ANNEX F – FEED 1 CONTRACTOR SUPPORTING INFORMATION FOR THE ASSESSMENT OF AMINES AND AMINE DEGRADATION PROCUCTS

This Annex provides further information provided by the FEED 1 contractor in relation to:

- Stack emissions of the solvent and solvent degradation species
- The derivation of Environmental Assessment Levels (EALs) relevant to the emitted solvent and solvent degradation species
- Kinetic data relevant to the emitted amines for use in the ADMS amine chemistry module

1. Amine and Amine Degradation Species Emitted from the carbon capture plant

1.1 Virgin (Starting) Solvent Amine Components

The FEED1 Contractor solvent is used as an amine aqueous solution, comprising the amine components shown in Table 1 together with the emission concentrations derived from FEED1 Contractor's simulated derivation verified by past internal measurement campaigns.

Table 1: FEED1 Contractor Solvent Amine Components

Abbreviation	Chemical name	CAS number	Emission Concentrations (mg/Nm^3)
AMP (Amine 1)	2-amino-2-methyl-1-propanol	124-68-5	0.99
PZ (Amine 2)	Piperazine	110-85-0	0.01

1.2 Chemistry and Degradation Product Emissions

The solvent chemistry leading to the formation of degradation compounds potentially emitted to the atmosphere involves mainly the following processes:

- Oxidative degradation
- Formation of nitrosamines and nitramines by reaction with NO_x

The list of expected degradation products and emission rates is provided in Table 2, based on from FEED1 Contractor's simulated derivation verified by past internal measurement campaigns.

Table 2: FEED1 Contractor Solvent Degradation Products

Group	Abbreviation	Chemical name	CAS number	Emission Concentrations (mg/Nm^3)
Amines	MA	Methylamine	74-89-5	<0.005
	DMA	Di-methylamine	124-40-3	<0.001
	DiEA	Di-ethyl-amine	109-89-7	<0.0001
	EA	Ethylamine	75-04-7	<0.01
Ammonia	NH_3	Ammonia	7664-41-7	1
Aldehydes	CH_2O	Formaldehyde	50-00-0	<3
	C_2H_4O	Acetaldehyde	75-07-0	<6
Ketones	C_3H_6O	Acetone	67-64-1	<8
Nitrosamines	NMAMP (Nitrosamine 1)	N-nitroso-2-methylamino-2-methyl-1-propanol	Not available	0 (Not detected)
	NPZ (Nitrosamine 2)	N-nitrosopiperazine	5632-47-3	Sum of 0.00495
	DNPZ (Nitrosamine 2)	Dinitrosopiperazine	140-79-4	
Nitramines	Nitro-AMP (Nitramine 1)	2-(nitro-amino)-2-methyl-1-propanol	1239666-60-4	0.0000495
	Nitro-PZ (Nitramine 2)	N-Nitropiperazine	42499-41-2	0.0000005

Note that the above amine emissions are indicative and for the purposes of air dispersion modelling, the FEED 1 contractor has provided an updated total amine emissions concentration of 1 mg/Nm^3 inclusive of both the solvent and solvent degradation amine components. For assessment purposes the total amines have been modelled based on a 99% to 1% split between Amine 1 and Amine 2. This recognises that the four degradation amine components are emitted only in trace quantities.

2. Environmental Assessment Levels for Amines and Amine Degradation Species

Among the components that can be released from the absorber stack, amines and nitrosamines are of special interest, due to the potential carcinogenicity of nitrosamines. These can be emitted directly or formed in the atmosphere from the emitted amines.

This section describes the proposed methodology to derive indicative EALs for the amines and nitrosamines emitted from a carbon capture plant using the from FEED1 Contractor solvent. Amines and nitrosamines/ nitramines (N-amines) are considered separately.

2.1 Amines

2.1.1 Reference: Monoethanol amine (MEA)

The Environment Agency (EA) have derived EALs for monoethanol amine (MEA)[1,2]:

- Maximum 1-hour mean: 400 µg/m^3
- 24-hour mean (long term): 100 µg/m^3

This is based upon a No Observed Adverse Effect Concentration (NOAEC) value of 10 mg/m^3. To derive the EAL, a safety factor of 25 has been applied to derive the 1-hour EAL, and a safety factor of 100 has been applied to derive the 24-hour EAL.

MEA is a strong respiratory, ocular, and skin irritant, there are equivocal indications that MEA could have skin and respiratory sensitizing properties, but MEA is currently not classified for these endpoints (ECHA Registration Dossier MEA).

For derivation of the short-term EAL, the critical effect considered is localized respiratory irritation. The pivotal study for derivation of a short-term EAL is the sub-acute duration rodent study submitted as evidence in support of an application under REACH (HSE 2016) with a No Observed Adverse Effect Concentration (NOAEC) of 10 mg/m^3. No correction for continuous exposure was applied because irritation is considered a concentration-dependent effect.

For derivation of the EALs, the critical health effects from long-term inhalation exposure are considered to be respiratory irritation and neurobehavioral toxicity. The pivotal study for derivation of a long-term EAL is the same sub-acute rodent study used for the short-term EAL (HSE 2016). No Uncertainty Factor (UF) for sub-acute to chronic duration is required because irritation is considered a concentration-based effect. An additional UF was included to take account of uncertainty over long-term effects.

The monoethanol amine REACH dossier also contains Derived No Effect Levels for the general population for local and systemic effects, and these are 280 and 180 µg/m^3, respectively. These are in the same order of magnitude as the EA's derived EALs.

2.1.2 Piperazine (FEED1 Contractor Amine 2)

The Environment Agency (EA) have derived an EAL for Piperazine[1,3]

- 24-hour mean (long term): 15 µg/m^3

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[1] Air emissions risk assessment for your environmental permit, updated 21 July 2025, https://www.gov.uk/guidance/air-emissions-risk-assessment-for-your-environmental-permit

[2] Environment Agency (2021)Consultation outcome, Appendix C: summary of toxicological evidence for MEA and NDMA https://www.gov.uk/government/consultations/environmental-assessment-levels-eals-used-in-air-emissions-risk-assessments/public-feedback/appendix-c-summary-of-toxicological-evidence-for-mea-and-ndma

[3] Environment Agency (2025) Environmental Assessment Level (EAL) Support Document, Dossier of substances included within our 2025 EAL Consultation, Version 1. https://consult.environment-agency.gov.uk/environment-and-business/development-of-environmental-assessment-levels-eal/supporting_documents/EAL%20Tech%20Summaries.docx

A long-term EAL of 15 µg/m^3 as a 24-hour mean was derived from a clinical case study (Belloni and Rizzoni, 1967 cited by ECB 2005[4]), where abnormal electroencephalogram changes were observed in children prescribed piperazine hexahydrate at a dose of 35 mg/kg body weight/day piperazine base for five days. ECB (2005) regarded the approximate 30 mg/kg body weight/day as an effect level as it was based on the therapeutic dose. This has been converted to a Lowest Observable Adverse Effect Concentration (LOAEC) of 45 mg/m3 by assuming a young child inhales 10 m^3 per day and weighs 15 kg. A total UF of 3,000 was applied (a factor of 10 for intraspecies variation, a factor of 10 for extrapolation from LOAEC to NOAEC, a factor of 10 to extrapolate to chronic exposures, and a factor of 3 for the quality of the database). ECB (2005) identified the importance of neurotoxicity in clinical case studies in humans, which were not observed in rodent laboratory studies. There is a lack of dose-response information. This EAL is considered protective of other toxic effects and potential carcinogenicity resulting from in vivo conversion of PZ to the corresponding nitrosamine.

A short-term EAL was not recommended due to constraints for practical compliance.

2.1.3 FEED1 Contractor Amine 1

Section 1.1 describes the amines used in the FEED1 Contractor solvent.

The main amine present in the absorber emission is Amine 1. The EA has not derived the final published EAL for this substance.

The critical effect for Amine 1 was identified as potential toxicity in the liver in relation to repeated exposure. A LOAEC (inhalation route, rats) of 700 mg/m^3 is selected based on the presence of very slight microscopic liver effects (REACH 2022b[5]). This point of departure is used as the basis for the calculation for proposed short term EAL. The uncertainty factor of 1000 is used as conservative approach.

Proposed short term EAL is calculated as below

Proposed short term EAL = N(L)OAEC/ (UF I x UF II x UF III)

= 700 mg/m^3 / (10 x 10 x 10)

= 0.7 mg/m^3 = 700 µg/m^3

The resulting short term EAL for Amine 1 is 700 µg/m^3.

A long-term EAL was not derived, as the long-term data on local effects by inhalation is not available.

As the short term EAL is less stringent than that derived for MEA, Amine 1 has been assessed against the 1 hour mean and 24-hour long-term mean EALs for MEA as a conservative approach.

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[4] ECB, 2005. European Union Risk Assessment Report. Piperazine. CAS No. 110-85-0

[5] REACH registration dossier https://chem.echa.europa.eu/100.004.282/dossier-view/7342c32c-1a67-48c2-9f39-27312e40004e , https://echa.europa.eu/brief-profile/-/briefprofile/100.004.282

2.2 N-Amines

The carbon capture process can emit Nitrosamine 2 and Nitramines 1 and 2.

The EA have derived an EAL for N-nitrosodimethylamine (NDMA)[2]

- Annual mean: 0.0002 µg/m^3

This is based on a Dose Level (BMDL10) of 0.023 mg/m^3. The EA also state: "NDMA is one of the most potent nitrosamines [in terms of carcinogenic potential]" and also state that NDMA is one of the most widely studied of the nitrosamines, recognizing that toxicology data for other nitrosamines is scarce, particularly for carcinogenic potential.

NDMA is one of the best-studied nitrosamines, and also one of the nitrosamines with the highest carcinogenic potential. Based on the available data, EA have derived an EAL of 0.2 ng/m^3 (as an annual mean).

The Danish Environmental Protection Agency published a report[6] aiming to derive health-based quality criteria and 'C-values' (similar to EALs) for nitrosamines and nitramines generated from amines during carbon capture processes, which included both NPZ and DNPZ. The study used extrapolation of literature TD50 values (the estimated does level causing cancer in 50% of test animals, generally rats or mice) to derive C-values for human exposure. For species where TD50 values were not available, read-across based on structural similarity was used. The C-values for are shown in Table 3.

Table 3. Relative toxicity of FEED1 Contractor nitrosamine emissions compared to NDMA

Species	TD50 value (mg/m^3)	C-value (mg/m^3)	Toxicity relative to NDMA
NDMA	0.0959 in rats	7 x 10 $^{-6}$	1
NPZ	8.78 in rats	6 x 10^{-4}	0.012 (86 times less toxic)
DNPZ	3.6 in mice	1 x 10^{-4}	0.07 (14 times less toxic)

The Danish study also derived C-values for three nitramines – these species were between five and 140 times less toxic than the corresponding nitrosamines providing further support to the wider literature suggesting than nitramines as a group show substantially lower toxicity than nitrosamines.

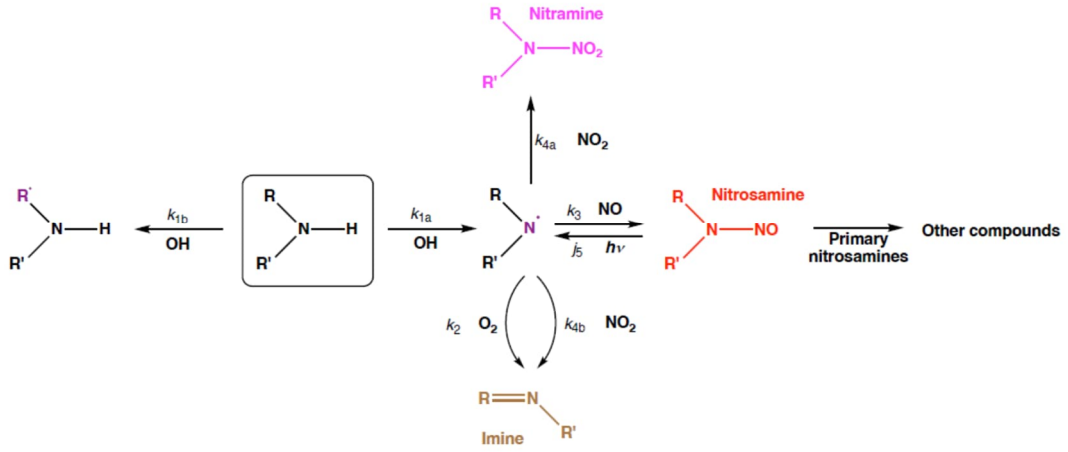
Based on available data, the EAL for NDMA of 0.2 ng/m^3 (annual mean) would serve as a very conservative EAL for assessment of the FEED1 Contractor nitrosamines and nitramines.

[6] Nitrosamines and nitramines - Evaluation of health hazards and proposal of health-based quality criteria and C-values for ambient air. Ministry of Environment of Denmark, Environmental Protection Agency, May 2023. https://www2.mst.dk/Udgiv/publications/2023/05/978-87-7038-518-3.pdf

3. Chemical Kinetics for Application in the ADMS amines chemistry module

3.1 Background Information

The ADMS amine chemistry module requires input values for kinetic constants of the reaction mechanism used which is widely accepted as best representation of the available experimental results:



Since the rate limiting step of the reaction mechanism is the initial reaction of the amine with OH radicals, the relative amounts of the different products formed depend on the ratios of the respective kinetic constants as follows:

- k_{1a}/k_1
- k_2/k_{4a}
- k_3/k_{4a}
- k_{4a}/k_{4b}

For the FEED1 Contractor constant values are required for:

- AMP (Amine 1)
- Piperazine (Amine 2)

3.2 Proposed Rate Constants

The proposed rate constants or kinetic parameters were provided based on the literature reviews for each of the amines, collated from the CERC report for the UK EA 'Improving Post-Combustion Carbon Capture Air Quality Risk Assessment Techniques' published in May 2024. Proxy substance data was used when specific information was not available.

Table 4. Amine 1 Chemistry Parameters

Parameter	Units	FEED 1 - Amine 1	Reference
k1 = Amine/OH radical reaction rate constant	ppb/s	0.7	Tan et al., 2021b
k2 = Amino radical/O_2 reaction rate constant	ppb/s	$3.75x10^{-9}$	Nielsen et al, 2010
k3 = Rate constant for formation of nitrosamine	ppb/s	$2.00x10^{-3}$	Nielsen et al., 2010
k4a = Rate constant for formation of nitramine	ppb/s	$8.00x10^{-3}$	Manzoor et al., 2015
k4 = Amino radical/NO_2 reaction rate constant	ppb/s	$8.00x10^{-3}$	Manzoor et al., 2015
Branching Ratio	dimensionless	0.30	Tan et al., 2021b
Ratio of J (nitrosamine) to NO_2	dimensionless	0.50	Nielsen et al. 2012a

Table 5. Amine 2 Chemistry Parameters

Parameter	Units	FEED 1 - Amine 1	Reference
k1 = Amine/OH radical reaction rate constant	ppb/s	7.0	Tan et al., 2021a
k2 = Amino radical/O_2 reaction rate constant	ppb/s	$3.75x10^{-11}$	Liu et al., 2019
k3 = Rate constant for formation of nitrosamine	ppb/s	$1.25x10^{-3}$	Liu et al., 2019
k4a = Rate constant for formation of nitramine	ppb/s	$8.00x10^{-3}$	Manzoor et al., 2015
k4 = Amino radical/NO_2 reaction rate constant	ppb/s	$8.00x10^{-3}$	Manzoor et al., 2015
Branching Ratio	dimensionless	0.20	Tan et al., 2021a
Ratio of J (nitrosamine) to NO_2	dimensionless	0.30	Tan et al., 2021a

Please note that all the References for the kinetics parameters were obtained from the CERC Report for UK EA in May 2024 (CERC, 2024. Improving Post-Combustion Carbon Capture Air Quality Risk Assessment Techniques).

The detailed references sources for each parameters are listed as below.

- Liu et al., 2019. *Mechanism and predictive model development of reaction rate constants for Ncenter radicals with O2*. Chemosphere, **237**, 124411.
- Manzoor et al., 2015. *A theoretical study of the reaction kinetics of amines released into the atmosphere from CO2 capture*. Int. J. Greenh. Gas Control, **41**, p219 – 228.
- Nielsen et al., 2010. *Atmospheric degradation of amines. Summary report: gas-phase photooxidation of 2-aminoethanol (MEA)*. CLIMIT project no. 193438
- Nielsen et al., 2012a. *Atmospheric Degradation of Amines (ADA). Summary report from atmospheric chemistry studies of amines, nitrosamines, nitramines and amides*. CLIMIT project no. 208122. ISBN 978-82-992954-7-5
- Tan et al., 2021a. *Experimental and Theoretical Study of the OH-Initiated Degradation of Piperazine under Simulated Atmospheric Conditions*. J. Phys. Chem. A, **125**, 1, 411-422.
- Tan et al., 2021b. *Atmospheric Chemistry of 2-Amino-2-methyl-1-propanol: A Theoretical and Experimental Study of the OH-Initiated Degradation under Simulated Atmospheric Conditions*. J. Phys. Chem., **125**, 34, 7502–7519.