






ASSESSMENT METHODOLOGY FOR
NITROGEN DIOXIDE AS AN
AIR POLLUTANT

NSW Environment Protection Authority

Assessment Methodology for Nitrogen Dioxide as an Air Pollutant

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1 INTRODUCTION

Todoroski Air Sciences has been engaged by the New South Wales Environment Protection Authority (NSW EPA) to undertake a study to evaluate methods for assessing nitrogen dioxide (NO₂) impacts. The study is based on a review of current regulatory approaches in similar jurisdictions.

The study includes a review of the current NO₂ assessment approaches in New South Wales (NSW) and other jurisdictions, an explanation of the science underpinning each approach, an evaluation of the methods in regard to their applicability in NSW, and a recommendation on the methods most appropriate for the assessment of NO₂ impacts in NSW.

2 OBJECTIVE

The objective of the study is to:

“Recommend methods for assessing concentrations of NO₂ arising from emissions of oxides of nitrogen (NO_x). The methods need to be based on current scientific understanding, reflect current world best practice, and be flexible to suit the range of emission sources present in NSW.”

3 PROJECT SCOPE

The project scope includes the following tasks:

1. Review current NO₂ assessment approaches in comparable jurisdictions and list the information sources considered;
2. Describe in detail the NO₂ assessment methods reviewed and their advantages and disadvantages, including but not limited to:
 - a. particular data requirements such as ambient measurements,
 - b. applicability to emissions source categories and types,
 - c. ease of use, including options to apply each method as a screening level and complex level of assessment, and
 - d. relative conservativeness of each method;
3. Compare the assessment methods in light of emissions in NSW; and,
4. Rank and recommend methods for use in NSW.

4 OXIDES OF NITROGEN

Oxides of nitrogen (NO_x) from anthropogenic sources are formed by the oxidation of fuel nitrogen and nitrogen in the air at high combustion temperatures. Oxides of nitrogen also arise from natural emissions such as the oxidation of ammonia and atmospheric nitrogen, releases from the soil and ocean and naturally occurring bushfires (Ferrari and Salisbury, 1997).

NO_x is mainly composed of nitric oxide (NO), lesser quantities of NO_2 and trace amounts of other nitrogen oxides. NO_2 is of primary concern as it affects human health at elevated levels, reacts to form acids, and is a precursor for the formation of other pollutants such as particulate matter, ozone (O_3) and other oxidants. Although NO alone is not a primary concern for health, it is oxidised in the atmosphere forming NO_2 mainly in the presence of O_3 .

NO_2 concentrations are generally highest during winter as lower temperatures and lesser sunlight in cooler months results in less photochemical oxidation of NO_2 into O_3 (NSW DECCW, 2010a) (refer to **Section 4.3**).

4.1 Sources of NO_2 in NSW

The NSW EPA Air Emissions Inventory for the Greater Metropolitan Region (GMR) in NSW estimates that in 2008, 96.9 per cent of the NO_x emissions in the GMR and 98.3 per cent in Sydney are human-made (NSW EPA, 2012a), as shown in **Figure 4-1**.

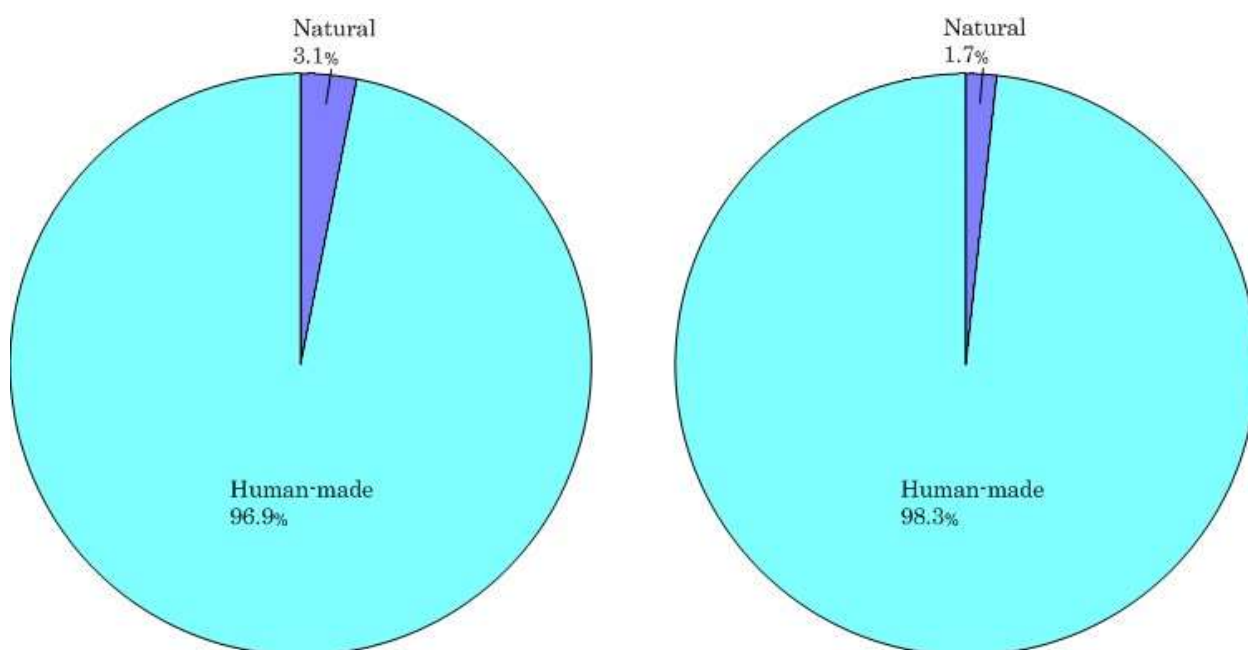


Figure 4-1: Natural and human-made NO_x in the GMR (left) and in Sydney (right) in 2008 (NSW EPA, 2012a)

The majority of NO_x emissions from human-made sources in the GMR arise from industrial sources followed by on-road mobile sources while in Sydney, on-road mobile sources are the major NO_x contributors followed by off-road mobile sources (see **Figure 4-2**).

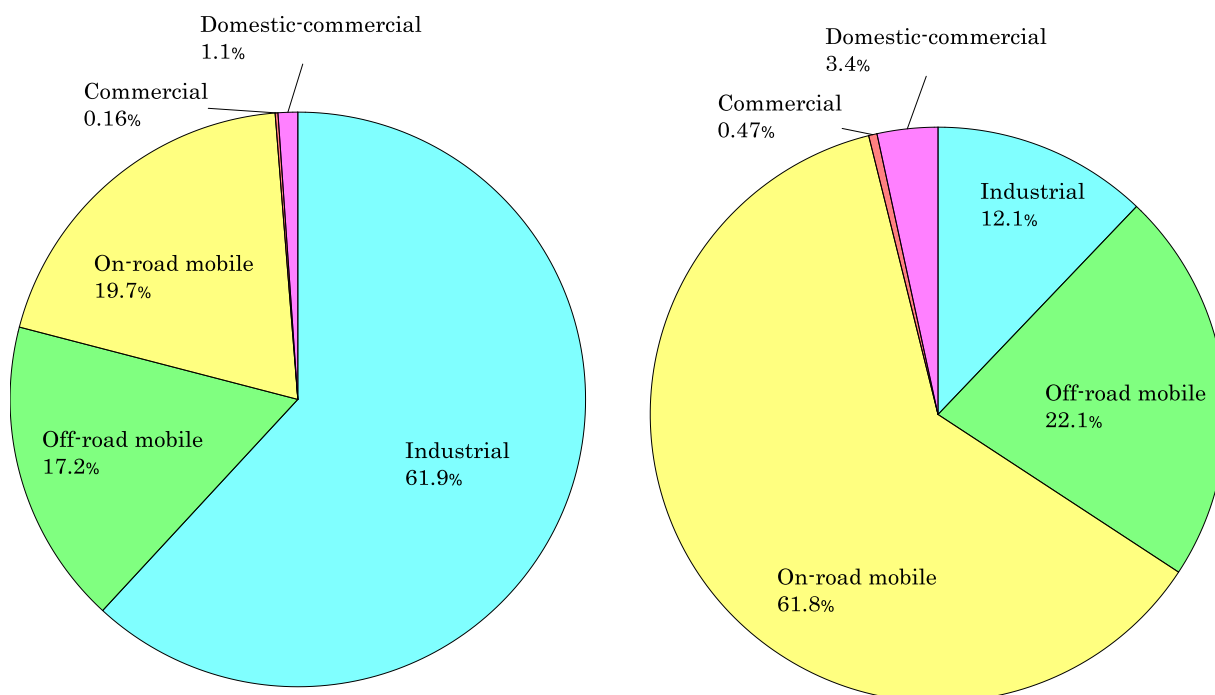


Figure 4-2: Sources of human-made NO_x in the GMR (left) and in Sydney (right) in 2008 (NSW EPA, 2012a)

Over the period from 1992 to 2008, the NO_x emissions from motor vehicles in Sydney fell by 27 per cent and "will continue to fall due to tighter vehicle emission standards such as ADR 80.03 (Euro 5) which will require nitrogen dioxide controls (such as selective catalytic reduction) on heavy duty vehicles by 2010/11" (NSW DECC, 2009). The NO_x emissions on-road will likely significantly fall further with the introduction of even tighter vehicle emission standards in the future such as the Euro 6 (Weiss et al., 2012).

However, over the same period, NO_x emissions from industry in Sydney have increased by 51 per cent and "are projected to grow a further 13% over the next 8 years to 2016" (NSW DECC, 2009).

The significant decrease in the total NO_x emissions from on-road mobile sources is likely to be responsible for the observed decrease in the NO₂ levels in Sydney (see **Section 4.3**). It may also be a significant factor affecting the O₃ levels in Sydney, which depending on the specific hour by hour conditions during periods of high ozone, may be significantly influenced by the prevailing NO_x concentrations. The relationship between NO₂ and Ozone in such periods is non-linear and complex, for further details refer to State of Knowledge: Ozone, (**NSW DECCW, 2010b**).

Although the NO₂ assessment methods promulgated by the NSW EPA are generally not specifically designed to be applicable to roads, on-road emissions information is important and may be applicable to assessable point source emissions in NSW.

NO₂ assessment methods that are generally applicable to a range of different situations, source types, or locations, are available. However, due to the complexity and the number of variables involved in the atmospheric reactions that determine the resulting levels of NO₂ (see **Section 4.2**), many of the NO₂ assessment methods are simplified, or are developed for specific emission sources or localities, by holding some of the many influencing variables constant. Thus, to be able to select and best use the

most appropriate assessment method for a specific situation, it is important to have an understanding of the main assessable NO_x sources in NSW.

4.1.1 NO_x from industrial sources

As shown in **Figure 4-3** the majority of NO_x emission from industrial sources in the GMR is estimated to occur in the non-urban regions. **Figure 4-4** to **Figure 4-8** show the proportion of NO_x emissions by industrial activity type in the GMR, Sydney, Newcastle, Wollongong and non-urban regions, respectively, in 2008.

The majority of the NO_x emissions in the GMR are dominated by emissions from coal-fired power stations. In the Sydney region, the industrial NO_x emissions arise predominantly from various industrial sources with a greater proportion from gas-fired power stations followed by petroleum products and fuel production. Ammonium production is the biggest source of NO_x emissions from industries in the Newcastle region, and in the Wollongong region the majority of NO_x emissions arise from iron or steel production.

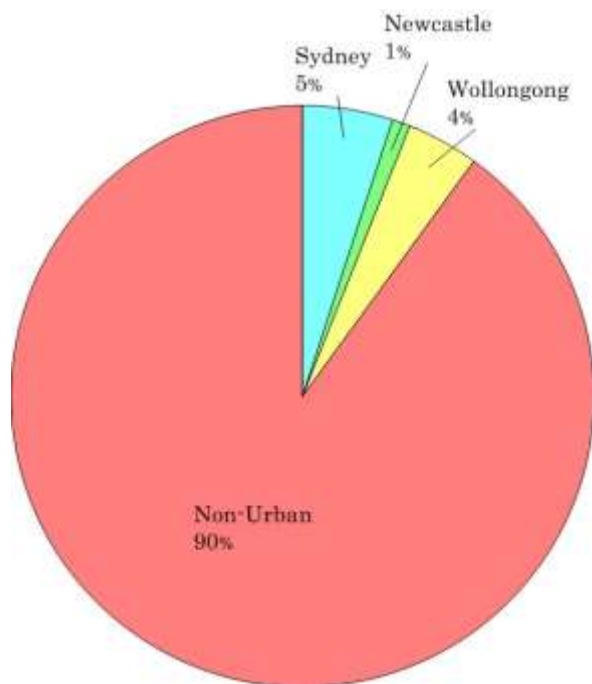


Figure 4-3: Proportions of NO_x emissions from industrial sources in each region of the GMR in 2008 (NSW EPA, 2012c)

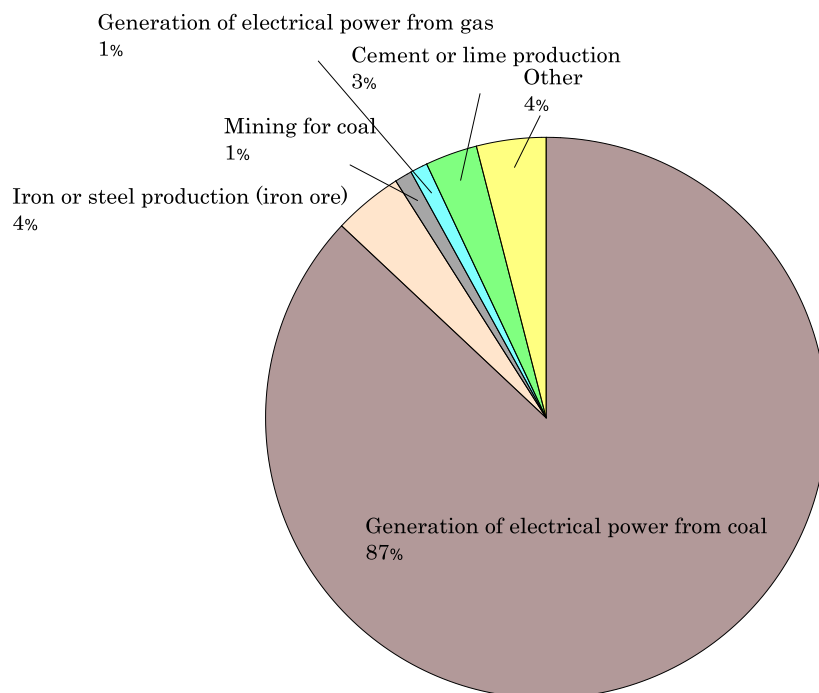


Figure 4-4: Proportion of NO_x emissions by industrial activity type in the GMR in 2008 (NSW EPA, 2012c)

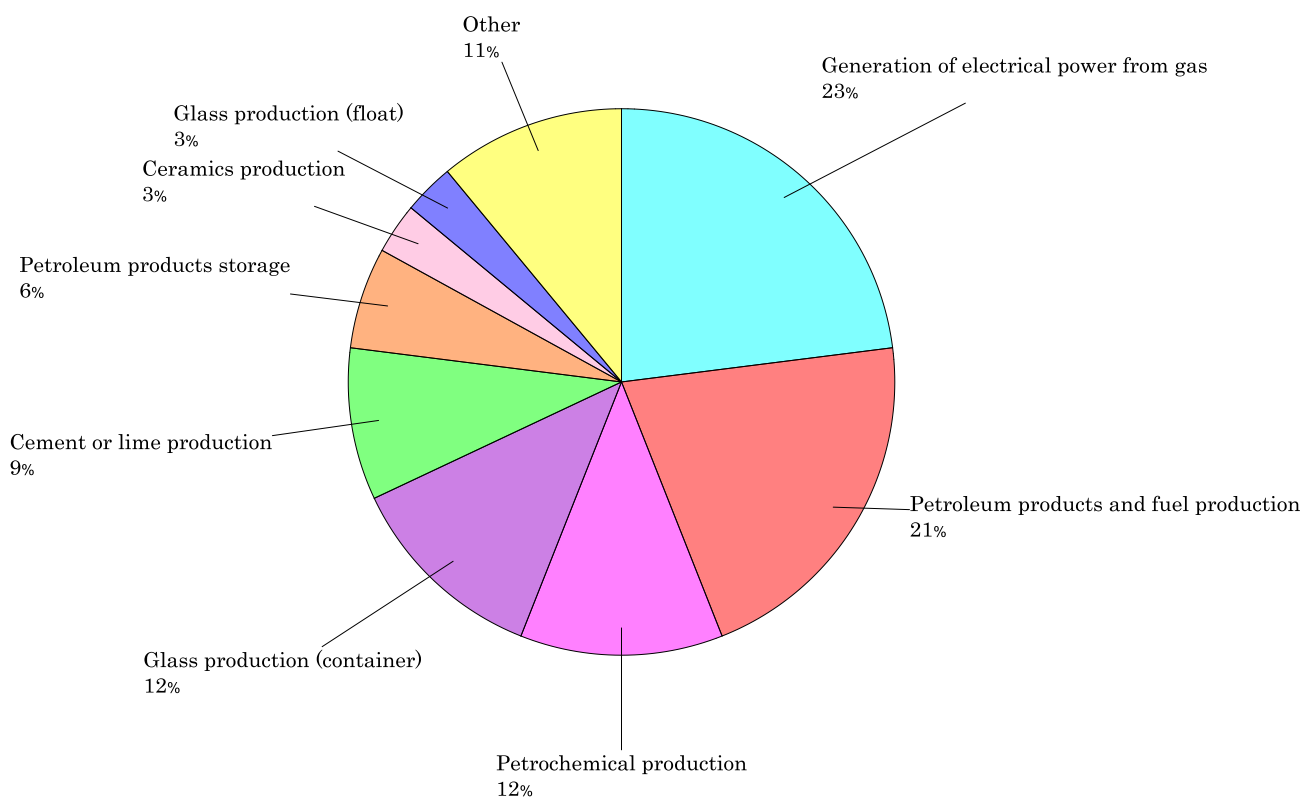


Figure 4-5: Proportion of NO_x emissions by industrial activity type in the Sydney region in 2008 (NSW EPA, 2012c)

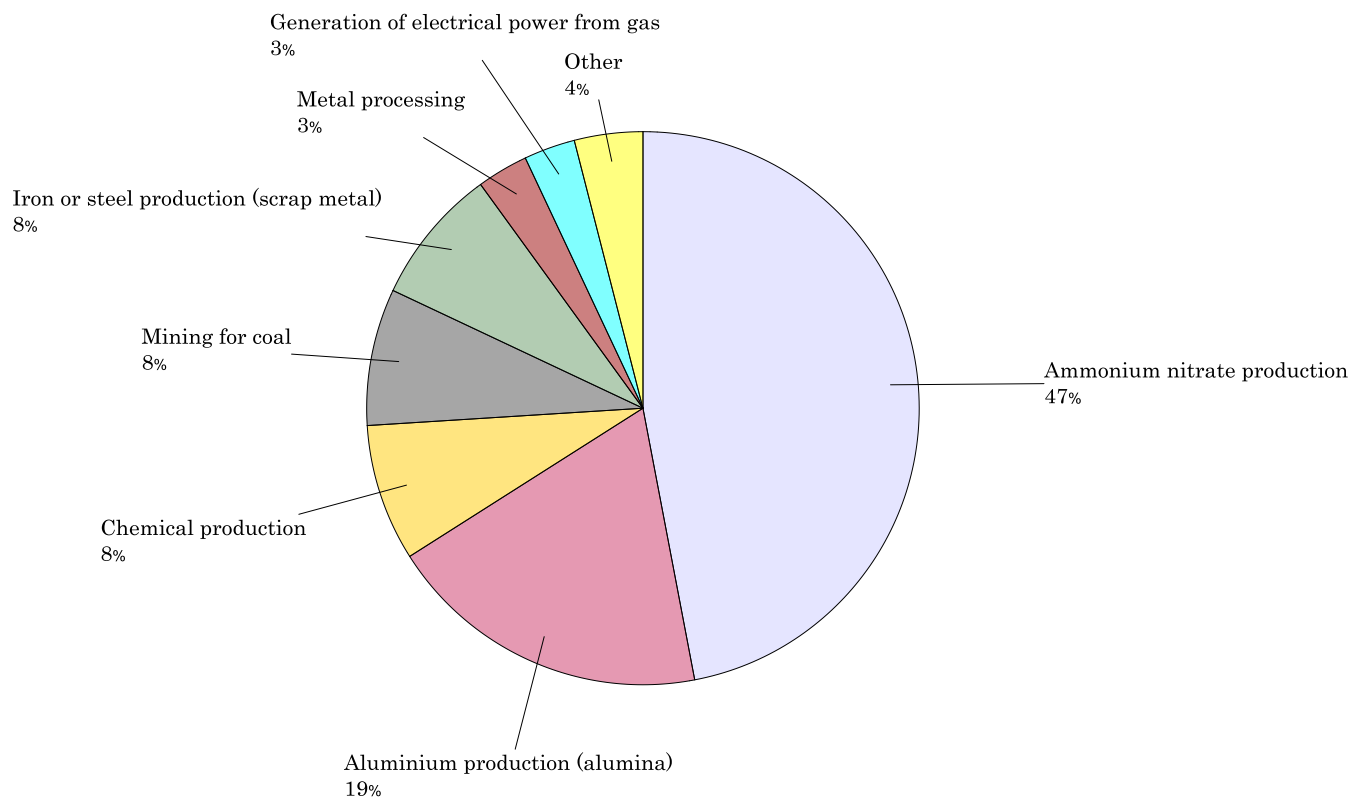


Figure 4-6: Proportion of NO_x emissions by industrial activity type in the Newcastle region in 2008 (NSW EPA, 2012c)

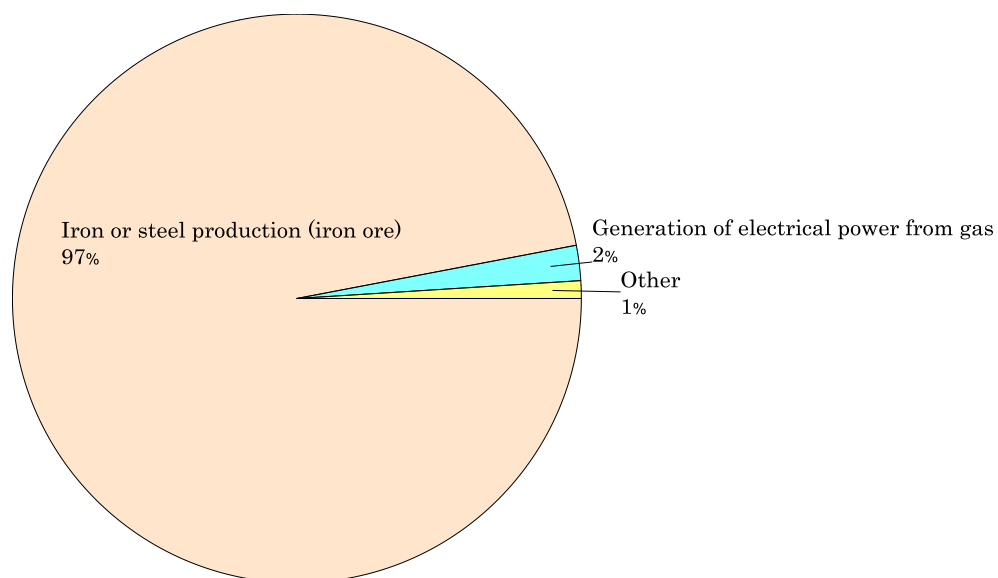


Figure 4-7: Proportion of NO_x emissions by industrial activity type in the Wollongong region in 2008 (NSW EPA, 2012c)

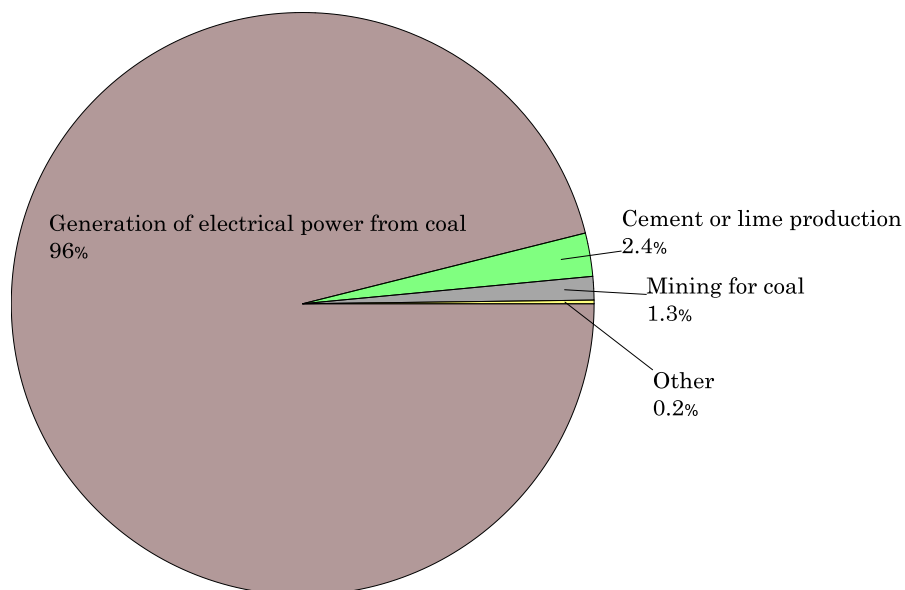


Figure 4-8: Proportion of NO_x emissions by industrial activity type in the non-urban region in 2008 (NSW EPA, 2012c)

4.1.2 NO_x from on-road mobile sources

Emissions from on-road mobile sources are the main source of NO_x emissions in the Sydney region, see **Figure 4-2**.

As shown in **Figure 4-9** the majority of the NO_x from on-road mobile sources in the GMR in 2008 arise in Sydney. **Figure 4-10** shows the breakdown of the various on-road mobile NO_x sources in the GMR in 2008, which is dominated by petrol passenger vehicles and heavy-duty diesel vehicles.

The distribution of NO_x emissions from each on-road mobile source for each region in the GMR is presented in **Figure 4-11** and shows a similar distribution that is typically dominated by petrol passenger vehicles and heavy-duty diesel vehicles.

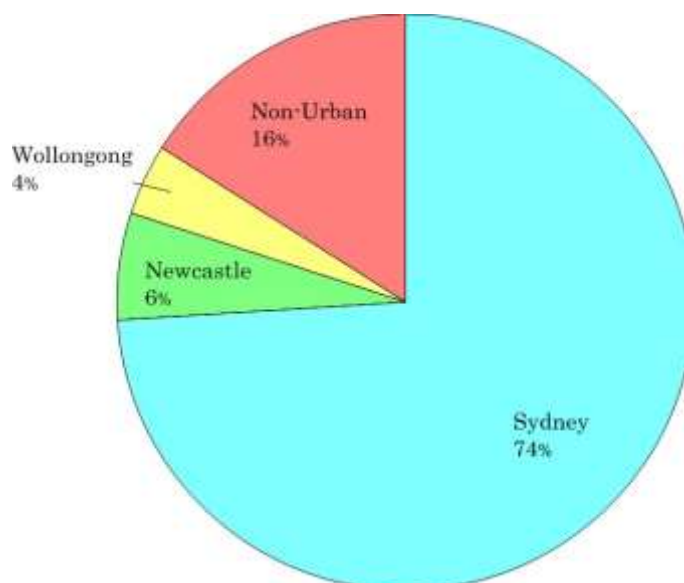


Figure 4-9: Proportions of NO_x emissions from on-road mobile sources in each region of the GMR in 2008 (NSW EPA, 2012b)

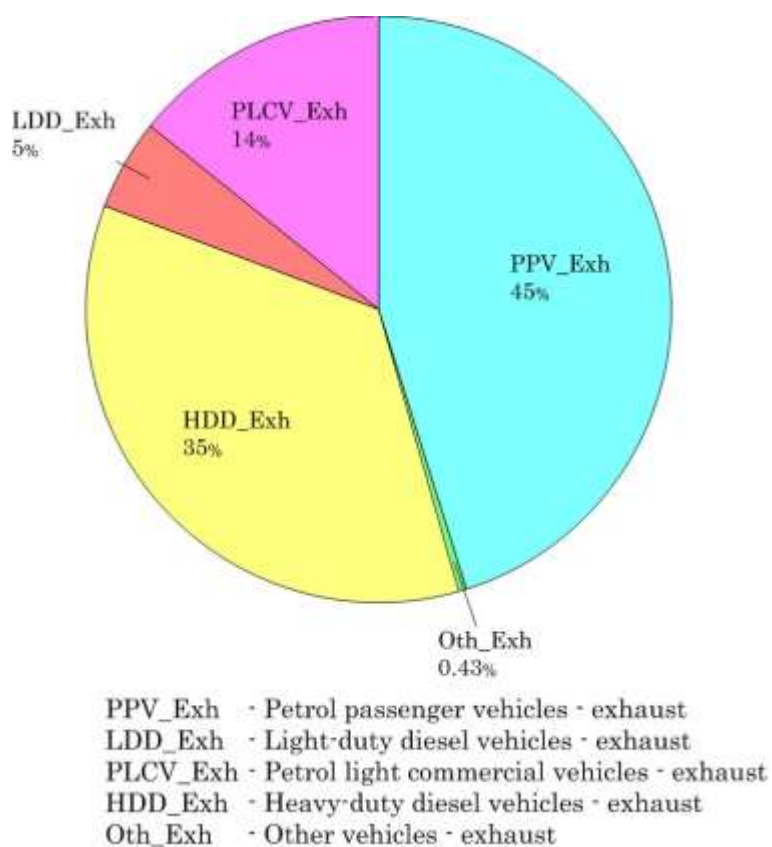


Figure 4-10: Proportion of NO_x emissions by on-road mobile source type in the GMR in 2008 (NSW EPA, 2012b)

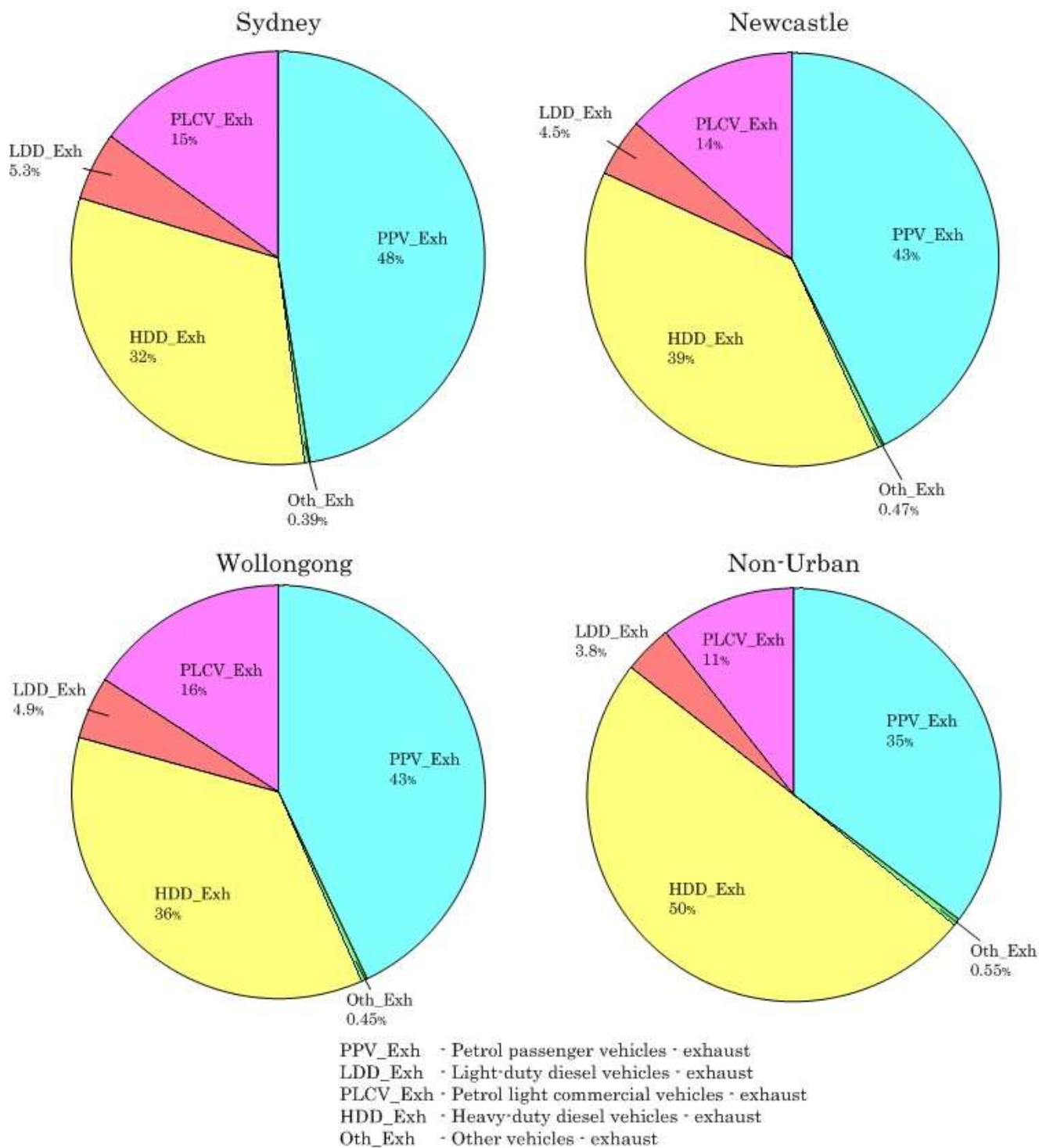


Figure 4-11: Proportion of NO_x emissions by on-road mobile source type in Sydney, Newcastle, Wollongong, and Non-Urban Regions (clockwise from upper left) in 2008 (NSW EPA, 2012b)

Observations of NO and NO₂ in Sydney's M5 East Tunnel suggest that the NO₂/NO_x ratio from motor vehicles is approximately 5-6 per cent (NHMRC, 2008). During the daytime the ratio was typically 5 per cent, while at night time higher ratios were observed due to both lower emissions and the lower likelihood of oxidant depletion (Holmes Air Sciences as cited in NHMRC, 2008).

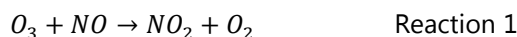
In London, although there has been a downward trend of NO_x concentrations at the roadside from 1997 to 2003, the NO₂ concentrations had no significant statistical trend over the same period (Carslaw, 2005). The relatively flat NO₂ concentrations contrasts with a downward trend in NO_x concentrations in London and is believed to be due to the increase of NO₂/NO_x emissions ratio from motor vehicles from approximately 5-6% in 1997 to approximately 17% in 2003, on the basis of "hourly modelling using a simple constrained chemical model" (Carslaw, 2005).

The increase in the NO₂/NO_x emissions ratio may be due to the increased use of catalytic diesel particulate filters using an oxidation catalyst, increased use of diesel cars and new engine technologies, and management approaches (Carslaw, 2005). The introduction of the more stringent Euro 6 emissions standards in Europe in 2014 would further decrease NO_x emissions at the roadside but would increase the NO₂/NO_x emissions ratio (Weiss et al., 2012).

These variations in on-road mobile NO_x over time highlight that it is important for NO₂ assessments to reflect the current and likely future trend of NO₂ and NO_x emissions from major sources such as vehicles which can potentially be inferred from historic trends and the available information on influencing factors such as the increasing uptake of new or future engine technologies.

4.2 NO₂ atmospheric reactions

The atmospheric reaction of NO₂ mainly involves the following reactions:



The oxidation of NO with O₃ (as illustrated in Reaction 1) is a fast reaction (typically a few minutes) in typical urban atmospheric conditions (ETC/ACM, 2011). In the presence of sunlight, the production of NO₂ is balanced by its photodissociation into NO and ground state oxygen molecule (O), as illustrated in Reaction 2 where $h\nu$ is the energy from a photon with a wavelength of less than 420nm (ETC/ACM, 2011).

As demonstrated by these two reactions, the concentration of NO₂ is dependent on the O₃ levels and the presence of sunlight. NO₂ concentrations are generally highest during winter as lower temperatures and lesser sunlight in cooler months results in less photochemical destruction of NO₂ into O₃ (NSW DECCW, 2010a), and also due to poorer dispersion of emissions.

Some of the ground state oxygen (O) produced in Reaction 2 would react with O₂ to form O₃ in the presence of some other molecule (M) as shown in Reaction 3 (ETC/ACM, 2011).



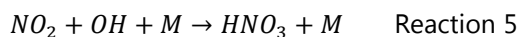
Reactions 1 to 3 show a cyclical interdependence of the concentrations of NO₂ and O₃ which is exemplified in the monitoring data for the Sydney region shown in **Section 4.3**.

The pathways for the oxidation of NO to NO₂ include reactions with volatile organic compounds (VOCs). The peroxy radicals (RO₂) generated by the oxidation of the VOCs would oxidise NO to NO₂ (ETC/ACM, 2011) as shown in Reaction 4.

Therefore the presence of VOCs may increase the NO₂ concentrations and, through Reactions 2 and 3, also increase the O₃ concentrations. Reaction 4 is a much slower reaction (typically of an hour or more) than Reaction 1 (which is typically of a few minutes) (ETC/ACM, 2011).



NO₂ in the atmosphere would eventually disappear through the following reaction (ETC/ACM, 2011):



The reaction of NO₂ with hydroxyl radical (OH) in the presence of other molecule (M) (Reaction 5) typically occurs between a few hours and a number of days (ETC/ACM, 2011).

The concentration of NO₂ in the atmosphere is dependent on a number of interrelated reactions involving oxidants whose production also involves a number of reactions, and the presence of sunlight and O₃, VOC 's and their reactive oxides, all of which react with and thus consume NO₂.

In other words, the NO₂ levels will vary with time and space away from the emissions source(s) depending on the composition and state of the receiving atmosphere, and it is very difficult to precisely model this situation. An accurate model that might represent these complex reactions would be unlikely to be practical to use for routine regulatory assessment purposes, and a simplified model becomes necessary.

Thus in any practical model that is suitable for routine use for NO₂ assessments, it is important that the model operates with a degree of conservatism (overestimation) in order to reasonably take into account the inherent inaccuracy that arises due to model simplifications.

4.3 Air quality in Sydney – NO₂ and O₃

The level of NO₂ and O₃ in the air shed is a significant factor to consider when conducting an NO₂ assessment. For example, as described in **Section 4.2**, there tends to be an inverse relationship between NO₂ and O₃ levels on average or over the longer term.

This section examines the long term, annual and one hour average concentrations of NO₂ measured in the Sydney air shed. This is one of the key NSW air sheds with potential for significant NO₂ and significant O₃ levels to occur.

The measured O₃ levels are also presented and illustrate the interrelationship between NO₂ and O₃ levels as described in **Section 4.2**. Many of the NO₂ assessment methods described in **Section 5.3** require such ambient data inputs to make the necessary calculations.

The 1-hour average and annual average concentration data are presented as these are the averaging periods applied to assess NO₂ levels per the relevant criteria (see **Section 5.1**).

The long term average NO₂ and O₃ concentrations at each monitoring station as a fraction of the maximum concentration are also presented in **Figure 4-12**. These levels do not correspond to assessment criteria averaging periods, but do illustrate the underlying trends that may not be apparent when examining any specific short term period. The long term average concentrations are computed as the average of the available monitoring data from 1990 to 2014. The fraction is normalised by dividing

the long term average concentration for each monitor by the highest of the long term averages among the monitors. Generally, the monitors which recorded higher NO₂ concentrations recorded lower O₃ concentrations and vice versa.

Figure 4-13 presents a spatial distribution plot of the measured long term average NO₂ concentration in the Sydney air shed. The figure indicates that the NO₂ concentrations (left) are highest close to the centre of traffic and industrial activity, but decline to the west where there is a lower density of on-road mobile sources. The spatial distribution of O₃ concentrations (right) shows an opposite trend to the NO₂ concentrations, where the lowest concentrations are found close to the centre of traffic and industrial activity and increase to the west.

This figure illustrates that over the long term, an inverse relationship between NO₂ and O₃ does arise in the Sydney basin, which provides a degree of confidence that assessment methodologies utilising both NO₂ and O₃ levels would be applicable in this air shed.

This analysis indicates that in areas with high NO_x concentrations, O₃ concentrations are typically depleted through the oxidation of NO to NO₂. Further examination of the available ambient NO or NO_x data would be useful to verify this and to examine any related trends in more detail. This is outside the scope for this project. Nevertheless, the trends in the freely available data indicate that it is likely that the ambient NO/NO₂ ratio would be higher in areas with high O₃ levels as more of the NO₂ would have transformed to NO and O₃.

It is recommended that it would be useful to extend the study in this regard, and to also examine the trend each year, to see how changes in industrial and residential development in the air shed may have spatially influenced the NO/NO₂ ratio and O₃ levels over time. This may also be a useful analysis to complete in other urban NSW air sheds with suitable data.

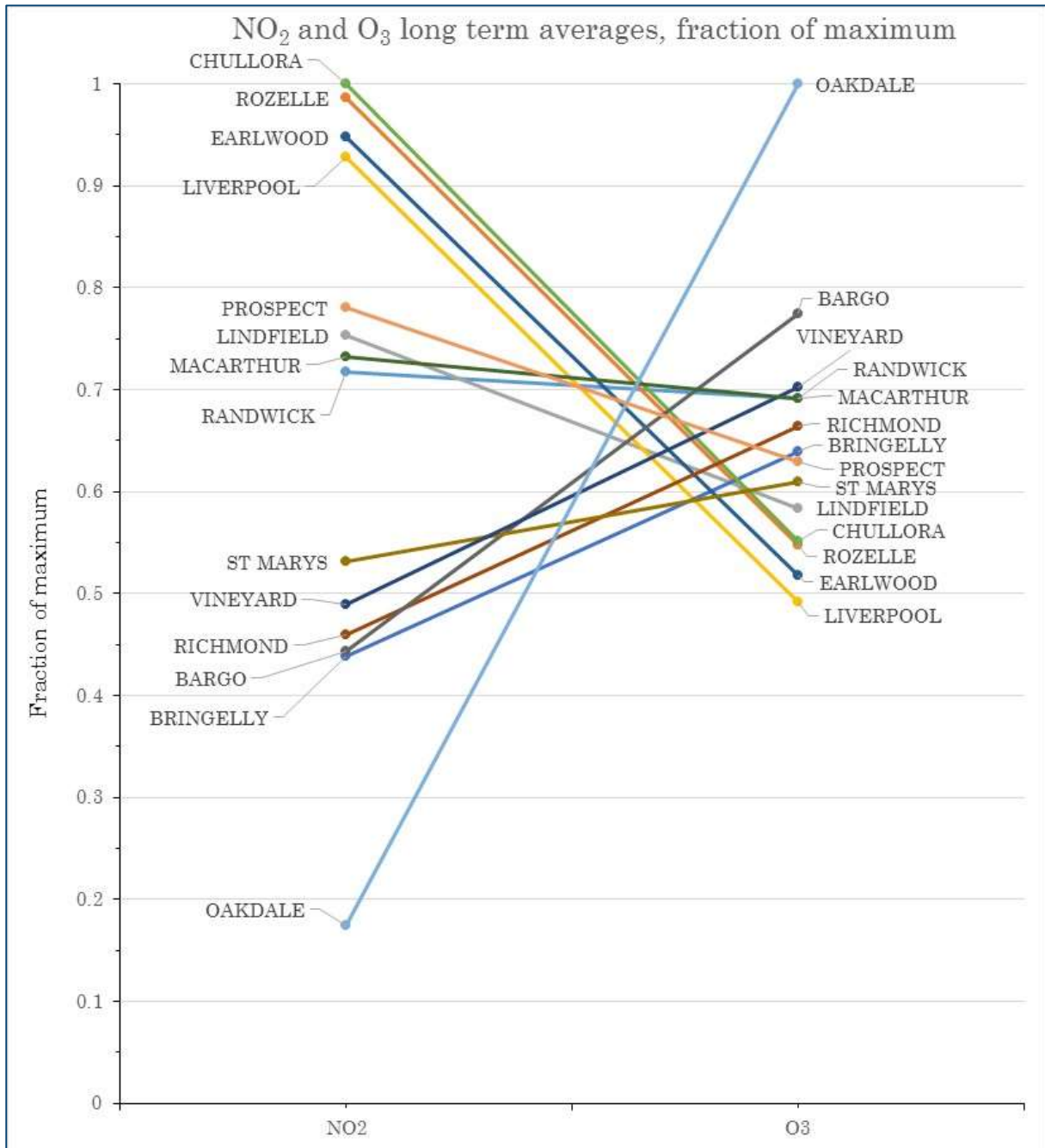


Figure 4-12: NO₂ and O₃ long term averages as a fraction of the maximum concentrations in Sydney (TAS, 2015)

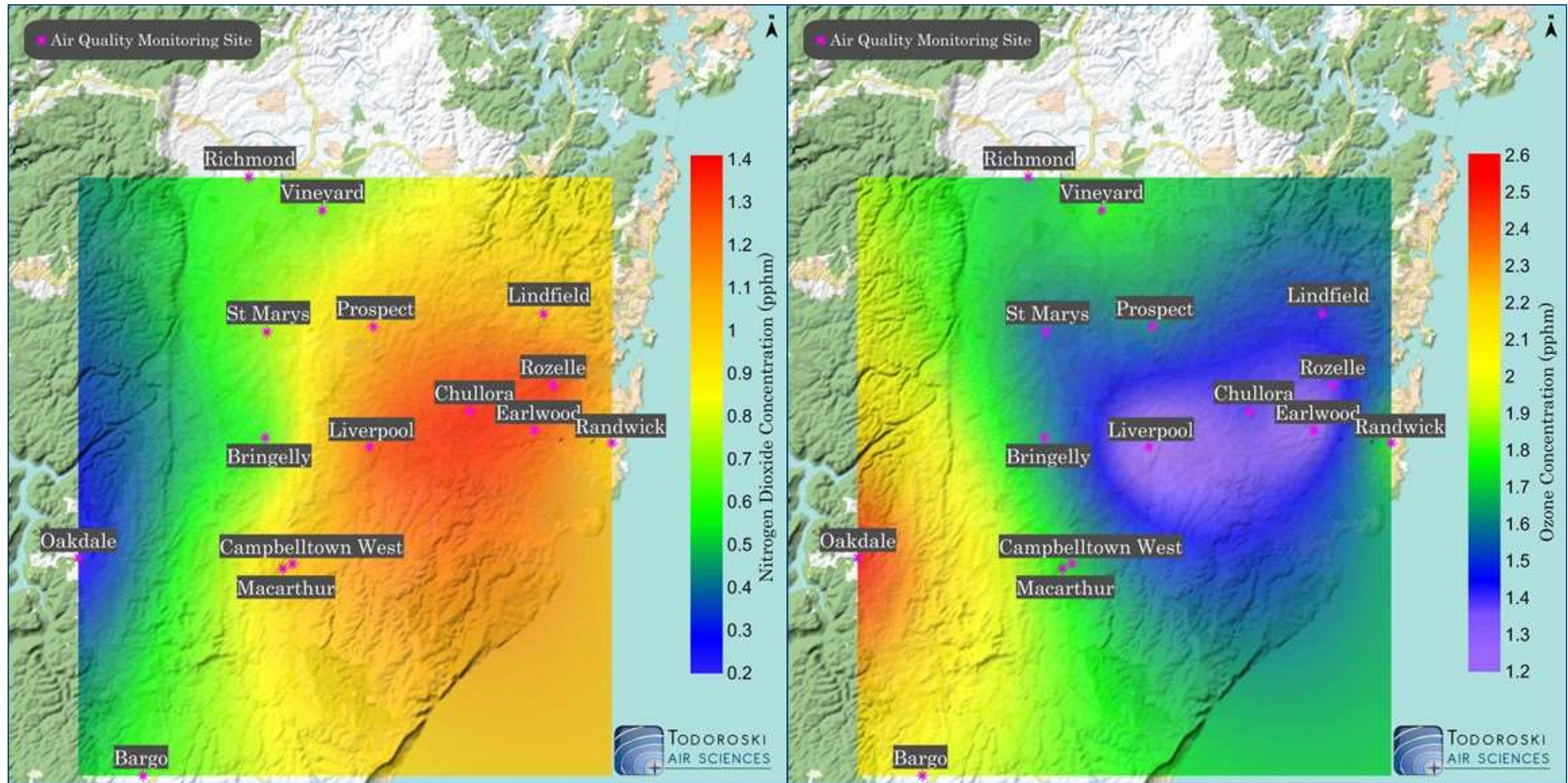


Figure 4-13: Long term average NO₂ (left) and O₃ (right) concentrations in Sydney (TAS, 2015)

Figure 4-14 and **Figure 4-15** present the measured daily maximum 1-hour average NO₂ and O₃ concentrations, respectively, in Sydney from 1990 to 2014. A seasonal variation in the daily maximum 1-hour concentrations of both species is apparent with NO₂ concentrations highest during winter and lowest during summer, with the opposite trend for O₃ concentrations.

During summer, there is more daylight for the photochemical production of O₃ and photolysis of NO₂ resulting in lower NO₂ levels and higher O₃ levels.

The 1-hour average NO₂ concentrations in the Sydney airshed are well below the criteria and the highest levels are approximately half of the criteria in recent years. The O₃ levels however exceed the criteria in some hours.

Figure 4-16 and **Figure 4-17** present the trend of the annual average NO₂ and O₃ concentrations, respectively, in Sydney from 1993 to 2014. The annual average NO₂ concentration declines over time, and levels off from approximately 2009 onwards while the annual average O₃ concentration increases over time and levels off from approximately 2004 onwards. In recent years the levels of NO₂ are well below the relevant criteria with the highest levels reaching approximately half of the criteria.

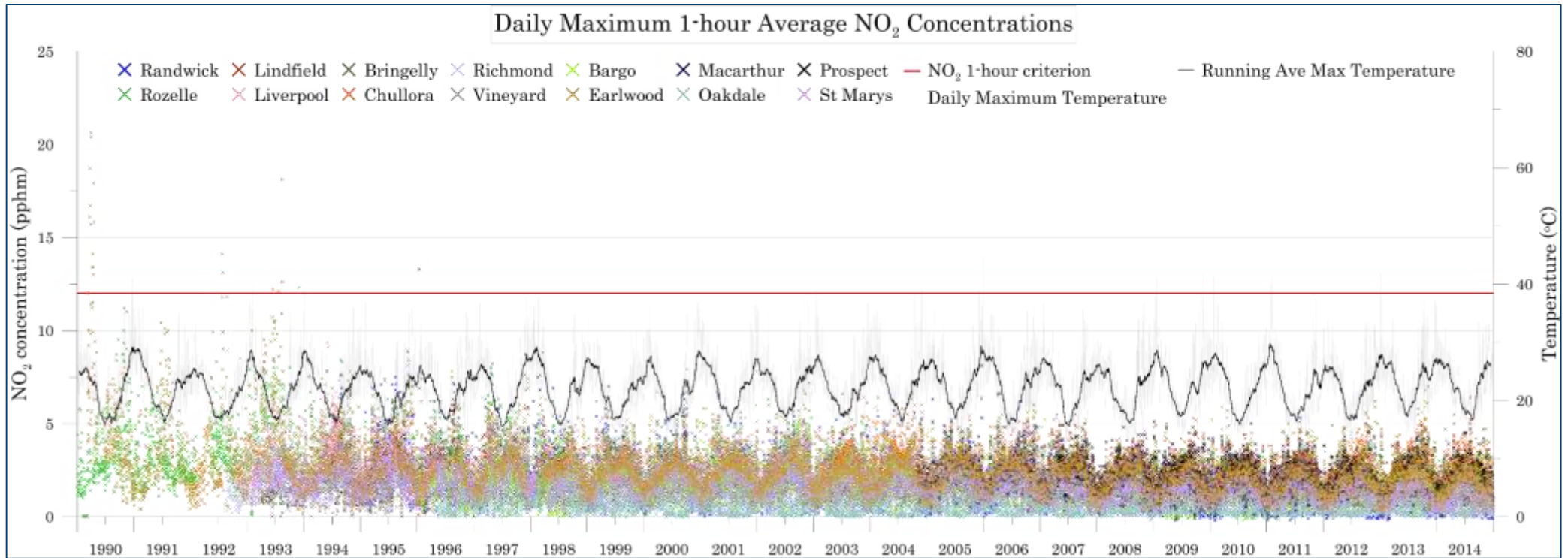


Figure 4-14: Daily maximum 1-hour average NO₂ concentrations in Sydney (TAS, 2015)

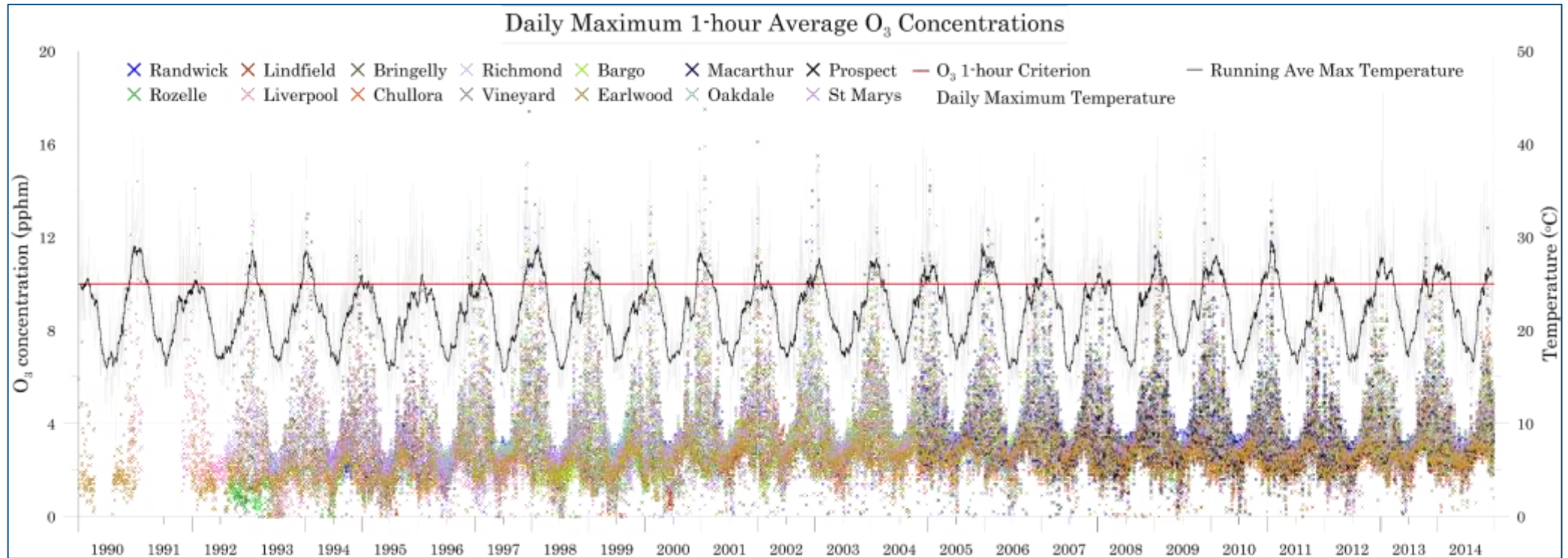


Figure 4-15: Daily maximum 1-hour average O₃ concentrations in Sydney (TAS, 2015)

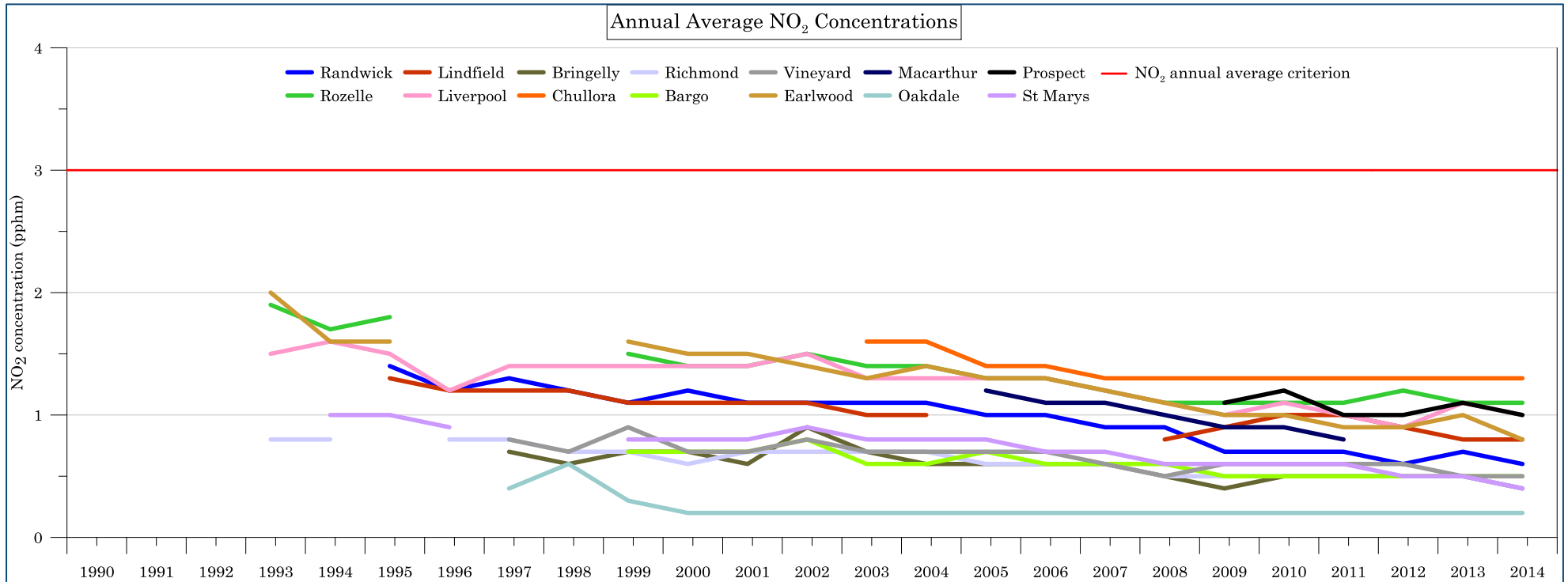


Figure 4-16: Annual average NO₂ concentrations in Sydney (TAS, 2015)

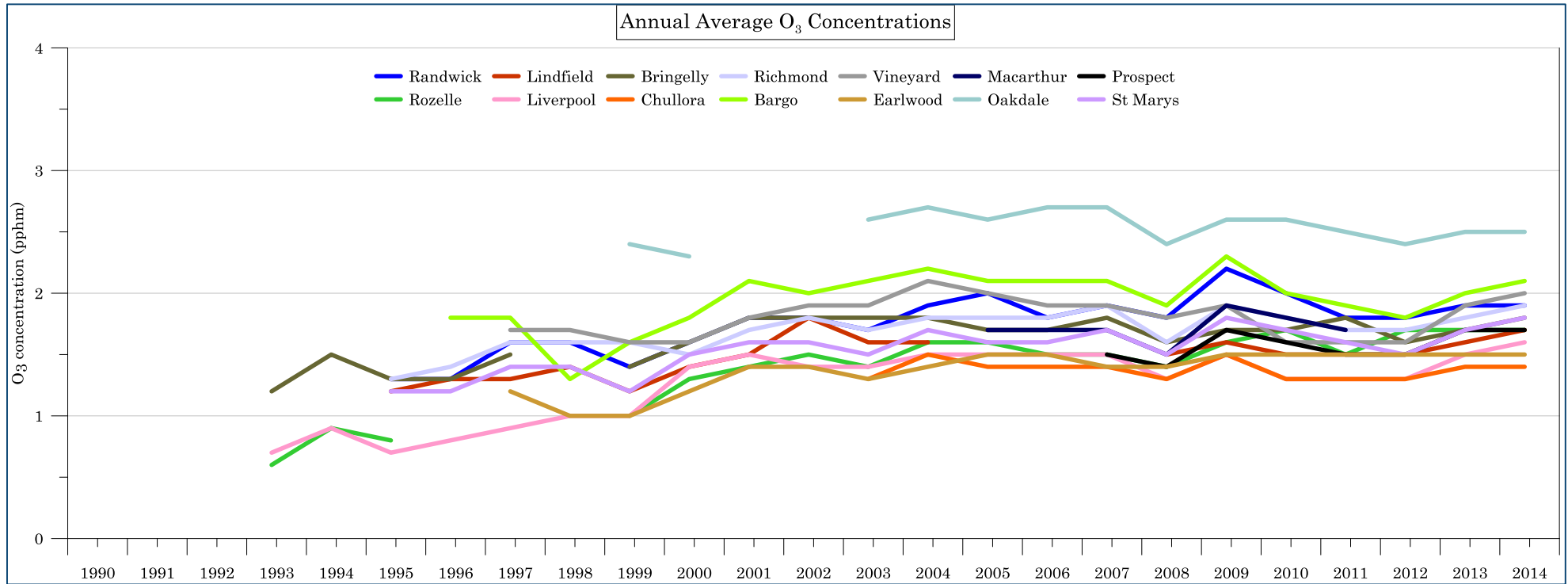


Figure 4-17: Annual average O₃ concentrations in Sydney (TAS, 2015)

5 REVIEW OF NO₂ IMPACT ASSESSMENT REQUIREMENTS

As outlined previously, NO₂ concentrations from anthropogenic sources arise from direct emissions and NO₂ that is produced from the atmospheric oxidation of NO. The chemistry involved in the atmospheric reaction is complex and involves many variables such as the presence of UV to catalyse the photochemical reactions involving NO_x, VOCs and O₃, and the inhomogeneous mixing of the reactants in the open atmosphere.

This complex chemistry in the production and depletion of NO₂ occurs while the reactants are dispersing in the atmosphere. Since the various mechanisms and variables involved in the production of NO₂ are difficult to simulate, simple approaches for predicting NO₂ impacts have been developed using easily obtainable information such as ambient O₃ concentrations. Such approaches may rely on formulae or variables specific to the various jurisdictions in which they are used to assess potential NO₂ impacts per the various criteria applicable in these jurisdictions. These factors need to be considered when determining the applicability of these approaches to NSW, along with the ability of the methods to produce results that can be assessed against the relevant NSW 1-hour and annual average periods for assessment (see **Section 5.1**).

5.1 Current approaches in NSW

To demonstrate compliance with relevant criteria, a Level 1 or Level 2 assessment may be employed as set out in the *Approved Methods for the Modelling and Assessment of Air Pollutants in New South Wales* (NSW DEC, 2005). **Table 5-1** summarises the air quality goals for the assessment of NO₂ in NSW.

Table 5-1: NSW EPA air quality impact assessment criteria

Pollutant	Averaging period	Criterion
Nitrogen dioxide (NO ₂)	1 hour	246µg/m ³
	Annual	62µg/m ³

Source: **NSW DEC, 2005**

5.1.1 Less refined assessment

The three current methods for nitrogen dioxide assessment set out in (NSW DEC, 2005) include the following, in order of simplicity;

Method 1: 100% conversion of NO to NO₂;

Method 2: NO to NO₂ conversion limited by ambient ozone concentration (OLM); and

Method 3: NO to NO₂ conversion using empirical relationship developed by Janssen et al. (1988).

Any of these methods can be used in the assessment of NO₂, however minor NO_x sources may only need the simplest assessment method while larger sources with more scope for impact may need the more detailed methods to demonstrate compliance with the relevant criteria.

5.1.2 Detailed assessment of NO₂

More detailed models for NO₂ assessment are outlined in (NSW DEC, 2005), and include the following methods developed by CSIRO.

Integrated Empirical Rate (IER) Reactive Plume Model. The IER Reactive Plume Model is a more refined assessment method than the methods specified above. It not only predicts changes in ambient NO₂ concentrations but also ambient O₃ concentrations (NSW DEC, 2005).

The Air Pollution Model (TAPM). *"CSIRO TAPM includes gas-phase photochemistry based on the semi-empirical mechanism, called the Generic Reaction Set (GRS). In chemistry mode, TAPM includes 10 reactions for the following 13 species: smog reactivity, radical pool, hydrogen peroxide (H₂O₂), NO, NO₂, O₃, SO₂, stable non-gaseous organic carbon, stable gaseous nitrogen products, stable non-gaseous nitrogen products, stable non-gaseous sulfur products, airborne particulate matter and fine particulate matter"* (NSW DEC, 2005).

Generally, the less refined methods are sufficient for most NO₂ impact assessment requirements.

5.2 Approaches in various other jurisdictions

Table 5-2 presents a summary of the NO₂ impact criteria and assessment approaches in various jurisdictions identified through a desktop literature review.

The scientific basis underpinning each of the methods presented in the table is briefly described in **Section 5.3**.

Table 5-2: Summary of the current NO₂ impact criteria and assessment approaches in various jurisdictions

Jurisdiction		Reference	Criteria			Methods
Country	State		1-hr average	24-hr average	Annual average	
Canada	Alberta	Air Quality Modelling Guideline (Alberta Environment, 2009) Draft Proposed Air Quality Modelling Guideline (Alberta ESRD, 2012) Alberta Ambient Air Quality Objectives and Guidelines Summary (Alberta Environment, 2013)	300µg/m ³ (159ppb)	-	45µg/m ³ (24ppb)	<ul style="list-style-type: none"> Total Conversion Method Plume Volume Molar Ratio Method (PVMRM) in AERMOD RIVAD/ARM3 Chemical Formulations in CALPUFF Ozone Limiting Method (OLM) Ambient Ratio Method (ARM)
Canada	British Columbia	Guidelines for Air Quality Dispersion Modelling in British Columbia (BC Ministry of Environment, 2008) British Columbia Ambient Air Quality Objectives (BC Ministry of Environment, 2014)	188µg/m ³ (100ppb)	-	60µg/m ³ (32ppb)	In order of priority: <ul style="list-style-type: none"> Total Conversion Method ARM OLM PVRM in AERMOD
Canada	Ontario	Air Dispersion Modelling Guideline for Ontario (Ontario Ministry of the Environment, 2009) Ontario's Ambient Air Quality Criteria (Ontario Ministry of the Environment, 2012)	400µg/m ³ (0.20ppm)	200µg/m ³ (0.10ppm)	-	Not specifically mentioned but refers to OLM and PVMRM as AERMOD options. Refers to post processing approaches described in the US EPA Guidelines on Air Quality Models.
Canada	Manitoba	Manitoba Ambient Air Quality Criteria (Manitoba Government, 2005)	Maximum Tolerable Level Concentration 1000µg/m ³ (0.53ppm)			Not specifically stated however indicates reference to US EPA Guidelines.
		Maximum Acceptable Level Concentration 400µg/m ³ (0.213ppm)				
		200µg/m ³ (0.106ppm)	100µg/m ³ (0.053ppm)			
		Maximum Desirable Level Concentration -				
Canada	Newfoundland Labrador	Guideline for Plume Dispersion Modelling (Newfoundland and Labrador DEC, 2012) Air Pollution Control Regulations (2004)	400µg/m ³	200µg/m ³	100µg/m ³	<ul style="list-style-type: none"> RIVAD/ISORROPIA for CALPUFF assessments PVMRM for AERMOD and AERSCREEN applications
Canada	Saskatchewan	Saskatchewan Air Quality Modelling Guideline (Saskatchewan Ministry of Environment, 2012) Ambient Air Quality Standards (The Clean Air Act, 2014)	400µg/m ³ (0.2ppm)	-	100µg/m ³ (0.05ppm)	<ul style="list-style-type: none"> Total Conversion Method ARM OLM PVMRM

Jurisdiction		Reference	Criteria			Methods
Country	State		1-hr average	24-hr average	Annual average	
Canada	Quebec	<p>Guide de la Modélisation de la Dispersion Atmosphérique (Québec Ministère du Développement durable, de l'Environnement et Parcs, 2005)</p> <p>Mise à jour des critères québécois de qualité de l'air (Québec Ministère du Développement durable, de l'Environnement et Parcs, 2010)</p> <p>Guide D'Estimation de la Concentration de Dioxyde D'Azote (NO₂) Dans l'Air Ambiant Lors de l'Application des Modèles de Dispersion Atmosphérique (Québec Ministère du Développement durable, de l'Environnement et Parcs, 2008)</p> <p>Power stations, oxides of nitrogen emissions, and photochemical smog: a modelling approach to guide decision makers (Wratt et al. 1992 cited in Québec Ministère du Développement durable, de l'Environnement et Parcs, 2005)</p>	414µg/m ³	207µg/m ³	103µg/m ³	<p>In order of priority:</p> <ul style="list-style-type: none"> Total Conversion Method OLM PVRM <p>For power generation plants located in plains of the St Lawrence – use Integrated Empirical Rate (IER) Model by Wratt et al. (Québec Ministère du Développement durable, de l'Environnement et Parcs, 2005)</p>
China	-	Ambient air quality standard (People's Republic of China, 1996)	1 st and 2 nd level criteria			Unable to find specific reference to recommended approach.
			0.12mg/m ³	0.08mg/m ³	0.04mg/m ³	
			3 rd level criteria			
			0.24mg/m ³	0.12mg/m ³	0.08mg/m ³	
China	Hong Kong	<p>Guidelines on Choice of Models and Model Parameters (HK Environmental Protection Department, 2015a)</p> <p>Air Quality Objectives (HK Environmental Protection Department, 2015b)</p>	200µg/m ³	-	40µg/m ³	<ul style="list-style-type: none"> ARM Discrete Parcel Method (DPM) available in CALINE4 OLM

Jurisdiction		Reference	Criteria			Methods
Country	State		1-hr average	24-hr average	Annual average	
Europe		Guide on modelling Nitrogen Dioxide (NO ₂) for air quality assessment and planning relevant to the European Air Quality Directive (ETC/ACM, 2011) Guidance on the use of models for the European Air Quality Directive (ETC/ACC, 2010)	Limit or target value			<ul style="list-style-type: none"> • Steady-state chemical models <ul style="list-style-type: none"> - AIRQUIS-EPISODE - IMMIS - IFDM-POLCA - OSPM - OSPM approach applied to annual averages • Distance dependent parameterised chemical models <ul style="list-style-type: none"> - CAR-FMI - CALINE4 - ADMS - OML-HIGHWAY • Statistical/empirical parameterised chemical models <ul style="list-style-type: none"> - ARM - Methodologies developed for DEFRA - Airviro - Romberg method - Standard Calculation Method in the Netherlands - SAPPHO - Keller - Oxidant Partitioning Model • Photochemistry models <ul style="list-style-type: none"> - GRS - EMEP - SAPRC99 and SARPC07 mechanism - CBM-IV - CB05 - RACM - MELCHIOR2
			200µg/m ³ 18 th highest hourly average in a year (99.78 percentile)	-	40µg/m ³	
			Lower assessment threshold			
			100µg/m ³ 18 th highest hourly average in a year (99.78 percentile)	-	26µg/m ³	
Upper assessment threshold						
			140µg/m ³ 18 th highest hourly average in a year (99.78 percentile)	-	32µg/m ³	

Jurisdiction		Reference	Criteria			Methods
Country	State		1-hr average	24-hr average	Annual average	
UK		Conversion Ratios for NO _x and NO ₂ (AQMAU, 2015) The Air Quality Standards Regulations 2010 The Air Quality (England) Regulations 2000 Review of methods for NO to NO ₂ conversion in plumes at short ranges (UK Environment Agency, 2007)	National UK Standard			Only appropriate for combustion processes where no more than 10% of NO _x is emitted as NO ₂ . <ul style="list-style-type: none"> • Screening/worst case scenario: 50% and 100% of modelled values should be used for short-term and long-term average concentration respectively • Worst case scenario: 35% for short-term and 70% for long-term average concentration • Case specific scenario: use of percentages lower than the worst case scenario should be justified. <ul style="list-style-type: none"> - The validity of an “ozone-limiting” procedure for assessment of likely maximum conversion of NO_x to NO₂ should be assessed on a case-by-case basis - Ozone photochemistry algorithms used in some models must have valid inputs of ozone concentrations, sunlight, etc.
			287µg/m ³	-	-	
			UK Air Quality Strategy Objective			
			200µg/m ³ not to be exceeded more than 18 times in a calendar year	-	40µg/m ³	
			Critical level for the protection of vegetation			
-	-	30µg/m ³ NO _x				
India		National Ambient Air Quality Standards (Central Pollution Control Board, 1994) National Ambient Air Quality Standards (Central Pollution Control Board, 1998)	Industrial area			Unable to find specific reference to recommended approach.
			-	120g/m ³ NO _x	80g/m ³ NO _x	
			Residential, rural and others			
			-	80g/m ³ NO _x	60g/m ³ NO _x	
			Sensitive areas			
			-	30g/m ³ NO _x	15g/m ³ NO _x	
			Industrial, residential, rural and others			
-	80µg/m ³	40µg/m ³				
South Africa		National Ambient Air Quality Standards (2009) National Regulations Regarding Air Dispersion Modelling (2014)	Ecologically sensitive area			<ul style="list-style-type: none"> • Tier 1: Total Conversion Method • Tier 2: ARM with the ratio of 0.8
			-	80µg/m ³	30µg/m ³	
			200µg/m ³ with 88 allowable exceedances		40µg/m ³	

Jurisdiction		Reference	Criteria			Methods
Country	State		1-hr average	24-hr average	Annual average	
Japan		Air Pollution Control Technology Manual (Overseas Environmental Cooperation Center, 1998)	-	Within the 0.04-0.06ppm zone or below.	-	<p>Exponential function model</p> $\frac{NO_2}{NO_x} = 1 - \frac{a}{1+b} (\exp(-kt) + b)$ <p>k = 0.0062UO_{3B} (stationary sources, vessels) or k = 0.208UO_{3B} (automobiles, houses) b = 0.3 a = 0.9 Here, t is time, U is velocity and O_{3B} is concentration of Ozone.</p> <p>Statistical model</p> $NO_2 = a[NO_x]b$ <p>Where a and b are determined using observed data.</p> <p>The exponential function is generally used in estimating NO₂ impacts from stationary sources and the statistical model is used for automobile influences.</p>
Australia	QLD	Environmental Protection (Air) Policy 2008	Health and wellbeing			Indicates reference to NSW EPA Guidelines.
			250µg/m ³ with allowable exceedance of 1 day per year	-	62µg/m ³	
			Health and biodiversity of ecosystems			
			-	-	33µg/m ³	
Australia	SA	EPA Guidelines - Air quality impact assessment using design ground level pollutant concentrations (DGLCs) (SA EPA, 2006)	In Adelaide metro areas			Unable to find specific reference to recommended approach.
			0.113mg/m ³	-	-	
			Outside Adelaide metro areas			
			0.158mg/m ³	-	-	

Jurisdiction		Reference	Criteria			Methods
Country	State		1-hr average	24-hr average	Annual average	
Australia	VIC	Guidance notes for using the regulatory air pollution model AERMOD in Victoria (VIC EPA, 2013) State Environment Protection Policy (Ambient Air Quality) (1999) State Environment Protection Policy (Air Quality Management) (2001)	Environmental quality objectives and goal			OLM and PVMRM option to be used with specific approval by EPA VIC
			0.12ppm maximum allowable exceedance of 1 day per year	-	0.03ppm	
			Design criteria			
			0.29mg/m ³ (0.1ppm)	-	-	
NZ		Good Practice Guide for Assessing Discharges to Air from Industry (NZ Ministry for the Environment, 2008a) Good Practice Guide for Assessing Discharges to Air from Land Transport (NZ Ministry for the Environment, 2008b) Good Practice Guide for Atmospheric Dispersion Modelling (NZ Ministry for the Environment, 2004)	National ambient air quality standards			From Industry <ul style="list-style-type: none"> Total Conversion Method OLM From Land Transport $Max\ 1hr\ NO_x = 0.325 \exp(-0.3d^{0.5}) \times N \times EF$ d = distance from roadside in metres N = number of vehicles in 1 hour (peak) EF = NO _x emission factor in g/km $Max\ 1hr\ NO_2 = NO_x \times C$ C = conversion factor from NO _x to NO ₂ Assumed to be 20% $24hr\ NO_2 = 0.325 \exp(-0.3d^{0.5}) \times (N/24) \times EF \times C \times 0.5$ d = distance from roadside in metres N = number of vehicles in 24 hours (high traffic day) EF = NO _x emission factor in g/km C = NO _x to NO ₂ conversion factor, 0.2
			200µg/m ³ with 9 allowable exceedances per year	-	-	
			Critical levels for protecting ecosystems			
			-	-	30µg/m ³	

Jurisdiction		Reference	Criteria			Methods
Country	State		1-hr average	24-hr average	Annual average	
US		<p>Revision to the Guideline on Air Quality Models: Adoption of a Preferred General Purpose (Flat and Complex Terrain) Dispersion Model and Other Revisions; Final Rule (US EPA, 2005)</p> <p>Applicability of Appendix W Modeling Guidance for the 1hr NO₂ National Ambient Air Quality Standard (US EPA, 2010a)</p> <p>Guidance Concerning the Implementation of the 1hr NO₂ NAAQS for the Prevention of Significant Deterioration Program (US EPA, 2010b)</p> <p>Additional Clarification Regarding Application of Appendix W Modeling Guidance for the 1hr NO₂ National Ambient Air Quality Standard (US EPA, 2011)</p>	100ppb 98 th percentile averaged over 3 years	-	53 ppb	<ul style="list-style-type: none"> • Tier 1 – Total Conversion • Tier 2 – ARM <ul style="list-style-type: none"> - use 0.80 default hourly ambient ratio without justification - use of 0.75 as annual national default ratio • Tier 3 – detailed screening method on a case-by-case basis requiring justification and approval by the Regional Office. <ul style="list-style-type: none"> -ISR of 0.50 for input to the PVMRM and OLM options within AERMOD in the absence of source specific info -Use of OLMGROUP ALL to apply combined plume scenarios in OLM calculations.
US	Colorado	FAQs on Air Quality Modeling Data and Techniques (Colorado Department of Public Health and Environment, 2015)	Federal Standard			<p>Use EPA's Tier 1</p> <ul style="list-style-type: none"> • If impacts are high, use Tier 3 (OLM)
US	Iowa	Air Dispersion Modeling Guidelines for Non-PSD, Pre-Construction Permit Applications (Iowa Department of Natural Resources Environmental Services Division, 2014)	Federal Standard			<p>Use of EPA's 3-tiered approach:</p> <p>Source-specific ISR should be used. If absent, default ISR of 0.50 may be used</p>

Jurisdiction		Reference	Criteria			Methods
Country	State		1-hr average	24-hr average	Annual average	
US	California	Modeling Compliance of The Federal 1-Hour NO ₂ NAAQS (CAPCOA, 2011) Nitrogen Dioxide – Overview (CARB, 2011)	California Standard			Use US EPA guidance (3-tiered approach) <ol style="list-style-type: none"> 1. Significant Impact Level (SIL) 2. Max Modeled + Max Monitor Value 3. Max Modeled + 98th Monitor value 4. 8th Highest Modeled + Max Monitor Value 5. 8th Highest Modeled + 98th Monitor Value 6. 5yr ave of the 98th percentile + Max Monitor Value 7. 5yr ave of the 98th percentile + 98th monitor value 8. 5yr ave of the 98th percentile + monthly hour-of-day (1st highest) 9. 5yr ave of the 98th percentile + Seasonal hour-of-day (3rd highest) 10. 5yr ave of the 98th percentile + Annual Hour-of-Day (8th Highest) 11. Paired-Sum (5yr Ave of the 98th percentile)
			0.18ppm	-	0.030ppm	
US	New York	NYSDEC Guidelines on Dispersion Modeling Procedures for Air Quality Impact Analysis (NYS DEC, 2006)	Federal Standard			Screening methods <ol style="list-style-type: none"> 1. Gaussian model with total conversion of NO_x to NO₂ 2. ARM using default of 0.75 ratio or site-specific ratio Refined method - Case-by-case analysis
US	Ohio	Engineering Guide #69: Air Dispersion Modeling Guidance (Ohio EPA, 2014)	Federal Standards			Refers to US EPA's guidelines
			Ohio EPA Generally Acceptable Incremental Impact			
			188µg/m ³	-	12.5µg/m ³	
US	Rhode Island	Rhode Island Air Dispersion Modeling Guidelines for Stationary Sources (Rhode Island Department of Environmental Management, 2013)	Federal Standards			US EPA approach
US	Texas	Air Quality Modeling Guidelines (Texas Commission on Environmental Quality, 2014)	Federal Standards			US EPA Approach

5.3 Description of methods for NO₂ assessment

5.3.1 Total Conversion Method

The Total Conversion Method assumes 100 per cent conversion of NO to NO₂. This is the simplest and most conservative method of evaluating NO₂ impacts from NO_x sources. Due to the conservative nature of the method, no justification is needed for its use and it is often applied as the screening method for the assessment of NO₂ impacts (Level 1 assessment) in various jurisdictions.

5.3.2 Ambient Ratio Method

The Ambient Ratio Method (ARM) uses an NO₂ to NO_x ratio to predict the NO₂ impact from the NO_x concentrations. The principle behind the ARM is that a source plume NO₂ to NO_x ratio will be the same in the long-term as the existing ambient NO₂ to NO_x ratio (OLM/ARM Workgroup, 1998). To determine the NO₂ to NO_x ratio, ambient NO₂ and NO_x data from monitoring stations located away from the source (approximately 15 to 60km downwind) (Hanrahan, 1999a) are needed.

Ambient NO_x monitoring however is not always sufficient to determine the ratio as the ambient concentrations are often below the minimum concentration threshold for NO_x of 20ppb (Hanrahan, 1999a). This is a potential limitation in NSW where hourly NO_x monitoring data would not appear to be publically available (i.e. it may be necessary to report this data if ARM is to be adopted). Further, NO₂ to NO_x ratios should only be determined using NO_x concentration data of at least 20ppb (OLM/ARM Workgroup, 1998 from Chu & Meyer, 1991). The inclusion of NO_x concentration data that are less than 20ppb would introduce *"potentially large errors introduced by small signal to noise ratios typical of current monitoring instrument at low ambient levels of NO_x"* (OLM/ARM Workgroup, 1998 from Chu & Meyer, 1991). This situation may have improved with advancements in monitoring equipment.

As the source plume will only achieve the ambient ratio on a long-term basis, the method has been originally used only for the estimation of the annual average NO₂ concentrations (US EPA, 2005). Chu and Meyer recommended using the daily average concentration during daylight hours to determine the annual average NO₂ and NO_x concentrations (OLM/ARM Workgroup, 1998). Night-time data should not be used to eliminate the low NO₂ bias to get a conservative NO₂ to NO_x ratio (OLM/ARM Workgroup, 1998 from Chu & Meyer, 1991).

The OLM/ARM Workgroup (1998) recommends using the annual average concentrations rather than the average daily average approach by Chu and Meyer as the ARM theory will only be true if the predicted and the observed NO₂ and NO_x concentrations are averaged in the same way.

The US EPA (2011) has recommended a fixed ratio of 0.8 for modelling hourly NO₂ concentrations when applying the ARM, based on ambient NO₂/NO_x ratios from studies by Wang et al (2011) and Jansenn et al (1991).

5.3.3 Ambient Ratio Method 2

The Ambient Ratio Method 2 (ARM2) is a modified version of the ARM. ARM2 is based on observed hourly NO₂/NO_x concentration ratios from a large data set with diverse source-monitor distances, atmospheric ozone concentrations, and atmospheric dispersion conditions (Podrez, 2015). The upper limits of the observed NO₂ to NO_x ratio with the observed NO_x concentration are used to derive the

empirical relationship and are found to perform better than ARM and produce comparable results for more refined 1-hour NO₂ modelling (RTP Environmental Associates, 2013).

Studies show that the NO₂ to NO_x ratio increases with distance from the source, and thus using the ARM method would tend to overestimate the NO₂ predictions near the source (RTP Environmental Associates, 2013).

A variable NO₂ to NO_x ratio with distance would predict a more realistic NO₂ concentration. By plotting the NO₂ to NO_x ratio as a function of the NO_x concentration, it was found to produce a similar relationship to plotting the ratio as a function of the inverse distance (Podrez, 2012).

Thus, the variable ratio has been developed for determining the NO₂ to NO_x ratio as a function of NO_x concentrations. This method removes challenges associated with distance to monitoring stations and the influence of other sources. The ARM2 approach has been incorporated into AERMOD version 14134 (Podrez, 2015).

5.3.4 Ozone Limiting Method

The Ozone Limiting Method (OLM) predicts the NO₂ concentration with the assumption that NO and O₃ react to form NO₂ in proportion to their receptor concentrations (Hanrahan, 1999a). It assumes total conversion of either NO or O₃, whichever is limiting, based on the receptor NO and O₃ concentrations. It requires an in-stack NO₂ concentration contribution to be added to the NO₂ concentration formed by reaction with ozone.

OLM neglects the oxidation of NO to NO₂ by oxidants other than ozone and ignores the photodissociation of NO₂ (Cole & Summerhays, 1979). *"The actual reactions occur in proportion to the moles of each reactant rather than in proportion to concentration"* which would make OLM theoretically valid if the reaction occurs in a closed system (Hanrahan, 1999a). However, as the atmosphere is an open system, there is practically an unlimited amount of O₃ available for reaction and some of the NO would have been converted to NO₂ as the plume travels to the receptor (Hanrahan, 1999a).

The US EPA limits the use of OLM to a single plume at a time unless the plumes overlap (US EPA, 2010).

5.3.5 Plume Volume Molar Ratio Method

The Plume Volume Molar Ratio Method (PVMRM) addresses some of the limitations of the OLM. PVMRM takes into account the expansion of the plume and the reaction of NO with O₃ as the plume expands downwind by "computing the number of moles of NO_x and O₃ that are contained within a plume segment as it reaches a receptor" (Hanrahan, 1999a). In a plume segment, the amount of primary NO_x remains the same as it travels downwind but the amount of O₃ increases as the segment expands downwind (Hanrahan, 1999a).

PVMRM has been found to predict close to the measured values while still being conservative (Hanrahan, 1999a and 1999b).

5.3.6 RIVAD/ARM3 in CALPUFF

The Acid Rain Mountain Mesoscale Model (ARM3) predicts acid deposition and air quality impacts with chemical transformation in complex terrain at mesoscale distances (Morris et al, 1989). ARM3 was found to perform as good as, or even better than, other mesoscale models in terms of transport or dispersion.

However its chemical transformation and deposition component has not been evaluated (Moore et al, 1990). RIVAD is one of the chemical transformation schemes available in the ARM3.

The RIVAD is a condensed pseudo-first-order chemical scheme available in CALPUFF as prepared for the ARM3 (Earth Tech, 2000). The scheme assumes a low VOC background concentration and is thus not suitable for urban areas (Earth Tech, 2000). The scheme includes solving the pseudo-steady-state concentrations of NO, NO₂ and O₃ from the photolysis of NO₂ to NO and O₃ and the reaction of NO and O₃ to NO₂ (Atmospheric and Environmental Research, 2008). In the revised RIVAD/ARM3 scheme of CALPUFF, the puff O₃ concentration is consumed by the oxidation of NO and is replenished by the background O₃ concentration (Atmospheric and Environmental Research, 2008).

Thus, the puff O₃ concentration is the average, weighted by the change in the puff volume, of the puff O₃ concentration for the previous time step and the background concentration (Atmospheric and Environmental Research, 2008). The original RIVAD/ARM3 scheme in CALPUFF does not take into account the depletion of O₃ in the plume and has still been retained as an option in CALPUFF as MCHM=3, while the revised RIVAD/ARM3 scheme is a new option as MCHM=5 (Atmospheric and Environmental Research, 2008). The difference in the results of the original and revised RIVAD/ARM3 was not significant in the case studies for which they were evaluated (Atmospheric and Environmental Research, 2008).

5.3.7 Discrete Parcel Method in CALINE4

The Discrete Parcel Method predicts the NO₂ impacts by assuming that the oxidation and dissociation of NO_x occurs in isolated discrete parcels of mixed reactants (Benson, 1989). The method assumes that the reactants are initially fully mixed within the mixing zone, the initial NO_x emissions are composed of 92.5 per cent NO and 7.5 per cent NO₂ by mass, and that the parcels of reactants are isolated for a certain time/distance before molecular diffusion takes place (Benson, 1989). Plume travel times are not long enough for diffusion to significantly take place in the discrete parcels for most of the microscale modelling applications (Benson, 1989).

As the reactions in the parcels occur independently from their dispersion, the time-averaged NO₂ concentrations are computed in CALINE4 by adjusting the initial NO₂ emission to be equal to the discrete parcel NO₂ concentration after time t for each element-receptor combination and then computes the time-averaged NO₂ concentration as with non-reactive species (Benson, 1989).

A study by Wang et al (2011) has found that CALINE4 predicts the NO_x profiles well but under predicts NO₂ concentrations at high wind speed. Also the initial emission of 5 per cent NO₂ by volume (or 7.5 per cent by mass) is not likely to be appropriate for most roadways (Wang et al, 2011). Another study by Levitin et al (2005) has found that CALINE4 predicts NO_x and NO₂ well and performs similarly to CAR-FMI. However the performance of either model deteriorates with decreasing wind speed and as the wind direction approaches a direction parallel to the road.

5.3.8 Methodologies developed for DEFRA

Empirical methods for calculating the NO₂ concentrations from the NO_x concentrations for the roadside have been developed in the UK. Derwent and Middleton (1996) developed an empirical relationship between hourly NO₂ and NO_x from monitoring data for a kerbside site in London (UK Environment Agency, 2007). The Derwent-Middleton curve has been used by a number of local authorities, as part

of the Aeolius street canyon model and in the ADMS model (UK Environment Agency, 2007). The Derwent-Middleton curve follows the equation (UK Environment Agency, 2007):

$$[NO_2] = 2.166 - [NO_x](1.236 - 3.348A_{10} + 1.933A_{10}^2 - 0.326A_{10}^3)$$

Where $A_{10} = \log_{10}([NO_x])$

Another study examined the relationship between NO_2 and NO_x concentrations (Dixon et al as cited in UK Environment Agency, 2007). The study uses a larger dataset of 12 study sites over 7 consecutive years of data (UK Environment Agency, 2007). The Dixon-Middleton-Derwent curve follows the equation (UK Environment Agency, 2007):

$$Y_2 = A + BA_{10} + CA_{10}^2 + DA_{10}^3 + EA_{10}^4$$

Where $Y_2 = [NO_2]/[NO_x]$ and A, B, C, D and E are published constants.

Laxen and Wilson used more stations and years in the dataset and provided a simpler relationship for the annual average NO_2 from NO_x measurements which is as follows (ETC/ACM, 2011):

$$[NO_2(road)] = (-0.068 \log([NO_x(total)]) + 0.53)[NO_x(road)]$$

Where $[NO_x(total)] = [NO_x(road)] + [NO_x(background)]$

5.3.9 Airviro

Airviro developed the following relationship to determined NO_2 concentrations from NO_x concentrations (ETC/ACM, 2011). The formula is based on the existence of a statistical relation between the NO_2/NO_x ratio to the absolute NO_x level, in that the ratio normally is higher for low NO_x concentration values.

$$[NO_2] = 0.73[NO_x]\exp(-0.00452[NO_x] + 0.003014[NO_x]^2)$$

5.3.10 Romberg Method

The Romberg method has been used in Germany within a number of models such as PROKAS, IMMIS and MISKAM and has the following relationship (ETC/ACM, 2011):

$$[NO_2] = \frac{A[NO_x]}{[NO_x] + B} + C[NO_x]$$

Where A, B and C are constants determined from monitoring data.

The parameters of the Romberg method were updated by Bächlin et al. using more recent NO_2 and NO_x monitoring data (Düring et al, 2011).

5.3.11 Standard Calculation Method in the Netherlands

An empirical relation for the calculation of NO_2 contributions from traffic emissions was developed and refined in the Netherlands. It is presently used in many Dutch legislated models as part of the "Standard Calculation Method (SCM)" applied in the Netherlands which is as follows (ETC/ACM, 2011):

$$\overline{\Delta NO_2} = F \cdot \overline{\Delta NO_x} + \beta \cdot \overline{O_3^a} \cdot \frac{(1 - F) \cdot \overline{\Delta NO_x}}{(1 - F) \cdot \overline{\Delta NO_x} + K}$$

Where $\overline{\Delta NO_x}$ is the average NO_x concentration contribution, $\overline{\Delta NO_2}$ is the average NO₂ concentration contribution, and F is the NO₂ to NO_x emission ratio.

For the annual average calculations in urban areas, K=100 and β=0.6. The results using the equation for the urban environment were found to agree well with measured concentrations (Wesseling and Sauter as cited in ETC/ACM, 2011) and with OSPM calculations (Nguyen and Wesseling, 2008).

In Dutch street canyons, β varies from 0.6 to 0.9 (ETC/ACM, 2011). For the annual average concentrations around open roads, β=0.1 and the concentration contribution is determined in 12 wind sectors and weighted averaged appropriately (ETC/ACM, 2011).

For hourly average concentrations for both urban street and open roads, β=0.1 (ETC/ACM, 2011). Results were found to agree with measured concentrations along roads although the calculated contributions tend to overestimate by approximately 5 per cent close to the road and underestimate by approximately 15 per cent far from the road (ETC/ACM, 2011). The value of K was found to be dependent on the road distance (ETC/ACM, 2011).

5.3.12 SAPPHO

A basic photochemical steady-state solution for NO₂ is as follows (ETC/ACM, 2011):

$$f_{NO_2}^2 - f_{NO_2}(1 + f_{O_x} + J') + f_{O_x} = 0$$

Where

$$f_{NO_2} = \frac{[NO_2]}{[NO_x]}, \quad f_{O_x} = \frac{[O_x]}{[NO_x]} \quad \text{and} \quad J' = \frac{J}{k_1[NO_x]}$$

This has a solution of the form

$$f_{NO_2} = \frac{(1 + f_{O_x} + J') - \sqrt{(1 + f_{O_x} + J')^2 - 4f_{O_x}}}{2}$$

An algorithm (SAPPHO) based on the above equation was presented in the Fifth National Environmental Report from RIVM but the factor J' and [O_x] have been determined from 8 years of annual average measurements in the Netherlands and are as follows (Erens and van Dam as cited in ETC/ACM, 2011):

$$J' = 0.27[NO_x] + 4.5$$

$$[O_x] = 1.3\sqrt{[NO_x]} + 27.4$$

5.3.13 Keller

An empirical formula for calculating NO₂ concentrations was also presented in the same report (Erens and van Dam as cited in ETC/ACM, 2011). Although its performance is considered satisfactory in Switzerland, it performs poorly in the Netherlands (ETC/ACM, 2011).

$$[NO_2] = 0.055[NO_x] + 55(1 - \exp(-(0.7 - 0.055)[NO_x]/55))$$

5.3.14 Oxidant Partitioning Model

Jenkin developed an empirical equation for the prediction of NO_2 by taking into consideration NO , NO_2 and O_3 as a set of chemically coupled species (ETC/ACM, 2011). The following is the empirical relationship used by Jenkin.

$$[\text{NO}_2] = (A[\text{NO}_x] + B) \cdot f(\text{NO}_x)$$

Where A is an empirical and site specific parameter representing the local oxidant contribution, B is the regional oxidant concentration and the function $f(\text{NO}_x)$ is the empirically fitted $\text{NO}_2:\text{O}_x$ ratio (ETC/ACM, 2011).

5.3.15 Limited mixing steady state approach applied to annual averages

Düring et al. (2011) has found that the equation used in the Operational Street Pollution Model (OSPM), as shown below, could predict the NO_2 concentrations well over the long term.

$$[\text{NO}_2] = 0.5(B - \sqrt{B^2 - 4([\text{NO}_x][\text{NO}_2]_o + [\text{NO}_2]_n/k\tau)})$$

With the variables

$$[\text{NO}_2]_n = [\text{NO}_2]_V + [\text{NO}_2]_B$$

$$[\text{NO}_2]_o = [\text{NO}_2]_n + [\text{O}_3]_B$$

$$B = [\text{NO}_x] + [\text{NO}_2]_o + \frac{1}{k} \left(J + \frac{1}{\tau} \right)$$

The J and k parameters in the above equation are dependent on meteorological parameters and can only be used in time series calculations (Düring et al, 2011).

Studies by BAST (Bundesanstalt für Straßenwesen) (Düring et al as cited in Düring et al, 2011) and the Landesumweltamt Brandenburg (Düring and Bächlin as cited in Düring et al, 2011) suggest that the equation can also be used for annual mean concentrations with the following parameters:

$$J = 0.0045 \text{ s}^{-1}$$

$$k = 0.00039 \text{ (ppb s)}^{-1}$$

$$\tau = 100 \text{ s (street canyons) or } 40 \text{ s (free dispersion)}$$

5.3.16 Janssen et al (1988)

Janssen et al (1988) proposed the relationship to describe the conversion of NO to NO_2 :

$$\text{NO}_2/\text{NO}_x = A(1 - \exp(-\alpha x))$$

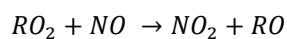
Where x is the distance from the source and A and α are parameters based on ozone concentration, wind speed and season of the year. Janssen et al (1988) determined the value of the parameters by collecting monitoring data using an aircraft at distances between 0.5 and 30km downwind of a number of power plants in the Netherlands.

5.3.17 Photochemistry models

Some of the available photochemistry models include the following schemes:

-
- ✦ Generic Reaction Set (GRS)
 - ✦ EMEP
 - ✦ SAPRC99 and SARPC07 mechanism
 - ✦ Carbon Bond-IV (CBM-IV)
 - ✦ CB05
 - ✦ RACM
 - ✦ MELCHIOR2

GRS is a relatively simple scheme which considers hydrocarbons as a single lumped term to generate a pool of radicals which enhance the oxidation of NO to NO₂ and increase in O₃ through photolysis (see equation below) (ETC/ACM, 2011). GRS is applied in TAPM and ADMS (ETC/ACM, 2011).



The other photochemistry models are based on a similar mechanism to GRS and are considered more 'complete' as the *"lumping of hydrocarbons is often carried out differently"* (ETC/ACM, 2011). The limitation of the photochemical schemes is that they do not describe near source reactions well as the emissions are often instantaneously diluted into the model grid volume (ETC/ACM, 2011).

Detailed examination of the available photochemical models is not part of the scope of this study.

6 ADVANTAGES AND DISADVANTAGES OF METHODS FOR NO₂ ASSESSMENT

Table 6-1: Summary of advantages and disadvantages of NO₂ assessment methods

Methods	Advantages	Disadvantages	Information requirements*
Total Conversion Method	Simple operation, unlikely to underestimate impact	Overestimates likely impact significantly.	None
Ambient Ratio Method (ARM)	Simple operation	Only applicable for localities with the required ambient monitoring data necessary to determine the NO ₂ /NO _x ratio.	Ambient NO ₂ and NO _x monitoring data from a suitable monitoring location to determine appropriate NO ₂ /NO _x ratio.
Ambient Ratio Method 2 (ARM 2)	Simple operation Programmed into AERMOD	Based on US monitoring data of NO ₂ and NO _x . Ratio may not be representative of jurisdictions outside the US. US EPA's ARM2 parameters have only been tested on sources with relatively low ISR (0.1-0.2) and typical ozone concentrations and thus may not be applicable with sources of higher ISR's and locations of higher ozone levels (Podrez, 2015).	Variable NO ₂ /NO _x ratio based on US monitoring data set.
Plume Volume Molar Ratio Method	Can simulate multiple industrial plumes Ambient NO _x monitoring is not required Programmed into AERMOD	Requires an initial in-stack NO ₂ /NO _x ratio. Requires ambient ozone concentrations. Not recommended in estimating NO ₂ from motor vehicle exhaust plumes due to potential for rapid oxidation.	Initial in-stack NO ₂ /NO _x ratio. Ambient ozone concentrations.
Ozone Limiting Method	Simple operation	Requires ambient ozone concentrations.	Initial in-stack NO ₂ /NO _x ratio. Ambient ozone concentrations.
RIVAD/ARM3	Incorporated into CALPUFF	Assumes low background VOCs making it suited for relatively clear non-urban areas. Requires knowledge of background concentrations of ozone and ammonia. Requires both NO and NO ₂ emission rates.	NO and NO ₂ emission rates (Initial in-stack NO ₂ /NO _x ratio). Ambient ozone concentrations. Ammonia concentrations.
Discrete Parcel Method	Incorporated in CALINE4 Computes NO ₂ concentrations without the need for an external background concentration file Capable of predicting NO _x concentrations. Suitable for road emissions	Only for roads. Under predicts NO ₂ concentrations under high wind velocity. Assumes initial NO _x emissions composing of 92.5% NO and 7.5% NO ₂ by mass.	Ambient ozone concentrations.

Methods	Advantages	Disadvantages	Information requirements*
Methodologies developed for DEFRA (UK)	Simple operation Suitable for road emissions	Only for roads. May not be representative of jurisdictions outside the UK.	NO ₂ and NO _x monitoring data to develop the empirical relationship.
Airviro (SE)	Simple operation	Algorithm may not be representative of jurisdictions outside Sweden.	None
Romberg Method (DE)	Simple operation Incorporated in models such as PROKAS, IMMIS and MISKAM	May not be representative of jurisdictions outside Germany. Requires NO ₂ and NO _x monitoring data. Requires ambient ozone concentrations.	NO ₂ , NO _x and ozone monitoring data required in derivation.
Standard Calculation Method in the Netherlands (NL)	Simple operation	May not be representative of jurisdictions outside Netherlands. Applicable for only road applications. Tends to overestimate by approximately 5 per cent close to the road and underestimates by approximately 15 per cent away from the road.	Initial NO ₂ to NO _x emission ratio. Ambient ozone concentrations .
SAPPHO (NL)	Simple operation	May not be representative of jurisdictions outside Netherlands.	None (in Netherlands)
Keller (CH)	Simple operation	May not be representative of jurisdictions outside Switzerland.	None (in Switzerland)
Oxidant Partitioning Model (UK)	Considers inter-relationships between NO, NO ₂ and ozone Considers source distance	May not be representative of jurisdictions outside UK. Applicable only to annual average concentrations.	Ambient ozone concentrations.
Limited mixing steady state approach applied to annual averages (DE)		May not be representative of jurisdictions outside Germany. Applicable only to annual average concentrations or in time series calculations. Determination of constants for time series calculations can be cumbersome Applicable for only road applications. Requires traffic station and background station monitoring data.	NO ₂ , NO _x and O ₃ monitoring data. Meteorological monitoring data.
Janssen et al (1988)	Simple operation	Assumes constant ozone and uses an empirical fit. Based on empirical data from power plant emissions in the Netherlands.	Ozone concentration, wind speed and season of the year. NO ₂ and NO _x concentrations to verify relationship and constant parameters. Distance from the source of receptor of interest.
Photochemistry models	Computer model based application	Costly, require specialist to operate, may take a long time to run.	Highly variable, depending on the approach.

* It is assumed that basic information needed to describe or quantify the emissions and to model their dispersion in the ambient air is available.

7 COMPARISON OF THE ASSESSMENT METHODS FOR USE IN NSW

Table 7-1 presents the summary weighting scales applied in the quantitative evaluation of the NO₂ assessment methods.

Table 7-2 to **Table 7-3** present an evaluation of each of the potential NO₂ assessment methods based on the following key factors:

- Simplicity, meaning the ease of correct use of the method, including by those with limited specialists skills;
- Data requirements, meaning the nature of the data necessary to operate the method, it's likely availability, costs and time needed to obtain the data;
- Conservatism/ accuracy, meaning the potential scale of any inherent overestimation of the likely actual impacts. Generally there is a trade-off between the simplicity and data requirements of a method and its conservatism/ accuracy; and,
- Applicability in NSW, an estimate of whether the approach would suit the typical situations encountered in NSW. This has been considered for urban areas, rural areas and other uses. As the other uses are generally outside of EPA's purview, no weighting has been applied, but the suitability of the method for wider application is indicated with a tick. The applicability of the methods are determined in the context of emission sector, release type and local environmental conditions in regard to how the methods are developed or would be adjusted for NSW. Methods for on-road sources of NO₂ are evaluated in a separate table.

Based on the methods' assumptions, its approach and calculation procedures and the similarity (or not) between NSW and the localities for which the methods were developed, the likely applicability and conservatism of the method in NSW was estimated, as shown in the weightings applied in **Table 7-2** and **Table 7-3**.

However, it is not possible within the scope of work for this study to precisely determine the actual conservatism/ accuracy and applicability in NSW of the majority of the methods. Many of the methods are developed for specific applications in specific locations outside NSW, thus there are no available data (e.g. cases of the model use in NSW) to determine whether these methods would be appropriate and accurate if used in NSW. Thus, such methods are presented in the tables but are not given a numerical evaluation based on their predictions (conservatism/ accuracy) and applicability in NSW.

The scale for conservatism/ accuracy is non-linear. Assuming accuracy increases on the vertical axis, and conservatism (overestimation increases on the horizontal axis, the relationship is assumed to be a hump shape, with maximum accuracy/ conservatism rating of four at the peak of the hump, and lower ratings lower down either side of the hump. A rating of 1 applies to either end of the base of the hump).

Table 7-1: Summary of weighting scales used to evaluate the various NO₂ assessment methods

Simplicity	Data requirements	Conservatism/accuracy	Applicability i. emission sector ii. release type iii. environmental conditions
1 Very complex 2 Complex 3 Neutral 4 Easy 5 Very easy	1 High 2 Medium 3 Low 4 None beyond minimum	1 Very over or very under conservative and inaccurate 2 Over or under conservative and moderately accuracy 3 Somewhat conservative and accurate 4 Ideally conservative and very accurate	1 Not applicable 2 Applicable in one of three 3 Applicable in two of the three 4 Applicable in all three

Table 7-2: Evaluation of assessment methods for generally all applications

Methods	Simplicity	Data requirement	Conservatism/accuracy	Applicability in NSW (8)			Total (22)
				Urban	Rural	Other uses (e.g. roads)	
Total Conversion Method	5	4	1	4	4	✓	18
Ozone Limiting Method	4	3	2	4	3	✓	16
Janssen et al (1988)	3	4	3	3	4	-	17
Ambient Ratio Method (ARM)	5	4	2	4	3	✓	18
Ambient Ratio Method 2	4	4	3	4	4	✓	19
Plume Volume Molar Ratio Method	2	3	4	4	4	✓	17
RIVAD/ARM3/ISORROPIA	1	3	-	-	-	-	4
Japan's exponential function method	2	2	-	-	-	-	4
SAPPHO	3	4	-	-	-	✓	7

* Most of these methods were developed for their specific jurisdictions. Each method needs to be tested to determine how it performs in terms of accuracy and conservatism in different applications in NSW. The parameters of the method may also need to be adjusted to reflect the conditions of NSW or specific region/locality of NSW to where it would be used.

Table 7-3: Evaluation of assessment methods for on-road sources

Methods	Simplicity	Data requirements	Conservatism/accuracy	Applicability in NSW	Total (18)
Discrete Parcel Method	1	3	3	3	10
Japan's statistical model	4	4	-	-	8
Methodologies developed for DEFRA (UK)	4	4	-	-	8
Airviro (SE)	4	5	-	-	9
Romberg Method (DE)	4	3	-	-	7
Standard Calculation Method in the Netherlands (NL)	3	2	-	-	5
SAPPHO (NL)	3	5	-	-	8
Keller (CH)	4	5	-	-	9
Oxidant Partitioning Model (UK)	4	3	-	-	7

* Most of these methods were developed for their specific jurisdictions. Each method needs to be tested to determine how it performs in terms of accuracy and conservatism in different applications in NSW. The parameters of the method may also need to be adjusted to reflect the conditions of NSW or specific region/locality of NSW to where it would be used.

8 DISCUSSION AND RECOMMENDATIONS

The study has identified that the majority of the approaches in use around the world have been developed empirically on the basis of observed data in a particular locality, and are suitable for application in those localities, or in areas with similar air quality. For example, the relationship and parameters of the SAPPHO algorithm have been developed using eight years of observed annual average data in the Netherlands. The empirical relationships and parameters in the method are applicable for determining the NO₂ concentrations in the Netherlands but may not perhaps ideally represent the potential NO₂ impacts arising in other locations.

Extensive modelling and assessment validation beyond the scope of this study would be necessary to test the applicability and accuracy of many of the methods identified in the report.

There appears to be some shift over time in the most impacted locations in Sydney (following the focus of traffic and industry further west). Hence it is important to note that many of the empirical methods may also only be applicable in those periods when the observed data were collected. Other conditions that affect the chemical reaction of NO_x may also change over time, such as changes in background ozone concentration and new technologies fitted to NO_x sources causing a change in the NO₂/NO_x ratio and NO_x emission concentration.

As the majority of the NO₂ in the urban air shed is from motor vehicle emissions, most of the approaches of NO₂ assessment are specific to roadside applications. The methods are predominantly empirical and different countries use different relationships developed specifically for their own situation.

These methods should be tested prior to formally sanctioning their application outside of the jurisdictions. For example, the Keller method which performs satisfactorily in Switzerland has been tested in Netherlands by Erens and van Dam and was found to not perform as well (ETC/ACM, 2011).

The methods that can be applied in NSW with an appropriate degree of confidence are those in the tables in **Section 7** where we have provided a complete evaluation of all of the criteria.

8.1 Methods for general applications

The methods recommended for further consideration for general application in NSW, in order of priority, are as follows:

1. Ambient Ratio Method 2 (ARM2)
2. Total Conversion Method
3. Ambient Ratio Method (ARM)
4. Janssen method
5. Plume Volume Molar Ratio Method (PVMRM)
6. Ozone Limiting Method (OLM)

Using the NO₂ and NO_x monitoring data from the NSW Office of Environment and Heritage (OEH) monitoring network over the most recent period of at least ten years is recommended to determine the

appropriate ARM ratio and ARM2 relationship. The development of the appropriate ARM ratio and ARM2 relationship could follow the method used for their development in the US. One ARM ratio and ARM2 relationship can be determined for the whole state of NSW. Alternatively, an ARM ratio and ARM2 relationship for each region (Sydney/Illawarra/etc. or urban/rural) can be developed and applied in the respective regions.

The use of a single ARM ratio and single ARM2 relationship across the whole state of NSW would require an ARM ratio and ARM2 relationship that would be conservative enough to use in all regions, but whilst this would reduce complexity, it may reduce accuracy.

The ARM and ARM2 relationship can be incorporated in current modelling applications which allow users to modify the source codes. ARM2 values specific for US applications are now incorporated in AERMOD (Podrez, 2015).

Since air quality impacts are of most concern in the most populated areas, these areas generally have air quality monitoring data available. Currently, NSW OEH NO₂/NO_x monitors are located in the Sydney, Illawarra, Lower Hunter, Upper Hunter and Central Coast regions. As the air quality differs across the state, it would be more accurate to have an ARM ratio and ARM2 relationship that would differ among the various regions.

To use the OLM and PVMRM methods, O₃ concentration data are needed. Currently, NSW OEH O₃ monitors are located in the Sydney, Illawarra, Lower Hunter and Central Coast regions. The assessors are to justify their use of their chosen O₃ concentration data. A conservative fixed O₃ concentration and/or a conservative hourly O₃ concentration for an entire year is recommended to be developed for applications in NSW to be applied in areas where no representative O₃ data are available.

A conservative fixed O₃ concentration could be set at some percentile of the available O₃ monitoring data across NSW or regions in NSW that would be representative of the maximum O₃ concentration across the state or the specific region in the absence of abnormal conditions. The conservative hourly O₃ concentration for an entire year could be set at a maximum hourly O₃ concentrations based on monitoring data but excluding measurements that may have been caused by abnormal events.

In-stack ratios (ISRs) are also required for the OLM and PVMRM. ISR values should be derived from source-specific data. Alternatively, data can be obtained from the literature on similar sources.

The other methods, namely RIVAD/ARM3/ISORROPIA, Japan's exponential function method, SAPHO, and Janssen, require evaluation of their performance in predicting NO₂ impacts in NSW. Some of the constant parameters may also need to be adjusted to make them suitable for NSW applications.

Janssen is a currently approved NO₂ assessment method in NSW. As the Janssen method was developed using data from power stations in Netherlands, the method may only be accurate for the situations from which it was developed (similar to some of the other methods). Evaluation of the method performance and/or refinement of the method for NSW conditions may be warranted to justify its continued use in NSW. The use of the Janssen method or its modified form, when verified for NSW, would be appropriate for application to industries in the GMR.

8.2 Methods for on-road sources

Most of the NO₂ assessment methods for on-road sources are either empirically-derived or have scientific basis with empirically-derived parameters. Each method needs to be evaluated for its performance in predicting NO₂ impacts from NSW roads. The equations may also need to be modified to be suitable for NSW applications. Some of the methods would only allow assessment of NO₂ at longer averaging periods (e.g. annual average).

The Discrete Parcel Method, although not empirically-derived, has some simplified assumptions, and also needs to be evaluated for NSW applications. The initial NO₂/NO_x ratio of the vehicle emissions may also not be appropriate.

The applicable methods listed in **Section 8.1** are recommended to be applied for on-road sources. These methods are more sound, conservative and easier to use.

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