Appendix 6C: Assessment of Amine Degradation Products

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6C. Air Quality – Assessment of Amine Degradation Products

6C.1 Introduction

6C.1.1 This Technical Appendix supports Chapter 6: Air Quality (ES Volume **I**) and describes the assessment of amine degradation products that has been undertaken to determine the potential impact on human health from these species as a result of the emissions from the operational Proposed Developments.

6C.1.2 The air quality assessment of emissions of amines from the Proposed Developments on human health and the environment has been included in Appendix 6B: Air Quality - Operational Phase (ES Volume **II**). However, amines can degrade to form other species, including nitrosamines and nitramines (collectively referred to as N-amines) which are potentially carcinogenic, therefore consideration of these species is also required within the air quality assessment. The assessment of these species is complex and therefore has been considered separately within this Appendix 6C.

6C.1.3 The assessment of N-amines includes direct N-amine emissions from the PCC plant absorber stacks. These are N-amines that form as a result of degradation within the carbon capture process itself and therefore are released directly from the stack as N-amines. The assessment also considered indirect N-amine impacts, which are the N-amines that form as a result of atmospheric processes following the release of amines from the PCC plant absorber stacks. This Technical Appendix has been prepared to describe the atmospheric processes effecting both these species and determine their potential impacts at receptor locations.

6C.2 Scope

PCC Plant Emissions

6C.1.4 When the Proposed Developments are operating with carbon capture, an amine-based solvent will be utilised as the scrubbing medium within the PCC plants, to remove the carbon dioxide (CO_2) within the flue gas streams from the VPI Site (used to describe GT1, GT2 and the two auxiliary boilers for the purpose of this appendix) and the Phillips 66 FCC. A small amount of ‘Amine slip’ can occur during the carbon capture process, resulting in direct emission of amines from the absorber stacks. Over time, the amine solvent used in the PCC plants can degrade, through for example, reaction with nitrogen dioxide (NO_2) within the flue gases, which can result in the generation of N-amines within the amine solvent. Degradation is minimised through continuous solvent replenishment, monitoring and process control, as will be required under the Environmental Permits covering the PCC plant activities. Nevertheless, the amine slip emission from the PCC plants is likely to include a very small fraction of N-amines, which is considered in this assessment as the ‘direct’ N-amine emission.

6C.1.5 Potentially of more significance is the subsequent atmospheric degradation of the amines released from the PCC plants absorber stacks. This is considered in the assessment as the ‘indirect’ N-amine emission.

6C.1.6 The atmospheric chemistry of amines and N-amines is complex, dependent on atmospheric ozone and NO_2 concentrations, and with the generation of hydroxyl (OH) 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.

6C.1.7 This Technical Appendix details the amine chemistry mechanisms likely to occur following release of amines and N-amines from the PCC plants absorber stacks, and the specific parameters used for the modelling assessment for N-amines from the Proposed Developments.

6C.1.8 The assessment has considered the impact of emissions on local air quality, under normal operating conditions, with the Proposed Developments operating in carbon capture mode for 8,760 hours per year.

6C.1.9 A comparison has been made between predicted model output concentrations, and the Air Quality Assessment Level (AQAL) for N-nitroso-dimethylamine (NDMA), as detailed in Chapter 6: Air Quality (ES Volume I).

6C.3 Sources of Information

6C.1.10 The assessment of N-amine emissions from the Proposed Developments has been undertaken using the advanced dispersion model ADMS (version V5.2.2), supplied by Cambridge Environmental Research Consultants Limited (CERC), as the assessment detailed in Appendix 6B: Air Quality – Operational Development (ES Volume II). CERC have developed an Amine Chemistry module to simulate the atmospheric chemistry of amines and N-amines following their release from stacks. The chemistry scheme is based on the reactions initiated by the attack of an emitted gaseous amine or N-amine by a hydroxl radical, and predicts the subsequent formation of nitrosamine and nitramines.

6C.1.11 The assessment includes pertinent information from:

- data on the amine and N-amine emission concentrations to atmosphere from Shell;
- details on the Proposed Developments' layouts;
- Ordnance Survey mapping;
- reaction rate constants required for the ADMS Amines Chemistry module, as provided by Shell for their specific solvent (CANSOLV);
- other constants required for the ADMS Amines Chemistry module derived from literature sources (as detailed throughout the text);
- Environment Agency Air Quality Modelling and Assessment Unit (AQMAU) 'AQMAU recommendations for the regulation of impacts to air quality from amine-based post-combustion carbon capture plant' AQMAU-C2025-RP01 (Environment Agency, 2021);
- AECOM's memo 'Amines Degradation Dispersion Modelling Memo to the Environment Agency' (AECOM, 2021); and
- meteorological data supplied by ADM Ltd.

6C.4 Discussion of Amines and N-amines

6C.1.12 The AQAL for NDMA is the only AQAL that has been derived to date for N-amine species. NDMA is the nitrosamine formed from dimethyl amine (DMA) degradation, and is the most widely studied nitrosamine, due to its known toxicity and carcinogenicity. As such, the AQAL proposed by the Environment Agency for the assessment of N-amines in the UK has been derived for NDMA. In the absence of other published values for N-amines, and assessment in order to ensure a conservative assessment, the AQAL for NDMA has been applied to all N-amines in this assessment.

Toxicity of N-Amines

6C.1.13 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 Nitrosodiethanolamine (NDELA)), the environmental toxicity of many of the other individual compounds is not well understood (Scottish Environmental Protection Agency (SEPA), 2015). NDMA is understood to be the most mutagenic (having the ability to cause a permanent change in an organism's genes) of the nitrosamines tested (Wagner et al., 2014).

6C.1.14 The World Health Organisation (WHO) has published a Concise International Chemical Assessment Document on NDMA (WHO, 2002), which states that laboratory studies have shown that exposure to NDMA results in tumours in all species examined; it is metabolised (in the body turned into new cells, energy and waste products by chemical processes) and does not bioaccumulate (build up within the tissues of an organism).

6C.1.15 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.

6C.1.16 There is less information available on the toxicity of nitramines, which include nitro (-NO_2) 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 currently all N-amines are assumed to be as toxic as the most toxic nitrosamine, can be carried out.

6C.1.17 The solvent licensor for the Proposed Developments is Shell, and although detailed toxicology data is considered to be commercially confidential for the N-amines that may be formed by the degradation of the amines within the Shell solvent, from research that has been carried out to date it is considered that the toxicity of the N-amines potentially formed is significantly lower than NDMA.

6C.1.18 Nitrosamines that can form through the use of the CANSOLV solvents have undergone *In vitro* mutagenicity analysis and comparison with NDMA. The nitrosamines formed from the use of the proposed CANSOLV DC-103 solvent are named as ‘CANSOLV N-1’ and ‘CANSOLV N-3’. The study found that NDMA was a mutagen. CANSOLV N-3 was also found to be a mutagen, but 52 times less potent than NDMA. CANSOLV N-1 was found to be a weak mutagen with a mutagenic potency approximately 2,100 times less than that of NDMA. CANSOLV N-1 would be the main nitrosamine formed from the CANSOLV DC-103 formulation, with CANSOLV N-3 being formed in lower amounts.

6C.1.19 In order to ensure a worst-case assessment is carried out, however, it is assumed that this direct N-amine emission occurs solely as NDMA and therefore comparison of the predicted process contributions to the NDMA AQAL is considered to be very conservative.

6C.5 N-Amine Emissions from Carbon Capture Processes

Direct N-Amine Emission

6C.1.20 The amine solvent used in the PCC plants will be contained and recycled within the PCC 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 PCC plant absorber stack can therefore occur through entrainment of the solvent within the exhaust gas.

6C.1.21 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 PCC plant is carefully controlled.

6C.1.22 Acid gas reactions can occur due to the other trace pollutant species present in the emission, in particular the NO_2 within the exhaust gases from the VPI Site and the Phillips 66 FCC. High NO_2 concentrations in the exhaust gas increases the rate of amine degradation to N-amines, and therefore the lower the overall NOx release, the less N-amines will be generated by this mechanism.

6C.1.23 Emission of NOx from the VPI Site are considered to be sufficiently low so as not to adversely affect the generation of N-amines within the solvent. The Phillips 66 FCC however, requires the addition of Selective Catalytic Reduction (SCR) abatement to reduce the NO_2 within the exhaust gas, prior to it entering the PCC plant. In addition, the Wet Gas Scrubber included as part of the Proposed Phillips 66 Development will reduce sulphur dioxide (SO_2) emissions and therefore reduce degradation of the solvent.

6C.1.24 The solvent inventory for both Sites will be managed to minimise the formation and release of degradation products through continuous bleed and regeneration of solvent within the process.

6C.1.25 It is considered that through best practice storage and management measures for the amine solvent, that its degradation within the PCC plants can be minimised, and this requirement will be managed through the Environmental Permits for the Sites. As a result, the direct emissions of N-amines into the atmosphere from the PCC plants absorber stacks, are expected to be at very low levels (i.e. in the parts per billion (ppb) range).

Indirect N-Amine Emission

6C.1.26 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.

6C.1.27 The amine degradation process in the atmosphere requires the presence of either an OH or a nitrate (NO_3) radical. The primary method for formation of N-amines in the atmosphere is a two-step process:

- an OH radical (daytime) or an NO_3 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 an NO group to form a nitrosamine, or an NO_2 group to form a nitramine.

6C.1.28 A variety of competing reactions 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 NO_2 and O_2 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.

6C.1.29 During daylight hours, atmospheric amine degradation is initiated by reaction with the OH radical (generated by photolysis of water (H_2O) by the action of ultraviolet (UV) 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 (O_3) to form NO_2 and subsequent reaction of NO_2 with O_3 to form the NO_3 radical; amine degradation is then initiated by reaction with the NO_3 radical to form N-amines. The nitrate radical is rapidly photolyzed (decomposed or separated by the action of light) in daylight and does not represent a likely reaction pathway during the daytime.

6C.1.30 The concentration of NOx and O_3 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.

6C.1.31 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%.

6C.1.32 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 6C.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	Nielson *et al.* 2011
Dimethylamine (DMA)	0.38 - 0.42	CERC 2012
Piperazine (Pz)	0.09	Onel *et al.* 2015

6C.1.33 As can be seen in Table 6C.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. Therefore, as other competing reactions may also occur, the likelihood of forming N-amine must also be lower than for a secondary amine; however, there is limited published data for tertiary amine reaction constants.

6C.1.34 Shell has provided specific branching ratios for the amines within their solvent, which have been determined by Professor Claus Nielson of the University of Oslo, the leading authority on amine atmospheric chemistry, through comparison of the characteristic of the amines within the Shell CANSOLV solvent with published data for other amine species with similar characteristics. Shell has provided data on two amine species present in the release, herein referred to as Amine 1 and Amine 2.

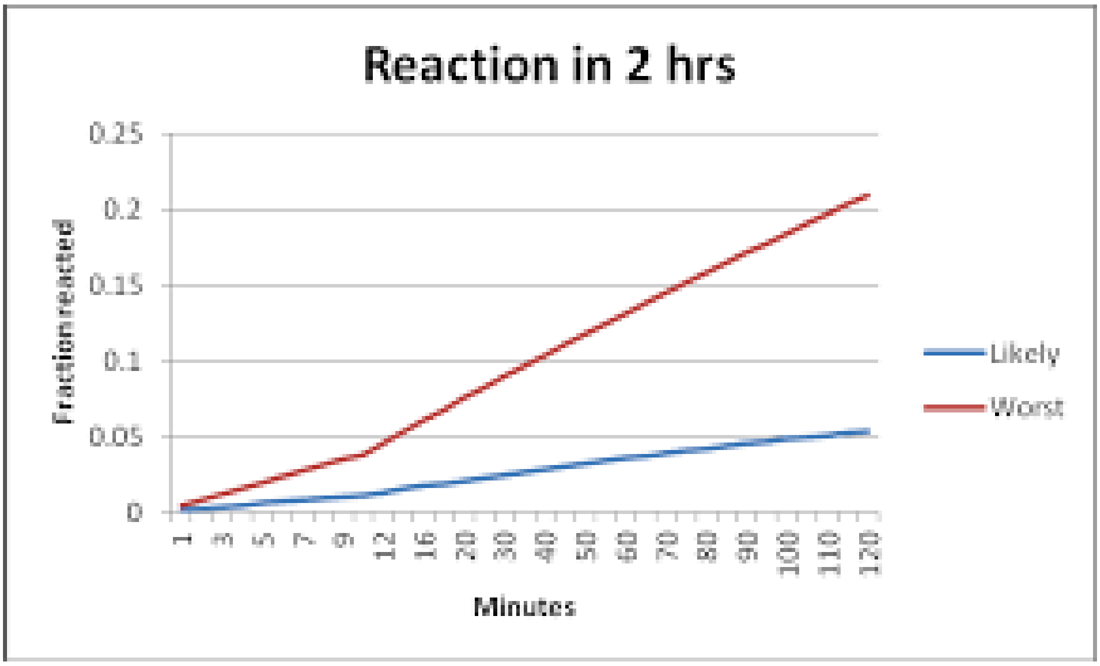
6C.1.35 In addition to the branching ratio, the concentration of ambient NOx also influences the generation of N-amines from amines. From laboratory tests, it is known that when more NOx is present, more amines are converted into N-amines. This function is called the ‘amino radical/ NO_2 reaction rate constant [k4]’.

6C.1.36 In the flue gas emitted from the PCC plants, the NOx is composed of around 90-95% NO to 5-10% NO_2. Once in the atmosphere, the NO will react with OH to form NO_2. The reaction of OH is preferential to NO rather than the 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 stacks. This is therefore considered to be very conservative.

6C.1.37 The time delay of the amine reaction is described by the work carried out by Tonnesen (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 Plate 6C.1.

6C.1.38 The fact that this time-delay is not taken into account in the ADMS amines chemistry module therefore is considered to result in an over-prediction in the process contributions predicted by the model.

Plate 6C.1: Conversion of Amines to N-Amine in the Atmosphere Over Time



6C.1.39 At night-time the NO_3 radical is formed from the reaction of O_3 with NO, and then NO_2. Therefore, the reaction of NO to NO_2 is likely to be preferential to the reaction of NO_2 to NO_3 or NO_3 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.

6C.1.40 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.

6C.6 Assessment Methodology

Dispersion Model Selection

6C.1.41 As stated previously, the assessment of emissions from the Proposed Developments has been undertaken using the advanced dispersion model ADMS (version V5.2.2), supplied by 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.

6C.1.42 CERC has 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 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 OH radicals in the atmosphere.

6C.1.43 The ADMS Amines chemistry module is currently the only commercially available modelling software for evaluating the potential impacts of amines and amine degradation products. 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.

6C.1.44 The module is based on established science considering published research on mechanisms of formation of toxic compounds. Although the module has not been validated, the ADMS air dispersion modelling algorithms are continually validated against real world situations, field campaigns and wind tunnel experiments.

6C.1.45 The Environment Agency's AQMAU recognise in their report (Environment Agency, 2021) that *"There are various aspects of the current version of the module that suggest the estimation of toxic products might be conservative, however, the level of uncertainties in other input parameters can counteract this."*

6C.1.46 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 individually for each component, and therefore any reactions between the amine components themselves are not accounted for.

6C.1.47 The module requires the amine-specific branching ratio and the kinetic constants, k values (specific to each subsequent reaction rate). The 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.

6C.1.48 Shell has provided specific k values for the two amines within the CANSOLV solvent, which again have been determined by Professor Claus Nielson of the University of Oslo through comparison of the characteristic of the amines within the Shell solvent with published data for other amine species with similar characteristics. This work was carried out in 2012, and therefore it is recognised that further information on the kinetic constants has been carried out since this time, and therefore those for the Shell solvent are currently under review by the University of Oslo. This review has not been completed at the time of writing.

Dispersion Model Input Parameters

6C.1.49 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 6C.2.

Table 6C.2: Amine Information for ADMS Model Set-Up

Parameter	Units	Notes
Amines Release	g/s	Emission concentrations for Amine 1 and Amine 2 present in the solvent have been provided by Shell.
Direct N-amine Release	g/s	Emission concentrations for N-amine 1 and N-amine 2 present in the solvent have been provided by Shell.
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 constants for Amine 1 and 2 provided by Shell for the reaction of the amine with the hydroxyl radical ('●') (OH●).
k2 = Amino radical/O_2 reaction rate constant	ppb/s	Rate constants for Amine 1 and 2 provided by Shell for the reaction of the amine● with O_2 (to form imine).
k3 = Rate constant for formation of nitrosamine	ppb/s	Rate constants for Amine 1 and 2 provided by Shell for formation of nitrosamine from amine● and NO.
k4a = Rate constant for formation of nitramine	ppb/s	Rate constants for Amine 1 and 2 provided by Shell for formation of nitramine from amine● and NO_2
k4 = Amino radical/NO_2 reaction rate constant	ppb/s	Rate constants for Amine 1 and 2 provided by Shell for the reaction of the amine● with NO_2 (to form imine or nitramine).

Parameter	Units	Notes
Branching Ratio	dimensionless	Branching ratios s for Amine 1 and 2 provided by Shell 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 for the Sites' location. Site specific value calculated following the 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 South Killingholme automatic monitor for the years of meteorological data used in the model.
NO$_2$ baseline	µg/m^3	
Ozone Baseline	µg/m^3	Hourly values obtained for Hull Freetown automatic monitor (being the closest site with O$_3$ data available) for the years of meteorological data used in the model

6C.1.50 These parameters are entered into an ADMS Additional Information (AAI) file, which characterises the amine chemistry for the amine or N-amine species being assessed.

6C.1.51 The specific input parameters used in the model are detailed in Table 6C.3. Shell has provided data on the two amine species present in the release, therefore these two species have been modelled separately. The specific Shell rate constants are considered to be subject to commercial confidentiality, and therefore are not provided, however where values are the same as those defined widely in literature, these have been provided.

6C.1.52 It is only possible to model one source with the Amines Chemistry module, and therefore the emissions from the two Proposed VPI Development PCC plant stacks have been combined into a single source for the model.

Table 6C.3: Amines Chemistry Module Model Set-Up

Parameter	Units	Amine 1	Amine 2	Source
VPI Amines	mg/Nm^3	0.27	0.023	Shell
	g/s	0.45	0.038	
Phillips 66 Amines	mg/Nm^3	1.04	0.052	
	g/s	0.077	0.0039	
VPI direct N-amine (assumed to be NDMA, as a worst case)	mg/Nm^3	0.0009	0.0004	Shell
	g/s	0.001	0.0007	
Phillips 66 direct N-amine (assumed to be NDMA, as a worst case)	mg/Nm^3	0.002	0.001	
	g/s	0.0001	0.00005	

Parameter	Units	Amine 1	Amine 2	Source
Ratio of NO_X to NO_2 in the exhaust gas	%	5 – 10%	5 – 10%	Typical range in combustion emissions
k1 = Amine/OH radical reaction rate constant	ppb/s	Considered to be commercially sensitive.		
k2 = Amino radical/O_2 reaction rate constant	ppb/s	Considered to be commercially sensitive.		
k3 = Rate constant for formation of nitrosamine	ppb/s	Considered to be commercially sensitive.		
k4a = Rate constant for formation of nitramine	ppb/s	7.82e-3	7.82e-3	CERC (2012) Manzoor (2014)
k4 = Amino radical/NO_2 reaction rate constant	ppb/s	Considered to be commercially sensitive.		
Branching Ratio	dimensionless	0.37	0.18	CERC (2012) Manzoor (2014) Lee & Wexler (2013)
Ratio of J (nitrosamine) to NO_2	dimensionless	0.34	0.34	Nielson (2010)
OH concentration constant c	Seconds	0.00101	0.00101	Specifically derived for the Sites location following CERC methodology.

6C.1.53 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 a higher process contribution (as shown in Annex 6C.A of this Appendix). The dilution and entrainment option has therefore been included for the main assessment for conservatism.

6C.1.54 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 not considered to be appropriate for the Shell amines, as advised by Shell.

6C.1.55 The stack parameters for both Proposed Developments, meteorology and structural parameters used in the dispersion modelling of N-amines are the same as those for other pollutants emitted from the PCC plant, and the underlying dispersion modelling approach is set out in Technical Appendix 6B: Air Quality – Operational Phase (ES Volume II).

Direct N-Amine Emissions

6C.1.56 Direct N-amine emissions have been assumed to occur at the concentration provided by Shell for the Proposed VPI Development and the Proposed Phillips 66 Development, as detailed in Table 6C.3. The Amines chemistry module has been used to determine the predicted process contributions of the Direct N-Amine emissions, taking account the atmospheric process that will occur to the N-amines following their release.

Indirect N-Amine Emissions

6C.1.57 Indirect N-amine emissions have been modelled as an amine release from the Proposed VPI Development and the Proposed Phillips 66 Development, as detailed in Table 6C.3.

6C.7 Model Results

Direct N-Amine Impacts

6C.1.58 The results of the Direct N-amine release emissions are shown in Table 6C.4 – Table 6C.6, and include the contributions of N-amines associated with the two amine species present within the emissions from the PCC plants. The results at the worst-case receptor are shown in **bold** type.

6C.1.59 The locations of the receptors are shown in Figure 6.1 (ES Volume III). The receptors are selected to be representative of residential dwellings in the area around the Proposed Developments. (OR = Operational Receptor).

Direct N-Amine Impacts Proposed VPI Development

Table 6C.4: VPI Future - Annual Average N-Amine Concentrations as a Result of Direct N-Amine Releases

Receptor	AQAL (ng/m^3)	Nitrosamine PC (ng/m^3)	Nitramine PC (ng/m^3)	Total N-Amines PC (ng/m^3)	PC/AQAL %
OR1	0.2	0.006	0.0002	0.006	3%
OR2		**0.045**	**0.0013**	**0.046**	**23%**
OR3		0.003	0.0003	0.003	1%
OR4		0.003	0.0005	0.004	2%
OR5		0.005	0.0007	0.006	3%
OR6		0.007	0.0008	0.007	4%
OR7		0.008	0.0011	0.010	5%
OR8		0.012	0.0013	0.013	7%
OR9		0.011	0.0010	0.012	6%
OR10		0.010	0.0013	0.012	6%
OR11		0.010	0.0008	0.011	5%
OR12		0.004	0.0004	0.004	2%
OR13		0.003	0.0005	0.004	2%

PC = Process Contribution, AQAL = Air Quality Assessment Level

6C.1.60 The results for the total direct N-amine emission for the Proposed VPI Development indicates that PCs at receptor locations are well within the AQAL for NDMA. The worst-case direct N-amine impacts are experienced at receptor OR2 – a single residential property on Station Road, however as detailed in Chapter 6: Air Quality (ES Volume I), this property is currently vacant, owned by Able Humber Ports Limited and proposed to be demolished as part of the proposed AMEP Enabling Works. Impacts at the next worst-case receptor are considerably lower, at only 7% of the AQAL.

Direct N-Amine Impacts Proposed Phillips 66 Development

6C.1.61 The results for the Proposed Phillips 66 Development are shown in Table 6C.5.

Table 6C.5: Phillips 66 Future - Annual Average N-Amine Concentrations as a Result of Direct N-Amine Releases

Receptor	AQAL (ng/m³)	Nitrosamine PC (ng/m³)	Nitramine PC (ng/m³)	Total N-Amines PC (ng/m³)	PC/AQAL %
OR1	0.2	0.008	0.0003	0.008	4%
OR2		0.006	0.0003	0.006	3%
OR3		0.002	0.0001	0.002	1%
OR4		0.002	0.0001	0.002	1%
OR5		0.002	0.0001	0.002	1%
OR6		0.004	0.0001	0.004	2%
OR7		0.007	0.0003	0.007	4%
OR8		**0.009**	**0.0003**	**0.009**	**5%**
OR9		0.008	0.0002	0.008	4%
OR10		0.007	0.0003	0.007	4%
OR11		0.004	0.0001	0.004	2%
OR12		0.002	0.0001	0.002	1%
OR13		0.001	0.0001	0.001	1%

PC = Process Contribution, AQAL = Air Quality Assessment Level

6C.1.62 The results for the total direct N-amine emission for the Proposed Phillips 66 Development indicates that PCs at receptor locations are well within the AQAL for NDMA. The worst-case direct N-amine impacts are experienced at receptor OR8 and represent 5% of the NDMA AQAL applied to the assessment.

Direct N-Amine Impacts for the In-Combination Proposed Developments

6C.1.63 The in-combination impacts from the Proposed Developments operating concurrently are shown in Table 6C.6. These are simply the Proposed VPI Development's impacts and the Proposed Phillips 66 Development's impacts summed, as it is not possible to model more than one source with the ADMS amines chemistry module.

Table 6C.6: In-Combination Future - Annual Average N-Amine Concentrations as a Result of Direct N-Amine Releases

Receptor	AQAL (ng/m³)	Nitrosamine PC (ng/m³)	Nitramine PC (ng/m³)	Total N-Amines PC (ng/m³)	PC/AQAL %
OR1	0.2	0.014	0.001	0.015	7%
OR2		**0.051**	**0.002**	**0.052**	**26%**
OR3		0.005	0.000	0.005	3%
OR4		0.005	0.001	0.006	3%
OR5		0.008	0.001	0.009	4%
OR6		0.010	0.001	0.011	6%
OR7		0.015	0.001	0.017	8%
OR8		0.021	0.002	0.022	11%
OR9		0.019	0.001	0.020	10%
OR10		0.017	0.002	0.019	10%
OR11		0.014	0.001	0.015	7%

Receptor	AQAL (ng/m^3)	Nitrosamine PC (ng/m^3)	Nitramine PC (ng/m^3)	Total N-Amines PC (ng/m^3)	PC/AQAL %
OR12		0.006	0.001	0.006	3%
OR13		0.005	0.001	0.005	3%

PC = Process Contribution, AQAL = Air Quality Assessment Level

6C.1.64 The results for the total direct N-amine emission for the in-combination Proposed Developments indicates that PCs at receptor locations are well within the AQAL for NDMA. As with the Proposed VPI Development results shown in Table 6C.4, the worst-case direct N-amine impacts are experienced at receptor OR2 – a single residential property on Station Road, which is unoccupied and proposed to be demolished. Impacts at the next worst-case receptor represent 11% of the NDMA AQAL.

6C.1.65 This assessment assumes that the whole of the N-amine direct emission from Proposed Developments occurs as NDMA, when it is considered that the N-amines formed from the Shell solvent are much less toxic than this nitrosamine species. It is therefore considered that the PCs presented within Table 6C.4 – Table 6C.6 represent a very much worst-case assessment of the potential impact from the direct N-amine releases from the Proposed Developments.

Indirect N-Amine Impacts

6C.1.66 The predicted modelling results of the In-direct N-amine concentrations that occur as a consequence of the amine emissions from the Proposed Developments are shown in Table 6C.7 – Table 6C.9.

Indirect N-Amine Impacts Proposed VPI Development

Table 6C.7: VPI Future - Annual Average Indirect N-Amine Concentrations as a Result of Amine Releases

Receptor	AQAL (ng/m^3)	Nitrosamine PC (ng/m^3)	Nitramine PC (ng/m^3)	Total N-Amines PC (ng/m^3)	PC/AQAL %
OR1	0.2	0.008	0.009	0.017	9%
OR2		**0.035**	0.051	0.086	43%
OR3		0.006	0.017	0.023	12%
OR4		0.009	0.026	0.035	17%
OR5		0.015	0.039	0.053	27%
OR6		0.018	0.042	0.059	30%
OR7		0.024	0.055	0.079	40%
OR8		0.029	0.063	0.092	46%
OR9		0.027	0.054	0.082	41%
OR10		0.029	**0.069**	**0.098**	**49%**
OR11		0.025	0.041	0.066	33%
OR12		0.009	0.020	0.029	14%
OR13		0.008	0.023	0.031	15%

PC = Process Contribution, AQAL = Air Quality Assessment Level

6C.1.67 The results for the total indirect N-amine emission for the Proposed VPI Development indicates that PCs at receptor locations are higher than those for the direct N-amine emission, but that they are still well within the AQAL for NDMA. The impacts at worst case receptor occur at OR10, and represented 49% of the NDMA AQAL.

Indirect N-Amine Impacts Proposed Phillips 66 Development

6C.1.68 The predicted modelling results of the indirect N-amine concentrations for the Proposed Phillips 66 Development are shown in Table 6C.8.

Table 6C.8: Phillips 66 Future - Annual Average In-direct N-Amine Concentrations as a Result of Amine Releases

Receptor	AQAL (ng/m^3)	Nitrosamine PC (ng/m^3)	Nitramine PC (ng/m^3)	Total N-Amines PC (ng/m^3)	PC/AQAL %
OR1	0.2	0.010	0.025	0.034	17%
OR2		0.006	0.021	0.026	13%
OR3		0.002	0.009	0.010	5%
OR4		0.002	0.007	0.009	4%
OR5		0.003	0.009	0.012	6%
OR6		0.005	0.013	0.018	9%
OR7		0.013	0.031	0.045	22%
OR8		**0.016**	**0.032**	**0.048**	**24%**
OR9		0.011	0.021	0.032	16%
OR10		0.012	0.031	0.043	22%
OR11		0.005	0.012	0.018	9%
OR12		0.002	0.007	0.009	4%
OR13		0.001	0.006	0.007	4%

PC = Process Contribution, AQAL = Air Quality Assessment Level

6C.1.69 The results for the total indirect N-amine emission for the Proposed Phillips 66 Development indicates that PCs at receptor locations are well within the EAL for NDMA. The worst-case receptor, OR8, is predicted to have a PC that represents 24% of the NDMA AQAL.

Indirect N-Amine Impacts In-Combination Proposed Developments

6C.1.70 The in-combination impacts from the Proposed Developments operating concurrently are shown in Table 6C.9. Again, the in-combination results are the Proposed VPI Development's impacts and the Proposed Phillips 66 Development's impacts summed, as it is not possible to model more than one source with the Amines Chemistry module.

Table 6C.9: In-Combination Future - Annual Average In-direct N-Amine Concentrations as a Result of Amine Releases

Receptor	AQAL (ng/m^3)	Nitrosamine PC (ng/m^3)	Nitramine PC (ng/m^3)	Total N-Amines PC (ng/m^3)	PC/AQAL %
OR1	0.2	0.017	0.034	0.051	26%
OR2		0.041	0.072	0.113	56%
OR3		0.007	0.026	0.033	17%
OR4		0.011	0.033	0.044	22%
OR5		0.017	0.048	0.065	33%
OR6		0.023	0.054	0.077	39%
OR7		0.038	0.086	0.124	62%
OR8		**0.046**	**0.095**	**0.140**	**70%**
OR9		0.039	0.075	0.114	57%
OR10		0.041	0.100	0.141	70%

Receptor	AQAL (ng/m^3)	Nitrosamine PC (ng/m^3)	Nitramine PC (ng/m^3)	Total N-Amines PC (ng/m^3)	PC/AQAL %
OR11		0.031	0.053	0.084	42%
OR12		0.011	0.027	0.037	19%
OR13		0.010	0.028	0.038	19%

PC = Process Contribution, AQAL = Air Quality Assessment Level

6C.1.71 The results for the total indirect N-amine emission for the in-combination Proposed Developments indicates that PC at receptor locations remain below the AQAL for NDMA. The worst-case In-direct N-amine impacts are experienced at receptor OR8 and represent 70% of the NDMA AQAL.

6C.1.72 Again, this assessment assumes that the N-amine PCs occur as NDMA, when it is considered that the N-amine formed from the Shell solvent are much less toxic than this. It is therefore considered that the PCs within Table 6C.7 - Table 6C.9 represent a worst-case assessment of the potential impact from the direct N-amine releases from the Proposed Developments.

Total N-Amine Impacts Proposed VPI Development

6C.1.73 The overall impact of the Direct N-amine release and the In-Direct N-amine impacts need to be considered together and compared with the AQAL.

Total N-Amine Impacts Proposed VPI Development

Table 6C.10: VPI Future – Total Annual Average N-Amine Concentrations

Receptor	AQAL (ng/m^3)	Nitrosamine PC (ng/m^3)	Nitramine PC (ng/m^3)	Total N-Amines PC (ng/m^3)	PC/AQAL %
OR1	0.2	0.014	0.009	0.023	12%
OR2		**0.080**	**0.052**	**0.133**	**66%**
OR3		0.008	0.018	0.026	13%
OR4		0.012	0.026	0.039	19%
OR5		0.020	0.039	0.059	30%
OR6		0.024	0.043	0.067	33%
OR7		0.033	0.056	0.089	44%
OR8		0.041	0.064	0.105	53%
OR9		0.039	0.055	0.094	47%
OR10		0.039	0.070	0.110	55%
OR11		0.035	0.042	0.077	38%
OR12		0.013	0.020	0.033	16%
OR13		0.012	0.023	0.035	17%

PC = Process Contribution, AQAL = Air Quality Assessment Level

6C.1.74 The results for the total N-amine impacts for the Proposed VPI Development indicates that PCs at receptor locations are well within the AQAL for NDMA. The impacts at the worst-case receptor (OR2, which is vacant and proposed to be demolished) represent 74% of the NDMA AQAL, or 63% at the next worst-case receptor (OR10).

Total N-Amine Impacts Proposed Phillips 66 Development

6C.1.75 The total N-amine results for the Proposed Phillips 66 Development are shown in Table 6C.11.

Table 6C.11: Phillips 66 Future - Total Annual Average N-Amine Concentrations

Receptor	AQAL (ng/m³)	Nitrosamine PC (ng/m³)	Nitramine PC (ng/m³)	Total N-Amines PC (ng/m³)	PC/AQAL %
OR1	0.2	0.018	0.025	0.043	21%
OR2		0.011	0.021	0.032	16%
OR3		0.004	0.009	0.013	6%
OR4		0.004	0.007	0.011	6%
OR5		0.005	0.009	0.014	7%
OR6		0.009	0.013	0.021	11%
OR7		0.020	0.032	0.052	26%
OR8		**0.025**	**0.032**	**0.057**	**29%**
OR9		0.019	0.021	0.040	20%
OR10		0.019	0.031	0.051	25%
OR11		0.009	0.013	0.022	11%
OR12		0.004	0.007	0.011	5%
OR13		0.003	0.006	0.008	4%

PC = Process Contribution, AQAL = Air Quality Assessment Level

6C.1.76 The results for the total N-amine impacts for the Proposed Phillips 66 Development indicates that PCs at receptor locations are well within the AQAL for NDMA. The worst-case receptor, OR8, is predicted to have a PC that represents 29% of the NDMA AQAL.

Total N-Amine Impacts In-Combination Proposed Developments

6C.1.77 The in-combination impacts from the Proposed Developments operating concurrently are shown in Table 6C.12. Again, the in-combination results are the Proposed VPI Development's impacts and the Proposed Phillips 66 Development's impacts summed, as it is not possible to model more than one source with the ADMS amines chemistry module.

Table 6C.12: In-Combination Future - Total Annual Average N-Amine Concentrations

Receptor	AQAL (ng/m³)	Nitrosamine PC (ng/m³)	Nitramine PC (ng/m³)	Total N-Amines PC (ng/m³)	PC/AQAL %
OR1	0.2	0.032	0.034	0.066	33%
OR2		**0.092**	**0.073**	**0.165**	**82%**
OR3		0.012	0.026	0.039	19%
OR4		0.016	0.034	0.050	25%
OR5		0.025	0.049	0.074	37%
OR6		0.033	0.055	0.088	44%
OR7		0.053	0.088	0.141	70%
OR8		0.066	0.096	0.162	81%
OR9		0.057	0.077	0.134	67%
OR10		0.059	0.101	0.160	80%
OR11		0.044	0.054	0.099	49%
OR12		0.016	0.027	0.044	22%
OR13		0.014	0.029	0.043	22%

PC = Process Contribution, AQAL = Air Quality Assessment Level

6C.1.78 The results for the total N-amine emission for the in-combination Proposed Developments indicates that PC at receptor locations remain below the AQAL for NDMA. The worst-case total N-amine impacts are experienced at receptor OR2 (vacant and proposed to be demolished) and represent 82% of the NDMA AQAL, or 81% at the next worst impacted receptor.

6C.1.79 As previously stated, this assessment assumes that the N-amine PCs occur as NDMA, when it is considered that the N-amine formed from the Shell solvent are much less toxic than this. It is therefore considered that the PCs within Table 6C.10 - Table 6C.12 represent a worst-case assessment of the potential impact from the total N-amine releases from the Proposed Developments.

6C.8 Assessment Limitations and Assumptions

6C.1.80 This section outlines the potential limitations associated with the dispersion modelling assessment. Where assumptions have been made, this is also detailed here.

6C.1.81 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.

6C.1.82 The Environment Agency recognises that the level of uncertainty within the ADMS amines chemistry model is high (Environment Agency, 2021), 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. The main model uncertainties are set out below.

No Time-Delay in N-amine Formation

6C.1.83 The amines chemistry module does not account for the time delay in the initiation of the amine degradation (Tonnesen, 2011). This time delay indicates that only around 15% of the amines that react to form N-amines would have done so within 1 hour, as a worst-case. 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 1km from the source 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 NOx 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 reaction completion at the point of calculation, and therefore it is considered that this is overly conservative.

No Interaction Between Different Amine Species

6C.1.84 The amines chemistry module does not allow for any interactions between different amines/ 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.

No Consideration of Other Potential Radical Species Present

6C.1.85 Other reactions with chlorine atoms, nitrate radicals are not taken into account, although these are considered to be less significant.

No Further Degradation Assumed after the Initial Reactions

6C.1.86 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, as discussed above.

Only Daytime Reactions are Considered

6C.1.87 The amines chemistry module accounts for diurnal variation in the photolysis (OH) reaction but does not account for the slower NO_2 degradation reaction that occurs during night-time.

No Consideration of Phase Partitioning

6C.1.88 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, however it is considered that the solubility of amines will put them out of the gas phase (Nielsen et al. 2012), therefore decreasing the amount of amines in the ambient air.

6C.1.89 In order to ensure a conservative assessment, and therefore to minimise the likelihood of under-estimating the impacts of N-amines from the absorber stacks, the following conservative assumptions have been made within the assessment:

- the operational Proposed Developments have 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 Humberside Airport meteorological station for the years 2017 to 2021 inclusive, with the highest result being reported for all years assessed; 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.

6C.9 Conclusions

6C.1.90 An assessment of the potential impacts associated with direct N-amine releases and the impact of atmospheric degradation of the amines released from the PCC plant stacks has been carried out for the Proposed Developments.

6C.1.91 The assessment methodology contains numerous conservative assumptions, and it is acknowledged that there is a high level of uncertainty in the use of the ADMS amines chemistry module.

6C.1.92 The 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 combined impacts of both the direct and indirect emission processes, and of both Proposed Developments. The sensitivity analysis of the model input parameters, presented in Annex 6C.A, supports this conclusion and supports the conservative nature of the assessment that has been carried out.

6C.10 References

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6C.11 Annex 6C.A – Model Sensitivity

A.1 Overview

6C.1.93 The sensitivity of the model to various input parameters has been tested and is reported in this annex. The parameters that have been varied in the model input include:

- sensitivity to the meteorological data and background data used in the model, comparing the maximum results presented to the results for the meteorological year returning the lowest results;
- the main model assumed a percentage of NO_2 within the NO_x emission of 5%. Sensitivity of the model has been tested at 10%;
- the main model was run with dilution and entrainment turned on. Sensitivity of the model has been tested with no dilution and entrainment; and
- an alternative constant value for k2 has been used in the model, which was recently advised for numerous amine species by the Carbon Capture and Storage Association (CCSA, 2021) in conjunction with Professor Claus Nielson. Although its suitability for the Shell solvent has not been confirmed, this is currently under discussion with the University of Oslo, however was not resolved at the time of writing.

6C.1.94 The results of the sensitivity testing are shown in Table 6C.A1 and 6C.A2 and represent the PCs of nitrosamine and nitramine combined as a percentage against the AQAL.

Table 6C.A1: Sensitivity of PC/ AQAL Results at the Worst-case Receptor OR2 for the Proposed VPI Development

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 %
Results presented in main assessment (Table 6C.10)	0.2	**0.080**	**0.052**	**0.132**	**66%**
Meteorological data (lowest year)		0.061	0.037	0.098	49%
NOx to NO_2 Ratio 10%		0.079	0.057	0.135	68%
No dilution and entrainment		0.062	0.062	0.124	62%
Alternative k2 Value CCSA		0.069	0.033	0.102	51%

Table 6C.A2: Sensitivity of PC/AQAL Results at the at the Worst-case Receptor OR8 for the Proposed Phillips 66 Development

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 %
Results presented in main assessment (Table 6C.11)	0.2	**0.025**	**0.032**	**0.057**	**29%**
Meteorological data		**0.008**	**0.008**	**0.016**	**8%**
NOx to NO_2 Ratio 10%		0.024	0.033	0.058	29%
No dilution and entrainment		0.015	0.031	0.046	23%
Alternative k2 Value CCSA		0.020	0.018	0.038	19%