Air Quality Modelling & Assessment Unit (AQMAU)

Environment Agency

AQMAU recommendations for the assessment and regulation of impacts to air quality from amine-based post-combustion carbon capture plants

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Summary

The Air Quality Modelling and Assessment Unit (AQMAU) was asked to review the available modelling techniques to support air quality impact assessments from amines and degradation products releases. The air quality model covers the dispersion, transformation and deposition of air pollutants. Our recommendations are based on the available evidence found by us and provided to us at the time of writing this report. This report is not intended to be a literature review of emissions to air from carbon capture technologies.

At the time of writing this report, the only commercially available modelling software to evaluate the potential impacts from amines and amine degradation products releases is the amines module within ADMS. The amines chemistry module is based on established science considering published research on mechanisms of formation of toxic compounds. Although the validation of the module is not possible at the moment, the ADMS air dispersion modelling algorithms are continually validated against real world situations, field campaigns and wind tunnel experiments. We do not endorse a specific modelling software and we acknowledge the level of uncertainty of the amines module is likely to be high.

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. Further experience, on-site measurements and validation exercises combined with sensitivity analysis and an alternative modelling software should be encouraged as the next steps. As a result of our analysis, we remain cautious, but consider the module to be a useful tool to inform decision-making. We expect applicants to have a sound understanding of the environmental implications of releasing these substances to air and address uncertainties following our guidance.

This report highlights some of the key knowledge gaps and considerations (section 3), summarises our recommendations for the regulation based on the modelling experience and review of evidence (section 4), and provides advice to applicants submitting air quality assessments based on the amines module (Appendix I). This report also incorporates comments from internal and external consultations. We anticipate that making Appendix I publicly available to applicants will help demonstrate robustness in the air quality assessments. We also propose a preliminary framework for next steps (Appendix II).

1 Understanding the implications of releasing amines and amine degradation products to ambient air

1.1.   The basic principle of amine capture process is to remove the carbon dioxide (CO_2) from the combustion flue gases through its reaction with amine-based solvents in an absorber tower. Amines are organic derivatives of ammonia (NH_3), wherein one or more hydrogen atoms are replaced by a substituent organic group (R). The type of amine depends on how many hydrogen atoms (H-atoms) are replaced by organic groups:

- Primary amine (R-NH_2) where 1 H-atom is replaced
- Secondary amine (R_2-NH) where 2 H-atoms are replaced
- Tertiary amine (R_3-N) where 3 H-atoms are replaced

1.2.   Amine-based solvents are commonly used in post-combustion carbon capture processes. The organic groups R can be alkyl, hydroxyl or aryl groups. The most common solvents tend to be the generic group of amines referred to as alkanolamines; a range of amine compounds consisting of hydroxyl (alcohol) and amino functional groups on an alkane backbone. These amine compounds can react with substances other than carbon dioxide to create new compounds both within the carbon capture process and after being released to the atmosphere.

1.3.   The fate of the substances released to air is determined by atmospheric processes such as chemical transformation, dispersion and deposition. The release of amines to air can lead to the formation of carcinogenic substances such as nitrosamines and nitramines (Nielsen et al. 2010a[1] b[2], 2011[3], 2012[4]) and other products. Whilst there is toxicity data available for a few of the more generally researched substances (e.g. N-nitrosodimethylamine NDMA), the environmental toxicity of many of the individual compounds is not well understood (SEPA 2015[5]).

1.4.   The mechanisms for formation of nitrosamines and nitramines in the atmosphere are complex. Published research indicates that they are generally initiated by hydroxyl radicals (OH), however, they can also result from reactions with chlorine atoms (Cl), nitrate radicals (NO_3) and ozone (O_3). Nitrosamines and nitramines are formed by reactions with nitrogen monoxide (NO) and nitrogen dioxide (NO_2), however, they can further degrade in the atmosphere (e.g. through photo-oxidation).

1.5.   The atmospheric reaction mechanisms for several types of amines have been studied by various authors (Nielsen et al. 2010, Manzoor et al. 2014[6]). The most widely published is the amine activation step by OH. OH radicals abstract an H-atom from the amine. The site of initial attack determines the type of species formed through two separate branches of reactions. A summary of the mechanisms of formation of nitrosamines and nitramines activated by OH is described below:

- The OH can attack either (a) the hydrogen on the nitrogen atom (N—H) or (b) one of the hydrogen atoms in the methyl groups (C—H).

- The ratio between the rate of attack on the C—H hydrogen and an N—H is known as the branching ratio i.e. the likelihood of the OH reacting with N—H rather than a C—H site. The branching ratio is dependent on the C chain length and the number and type of organic groups (e.g. alkyl or alcohol).

- Once the H atom has been removed from the N—H bond, the resulting amino radical species react with NO or NO_2 present in the atmosphere, to form nitrosamines or nitramines and other products, respectively. The amount of nitrosamines and nitramines formed depend on the amount of oxides of nitrogen (NO_X) and the ratio of NO to NO_2 (CERC 2012b[7]).

- The production of nitramines and nitrosamines depend on the branching ratio for the abstraction at the N–H site (CERC 2012a[8], Onel et al. 2015[9]).

1.6.   The steady state concentration of nitrosamines and nitramines formed in the air can be calculated using reaction rate laws or based on percentage conversions measured through experimental studies. Steady state conversions (i.e. emitted amines converted to nitrosamines in ambient air) from chamber experiments are reported to be typically between 0 and 10% (SEPA 2015). However, there are uncertainties in these methods due to the complex multiphasic chemical reactions and the potential that the chemistry of specific nitrosamines might not represent the behaviour of a whole group.

1.7.   The flue gases entering the absorber tower may contain potential amine oxidants. They can react with amine-based solvents and form degradation products that will be directly released to air, including potentially stable nitrosamines (i.e. directly-emitted nitrosamines).

1.8.   A number of modelling tools have been used for research purposes to quantify impacts of amine and degradation product releases to ambient air. These include amine chemistry schemes incorporated into open source models such as Weather Research and Forecasting Models (WRF) with the Unified European Monitoring and Evaluation Program (WRF-EMEP) and chemistry and aerosols (WRF-Chem) and the United States Environmental Protection Agency (US EPA) CALPUFF. Others include the Consortium for Small-scale Modeling Multi-Scale Chemistry Aerosol Transport (COSMO-MUSCAT) and The Air Pollution Model (i.e. TAPM) (Helgesen et al., 2016[10]). The amines chemistry module incorporated in the Air Dispersion Modelling Software (ADMS) created by Cambridge Environmental Research Consultants (CERC) is the only modelling tool commercially available at the time of writing this report.

2   Understanding the amines chemistry model

2.1   An air dispersion model is a computational procedure that predicts concentrations of air pollutants emitted from a source based on knowledge of emission characteristics, terrain, obstacles and level of turbulence in the atmosphere. It is a mathematical model that incorporates transport, dispersion and transformation of compounds.

2.2   Gaussian air dispersion models are the most commonly used models for industrial regulation. They assume that pollutant concentrations follow a Gaussian (normal probability) distribution profile within the plume and a parameterisation of the turbulence within periods of time. Therefore, resultant pollutant concentrations are estimates of actual concentrations with a level of uncertainty. In consideration of these uncertainties, the commercially available models have been subject to a number of validation exercises[11] showing correlations of modelled versus observed concentration values for a wide range of cases.

2.3   The ADMS software created by CERC is a steady state Gaussian model. The model calculates the concentration of pollutants after they are emitted from a stack at each receptor point using the standard ADMS dispersion algorithms.

2.4   ADMS (version 5) offers an amines module incorporating a chemistry scheme that attempts to mimic the chemical transformation of released amines in ambient air. The chemistry scheme is based on mechanisms from published research (i.e. Nielsen et al. 2010) summarised in previous section 1.5, calculating steady state concentrations using each reaction rate (refer to section 1.6). The module is designed so that it can be applied to a variety of amines, provided the amine-specific information on atmospheric reactions is available. Our interpretation of the approximation is shown in the Figure 1 below, whereas a summary of the key input information is presented in Table 1. Our interpretation of the key aspects of the module are described as follows:
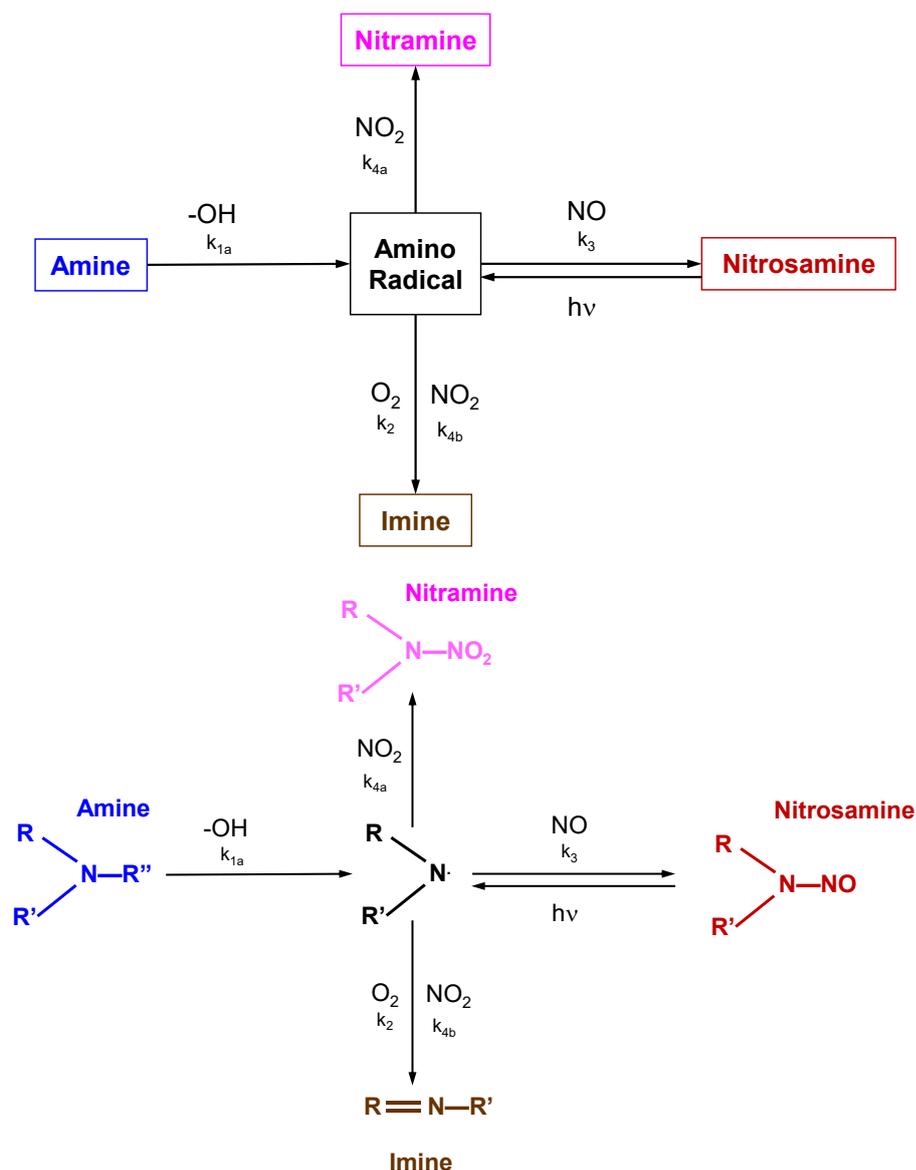
Figure 1 – Summary of the reactions considered in the CERC ADMS amines chemistry scheme and example for a generic tertiary amine [Adapted from CERC and Nielsen et al., 2012 CLIMIT project]. Refer to Table 1 for the description of the k values as subscripts vary in the published research.

- The module defines every amine-based species with generic names "AMINE", "NITROSAMINE" and "NITRAMINE". However, the substance-specific parts per billion by volume (ppbv) to mg/Nm^3 conversion needs to be specified in the modelling software.

- The amino "RADICAL" resultant from the attack of OH (i.e. amine activation step) interacts with NO_2, NO and O_2 to form NITRAMINE, NITROSAMINE and other products.

- Each released amine undergoes atmospheric reactions at their specific rates. The module uses chemical reaction equations from published research (Nielsen et al.) corresponding to the reactions in Figure 1. Therefore, it requires a number of amine-specific inputs such as the kinetic constants/k values (refer to Table 1) and the branching ratio (described in section 1.5). Kinetic data is available from published research for a variety of amine-based substances (e.g. monoethanolamine - MEA, dimethylamine - DMA, ethylamine - EA, etc.). Therefore, there is a need to identify and quantify the species released to air.

- The amines module works in conjunction with the NO_X chemistry module already incorporated in the ADMS modelling software. It considers hourly photochemical reactions of O_3, NO_2 and nitrosamines, taking into account the flux of sunlight from the meteorological station data, background hourly monitored NO_2, NO_X and O_3 concentrations, and the amine-specific ratio of photolysis of NO_2 and nitrosamines (j_s/jNO_2) available from published research.

- Annual background OH concentration is considered to set up the constant, c, allowing the model to calculate OH radical values for every hour of the year. The equation considers that OH radicals are produced from ozone photolysis, thus the formation is directly proportional to the levels of sunlight and O_3 available. This is considered in conjunction with the NO_X photochemical reactions.

- The model predicts concentrations of NITROSAMINES, NITRAMINES and AMINES at any location, which can be directly compared against their relevant Environmental Standards.

Table 1 – Summary of the key information specific to the amines chemistry module

Description	Potential source of information
Mass emission rates for each pollutant (g/s) • Amines, nitrosamines, nitramines and NO_X	Applicant
Species molecular weight (g/mol)	
Ratio of NO_X to NO_2 at the stack (dimensionless)	
Amine-specific atmospheric reaction rate parameters (refer to Figure 1): • k_{1a} - Amine/OH reaction rate constant (/ppbv/s) • k_2 - Amino radical/O_2 reaction rate constant (/ppbv/s) • k_3 - Rate constant for the formation of nitrosamines (/ppbv/s) • k_{4a} - Rate constant for formation of nitramine (/ppbv/s) • k_4 - Amino radical/NO_2 reaction rate constant (/ppbv/s) i.e. k_{4a} + k_{4b} • k_{1a}/k_1 - Branching ratio for amine/OH reaction (dimensionless) • j_s/jNO_2 - Amine-specific ratio of photolysis (hν) rates between nitrosamine and NO_2 (dimensionless)	Published research
OH annual average background concentration (ppbv)	Published research or ambient air measurements
Hourly background concentration values for NO_X, NO_2 and O_3 ($\mu g/m^3$)	Ambient air measurements

2.5 The amines chemistry module considers the mass and type of species released from the stack to ambient air. These undergo atmospheric chemical transformation according to the assumed scheme presented in Figure 1, in addition to dispersion and deposition. At the time of writing this report, the available version of the amines module does not consider parallel reactions (the available OH), therefore, each released species needs to be modelled individually according to their specific kinetics i.e. one substance at a time (e.g. MEA, NDMA, etc.). A conceptual visualisation of the CERC amines module is presented as follows:
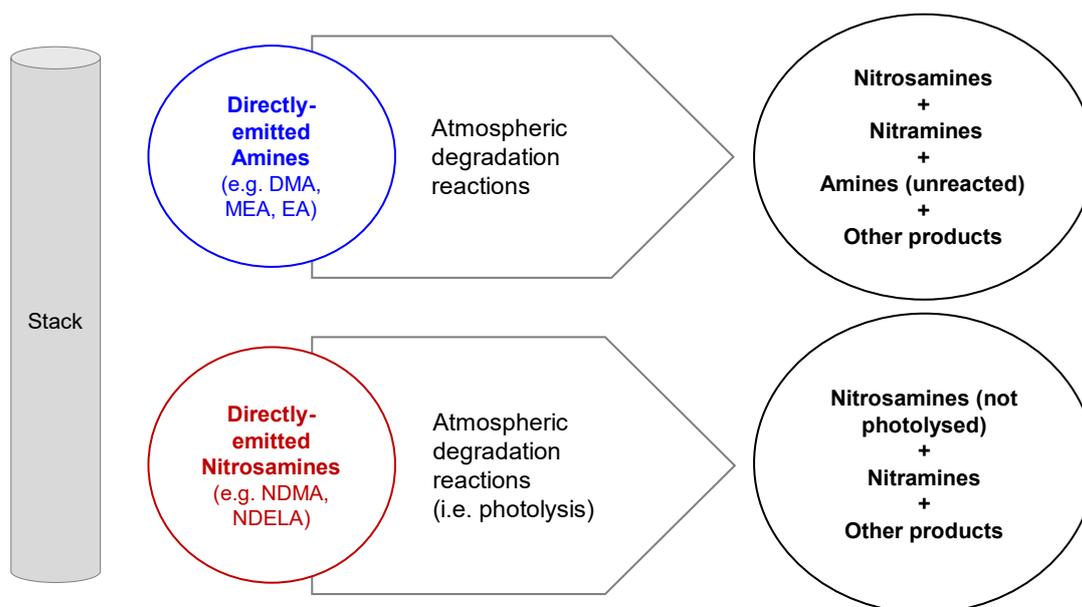
Figure 2 – Conceptual visualisation of the ADMS amines chemistry module

3   Key knowledge gaps and considerations

Atmospheric chemistry

3.1   Once emitted to air, amines, nitrosamines and nitramines undergo dispersion, transformation through complex chemical reactions and deposition. These processes involve multiphase chemistry i.e. gas, aqueous (aerosols, cloud droplets, fog and rain) and particle phase (aerosol), therefore, the mass of starting species may be partitioned (e.g. gas or aqueous phase). There is available research on the fate of various types of amines and their derivation products in aqueous phases (NILU 2012[12]). We highlight:

- An advanced aqueous partitioning scheme (CERC 2012b) was incorporated in the CERC modelling work for the Mongstad pilot plant, however, it is not included in the commercially available version.

- The solubility of amines will put them out of the gas phase (Nielsen et al. 2012[13]), decreasing the amount of pollutants in the ambient air. Publications associated with the Mongstad pilot plant (e.g. Gjernes 2013[14]) indicate that the formation of toxic products in ambient air was dominated by gas phase reactions, supporting the current version of the ADMS amines module.

3.2   With regard to the atmospheric chemical reactions, published research considers theoretical (e.g. quantum chemical methods or statistical rate theory) and experimental methods to validate reaction mechanisms. We highlight:

- Findings from the research associated with the Mongstad pilot plant suggest that the atmospheric reaction of amines with OH during daytime and NO_3 radical during night time are those to consider in the formation of toxic products under the pilot plant conditions (Nielsen et al., 2012, 2011[15], Helgesen et al., 2016). In the comparison between amine reactions with OH versus NO_3 radicals, these studies indicate that reactions with OH radicals are dominant, which supports the current CERC approximation presented in Figure 1. The modelling undertaken by CERC for the pilot plant incorporating the NO_3 route for research purposes (CERC 2012b) also supports this statement, despite the differing dispersion pattern due differences in atmospheric conditions between day and night.

- The research suggests that the atmospheric chemistry established as a result of the Mongstad project considered a generic approach meant to be applicable for all

amines, although investigations were focused on a range of alkyl, alkanol and aryl amines[1] (Helgesen 2016). However, depending on the released substances, kinetic parameter data might not be available, or the published research might not cover their atmospheric chemistry.

- For a given amine, the atmospheric kinetic parameters can differ in various published research. Testing sensitivity to potential parameters to understand variability in predictions for each amine can increase the complexity of evaluating uncertainties and decision-making.

- As mentioned in point 2.5, the amines module does not consider parallel atmospheric reactions of released blends of amines/degradation products, thus it does not consider the available radicals in the activation step. We found no published research covering this aspect in the atmospheric modelling.

- An alternative method to estimate the formation of nitrosamines and nitramines from released amines is assuming steady state conversions based on published research and experimental studies. However, as mentioned in previous points 1.6 and 3.1, these can be uncertain.

Modelling tools

3.3   The ADMS amines module assumes that steady state is achieved each hour throughout the year. The non-steady state modelling was investigated for the Mongstad pilot plant (DNV 2012) in which an amine chemistry scheme was inserted into the CALPUFF US EPA Fortran code. The results indicated that dispersion process were generally faster than the atmospheric chemical reactions and transfer of amine into the aqueous phase reduced peak concentrations of nitramines and nitrosamines. This finding suggests that compounds achieve their full yield very slowly relative to the time scale for dispersion. Thus, the ADMS module might lead to a potential overestimation of pollutant concentrations within each hour. Nonetheless, considering the unavailability of measurements or alternative modelling software to test the steady-state assumption, it is reasonable to consider this a knowledge gap.

3.4   It is worth noting that the ADMS air dispersion models are continually validated against available measured data obtained from real world situations, field campaigns and wind tunnel experiments. However, such measurements would be required to either refine or validate the amines chemistry module.

3.5   Experiences from the modelling of the Mongstad pilot plant refer to a set of methods developed as a framework to assess impacts named the Amine Quantification Toolbox, which includes the ADMS amines chemistry module. This toolbox was subject to an independent evaluation by a group of experts on analytical chemistry, atmospheric modelling, human health and toxicology (Helgesen 2016). In the evaluation of the ADMS amines module against alternative research models, some of which are mentioned in point 1.8, the conclusion was that "although results differ between dispersion models, the combined usage of more than one gave a broader understanding of the estimated exposure". This model inter-comparison study also suggests that incorporating aqueous partitioning (refer to 3.1 and 3.3), model results are more realistic (Helgesen 2016).

Other considerations

3.6   There is currently limited knowledge on parameters to model dry and wet deposition of amines and related compounds. Assumptions on deposition behaviour similar to ammonia have been suggested (CERC 2012[16]), which can be considered reasonable.

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[1] The solvents investigated for the Mongstad project were ethanolamine, diethanolamine, triethanolamine, pyrrolidine, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine and piperazine (Helgesen 2016)

The approach to deposition can be refined in the future as more information becomes available.

3.7 In relation to baseline levels, we found no ambient air measurements of amines, nitrosamines or nitramines in the UK. Norwegian studies indicate that relatively high concentrations of hydrocarbons in air reduce concentration of OH radicals hence reducing the rate of the initial amine activation step (DNV 2010). However, this situation might not be representative of a UK cluster.

Table 2 – Interpretation of the key evidence regarding the amines chemistry module

Consideration	Summary of what the published research suggests
Model validation	• Amines chemistry module validation is not possible at the moment, however, the ADMS air dispersion model algorithms are continually validated.
Atmospheric chemical reactions mechanisms	• Reactions with OH radicals in the gaseous phase are dominant. Alternative routes of formation are relatively less significant in the formation of toxic compounds. • The generic approach devised at Mongstad is meant to be applicable for all amines, although investigations are focused on a range of alkyl, alkanol and aryl amines. • Depending on the substances, atmospheric kinetic parameters can differ in various published research, data might not be available or research might not cover their atmospheric chemistry.
Aqueous phase partition	• The formation of toxic compounds is dominated by the gaseous phase. • Transfer of soluble amine into the aqueous phase reduces the peak concentrations of nitramine and nitrosamine. • Incorporating atmospheric chemistry and aqueous partitioning, model results are likely to be less conservative.
Steady-state assumption	• Dispersion is generally faster than chemical reactions, thus compounds achieve their full yield very slowly relative to the time scale for dispersion.
Alternative modelling software	• Although results differ between dispersion models, the combination of more than one gives a broader understanding of the estimated exposure.

4 Advice for regulators

4.1 In our modelling guidance[17], we state that "the model must be fit for purpose, based on established science, and be validated and independently reviewed". The ADMS air dispersion models are continually validated, however, measurements would be required to either refine or validate the amines chemistry module. We do not endorse a specific modelling software and we acknowledge the level of uncertainty is likely to be high in this case. Nonetheless, the ADMS amines module follows first principles, considers the available science on mechanisms of formation of toxic pollutants and the evidence suggests the module has been scrutinised as a tool. We consider the amines module to be a useful tool to inform decisions, however, we would expect applicants to address uncertainties and give us confidence in the conclusions drawn from the modelling exercises. The Appendix I of this report provides advice to applicants on air

quality assessments based on the amines chemistry module. The Appendix II proposes a preliminary framework for the next steps.

4.2 Uncertainty in the identity and quantities emitted has the potential to make the modelling exercise misleading. Kinetic parameters are substance-specific but vary in the available published research, while the Environmental Assessment Levels (EALs) are also substance specific. Some published modelling exercises[7] suggest that the directly-emitted stable nitrosamines can potentially contribute more significantly to ambient air concentrations than those nitrosamines formed through atmospheric reactions. This underpins that the air dispersion modelling exercise is likely to be a useful tool to inform operations and regulatory decisions. Therefore, we strongly advise the uncertainty in relation to the species and amounts emitted to be understood and minimised.

4.3 In addition to knowing the substances released to the environment, we need to know the risk assessment criteria. The published EALs for MEA and NDMA are presented in Table 3. According to the air emissions risk assessment guidance[18], where an environmental standard or EAL is not listed for the substance assessed, the applicant can propose an EAL using the hierarchy included within the consultation document[19]. For amine-based post-combustion carbon capture facilities, the applicant is required to be transparent in the chemical composition of the solvent and degradation products, proposing EALs for each substance if not defined, justifying that values are appropriate. In addition to these already established regulatory processes to devise risk assessment criteria, when deemed appropriate, we recommend steer on the following to streamline risk assessments as experience increases:

- In-depth understanding of likelihood of emissions, longevity, relative toxicity, additional pathways of exposure (e.g. via ingestion), and developing practical risk assessment approaches able to supersede detailed modelling.

- Derivation of precautionary risk-based assessment criteria (e.g. one EAL for total nitrosamines, another for total nitramines) or grouped substances approaches, where these may be appropriate and based on sound criteria. This is practical for the following reasons:

  - The amines chemistry module needs to be run with a single species at a time (refer to point 2.5). Having a single grouped EAL opens the possibility to model a group of species, allowing the focus on detailed sensitivity analysis for individual species, where the group does not screen out.

  - Ultimately, this might set the basis to devise Emission Limit Values (ELVs) for groups of substances in the future, based on sound criteria, once monitoring standards have been devised.

Table 3 - EALs for MEA and NDMA

Compound	MEA	NDMA
Short-term EAL	400 µg/m^3	none
Long-term EAL	100 µg/m^3 (24-hour means)	0.2 ng/m^3

4.4 In relation to factors that can be considered in decisions related to environmental permit determinations, we recommend the following:

- Agreeing with the operator on emission limit values (ELVs) (e.g. maximum annual emission of secondary/tertiary amines, directly-emitted stable nitrosamines, etc.), so that the uncertainty in the emissions is minimised (as referred in point 4.2).

- Suitable solvent management and reclaiming strategies (following Best Available Techniques[20]) to minimise the direct emissions of toxic products to ambient air and increase confidence in the modelled species.

- Improvement conditions (ICs) to update the air dispersion model with representative site-specific input parameters, stack monitored data, updated scientific evidence, validation, etc.; or ICs requesting the operator to present sound evidence to justify the modelling is likely to be reasonably appropriate (for example, modelled emissions derived from stack monitoring representative of the changing emissions profile due to gradual solvent degradation).

4.5 Based on operational experience, measurements and updated knowledge, we recommend consideration to screening methods with the potential to supersede the need for detailed modelling, such as, benchmark amines to nitrosamine conversions. There is published research on worst-case studies for risk-assessment purposes, however, these results are site specific and are not recommended to be scaled or used for other locations (Tonnesen 2011[21]).

4.6 We recommend consideration to the knowledge gaps identified in the previous section 3. Although these are not exhaustive, they attempt to address key aspects related to modelling amine and degradation product releases to air.

5 Concluding remarks

5.1 In our modelling guidance, we state that "the model must be fit for purpose, based on established science, and be validated and independently reviewed". Validation of the amines chemistry module by comparing modelled with observed concentrations is not possible at the moment. However, the module is based on established science considering published research on mechanisms of formation of nitrosamines and nitramines. In addition, the ADMS air dispersion modelling algorithms have been subject to validation exercises and the amines chemistry was considered by independent reviewers as an additional tool to assess impacts of these substances.

5.2 There are various aspects of the ADMS amines module that suggest the estimation of toxic products might be conservative, for example, considering the substance by substance approach, mechanisms of formation of nitrosamines (section 3.2), steady state vs. non-steady state (sections 3.3 to 3.4), and solubility of amines (section 3.1). However, the level of uncertainty in other input parameters can counteract this. Further experience, on-site measurements and validation exercises combined with sensitivity analysis to alternative modelling software should be encouraged as the next steps. We suggest a preliminary framework for future steps in Appendix II.

5.3 As a result of our analysis, we remain cautious and recommend consideration to the key knowledge gaps (section 3) and follow our advice for regulation and permit determinations (section 4). Applicants can use the amines chemistry model as a tool to quantify impacts with special attention to uncertainties, for which we have provided recommendations (Appendix I).

Appendix I - Advice for applicants using the amines module (external)

These are guidelines to support applicants in the air quality assessments based on the ADMS amines module. The applicant is expected to follow our published guidance:

- Air emissions risk assessment: https://www.gov.uk/guidance/air-emissions-risk-assessment-for-your-environmental-permit

- Air dispersion modelling reports: https://www.gov.uk/guidance/environmental-permitting-air-dispersion-modelling-reports

- Derivation of new Environmental Assessment Levels (EALs) to air: https://www.gov.uk/government/consultations/derivation-of-new-environmental-assessment-levels-to-air

Enhanced pre-application advice service is available and can be requested at https://www.gov.uk/government/publications/environmental-permit-pre-application-advice-form.

Understanding the implications of releasing amines and degradation products to ambient air

1. The applicant is expected to demonstrate a sound understanding of the environmental implications of releasing amine and degradation products based on the best available science at the time of the submission, recognising knowledge gaps. This involves an understanding of emissions and their environmental fate.

2. Where an environmental standard or EAL is not listed for the substance assessed, the applicant can propose an EAL.

Assumptions and model inputs

3. Model inputs and assumptions must be clearly justified and evidenced with reference to available published research, manufacturer's data, calculations, process simulations, etc., demonstrating the data is representative. We expect the applicant to provide the key information presented in the table below with consideration to the following aspects:

- Type and identity of each amine and degradation product released from the stack(s) and whether stable nitrosamines will be emitted and/or formed in ambient air, explaining how these were modelled.

- Some stack source parameters, emissions limit values and operational hours might be added to the environmental permit on a case by case basis, we suggest providing:

  - An explanation of the modelled emission scenarios and how they represent annual and peak operations, including aspects such as pollutant emissions as the solvent degrades, periods when the carbon capture plant is in operation, the effect of start-up/shut-downs.

  - Pollutant emission rates of NO_X, amines, nitrosamines and nitramines (and others pollutants such as ammonia), and NO_X to NO_2 ratio at the stack with supporting evidence that they are representative. The applicant should identify achievable emission levels, so that pollutant emissions are outside the uncertainty analysis.

  - Representative actual volume flows, clearly specifying conditions of exhaust temperature, moisture, oxygen and carbon dioxide.

- Justification that the additional inputs are reasonably representative:

  - Amine-specific reaction parameters, referencing the source of information and explaining the choice is appropriate. Assumptions and/or source of information of annual OH concentration.

  - Hourly background concentrations for NO_X, NO_2 and O_3. If available, background concentrations for amines, nitrosamines and nitramines.

4. The applicant is expected to explain how the modelled predictions represent actual operations and estimate the level of uncertainty in the predicted values as specified in our modelling guidance, demonstrating the approach to address uncertainties. For this evaluation exercise, we recommend:

- Carry out a sensitivity run without amines chemistry (i.e. assuming no chemical transformation of pollutants) as an indication to differentiate the effect of predictions between dispersion and atmospheric reactions.

- Carry out sensitivity analysis to deal with variability in the input data, in particular, considering the input parameters that can be potentially managed (e.g. pollutant emissions, volume flows, NO_X emissions, operational hours, etc.). The sensitivity analysis should include evaluating which key parameters would affect predictions (e.g. the most "sensitive" parameters) and those that would outweigh the level of uncertainty most significantly. Sensitivity analysis is our recommended approach to deal with the variability in the published kinetic parameters until a database of values is established.

- Provide numerical predictions for each likely emission scenario and pollutant i.e. Nitrosamines (differentiating directly-emitted against those formed through atmospheric reactions), nitramines, amines.

- Include a discussion of results (what they mean and their significance) before the final conclusion, considering any subsequent validation document.

Conclusion

5. The applicant should clearly present the conclusion and a discussion on uncertainties referring to the sensitivity analysis. If the assumptions would make the predictions conservative, showing exceedances of an EAL, the applicant might need to either present more realistic predictions or provide a justification that these exceedances are not likely. The proposed operation and air quality assessment should outweigh uncertainties on potential impacts at sensitive receptors based on the current knowledge.

Table – Summary of the key information specific to the amines chemistry module

Description	Potential source of information
Mass emission rates for each pollutant (g/s) • Amines, nitrosamines, nitramines and NO_X	Applicant
Species molecular weight (g/mol)	
Ratio of NO_X to NO_2 at the stack (dimensionless)	
Amine-specific atmospheric reaction rate parameters: • k_{1a} - Amine/OH reaction rate constant (/ppbv/s) • k_2 - Amino radical/O_2 reaction rate constant (/ppbv/s) • k_3 - Rate constant for the formation of nitrosamines (/ppbv/s) • k_{4a} - Rate constant for formation of nitramine (/ppbv/s) • k_4 - Amino radical/NO_2 reaction rate constant (/ppbv/s) i.e. $k_{4a} + k_{4b}$ • k_{1a}/k_1 - Branching ratio for amine/OH reaction (dimensionless) • j_s/jNO_2 - Amine-specific ratio of photolysis rates between nitrosamine and NO_2 (dimensionless)	Published research
OH annual average concentration (ppbv)	Published research or ambient air measurements
Hourly background concentration values for NO_X, NO_2 and O_3 (µg/m^3)	Ambient air measurements

Appendix II – Preliminary framework for future work

This appendix suggests a preliminary framework for potential next steps based on our findings, advice for regulation and identified knowledge gaps at the time of writing this report.

Modelling toolkit

1- Improvements to the current amines module within the ADMS software, primarily incorporating the ability to model a mix of releases, secondly, including phase partitioning, and lastly the potential incorporation of the nitrites radical route (refer to sections 3.1 and 3.2).
2- Validation of the amines module incorporated in ADMS, including the validation of the chemistry scheme for a wide range of substances (refer to sections 3.2, 3.4, and 3.5).
3- Alternative non-steady state modelling software covering the aspects mentioned in point 1 (refer to section 3.3).
4- Kinetic parameters/chemistry database (refer to section 3.2).

Regulation

1- Transparency in the emissions to air, nature, quantities and uncertainties (refer to section 4.2 and 4.3).
2- Human health and habitats risk assessment criteria (refer to section 4.3), considering toxicity, longevity, environmental fate, etc.
3- Stacks monitoring and operational modes directly affecting releases (refer to sections 4.4 and 4.5).
4- Ambient air measurements (refer to sections 3.7, 4.4 and 4.5).
5- Technology benchmark values: Operational data, emissions, stack heights, potential ELVs, etc.
6- When deemed appropriate, robust risk-based methods able to supersede the need for detailed modelling of emissions to air (refer to section 4.5).

Appendix III - References

[1] Nielsen et al., 2010 a. Theoretical Evaluation of the Fate of Harmful Compounds Post Emission. Tel-Tek. 2010

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