



Net Zero Teesside – Environmental Statement

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Volume III – Appendices

Appendix 8C: Air Quality Assessment of Amine Degradation Products

The Infrastructure Planning (Environmental Impact Assessment) Regulations 2017 (as amended)



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8C Air Quality – Amine Degradation Assessment

8.1 Introduction

Overview

- 8.1.1 An assessment of amine degradation products has been undertaken to determine the potential impact on human health from these species as a result of the emissions from the operational Proposed Development, as summarised in Chapter 8: Air Quality (Environmental Statement (ES) Volume I, Document Reference 6.2).
- 8.1.2 The air quality assessment of emissions of amines from the Proposed Development on human health and the environment has been included in ES Appendix B: Air Quality - Operational Assessment (ES Volume III, Document Reference 6.4). Amines can degrade to form other species, including nitrosamines and nitramines (collectively referred to as N-amines) and some N-amines are potentially carcinogenic, therefore consideration of these species is also required within the air quality assessment; however the assessment of these species is more complex and therefore has been considered separately within this Appendix.
- 8.1.3 The assessment of N-amines includes direct N-amine emissions from the stack, that form as a result of degradation within the carbon capture process, and indirect N-amine emissions that form as a result of the atmospheric degradation following release of amine from the stack. This Technical Appendix has been prepared to describe the assessment of amine degradation products.

8.2 Scope

Carbon Plant Emissions

- 8.2.1 When the Proposed Development is operating with carbon capture, a proprietary amine solvent will be utilised as the scrubbing medium within the carbon capture plant, to remove the CO₂ within the flue gas stream from the Combined Cycle Gas Turbine (CCGT) unit.
- 8.2.2 As with ammonia in the Selective Catalytic Reduction (SCR) process for NO_x reduction from the CCGT flue gas, 'amine slip' can occur during the carbon capture process, resulting in direct emission of amines from the Capture plant stack.
- 8.2.3 The proprietary amine solvent used in the carbon capture plant overtime, degrades through, for example, reaction with nitrogen dioxide (NO₂) within the flue gas, resulting in the generation of N-amines. This is minimised through continuous solvent replenishment, monitoring and process control parameters, as described in Chapter 4: Proposed Development (ES Volume I, Document Reference 6.2). Nevertheless, the amine slip emission from the

carbon capture plant is likely to include a small fraction of N-amines, which is considered in the assessment as the ‘direct’ N-amine emission.

- 8.2.4 Potentially of more significance, is the subsequent atmospheric degradation of the amines released from the carbon capture stack. The atmospheric chemistry of amines that react to form N-amines is complex, dependent on ozone and NO₂ concentrations, and with the generation of hydroxyl radical intermediates and other unstable intermediate species in UV light, however the principal mechanisms are understood and many studies have been made of the primary reaction rates and subsequent interactions between degradation products and these atmospheric species. This is considered in the assessment as the ‘indirect’ N-amine emission.
- 8.2.5 This Technical Appendix details the amine chemistry mechanisms likely to occur following release of amines from the carbon capture plant absorber stack, and the specific parameters used for the modelling assessment for N-amines from the Proposed Development.
- 8.2.6 Due to the use of proprietary solvents, the technology licensors will not confirm the specific amines species present in their solvents, due to Commercial Confidentiality issues. This issue is currently being discussed by the Carbon Capture and Storage Association (CCSA), the Environment Agency and The Department of Business, Energy and Industrial Strategy (BEIS), however until resolved, this assessment has been carried out to encompass a number of worst-case assumptions to ensure a conservative assessment, based on the data that has been made available.
- 8.2.7 The assessment has considered the impact of emissions on local air quality, under normal operating conditions, with the Low Carbon Electricity Generating Station operational for 8,760 hours per year. The assessment considers impacts in the year in which the Proposed Development is due to commence operation, 2026.
- 8.2.8 A comparison has been made between predicted model output concentrations, and the proposed Air Quality Assessment Level (AQAL) for N-nitroso-dimethylamine (NDMA), as detailed in Chapter 8: Air Quality (ES Volume I, Document Reference 6.2).

Sources of Information

- 8.2.9 This assessment includes pertinent information from:
- Chapter 4: Proposed Development (ES Volume I, Document Ref. 6.2);
 - Data on emissions to atmosphere from technology licensors;
 - Details on the site layout;
 - Ordnance Survey mapping;
 - Various literature sources for the derivation of reaction rate constants (as detailed throughout the text);
 - Environment Agency “AQMAU recommendations for the regulation of impacts to air quality from amine-based post-combustion carbon capture plant” (Environment Agency, 2020);

- AECOM's memo "Amines Degradation Dispersion Modelling Memo to the Environment Agency" (AECOM, 2021); and
- Meteorological data supplied by ADM Ltd.

8.3 Discussion of Amines and N-Amines

General Amine Information

- 8.3.1 The group of chemicals known as amines are hydrocarbon derivatives of ammonia (NH₃). Primary amines have one hydrogen (H) atom replaced with an organic (hydrocarbon-based) functional group, secondary amines have two H atoms replaced, and tertiary amines have three H atoms replaced.
- 8.3.2 The most widely trialled amine-based solvents for carbon capture are based on monoethanolamine (MEA), a primary amine (or alkanolamine) which features a primary amine functional group and a hydroxyl (OH) group.
- 8.3.3 Carbon capture solvent research has included detailed studies and pilot trials of other amines, such as monomethylamine (MMA), ethanolamine; secondary amine such as dimethylamine (DMA), diethylamine, and tertiary amines trimethylamine and triethanolamine. This has resulted in the development of proprietary solvents that demonstrate improved performance, in terms of carbon capture efficiency, lower energy requirements and reduced emissions as a result of lower volatility. Such amine solvents may include tertiary amines and alkanolamines, and cyclic amines, such as piperazine (Pz).

General N-Amine Information

- 8.3.4 Nitrosamines are nitroso- (-NO) compounds of the original amine. The stability of the N-amines produced through amine degradation varies, for example, primary amines MEA and MMA are not considered to form stable nitrosamines, such that, following formation, the nitrosamine either reverts to the amine radical intermediate or rapidly isomerises (changes structure) and then reacts very quickly with O₂ to form an imine (R-N group) (Neilson, 2011). However, MEA can degrade to the nitrosamine N-Nitrosodiethanolamine (NDELA) via the secondary amine diethylamine (DEA).
- 8.3.5 Secondary amines can form more stable nitrosamines (Neilson, 2011), as can tertiary amines although they are less likely to do so than secondary amines.
- 8.3.6 N-nitroso-dimethylamine (NDMA) is the nitrosamine formed from DMA degradation, and is the most widely studied nitrosamine, due to its toxicity. As such, the proposed AQAL for the assessment of N-amines in the UK has been derived for NDMA.
- 8.3.7 The AQAL for NDMA is to be applied to all N-amines in order to ensure a conservative assessment.

Toxicity of N-amines

- 8.3.8 Many nitrosamines and nitramines are known or potential carcinogens. Whilst there is toxicity data available for a few of the more generally researched substances (e.g. NDMA and NDELA), the environmental toxicity

of many of the other individual compounds is not well understood (SEPA 2015). NDMA is understood to be the most mutagenic of the nitrosamines tested (Wagner et al. 2014).

- 8.3.9 There is less information available on the toxicity of nitramines, which include nitro (-NO₂) compounds of the amine, such as dimethylnitramine (DMNA), however it is generally considered that they are of lower toxicity than nitrosamines. Although they are suspected carcinogens, none are classified as such by the International Agency for Research on Cancer (IARC). Animal carcinogenicity studies have indicated that DMNA is at least 6 times less toxic than NDMA (Gjernes et al. 2013). This paper goes on to state that further quantitative evaluation of relevant nitramines is required to rank them against nitrosamine toxicity, in order that more refined and less conservative assessments, where all N-amines are assumed to be as toxic as the most toxic nitrosamine, can be carried out.
- 8.3.10 The World Health Organisation (WHO 2002) have published a Concise International Chemical Assessment Document on NDMA, which states that laboratory studies have shown that exposure to NDMA results in tumours in all species examined; it is metabolized and does not bioaccumulate.
- 8.3.11 NDMA can be produced during water treatment processes involving chlorination and is also found in low levels in cured meat, fish, beer and tobacco smoke. Recently NDMA gained publicity due to it being found to be present in the pharmaceutical product ranitidine.

N-Amine Emissions from Carbon Capture

Direct N-Amine Emissions

- 8.3.12 The proprietary amine solvent used in the Capture plant is contained and recycled within the plant. Within the process the amine solvent can degrade to N-amines through oxidation, thermal degradation and acid gas/ trace impurity reactions. Losses via the absorber stack can therefore occur through entrainment of the solvent within the exhaust gas.
- 8.3.13 The main cause of degradation of the amine solvent is understood to be thermal degradation and therefore this can be reduced by ensuring that the maximum operating temperature of the re-boiler and stripper in the carbon capture plant is carefully controlled to reduce this.
- 8.3.14 Acid gas reactions can occur due to the other trace pollutant species present in the emission, in particular the NO₂ within the gases present in the exhaust gas from the CCGT plant. High NO₂ concentrations in this exhaust gas increase the rate of amine degradation to N-amines, and therefore the lower the overall NO_x release from the CCGT plant, the less N-amines will be generated by this mechanism.
- 8.3.15 The CCGT plant at the operational Proposed Development is likely to use SCR to remove NO_x from the exhaust gas, prior to it entering the carbon capture plant. Trace levels of other species such as sulphur dioxide SO₂ would be negligible from gas fired plant, and therefore are considered to have negligible effect on degradation of the solvent.
- 8.3.16 The solvent inventory will also be managed to minimise the formation and release of degradation products through a reclamation process which may

be batch or a continuous bleed and replenishment of solvent within the process.

- 8.3.17 It is considered that through best practice storage and management measures for the amine solvent, that its degradation within the carbon capture plant can be minimised. As a result, the direct emissions of N-amines into the atmosphere from the carbon capture absorber stacks, are expected to be at very low levels (i.e. in the parts per billion (ppb) range).
- 8.3.18 In order to ensure a worst-case assessment is carried out for the purpose of the assessment, it is assumed that this direct N-amine emission occurs solely as NDMA.

Indirect N-Amine Emissions

- 8.3.19 The majority of N-amines resulting from releases from the carbon capture process are considered to form through reactions in the atmosphere post release. These atmospheric reactions are complex, and the rate of N-amine formation and subsequent destruction depends upon a range of factors.
- 8.3.20 The amine degradation process in the atmosphere requires the presence of either an OH or a NO₃ radical. The primary method for formation of N-amines in the atmosphere is a two-step process:
- The OH radical (daytime) or an NO₃ radical (night-time) removes a single hydrogen atom in the amine molecule to form a highly unstable amine radical; then
 - The amine radical reacts with either a NO group to form a nitrosamine, or an NO₂ group to form a nitramine.
- 8.3.21 A variety of competing reaction can also take place, preventing the formation of N-amines:
- The amine can degrade to other radical species via removal of a non-amine hydrogen, or methyl group (this potential is known as the branching ratio);
 - The amine radical can undergo competing reactions, with NO₂ and O₂ to form an imine (stable, and not toxic (Helgesen/Gjernes 2016)); and
 - The nitrosamine or nitramine can undergo further degradation or reverse reaction to the radical.
- 8.3.22 During daylight hours, atmospheric amine degradation is initiated by reaction with the OH radical (generated by photolysis of water (H₂O) by the action of ultraviolet light from sunlight). At night, in the absence of UV light, no OH radical is generated. Night-time reactions instead proceed by the much slower pathway of NO with ozone (O₃) to form NO₂ and subsequent reaction of NO₂ with O₃ to form the NO₃ radical; amine degradation is then initiated by reaction with the NO₃ radical to form N-amines. The nitrate radical is rapidly photolyzed in daylight and does not represent a likely reaction pathway during the daytime.
- 8.3.23 The concentration of NO_x and O₃ available in the atmosphere therefore influences the reaction of amine to N-amines. The night-time reactions are slower than the daytime reactions as a result of the intermediate reaction

step, therefore a higher rate of formation of N-amines results from daytime reactions.

- 8.3.24 The steady state concentration of N-amines can be calculated using reaction rate constants, usually derived through experimental studies. Such studies have indicated that not all amines released would convert to N-amines in the atmosphere, and the conversion of those amines that would degrade in the atmosphere to N-amines can take many hours to occur. Typical conversion rates are <1% although chamber experiments show a range of between 0 and 10%.
- 8.3.25 The ratio of reaction coefficients in the formation of (1) the amine radical (that can proceed to N-amine formation) or (2) an alternative species radical (that does not form N-amine) is described as the Branching Ratio; and for several amine species these have been published, although values range between published sources. The higher the Branching Ratio of the amine, the more likely it is to form N-amines.

Table 0C-1: Amine Branching Ratios

Amine Species	Branching Ratio	Source
Monoethanolamine (MEA)	0.05 – 0.15	CERC 2012 and Karl et al. 2012
Monomethylamine (MMA)	0.25	Neilson <i>et al.</i> 2011
Dimethylamine (DMA)	0.38 - 0.42	CERC 2012
Piperazine	0.09	Onel <i>et al.</i> 2015

- 8.3.26 As can be seen in Table 8C-1, the branching ratios for the primary amines MEA and MMA, and piperazine, are lower than that for the secondary amine, DMA, therefore secondary amines are more likely to form N-amines. Tertiary amines must first degrade to a primary or secondary amine, through elimination of a hydrocarbon group, before further reaction to N-amine or other species can occur, and therefore as other competing reaction may also occur, the likelihood of forming N-amine must also be lower than for secondary amine; however there is limited published data for tertiary amine reaction constants.
- 8.3.27 In addition to the Branching Ratio, the concentration of ambient NO_x also influences the generation of N-amines from amines. From laboratory tests it is known that when more NO_x is present, more amines are converted into N-amines. This function is called the “amino radical/NO₂ reaction rate constant [k₄]”.
- 8.3.28 There is a relatively limited data set available for establishing the proportion of amine that forms N-amines, upon which a simulation of atmospheric chemistry can be based. The reaction rate data that has been identified from laboratory experiments for DMA is set out in Table 8C-2. Within this data set, the NO_x concentrations, and whether the simulation is undertaken for daytime or night-time simulations, is identified.

Table 0C-2: Influence of the NO_x Concentration on the Proportion of DMA Converted to N-amines in Laboratory Trails

Final environmental species	NO _x / NO ₂ concentration in the experiment	Proportion of amine converted to N-amine	Reference	Comments
Nitramines	0.2 – 10ppb	<2.5%	Nielsen <i>et al.</i> (2011)	Daytime simulation
	20 – 50ppb	<8%	Nielsen <i>et al.</i> (2011)	Daytime simulation
	0.2 – 10ppb	<0.6%	Nielsen <i>et al.</i> (2011)	Daytime simulation
	20 – 50ppb	<2.3%	Nielsen <i>et al.</i> (2011)	Daytime simulation
	0.08ppm NO - 0.16ppm NO ₂	1%	Grosjean <i>et al.</i> (1991) citing Pitts J. <i>et al.</i> (1978)	Night-time simulation
Nitrosamines	2ppm NO ₂ - 2ppm NO	10 – 30%	Grosjean <i>et al.</i> (1991) citing Hanst <i>et al.</i> (1977)	Night-time simulation. This experiment is acknowledged by SEPA to have been undertaken at particularly high Nitrous Acid/NO _x concentrations, at nearly 20 times the short-term ambient NO ₂ air quality standard. This concentration would typically only be observed within a stack flue gas before abatement.

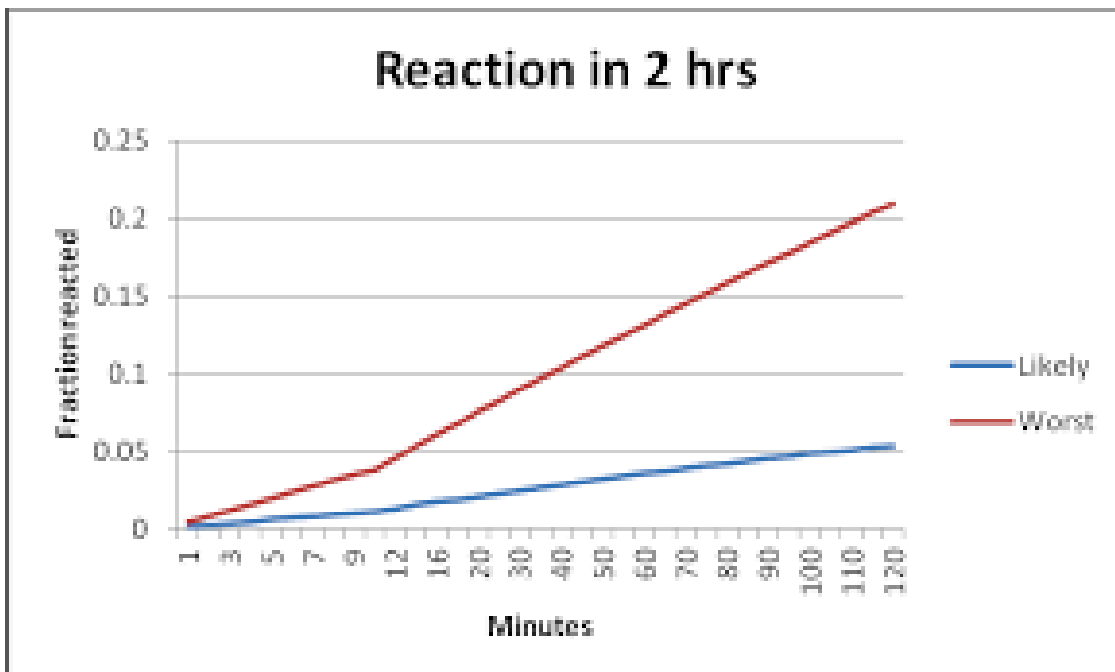
8.3.29 In the flue gas from the carbon capture plant, the NO_x is composed of around 90-95% NO to 5-10% NO₂. Once in the atmosphere the NO will react with OH to form NO₂. The reaction of OH is preferential to NO rather than amine as NO is more reactive. Therefore, as NO concentrations decrease spatially due to reaction with OH, there becomes more available OH radicals to react with the amines, so amine reaction will occur at greater distance from the stack. The details of this process are too uncertain to be accurately represented in the ADMS amines chemistry model and therefore the model does not include this time-delay in the initiation of the amine degradation reaction, assuming that this occurs instantly on release, therefore potentially resulting in higher concentrations in close proximity to the stack. This is therefore considered to be very conservative.

8.3.30 At night-time the NO₃ radical is formed from the reaction of ozone with NO, and then NO₂. Therefore, the reaction of NO to NO₂ is likely to be preferential to the reaction of NO₂ to NO₃ or NO₃ reacting with amines, which again will slow down the formation of N-amines. These details again are too uncertain to be accurately represented in the amines chemistry module and therefore are not included.

8.3.31 Only a proportion of the N-amines released or generated will remain as N-amines, as during daylight hours, N-amines are degraded to more basic amines, amides, ethanoic acid, ketones and simple nitrogen compounds in the presence of sunlight. At night no destruction of N-amines occurs.

- 8.3.32 The WHO document (WHO 2002) states that photolysis is the major pathway for the removal of NDMA from surface water, air, and land and that it is unlikely to be transported over long distances in air or to partition to soil and sediments.
- 8.3.33 Not all amines released would convert to N-amine in the environment and the conversion of those amines that would degrade in the atmosphere to N-amine can take many hours to occur. This is described by the work carried out by Tonnesen in 2011 (Tonnesen 2011), which demonstrated that less than 5% of the amines that would convert to N-amines would have done so in the first 10 minutes after release. After 2 hours, only 20% of the amines that would convert to N-amine would have done so. The work then goes on to estimate that it would take in the order of 10 hours for 100% conversion to occur. A graph showing this process is provided in Figure 8C-1.

Diagram 8C-1. Conversion of Amines to N-Amine in the Atmosphere Over Time



8.4 Assessment Methodology

Dispersion Model Selection

- 8.4.1 The assessment of emissions from the Proposed Development has been undertaken using the advanced dispersion model ADMS (version V5.2.2), supplied by Cambridge Environmental Research Consultants Limited (CERC). ADMS is a modern dispersion model that has an extensive published validation history for use in the UK. This model has been extensively used throughout the UK to demonstrate regulatory compliance.

Direct N-amine Emissions

- 8.4.2 Direct N-amine emissions have been to occur at the maximum concentration provided by licensors, and no atmospheric chemistry has been assumed to occur. These have therefore been modelled as a direct release within the

ADMS model at a concentration of 0.002mg/m^3 (assumed to be NDMA, as a worst case).

Indirect N-amine Emissions

- 8.4.3 CERC have generated a specific amine chemistry module for use with the ADMS software, for the assessment of emissions of amines and their atmospheric degradation products. The ADMS amines chemistry module is the only commercially available modelling software that can be used to evaluate potential impacts on air quality from amines and amine degradation products releases.
- 8.4.4 The model calculates the rate of amine degradation taking into account the reaction of amines with other species present in the exhaust gas (i.e. NO_2) and also with hydroxyl (OH) radicals in the atmosphere. Whilst the ADMS model itself has been validated, the specific amines module has not been, and therefore the results should be regarded as indicative rather than definitive.
- 8.4.5 Within the ADMS amines chemistry module it is necessary to specify the amine, nitrosamine, nitramines and radical species that are being modelled, therefore an emission of a solvent with multiple amine components would need to be modelled for each component, and therefore any reactions between the amine components themselves are not accounted for.
- 8.4.6 The module requires the amine-specific branching ratio (Table 8C-1) and the kinetic constants, k values (specific to each subsequent reaction rate). These values have been derived for very few species, and different sources contain different rates for the same species. Other input data, such as the hydroxyl radical (OH) concentration, also has limited data available. Further detail on the uncertainties within the ADMS amine chemistry module are discussed below.

Limitations of the Assessment

- 8.4.7 The Environment Agency recognise that the level of uncertainty within the ADMS amines chemistry model is high (Environment Agency 2020), however, as the only commercially available model, recognises that it follows first principles and considers available knowledge on the mechanisms of formation of toxic pollutants from amine emissions in ambient air. As such, they recommend that uncertainties are addressed by testing the sensitivity of the model to different input parameters, and also that validation exercises are undertaken. In order to validate the model outcome, an operational carbon capture plant utilising the specific amine being assessed would be required.

ADMS Amines Chemistry Module

- No time-delay in N-amine formation
- 8.4.8 The amines chemistry module does not account for the time delay in the initiation of the amine degradation (Tonnesen 2011), which indicates only around 15% reaction completion as worst-case within 1 hour. The ADMS model assumes that a "steady state" is achieved within 1 hour (N-amine formation/ destruction). The time taken for the peak concentration to reach a receptor at 1 km is between 1 - 30 minutes. The model only calculates spatial

dispersion, not temporal change. In the real world, as the plume travels further from the source, the amine concentration reduces but the OH concentration may increase (less NO_x for the preferential reaction to occur) leading to higher potential N-amine formation, but when balanced against N-amine and amine dispersion the result is a lower N-amine concentration with distance. The model has to assume the reaction completion at the point of calculation, and therefore it is considered that this is overly conservative.

- No interaction between different amine species

8.4.9 The amines chemistry module does not allow for any interactions between different amine degradation species as only one amine species can be modelled at a time. This could result in missing N-amine removal pathways and therefore result in higher predicted results.

- N-amine degradation processes not accounted for in the module

8.4.10 Once the N-amine has formed in the atmosphere, further degradation/destruction processes will occur due to photolysis by sunlight, however this destruction of N-amine is not accounted for in the model. It is therefore considered that this leads to potentially significant overprediction of the potential impact.

8.4.11 Furthermore, no photolysis of the direct N-amine emission is considered in the model, and this will again lead to an overprediction of the potential impact.

8.4.12 The amines chemistry module also does not account for further amine degradation, for example the primary amine MEA can degrade to the secondary amine DEA (which could subsequently degrade into NDMA). This could result in an increase in N-amine formation but over longer time periods which could be counterbalanced by the destruction of N-amine over time discussed above.

- Only day-time reactions considered

8.4.13 The amines chemistry module accounts for diurnal variation in the photolysis (OH) reaction, but does not account for the slower NO₂ degradation reaction that occurs during night-time. This would lead to an underprediction of N-amine generation at night-time.

- No consideration of phase partitioning

8.4.14 Once emitted to the air, amines, nitrosamines and nitramines undergo multiphase chemistry, i.e. gas, aqueous (aerosols, cloud droplets, fog and rain) and particle phase (aerosol). Therefore, the mass of starting amine may be partitioned (e.g. gas or aqueous phase). The amines chemistry module is only concerned with the gaseous phase.

Other Assessment Limitations

- Limited reaction rate constants available

8.4.15 The majority of published data for amine degradation to nitrosamine and nitramines are presented as relative rates of reaction (for example for the reaction of the amine radical to form either the imine or nitramines, and the k_{1a}/k₁ branching ratio), rather than the absolute rates for each reaction required for the Amines module (i.e. k₁, k₂, k₃, k_{4a} and k₄). The absolute

rates of reaction may be derived through scientific research through experimental observation, for the more stable intermediate reaction species, or through theoretical computational calculations such as Transition State Theory. A review of the available literature indicates that the availability of published absolute reaction rates for a whole amine reaction scheme is currently limited to a few primary and secondary amine species (namely MEA, DMA and MMA). In addition, some kinetic parameters reported for the same type of amine show different values in published reports. Sensitivity testing to the range of kinetic parameters published is therefore required, and has been carried out as part of this assessment.

- OH Value

- 8.4.16 The main reaction of amines in the atmosphere is with the OH radicals and it is this reaction on which the ADMS amine module is based. The model set up therefore requires a OH value to calculate the "c-value" for the reaction rate. The modelled predicted impact is directly proportional to c-value, and therefore it is important that local data is obtained and used in the model set-up. Halving of the OH value would result in a halving of the modelled N-amine impact.
- 8.4.17 There is limited data on OH concentrations in atmosphere and the concentration is highly variable with sunlight, ozone concentration, NO_x concentration etc. and the radical is short-lived.
- 8.4.18 This therefore represents a significant uncertainty in the modelled results.
- Use of the NDMA AQAL for all N-amines
- 8.4.19 The use of the NDMA AQAL for the assessment of all N-amines is likely to lead to an over-prediction of the potential impact. As previously stated, NDMA is considered to be one of the most toxic nitrosamines, with nitramines being considered much less so. It is therefore reasonable to assume that were AQALs to be developed for other N-amine species that these would be higher than that proposed for NDMA.
- 8.4.20 The model output typically presents much higher predicted concentrations of nitramines (three to ten times higher) than for nitrosamines. For comparison against the AQAL for the purpose of assessment, the nitrosamine and nitramine predicted concentrations have been combined. As stated previously, nitramines are known to be less toxic than nitrosamines, and therefore it is considered that this leads to an overly conservative assessment.

First Stage - Screening Assessment Approach for Indirect N-amine Emissions

- 8.4.21 Given the limitations in the use of the ADMS amines chemistry module and other assessment parameters, it has been considered appropriate to carry out a staged assessment approach for indirect N-amines, comprising an initial screening assessment, based on literature assumptions on amine degradation, and a second stage of assessment utilising the ADMS amines chemistry module.
- 8.4.22 Two aspects for the preliminary screening assessment have been taken into account:

- The proportion of amine that can convert to N-amines in the atmosphere. This depends on the actual amine species released, with reported conversions of different amines being between 0.6 – 10%, based on information from Nielson (2011). An average conversion rate of 5% has therefore been assumed for this screening assessment.
- The fraction of reacted amine that can convert to N-amines based on the time taken to reach the identified receptors. This has been based on the average wind speed in the area and the distance to the identified receptors. The specified receptors included in the model are between 800m and 2 km from the emission sources, and therefore considering that the average wind speed in the study area is approximately 4.5 m/s, the pollutants released from the stacks would take approximately 3 – 7.5 minutes to reach these receptors. Due to the slow rate of the degradation of amine to N-amines in the atmosphere (especially in an area with low background NO₂ concentrations) it is considered that less than 1% of the amine that could degrade to N-amines would have done so by the time it reaches the identified receptors (Tonneson 2011).

8.4.23 Taking both these factors into account, a total of 0.05% of the total amine released would have been converted to N-amine by the time the plume reaches the sensitive receptors. This has therefore been derived from the amine PC presented in Appendix 8B (ES Volume III, Document Ref. 6.4), and applying the 0.05% conversion.

8.4.24 It is considered that this screening assessment would lead to an overestimation of the potential N-amines in the atmosphere, as it does not take into account the destruction of N-amines within the atmosphere, which occurs following the initial conversion process by photolysis, as described above.

Second Stage - Amines Chemistry Module

8.4.25 As discussed above, the treatment of chemistry within the ADMS amines model requires a suite of reaction rate parameters derived from laboratory studies and other sources. The parameters required by the model in order to simulate amine chemistry for a specific amine(s) are detailed in Table 8C-3. Within Table 8C-3 ● denotes a radical species.

Table 8C-3: Amine Information for ADMS Model Set-Up

Parameter	Units	Notes
Amines Release	g/s	As per the emission rate for the main assessment (5.5 mg/m ³).
Direct N-amine Release	g/s	Assessed as NDMA as a worst case at the maximum value provided.
Ratio of NO _x to NO ₂ in the exhaust gas	%	Sensitivity tested at 5% and 10%.
k1 = Amine/OH radical reaction rate constant	ppb/s	Rate constant for the reaction of the amine with the hydroxyl radical. (OH●).

Parameter	Units	Notes
k2 = Amino radical/O ₂ reaction rate constant	ppb/s	Rate constant for the reaction of the amine● with O ₂ (to form imine).
k3 = Rate constant for formation of nitrosamine	ppb/s	Rate constant for formation of nitrosamine from amine● & NO.
k4a = Rate constant for formation of nitramine	ppb/s	Rate constant for formation of nitramine from amine● and NO ₂
k4 = Amino radical/NO ₂ reaction rate constant	ppb/s	Rate constant for the reaction of the amine● with NO ₂ (to form imine or nitramine).
Branching Ratio	dimensionless	Branching ratio for the amine / OH● reaction – representing the reaction split, in formation of amine radical (amine● which further reacts to nitrosamine/nitramine) and alternative hydrocarbyl radical species.
Ratio of J (nitrosamine) to NO ₂	dimensionless	The ratio of the photolysis rate constants for the nitrosamine and NO ₂ - representing the relative atmospheric fluctuations of NO ₂ and nitrosamine formation as a result of UV light action.
c = OH concentration constant	s	OH concentration constant, derived for typical daytime atmosphere. Calculated following derivation of J(NO ₂).
Atmospheric oxygen concentration	ppb	Representing 21% O ₂ in air.
NO _x baseline	µg/m ³	Hourly values obtained for Dormanstown automatic monitor the years of meteorological data used in the model.
NO ₂ baseline	µg/m ³	
Ozone Baseline	µg/m ³	

8.4.26 These parameters are entered into an ADMS Additional Information (AAI) file, which characterises the amine chemistry for the amine species being assessed.

8.4.27 The majority of published data for amine degradation to nitrosamine and nitramines are presented as relative rates of reaction (for example for the reaction of the amine radical to form either the imine or nitramines, and the k1a/k1 branching ratio), rather than the absolute rates for each reaction required for the Amines module (i.e. k1, k2, k3, k4a and k4). The absolute rates of reaction may be derived through scientific research through experimental observation, for the more stable intermediate reaction species,

or through theoretical computational calculations such as Transition State Theory.

- 8.4.28 A review of literature indicates that the availability of published absolute reaction rates for a whole amine reaction scheme is currently limited to a few primary and secondary amine species (namely monoethanolamine (MEA), dimethyl amine (DMA), monomethylamine (MMA)). Notably, there is scant data published for tertiary amines or sterically hindered amines (such as aminomethyl propanol or piperazine derivatives). A number of papers provide theoretically derived rate constants (Wen Tan, Liang Zhu *et al.* 2018 and Helgesen/Gjernes 2016), based on relative reaction rates, however these values have not verified experimentally.
- 8.4.29 Given the limited data set available for these parameters, the assessment has been carried out using the data available for MEA and DMA, assuming that the whole of the amine emission is either as MEA, or as DMA, and reporting the results of both species against the NDMA AQAL. It is considered that this is a reasonable worst-case assumption, given that the majority of primary amines will react similarly in the atmosphere to MEA, and that the majority of secondary amines will react similarly in the atmosphere to DMA.
- 8.4.30 That said, this approach is also likely to lead to an over-estimation of the level of impact, as it is likely that primary amines would make up a greater proportion of any solvent solution, with a much smaller proportion comprising secondary amines, although it is recognised that this is not necessarily the case for all proprietary solvents.
- 8.4.31 As tertiary amines do not feature a labile -H (hence their desired characteristics for their use as a carbon capture solvent of both thermal stability and the limited propensity to form nitrosamine), for assessment purposes, it is cautiously assumed that primary amine nitrosamine formation rates, which are lower than secondary amine nitrosamine formation rates, are representative of tertiary amines nitrosamine formation rates in the absence of other data. However, where primary amines are not expected to form stable nitrosamine, this is not necessarily the case for tertiary amine, which is taken into consideration in the discussion of validity of results.
- 8.4.32 In combination with the other worst-case assumptions used in the assessment, such as the using the maximum emission concentration of all technology licensors and the fact that photolysis of the N-amines is not taken into account, it is considered that there is a large degree of conservatism built into the assessment.
- 8.4.33 As stated previously, there is variability in the published branching ratios and kinetic parameters reported for the same type of amine. As such, the range of reported values for MEA and DMA are presented in Table 8C-4. For the main assessment, the mid-point of these reported values has been used, with sensitivity for the upper and lower end of the range being carried out and reported in Annex A. The validity of any particular published reaction rate value is not possible to confirm with the currently available information and therefore this approach is considered to be reasonable until plant trials allow for further verification of data.

Table 0C-4: MEA and DMA ADMS Model Set-Up

Parameter	Units	MEA	DMA	Source
Amines Release	g/s	5.9	4.3	Appendix 8B: Air Quality – Operational Assessment (ES Volume III, Document Ref. 6.4).
Direct N-amine Release (assumed to be NDMA, as a worst case)	g/s	0.017	0.017	Licensors
Ratio of NO _x to NO ₂ in the exhaust gas	%	5 – 10%	5 – 10%	-
k1 = Amine/OH radical reaction rate constant	ppb/s	1.87 – 2.26	1.54 – 1.63	CERC (2012) Lee & Wexler (2013)
k2 = Amino radical/O ₂ reaction rate constant	ppb/s	3.1e-9* - 9.5e-8*	3.1e-9* - 8.9e-8*	CERC (2012) Manzoor (2014)
k3 = Rate constant for formation of nitrosamine	ppb/s	1.4e-3 – 6.0e-3	2.0e-3 – 2.1e-3	CERC (2012) Manzoor (2014)
k4a = Rate constant for formation of nitramine	ppb/s	2.1e-4 - 7.8e-3	7.75e-3 - 7.82e-3	CERC (2012) Manzoor (2014)
k4 = Amino radical/NO ₂ reaction rate constant	ppb/s	3.1e-4 - 8.6e-3	8.0e-3 – 9.7e-3	CERC (2012) Manzoor (2014)
Branching Ratio	dimensionless	0.05 – 0.15	0.38 – 0.42	CERC (2012) Manzoor (2014) Lee & Wexler (2013)
Ratio of J (nitrosamine) to NO ₂	dimensionless	-	0.53* - 0.25*	Nielson (2010)
OH concentration constant c	Seconds	7.1e-4 – 3.9e-3	7.1e-4 – 3.9e-3	CERC (2012) Jackson <i>et al.</i> (2009)

*Upper & Lower values defined according to effect on maximum PC – increase in k2 results in decrease in PC, similarly for JNS:JNO₂.

8.4.34 The model includes an option to take into account the effects of dilution of pollutant species and the entrainment of background pollutants. This “dilution and entrainment” effect can be switched on and off, however it is recommended that it is switched on for all model runs involving amine chemistry. This is employed in the ADMS chemistry module (and recommended by CERC for low concentration plumes for the Amines module) to represent slower mixing of the ambient air within the plume – rather than instantaneous mixing with an ambient air “parcel” at plume release. The use of the dilution and entrainment option leads to substantially higher PC (as shown in Annex A). The dilution and entrainment option has therefore been included for the main assessment for conservatism.

- 8.4.35 In addition, the amine module includes an option for modelling unstable nitrosamines, which can be employed when modelling primary amines that do not form stable nitrosamines. In effect, this means that the model results generated when this option is selected include no nitrosamine component, with only nitramines being predicted to form. This option has not been included in the assessment, as it is considered that the results would also be valid for predicting likely concentrations of tertiary amines, as they are more likely to form stable nitrosamines than primary amines.
- 8.4.36 The stack parameters, meteorology and structural parameters used in the dispersion modelling of the amines are the same as those for other pollutants emitted from the carbon capture plant, and the underlying dispersion modelling approach is set out in Technical Appendix 8B: Air Quality – Operational Assessment (ES Volume III, Document Ref. 6.4).

8.5 N-Amines Modelling Results

Direct N-Amine Emissions

- 8.5.1 Total direct N-amine emissions have been modelled at an emission concentration of 0.002mg/m³, without the Amines module (as the module does not include degradation of N-amine direct release), assuming that this release occurs entirely as NDMA, as a worst-case. The results are shown in Table 8C-5.

Table 8C-5: Predicted Change in Annual Average N-Amine Concentrations as a Result of Direct Amine Releases

Receptor	AQAL (ng/m ³)	Total N-Amines PC (ng/m ³)	PC/AQAL %
Max anywhere		0.07	35%
OR1		0.03	13%
OR2		0.05	25%
OR3		0.02	8%
OR4		0.01	7%
OR5	0.2	0.04	20%
OR6		0.01	7%
OR7		0.03	15%
OR8		0.01	7%
OR9		0.03	13%
OR10		0.01	7%

PC = Process Contribution, AQAL = Air Quality Assessment Level

- 8.5.2 The results for the total direct N-amine emission indicate that PCs at receptor locations are well within the AQAL for NDMA. This assessment assumes that all the N-amine emission occurs as the nitrosamine NDMA, when this may only make up a small proportion (if any) of the direct release, with the total release comprising a number of nitrosamines and nitramines that are likely to be less toxic than NDMA. It is therefore considered that the PCs within

Table 8C-5 represent a worst-case assessment of the potential impact from the direct N-amine releases.

Indirect Releases - Screening Assessment

- 8.5.3 As stated previously, the screening assessment assumes that 0.05% of the amine release could degrade into N-amines at receptor locations following release from the emission stack.
- 8.5.4 Obviously over a greater distance, further degradation would occur, and therefore this could result in N-amine concentrations increasing with distance from the absorber stack, although this would be countered to some extent by the additional dispersion of the plume over the greater distance and the removal of N-amines from the atmosphere through the various pathways described previously.
- 8.5.5 Taking the outlined assumptions into account, the screening assumptions have been applied to the reported amine concentrations from Appendix 8B, to derive the N-amine PCs from atmospheric degradation processes. These results are shown in Table 8C-6.

Table 8C-6: Predicted Change in Annual Average N-Amine Concentrations as a Result of Indirect Amine Releases – Screening Assessment

Receptor	AQAL (ng/m ³)	Total N-Amines PC (ng/m ³)	PC/AQAL %
Max anywhere		0.09	46%
OR1		0.04	18%
OR2		0.07	34%
OR3		0.02	11%
OR4		0.02	9%
OR5	0.2	0.05	27%
OR6		0.02	10%
OR7		0.04	21%
OR8		0.02	9%
OR9		0.04	18%
OR10		0.01	7%

PC = Process Contribution, AQAL = Air Quality Assessment Level

- 8.5.1 The screening assessment results indicate that at the receptor experiencing the maximum impact, the PC represents 34% of the AQAL for NDMA. This is therefore well below the AQAL and demonstrates that based on the screening criteria applied, an exceedance of the AQAL would be unlikely at receptor locations as a result of the atmospheric degradation of amines.
- 8.5.2 Together with the direct amine release PCs provided in Table 8C-5, the combined PCs would remain within the AQAL for NDMA.

Indirect Releases – ADMS Amines Module Assessment

- 8.5.3 The assessment using the mid-point of the reaction rate constants for MEA and DMA, as shown in Table 8C-4, are presented in Tables 8C-7 and 8C-8

respectively. These results presented included the dilution and entrainment option, as advised by CERC, the model developers.

Table 0C-7: Predicted Change in Annual Average N-Amine Concentrations as a Result of Indirect Amine Releases – Amines Module Assessment – MEA Results

Receptor	AQAL (ng/m ³)	Nitrosamine PC (ng/m ³)	Nitramine PC (ng/m ³)	Combined PC (ng/m ³)	Combined PC/AQAL %
Max anywhere		0.026	0.012	0.038	19%
OR1		0.006	0.002	0.008	4%
OR2		0.019	0.007	0.025	13%
OR3		0.007	0.006	0.013	6%
OR4		0.007	0.005	0.013	6%
OR5	0.2	0.017	0.007	0.024	12%
OR6		0.007	0.003	0.010	5%
OR7		0.013	0.005	0.018	9%
OR8		0.006	0.003	0.010	5%
OR9		0.011	0.005	0.016	8%
OR10		0.006	0.002	0.008	4%

Table 0C-8: Predicted Change in Annual Average N-Amine Concentrations as a Result of Indirect Amine Releases – Amines Module Assessment – DMA Results

Receptor	AQAL (ng/m ³)	Nitrosamine PC (ng/m ³)	Nitramine PC (ng/m ³)	Combined PC (ng/m ³)	Combined PC/AQAL %
Max anywhere		0.030	0.066	0.097	48%
OR1		0.008	0.012	0.020	10%
OR2		0.025	0.037	0.061	31%
OR3		0.004	0.032	0.036	18%
OR4		0.004	0.031	0.035	18%
OR5	0.2	0.020	0.037	0.057	29%
OR6		0.008	0.018	0.026	13%
OR7		0.014	0.029	0.043	22%
OR8		0.006	0.019	0.026	13%
OR9		0.012	0.027	0.039	20%
OR10		0.008	0.012	0.020	10%

8.5.4 It can be seen that, when using the mid-point value for the reaction rate constants for both MEA and DMA, the predicted PCs are lower than those predicted in the screening assessment shown in Table 8C-6.

- 8.5.5 The results for MEA show a greater proportion of the total N-amine release being present as the nitrosamine, whereas the DMA results show a higher proportion as the nitramine. Therefore, although the PCs for DMA result in a higher PC/AQAL, the proportion of the potentially less toxic nitramine is greater. This again means that the comparison against the NDMA AQAL is very conservative.
- 8.5.6 If, for example, the nitramine was assumed to be 6-fold less toxic than the nitrosamine (Gjernes *et al.* 2013), then the predicted nitramine PC could be reduced by a factor of 6 for comparison with the NDMA AQAL. This would then result in a maximum PC that occurs anywhere of:
- $$\text{nitrosamine (0.03 ng/m}^3\text{)} + \text{nitramine (0.066 ng/m}^3\text{ / 6)} = \text{0.041 ng/m}^3$$
- 8.5.7 This would represent 20.5% of the AQAL, compared to the 48% reported in Table 8C-8 above.
- 8.5.8 In combination with the direct releases from Table 8C-5, both the MEA and DMA results would remain below the AQAL.
- 8.5.9 Further sensitivity testing of the inputs into the Amines module has been carried out and is discussed in Annex A of this Appendix.

8.6 Assessment of Limitations and Assumptions

- 8.6.1 This section outlines the potential limitations associated with the dispersion modelling assessment. Where assumptions have been made, this is also detailed here.
- 8.6.2 The greatest uncertainty associated with any air quality modelling assessment arises through the inherent uncertainty of the dispersion modelling process itself. The use of dispersion modelling is nevertheless a useful and widely applied and accepted approach for the prediction of impacts from industrial sources.
- 8.6.3 The amines module itself has not been validated, and the limitations of the model are highlighted in Section 8.4.
- 8.6.4 In order to minimise the likelihood of under-estimating the N-amine PC to ground level concentrations from the main stack, the following conservative assumptions have been made within the assessment:
- The operational Proposed Development has been assumed to operate on a continuous basis i.e. for 8,760 hours per year, although in practice the plant would require routine maintenance periods;
 - The modelling predictions are based on the use of five full years of meteorological data from Durham Tees Valley meteorological station for the years 2015 to 2019 inclusive, with the highest result being reported for all years assessed;
 - The largest possible building sizes within the Rochdale Envelope as outlined in Chapter 4: Proposed Development (ES Volume I, Document Ref. 6.2) have been included;

- The lowest emission temperature of 35°C has been used for the N-amine assessment as the results obtained for Appendix 8B indicated that this led to the worst-case impacts at human health receptors;
- Emission concentrations of amines and direct N-amine have been based on the maximum concentrations indicated by all the technology licensors consulted; and
- All N-amines have been assessed against the AQAL for NDMA, when it is likely that there will be different N-amine species present in the PC, the majority of which will be less toxic than NDMA.

8.7 Conclusions

- 8.7.1 An assessment of the potential impacts associated with direct N-amine releases and the impact of atmospheric degradation of the amines released from the carbon capture stack has been carried out for the Proposed Development.
- 8.7.2 The assessment methodology contains numerous conservative assumptions, and there is a high level of uncertainty in the use of the ADMS Amines chemistry module.
- 8.7.3 The main reported assessment results show that the predicted impacts are unlikely to result in an exceedance of the proposed AQAL for NDMA, even when considering the impacts of both the direct and in-direct emission processes. The sensitivity analysis of the model input parameters largely supports this conclusion and supports the conservative nature of the assessment that has been carried out.

8.8 References

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Annex A: Model Sensitivity

The sensitivity of the model to various amine input parameters has been tested and is reported in this Annex. The results in the main assessment presented above are for the mid-point values for the branching ratios and reaction rate constants available for the amines MEA and DMA. In addition, the main results include the dilution and entrainment function, as advised by the model developers.

The parameters that have been varied in the model input include:

- Mid-Point rate constant and branching ratio values with no dilution and entrainment;
- Lowest rate constant and branching ratio values with dilution and entrainment; and
- Highest rate constant and branching ratio values with dilution and entrainment.

In addition, the percentage of NO₂ within the NO_x emission was tested at 5% and 10%, however this did not change the results.

The results of the sensitivity testing are shown in Table 8C-9, and represent the process contribution of nitrosamine and nitramine combined as a percentage against the AQAL.

Table 0C-9: Summary of PC/AQAL Results at the Maximum Location for Various Amine Input Parameters

Model Input Varied	AQAL (ng/m ³)	Nitrosamine PC (ng/m ³)	Nitramine PC (ng/m ³)	Combined PC (ng/m ³)	Combined PC/AQAL %
MEA					
Mid-Point Values with Dilution and Entrainment (as main assessment)		0.026	0.012	0.038	19%
Mid-Point Values No Dilution and Entrainment	0.2	0.002	0.005	0.008	4%
Lowest Values With Dilution and Entrainment		0.0009	0.00005	0.0010	0.5%
Highest Values With Dilution and Entrainment		0.46	0.48	0.94	470%
DMA					
Mid-Point Values with Dilution and Entrainment (as main assessment)	0.2	0.030	0.066	0.10	48%

Model Input Varied	AQAL (ng/m ³)	Nitrosamine PC (ng/m ³)	Nitramine PC (ng/m ³)	Combined PC (ng/m ³)	Combined PC/AQAL %
Mid-Point Values No Dilution and Entrainment		0.0031	0.030	0.033	16%
Lowest Values With Dilution and Entrainment		0.005	0.009	0.014	7%
Highest Values With Dilution and Entrainment		0.33	0.97	1.29	647%

It can be seen from the results presented in Table 8C-9 that, the inclusion of the dilution and entrainment option increases the results up to 5-fold for MEA and nearly 3-fold for DMA, therefore its inclusion in the main assessment is considered to result in a conservative assessment.

When the lowest branching ratios and rate constants are used in the assessment, the results are considerably lower than those reported in the main assessment.

Using the highest branching ratios and rate constants values leads to a significant increase in the predicted results, with results nearly 25 times higher for MEA and 13 times higher for DMA.

Further analysis of the rate constant inputs (which included varying each value at a time) showed that the parameter that has the greatest impact on the predicted PC is the k₂ (Rate constant for the reaction of the amine● with O₂ (to form imine)), which could lead to variations in the predicted PCs of up to 495% for the nitrosamine generated and 996% of the nitramine generated from MEA, with values of a similar order of magnitude for DMA.

The k₂ rate constant is effectively a radical “sink” (or loss) from the reaction scheme, and therefore an increase in k₂ leads to a decrease in the formation of nitrosamine and nitramine (and consequently a lower PC). The model run to obtain highest values for the sensitivity analysis therefore, used the lower end of the range of values reported for k₂, as this leads to a higher PC as it favours the nitrosamine formation.

The published data for k₂ varies by nearly a factor of 10, and therefore it is considered that the value of k₂ represents significant uncertainty in the assessment.

Other parameters have a less marked effect varying the predicted PCs. Further sensitivity modelling has been carried out to demonstrate this, with all the rate constants at their upper values, except for k₂, which has been kept at the mid-point value. The results of this model are shown in Table 8C-10.

Table 0C-10: PC/AQAL Results at the Maximum Location for k2 Sensitivity

Model Input Varied	AQAL (ng/m ³)	Nitrosamine PC (ng/m ³)	Nitramine PC (ng/m ³)	Combined PC (ng/m ³)	Combined PC/AQAL %
MEA					
Mid-Point Values with Dilution and Entrainment (as main assessment)	0.2	0.026	0.012	0.038	19%
Upper Values for all constants except k2 at mid-point With Dilution and Entrainment		0.091	0.050	0.14	70%
DMA					
Mid-Point Values with Dilution and Entrainment (as main assessment)	0.2	0.030	0.066	0.10	48%
Upper Values for all constants except k2 at mid-point With Dilution and Entrainment		0.060	0.10	0.16	80%

When all other values are at the upper values reported in literature, and the k2 value is at the mid-point, the PCs remain below the NDMA AQAL, even when dilution and entrainment are factored into the model.

The sensitivity analysis shows that several parameters, such as the k2 value and the inclusion of dilution and entrainment can lead to substantially different predicted concentrations of nitrosamine and nitramine. As such, this leads to significant uncertainty in modelled PCs.

Nevertheless, the assumed mid-range values, for the typical stack emission parameters modelled, indicate that amine emission concentrations would be within the range for control of nitrosamine and nitramine to within the AQAL.