ANNEX G – FEED 2 CONTRACTOR SUPPORTING INFORMATION FOR THE ASSESSMENT OF AMINES AND AMINE DEGRADATION PROCUCTS

This Annex provides further information provided by the FEED 2 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 FEED 2 Contractor Solvent (DC-103) is used as an amine aqueous solution, comprising the amine components shown in Table 1.

Table 1: DC-103 Solvent Amine Components

Component	Chemical name	CAS number
Amine 1	1-Piperazineethanol	103-76-4
Amine 2	Piperazine	110-85-0
Amine 3	1,4-Piperazinediethanol	122-96-3

1.2 Chemistry and Degradation Products

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

- Oxidative degradation:
  - Oxidation of amine or hydroxyl functionalities, leading primarily to low molecular weight organic acids and ammonia.
  - Formation of heavier molecular weight species by reaction with oxygen, free radicals or organic acids, leading to non-alkaline compounds such as formamides or ketone-type species such as amides.
- Formation of nitrosamines by reaction with NO_2- (nitrite).

Note tertiary amines will not form nitrosamines, and therefore there is no nitrosamine associated with Amine 3.

The list of potential degradation products is provided in Table 2.

Table 2: DC-103 Solvent Degradation Products

Status	Type	Components	Chemical name [2]	CAS number [2]
Confirmed degradation products	-	N-amine 1	4-Nitroso-1-piperazineethanol	48121-20-6
		N-amine 2	1-nitrosopiperazine	5632-47-3
		Amide 1	4-(2-Hydroxyethyl) piperazin-2-one	23936-04-1
		Formamide 1	1-formyl-4-(2-hydroxyethyl) piperazine	25209-64-7
		Amide 2	Piperazin-2-one	5625-67-2
		Formamide 2	1-formylpiperazine	7755-92-2
		Ammonia	Ammonia	7664-41-7
	Organic acids	Formate	-	-
		Glycolate	-	-
		Oxalate	-	-
		Acetate	-	-
		Sulfamate	-	-
Possible degradation products [1]	-	Formaldehyde	-	-
		Acetonitrile	-	-
		Acetaldehyde	-	-
		Ethanol	-	-
		Acetone	-	-
		MEA	Mono Ethanol Amine	141-43-5

Note 1: compounds not linked to an established degradation pathway but detected in some instances in the absorber treated gas in amounts that indicate at least a partial origin in solvent chemistry.
Note 2: For DC-103 specific components.

1.3 Emissions to Atmosphere

The solvent components and degradation compounds detailed in Table 1 and 2 above will have a zero vapour pressure over the solvent if they are ionized. This will be the case for the organic acids.

The other components have the potential to be present in the emissions from the absorber, and water and acid wash systems can be used to control the amounts emitted to the atmosphere to low levels.

In the case of the CANSOLV DC-103 system, the oxidative degradation pathways favour the formation of heavier compounds that will have a low vapor pressure which have been shown to be effectively controlled with a single stage water-wash (as demonstrated in the operating units of Boundary Dam and Brothers CISA, and in further pilot campaigns). The low amounts of lighter products, in particular ammonia, are also well controlled with this water wash system and usually do not mandate the addition of an acid wash stage.

Monitoring of the emissions of the Boundary Dam unit has included the amine and nitrosamine emissions, relevant to the concern of nitrosamine levels in the environment.

An advanced PTR-TOF-MS instrument, with full spectrum analysis capabilities, has been used on several pilot and demonstration scale campaigns, has been used to detect the confirmed and suspected degradation products mentioned in Table 2 in the treated gas (instrument installation, calibration, maintenance and data analysis performed by specialists at the University of Oslo, also owner of the PTR-TOF-MS instrument).

Concurrent extractive sampling with impinger trains followed by LCMS analysis has been used to confirm emission levels for targeted components.

Table 3 summarizes components known to be potentially emitted to atmosphere, which includes the solvent components (Table 1) as well as the degradation products (Table 2, with the exception of organic acids that are not volatile in their ionized form).

Table 3: Components Potentially Emitted to Atmosphere

Status	Components
Solvent components	Amine 1
	Amine 2
	Amine 3
Confirmed degradation products	N-amine 1
	N-amine 2
	Amide 1
	Formamide 1
	Amide 2
	Formamide 2
	Ammonia
Possible degradation products (1)	Formaldehyde
	Acetonitrile
	Acetaldehyde
	Ethanol
	Acetone
	MEA

Note 1: compounds not linked to an established degradation pathway but detected in some instances in the absorber treated gas in amounts that indicate at least a partial origin in solvent chemistry.

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 CANSOLV DC-103 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.

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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

2.1.2 Piperazine (CANSOLV DC-103 Amine 2)

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

- 24-hour mean (long term): 15 µg/m^3

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 European Chemicals Bureau (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 CANSOLV DC-103 Amine1 and Amine 3

Section 1.1 describes the amines used in the CANSOLV DC-103 solvent. These amines are structural analogues, consisting of a heterocyclic di-amine (Amine 2), with an alkanol group substitution on one (Amine 1) or both (Amine 3) amine functions.

Amine 1 has low vapor pressure and is considered to be a strong ocular and skin irritant. Available data are summarized in Table 4 below.

Amine 3 is a minor component of the DC-103 solvent with low volatility and is generally not detected at stack. DC-103 amine 3 is an amine with low vapor pressure, and is considered to be a strong ocular and skin irritant. Available data are summarized in Table 4 below.

Due to their common active group (the amine group), the overall toxicity of all aliphatic amines is similar, with some potency differences depending on the aliphatic parts. Based on a review of the toxicological properties of alkanol-amines, cyclic amines and aliphatic amines, supplemented with modelling of the structure-activity relationship, the following can be summarized regarding the toxicity of these compounds in the human body:

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[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

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

- Amines are metabolized by oxidation into the corresponding aldehydes, a process accompanied by the release of ammonia. The aldehydes are then metabolized into carboxylic acids and, ultimately, into CO_2 (that is subsequently exhaled).
- Aliphatic amines and alkanolamines are of relatively low acute toxicity, with LD50 levels (Lethal Dose for 50% of the test animals) in the order of grams per kilogram bodyweight. The cyclic amines have a lower threshold of toxicity (LD50 levels in the order of 100s of milligrams per kilogram bodyweight), but are still of relatively low acute toxicity.
- Except for tertiary amines, the range of aliphatic amines, alkanolamines, as well as cyclic amines are to some degree corrosive or highly irritating to the skin, eyes and/or respiratory tract.
- With the exception of piperazine, amines are no skin or respiratory sensitizers.
- Overall, amines are not mutagenic or carcinogenic and, with exception of piperazine, amines are not expected to affect human development or reproduction.

Overall, amines will pose minimal risk to members of the general public. However, due to their corrosive properties risk management measures need to be in place for workers.

The main amine present in the absorber emission is Amine 1. Based on available data, as well as modelling data, all DC-103 amines are expected to be of low systemic toxicity with no alerts for carcinogenicity, mutagenicity or reproductive toxicity. Like MEA, the main effect would be local irritation.

It should be noted that all chemicals imported to the UK are subject to the UK REACH regulation. It is anticipated that additional information will be generated for the REACH registration of Amine 1. This will include longer-term repeated dose studies that will confirm a NOAEL and can be used to substantiate the current EAL derivation. The current EAL derivation however is considered to be conservative, and based on inhalation effects from MEA. Due to the low vapor pressure of Amine 1 compared to MEA, exposure levels are estimated to be well below the EAL, and this has been demonstrated by the dispersion modelling carried out for the project.

Analysis of the No Observed Adverse Effect Levels (NOAEL) of the DC-103 amines and MEA, support that there is no concern for systemic toxicity from the DC-103 amines. The NOAELs for Amine 2 and Amine 3 are 627 and 1,000 mg/kg bw/d for systemic effects, which is above the systemic NOAEL of MEA of 300 mg/kg bw/d.

To date, a NOAEL has not been derived for Amine 1, however based on structural similarity with Amine 2 and Amine 3, Amine 1 is expected to have a systemic NOAEL of the same order of magnitude. Given that the NOAELs for Amine 2 and 3 are higher than that derived for MEA, it is reasonable to assume that for systemic effects, the EAL derived for MEA would represent a worst-case, and that the EAL protective for systemic effects from exposure to MEA, should also be protective for systemic effects of all three of the DC-103 amines.

For short-term, local effects, all DC-103 amines are ocular and skin irritants. In addition, Amine 2 is classified as a respiratory sensitizer. However, based on its REACH registration dossier, the substance could be considered an asthmagen (causing asthma by non-immunological mechanism) rather than a respiratory allergen (causing asthma by an immunological mechanism). Amines 1 and 3 have the same local irritating effects as MEA. It is therefore reasonable to assume that the EAL protective for local irritating effects from exposure to MEA, should also be protective for local irritating effects of DC-103 amines.

Table 4 provides a summary of the available toxicity date available for MEA and DC-103 amine 1 and amine 3.

Table 4: Summarized toxicity data for MEA and DC-103 amines

Amine	Irritation	Sensitization	Geno-toxicity	NOAEL (mg/kg bw/day)	NOAEC (mg/m^3)	STEL (mg/m^3)	OEL or DNEL (mg/m^3)
Mono-ethanol Amine (MEA)	H314	Not classified	Negative	300	10	7.6	2.5 0.28* 0.18**
Amine 1	H315 H318 No clinical signs after exposure to saturated vapors	Not classified	Negative	N/A	***	N/A	N/A
Amine 3	H318	N/A	Negative	1000	***	N/A	N/A

* General population DNEL local effects

** General population DNEL systemic effects

*** Due to the low vapor pressure it is unlikely that the substance will be available as a vapor.

STEL – Short-term Exposure Limit, OEL = Occupational Exposure Limit

In summary, based on the absence of significant systemic toxicity and similar local effects (irritation) the proposed EALs for DC-103 amine1 and amine 3 are similar to those of MEA, which is 400 $\mu g/m^3$ and 100 $\mu g/m^3$ for short-term and long-term exposure, respectively.

The DC-103 amine EALs are summarized in Table 5.

Table 5: Environmental Assessment Level (EAL) for MEA and DC-103 amines

Amine	1-hour EAL ($\mu g/m^3$)	Long term 24-hour EAL ($\mu g/m^3$)
Mono ethanol amine	400	100
Amine 1	400	100
Amine 2	None	15
Amine 3	400	100

As Amine 3 is a minor component of the DC-103 solvent and is generally not detected at stack and the same EAL is being applied for assessment of Amine 1 and Amine 3, for the purposes of dispersion modelling, Amine 1 and Amine 3 have been modelled as a single component, namely Amine 1.

2.2 N-amines

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

The EA have derived an EAL for N-nitrosodimethylamine (NDMA)[5]

- 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.

Nitrosamine 1 has no carcinogenic data currently available. Nitrosamine 2 has been studied for carcinogenic potential and it has been demonstrated to be 45 times less potent than NDMA.

Mutagenic potency of Nitrosamine 1, Nitrosamine 2 and NDMA (as a positive control) have been investigated in a modified Ames test[6], using bacterial strains sensitive to nitrosamines. The mutagenic potency of Nitrosamine 1 was found to be 2,000 times less than that of NDMA, and the mutagenic potency of Nitrosamine 2 was found to be 50 times less than that of NDMA.

An overview of data is presented in Table 6.

Table 6: Mutagenic and carcinogenic potency of NDMA and DC-103 nitrosamines

Nitrosamine	**Mutagenic potency (µmol)$^{-1}$**	**Carcinogenic potency based on animal data (mmol/m^3)$^{-1}$**	**EAL (ng/m^3) annual mean**
NDMA	1	300	0.2
DC-103 nitrosamine 1	0.043	N/A	0.2 proposed
DC-103 nitrosamine 2	0.001	6.6	0.2 proposed

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). Based on available data on the mutagenic and carcinogenic potency of DC-103 nitrosamines and NDMA, it is expected that NDMA is the most potent mutagen and carcinogen. Hence, the EAL for NDMA of 0.2 ng/m^3 (annual mean) would serve as a very conservative EAL for DC-103 nitrosamines. As discussed in Annex A, available literature suggests that nitramines as a group show substantially lower toxicity than nitrosamines and hence the EAL for NDMA would also provide a very conservative EAL for the assessment of nitrosamines and nitramines as a group.

[5] 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

[6] Plewa et al. University of Illinois. (2013). Technical Service Report on the Mutagenicity Analyses of Cansolv Nitrosamine Samples.

2.3 EAL's for DC-103 amines amide and formamide degradation products

There is limited relevant human and environmental toxicity data relating directly to the amide and formamide degradation products that have been identified. The lack of information leads to a difficulty in assigning EALs for these products. The best approach is to use a scientifically justified read across from similar chemicals with established human and environmental toxicity data.

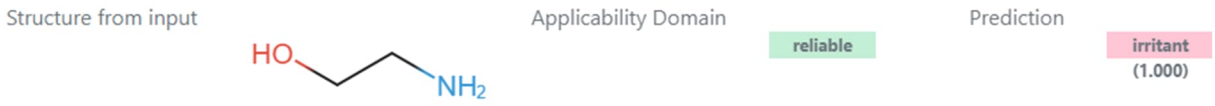
Additionally, it must be recognised that these chemicals tend to be very reactive in air and therefore quickly react in the atmosphere so that they are no longer present. This should be considered when assigning any environmental limits.

This document sets out the use of Quantitative Structure-Activity Relationship (QSAR) methods to derive EAL values by reading across to chemicals with established EALs and known toxicological profiles.

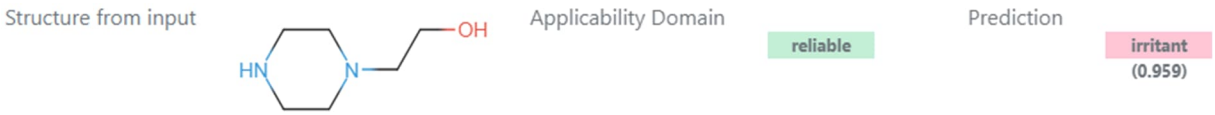
2.3.1 Modelling of Respiratory effects

The RespiraTox project developed a QSAR model for identifying potential human respiratory irritants using a novel in silico strategy. Using the RespiraTox modelling software for respiratory irritation and tissue damage the model returned the following results for MEA and the degradation products in question:

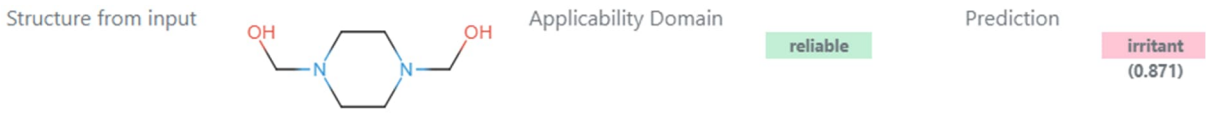
RepiraTox prediction of respiratory irritation for MEA:



RepiraTox prediction of respiratory irritation for amine 1:

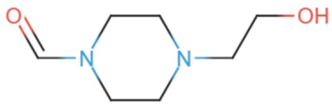


RepiraTox prediction of respiratory irritation for amine 3:



The degradation products requiring EALs are:

1- **Formamide HEP (CAS: 25209-64-7)**



Formamide HEP does not have any data available. 3rd party Safety Data Sheets (SDSs) report[i]:

H315 Skin corrosion/irritation Category 2

H319 Serious eye damage/eye irritation Category 2

H335 Specific target organ toxicity (single exposure: respiratory irritation) Category 3

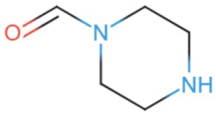
Based on respiratory irritation being the point of departure and running formamide HEP through Respiratox shows an 85% similarity to amine 1 and a 62% similarity to MEA.

Recommendation: follow the guidance suggested for amine 1 and read-across EAL from MEA based on respiratory irritation as the critical end point.

Proposed EALs:

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

2- **Formamide piperazine (CAS: 7755-92-2)**



Formamide piperazine also lacks any data, European Chemicals Agency (ECHA) Classification and Labelling (C&L) notifiers have reported[ii]:

H302 Acute Tox. category 4 (Oral)

H315 Skin corrosion/irritation Category 2

H318 Serious eye damage/eye irritation Category 1

H335 Specific target organ toxicity (single exposure: respiratory irritation) Category 3

Based on respiratory irritation being the point of departure and running formamide piperazine through Respiratox shows an 83% similarity to amine 1, although formamide piperazine has an 85% similarity to piperazine this is only in the context of predicting respiratory irritation and not sensitisation for which there is no indication. Based on this the recommendation is to follow the same scientific basis for read-across as amine 1.

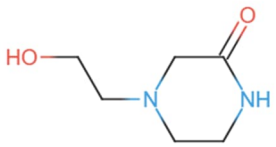
Recommendation: follow the guidance suggested for amine 1 and read-across EAL from MEA based on respiratory irritation as the critical end point.

Proposed EALs:

- Maximum 1-hour mean: 400 µg/m^3

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

3- <u>Amide HEP (CAS: 23936-04-1)</u>



Amide HEP also lacks any data, 3rd party SDS has this classified as[iii]:

H302: Acute Tox. Category 4 (oral)

H315: Skin Irrit. category 2

H319: Eye Irrit. category 2

<u>H335: STOT SE (respiratory irritation) category 3</u>

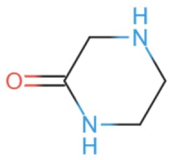
Once again, respiratory irritation seems to be a common critical end point for these substances. Based on respiratory irritation being the point of departure and running amide HEP through Respiratox shows an 89% similarity to amine 1, therefore, we recommend to apply the same scientific basis for read-across as amine 1 i.e., MEA.

Recommendation: follow the guidance suggested for amine 1 and read-across EAL from MEA based on respiratory irritation as the critical end point.

<u>Proposed EALs:</u>

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

4- <u>Amide piperazine (CAS: 5625-67-2)</u>



Out of all the degradation products only amide piperazine has data available for human and environmental health impacts. According to the submitted dossier on the ECHA website the classification for amide piperazine is[iv]:

H315 Skin Irrit. category 2/ H314 Skin Corr. category 1B

H317 Skin Sens. category 1

H319 Eye Irrit. category 2/H319 Eye Irrit. category 2A/ H318 Eye Dam. category 1

H335 STOT SE (respiratory irritation) category 3

The Classification and Labelling (C&L)notifier information highlights the difficulty ascertaining the correct relevant information. Here we see different self-classifications for skin and eye

irritation endpoints. However, for our purpose the data available for amide piperazine clearly points to respiratory irritation to be the most relevant end point for consideration in our proposed application. Based on this and running the chemical through Respiratox; the results indicate that amine 1 is 78% similar to amide piperazine, although piperazine is 83% similar that would only be relevant is the endpoint in consideration was respiratory sensitisation. However, with respiratory irritation being the end point it is scientifically justifiable to conclude reading across to MEA to be the best approach for establishing EALs.

Recommendation: follow the guidance suggested for amine 1 and read-across EAL from MEA based on respiratory irritation as the critical end point.

Proposed EALs:

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

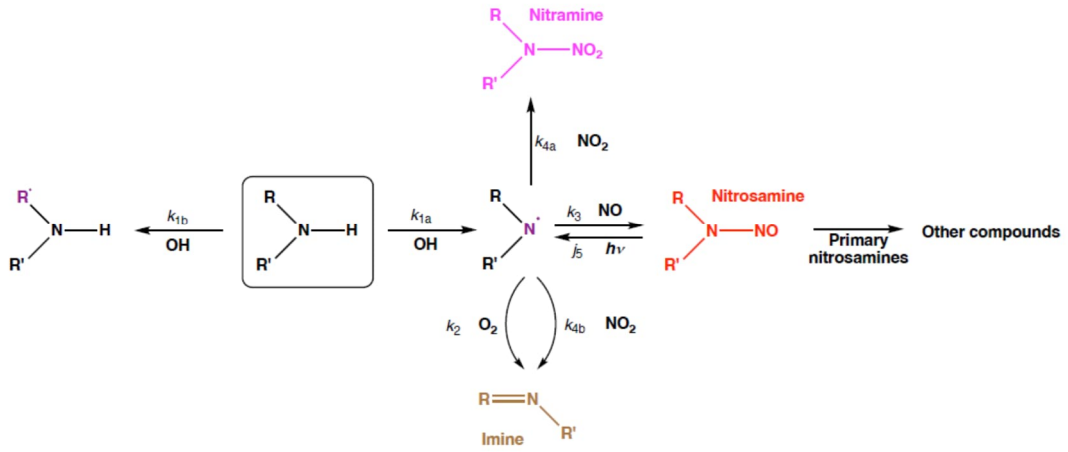
In conclusion, it is proposed to follow the same logic used in assigning EAL for amine 1 and amine 2 in the case of these degradation products. This takes into account the most relevant point of departures, which is respiratory irritation and takes into consideration high reactivity in air of the degradation products in question. Using MEA as a read across therefore will capture any uncertainty and still be a sufficiently cautious EAL to be safe and sustainable moving forward.

As the same EAL is being applied for assessment, for the purposes of dispersion modelling, AMIDE 1 and AMIDE 2 have been modelled as a single species (AMIDE 1) and FORMAMIDE 1 and FORMAMIDE 2 have been modelled as a single species (FORMAMIDE 1).

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 CANSOLV DC-103 constant values are required for:

- (2-Hydroxyethyl)piperazine (HEP) (Amine 1)
- Piperazine (Amine 2)

While some proposed values for piperazine can be found in the literature, none are available for HEP. In 2014 Pr. Nielsen, University of Oslo, was requested to recommend values for HEP for the Boundary Dam project.

In 2024 Shell instructed Pr. Nielsen to reassess the findings of his original report based on new data available in the literature (where available), as well as progress in theoretical tools since the 2014 work.

In 2025 Pr. Nielsen completed a full literature review of the atmospheric chemistry of piperazine and reviewed the theoretical quantum chemistry calculations to provide a proposed set of rate constants for HEP. The review demonstrates that piperazine is a good read-across for HEP.

3.2 Proposed Rate Constants

As 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. This means that atmospheric chamber experimental studies can only access these ratios and cannot provide absolute rate constant values. It is therefore not considered appropriate to select individual rate constants from different literature sources, such

as the proposed k_2 value of 1.3×10^{-21} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ from Liu et al., 2019[7] and a k_3 value of 7.2×10^{-11} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ from Ma et al., 2018[8] as detailed in the CERC report[9].

Additionally, whilst the CERC report details a value for k_2 from Liu et al., 2019, and this was identified by the EA as being the most conservative value for use in the ADMS amines module, Pr. Nielsen has expressed caution over the use of this value as the calculations are ill-documented and difficult to peer review, and display a wide scatter of values. It should also be noted that the value of 1.24×10^{-20} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ for k_2 provided in Table 3.8 of the CERC report is incorrect, and based on the ratio of k_2/k_{4a} should be 4.99×10^{-20}.

The branching ratios are usually specified relative to k_{4a}, and constants can be obtained by setting an arbitrary value of k_{4a} consistent with the aminyl radical being the limiting step, i.e. ensuring that:

$$k_2 \cdot [O_2] + k_3 \cdot [NO] + k_{4a} \cdot [NO_2] + k_{4b} \cdot [NO_2] \approx 1\ s^{-1} \text{ (or larger)}.$$

Pr. Nielsen advises that the value used for k_{4a} to derive proposed values for the kinetic constants correspond to the experimental value obtained by Lazarou et al[10] (3.18×10^{-13} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$).

It follows from the above that:

- Direct specification of individual constants from different sources will lead to an inconsistent set of constants for the overall mechanism.
- Unless it is clearly established that the value of the arbitrary fixed constant is identical, comparison of constants is irrelevant and only branching ratios should be compared.

Only specification of a consistent full set of constants, derived from a full set of branching ratios, is considered meaningful, and should be used in the ADMS chemistry module.

Several of the values reported in the literature for piperazine, and resulting from theoretical studies, should be considered with caution. The most reliable source is considered to be the article of Tan et al.[11], which states:

Table 1: Tan et al 2021 Reaction Ratios ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for Piperazine

k_{1a}/k_1	k_2/k_{4a}	k_3/k_{4a}	k_{4b}/k_{4a}
0.18	1.57×10^{-7}	1.7	0

[7] Liu et al., 2019. Mechanism and predictive model development of reaction rate constants for N center radicals with O2. Chemosphere, 237, 124411.
[8] Ma et al., 2018. Atmospheric Oxidation of Piperazine Initiated by ·Cl: Unexpected High Nitrosamine Yield. Environ. Sci. Technol., 52, 17, p9801 – 9809
[9] CERC (2024). Improving Post-Combustion Carbon Capture Air Quality Risk Assessment Techniques. Final Report Prepared for the Environment Agency, FM1384/R6/24. Available: https://www.cerc.co.uk/environmental-research/assets/data/CERC_2024_Improving_Post-Combustion_Carbon_Capture_Air_Quality_Risk_Assessment_Techniques.pdf
[10] Lazarou, Y.G., K.G. Kambanis, and P. Papagiannakopoulos, *Gas-Phase Reactions of $(CH_3)_2N$ Radicals with NO and NO_2*. Journal of Physical Chemistry, 1994. **98**(8): p. 2110-2115.

[11] Tan, W., et al., *Experimental and Theoretical Study of the OH-Initiated Degradation of Piperazine under Simulated Atmospheric Conditions*. The Journal of Physical Chemistry A, 2021. **125**(1): p. 411-422.

The k_1 value reported in Tan et al. (2.80×10^{-10} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) is not considered to be accurate as particle formation was experienced during the experiments, and therefore the values of 2.38×10^{-10} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ from Onel et al., 2014[12] based on experimental studies is considered to be the most appropriate value to use.

The full set of rate constants for the ADMS Amines Module for Piperazine is shown in Tables 2 (in $cm^3.molecule^{-1}.s^{-1}$) and 3 (in $ppb.^{s-1}$).

Table 2: Rate Constants for use in ADMS for Piperazine ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$)

k_1	j_{rel}	k_{1a}/k_1	k_2	k_3	k_{4a}	k_4
2.38×10^{-10}	0.34	0.18	4.99×10^{-20}	5.41×10^{-13}	3.18×10^{-13}	3.18×10^{-13}

Table 3: Rate Constants for use in ADMS for Piperazine ($ppb^{-1} \cdot s^{-1}$)

k_1	j_{rel}	k_{1a}/k_1	k_2	k_3	k_{4a}	k_4
5.95	0.34	0.18	1.25×10^{-9}	0.0135	0.00795	0.00795

The 2025 Pr. Nielsen theoretical study shows that for HEP:

- Three aminyl radicals can be formed with a total yield of 17% ($k_{1a}/k_1 = 0.17$).
- Two of those are similar to the radical formed by piperazine and quantum potential are shown to be similar, supporting also similar branching ratios.
- The third aminyl radical is formed with an about 200 times lower yield than for the two other radicals, leading to a negligible contribution to the total nitrosamines and nitramines yield.
    - the aminyl group structure is similar to the diethyl aminyl radical structure and potentials are expected to be similar.
    - The yield of this aminyl radical is predicted to be about 200 times lower than for the two other radicals, leading to a negligible contribution to the total nitrosamines and nitramines yield.

The contribution from the third radical can thus be ignored and again a single reaction mechanism can be considered with the aggregated piperazine radicals branching ratios, which form a consistent set of data.[v]

The proposed rate constants for the ADMS amine model are therefore the same as those proposed for piperazine shown in Table 3 above, however the value for k_1 from Pr. Nielsen's 2014 study should be applied (i.e. 6.25 $ppb^{-1} \cdot s^{-1}$) with the k_{1a}/k_1 branching ratio of 0.17.

[12] Onel et al., 2014a. Atmospheric oxidation of piperazine by OH has a low potential to form carcinogenic compounds. Environ. Sci. Technol. Lett., 1, 9, p367 – 371.