDS

Previous studies undertaken at both the Wagerup and Pinjarra facilities identified the VOC compounds that are estimated to be emitted in largest quantities on an annual mass emission basis. Appendix A lists the quantified VOC compounds emitted to air grouped according to the percentage contribution of each individual compound to the total VOC emissions to air from the Pinjarra refinery. This compound speciation and prioritisation was used as the basis for investigating VOC emissions from the Wagerup refinery.   Further quantification (VOC sampling and analysis programmes undertaken between July 2002 – December 2004) of these compounds and prioritisation based on their percentage contribution of each individual compound to the total VOC emissions from the facility indicated that 14 VOCs (out of a total of 97 compounds) contribute in excess of 85% of the total quantifiable VOC emissions from the Wagerup refinery, as determined in the emissions inventory program (*Note that the total mass emissions of all modelled compounds including VOCs accounts for about 96% of the total mass emissions to air from the refinery*). The emission rates therefore determined for the base and expansion scenarios are presented in Table 3.0.

Table 3.0: Summary of VOC emission rates for Scenarios Assessed

Analytes	Emission Rates -Base Case		Emission Rates – Expansion	
	Average (kg/yr)	Peak (kg/yr)	Average (kg/yr)	Peak (kg/yr)
Acetone	3.56 E+04	8.34 E+04	3.92 E+04	4.1 E+04
Acetaldehyde	1.21 E+04	2.54 E+04	1.98 E+04	2.14 E+04
Formaldehyde	1.71 E+04	3.63 E+04	2.23 E+04	2.41 E+04
2-Butanone	3.52 E+03	9.90 E+03	4.71 E+03	4.96 E+03
Benzene	2.05 E+03	5.45 E+03	2.60 E+03	2.76 E+03
Toluene	3.27 E+03	5.82 E+03	1.44 E+03	1.50 E+03
Xylenes	7.15 E+02	7.79 E+02	1.75 E+02	1.90 E+02
Acrolein	1.20 E+03	1.39 E+03	2.35 E+03	2.56 E+03
Ethylbenzene	4.62 E+01	5.47 E+01	7.29 E+01	8.04 E+01
Methylene Chloride	5.11 E+03	7.66 E+03	4.65 E+03	5.03 E+03
Styrene	2.22 E+02	2.30 E+02	1.45 E+02	1.60 E+02
1,2,4-Trimethyl benzene	2.23 E\+01	3.72 E+01	1.14 E+01	1.27 E+01
1,3,5-Trimethylbenzene	1.40 E+01	1.98 E+01	1.77 E+01	1.98 E+01
Vinyl Chloride	7.52	8.66	1.47 E+01	1.64 E+01

Notes:
1. Emissions reported to the nearest 100 kg/y.

Table 4.0: Relative Contribution of the Individual VOC Air Emissions Assessed (base Average Scenario)

Analytes	kg/y [2]	% contribution
Acetone	3.56E+04	44.0%
Formaldehyde	1.71E+04	21.11%
Acetaldehyde	1.21E+04	14.94%
Methylene Chloride	5.11E+03	6.31%
2-Butanone	3.52E+03	4.35%
Toluene	3.27E+03	4.04%
Benzene	2.05E+03	2.54%
Acrolein	1.20E+03	1.49%
Vinyl Chloride	7.50E+00	1.00%
Xylene	7.15E+02	0.88%
Styrene	2.22E+02	0.27%
Ethylbenzene	4.62E+01	0.06%
1,2,4-Trimethylbenzene	2.23E+01	0.03%
1,3,5-Trimethylbenzene	1.40E+01	0.02%

Notes:
1. Figures are rounded, therefore the total does not exactly equate to 100%.
2. Emissions reported to the nearest 100 kg/y.

These compounds were selected as the VOCs to undergo air dispersion modelling for the HRA. Organic compounds not included in dispersion modelling for the HRA were those that (i) individually and cumulatively make up a very small proportion of the total mass emissions from the refinery and that (ii) do not have a high toxicity/corresponding low health thresholds, guidelines or criteria warranting their inclusion despite their low mass emissions contribution. This risk based approach means that some compounds that have very low overall mass emission contribution were assessed (eg Trimethylbenzene) since they have low acute or chronic health guidelines.

6.3 PAH'S

PAHs are a complex class of organic compounds that consist of two or more fused aromatic rings, and typically contain only carbon and hydrogen atoms (EA, 2001). The relative carcinogenic potency of indicator PAHs has been published by the WHO relative to Benzo[a]pyrene (BaP), a widely reported PAH known for its carcinogenic potency. BaP is widely regarded as an appropriate indicator for the carcinogenic PAHs in the air given present knowledge and existing published data. Therefore to assist with characterising the potential health risk associated with PAH emissions from the refinery, the make-up of individual PAH compounds likely to be present in emissions were derived.

Emissions monitoring have identified the presence of specific PAH compounds in the SVOC monitoring program conducted at the Wagerup refinery with the relative percentage of each of the PAH compounds presented in Table 5.0.

Table 5.0: Relative Composition of PAH Emissions Detected for the Wagerup Refinery

PAH Compound	Indicative Composition (%)
Naphthalene	58.1
2-Methylnaphthalene	41.3
Phenanthrene	0.4
Acenaphthene	0.1
Fluoranthene	0.1

The contributions for each individual PAH was summarised into a total BaP equivalent dose (assuming there carcinogenic effects to be additive). Table 6 presents the BaP equivalent emission rates for the scenarios considered in the QHRA.

Table 6.0: Summary of emission for Relative Composition of PAH Emissions Detected for the Wagerup Refinery

	Emission Rates - Base case		Emission Rates - Expansion Case	
Analytes	Average (kg/yr)	Peak (kg/yr)	Average (kg/yr)	Peak (kg/yr))
BaP equivalents	6.17 E-01	8.60 E-01	3.76 E-01	4.05 E-01

6.4 DIOXINS AND FURANS[1]

Dioxins and Furans are not assessed further in this QHRA as previous toxicological studies undertaken for Alcoa (*Toxikos 2003*) at the Pinjarra refinery indicate that the dioxin dose from direct inhalation is at most 0.002% of background intake and is therefore a negligible contributor to total dioxin intake and body burden. In undertaking the risk assessment for dioxins the consultant (Toxikos) used the highest of any of the concentrations that occurred by modelling and at any of the modeled receptor locations. The comprehensive justification for the exclusion of Dioxins is provided in the Toxikos report TR121003-RJd2. Furthermore, at the Wagerup Refinery, unlike at Pinjarra, none of the 23 cogeners of polychlorinated dibenzo dioxins and furans that attract a WHO toxic equivalency rating (TEQ) were detected in emissions monitoring. This means that the dioxins and

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[1] The information was extracted from the Alcoa Pinjarra Refinery QHRA, report Toxikos Document: TR121003-RJd2

furans TEQ emission rate at Wagerup is zero, whereas at Pinjarra there was a small TEQ emission rate for the refinery.

6.5 HEAVY METALS

Sampling programs in accordance with US EPA methodology (US EPA method 29) were undertaken for the following analytes: antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, phosphorous, selenium, silver, thallium and zinc. The results of the sampling program identified seven metals that contributed to the majority of heavy metal emission from the facility. Some metals-for instance, lead were not detected in the emission from any of the point sources tested in both the original emission inventory and follow-up monitoring undertaken at Wagerup (*pers. comm. P. Coffey 2005*). The mass emission rates for heavy metals are presented in Table 7.0.

Table 7.0: Summary of Heavy Metal Emission Rates

	Emission Rates - Base case		Emission Rates - Expansion Case	
Analytes	**Average (kg/yr)**	**Peak (kg/yr)**	**Average (kg/yr)**	**Peak (kg/yr))**
Arsenic	8.04 E+01	1.1 E+02	2.21 E+02	2.30 E+02
Selenium	3.22 E+01	3.63 E+01	3.13 E+01	3.82 E+01
Manganese	3.05 E+02	5.46 E+02	1.83 E+02	2.34 E+02
Cadmium	7.02 E-03	7.02 E-03	1.40 E-02	1.40 E-02
Chromium (VI)	6.60 E-01	6.6 E-01	9.72 E-01	1.06 E+00
Nickel	1.63 E+01	2.6 E+01	8.97 E+00	1.49 E+01
Mercury	1.84 E+02	1.84 E+02	1.07 E+02	1.07 E+02

The analytes sampled for and the results of the monitoring program have been cross verified with mass balance equations based on raw material usage and NPI reporting data.

6.6 INORGANICS - AMMONIA

The ammonia emissions were confirmed by point source monitoring undertaken between 2002 and 2004. A summary of the emission rates for the base and Expansion scenarios are presented in Table 8.0.

Table 8.0: Summary of Ammonia emissions

	Emission Rates - Base case		Emission Rates - Expansion Case	
Analytes	**Average (kg/yr)**	**Peak (kg/yr)**	**Average (kg/yr)**	**Peak (kg/yr))**
Ammonia	2.17 E+04	2.57 E+04	3.51 E+04	3.52 E+04

6.7 DIFFUSE SOURCE EMISSIONS

Diffuse sources at Wagerup such as the RDA's, bauxite stockpiles, ROWS (Run-off Water Storage) pond, cooling lakes and lower dam are a potential source of air emissions and may be significant in terms of potential off-site impacts as a result of their very large surface areas and their close proximity to sensitive receptors.

Current available technology for sampling area sources is limited with some inherent inaccuracies in the sampling techniques due to the number of environmental variables that influence the rate of air emissions. Alcoa and its consultants utilised current best practice in quantifying air emission from diffuse sources. Sampling areas were broken up on the basis of similarity of surface type, for example the cooling ponds were broken into a turbulent hot entry zone and a quiescent warm zone covering the remainder of the cooling pond. Drying areas were broken into wet and dry residue and wet sand areas and each area sampled separately. Source sampling was undertaken by GHD Consultants for VOC's, carbonyls and odour emissions using a USEPA (United States Environmental Protection Authority) emission isolation flux chamber. Fugitive dust emissions were estimated based on site specific emission factors (against each activity) developed and verified against comprehensive ambient dust monitoring data from Alcoa's RDA dust monitoring network. A summary of the estimated dust emission rates form diffuse sources are presented in Table 8.0.

Table 8.0 Estimated PM$_{10}$ Emissions from Wagerup Fugitive sources for 2003/2004[2]

Source	Units	Normal Operations					RDA Construction		
		Stockpile Wind	Stockpile Activity	RDA Wind	RDA Activity	Total	Wind	Construct. Activity	Total
Maximum	g/s	159	8.2	469	6.0	637	154	26	180
99 Percentile	g/s	55.9	5.5	177	6.0	240	40.5	26	44.2
95 Percentile	g/s	10.6	3.4	44.5	6.0	60.8	7.2	26	26
90 Percentile	g/s	1.7	2.5	15.2	6.0	22.6	1.5	10.4	18.2
Average	g/s	2.2	1.3	8.4	1.9	13.8	1.5	2.3	3.8
Minimum	g/s	0.0	0.4	0.0	0.54	0.9	0.0	0.0	0.9
Annual	tpa	70	40.3	266	60	436.3	48.5	72.8	121.3

Further validation and ground truthing using ambient odour and VOC measurements and back calculating using Windtrack^{TM} was undertaken to provide confidence in the flux measurements. The results of the field VOC measurements and the contaminants detected during the VOC monitoring programs are summarised with emission rates in Table 9.0 & 10.0.

Table 9.0: Estimated VOC Emissions for the Base Case[3]

Source	Area	BaP Equivalents	Acetone	Acetaldehyde	Formaldehyde	2-Butanone	Benzene	Toluene	Xylenes	Odour
	(ha)	(g/s)								(ou/s)
Dry Stacked Areas	186.52	0	1.70E-02	3.08E-03	3.16E-03	5.22E-04	3.85E-04	1.81E-03	0	74,000
Lower Dam	17.7	0	7.38E-04	2.07E-04	1.62E-03	0	0	0	0	9,710
ROCP1	8.217	0	3.42E-04	9.59E-05	7.53E-04	0	0	0	0	2,530
ROCP2	4.58	0	1.91E-04	5.34E-05	4.20E-04	0	0	0	0	1,410
RDA2-1 Liquor Southern	8.0	0	1.55E-02	1.16E-02	1.73E-04	1.96E-03	6.67E-05	2.13E-04	0	49,300
RDA2-2 Wet Mud - North	7.36	0	3.09E-03	1.07E-03	5.40E-04	3.43E-04	6.13E-05	3.68E-05	0	20,600
Super Thickener	0.461	1.06E-08	5.94E-03	4.36E-03	5.99E-05	5.86E-04	8.45E-05	3.46E-04	5.46E-05	6,670

[2] Emission rates extracted from Air Assessments, RDA Air Quality Assessment, 2005
[3] Emission rates extracted from Air Assessments, RDA Air Quality Assessment, 2005

Source	Area (ha)	BaP Equivalents (g/s)	Acetone (g/s)	Acetaldehyde (g/s)	Formaldehyde (g/s)	2-Butanone (g/s)	Benzene (g/s)	Toluene (g/s)	Xylenes (g/s)	Odour (ou/s)
Cooling Pond	15.52	2.33E-08	3.42E-02	2.57E-02	2.07E-04	5.10E-03	5.43E-04	7.76E-04	1.81E-04	11,000
Oxalate Pond	1.888	0	7.87E-05	2.20E-05	1.73E-04	0	0	0	0	116
ROWS	33.28	0	1.39E-03	3.88E-04	3.05E-03	0	0	0	0	200
Sand Cannon	0.5	0	2.10E-04	7.25E-05	3.67E-05	2.33E-05	4.17E-06	2.50E-06	0	1,400
Sand Lake	4.34	0	7.63E-03	5.64E-03	1.20E-04	9.64E-04	3.62E-05	1.05E-04	0	25,100
Total		**3.39E-08**	**8.63E-02**	**5.23E-02**	**1.03E-02**	**9.50E-03**	**1.18E-03**	**3.29E-03**	**2.36E-04**	**303,000**

Table 10.0: Estimated VOC Emissions for the Expansion Case[4]

Source	Area (ha)	BaP Equivalents (g/s)	Acetone (g/s)	Acetaldehyde (g/s)	Formaldehyde (g/s)	2-Butanone (g/s)	Benzene (g/s)	Toluene (g/s)	Xylenes (g/s)	Odour (ou/s)
Dry Stacked Areas	275	0	2.56E-02	4.70E-03	5.95E-03	7.69E-04	5.67E-04	2.66E-03	0	117,000
Lower Dam	17.7	0	7.38E-04	2.07E-04	1.62E-03	0	0	0	0	9,710
ROCP1	8.217	0	3.42E-04	9.59E-05	7.53E-04	0	0	0	0With the Expansion case	2,530
ROCP2	4.58	0	1.91E-04	5.34E-05	4.20E-04	0.	0	0	0	1,410
Super Thickener	0.461	1.06E-08	6.09E-03	4.40E-03	3.84E-04	5.86E-04	8.45E-05	3.46E-04	5.46E-05	8,610
Cooling Pond	15.52	3.49E-08	5.14E-02	3.86E-02	3.10E-04	7.64E-03	8.15E-04	1.16E-03	2.72E-04	165,000
Oxalate Ponds	2.888	0	1.20E-04	3.37E-05	2.65E-04	0	0	0	0	178
ROWS	33.28	0	2.77E-03	7.77E-04	6.10E-03	0	0	0	0	3990
Sand Cannon	0.5	0	2.10E-04	7.25E-05	3.67E-05	2.33E-05	4.17E-06	2.50E-06	0	1,400
Sand Lake	4.59	0	7.74E-03	5.68E-03	1.38E-04	9.76E-04	3.83E-05	1.06E-04	00	25,800
Total		**4.55E-08**	**9.51E-02**	**5.46E-02**	**1.60E-02**	**1.00E-02**	**1.51E-03**	**4.28E-03**	**3.26E-04**	**336,000**
Percentage of Base Case emissions			134	110	104	155	105	128	130	138	111

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[4] Emission rates extracted from Air Assessments, RDA Air Quality Assessment, 2005

7.   AIR DISPERSION MODELING

The exposure assessment component of the QHRA is based on ground level concentrations predicted by air dispersion modelling. Air dispersion modelling using TAPM and CALPUFF was used to predict ground level concentrations at near-by receptors for input into the QHRA for those pollutants selected and prioritised from the above studies. Refer to the modelling report for details of the air dispersion modelling approach (CSIRO 2004, Air Assessments 2005). The substances selected for use in the dispersion modelling are appropriate for use in the QHRA.

8.   HEALTH RISK ASSESSMENT

Predicted ground level concentrations from the dispersion modelling for compounds present in the emissions from the refinery and the RDA for both scenarios (current refinery and expansion, average and peak emissions) will be used to estimate the exposure concentrations at sensitive receptors. These exposure concentrations will then be used as input to hazard evaluation and risk assessment in the QHRA being performed by an external consultant.

The receptor locations were identified by Alcoa to represent populations or individual residences that could potentially be exposed to refinery or RDA emissions (Annex C).

The potential health effects arising from the predicted short-term (acute) and long-term (chronic) exposure to non-carcinogenic compounds, and potential carcinogenic risks will be considered in the QHRA by comparing the predicted exposure concentrations at the receptor locations with health protective guidelines for ambient air developed by reputable authorities such as the National Environment Protection Council (NEPC), World Health Organisation (WHO) and the U.S Environmental Protection Agency (USEPA).

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10.   ABBREVIATIONS

ALD	Alumina Leach Dryer
Alcoa	Alcoa World Alumina Australia
ASTM	American Society for Testing and Materials
ARB	Air Resources Board, California
BaP	Benzo(a)pyrene
COU	Chemical Odour Unit
CO	Carbon Monoxide
DoE	Department of Environment
EPA	Environmental Protection Authority
EPS	Environmental Protection Statement
ECS	Environmental Consultancy Services
GTs	Gas Turbines
GLC	Ground Level Concentration
HPLC	High Performance Liquid Chromatography
HiVol	Hi-volume particulate air sampler
HRSG	Heat Recovery Steam Generator
IRIS	Integrated Risk Information System
NPI	National Pollutant Inventory
NEPM	National Environment Protection Measure
NOx	Oxides of Nitrogen
NO_2	Nitrogen Dioxide
NO	Nitric Oxide
NATA	National Association of Testing Authorities
NATO	North Atlantic Treaty Organisation
OU	Odour Unit
OC2	Operating Centre 2
OEHHA	Office of Environmental Health Hazard Assessment, Californian
PM_{10}	Particles with an aerodynamic diameter of less than 10 microns
$PM_{2.5}$	Particles with an aerodynamic diameter of less than 2.5 microns
PAHs	Polycyclic Aromatic Hydrocarbons
POHC	Principal Organic Hazardous Constituents
PQL	Practical Quantifiable Limit
QHRA	Quantitative Health Risk Assessment
QA/QC	Quality Assurance/Quality Control
ROCs	Reactive Organic Compounds

RDA	Residue Disposal Area
RTO	Regenerative Thermal Oxidiser
SRG	Stakeholder Reference Group
SWIS	South-West Interconnected System
SO_2	Sulphur Dioxide
SVOCs	Semi-volatile Organic Compounds
STL	Severn Trent Laboratories
STP	Standard Temperature and Pressure
TSP	Total Suspended Particulate
TEOM	Tapered Element Oscillating Microbalance
TEQ	Toxic Equivalents
USEPA	U.S. Environmental Protection Agency
VOCs	Volatile Organic Compounds
VOST	Volatile Organic Sampling Train
VEPA	Victorian Environmental Protection Authority
QHRA	Quantitative Health Risk Assessment
WHO	World Health Organisation

Appendix A

VOC Screening List

Table 1: Individual Relative Contribution to Total VOC Air Emissions Estimated for the Pinjarra Refinery

> 1%	Kg/Y [6]	%	≤ 1% And > 0.1%	≤ 0.1% And > 0.01%	≤ 0.01% And > 0.001%	≤ 0.001%
Acetone	86,200	46.6	1,2,4-Trimethylbenzene	Isopropylbenzene	Acrolein	1,2,4-Trimethylpentane
Acetaldehyde	24,200	13.1	Butenal	Methyl isobutyl ketone [4]	Methylcyclohexane	1,2-Dimethyl-3-ethylbenzene
Formaldehyde	23,800	12.9	Dibromomethane	Cyclopentadiene	2,4-Dimethyl-3-pentanone	3,5-Dimethylcyclopentane
Toluene	13,600	7.3	2-Methylpropanal	Naphthalene	Methylcyclopentane	Chloromethane
Methyl ethyl ketone [1]	13,000	7.0	Tribromomethane	Iodomethane	1,2,3-Trimethylcyclopentane	Ethylcyclopentane
Propanal	3,300	1.8	Butanal	Pentanal	Bromomethane	1-Methyl-4-isopropylbenzene
Benzene	3,200	1.7	Methylene chloride [3]	Hexanal	3-Methyl-1-ethylbenzene	1,3-Dichlorobenzene
2-Pentanone	2,300	1.2	Benzaldehyde	Dichloromethane	Trimethyl-1,3-cyclopentadiene	Methyl cyclopentadiene
Xylenes [2]	2,000	1.1	1,3,5-Trimethylbenzene	2-Hexanone	1,2-Dimethylcyclopentane	Nonane
			Ethylbenzene	Dichlorodifluromethane	1,2-Dichloroethene	Isopropyltoluene
			Isopropanol	Dimethyl disulphide	2-Methylpentane	1,2-Dichlorobenzene

> 1%	Kg/Y [6]	%	≤ 1% And > 0.1%	≤ 0.1% And > 0.01%	≤ 0.01% And > 0.001%	≤ 0.001%
			Methacrolein	Trichlorofluromethane	3-Methylcyclopentane	2,2,4-Trimethylpentane
			Hexane	3-Methylpentane	Trimethylcyclopentadiene	n-Butylbenzene
			n-Propylbenzene	Chlorodibromomethane	1,4-Dimethyl-2-ethylbenzene	Carbon disulphide
			2-Methylbutane	sec-Butylbenzene	Cyclohexane	p-Propylbenzene
			Tolualdehyde	Styrene	Carbon tetrachloride	Vinyl chloride (Chloroethene)
					Ethylcyclohexane	p-Isopropyltoluene
					1,2-Dimethyl-1,3-cyclopentadiene	Undecane
					1-Methyl-2-ethylbenzene	1,1-Dimethyllindan
					Pentane	2-Methyl-1-propenylbenzene
					3-Methylcyclohexane	Bromochloromethane
					2,3,5-Trimethylfuran	5-Methylindan
					2-Methylnaphthalene	Chlorobenzene

> 1%	Kg/Y [6]	%	≤ 1% And > 0.1%	≤ 0.1% And > 0.01%	≤ 0.01% And > 0.001%	≤ 0.001%
					1,2,3-Trimethylbenzene	1,2,3,4-Tetrahydro-5-methylnapthalene
					3,3-Dimethy-1,3-cyclopentadiene	Decane
					Diethylbenzene	3-Hexanone
					1-Ethyl-4-ethylbenzene	2,2 Dichloropropane
					1-Methylindan	Chloroethane
Totals [5]		*92.7%*	*7.3%*	*0.9%*	*0.1%*	*0.01%*

Notes:
1. Synonyms: MEK, 2-butanone
2. Synonym: dimethylbenzene.
3. Synonym: dichloromethane.
4. Synonym: MIBK.
5. Figures are rounded, therefore the total does not exactly equate to 100%.
6. Emissions reported to the nearest 100 kg/y.

Appendix B

QHRA Screening Methodology

QUANTITATIVE HEALTH RISK ASSESSMENT COMPOUND SCREENING METHODOLOGY

1. INTRODUCTION

The compound screening methodology is based on guidance from the United States Environmental Protection Agency (USEPA) for facilities that emit a complex mixture of compounds where it is considered necessary to refine the list of compounds that are explicitly considered as part of a Quantitative Health Risk Assessment (QHRA). The benefit of such an approach is that it enables the emissions estimation and exposure assessment stage of the QHRA to focus on those compounds most likely to exhibit the greatest potential health risks, enhancing the exposure assessment component of the QHRA.

2. OVERVIEW OF SCREENING METHOD

The screening methodology identifies the compounds most likely to exhibit the greatest potential health risk using the ratio of total facility emissions divided by the relevant ambient air quality guideline for acute (i.e. short-term) and chronic (i.e. long-term) exposures as an indicator of the relative acute or chronic potential health risk compared to other compounds.

$$R(acute) = \frac{\dfrac{E}{Gdl(acute)}}{\sum_{1}^{n} \dfrac{E_n}{Gdl(acute)_n}} \times 100 \qquad \textbf{\textit{Equation 1}}$$

$$R(chronic) = \frac{\dfrac{E}{Gdl(chronic)}}{\sum_{1}^{n} \dfrac{E_n}{Gdl(chronic)_n}} \times 100 \qquad \textbf{\textit{Equation 2}}$$

Where:

E = total emission rate released from facility (kg/y)

$Gdl(acute)$ = acute ambient air quality guideline ($\mu g/m^3$; 24-hour average)

$Gdl(chronic)$ = chronic ambient air quality guideline ($\mu g/m^3$; lifetime or annual average)

$R(acute)$ = relative contribution to potential acute health risk (%)

$R(chronic)$ = relative contribution to potential chronic health risk (%)

It should be noted that this screening approach assumes that the total facility emission rate is directly correlated to the expected ground level concentrations at nearby sensitive receptors. This is not necessarily the case as in addition to the pollutant emission rate, the release height and other emission characteristics such as volume and temperature, together with the prevailing meteorological conditions, also influence the ground level concentration. However, we believe that this will be less of a problem for the Pinjarra refinery emissions due to the fact that the closest residential property is located approximately 3.5 km from the refinery.

3. Pinjarra Refinery Emission Estimates

For the Pinjarra refinery compound screening, facility emission estimates were based on emission estimates report to the National Pollutant Inventory for the 2002/2003 reporting period.

4. Ambient Air Quality Guidelines

The ambient air quality guidelines used in the screening approach were confined to the following references (in order of priority):

- World Health Organisation (WHO);
- USEPA's Integrated Risk Information System (IRIS); and
- Californian Office of Environmental Health Hazard Assessment (OEHHA) /Air Resources Board (ARB) guidelines.

For those pollutants for which the relevant acute ambient air quality guideline is not specified as a 24-hour average, the power law (Hanna *et al*, 1977) has been used to calculate an equivalent 24-hour standard to ensure a consistent basis for the calculation of relative risk for each compound.

It should be noted that there are no acute and/or chronic ambient air quality guidelines published by the WHO, USEPA's IRIS or the OEHHA/ARB for some of the pollutants reported in the NPI

[5], and therefore these pollutants were excluded from further consideration for the purposes of the compound screening. This was considered appropriate on the basis that these compounds were either considered to be of no known concern to these health authorities or there is inadequate information available to define their health effects. It should however be noted that the health risk assessment considered exposure to the full suite of organic compounds measured from the Pinjarra refinery. The methodology to enable this is discussed within the health risk assessment report (Toxikos, 2003).

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[5] Acute: Acetone, Beryllium & compounds, Cadmium & compounds, Chromium (III) compounds, Chromium (VI) compounds, Cobalt & compounds, Lead & compounds, Dioxins & Furans, PAHs, Selenium & compounds, Total VOCs, Zinc & compounds.
Chronic: Acetone, Chromium (III) compounds, Cobalt & compounds, Total VOCs.