Cambridge Environmental Research Consultants

Improving Post-Combustion Carbon Capture Air Quality Risk Assessment Techniques

Final report

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CERC

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Executive Summary

CERC was awarded the contract by the Environment Agency to deliver this project to help improve air quality risk assessment techniques for post-combustion carbon capture as an emerging technique. The main focus of the project is a technical investigation of the use of the amine chemistry module in ADMS for the assessment of amines and their atmospheric degradation products.

A key aim of the project is to address the uncertainties of ADMS input data and assumptions, help users to calculate input parameters, improve accuracy of modelling, and improve transparency and significance of the assessment process. The project aims to increase confidence and understanding of the ADMS approach and assessment strategies, including the current limitations, to inform better risk-based decisions.

A key outcome of the project is a preliminary framework for appropriate and robust sensitivity assumptions for risk assessments. The framework development entails improving the evidence and practical use of the current ADMS amine chemistry module approximations, addressing or reducing the uncertainty in the predicted concentrations and decision-making in accordance with seven objectives outlined by the Environment Agency's Air Quality Modelling and Assessment Unit (AQMAU).

The project includes the following subtasks:

- A literature review of substance specific atmospheric reactions and data collation:
    - List of amines and their corresponding nitrosamine and nitramine species
    - List of atmospheric kinetic parameters
    - List of Henry's law constants
    - Other input data
- Sensitivity testing for risk-based decision-making and practical use:
    - ADMS amines chemistry scheme (i.e. gas reactions with OH radicals)
    - ADMS amines aqueous scheme (i.e. partitioning of amines into plume water droplets)
- Development of an additional ADMS input tool
- Literature reviews to increase confidence and understanding of the ADMS approach and assessment strategies, and further the understanding of model and data limitations
- Recommendations for future work

The work is focused on a specific group of amines considered to be the most relevant to current and future carbon capture facilities, along with their corresponding nitrosamines and nitramines. This list comprises 23 core amines, plus some additional relevant species, and includes well-studied amines such as monoethanolamine (*MEA*), 2-amino-2-methyl-propanol (*AMP*) and piperazine (*PZ*). It includes different types of amines, including primary, secondary and tertiary amines in straight-chain and cyclic arrangements. A mix of simple and more complex, sterically-hindered amines are included, as well as those containing alcohol (hydroxyl) groups and other functional groups.

The literature review of kinetic parameters has involved extensive research and collation of published values for all of the atmospheric kinetic parameters required in the ADMS amine chemistry scheme, including values derived from: experiments, detailed theoretical calculations, and predictions. The parameters comprise: the initial (first step) reaction of OH radical with amine (k_1); the branching ratio of this reaction; the rate constants for the subsequent reactions of the amino radicals to form the nitrosamine, nitramine and other products (k_2, k_3, k_{4a}, k_{4b}); and the photolysis constant, $J_{nitrosamine}/J_{NO2}$.

Relationships and patterns in the atmospheric reaction parameters for different species are discussed, and an analysis of the range/differences in values for a given species. Structure Activity Relationship (SAR) predictions are discussed. Where differences in reported values are highlighted by authors, such as problems in experimental methodology, or criticism of theoretical calculation, this is included in the discussion.

The amine chemistry scheme in ADMS 6 includes an option to model the partitioning of amines to any liquid water contained in the dispersing plume, and the resultant slowing of gaseous phase reactions. The solubility of the amine species was therefore investigated. A literature review was carried out, and published values for Henry's Law constants (a measure of the solubility of species) collated.

The collation of the kinetic data and solubility values enables model users to compare the ranges of the values, identify outliers, set ranges of data to use in sensitivity tests and make informed decisions.

Literature reviews were also carried out to investigate values for other key model input data relating to the amine chemistry. This includes spatial and temporal considerations for ambient hydroxyl radical concentrations in the UK.

The inputs and results of a range of sensitivity tests are reported, with the aim of assisting risk-based decision-making and practical use. The focus is on amine-specific parameters, specifically those parameters over which site operators have some control (e.g. type of solvent, exhaust temperature) and over which model users have an element of choice (e.g. due to uncertainty in values).

Those tests involving only the standard (gaseous phase) amine chemistry showed that the following key parameters result in the lowest sum of concentrations of nitrosamines and nitramines:

- Low k_1 (k_{OH})
- Low k_{1a}/k_1 branching ratio
- Lower ambient ozone concentrations
- Low ambient OH

Those tests involving aqueous phase partitioning showed that the following key conditions that result in the lowest sum of concentrations of nitrosamines and nitramines:

- Higher emission temperature (at a constant water content)
- Saturated water content (with associated higher emission temperature).

Additionally, a user input tool has been developed as part of this project, to help model users calculate and document the amine-related input parameters. The tool has been designed to be user-friendly, and to help calculations of input data to be transparent, repeatable and auditable. It is also designed to be useful for planning and carrying out sensitivity tests and analysis of data in a systematic matter (e.g. hourly-varying hydroxyl radical concentrations).

Further explanations of the underlying calculations and assumptions of the amine chemistry module are provided, via literature reviews of research on the key atmospheric chemistry and dispersion processes. These explanations are included in order to address questions that have arisen during the project, via the CERC technical support helpdesk, and through stakeholder engagement, and include an explanation of how chemistry calculations over small timesteps are included in ADMS: the 'dilution and entrainment' option, and the delay in amine chemistry due to initial high NO concentrations.

The preliminary assessment Framework resulting from this project comprises the following:

- A database of collated kinetic parameter values:
  - k_1 to k_4 rate constants
  - Branching ratios
  - Photolysis constants
- A database of collated aqueous partitioning parameters:
  - Henry's Law constants
- A User Input Tool, for the preparation of model input data
  - Unit conversion
  - Calculation of the constant, 'c'

A summary of the recommendations for future work is as follows:

- Reliable measurement methods should be developed that are sufficiently sensitive to measure nitrosamines and nitramines in ambient air
- Further research on the amine scheme rate constants should be carried out, particularly:
  - concentrating on the amines used, or likely to be used, in full-scale carbon capture facilities
  - further measurements and/or calculations of key atmospheric reaction rate constant data
  - the creation and ongoing development of a central database of rate constant values
  - detailed analysis of the accuracy and uncertainty of the values, carried out by experts in the field of rate constant measurement and modelling
  - further development of structure activity relationships (SARs) for amine reactions
- Further research on the reaction of amines with the chlorine radical (Cl), including:
  - Further measurements and/or calculations of the rate constants, for more amine species
  - Research on typical atmospheric Cl radical concentrations in different areas (urban, rural, industrial, marine), and other spatial variation considerations.
  - Research on the time variation of Cl radicals in the atmosphere.

1 Introduction

1.1 Report overview

CERC was awarded the contract to carry out this Environment Agency led project, instigated by the Environment Agency Air Quality Modelling and Assessment Unit (AQMAU), to help improve air quality risk assessment techniques for post-combustion carbon capture.

An AQMAU recommendations document (AQMAU, 2021) identifies and describes knowledge gaps and limitations of modelling tools. Based on the findings of this document, the proposal for this project describes the overall objective:

Through this project, we want to gather evidence to increase confidence in the current risk-assessment methods, decrease the uncertainty and incorporate practical tools and sound evidence into risk-based decision-making.

Specifically, the proposal outlines the following seven objectives identified by the Environment Agency as being particularly important for current risk assessment methodologies and tools:

1. *The only commercially available estimation tool at the moment is the ADMS amines module. Alternative models were developed for research purposes, however, they are not widely available for use by UK regulators, operators or air quality professionals.*

2. *The available ADMS amines module cannot model a mixture of released amines i.e. each released species needs to be modelled individually according to their specific kinetics, thus each amine reacts with all the available hydroxyl radical*

3. *Published research where an amines chemistry scheme was incorporated into the US EPA CALPUFF air dispersion model indicated that dispersion processes were generally faster than chemical reactions and transfer of amines into aqueous phase reduce nitrosamines and nitramines peak concentrations (Fowler and Vernon, 2012).*

4. *An alternative method to estimate the formation of compounds from released amines is assuming steady state conversions based on published research and experimental studies. However, these can be uncertain due to the complex multiphasic chemical reactions and the potential that the chemistry of specific compounds might not represent the behaviour of a whole group.*

5. *The ADMS chemistry scheme is based on the atmospheric chemistry (Nielsen et al. 2010) which considered a generic approach meant to be applicable for all amines despite investigations were focused on a range of alkyl, alkanol, and aryl amines (Helgesen and Gjernes, 2016). However, depending on the released substances, kinetic parameter data might not be available, or the published research might not cover their atmospheric chemistry. In addition, for a given amine, the atmospheric kinetic parameters can differ in various published research. When using the ADMS amines chemistry module, testing sensitivity to potential kinetic parameters to understand variability in predictions for each amine can increase complexity of evaluating uncertainties and decision-making.*

6. *Sensitivity analysis is the determination of the effects of change in model input parameters on the predicted concentrations. Our guidance states that applicants must carry out sensitivity analysis and estimate the level of uncertainty in predictions. Particularly, the applicant needs to show how the model is affected by meteorological data, receptor grid resolution, terrain and buildings, and emission parameters (typically in scope of an environmental permit) such as stack parameters, pollutant emissions and operational scenarios. However, due to the variability, uncertainty, and number of input parameters (including atmospheric reaction kinetic parameters), the number of variables is high and robust decisions on sensitivity analysis using the ADMS chemistry module can be complex. This additional multivariable model output complexity has an impact in operator's design and regulator's decision-making.*

7. *The ADMS air dispersion models are continually validated against 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 ADMS amines chemistry module and there must be a roadmap of developments in the module towards validation.*

This report presents the work undertaken in this project to address these specific objectives, structured as follows:

- Section 1 provides context and background information regarding amines and their atmospheric degradation
- Section 2 presents a description of the current risk assessment methods/tools, focussing on the ADMS amine chemistry scheme, as this is the only commercially available software for this purpose. This is intended as a baseline on which to base an improved framework.
- The development of this Framework is described in Section 3.
- Section 4 presents the inputs and assumptions, and the results, of sensitivity tests.
- Recommendations for future work are outlined in Section 5.
- Finally, contour plots for the sensitivity tests are given in Appendix A.

## 1.2 Introduction to amines and key chemical terms

1.2.1 Amines and their degradation products

Amines are substances used in the solvent formulation of carbon capture plants due to their ability to react with the CO_2 from flue gas. They absorb the CO_2 at low temperatures in an absorber tower and then this is 'stripped' (released) at high temperatures. Although they are employed within a closed system, where the amine solvent is recycled, there is some loss to the atmosphere.

Amines are nitrogen-containing compounds similar to ammonia (NH_3), but where one or more of the hydrogen (H) atoms have been replaced with a hydrocarbon or other group. Dimethylamine, for example, has the following structure, where 'CH_3' is a methyl group:

H_3C
H_3C N — H
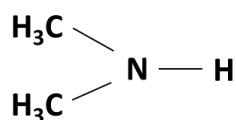
Amines used in carbon capture can react with other species in the flue gas (such as O_2 and NO_x) and in the atmosphere to produce degradation products (including nitrosamines and nitramines) that are potentially harmful. Nitrosamines consist of a nitroso (-N=O) group bonded to an amine group. The nitrosamine formed from dimethylamine, for example, is called N-Nitroso dimethylamine (often abbreviated to *NDMA*), and has the following structure:

H_3C
H_3C N — N = O
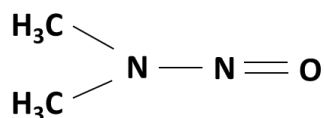
Nitramines (or, more formally, nitroamines) consist of a nitro (-NO_2) group bonded to an amine group. The nitramine formed from dimethylamine is called N-nitro dimethylamine or dimethylnitramine (sometimes abbreviated to *DMN*) and has the following structure:

H_3C
H_3C N — NO_2
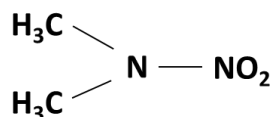
1.2.2 Key chemistry terminology

This section introduces terms and concepts that are used in this report.

1.2.2.1 Basic kinetic terminology

Chemical kinetics (usually called simply 'kinetics') is the branch of chemistry that concerns the measurement and study of the rate of chemical reactions. The following is a brief description of rate constants and the basic form of rate equations.

For a chemical reaction:

$$A \ + \ B \ \rightarrow \ C$$

The rate of consumption of A (the reactant) can be written as:

$$-\frac{d[A]}{dt}$$

Where the square brackets denote the concentration, so that [A] is the concentration of species A. Note the negative sign, which denotes that the species is being consumed within a period represented by 't'. A similar expression can also be written for species B.

Similarly, the rate of formation of C (the product) can be written as:

$$\frac{d[C]}{dt}$$

The rate of the reaction = k [A] [B]

Where k is known as the reaction rate constant or rate coefficient.

Reaction rate constants are kinetic parameters that define the chemical reaction rate equations and transformation of reagents. They have traditionally been measured empirically, by experimental measurement methods. In recent years, they have also been calculated by theoretical, computational methods, although experimental measurements maintain a vital role. The computational methods include quantum chemical methods and theoretical kinetic methods.

Although it is strictly a rate coefficient, and not a constant (because the values vary with temperature), the terms 'rate constant' and 'rate coefficient' are used interchangeably in this report, as is customary in the literature.

A set of reactions is often called a reaction scheme, where the rate equations and rate constants are considered together to determine the extent of production of the final products.

1.2.2.2 Molecular structure

Isomerisation

Isomerisation is a process in which a molecule is converted to another with the same composition and molecular formula, but with a different molecular structure.
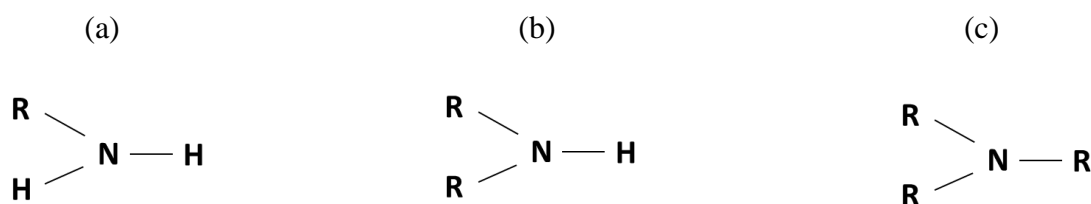
Functional groups

Functional groups are specific parts of molecules that affect the chemical reactions and physical properties. Different functional groups give molecules characteristic properties. Examples include amine (e.g. $-NH_2$), hydroxyl/alcohol (-OH) and carboxyl (-COOH) groups.

An alkyl functional group comprises one or more carbon atoms bonded to hydrogen atoms. The simplest example is a methyl group, with a single carbon ($-CH_3$), and alkyl groups comprise chains of carbon atoms when there is more than one carbon (e.g. ethyl, $-C_2H_5$).

Primary, secondary and tertiary amines

Amines (and many other types of compounds) can be classified as primary, secondary or tertiary, according to their structure with respect to the amine functional group. This property is sometimes called the degree of substitution, and has important implications for amine reaction mechanisms and rates, as discussed later in this report. Whether an amine is classed as primary, secondary or tertiary is determined by how many carbons (e.g. alkyl groups) to which the nitrogen atom is bonded. Primary amine groups are bonded to one carbon atom, secondary to two, and tertiary to three. Because each nitrogen atom in amines bonds to three atoms in total, this means that primary amines are bonded to two hydrogen atoms, secondary to one and tertiary to zero. Figure 1.1 shows the general structure of each type of amine, where 'R' represents an alkyl or other similar functional group.

Figure 1.1: Structure of primary (a), secondary (b) and tertiary (c) amines

Note that the way in which amines are designated primary, secondary and tertiary is different to most other types of compound. For alcohols, for example, it is the carbon bonded to the alcohol (OH) functional group that determines this, and the *carbons* can be labelled as primary, secondary, etc. Where a carbon is bonded to one other carbon atom, the carbon is a primary carbon, and hence the alcohol is denoted as a primary alcohol (secondary and tertiary alcohols have -OH groups bonded to a carbon that are bonded to two and three other carbons, respectively).

This distinction between how amines and alcohols (and many other compounds) are grouped as primary, etc. is important to note, to avoid potential confusion in their classification, because several of the amines in CO_2 capture solvents are both alcohols and amines (have both a hydroxyl and an amino group). Similarly, molecules with bulky alkyl chains are often discussed according to their carbon atoms. There is therefore potential for confusion with amines such as *tert*-butylamine; this is a *primary* amine, with this informal name deriving from its central, tertiary, carbon atom. Species that *are* tertiary amines include trimethylamine and triethylamine. This distinction is particularly important because primary amines are generally considered to produce unstable nitrosamines that very quickly isomerize to a different species.

Steric effects

Steric effects are effects on chemical reactions that are caused by the physical structure of the molecule. Steric hindrance is the prevention or slowing of a particular chemical reaction due to the bulk of one or more groups within molecules. The molecules do not just have to collide in order for a reaction to occur, but the specific functional groups involved in the reaction must be aligned correctly. The presence and location of bulky groups can affect this alignment, and therefore affect the rate of reaction. This is an important concept for atmospheric reactions of amines because amines with bulky functional groups (such as 2-amino-2-methyl-propanol (*AMP*)) are often employed as carbon capture solvents, as this is an important property with respect to their CO_2 absorption capability (e.g. Yoon et al, 2022).

Structure activity relationships

In chemistry, a structure activity relationship, or SAR (sometimes called a quantitative structure activity relationship, or QSAR) is the relationship between its molecular structure and its behaviour. In the context of this report, this behaviour is the propensity of a given molecule to react with another species, specifically the rate of reaction. The structural properties in question can be the presence of specific functional groups, bulky groups, etc.

The vast number of species and their reactions in the atmosphere mean that the time and effort involved in employing experimental and detailed theoretical methods for determining rate constants for all individual reactions is prohibitive. Therefore, the data collected from those measurements and calculations that *have* been carried out can be used to identify trends and develop SARs. These SARs can then be used as very useful predictive tools for estimating rate constants. These have been used for amine species, due to the wide range of prospective species used and proposed for CO_2 capture solvents.

Although SARs vary in their level of sophistication, their results are, by their inherent nature, less reliable than those of kinetic measurements and detailed calculation methods. As they are fundamentally based on the premise that molecules with similar structures have similar properties, they are susceptible to failing wherever this premise does not hold.

Solubility

The solubility of different chemical species is highly dependent on their molecular structure. Hydrophilic molecules or functional groups are those that are attracted to, and are readily dissolved in, water. Hydrophobic molecules or functional groups are those that are not attracted to, and are not readily dissolved in, water.

Examples of hydrophilic functional groups are hydroxyl (alcohol) groups and amine groups. In addition, the carboxy (carboxylic acid) group is also highly hydrophilic; this group is found in amino acids, such as glycine, which are potential carbon capture solvents.

In contrast, alkyl groups tend to be hydrophobic, and hence their presence tends to make molecules less soluble, and, in general, the longer the alkyl chain the less soluble the molecule.

Solubility is an important consideration when selecting amine solvents, as amine species with low solubility (and hence high volatility) are more likely to be lost from the capture process and emitted to ambient air (Nwaoha et al., 2017).

1.2.2.3 Other species and terms of relevance to this report

Radicals

A radical (or free radical) is a species that has one or more unpaired electrons, and is therefore highly unstable and very chemically reactive. As a result, they tend to have very short atmospheric lifetimes. Radicals play an instrumental part in atmospheric chemistry.

Hydroxyl radicals (˙OH) are the main species that initiate the atmospheric degradation process for amines.[1] A common reaction mechanism of the hydroxyl radical with many species in the atmosphere is the removal of a hydrogen atom. This is known as abstraction of the hydrogen atom. Abstraction leads to the formation of another radical, and in the case of ˙OH reacting with an amine, the result is an amino (sometimes called an aminyl) radical. Other radical species that can abstract a hydrogen atom to initiate the atmospheric degradation of amines include nitrate (NO_3˙) radicals and chlorine (Cl˙) radicals (e.g. Lee and Wexler, 2013).

Imines

An imine is a compound with a carbon-nitrogen double bond. Imines are formed during the OH-initiated atmospheric reactions of amines, but as they are not generally species of interest in the assessment of amine degradation products in the atmosphere, they are generally considered to be incidental species in this context.

Heterocyclic species

A heterocyclic molecule is a cyclic molecule (that is, formed of a ring) with at least two different types of atom within the ring structure. An example is piperazine (shown below), which has carbon atoms forming the main structure of the ring, and also two nitrogen atoms within the ring structure.

Photolysis

Photochemical reactions are those that involve the absorption of solar radiation by a molecule. If the molecule dissociates (breaks apart), as a result of this absorption, this is called photolysis. The rate of photolysis is quantified using a photolysis rate coefficient, denoted by 'J'.

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[1] Radicals are often written with a dot to indicate their unpaired electron. Sometimes this is useful, particularly when describing reaction schemes, but other times it is unnecessary, and is omitted for the sake of simplicity. The dot is omitted for the hydroxyl radical for the majority of this report, a common convention in atmospheric chemistry literature.

1.2.3 How do amines react in the atmosphere to form the degradation products?

A radical such as the hydroxyl radical (OH) can initiate the reaction process by the abstraction (removal) of a hydrogen atom from the amine. The site of initial attack determines the type of species formed, through separate branches of reactions.

For amines in general, the $^\bullet$OH can attack:
a hydrogen atom on the N atom (N—**H**)
a hydrogen atom in the methyl groups (C—**H**)
other hydrogen atoms, such as those that form part of alcohol groups (O—**H**)

The ratio between the rate of attack on an N—**H** hydrogen and the rates of attack of other hydrogen atoms is known as a *branching ratio.*

The abstraction of the hydrogen atoms leads to the formation of other radical species. The abstraction of an N—**H** hydrogen atom forms an amino radical (also known as an aminyl radical, or an N-centred radical), and it is only this radical that can eventually result in the formation of nitrosamines and nitramines.

If the amino radical reacts with nitric oxide (NO) then this forms a nitrosamine. If it reacts with nitrogen dioxide (NO_2), then a nitramine is formed. Once formed, the nitrosamine can be photolysed by the action of solar radiation, which leads to the regeneration of the amino radical.

Figure 1.2 shows an overview of the hydrogen abstraction, the formation of products from the amino radical, and subsequent photolysis of the nitrosamine, for the example amine of dimethylamine.

Figure 1.2: Schematic diagram of the key atmospheric reactions of amines
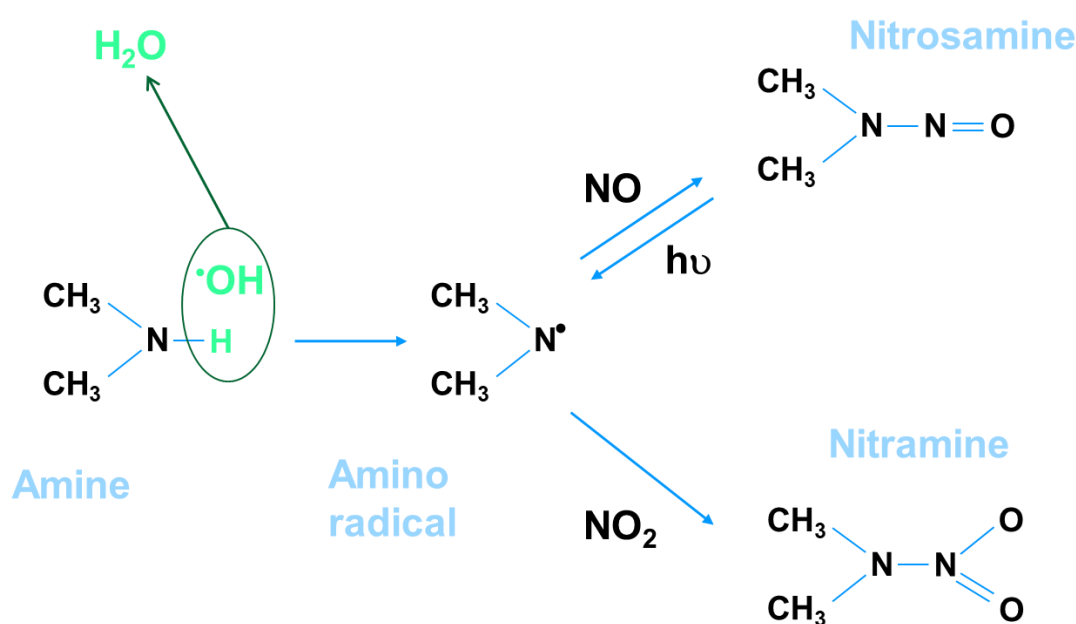
2 Current risk assessment methods/tools

2.1 Overview of dispersion models and amine chemistry

This section provides an overview of the current risk assessment methods and tools used to conduct air quality risk assessment for Post-Combustion Carbon Capture and to assess their limitations and needs for improvements. The focus here is on the amine chemistry module in ADMS. The "*AQMAU recommendations for the assessment and regulation of impacts to air quality from amine-based post-combustion carbon capture plants*" (AQMAU, 2021) document gives an overview of the status of amine chemistry modelling tools as follows:

"*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). 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.*"

ADMS was one of the models selected for the implementation of amine chemistry, as part of a large, comprehensive research program in 2011: "Health and Environmental Technology Qualification Program for Amines" part of the Norwegian full-scale CO_2 capture project Mongstad, known as CCM (Helgesen and Gjernes, 2016). During an early stage of the CCM project, the issue of emissions to air and the potential for atmospheric formation of harmful compounds was identified as a major potential constraint. It was recognised that the risk would need to be assessed, and that there were significant knowledge gaps. A comprehensive program was set up to address this, including research into the toxicological implications, the many aspects of the atmospheric chemistry reaction schemes and kinetics, and evaluation and development of dispersion models to incorporate atmospheric amine chemistry.

Several models were assessed in these early stages of the CCM project, for their suitability for the inclusion of atmospheric amine chemistry. ADMS was used for indicative case study modelling by both CERC (Price et al., 2010) and Det Norske Veritas (DNV) (Yiannoukas et al., 2010). Amine chemistry schemes within ADMS and CALPUFF were then developed in parallel by CERC and DNV, respectively, in the next stages of the project, and used to run case studies (Price, 2012a; Fowler and Vernon, 2012). The reports for this work and for several other related studies funded through Gassnova can be found on the website: https://ccsnorway.com/hse-studies/.

CALPUFF is a non-steady state meteorological and air quality modelling system. It is a Lagrangian Gaussian puff model, which simulates the effects of time- and space-varying meteorological conditions on pollution transport, transformation and removal over long timescales (more than a day) and large distances (tens to hundreds of kilometres). The spatial extent of each puff is defined using a Gaussian formulation, similar to a Gaussian plume in the vertical and crosswind directions, but including along-wind Gaussian growth and decay.

The Norwegian Institute for Air Research (NILU) joined the latter stages of the CCM project, running the WRF-EMEP model (Karl et al., 2014), where WRF is the Weather Research and Forecasting model and EMEP is the Unified European Monitoring and Evaluation Program model.

The EMEP model (Simpson et al., 2012) is an Eulerian chemical transport model (CTM) that is widely used for regional and national scale air quality assessments. It is an open source model developed at the Norwegian Meteorological Institute.

The EMEP model can be used in combination with data from various meteorological models. The option used by NILU in the CCM project was the WRF (Weather Research and Forecasting) model, which is an open source meteorological model developed at the US National Centre for Atmospheric Research (NCAR).

These dispersion models (i.e., ADMS, CALPUFF and EMEP-WRF), and their application in the CCM project, along with the comprehensive compilation of data, methods and improved understanding of best practice, was collectively known as the Amine Qualification Toolbox. This Toolbox, including the dispersion modelling, was independently assessed by a group of experts on analytical chemistry, atmospheric dispersion modelling and toxicology, and found to be fit for the purpose of comparing different amine-based technologies for the full scale Mongstad plant. After the termination of the CCM project, the Toolbox was used for the assessment of the emissions from testing programs of several vendors at Mongstad, as part of a related project, the Technology Centre Mongstad (TCM) project (Gjernes et al., 2013). In their 2016 summary of the Toolbox, Helgesen and Gjernes (2016) concluded, of the Toolbox, that "*It is highly recommended that this practice is implemented in any future post combustion project based on amine or amino acid solvents*".

During this TCM project the Leibniz Institute for Tropospheric Research (IfT) used the COSMO-MUSCAT model to assess amine chemistry effects. COSMO-MUSCAT is a multiscale model system developed by the Leibniz Institute for Tropospheric Research (TROPOS). It comprises the regional weather model COSMO (COnsortium for Small scale MOdelling) and the chemistry transport model MUSCAT (MUltiScale Chemistry Aerosol Transport. A complex multiphase monoethanolamine (*MEA*) chemistry mechanism was developed for the model, to represent multiphase processes related to *MEA*, focusing mainly on the chemical fate and lifetime of *MEA* and its reaction products such as nitramines and nitrosamines as well as their removal.

Similar modelling has been carried out in other projects. As part of a CLIMIT project, NILU included a chemical scheme for *MEA* reactions in WRF-Chem (Weather Research and Forecasting Chemistry), and used this to model *MEA* emissions for a case study (Karl et al., 2015). They compared the results of this model with those from their WRF-EMEP modelling (using the same general input data and model setup), including an investigation of the effects of varying the calculation grid resolution.

Note that the above modelling tools incorporating amine chemistry schemes were part of the aforementioned research and are not commercially available at the time of writing this report.

2.2　The ADMS amine chemistry module

As described in Section 2.1, the amine chemistry module in ADMS was developed as part of the Norwegian full scale CO_2 capture Mongstad (CCM) project. Novel aspects of the module were a mixing model for the 'instantaneous' rather than 'ensemble' plume and the incorporation of the generic gas phase reaction scheme for amine chemistry derived under the CCM project, as described in the ADMS Amine Chemistry supplement user guide (CERC, 2023b). The amine reaction scheme was made widely available through the release version of ADMS 5 in 2012.

The ADMS amine chemistry module was designed to be versatile and adaptable, to allow a wide range of amines to be modelled (e.g. primary and tertiary, and those with alcohol groups), specified using generic names for the various species. These are simply 'AMINE', 'NITROSAMINE' and 'NITRAMINE'. The amino radical species is denoted 'RADICAL', and can also be output by the model. Specific amine species are defined by the kinetic parameters and other amine-specific parameters input by the model user, such as unit conversion factors that reflect their molecular mass. The model user can also specify whether a stable nitrosamine is formed for primary amines.

The amine reaction scheme also involves interaction with NO_x emissions and background concentrations and ozone background concentrations. It uses information from the ADMS meteorological pre-processor to determine photolysis rates on an hourly basis, and interacts with the NO_x chemistry module.

It is also possible to model directly-emitted nitrosamines and nitramines, as these can form within the absorber/exhaust gas stream, before the stack exit.
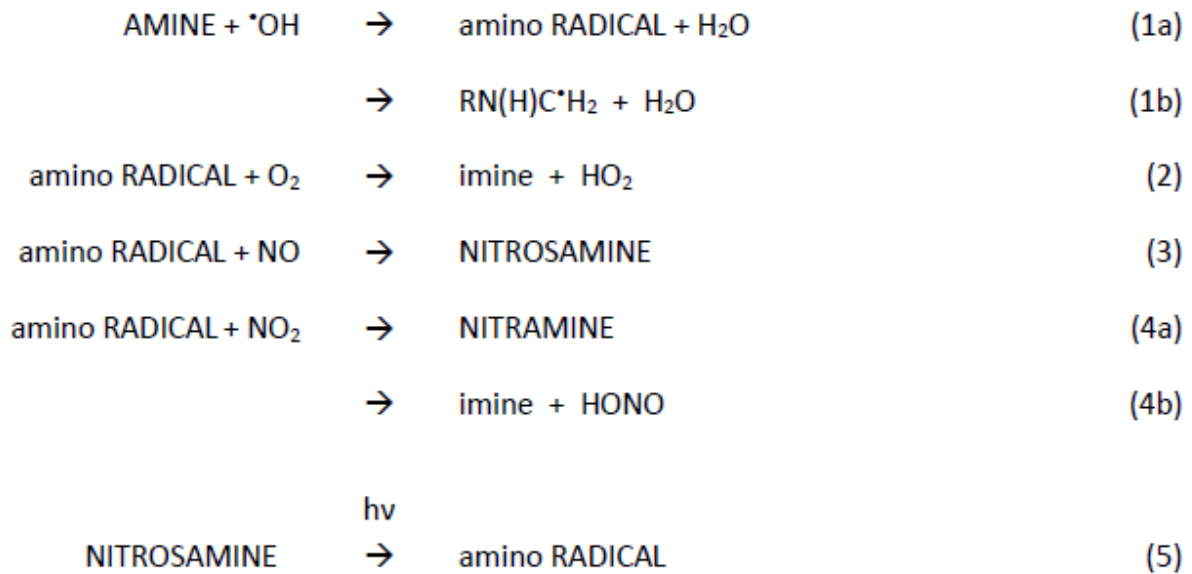

2.2.1　Reaction scheme

Figure 2.1 shows the reaction scheme that forms the basis of the amine scheme in ADMS. It is a scheme originally based on dimethylamine, as determined in the Atmospheric Degradation of Amines (ADA) project, described in Nielson et al. (2011). Note that 'hν' denotes a photon of energy, and is often used to represent a photolysis reaction, here the photolysis of the nitrosamine.

Figure 2.2 shows the reaction equations used to model the amine chemistry.

Figure 2.3 shows an illustration of the inter-relationships of the various aspects of the amine chemistry scheme with other ADMS processes and data. The red boxes indicate user input data and the green boxes represent data calculated by ADMS. The diagram shows how the amine chemistry scheme interacts with the ADMS NO_x chemistry scheme, which is based on the Generic Reaction Set (GRS) of equations (Azzi and Johnson, 1992).

Figure 2.1: ADMS amine chemistry scheme

AMINE + ˙OH	→	amino RADICAL + H_2O	(1a)
	→	$RN(H)C\dot{}H_2$ + H_2O	(1b)
amino RADICAL + O_2	→	imine + HO_2	(2)
amino RADICAL + NO	→	NITROSAMINE	(3)
amino RADICAL + NO_2	→	NITRAMINE	(4a)
	→	imine + HONO	(4b)
NITROSAMINE	$\xrightarrow{hv}$	amino RADICAL	(5)

Where $RN(H)C\dot{}H_2$ is another radical (often called a 'carbon-centred' radical), that does not lead to nitrosamine or nitramine formation, and HO_2 and HONO are reaction by-products.

Figure 2.2: Reaction equations in ADMS

1. Loss of the AMINE

$$\frac{d[AMINE]}{dt} = -k_1[AMINE][OH]$$

2. Production of the amino RADICAL

$$\frac{d[RADICAL]}{dt} = k_{1a}[AMINE][OH] + j_5[NITROSAMINE] - k_2[RADICAL][O_2]$$
$$-k_3[RADICAL][NO] - k_4[RADICAL][NO_2]$$

3. Production of NITRAMINE

$$\frac{d[NITRAMINE]}{dt} = k_{4a}[NO_2][RADICAL]$$

4. Production of NITROSAMINE

$$\frac{d[NITROSAMINE]}{dt} = k_3[RADICAL][NO] - j_5[NITROSAMINE]$$

Figure 2.3: Schematic diagram of the interactions of the various aspects of ADMS and its amine chemistry scheme (red boxes denote user input data and green boxes data calculated by ADMS)
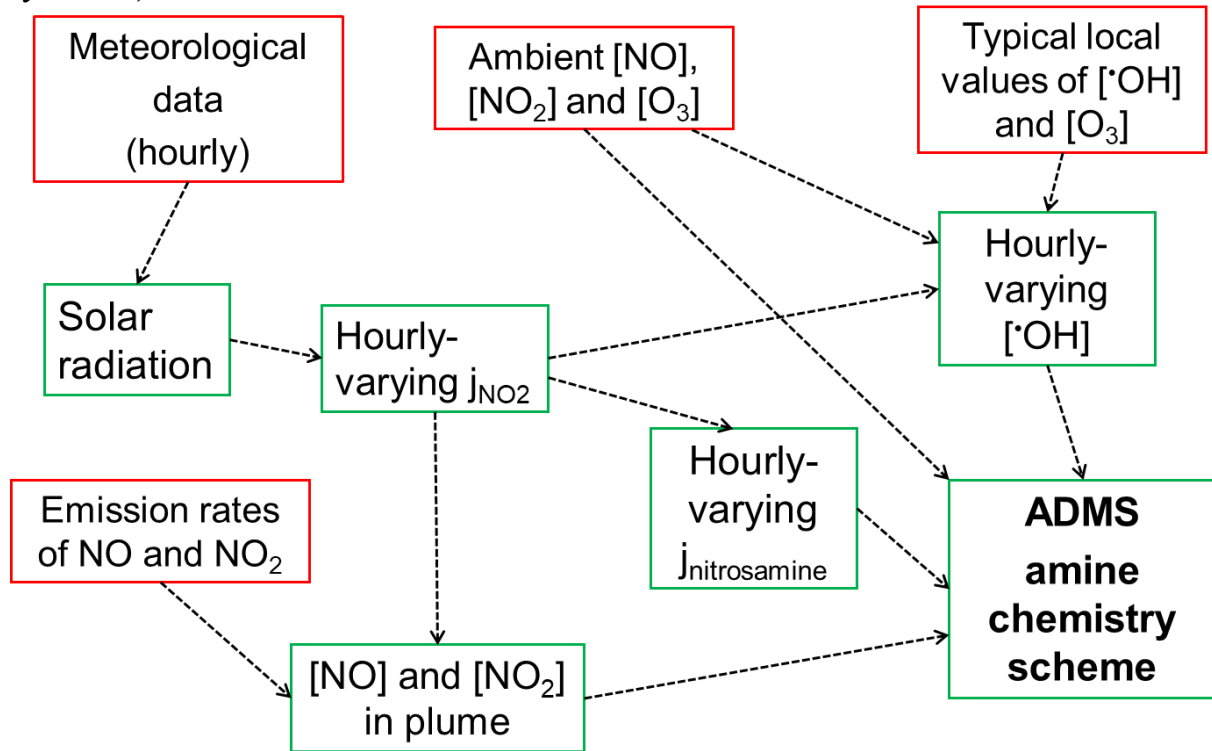
Further details on the amine chemistry scheme can be found in the amine chemistry user guide supplement (CERC, 2023b). Further information on the NO_x chemistry, and all other aspects of the ADMS model can be found in the ADMS 6 User Guide (CERC, 2023a) and the online Technical Specification documents (CERC, 2023c).

2.2.2 Photolysis

The photolysis of nitrosamines is parameterised in the ADMS amine chemistry scheme by means of the parent amine-specific, user-defined parameter $J_{nitrosamine}/J_{NO2}$. This is a ratio of the photolysis rate of the nitrosamine to that of NO_2. As the NO_x chemistry scheme calculates the diurnal variation of J_{NO2} according to the solar radiation variation in the input meteorological data, the diurnal variation in the nitrosamine photolysis is varied accordingly.

The photolysis of the directly-emitted nitrosamines can also be modelled if the model user specifies the emission as 'nitrosamine', activates the amine chemistry module, and inputs an appropriate value for the photolysis rate; the amino radicals regenerated during the photolysis process are then available for further reaction.

2.2.3 User input data

Table 2.1 summarises the data required by the ADMS amine chemistry scheme. Figure 2.4 shows an illustration of the amine chemistry scheme and its use of the parameters.

Table 2.1: User input data requirements specific to the amine chemistry scheme

Name in ADMS	Description	Symbol	Units
Amine/OH reaction rate constant	Rate constant for the reaction of the amine with hydroxyl radical (also known as k_{OH})	k_1	$ppb^{-1} s^{-1}$
Amino radical/O_2 reaction rate constant	Rate constant for the reaction of the amino radical with oxygen	k_2	
Rate constant for formation of nitrosamine	Rate constant for the reaction of the amino radical with NO to form the nitrosamine	k_3	
Rate constant for formation of nitramine	Rate constant for the reaction of the amino radical with NO_2 to form the nitramine	k_{4a}	
Amino radical/NO_2 reaction rate constant	Rate constant for the overall reaction of the amino radical with NO_2	k_4	
Branching ratio for amine/OH reaction	Branching ratio for the abstraction of hydrogen from the nitrogen atom	k_{1a}/k_1	None
Ratio of $J_{nitrosamine}$ to J_{NO2}	The photolysis rate constant, expressed as a ratio of the photolysis rate of the nitrosamine to that of NO_2	$J_{nitrosamine}/J_{NO2}$	
Constant for OH concentration calculations	A value used by the model to generate hourly concentrations of OH, along with hourly values of O_3 and J_{NO2}	c	s

Note that $k_1 = k_{1a} + k_{1b}$ and $k_4 = k_{4a} + k_{4b}$. Refer to Figure 2.1 for the reactions to which these rate constants relate. Note that 'ppb' here, and throughout this report, refers to ppbv (parts per billion by volume)

Figure 2.4: Schematic of the amine chemistry scheme in ADMS, depicting the depicting the user input data requirements shown in Table 2.1
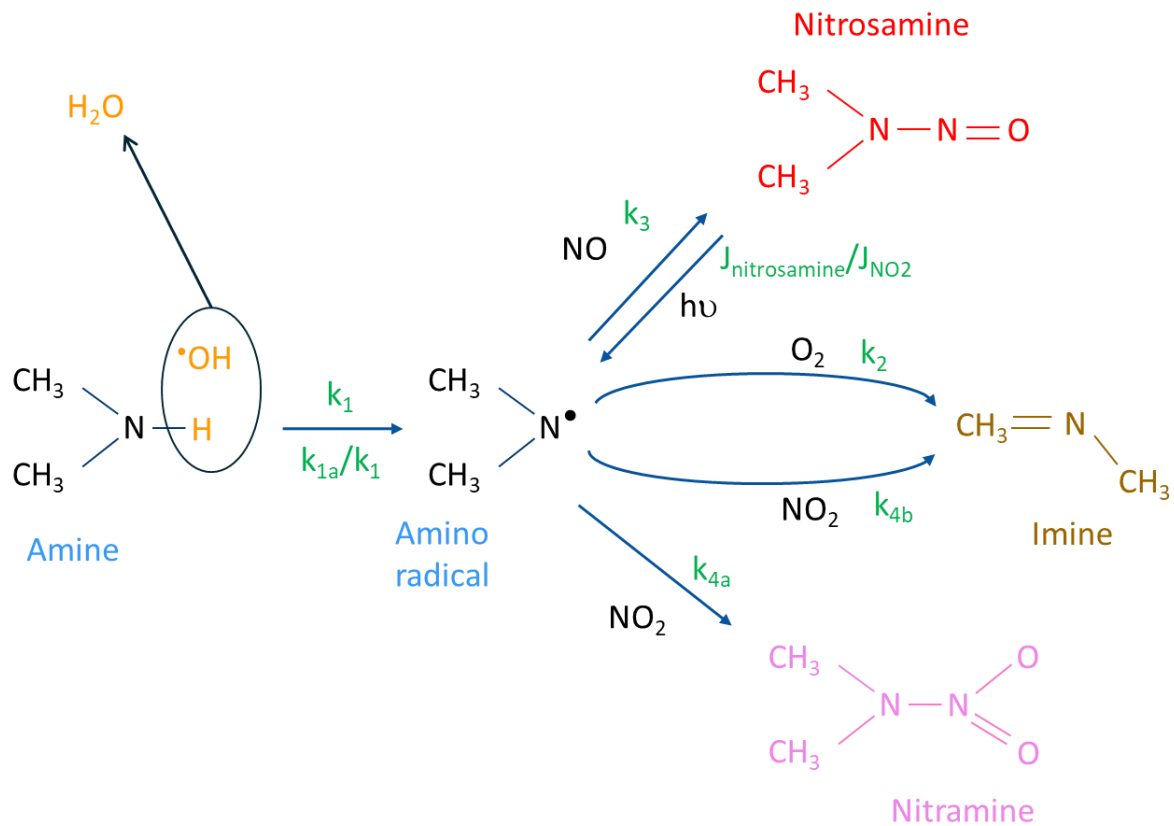
In addition, the model requires the following data that relate to the amine chemistry scheme:

- Emission rates (in g/s) for the amine; any directly-emitted nitrosamine or nitramine, NO_x and NO_2 (NO is then calculated by ADMS).

- Conversion factors for $\mu g/m^3$ to ppbv, which is dependent on the molecular mass of each species (including the nitrosamine and nitramine as well as the amine).

- Hourly varying local background data for NO, NO_2 and O_3

- An indication of whether the amine will not form stable nitrosamines (i.e. if it is a primary amine)

2.2.4 Short timescale incremental mixing

ADMS has a 'Low concentration dilution and entrainment' scheme, and model users must ensure that this is switched on whenever modelling amine chemistry. This is described below.

For the purposes of modelling amine reactions, it was necessary to modify the standard ensemble plume mixing model to take account of instantaneous plume mixing. Figure 2.5 shows a schematic diagram of the ensemble mean and instantaneous plumes, and entrainment of background species.

The standard ADMS dispersion algorithms calculate and store the plume sizes at small timesteps (seconds) over an internal grid. Figure 2.6 shows an example of the variation of the horizontal plume spread parameter, σ_y, a measure of the horizontal plume width, over the first minute of modelled plume dispersion for seven different meteorological conditions, specifically the Pasquill-Gifford stability categories. The letters A to G in the graph correspond to these categories, where A represents very convective (unstable) meteorological conditions, D represents neutral conditions, and G denotes very stable conditions.

The standard ADMS dispersion algorithms also calculate the concentrations and age of the primary (emitted) pollutants at each output point. The dilution and entrainment scheme first takes these concentrations and adjusts them to remove the effects of dilution, using the plume spread parameters and ages, according to the following ratio (where σ_z describes the vertical plume width):

$$\frac{\left(\sigma_y \sigma_z\right)_{t=0}}{\left(\sigma_y \sigma_z\right)_{t=t_{age}}}$$

The equations that represent the chemical reactions are applied to all of the relevant pollutants over many small timesteps, each with duration δt (on the order of seconds or less), over the period between t_0 and t_{age}. For a given timestep, δt, there will be a corresponding instantaneous concentration, which is then adjusted back to correspond to the ensemble mean plume, based on the relative plume sizes as described above.

So, although the model timescale in ADMS is ostensibly an hour, in the sense that variations in meteorology, emissions and background concentrations may occur each hour, the chemistry and dispersion calculations are carried out over much smaller timesteps, and converted to an hourly 'ensemble' plume only at the end of the process.

This more realistic modelling approach for plume mixing results in higher concentrations of nitrosamines and nitramines than would result if the dilution and entrainment option were not applied to the chemistry calculations. Figure 2.7 shows an example of output nitrosamine concentrations modelled with and without the dilution and entrainment option applied. The y axis represents the nitrosamine concentration normalised using output concentrations of an inert tracer (carbon monoxide), in order to isolate and illustrate the effect. This clearly shows that not using the dilution and entrainment option would lead to a significant underprediction of potentially several orders of magnitude.

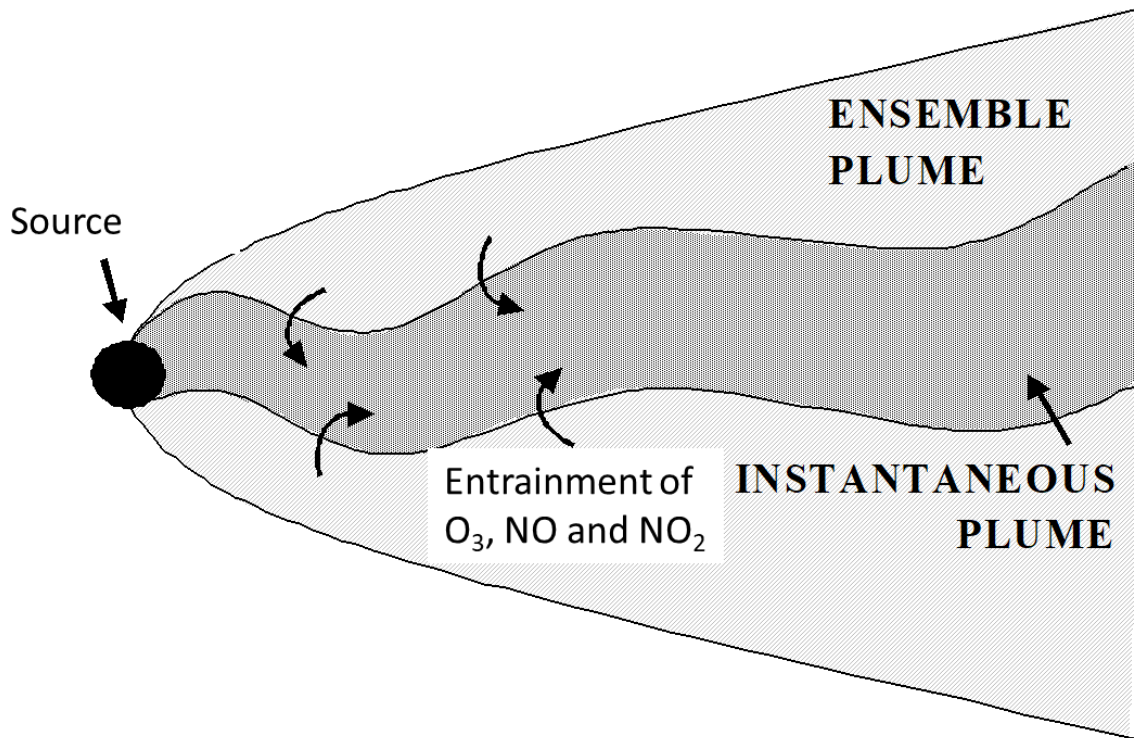*Figure 2.5: Schematic diagram of the mean and ensemble plumes*

Figure 2.6: Illustration of the variation of horizontal plume spread, σ_y, over time, for different meteorological conditions (Pasquill-Gifford stability classes)
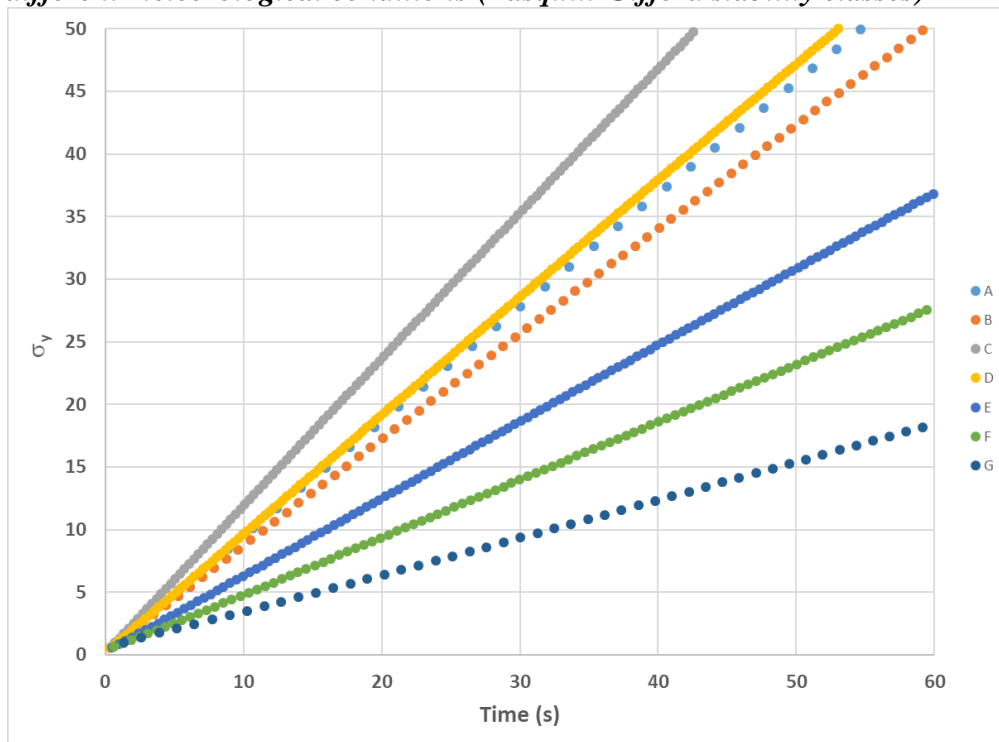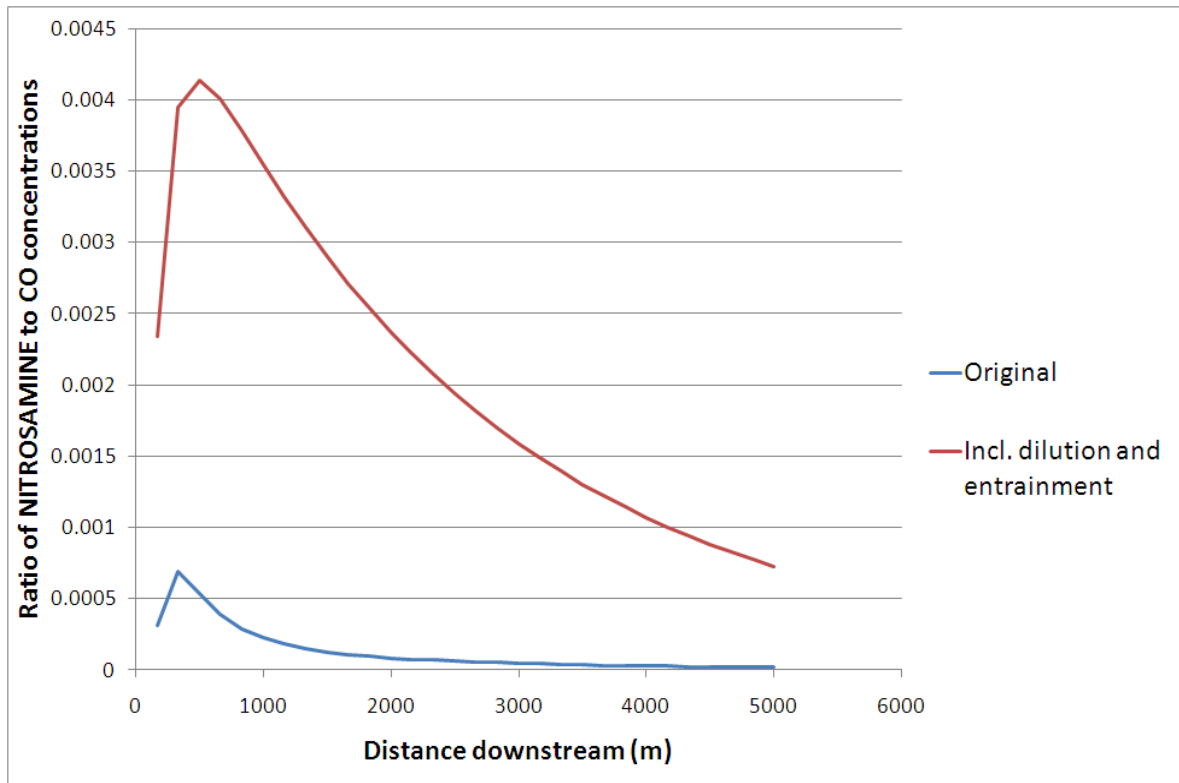
Figure 2.7: An example of the effect of the dilution and entrainment scheme on nitrosamine formation, represented by the variation of nitrosamine/inert tracer concentrations with downwind distance

2.3 Developments for ADMS 6 as part of the SCOPE project

2.3.1 Summary of developments

At the start of this project, the release version of the ADMS amine chemistry module was ADMS 5, and the amine scheme was the original released version, as described in Section 2.1. Just prior to the start of this project, several improvements to the amine chemistry scheme were being implemented, as part of a different project, the SCOPE (Sustainable OPEration of post-combustion Capture plants) research project (https://www.scope-act.org/). These improvements were included in the release of ADMS 6 in March 2023.

This section of the report describes these developments of the amine chemistry scheme as implemented in ADMS 6.

The following three developments were carried out under the SCOPE project:

- Multiple sources can now be modelled in a single run, with each source modelled individually.

- Multiple amine species can now be modelled in a single run. Note that this was designed so that there is limited interaction (and competition for OH) between the amine species.

- A new option is included, to calculate absorption of amines, nitramines and nitrosamines into the liquid water content of the plume. It also includes a new option to calculate water droplet nucleation around salt particles.

The first development was carried out because it is highly likely that amine solvents employed in full-scale technology will be blends containing two or more amine species (see, for example, the discussion by Nwaoha et al., 2017).

The second development addressed the fact that an important feature of carbon capture is that the infrastructure is designed to be grouped into areas, often called 'clusters', with many sites using carbon capture. In ADMS 5, the user could only model a single source in a single run, so each source was modelled by carrying out separate runs and post-processing the output files, which was also highlighted as a potential limitation.

The third development was carried out because many amines, particularly those with alcohol or carboxyl functional groups are highly soluble, and have the potential to partition into water droplets in the atmosphere. Note that an aqueous partitioning scheme was previously developed as part of the CCM project, but not included as part of the amine chemistry scheme in ADMS 5. This is described in the next section of the report.

2.3.2 Aqueous partitioning in the atmosphere

In the atmosphere, interactions between the gaseous phase and the aqueous phase are likely; a gaseous plume can co-exist with a 'cloud droplet' or 'condensed water' or 'wet' plume. The wet plume is likely to form almost immediately after the emission to air of flue gas containing significant quantities of water vapour.

As the plume moves downstream, it is diluted by entrainment of ambient air. This will change the water content of the plume, depending on the humidity of the ambient air and other meteorological conditions, including temperature; it is most likely that the water content of the plume will reduce.

In most cases, the relative humidity of the plume may fall below 100% and the droplets evaporate. Small amounts of water will be retained within cloud condensation nuclei (CCN), which are airborne particles made up of salts (ammonium sulphate, sodium chloride, etc).

Alternatively, the 'wet' plume may persist for some kilometres downstream. In either case, the plume may encounter higher humidity air and cloud further downstream, which may have a significant impact on the liquid water in the plume. By this time, however, the plume will be very dilute; therefore, the focus of developing this partitioning scheme in ADMS was on the impact of the formation of a wet plume soon after the gases are released.

2.3.3 The aqueous partitioning scheme in ADMS 6

The aqueous partitioning scheme in ADMS quantifies the transfer of the amines, nitrosamines and nitramines between the gaseous phase and the aqueous phase. The aqueous phase is treated as a sink for the gaseous amines, and the production of nitrosamines and nitramines in the gaseous phase chemistry schemes is limited as a result. Note that this is a partitioning scheme only; no aqueous phase chemistry is included, based on the conclusion from a comprehensive body of work that the formation of nitrosamines and nitramines in the atmosphere is very much dominated by gas phase reactions (Helgeson and Gjernes, 2016).

When using the aqueous partitioning scheme, the emissions of the amine represent the combined total of the emitted amine partitioned in the gaseous and the aqueous phases. The model user, therefore, does not need to know/estimate how much of the amine is in each phase at the point of release.

At each timestep, as the plume spreads and dilutes, the model calculates the total water content of the plume, from the initial water content plus the impact of entrainment. It then calculates the liquid water content of the plume, and partitions the amines between gaseous and aqueous phase according to the Henry's Law constant. The gas phase reactions are then carried out for the gaseous amines.

It is also possible for the model user to investigate the partitioning of nitrosamines and nitramines into the aqueous phase by entering Henry's Law constant values for these species, though, as described further in Section 3.2.6, this is not necessarily advisable, as there are very few reliable data available for these species.

The aqueous partitioning scheme in ADMS was designed to allow for the future inclusion of wet deposition of cloud droplets by raindrops through a washout coefficient formulation. This means that advanced treatment of the washout of cloud droplets and gaseous phase by rain could be implemented in the ADMS model in the future if required. This would model the transfer of the amines, nitrosamines and nitramines from the aqueous phase to ground level via wet deposition.

The model user can select either the standard aqueous partitioning only, or combine it with the Plume Droplet scheme, within the Plume Visibility options in ADMS. The standard scheme requires a Henry's Law constant for the amine (and the corresponding nitrosamine and nitramine if modelling their partitioning), and a value for the initial water content of the emitted plume (kg of water per kg of dry release).

The Plume Droplet Scheme includes the nucleation of water drops by CCN, and requires the following parameters:

- the number of ions in dissociation for the salt
- the concentration of salt particles
- the molecular mass of the salt particles
- the number of salt particles per cm^3

Full details of the aqueous scheme and the required model set up and additional inputs, are given in the ADMS amine chemistry scheme user guide supplement (CERC, 2023b).

In this project, the significance of the aqueous partitioning was investigated by collating ranges of Henry's Law constant data (see Section 3.2.6) and carrying out sensitivity tests using representative vales the aqueous scheme (see Section 3.3.2).

2.4   AQMAU recommendations document

The Environment Agency published guidance is available at [Environmental permitting: air dispersion modelling reports - GOV.UK (www.gov.uk)](#) and [Air emissions risk assessment for your environmental permit - GOV.UK (www.gov.uk)](#), which set the expectations from applicants/operators for environmental permits. In relation to air dispersion modelling software, the guidance states that: "The model you use must be fit for purpose, based on established science, and be validated and independently reviewed".

The current risk assessment of amine atmospheric degradation products is described in the AQMAU document, "*AQMAU recommendations for the assessment and regulation of impacts to air quality from amine-based post-combustion carbon capture plants*" (AQMAU, 2021). The document was drafted in consultation with stakeholders and provides summaries of:

- modelling techniques available for air quality impact assessments,
- some of the key knowledge gaps and considerations,
- recommendations for regulating emissions,
- guidelines to support applicants in the air quality assessments based on the ADMS amines module (ADMS 5), and
- a preliminary framework for future work.

3 Development of the Framework

The framework development entails improving the evidence and practical use of the current ADMS amine chemistry module approximations, addressing or reducing the uncertainty in the predicted concentrations and decision-making in accordance with the objectives given in Section 1.1.
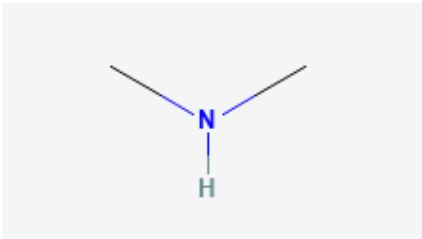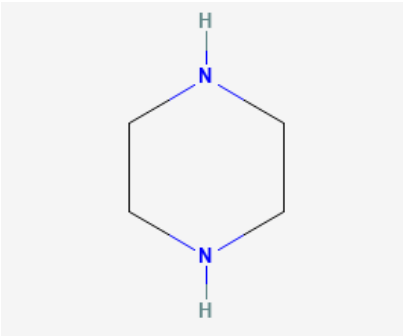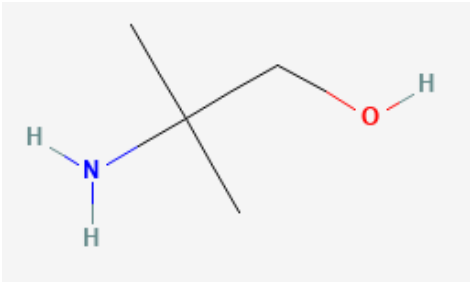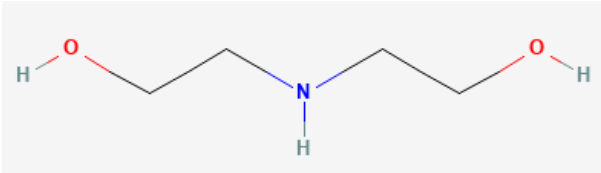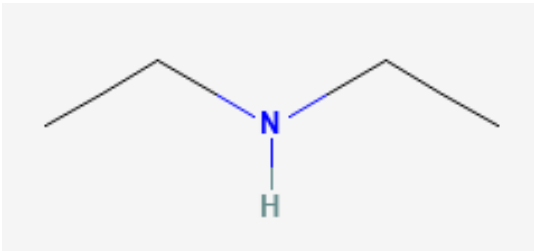
3.1 Key amine solvent species

A group of 23 amines was selected for specific consideration in this framework. At the time of this project, we found that these are amines that are likely to be contenders for use as carbon capture solvents in the UK, and are of higher priority with respect to potential toxicological impacts. They were based on those species derived in a project on Environmental Assessment Levels (EALs), led by the Environment Agency to prioritise toxicological reviews, now publicly available at Prioritisation-of-carbon-capture-chemicals-interim-report_FINAL-1.pdf (ukccsrc.ac.uk).
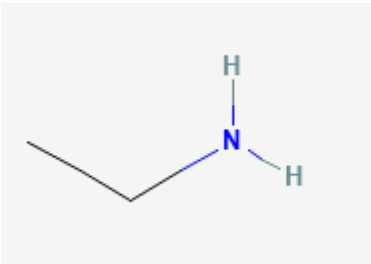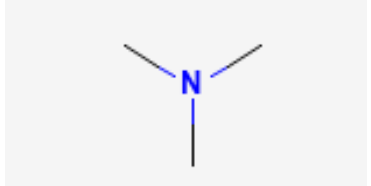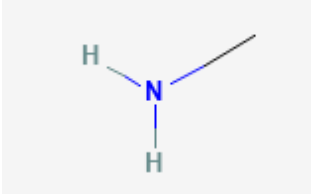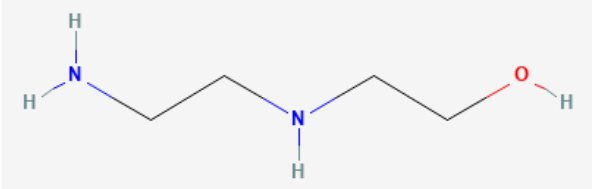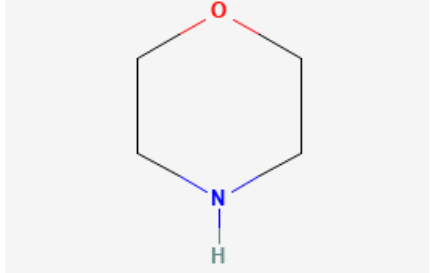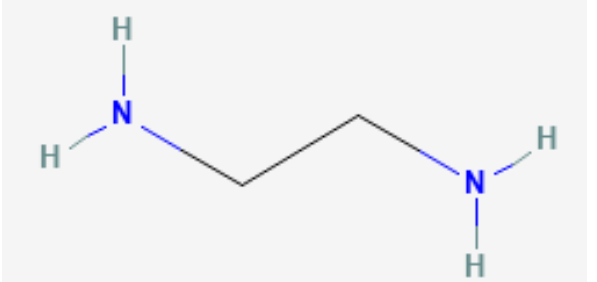
The list of selected amines is given in Table 3.1, including the chemical structure of each of the selected amine species (Kim et al., 2023). Note that, in order to show an uncluttered structure, so that the key functional groups are clear, the species are presented as skeletal structural formulae. In these, the lines represent bonds between atoms. Carbon atoms and most hydrogen atoms are not shown explicitly in the structures, but each junction and bare end of a line indicates the presence of a carbon atom.
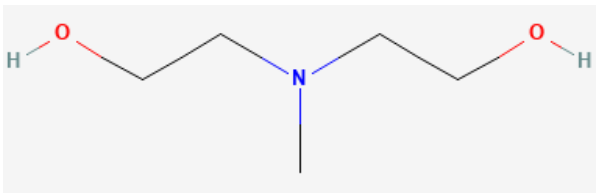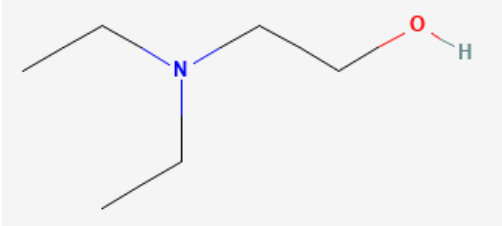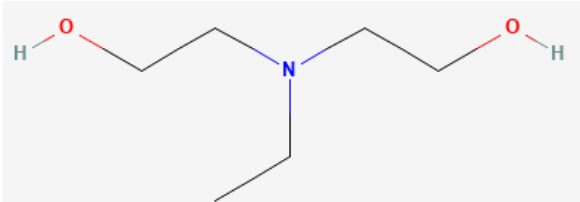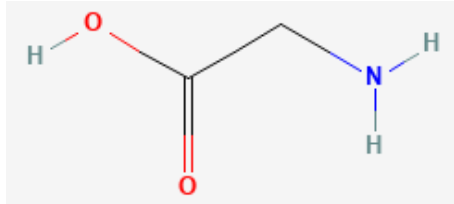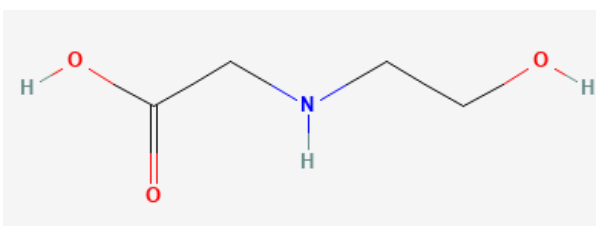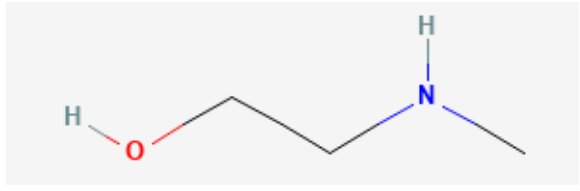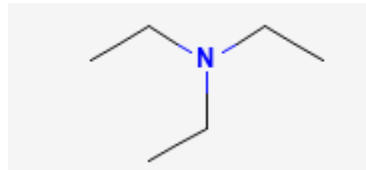
The common abbreviations are also shown in Table 3.1. These are not unique identifiers of the amines, but are intended as informal reference aids only. Note that different authors often use different abbreviations for the same amine (or even the same abbreviation for two different amines), particularly those less commonly studied, so caution is advised when dealing with such abbreviations.

Table 3.2 shows basic information for each amine: relative molecular mass (Mr) values; whether the species is a primary (1°), secondary (2°) or tertiary (3°) amine; and whether the amine species is a diamine (that is, has two amine groups per molecule).

Table 3.1: Name and structure of each of the selected amines

Substance	Common abbreviation	Structure
Dimethylamine	DMA	
Piperazine	PZ	
2-amino-2-methyl-propanol	AMP	
Diethanolamine	DEA	
Diethylamine/ ethylethanamine	DiEA	

Substance	Common abbreviation	Structure
Ethylamine	EA	
Trimethylamine	TMA	
Methylamine	MMA/MA	
N-(2-hydroxyethyl) ethylenediamine	HEEDA	
Morpholine	MOR	
Ethylenediamine	EDA	

Substance	Common abbreviation	Structure
Methyldiethanolamine	MDEA	
2-(diethylamino)ethanol	DEELA	
N-ethyldiethanolamine	EDELA	
Glycine	GLY	
N-(2-hydroxyethyl) glycine	HEGLY	
Methylethanolamine	MMEA	
Triethylamine	TEA	
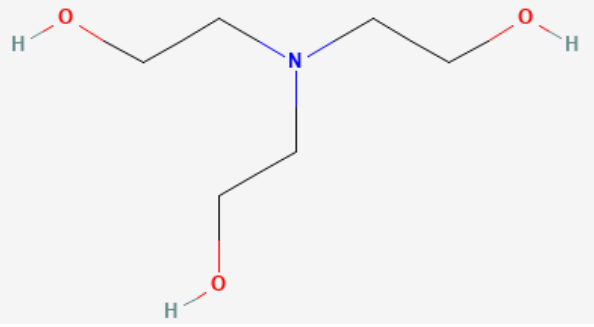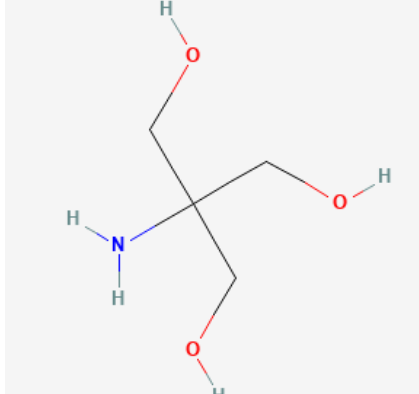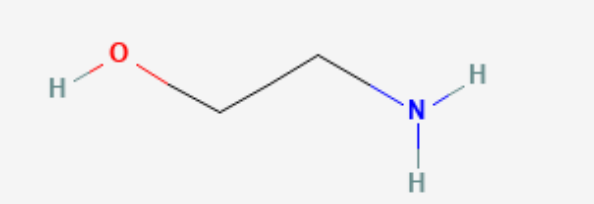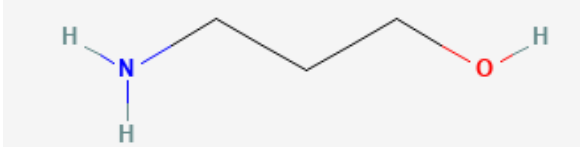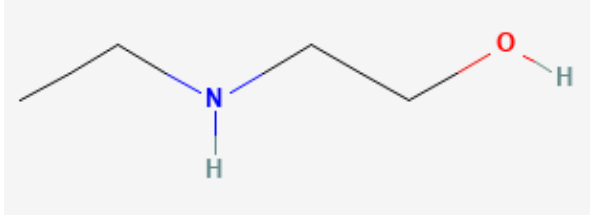
Substance	Common abbreviation	Structure
Triethanolamine	TELA	
Tris(hydroxymethyl)amino methane	TRIS	
Monoethanolamine	MEA	
3-aminopropanol	-	
2-(ethylamine) ethanol	-	

Table 3.2: Basic information for each of the selected amines

Substance	Common abbreviation	CAS number	Mr	Type	Diamine?
Dimethylamine	DMA	124-40-3	45.1	2°	No
Piperazine	PZ	110-85-0	86.1	2°	Yes
2-amino-2-methyl-propanol	AMP	124-68-5	89.1	1°	No
Diethanolamine	DEA	111-42-2	105.1	2°	No
Diethylamine/ethylethanamine	DiEA	109-89-7	73.1	2°	No
Ethylamine	EA	75-04-7	45.1	1°	No
Trimethylamine	TMA	75-50-03	59.1	3°	No
Methylamine	MMA/MA	74-89-5	31.1	1°	No
N-(2-hydroxyethyl) ethylenediamine (dihydrochloride)	HEEDA	111-41-1	104.2	1° and 2°	Yes
Morpholine	MOR	110-91-8	87.1	2°	No
Ethylenediamine	EDA	107-15-3	60	1°	Yes
Methyldiethanolamine	MDEA	105-59-9	119.2	3°	No
2-(diethylamino)ethanol	DEELA	100-37-8	117.2	3°	No
N-ethyldiethanolamine	EDELA	139-87-7	133.2	3°	No
Glycine	GLY	56-40-6	75.1	1°	No
N-(2-hydroxyethyl) glycine	HEGLY	5835-28-9	119.1	2°	No
Methylethanolamine/ monomethylethanolamine	MMEA	109-83-1	75.1	2°	No
Triethylamine	TEA	121-44-8	101.2	3°	No
Triethanolamine	TELA	102-71-6	149.2	3°	No
Tris(hydroxymethyl) aminomethane	TRIS	77-86-1	121.1	1°	No
Monoethanolamine	MEA	141-43-5	61.1	1°	No
3-aminopropanol	-	156-87-6	75.1	1°	No
2-(Ethylamine) ethanol or Monoethylaminoethanol	-	110-73-6	89.1	2°	No

CERC

3.2 Literature reviews

3.2.1 Kinetic parameter data

A literature review was carried out to investigate and collate values of the kinetic parameters required to be input to ADMS, for the selected list of amines and other relevant amines. These other amines include those for which there has been significant attention, and those that can shed light on the parameters of amines that are within the selected list. *Tert* butylamine, for example, was included because it is used in several studies, as a proxy molecule to represent *AMP*; Tan et al. (2018) describe how it is almost identical to *AMP* in structure, but without the alcohol (OH) functional group that makes *AMP* difficult to study, both for experiments and theoretical calculations. Note that later work by the same research group focused on *AMP* itself.

Reaction rate constants, including those for reactions of amine species, have traditionally been determined by experimental measurements. More recently, the rate constants have also been calculated by theoretical methods, including: various quantum chemical methods; transition state theory (TST); and Rice–Ramsperger–Kassel–Marcus (RRKM) theory. Vereecken and Francisco (2012) give a useful overview of these and other theoretical methods commonly used for studying atmospheric reactions and determining rate constants. Structure activity relationships, or SARs (as defined in Section 1.2.2.2) are also used to predict rate constants for amine species.

3.2.1.1 Rate constants for reactions of the amine with OH: k_{OH} (k_1) values

3.2.1.1.1 Collated data

A literature review was carried out to investigate and collate values of k_{OH} (k_1 in ADMS notation, as described in Section 2.2), for the selected list of amines and other relevant amines. Several authors have carried out similar reviews and collated values for selected amines (e.g. Carter, 2008; Nielsen et al., 2012b; Borduas et al., 2016; Barnes et al., 2016; Speak, 2021; Hazell-Marshall & Nielsen, 2022; Shen et al., 2023) and these were used as an initial basis for the review. In addition, a comprehensive review of other published work of experimental and theoretical calculations was carried out.

Estimation Programs Interface Suite (EPI Suite) is a screening-level tool, developed by the US EPA and Syracuse Research Corp. (US EPA, 2012). It comprises a collection of physical/chemical property and environmental fate estimation programs. It includes a program, AOPWIN™, that uses the well-known Structure Activity Relationships (SARs) developed by Atkinson and co-workers (e.g. Kwok and Atkinson, 1995) to estimate rate constant values for the reaction of hydroxyl radicals with amines. For those amine species for which no data was available, AOPWIN was run within EPI Suite to calculate k_{OH} values within this project.

Table 3.3 shows the collated and calculated data for k_{OH}. Values from experimental studies are denoted by 'E' and those predicted from theoretical calculations by 'P'. Values calculated using a SAR calculation are denoted 'S'. Of these, values calculated using the SAR calculations within the AOPWIN program in EPI Suite are marked in the 'Notes' column. Note that those values calculated by da Silva et al., 2010 using EPI Suite were recalculated as part of the current

work, using the latest version of EPI Suite, and found to be the same values, despite updates to the EPI Suite program in the meantime.

Figures 3.1 to 3.3 show plots of the values shown in Table 3.3. The red data markers indicate the values calculated in EPI Suite using its SAR method. Figure 3.1 indicates those amines that are primary, secondary and tertiary, respectively. Note that amine no. 9, *HEEDA*, contains both a primary and a secondary amine group. Figure 3.2 indicates those amines that contain alcohol (hydroxyl) functional groups and those that are heterocyclic molecules. Finally, Figure 3.3 indicates those amines that are diamines, and those that have a tertiary carbon atom adjacent to the nitrogen atom.

Table 3.3: Collated and calculated values of k_{OH} for the selected amines (No. 1 to 23) and other relevant amines (24 to 26). Where E = experimental, P = predicted and S = SAR.

	Amine	Abbr.	k_{OH} (cm³ molecule⁻¹ s⁻¹)	Reference	Type	Notes
1	Dimethylamine	DMA	6.54×10^{-11}	Atkinson, 1978	E	
			6.49×10^{-11}	Carl and Crowley, 1998	E	
			5.2×10^{-11}	Galano and Alvarez-Idaboy, 2008	P	
			6.55×10^{-11}	da Silva et al., 2010	S	EPI Suite
			7.10×10^{-11}	Nielsen et al, 2011a	E	
			6.27×10^{-11}	Onel et al., 2013	E	
			6.26×10^{-11}	Manzoor et al., 2014, 2015	P	
			6.55×10^{-11}	Manzoor et al., 2015	S	EPI Suite
			5.20×10^{-11}	Butkovskaya and Setser, 2016	E	
			6.32×10^{-11}	Borduas et al., 2016	S	
2	Piperazine	PZ	1.69×10^{-10}	da Silva et al., 2010	S	EPI Suite
			2.38×10^{-10}	Onel, 2014a	E	
			2.88×10^{-10}	Borduas et al., 2016	S	
			2.86×10^{-10}	Sarma et al., 2017	P	
			2.41×10^{-10}	Ren and da Silva, 2019	P	
			2.80×10^{-10}	Tan et al., 2021a	E	
3	2-amino-2-methyl-propanol	AMP	2.80×10^{-11}	Harris and Pitts, 1983	E	
			2.55×10^{-11}	da Silva et al., 2010	S	EPI Suite
			3.05×10^{-11}	Borduas et al., 2016	S	
			2.80×10^{-11}	Tan et al., 2021b	P	
4	Diethanolamine	DEA	1.01×10^{-10}	Carter, 2008	S	
			9.27×10^{-11}	da Silva et al., 2010	S	EPI Suite
5	Diethylamine	DiEA	8.07×10^{-11}	da Silva et al., 2010	S	EPI Suite
			7.40×10^{-11}	Nielsen et al, 2012a	E	
			1.19×10^{-10}	Tuazon et al., 2011	E	
			7.29×10^{-11}	Borduas et al., 2016	S	
			7.36×10^{-11}	Barnes et al., 2016	E	
6	Ethylamine	EA	2.77×10^{-11}	Atkinson, 1978	E	
			2.38×10^{-11}	Carl and Crowley, 1998	E	
			1.2×10^{-11}	Galano and Alvarez-Idaboy, 2008	P	
			2.99×10^{-11}	da Silva et al., 2010	S	EPI Suite
			2.50×10^{-11}	Onel et al., 2013	E	
			3.15×10^{-11}	Borduas et al., 2016	S	

	Amine	Abbr.	k_{OH} (cm³ molecule⁻¹ s⁻¹)	Reference	Type	Notes
7	Trimethylamine	TMA	6.09×10^{-11}	Atkinson, 1978	E	
			3.58×10^{-11}	Carl and Crowley, 1998	E	
			6.98×10^{-11}	da Silva et al., 2010	S	EPI Suite
			5.10×10^{-11}	Nielsen et al, 2011a	E	
			5.78×10^{-11}	Onel et al., 2013	E	
			4.40×10^{-11}	Butkovskaya and Setser, 2016	E	
			4.68×10^{-11}	Borduas et al., 2016	S	
8	Methylamine	MMA/ MA	2.20×10^{-11}	Atkinson, 1977	E	
			1.73×10^{-11}	Atkinson, 1978	E	
			1.73×10^{-11}	Carl and Crowley, 1998	E	
			5.2×10^{-12}	Galano and Alvarez-Idaboy, 2008	P	
			2.23×10^{-11}	da Silva et al., 2010	S	EPI Suite
			1.97×10^{-11}	Onel et al., 2013	E	
			2.22×10^{-11}	Manzoor et al., 2014, 2015	P	
			2.00×10^{-11}	Butkovskaya and Setser, 2016	E	
			2.66×10^{-11}	Borduas et al., 2016	S	
9	N-(2-hydroxyethyl) ethylenediamine	HEEDA	1.20×10^{-10}	This work	S	EPI Suite
10	Morpholine	MOR	8.00×10^{-11}	SenGupta et al., 2010	E	
			1.40×10^{-10}	Rashidi et al., 2014	E	
			1.95×10^{-10}	Gao et al., 2015	P	
			1.38×10^{-10}	This work	S	EPI Suite
11	Ethylenediamine	EDA	6.34×10^{-11}	This work	S	EPI Suite
12	Methyldiethanolamine	MDEA	9.70×10^{-11}	da Silva et al., 2010	S	EPI Suite
13	2-(diethylamino) ethanol	DEELA	9.86×10^{-11}	This work	S	EPI Suite
14	N-ethyldiethanolamine	EDELA	1.05×10^{-10}	This work	S	EPI Suite
15	Glycine	GLY	2.80×10^{-11}	This work	S	EPI Suite
16	N-(2-hydroxyethyl) glycine	HEGLY	No data found and species not in EPI Suite database			
17	Methylethanolamine	MMEA	8.26×10^{-11}	Onel et al., 2015	E	
			7.91×10^{-11}	This work	S	EPI Suite
18	Triethylamine	TEA	5.57×10^{-11}	Carter, 2008	P	SAR
			9.26×10^{-11}	da Silva et al., 2010	S	EPI Suite
			7.70×10^{-11}	Nielsen et al, 2011a	E	

	Amine	Abbr.	k_{OH} (cm^3 molecule^{-1} s^{-1})	Reference	Type	Notes
			6.14×10^{-11}	Borduas et al., 2016	S	
			1.09×10^{-10}	Barnes et al., 2016	E	
19	Triethanolamine	TELA	8.04×10^{-11}	Carter, 2008	P	SAR
			1.11×10^{-10}	da Silva et al., 2010	S	EPI Suite
20	Tris(hydroxymethyl)aminomethane	TRIS	3.35×10^{-11}	This work	S	EPI Suite
21	Monoethanolamine	MEA	4.41×10^{-11}	Carter, 2008	S	SAR
			3.58×10^{-11}	da Silva et al., 2010	S	EPI Suite
			9.20×10^{-11}	Karl, 2012a	E	
			7.61×10^{-11}	Onel et al., 2012	E	
			7.02×10^{-11}	Borduas, 2013	E	
			7.27×10^{-11}	Xie, 2014	P	
			9.20×10^{-11}	Manzoor et al., 2014, 2015	P	
			3.58×10^{-11}	Manzoor et al., 2015	S	EPI Suite
			6.39×10^{-11}	Borduas et al., 2016	S	
22	3-aminopropanol	-	3.73×10^{-11}	This work	S	EPI Suite
23	2-(Ethylamine) ethanol	-	8.67×10^{-11}	This work	S	EPI Suite
24	Piperidine	-	7.40×10^{-11}	Nielsen et al, 2012a	E	
			9.65×10^{-11}	Borduas et al., 2016	S	
			8.86×10^{-11}	This work	S	EPI Suite
25	tert-butylamine	TBA	1.20×10^{-11}	Koch et al., 1996	E	
			6.73×10^{-11}	Borduas et al., 2016	S	
			8.40×10^{-12}	Tan et al., 2018	E	
			1.66×10^{-11}	Speak et al., 2021	E	
			2.15×10^{-11}	This work	S	EPI Suite
26	N,N-dimethyl ethanolamine	DMEA	4.7×10^{-11}	Harris and Pitts, 1983	E	
			1.03×10^{-10}	Anderson and Stephens, 1988	E	
			8.34×10^{-11}	da Silva et al., 2010	S	EPI Suite
			7.29×10^{-11}	Onel et al., 2015	E	

Note: 'This work' means that the value was calculated for this report, by runniing AOPWIN within EPI Suite.

Figure 3.1: Plot of values in Table 3.3, with SAR-calculated values shown in red (and labelled as 'S' in the table). The primary, secondary and tertiary amines are denoted by '1•', '2•' and '3•', respectively.
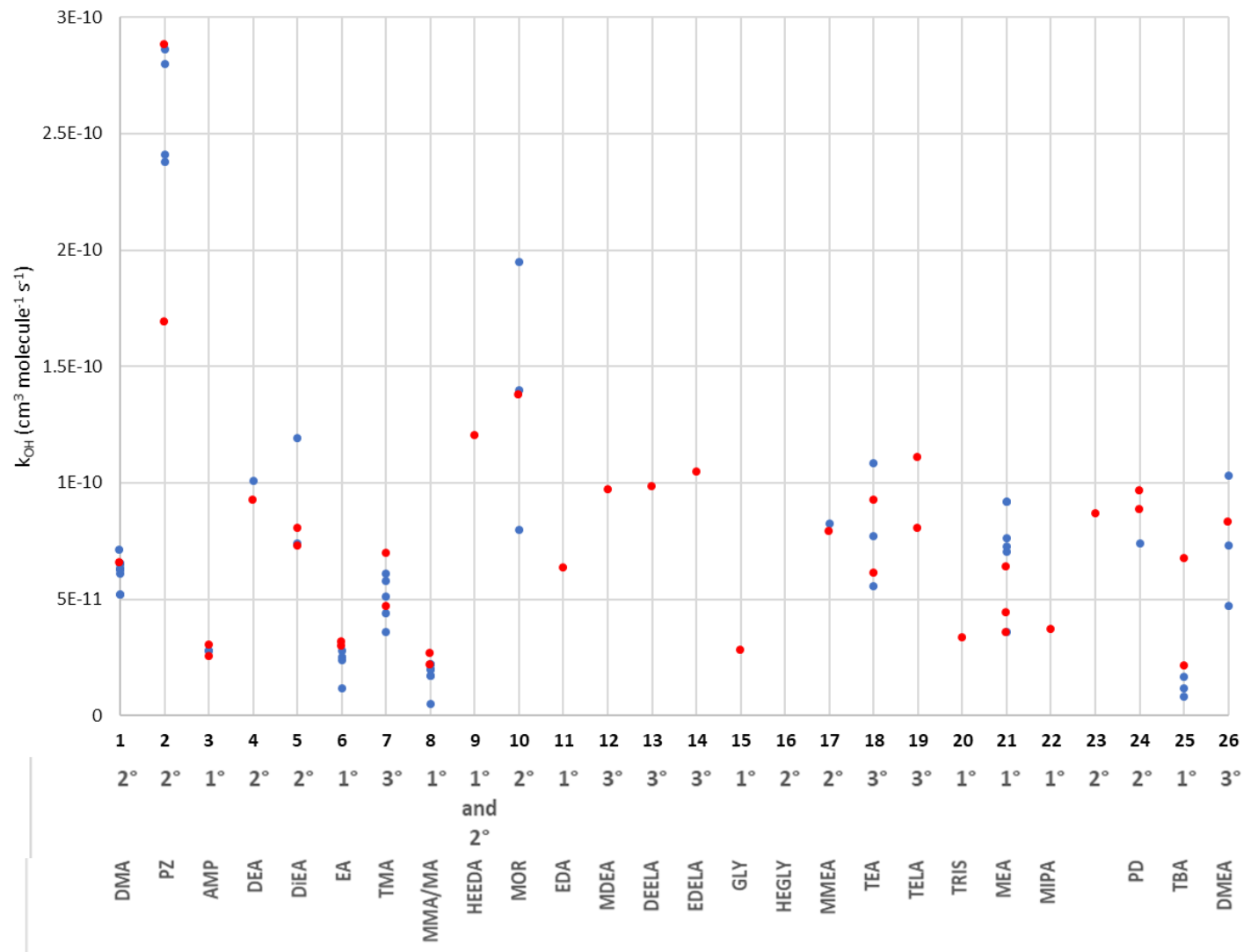
Figure 3.2: Plot of values in Table 3.3, with SAR-calculated values shown in red (and labelled as 'S' in the table). The heterocyclic amines are denoted by 'H' and those amines with alcohol groups by 'A'
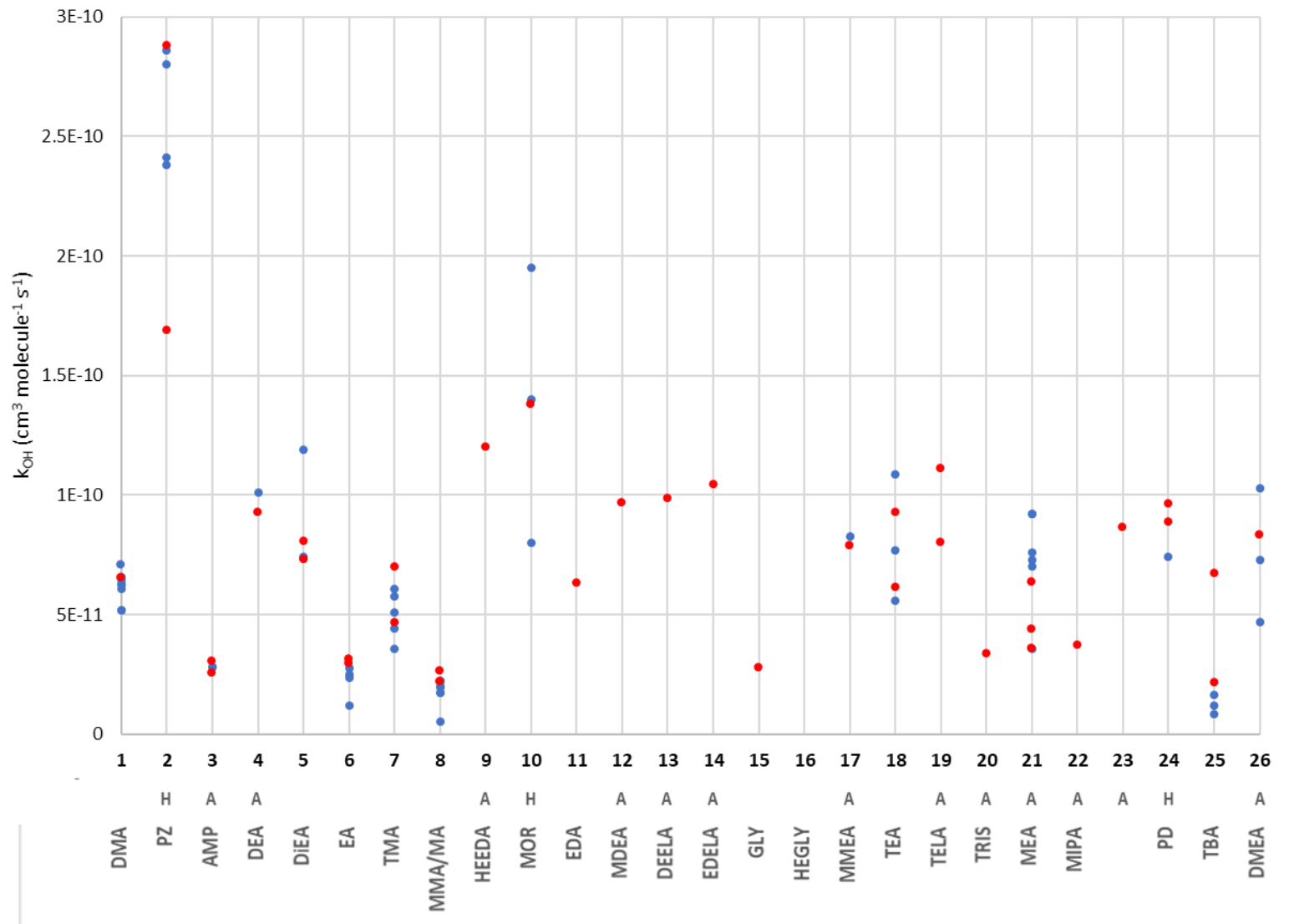
Figure 3.3: Plot of values in Table 3.3, with SAR-calculated values shown in red (and labelled as 'S' in the table). Those amines that are diamines are denoted by 'D', and those that have tertiary carbon atoms adjacent to the amine group are denoted by 'T'
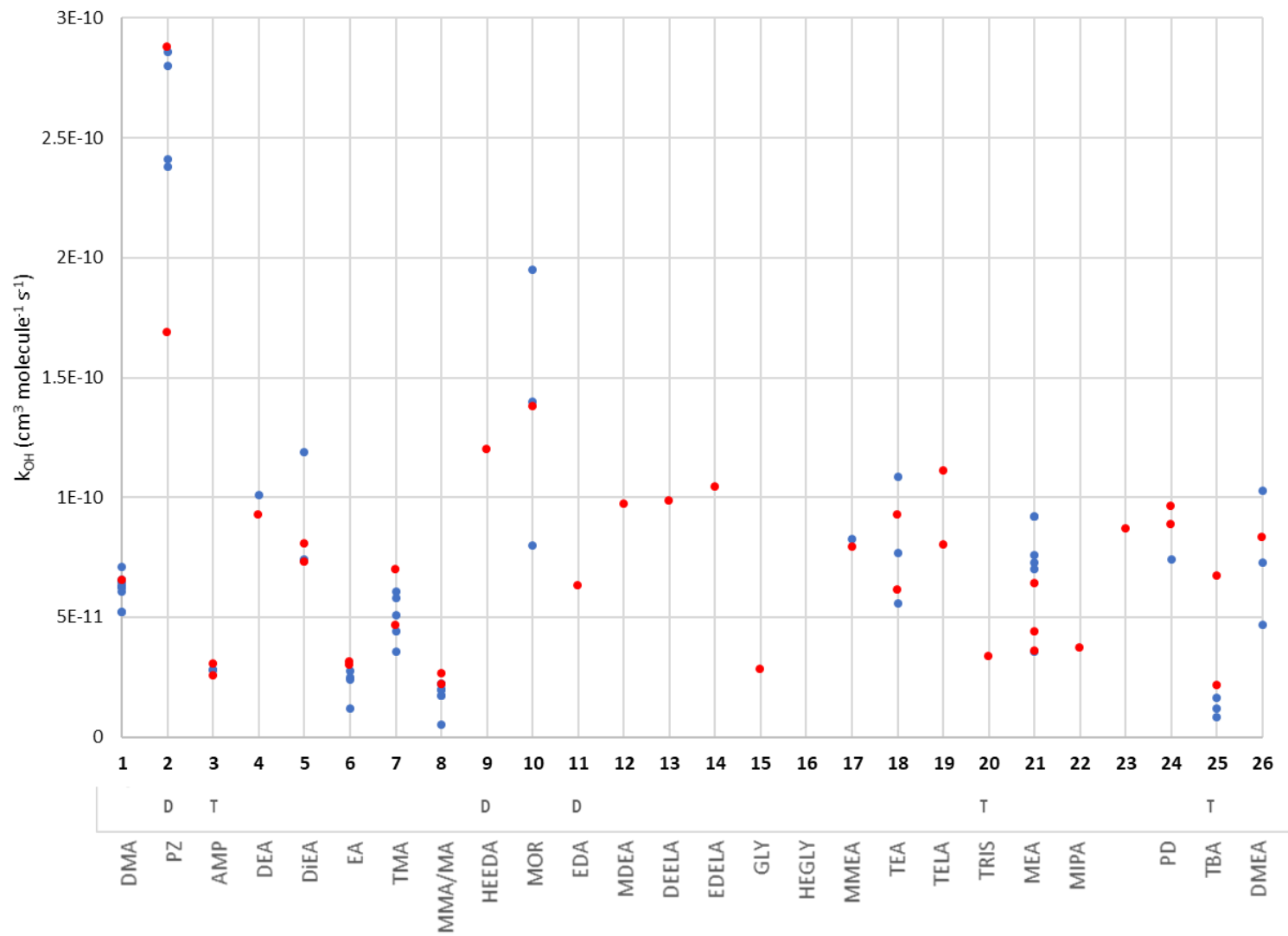
3.2.1.1.2 Discussion of k_{OH} values

Where there are sufficient data points for particular types of amine, the plots highlight some general patterns, and it is clear that there is good agreement between the values (i.e. a smaller spread of data) for some amines, and much less good agreement for others; this is discussed below.

Simple vs complex amines:

For those amines that have enough data points to meaningfully compare values by different methods and research groups, there is particularly good agreement for dimethylamine, ethylamine and methylamine, which are all simple, small alkyl amines. Conversely, there is generally poor agreement for piperazine, trimethylamine, morpholine, triethylamine and monoethanolamine (*MEA*), which are all significantly larger and/or more complex molecules. This is as expected, as there are fewer permutations for reactions in smaller molecules and those with fewer functional groups, which makes calculations more straightforward.

The overall agreement for diethylamine appears poor, but Barnes et al. (2016) highlight the clear difference between the value reported by Tuazon et al. (2011) and the other values. Barnes et al. (2016) describe how this value is possibly due to errors relating to wall-loss of diethylamine, and its reaction with ozone. With the Tuazon et al. (2011) value omitted, there is excellent agreement between the remaining values. This aligns with the good agreement in values for small, simple alkyl amines, as diethylamine is also a relatively small and simple molecule.

Primary, secondary and tertiary amines:

Figure 3.1 shows that there is good agreement between values for the primary amines, with the exception of *MEA*. For tertiary amines, there is less good agreement in general. The level of agreement for secondary amines is mixed; many show very good agreement, while others significant disagreement. The two secondary amines that show the least agreement are piperazine and morpholine, which are both heterocyclic molecules (as shown in Figure 3.2). Several authors have noted a general increase in the k_{OH} value for secondary amines with increasingly large alkyl groups (e.g. da Silva et al. 2010, Barnes et al., 2016), and this is generally borne out by the data in Table 3.3.

Note that tertiary amine groups do not have any nitrogen-bound hydrogens available for abstraction. This means that hydroxyl radical attack must be via a slightly different mechanism, with some initial steps occurring before the amino radical is formed. For trimethylamine, for example, the OH abstracts one of the hydrogen atoms from the carbon atom of one of the methyl groups, and the subsequent breaking of the C-N bond between the methyl group and the amine group nitrogen atom then forms the amino radical (e.g., Nielsen et al., 2012b). The identities of the products are therefore not as straightforward to predict as they are for the primary and secondary amines. This should be taken into consideration when carrying out dispersion modelling, for several reasons; one is that the calculation of the 'µg/m^3 to ppb' conversion rate for the nitrosamine and/or nitramine species for input to ADMS is dependent on the molecular mass, and hence the structure of the species.

Amines with alcohol functional groups:

Figure 3.2 indicates those amines that contain alcohol functional groups. There is a lack of data points for the majority of these amines, which makes comparison difficult. The lack of rate constant data for these amines is itself of note, and perhaps reflects, at least in part, the sampling and reaction challenges involved in analysing species containing alcohol groups (e.g. Li et al., 2020).

Sterically-hindered amines:

Figure 3.3 indicates those amines with a tertiary carbon adjacent to the nitrogen atom (sterically hindered amines), and diamines. It is difficult to draw out any trends regarding these molecular properties, as there are few species and few data points, but in general, the diamines have relatively large rate constant values, and the sterically hindered amines have relatively small values. These two types of amines are discussed further below.

Regarding sterically-hindered amines, Barnes et al. (2016) state that: "*It would appear from the present work and the study of Koch et al. that the reactivity toward OH of alkylamines that have a tertiary carbon atom adjacent to the nitrogen atom will be reduced compared to those which contain H atoms.*" This is indeed evident in the values collated here; those amines that have tertiary carbon atom adjacent to the nitrogen atom (*AMP* and *tert*-butylamine) have noticeably lower k_{OH} values. Barnes et al. do not elaborate on the possible reasons for this lower reactivity to OH radicals, but this is likely to be due, at least in part, to the resulting steric hindrance (and this is put forward in the work by Koch et al. (1996) that they cite). Tan et al. (2018), describe how they were the first to present insights into the reaction mechanisms of the reaction of OH with an amine that has a tertiary carbon atom adjacent to the nitrogen atom (*tert*-butylamine).

The apparently low k_{OH} values for sterically-hindered amines has potentially important implications, because sterically hindered amines have many favourable properties that make them particularly suitable for carbon capture solvents, including a higher CO_2 loading capacity, and a reduced tendency for solvent degradation (Tan et al., 2018). If these amines are chosen (due to their superior solvent properties), it may be the case that they lead to lower nitrosamine and nitramine concentrations in air than other amines that could be used. Note that the value used for the 'k_1 min' sensitivity test in Section 4.1 is that reported by Tan et al. (2018), for tert butylamine, so this gives an indication of the difference between the nitrosamine and nitramine yield for this species compared with that of dimethylamine (which was assumed for the base case run).

Diamines:

Regarding diamines, piperazine (*PZ*) has a noticeably higher k_{OH} value than any of the other species. As shown in Table 3.3 and Figures 3.1 to 3.3, this is a heterocyclic diamine, where both amine groups are secondary. *HEEDA* (no. 9) and *EDA* (no. 11) are also diamines, but the only values available are those derived from SARs, which makes comparison difficult. Angove et al. (2013) highlighted that caution should be used when applying the Kwok and Atkinson SAR and other SARs to *PZ*, and they note that the presence of two amine groups in a single molecule had not been included in these SARs. Results from subsequent experimental and predictive studies have suggested that this recommendation of caution is justified, as these studies have all given significantly higher values for k_{OH}. This suggests that the EPI-Suite values for the other diamines might also be too low.

Structure activity relationships (SARs):

SARs (defined in Section 1.2.2.2), such as the Atkinson SAR included in EPI Suite, can be very useful tools and their development and use for determining the reaction of amines with OH has been discussed by multiple authors (e.g. Braten et al., 2008; da Silva et al., 2010; Nielsen et al., 2012b; Barnes et al., 2016; Borduas et al., 2016; Speak et al., 2021). The consensus is that the Atkinson SAR calculation included within EPI Suite tends to give relatively good agreement with values from kinetic experiments and higher-level prediction methods for some types of amines, and less good agreement for other types of amines. Da Silva et al. noted in 2010 that it seemed to give reliable results for primary amines, but that for tertiary amines, there was not enough experimental data to derive a good SAR, and therefore they advised caution for its use to derive k_{OH} for tertiary amines.

More recently, Speak et al. (2021) discuss the Atkinson SAR, and the subsequent SARs of Nielsen et al. (2012) and Borduas et al. (2016). They conclude with the following: "*The current work and comparison of the SARs with site specific rate coefficients suggests that there is more work to be done in refining the SARs. Such work is of great importance…Experimental determinations of site specific reactivity will be challenging and therefore a fully validated SAR would be of great benefit.*". The term 'site-specific' here refers to the rates of the branching reactions (e.g. k_{1a}), as opposed to the overall reaction (e.g. k_1).

For the collated data in Table 3.1, the most notable deviation of the Atkinson/EPI Suite SAR value from the other data is the large underprediction for piperazine. This is perhaps not surprising, due to the unusual nature of piperazine, being both a cyclic molecule and possessing two amine groups.

Regarding sterically hindered amines (with tertiary carbon atoms), and the applicability of the Atkinson SAR to these species, Barnes et al. (2016) note that their results suggest the following: "*…the RNH2 parameter used in the rate coefficient estimate in the SAR is too large when the amine has a tertiary carbon atom next to the nitrogen atom, such as in tert-amylamine*". The data in Table 3.3 and Figure 3.3, however, does not show a strong tendency for the SAR to overpredict k_{OH} values for the amines with adjacent tertiary carbons considered here; although there are only two such species that have enough data points to make such a comparison.

3.2.1.2 Rate constants for reactions of the amino radical: k_2, k_3, k_{4a} and k_{4b} values

3.2.1.2.1 Collated data

A literature review was carried out to investigate and collate values for the rate constants for the reaction of the amino radical with the following species, for the selected list of amines and other relevant amines:

- Reaction with O_2 to form the imine (k_2 in ADMS notation)
- Reaction with NO to form the nitrosamine (k_3 in ADMS notation)
- Reaction with NO_2 to form the nitramine (k_{4a} in ADMS notation)
- Reaction with NO_2 to form the imine (k_{4b})

These rate constants are described in Section 2.2.1. Note that ADMS requires the input of k_{4a} and k_4, where $k_4 = k_{4a} + k_{4b}$.

Tables 3.4 and 3.5 show the collated and calculated data for k_2 and k_3, respectively. Figures 3.4 and 3.5 show plots of these values; note that the values for k_3 in Figure 3.5 are shown on a logarithmic y axis, as the range of values is very large. Table 3.6 gives the very limited available data found for k_{4a} and k_{4b}.

In all tables, values from experimental studies are denoted by 'E' and those predicted from theoretical calculations by 'P'. Note that the values for k_3 from the Lui et al. reference are the values given for ambient NO concentrations of 5 ppb, as these are more representative of background NO levels at UK carbon capture plant sites than the other set of k_3 values, which correspond to ambient NO concentrations of 5 ppt.

A particular type of experimental method is to use the photolysis of a nitrosamine to generate amino radicals, which can then be used to determine the rates of reaction of the amino radical with O_2, NO and NO_2, to determine k_2, k_3 and k_{4a}, respectively (e.g. Nielsen et al., 2012a). The rate constant data from these types of experiments are inherently in the form of ratios (e.g. k_2/k_{4a}), rather than absolute rate constant values. This is the method used by Lindley et al. (1979), Nielsen et al. (2012a) and Tan et al. (2021a), and their reported values are given in Table 3.7. Note that the values given in this table for piperazine (*PZ*) for Tan et al. (2021a) are taken from Table S13 of the Supporting Information of that reference, as the values given in the main text are of the wrong order of magnitude and contradict those in the Supporting Information.

Absolute rate constant values can be determined from these ratios by using a known absolute value for one of the rate constants. As the values in the aforementioned experiments are reported normalised to k_{4a}, it is useful to use a known absolute rate constant value for k_{4a} for this purpose. The only direct experimental measurement of k_{4a}, to our knowledge, is that determined by Lazarou et al. (1994), for *DMA*. The ratios, and our calculated absolute values, based on the Lazarou et al. k_{4a} value of 3.18×10^{-13} cm^3 molecule s^{-1} are given in Table 3.8.

Table 3.9 shows values given in a Position paper published by the Carbon Capture and Storage Association (CCSA) (Hazell-Marshall & Nielsen, 2022).

Table 3.4: Collated and calculated values of k₂ for the selected (no. 1 to 23) and other relevant amines (24 and 25). Where P = predicted.

	Amine	Abbr.	k_2 (cm^3 molecule^{-1} s^{-1})	Reference	Type
1	Dimethylamine	DMA	3.64×10^{-18}	Manzoor et al., 2015	P*
			1.89×10^{-20}	Manzoor et al., 2015	P†
			5.54×10^{-20}	Liu et al., 2019	P
2	Piperazine	PZ	2.40×10^{-21}	Ma et al., 2018	P
			1.30×10^{-21}	Liu et al., 2019	P
3	2-amino-2-methyl-propanol	AMP	0	Carter, 2008	P
			0	Tan et al., 2021b	P
4	Diethanolamine	DEA	1.78×10^{-20}	Liu et al., 2019	P
5	Diethylamine	DiEA	2.26×10^{-19}	Liu et al., 2019	P
6	Ethylamine	EA	2.53×10^{-18}	Liu et al., 2019	P
7	Trimethylamine	TMA	No data found		
8	Methylamine	MMA/ MA	3.64×10^{-18}	Manzoor et al., 2015	P*
			1.89×10^{-20}	Manzoor et al., 2015	P†
			3.60×10^{-17}	Alam et al., 2019	P
			1.08×10^{-18}	Liu et al., 2019	P
9	N-(2-hydroxyethyl) ethylenediamine	HEEDA	No data found		
10	Morpholine	MOR	2.60×10^{-21}	Liu et al., 2019	P
11	Ethylenediamine	EDA	1.42×10^{-18}	Liu et al., 2019	P
12	Methyldiethanolamine	MDEA	No data found		
13	2-(diethylamino) ethanol	DEELA			
14	N-ethyldiethanolamine	EDELA			
15	Glycine	GLY			
16	N-(2-hydroxyethyl) glycine	HEGLY			
17	Methylethanolamine	MMEA			
18	Triethylamine	TEA			
19	Triethanolamine	TELA			
20	Tris(hydroxymethyl)amino methane	TRIS			
21	Monoethanolamine	MEA	1.20×10^{-19}	Nielsen et al, 2010	E
			2.49×10^{-16}	Manzoor et al., 2015	P*
			3.86×10^{-18}	Manzoor et al., 2015	P†
			2.90×10^{-18}	Xie et al., 2015	P
			1.47×10^{-18}	Liu et al., 2019	P
22	3-aminopropanol	-	6.30×10^{-18}	Liu et al., 2019	P
23	2-(Ethylamine) ethanol		No data found		
24	Piperidine		1.37×10^{-20}	Liu et al., 2019	P
25	tert-butylamine	TBA	0	Carter, 2008	P

*Calculated using RRKM theory
†Calculated using TST theory

Figure 3.4: Plot of k₂ values in Table 3.4: a) All values shown, and b) Highest two values excluded to show range of lower values

a)

b)

Improving post-combustion carbon capture air quality risk assessment techniques
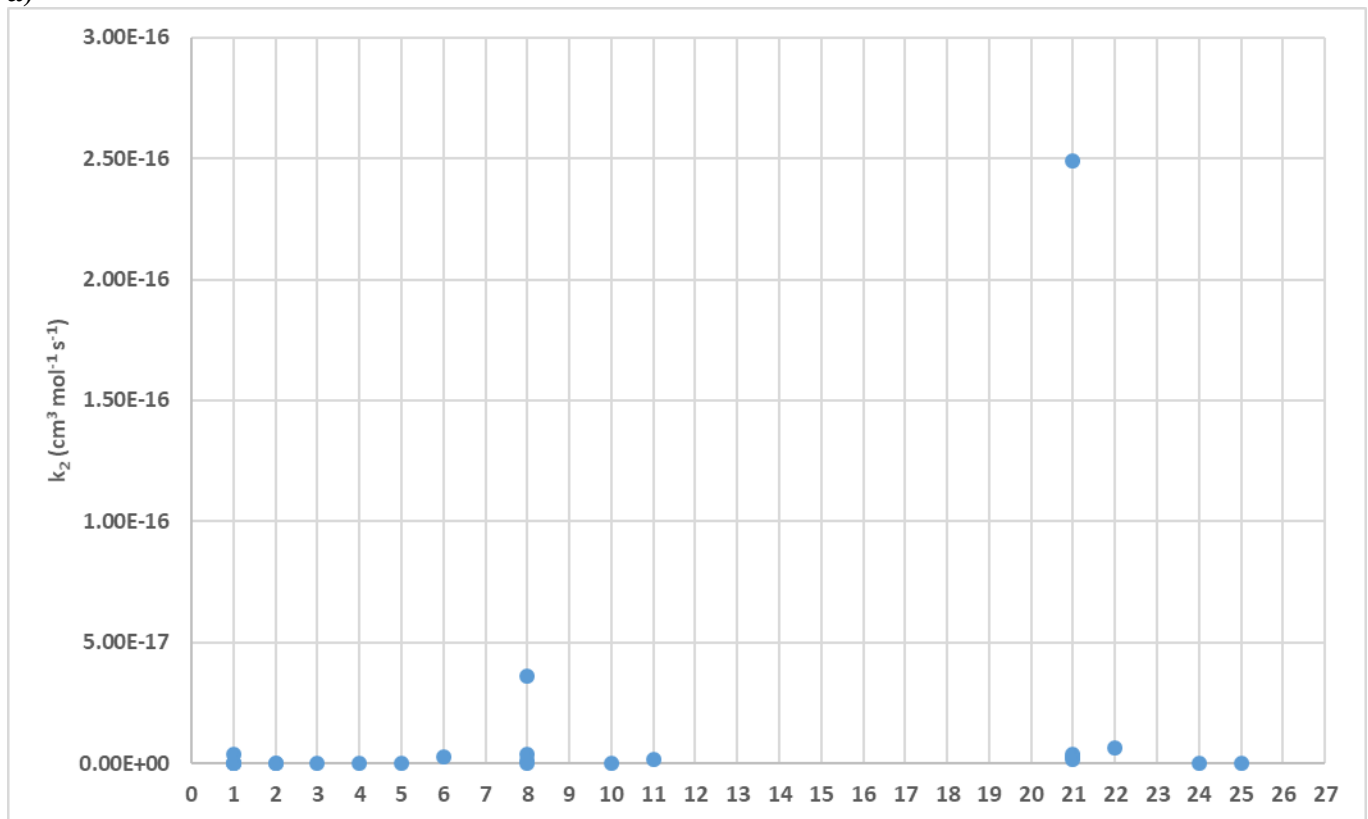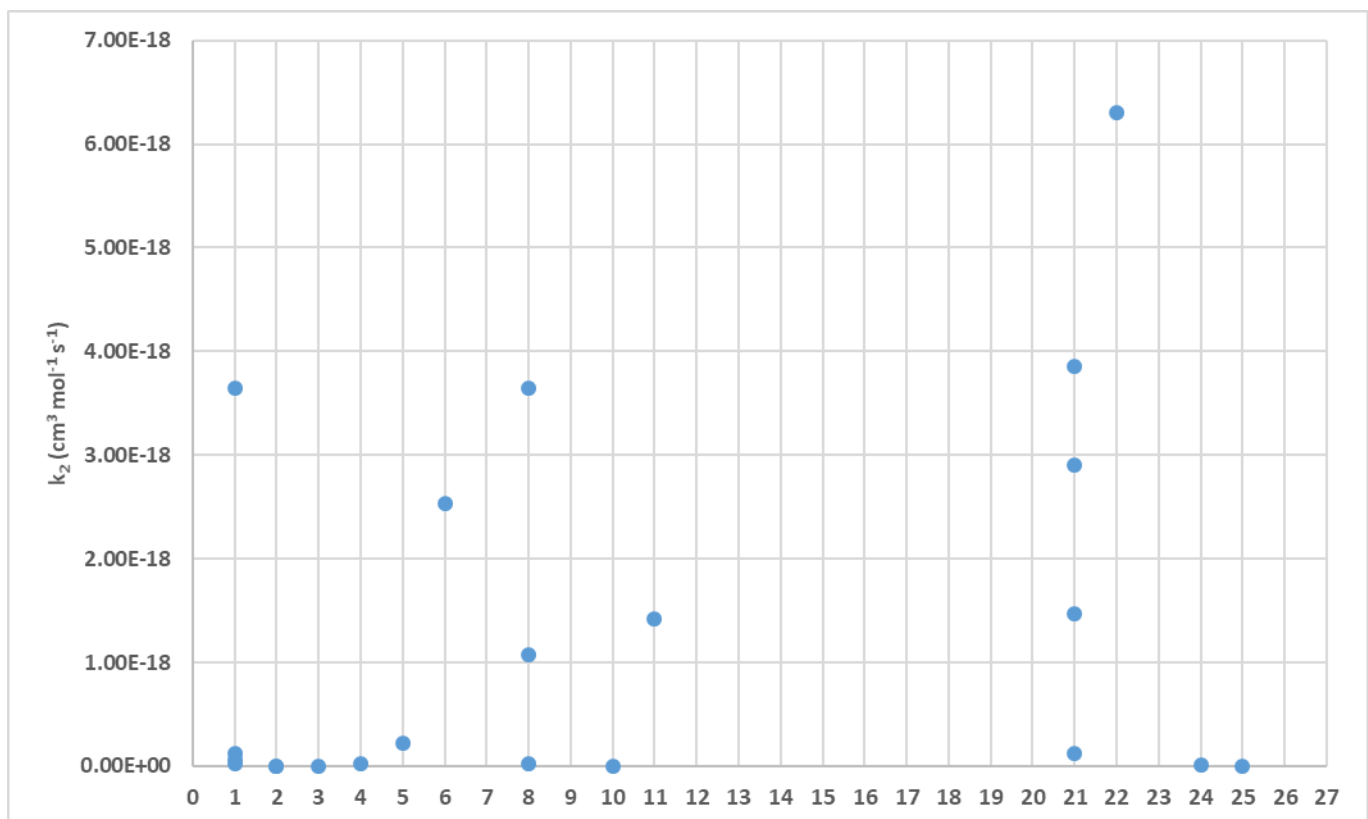
Table 3.5: Collated and calculated values of k_3 for the selected amines. Where E = experimental and P = predicted.

	Amine	Abbr.	k_3 (cm³ molecule⁻¹ s⁻¹)	Reference	Type
1	Dimethylamine	DMA	8.53×10^{-14}	Lazarou et al., 1993	E
			8.37×10^{-14}	Manzoor et al., 2015	P
			2.22×10^{-12}	Liu et al., 2019	P
2	Piperazine	PZ	7.20×10^{-11}	Ma et al., 2018	P
			5.20×10^{-14}	Liu et al., 2019	P
3	2-amino-2-methyl-propanol	AMP	No data found (and primary amine)		
4	Diethanolamine	DEA	7.12×10^{-13}	Liu et al., 2019	P
5	Diethylamine	DiEA	9.04×10^{-12}	Liu et al., 2019	P
6	Ethylamine	EA	1.01×10^{-10}	Liu et al., 2019	P
7	Trimethylamine	TMA	No data found		
8	Methylamine	MMA/ MA	7.30×10^{-11}	da Silva, 2013	P
			1.70×10^{-12}	Manzoor et al., 2015	P
			4.32×10^{-11}	Liu et al., 2019	P
9	N-(2-hydroxyethyl) ethylenediamine	HEEDA	No data found		
10	Morpholine	MOR	1.04×10^{-13}	Liu et al., 2019	P
11	Ethylenediamine	EDA	5.68×10^{-11}	Liu et al., 2019	P
12	Methyldiethanolamine	MDEA	No data found		
13	2-(diethylamino) ethanol	DEELA			
14	N-ethyldiethanolamine	EDELA			
15	Glycine	GLY			
16	N-(2-hydroxyethyl) glycine	HEGLY			
17	Methylethanolamine	MMEA			
18	Triethylamine	TEA			
19	Triethanolamine	TELA			
20	Tris(hydroxymethyl)aminomethane	TRIS			
21	Monoethanolamine	MEA	8.53×10^{-14}	Nielsen et al., 2010	E
			5.62×10^{-14}	Manzoor et al., 2015	P
			6.99×10^{-11}	Xie et al., 2015	P
			5.88×10^{-11}	Liu et al., 2019	P
22	3-aminopropanol	-	No data found		
23	2-(Ethylamine) ethanol	-			

Figure 3.5: Plot of k₃ values in Table 3.5; note that values are shown on a logarithmic y axis
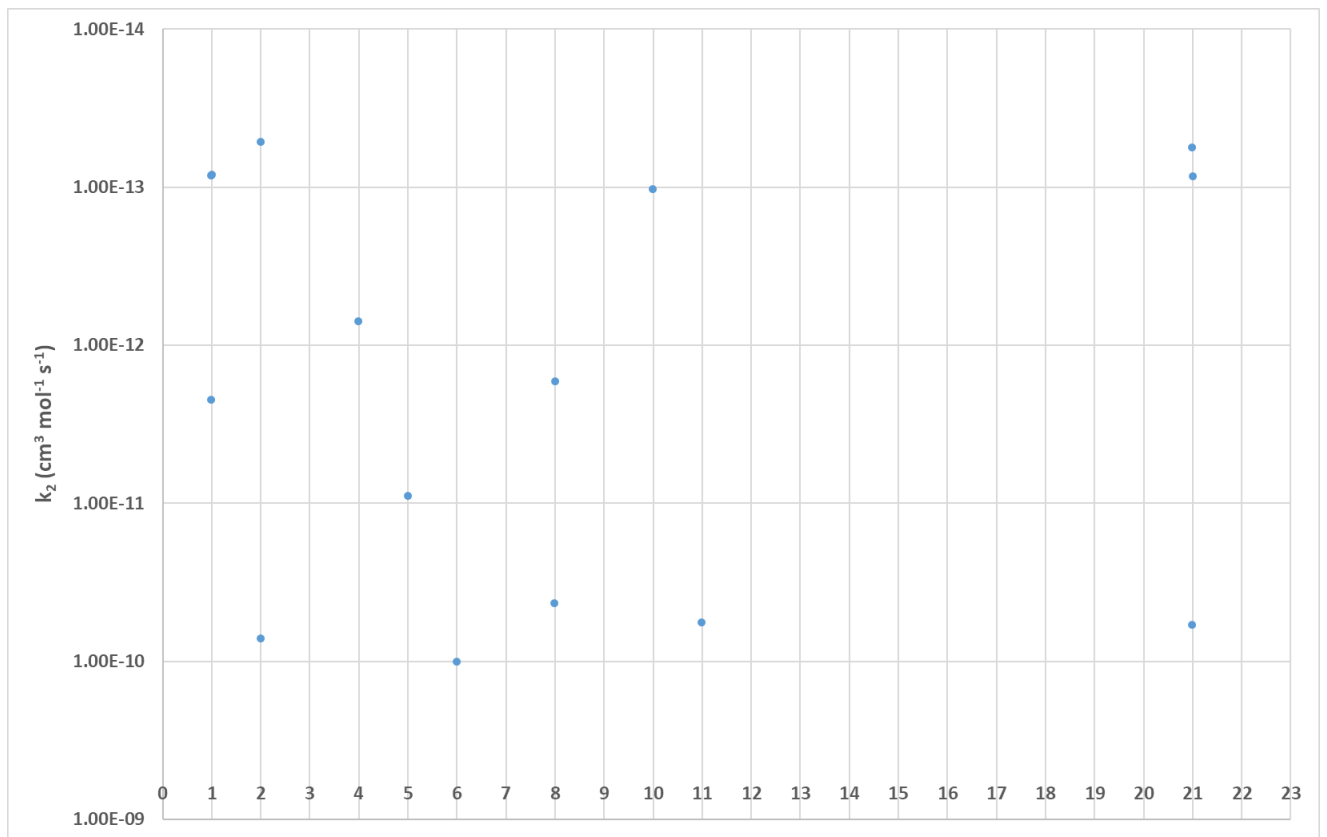
Table 3.6: Collated and calculated values of k₄ₐ and k₄ᵦ for the selected amines. Where E = experimental and P = predicted

	Amine	Abbr.	k_{4a}	k_{4b}	Reference	Type
			(cm^3 molecule^{-1} s^{-1})			
1	Dimethylamine	DMA	3.18 x 10^{-13}		Lazarou et al., 1993	E
			3.15 x 10^{-13}	1.10 x 10^{-14}	Manzoor et al., 2015	P
2	Piperazine	PZ				
3	2-amino-2-methyl-propanol	AMP				
4	Diethanolamine	DEA		No data found		
5	Diethylamine	DiEA				
6	Ethylamine	EA				
7	Trimethylamine	TMA				
8	Methylamine	MMA/MA	9.70 x 10^{-13}	2.02 x 10^{-13}	Manzoor et al., 2015	P
9	N-(2-hydroxyethyl) ethylenediamine	HEEDA				
10	Morpholine	MOR				
11	Ethylenediamine	EDA				
12	Methyldiethanol amine	MDEA				
13	2-(diethylamino) ethanol	DEELA				
14	N-ethyldiethanolamine	EDELA		No data found		
15	Glycine	GLY				
16	N-(2-hydroxyethyl) glycine	HEGLY				
17	Methylethanolamine	MMEA				
18	Triethylamine	TEA				
19	Triethanolamine	TELA				
20	Tris(hydroxymethyl) aminomethane	TRIS				
21	Monoethanolamine	MEA	8.40 x 10^{-15}	4.14 x 10^{-15}	Manzoor et al., 2015	P
22	3-aminopropanol	-				
23	2-(Ethylamine) ethanol	-		No data found		
24	Piperidine	-				

Table 3.7: Collated and calculated values from nitrosamine photolysis experiments, for the selected amines

Amine	Abbr.	Branching ratios			Reference
		k_2/k_{4a}	k_{4b}/k_{4a}	k_3/k_{4a}	
Dimethylamine	DMA	3.90×10^{-7}	0.22	0.26	Lindley et al., 1978[†]
Piperazine	PZ	1×10^{-7}*	0.3*	0.3*	Nielsen et al., 2012a
		1.57×10^{-7}	0	1.7	Tan et al., 2021a[‡]

*These parameters were constrained

[†]Normalised to k_{4a} by Nielsen et al. (2012a)

[‡] Note that the values quoted in the main text contradict those in Table S13 of the Supporting Information The values shown are those from the Supporting Information, as the values given in the main text are of the wrong order of magnitude.

Table 3.8: Calculated absolute values from the ratios in Table 3.7, based on the k_{4a} value for DMA, from Lazarou et al. (1994)

Amine	Abbr.	Rate constants (cm³ molecule⁻¹ s⁻¹)			Reference
		k_2	k_3	k_{4b}	
Dimethylamine	DMA	1.24×10^{-19}	8.27×10^{-14}	7.00×10^{-14}	Lindley et al., 1978
Piperazine	PZ	1.24×10^{-20}	5.41×10^{-13}	0	Tan et al., 2021a

Table 3.9: Values from the CCSA Position paper

Amine	Abbr.	Rate constants (cm³ molecule⁻¹ s⁻¹)			
		k_2	k_3	k_{4a}	k_4
Dimethylamine	DMA	1.24×10^{-19}	8.53×10^{-14}	3.18×10^{-13}	3.88×10^{-13}
Ethylamine	EA	1.24×10^{-19}	8.27×10^{-14}	3.18×10^{-13}	3.18×10^{-13}
Methylamine	MMA/MA	1.24×10^{-19}	8.27×10^{-14}	3.18×10^{-13}	3.88×10^{-13}
Monoethanolamine	MEA	1.24×10^{-19}	8.53×10^{-14}	3.18×10^{-13}	3.88×10^{-13}

3.2.1.2.2 Discussion of k_2, k_3, k_{4a} and k_{4b} values

Value ranges:

From a comparison of Tables 3.4 and 3.5 it is immediately evident that the values for k_2 are several orders of magnitude smaller than those for k_3, a conclusion shared by several authors (e.g. Tang and Nielsen, 2012). This difference in magnitude is partially counterbalanced by the difference in magnitude of ambient concentrations of O_2 and NO.

It is clear that there are very large variations in the values of both k_2 and k_3 for different species. This is unsurprising, as many authors have noted the strong dependence of amine structure and functional groups on the reactivity of amino radicals (e.g. Liu et al., 2019; Shen et al., 2023). There is, however, also a wide range of reported values for the same species, for almost all species for which there are multiple values.

k_2 values:

Considering first the k_2 values, Manzoor et al. (2015) reported considerable disagreement between values that they predicted using different theoretical methods, with values of k_2 calculated using a method based on Transition state theory (TST) being much lower than those calculated using Rice–Ramsperger–Kassel–Marcus (RRKM).

For both *DMA* and *MEA*, the k_2 values calculated by Manzoor et al. using RRKM theory are around two orders of magnitude higher than the other reported values for the same amine. Their value calculated using the TST theory, however, shows much better agreement with the other values, including the value for *DMA* derived from experiments (as given in Table 3.8 and 3.9). The large discrepancy between these RRKM values and other values challenges the decision of the authors to use these RRKM values for their subsequent calculations and atmospheric dispersion modelling.

For *MMA*, however, it is the value calculated using RRKM theory by Manzoor et al. which shows better agreement with the two other *MMA* values in Table 3.5. These other values, reported by Alam et al. (2019) and Liu et al. (2019), were calculated using RRKM and TST theory, respectively.

The only other amine in Table 3.5 with more than one value for k_2 is piperazine. The two values (Ma et al., 2018 and Liu et al., 2019) show very good agreement with one another, and are much lower than the values reported for most of the other amines.

The reported k_2 value of zero for *AMP* (Tan et al., 2021b) is of note; they explain that this is due to an absence of hydrogen atoms in the *AMP* amino radical that are in a suitable position for the reaction of O_2.

It is of note that Liu et al. (2019) have developed a SAR model for the determination of rate constants of the reaction of amino radicals with oxygen (k_2). Their model was constructed based on values determined for amino radicals from 28 amine species, using sophisticated quantum chemistry methods (some of which are shown in Table 3.2). The SAR model was then tested for a further set of six amines, with results reported as promising. This SAR model could be a useful resource for emerging amine species for which no other data is available.

k₃ values:

For k_3, the reported values also show a wide variation in magnitude, both between different species, and for different reported values for the same species. It should be noted that (unlike their values for k_2) the values reported by Liu et al. (2019) for k_3 are only estimations; if these values are disregarded for comparison purposes here, the remaining values show good agreement for *DMA*; these remaining values still show relatively poor agreement for *PZ*, *MMA* and *MEA*, however.

For *MEA*, the value calculated by Manzoor et al. (2015), shows much better agreement with the experimental value reported by Nielsen et al. (2010) than the other predicted values for *MEA*. Note that the Manzoor et al. value was calculated using RRKM theory.

Primary amines are not generally thought to give stable nitrosamines, so it might be expected that there has been little focus on the determination of values for k_3 for those amines that are primary. Nevertheless, there are values for several of the primary amines, including ethylamine (*EA*) and methylamine (*MMA*); this is important because the reaction represents a sink for the amino radical.

k₄ₐ and k₄ᵦ values:

For k_{4a} and k_{4b}, there are very few values with which to make a robust comparison. Of note is the value of k_{4b}/k_{4a} of 0, presented by Tan et al. (2021a) for *PZ*, with the explanation that the formation pathway of the imine from the reaction of the amino radical with NO_2 is blocked. This means that the reaction of the amino radical with NO_2 would form only the nitramine, and therefore that k_4 would be equal to k_{4a} for *PZ*.

There are very few values of k_{4a} and k_{4b} available for the selected amines (and for amines in general), so it is not possible to make any comparisons of values for any of the amines, except for k_{4a} for methylamine. Here there is relatively good agreement of the two available values, determined by experimental and prediction methods, respectively.

3.2.1.3 k_{OH} branching values: k_{1a}/k_1

3.2.1.3.1 Collated data

A literature review was carried out to investigate and collate values for the branching ratio of k_{OH} (k_{1a}/k_1 in ADMS notation), for the selected list of amines and other relevant amines. This branching ratio is the ratio between the rate of abstraction of an N—H hydrogen (as shown in Figure 1.2) and the rates of abstraction of other hydrogen atoms, as described in Section 1.2.3.

Table 3.10 shows the collated and calculated data. Values from experimental studies are denoted by 'E' and those predicted from theoretical calculations by 'P'. Values calculated using a SAR calculation are denoted 'S'. Note that, for tert-butylamine (*TBA*), the two values shown for Tan et al., 2018 refer to the use of two different models for the calculation. The SAR values labelled 'Borduas et al., 2016' are values reported by Speak et al. (2021), based on the SAR developed by Borduas et al.

No values could be found for many of the amine species.

Table 3.10: Collated values of k_{OH} branching ratio (k_{1a}/k_1) for the selected amines (1 to 23) and other relevant amines (24 to 26). Where E = experimental, P = predicted and S = SAR.

	Amine	Abbr.	k_{1a}/k_1	Reference	Type
1	Dimethylamine	DMA	0.37	Lindley et al., 1979	E
			0.48	Galano and Alvarez-Idaboy, 2008	P
			0.42	Nielsen et al., 2011a	E
			0.41	Onel et al., 2014b	E
			0.38	Manzoor et al., 2014, 2015	P
			0.34	Butkovskaya and Setser, 2016	E
			0.98	Borduas et al., 2016	S
2	Piperazine	PZ	0.09	Onel et al., 2014a	E
			0.45	Borduas et al., 2016	S
			0.07	Sarma, 2017	P
			0.011	Ren and da Silva, 2019	P
			0.18	Tan et al., 2021a	E
3	2-amino-2-methyl-propanol	AMP	0.8	Carter, 2008	P
			0.24	Tan et al., 2021b	E and P
4	Diethanolamine	DEA	No data found		
5	Diethylamine	DiEA	0.6	Nielsen, 2012	E
6	Ethylamine	EA	0.02	Galano and Alvarez-Idaboy, 2008	P
			0.09	Nielsen, 2012	E
			0.83	Borduas et al., 2016	S
7	Trimethylamine	TMA	0.6	Nielsen et al., 2011a	E
8	Methylamine	MMA/MA	0.2	Galano and Alvarez-Idaboy, 2008	P
			0.26	Tian et al., 2009	P
			0.25	Nielsen et al., 2011a	E
			0.24	Onel et al., 2014b	P
			0.35	Manzoor et al., 2014, 2015	P
			0.26	Butkovskaya and Setser, 2016	E
			0.98	Borduas et al., 2016	S
9	N-(2-hydroxyethyl) ethylenediamine	HEEDA			
10	Morpholine	MOR	0.2	Gao et al., 2015	P
11	Ethylenediamine	EDA	No data found		
12	Methyldiethanolamine	MDEA			
13	2-(diethylamino) ethanol	DEELA			
14	N-ethyldiethanolamine	EDELA			
15	Glycine	GLY			
16	N-(2-hydroxyethyl) glycine	HEGLY			
17	Methylethanolamine	MMEA	0.52	Onel et al., 2015	E
			0.74	Onel et al., 2015	S
18	Triethylamine	TEA	No data found		
19	Triethanolamine	TELA			
20	Tris(hydroxymethyl)aminomethane	TRIS			

	Amine	Abbr.	k_{1a}/k_1	Reference	Type
21	Monoethanolamine	MEA	0.08	Nielsen et al., 2010	E
			0.15	Karl et al., 2012a	P
			0.17	Xie et al., 2014	P
			0.05	Manzoor et al., 2014, 2015	P
			0.38	Onel et al., 2015	E
			0.47		S
22	3-aminopropanol	-			
23	2-(Ethylamine) ethanol	-		No data found	
24	Piperidine	-			
25	tert-butylamine	TBA	0.97	Carter, 2008	P
			0.39	Borduas et al., 2016	S
			0.96	Tan et al., 2018	P
			0.8	Tan et al., 2018	P
			0.59	Speak et al., 2019	E and P
			0.87	Speak et al., 2021	E and P
26	N,N-dimethyl ethanolamine	DMEA	0.66	Onel et al., 2015	S

3.2.1.3.2 Discussion of k_{1a}/k_1 values

It is clear that there are very large variations in the reported values of k_{1a}/k_1 for different species, and, for some amines, also a wide range of reported values for the same species.

It should be noted that the values reported by Borduas et al. (2016) are only estimations, based on a SAR model; if these values are disregarded for comparison purposes here, the remaining values show relatively good agreement for almost all of those amines with multiple values. Notable exceptions are *AMP* and *MEA*.

For *AMP*, Tan et al. (2021b) derived their value from a combination of their experimental data and a quantum chemistry theoretical model. In contrast, they highlight the challenges experienced in the experiments of Carter (2008), in which wall loss and the "sticky" nature of *AMP* caused significant problems, as acknowledged by the author: "*Although the experiments carried out for this project were useful in testing mechanisms in a qualitative sense… they were not particularly useful for quantitative mechanism evaluation. This is because amines are extremely "sticky" compounds that are difficult to reliably inject or monitor in the gas phase, and attempts to develop methods to quantitatively monitor these compounds in the gas phase were unsuccessful.*" (Carter, 2008).

For *MEA*, the values reported by Onel et al. (2015) are significantly higher than all of the others. The discrepancy in the SAR value is unsurprising, as it has often been noted that the Atkinson SAR used in EPI Suite is not able to give a good indication of where the hydrogen abstraction occurs in the amine molecule (e.g. da Silva et al., 2010, Nielsen et al., 2012) and so is not a useful tool for estimating the k_{1a}/k_1 branching ratio. But the value that they derive from their experiments is also much higher than the other values in Table 3.10.

This can be explained, at least in part, by the fact that they only considered abstraction from one of the methyl hydrogen atoms in their calculation of the abstraction from the nitrogen hydrogen atom (thereby ignoring the extent of abstraction of the other types of hydrogen atoms). This is echoed in their acknowledgement that their k_{1a}/k_1 value "*represents an upper limit for the carcinogenic compound production*".

The k_{1a}/k_1 branching ratio values determined from theoretical calculations for *MMA*, *DMA* and *EA* by Galano and Alvarez-Idaboy (2008) have been challenged. Bråten et al. (2008) claim that "*Again, any resemblance to experimental values is merely accidental*". This is discussed further in Nielsen et al., 2012, along with the results of Tian et al. (2009), who used a similar method: "*Although the published theoretical studies capture essential features of amine + OH reactions, the employed levels of computation are inadequate as a basis for* modelling the observed kinetics".

It is notable that the k_{1a}/k_1 branching ratio values for *PZ* are very low, as this tempers the very high k_1 values reported. A low k_{1a}/k_1 branching ratio is the reason given by Onel et al. (2014a) for the claim that the atmospheric reaction of *PZ* with OH has a low potential to form nitrosamines and nitramines.

3.2.1.4 Photolysis rate constants for nitrosamines

3.2.1.4.1 Collated data

A literature review was carried out to investigate and collate values of $J_{nitrosamine}/J_{NO2}$, for the selected list of amines and other relevant amines.

Table 3.11 shows the collated and calculated data for $J_{nitrosamine}/J_{NO2}$. Values from experimental studies are denoted by 'E' (i.e. all of the values here are derived from experiments). Those species that are primary amines are shown in grey text in the table; primary amines are generally considered to produce unstable nitrosamines that undergo immediate isomerisation, and hence the consideration of nitrosamine photolysis is not relevant for these species.

Calculations of nitrosamine photolysis are reported by Manzoor et al (2015). The authors state that "*primary nitrosamines are formed that are unstable and follow different dissociation pathways to form stable products…*", which is in line with the general scientific consensus, as noted above. But they then provide values of 'J/J(NO₂)' for N-nitroso methylamine and N-nitroso monoethanolamine, both of which are primary nitrosamines. Although these calculations represent valid photolysis calculations of the relevant chromophores in the molecules, what comprises a photolysis rate for an already highly unstable molecule is unclear. Therefore, it is not clear exactly what these values (and by extension, the value provided for N-nitroso dimethylamine), represent, and they have not been included here.

Table 3.11: Collated and calculated values of $J_{nitrosamine}/J_{NO2}$ for the selected amines (1 to 23) and other relevant amines (24). Where E = experimental and P = predicted

	Amine	Abbr.	$J_{nitrosamine}$ /J_{NO2}	Reference	Type
1	Dimethylamine	DMA	0.53	Tuazon et al., 1984	E
			0.34	Nielsen et al. 2012a	E
			0.13*	Larsen, 2011	P
2	Piperazine	PZ	0.12*†	Larsen, 2011	P
			0.24*‡	Larsen, 2011	P
			0.34	Nielsen et al. 2012a	E
			0.34	Tan et al., 2021a	E
3	2-amino-2-methyl-propanol	AMP			
4	Diethanolamine	DEA	0.15*	Larsen, 2011	P
5	Diethylamine	DiEA	0.30	Nielsen et al. 2012a	E
6	Ethylamine	EA			
7	Trimethylamine	TMA			
8	Methylamine	MMA/MA			
9	N-(2-hydroxyethyl) ethylenediamine	HEEDA			
10	Morpholine	MOR	0.34	Nielsen et al. 2012a	E
			0.13*	Larsen, 2011	P
11	Ethylenediamine	EDA			
12	Methyldiethanolamine	MDEA			

13	2-(diethylamino) ethanol	DEELA			
14	N-ethyldiethanolamine	EDELA			
15	Glycine	GLY			
16	N-(2-hydroxyethyl) glycine	HEGLY			
17	Methylethanolamine	MMEA	0.17*	Larsen, 2011	P
18	Triethylamine	TEA			
19	Triethanolamine	TELA			
20	Tris(hydroxymethyl)amino methane	TRIS			
21	Monoethanolamine	MEA			
22	3-aminopropanol	-			
23	2-(Ethylamine) ethanol	-			
24	Piperidine	-	0.31	Nielsen et al. 2012a	E

* The mean of the reported values for the lowest reported altitude of 500 m.

† Corresponds to 1-nitrosopiperazine

‡ Corresponds to 2-nitrosopiperazine

3.2.1.4.2 Discussion of photolysis rate values

A report by Tel-Tek for Gassnova (Nielsen, 2011b) concludes that: "*There is now an extensive, high-quality experimental data set available for gas phase nitrosamine photolysis under very different conditions (actinic flux and NO_x). All results point to a relative photolysis rate coefficient of jNitrosamine = (0.32 ± 0.03) × j_{NO2}.* A recommendation of the report is to use jNitrosamine = $0.32 \times j_{NO2}$ for all nitrosamines in dispersion modelling.

The more recent value of Tan et al. (2021a) also supports the advice given in the 2011 Tel-Tek report.

The value reported by Tuazon et al. (1984) is the highest of those in Table 3.11. This value is discussed by Nielsen et al. (2012): "*They employed O_3 in large excess in their photolysis experiments to prevent back-reaction of NO with the dimethylamino radical …We note, however, that under such experimental conditions NO_3 radicals are formed and the obtained result for jNDMA/jNO2 thus only represent an upper limit to the nitrosamine relative photolysis rate.*"

The theoretical values calculated by Larsen (2011) are lower than the other, experimentally-determined, values.

3.2.1.5 Important considerations for kinetic parameter values

For some amine species, the collated rate constants and branching ratios span a wide range of values, and the question arises of which values are most reliable, and therefore best to use for air emissions risk assessment purposes. It is recommended that care is taken when selecting and/or researching kinetic data. It is also important to consider the fact that some kinetic parameters have a greater influence on modelled concentrations than others; see Section 4 for sensitivity testing of these and other input parameters.

In a situation where a published value from a detailed theoretical calculation is very different value to a published experimental value for the same amine species, it is important to consider which value is more reliable, and why.

Important considerations when comparing values of kinetic parameters include:
- The level of sophistication of the respective experiments/calculations.
- Whether the methods used are fit for purpose
- The possibility of experimental artefacts or interferences
- Whether the two values should be compared; are they, for example, based on different assumptions for the reaction pathway mechanisms?
- Recognition of the strengths and weaknesses of different methods; e.g. some theoretical calculations are useful for determining reaction pathway mechanisms, but less useful for determining rate constant values.
- Whether the studies are independent of one another. e.g. researchers may constrain values or otherwise modify their measured or calculated values, based on the findings of other authors
- The complexity of the molecule. Simple, smaller molecules are usually easier to study with molecular modelling methods, and certain functional groups, such as alcohol groups, can pose experimental challenges

A further consideration is whether researchers have used a combination of experimental and predictive techniques in order to gain a more thorough understanding of the reaction mechanisms and kinetic data.

The development and use of theoretical calculations for the determination of rate constants in atmospheric chemistry is a rapidly evolving field. Vereecken and Francisco stated in their 2012 paper that "*experimental work remains the tool of choice*" for accurate determination for rate constants, but that "*computational chemistry has provided a major paradigm shift in the field of atmospheric chemistry*" They go on to say: "*More important, though, is the excellent complementarity of theoretical studies to experimental work and kinetic modeling. Examples where experimental work remains the tool of choice are the accurate determination of rate coefficient*".

CERC

3.2.2 Ambient OH concentrations

3.2.2.1 Annual average values in the UK

The ADMS amine chemistry scheme requires a typical local concentration of hydroxyl radical (OH) to be used to calculate a parameter, 'c', which is used to parameterise the hour-by-hour variation in OH. The OH concentration is a key parameter in amine chemistry, and as demonstrated in the modelling in Section 4.1, the production of nitrosamines and nitramines is highly sensitive to the starting value used. Therefore, a literature review was carried out to investigate typical values relevant to the UK, and the likely variation and uncertainty in values.

Hydroxyl radicals (OH) are formed primarily by the photolysis of ozone and reaction of the resulting oxygen atom with water vapour. The concentrations are therefore dependent on latitude, due to a combination of solar angle, variation in protection from UV light by stratospheric ozone, and the abundance of water. All three of these factors act so that there are higher concentrations at lower latitudes and lower concentrations at higher latitudes.

Because of the dependence on photolysis, the formation, and hence concentration, of OH is highly dependent on the time of day and the time of year. The existence of secondary means of production of OH, as described in Section 3.2.2.2, means that OH concentrations are not necessarily zero at night, but they are significantly lower. (e.g. Khan et al., 2008).

There are also spatial variations in OH concentrations according to the local environment, with different typical values in urban, rural, marine, etc areas. As an illustration of typical values, and of how the OH concentrations can vary on a relatively local spatial scale. Figure 3.6 shows OH concentrations over the UK and Ireland from a run carried by the UK Centre for Ecology & Hydrology (UKCEH) (CEH, 2022) for 2019, using the atmospheric chemistry transport model, EMEP4UK (CEH, 2023). This shows annual average ground level concentrations of OH in units of 10^5 molecules/cm^3.

Figure 3.6: Annual average OH concentrations (10^5 molecules/cm^3) from EMEP4UK model
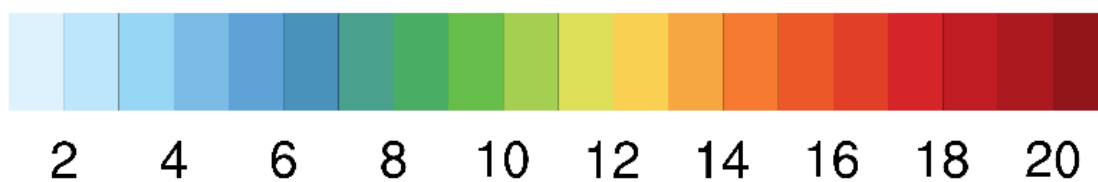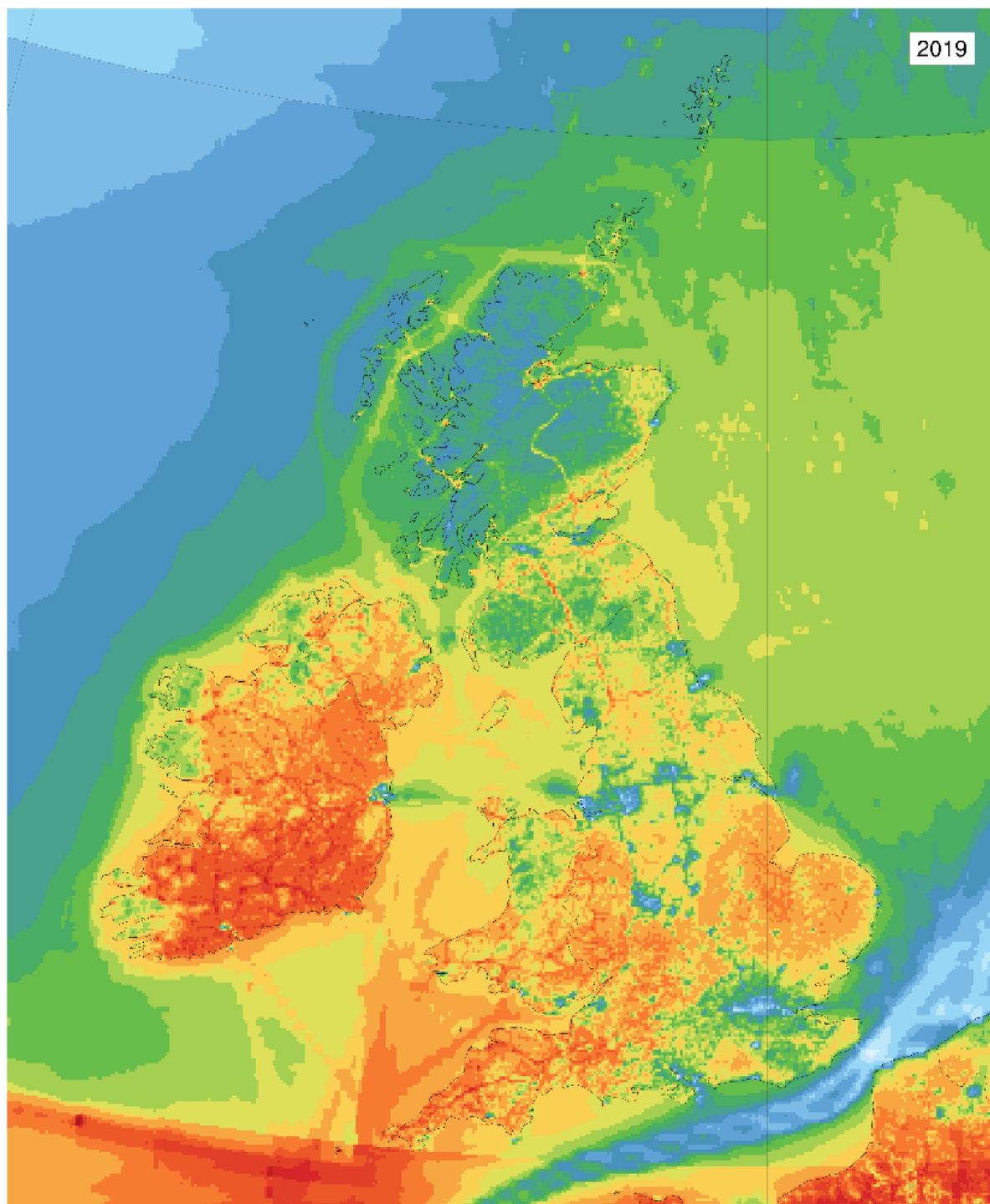
3.2.2.2 Modelling mixtures of amines and potential competition for OH

As described in Section 2.3, ADMS 6 has the ability to model several amine species in a single run, and also the ability to model two or more sources simultaneously. This treatment for multiple species and sources was designed so that there is no competition for the hydroxyl radical. The question has been raised as to whether two or more amine species released simultaneously would compete for the same OH, and if so, whether this should be taken into account in the ADMS amine chemistry scheme. Therefore, a literature survey was carried out to investigate whether there would be competition for OH.

The OH radical reacts with a wide range of species in the atmosphere, and the rate constant of the consumption of OH radicals by a reacting species is called the 'OH reactivity'. The total OH reactivity is a quantification of the total amount of OH-reactive species in an atmosphere. It is the loss frequency of OH radicals, with units of s^{-1}, and is the inverse of the OH atmospheric lifetime.

Important species for OH reactivity include carbon monoxide (CO) and volatile organic compounds (VOCs). The atmospheric chemistry of OH is highly complex and the balance of species dominating the reactions are different in different environments (urban, rural, marine, industrial etc), and this also depends on the origin (and hence pollutant loading) of the air mass brought in to an area. (e.g. Sinha et al., 2012; Stone et al., 2012; Woodwood-Massey et al., 2023).

The atmospheric lifetime of the OH radical is very short (of the order of a second, depending on the environment), and the OH radicals are rapidly regenerated and recycled via many different processes (e.g. Whalley et al., 2018).

Rohrer and Berresheim, (2006) carried out a detailed analysis of OH concentration measurements spanning a five-year period demonstrated that, and found that, despite the highly complex nature of the multitude of OH consumption and regeneration reactions, the concentration of OH in the atmosphere can be predicted using the intensity of ultraviolet light only: "*We find that the concentration of OH can be described by a surprisingly linear dependence on solar ultraviolet radiation throughout the measurement period, despite the fact that OH concentrations are influenced by thousands of reactants.*"

The specific parameter representing the UV intensity is the photolysis rate constant for atomic oxygen, called $J(O^1D)$. The dependency was shown to be due to the highly efficient recycling of OH by a radical called the hydroperoxyl radical, which in turn depends on $J(O^1D)$. They found that this parameter can be used to calculate OH concentrations over a range of timescales, down to as little as five minutes. They also demonstrated this relationship with other measurement datasets. This strong dependency has also been demonstrated by other researchers, albeit with some variations in the nature of the relationship for different environments (e.g. Stone et al., 2012; Lelieveld et al., 2016; Woodwood-Massey et al., 2023).

In conclusion, despite there being many different species in the atmosphere that react with and hence consume OH radicals, the OH is rapidly and efficiently recycled. Some of these OH-reactive species are present in the atmosphere at high concentrations, much higher than concentrations of amines in plumes, even when the requirement for ambient air entrainment into the plume is taken into account. It is therefore concluded that any OH competition posed by a mixture of amines is therefore likely to be insignificant.

3.2.3 Delayed OH and amine reactions through O_3 titration

A subject that has been discussed in relation to amine chemistry and dispersion is the potential for delayed amine chemistry within the plume. More specifically, the presence of reduced concentrations of O_3 (compared with ambient levels), and hence lower concentrations of OH, in the early stages of the plume, caused by the preferential 'titration' reaction of the O_3 with NO; with a resultant delay in the reactions that lead to the formation of nitrosamines and nitramines. Tønnesen (2011), for example, suggests that "*The reactions with OH will not start immediately after emissions due to the presence of NO in the plume after release. Approximately 2 to 4 minutes will pass before the NO is oxidized to NO_2 and no OH would be present in the plume until that has happened.*"

It is sometimes questioned whether ADMS is able to take this delaying titration effect into account, and it has further been suggested that the results of the ADMS amine chemistry scheme are overly-conservative as a result. This section demonstrates that the assertion that that ADMS does not account for the initial delay in the formation of nitrosamines and nitramines due to NO titration effects is unfounded.

This section describes the nature of the NO effects and delay, and demonstrates how these are included in the amine chemistry scheme in ADMS through the NO_x chemistry scheme (which works alongside the amine chemistry scheme). Information for NO_x chemistry is introduced to ADMS by the model user in two ways: emissions of NO_x from the source are input (including a quantification of primary NO_2), and hourly-varying ambient background concentrations of NO, NO_2 and O_3 are also input.

There are many descriptions of the O_3 titration effect within plumes. Song et al. (2003) provide a particularly clear and relevant illustration and description of this in their investigation of chemical evolution and mixing effects in ship plumes. They modelled both the dispersion and key photochemical reactions of the plume. Their results for daytime springtime chemistry in mid-latitude conditions show initial ozone and OH depletion in the early stages of the plume evolution, followed by restoration of these levels. Although the research was carried out on ship plumes in the marine boundary layer, the overall conditions, of a plume with relatively high NO_x (particularly NO) concentrations in ambient conditions conducive to high O_3 and OH production (i.e. high solar radiation), is broadly relevant to the amine chemistry situations considered in this report.

Song et al. define the earliest phase of the evolution of their modelled plume as 'stage 1', in which there are very high concentrations of NO_x within the plume, mainly in the form of NO. They demonstrate clear depletion of O_3 (with respect to background levels) in this early period, and explain that this is mainly due to the following reaction in their chemical scheme:

$$NO \; + \; O_3 \; \rightarrow \; NO_2 \; + \; O_2$$
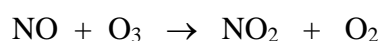
denoted as [R1].

The amine chemistry scheme in ADMS uses this same reaction. It is denoted as Reaction (1) in the ADMS 6 NO_x chemistry Technical Specification (CERC, 2023c). This, unsurprisingly, has the same effect as [R1] in the Song et al. chemical scheme, which is to keep the O_3 at low levels in the early stages of the plume evolution. The Technical Specification describes how

"*When the solar radiation is weaker (1) is the main reaction with generation of NO₂ until either NO and/or O₃ are reduced to low levels when further reaction proceeds only slowly*".

Song et al. go on to describe how the low levels of O_3 in the early stages of the plume have a strong influence on OH concentrations, as there is little O_3 available to form OH. This conversion of O_3 to OH is controlled by the following two reactions in their chemical scheme:

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$
$$O(^1D) + H_2O \rightarrow 2OH$$
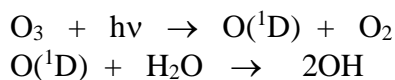
denoted as [R12] and [R15], respectively.

The first reaction, [R12], represents the photolysis of ozone, and the $O(^1D)$ is an excited oxygen atom, which goes on to form OH by reaction with a water molecule. The amine scheme in ADMS parameterises these two reactions in the form of the following expression:

$$[OH] = c [O_3] JNO_2$$

While this is not treated in exactly the same way as the scheme used in the Song et al. work (that is, in the form of explicit equations) the effect, which is essentially the same because the reaction rates for [R12] and [R15] are both very fast, is that the reduction of O_3 in the early stages of the plume history is translated to a corresponding reduction in OH concentrations. The J_{NO2} and c terms in combination act as a proxy for the explicit photolysis of O_3. This has the same effect as the [R12] and [R15] reactions of the Song et al. scheme, in that low concentrations of O_3 give low concentrations of OH.

Song et al. then go on to describe Stage 2 of the plume evolution, which is the generation of significantly higher levels of OH in the plume. They state that the NO titration reaction described above converts the NO to NO_2, and these high levels of NO_2 lead to the recovery of O_3, governed by the following reactions:

$$NO_2 + h\nu \rightarrow O(^3P) + NO$$

$$O(^3P) + O_2 \rightarrow O_3$$
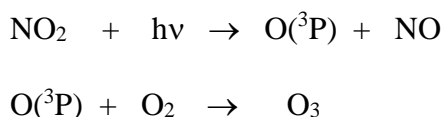
denoted as [R3] and [R5] in their chemical scheme, where $O(^3P)$ is another type of oxygen atom.

The amine chemistry scheme in ADMS uses these same reactions, combined into a single reaction expression:

$$NO_2 + h\nu \rightarrow NO + O_3$$
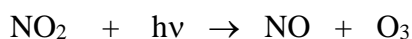
This is denoted as Reaction (2) in the ADMS 6 NO_x chemistry Technical Specification (CERC, 2023c). While this reaction is important, it is the entrainment of ambient O_3 into the plume which then increases O_3 and hence OH concentrations within the plume.

To demonstrate the O_3 titration in ADMS, a model run was carried out, set up to reflect typical values that might be expected for a combustion source with carbon capture. NO_x emission rate of 5 g/s, with primary NO_2 of 10%. An inert tracer was also modelled, in order to isolate the

effects of dilution, and isolate the effects of the chemical reactions; the tracer compound was modelled with a unit emission rate, that is the emission rate value was set to 1 g/s.

A single line of meteorological data (i.e. a single hour) was run, corresponding to a sunny, cloudless day, with a wind speed of 5m/s, and background concentrations of O_3 were set to 30 ppb; these parameters were selected to broadly match the daytime springtime conditions and ambient concentrations in the Song et al. scenario described above. Background NO and NO_2 concentrations were set to zero, so that the effects on the emitted NO and NO_2 could be isolated, for clarity.

Figure 3.7 shows the variation of normalised plume centreline concentrations of O_3, nitrosamine, NO and NO_2, with time. The concentrations of each species were normalised by dividing by the concentrations of the inert tracer, to remove the effects of dilution. The initial low (zero) levels of O_3 can be seen, followed by an increase in this O_3 over time.

ADMS uses the O_3 calculated using the above equations for each small timestep of the *dilution and entrainment* scheme (as described in Section 2.2.4) to calculate the OH concentration at each of these timesteps.

Figure 3.8 shows the equivalent concentration of OH, calculated from the plume centreline output O_3, the value of J_{NO2} for the modelled hour, and the input value of 'c'. The initial low (zero) levels of OH can be seen, followed by an increase in the OH over time. The normalised concentration of OH has still not reached its maximum level (equivalent to the 30 ppb ambient concentration of ozone) after ten minutes, which (for the particular meteorological condition modelled), represents a distance of over four kilometres from the source.

These figures demonstrate how ADMS accounts for an initial delay in the formation of nitrosamines and nitramines due to initial suppression of O_3, and hence OH, levels within the plume.

Figure 3.7: Variation in normalised plume centreline concentrations of a) O₃ and nitramine and b) NO and NO₂ over time

a)
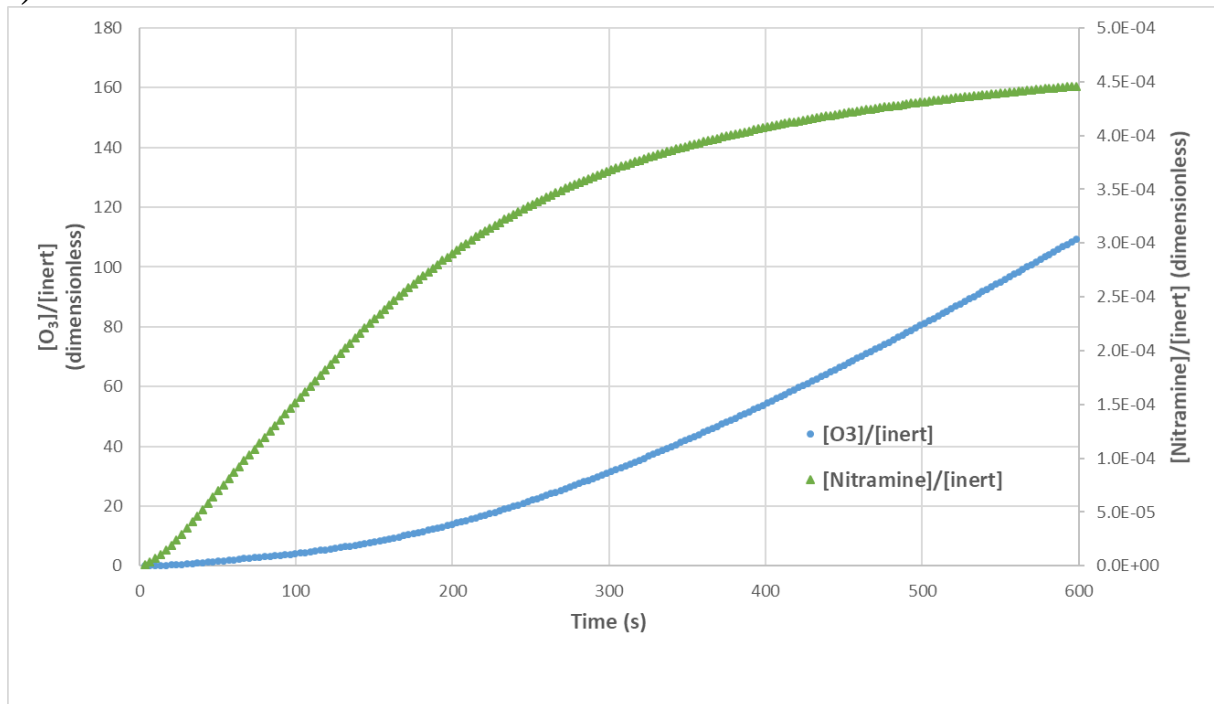
b)
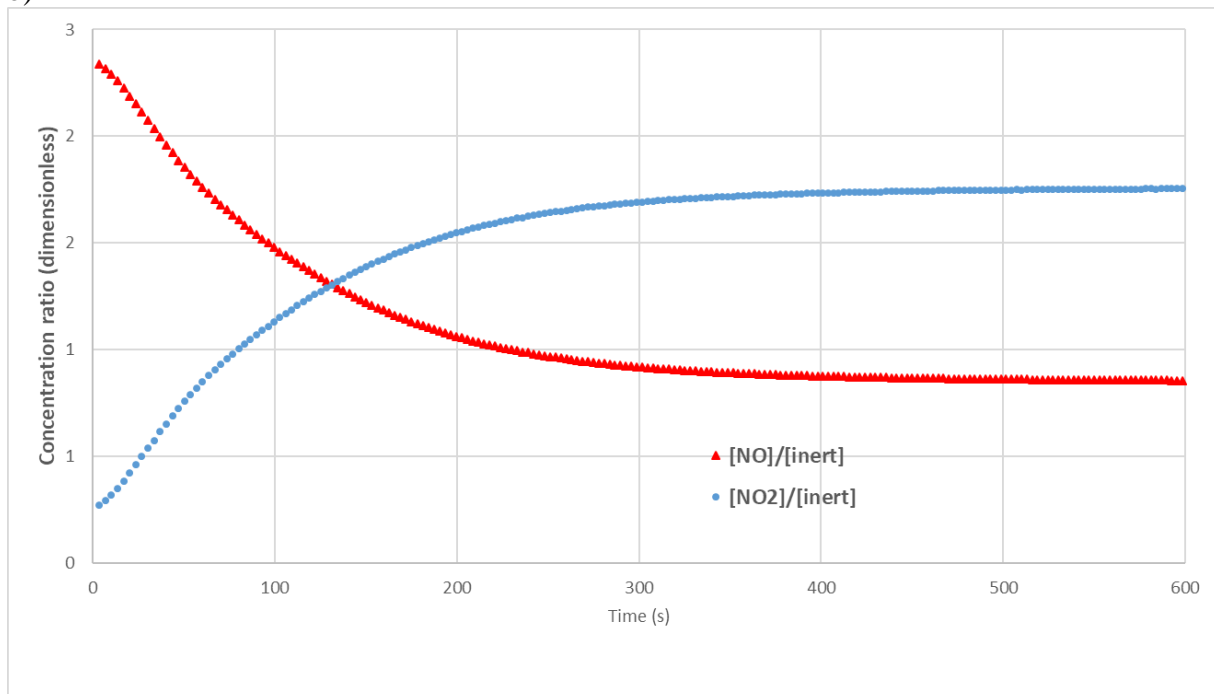
Figure 3.8: Variation in normalised plume centreline concentrations of OH with time
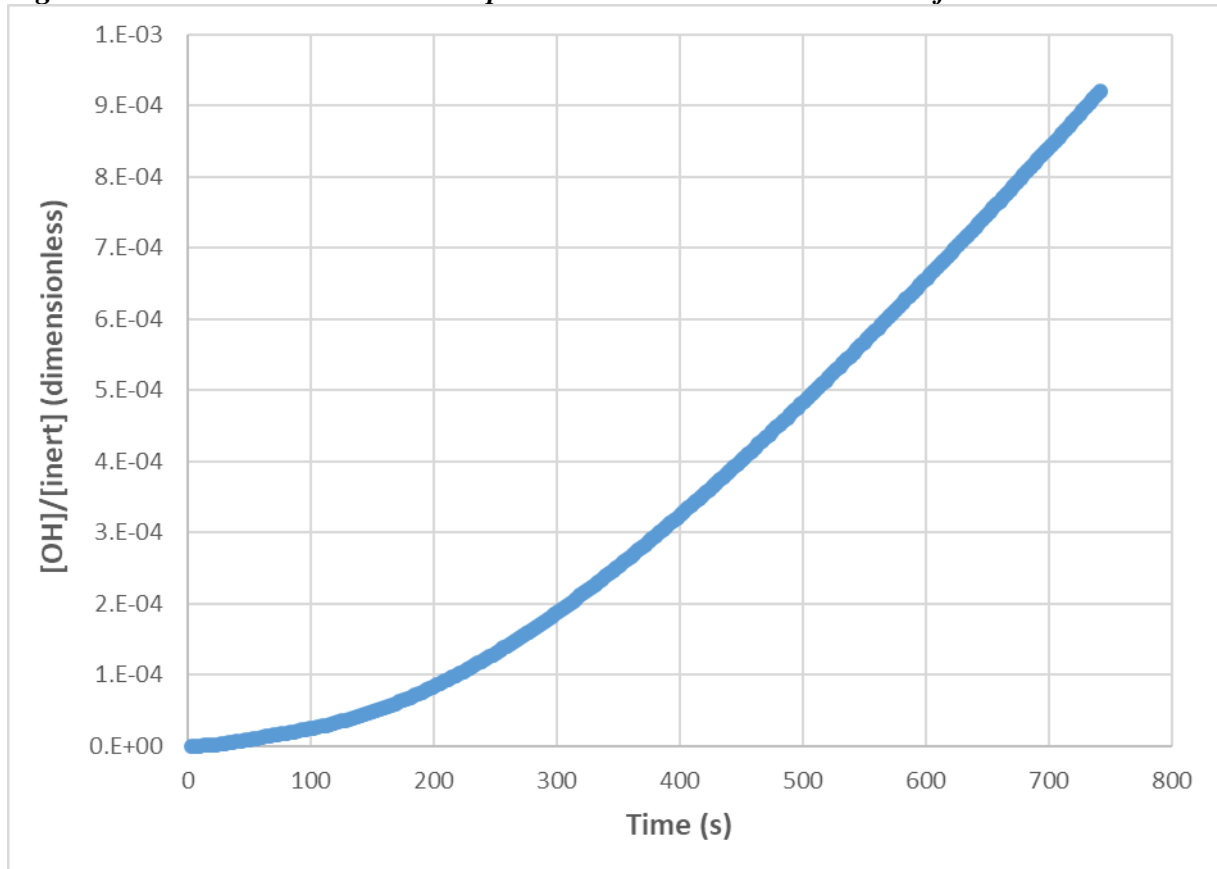
The United States Environmental Protection Agency (EPA) are proposing to revise their *Guideline on Air Quality Models (Appendix W)*. One of the proposals is to include the Generic Reaction Set Method (GRSM), a NO_x chemistry scheme method developed by CERC and included as a beta option in the AERMOD release version 22112, and is still included (as a beta option) in the latest version, 23132. The method is also known as the ADMSM method, as it uses the same key reactions and approach as the NO_x chemistry scheme in ADMS.

A key driver for the inclusion of this method in AERMOD and the EPA Guideline is its explicit modelling of ozone titration effects: "*The primary motivation behind the formulation and development of the GRSM NO_2 screening option was to address photolytic conversion of NO_2 to NO and to address the time-of-travel necessary for NO_X plumes to convert the NO portion of the plume to NO_2 via titration and entrainment of ambient ozone.*" (US EPA, 2023).

3.2.4 The use of fixed amine chemical conversion rates in dispersion modelling

Before amine chemistry schemes were developed for use in dispersion models, early dispersion modelling of the potential impact of the release of amines to air from carbon capture employed fixed percentage rates for the conversion of amines to their degradation products. It is sometimes suggested that this approach could be used for the risk assessment of atmospheric degradation products of amines.

A review of amine emissions by the Scottish Environmental Protection Agency (SEPA) includes a summary of studies that used a fixed-rate approach, including the percentage rates used in each case (SEPA, 2015).

The interactions between dispersion and chemical transformations are complex, and are highly dependent on the specific ambient conditions. For example, when conditions are conducive to OH formation (high solar radiation), they will also favour photolysis of nitrosamines. Furthermore, these conditions will also be favourable for the photolysis of NO_2.

Meteorological parameters that determine dispersion, such as wind speed and direction, and those that are important for chemical transformations, such as solar radiation, often show interrelationships. The wind conditions and solar radiation together determine the stability of the atmosphere, and the fact that OH-initiated amine chemistry is mostly restricted to the daytime means that nitramines and nitrosamines will only tend to form during certain stability conditions, and hence this tends to restrict product formation to specific dispersion patterns.

Modelling carried out by CERC for the Mongstad site in Norway, comparing the dispersion of chemically inert tracer in ADMS with output from the amine chemistry scheme found that the inert tracer maximum locations tend to occur in different locations to those of the nitrosamine/nitramine (using the amine chemistry scheme). This would also be expected to be the case for similar modelling for the UK. This suggests that calculations based on applying a fixed percentage to inert pollutants only, could give spatially unrealistic results. Figure 3.9 shows contour plots from this modelling, showing a) concentrations of nitramines and b) concentrations of an inert species modelled without any chemistry. The contour plots show that the maximum concentrations are to the southeast of the stack for nitramines, but to the north west for the inert tracer.

Figure 3.9: Contour plots of a) Nitramine concentrations and b) Inert tracer concentrations, for the same model setup
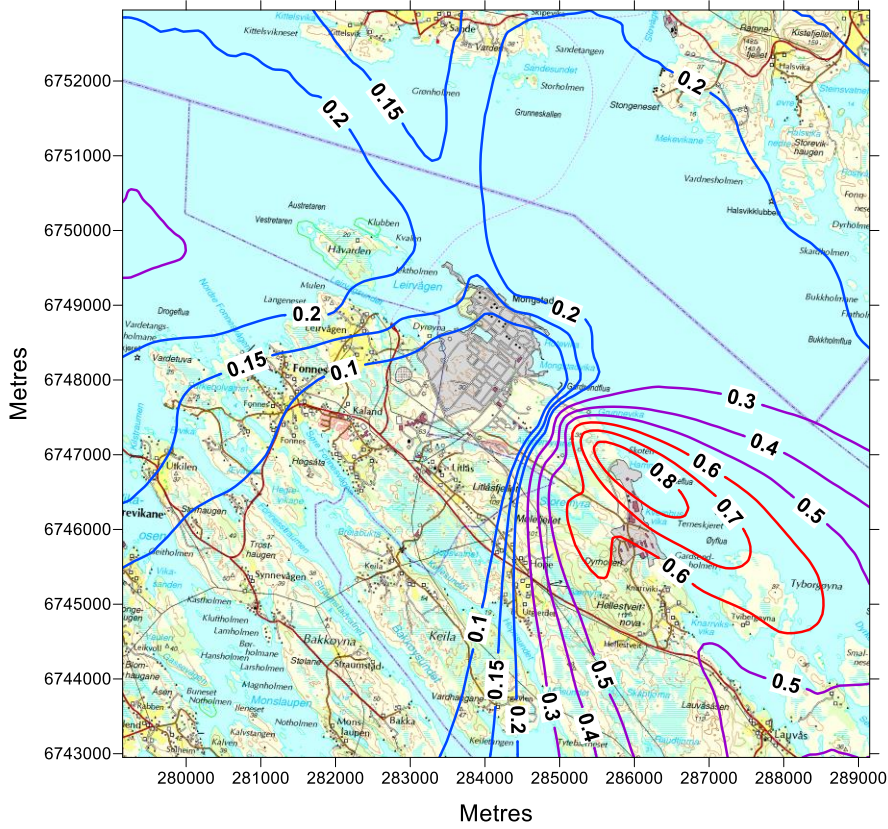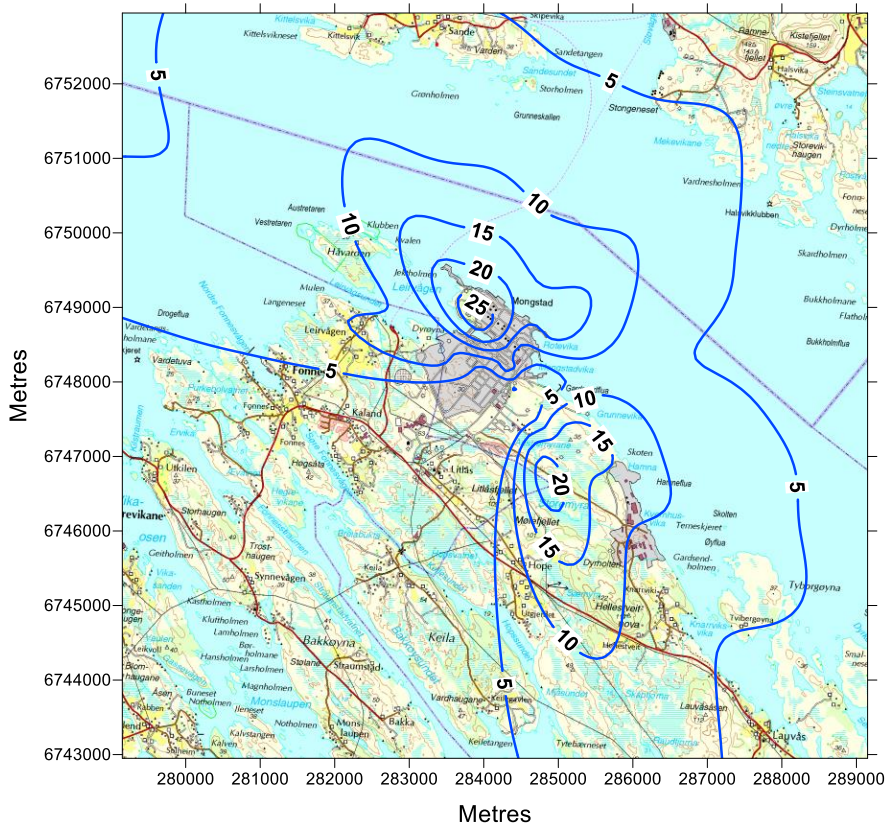
3.2.5 Aqueous partitioning

As described in Section 2.3, the aqueous partitioning of amines and related species into ambient liquid water droplets was originally developed in ADMS under the CCM project (Price, 2012b) and incorporated into the release version of ADMS as part of the SCOPE project (CERC, 2023b).

This partitioning into the aqueous phase can act like a sink for the amine and affect the amine chemistry, and hence gaseous nitrosamine and nitramine concentrations. The extent of this effect will depend on the solubility of the amine species, which is quantified in ADMS by user-defined value of Henry's Law constants. A literature review was carried out of Henry's Law Constant values for the selected amines.

The effect of Henry's Law constants, as well as other parameters involved in the aqueous partitioning scheme, is investigated further via sensitivity tests, as described in Section 4.2.

3.2.5.1 Henry's Law constants

The aqueous partitioning scheme in ADMS 6 requires a Henry's Law constant value for each amine, nitrosamine and nitramine species for which aqueous partitioning is to be modelled. Henry's law applies to solutions at the low concentrations typical of pollutant transfer into droplets in the atmosphere. It states that "*the abundance of a volatile solute dissolved in a liquid is proportional to its abundance in the gas phase*" (Sander et al. 2021).

The Henry's Law constant quantifies the distribution between the two phases. There are several different ways in which Henry's Law constants can be presented, depending on whether gas phase or liquid phase concentrations are of interest for a particular application, and hence whether the volatility or solubility needs to be quantified, respectively. They also vary depending on the quantity used to define the constant (concentration, mass fraction, molality, etc). The result is a complicated mix of different expressions and units for Henry's Law constants.

The values of Henry's Law solubility constants and volatility constants (expressed using the same quantities) are the inverse of one another. This means that the greater the value of Henry's Law solubility constants, the more soluble the species is in the solvent (usually water), but for Henry's Law volatility constants, the higher the value, the less soluble the species is in the solvent.

The International Union of Pure and Applied Chemistry (IUPAC) recommends eight variants of Henry's Law constants (different combinations of solubility/volatility and expressions of quantity), as described by Sander et al. (2021).

The ADMS 6 aqueous partitioning scheme requires the model user to input a Henry's law *solubility* constant, based on the concentration (number of moles per unit volume) of a species in the liquid phase, and the partial pressure of that species in the gas phase. In the notation used in Sander et al., this is the H_s^{cp} variation, and is the value where the molar concentration is the numerator and the partial pressure is the denominator. The specific units required for ADMS are mol/L/atm.

Due to the complex array of Henry's Law constant variations, users of the ADMS aqueous partitioning scheme may be uncertain of the format and units of any Henry's Law data they may have for a particular amine. They are advised to refer to the aforementioned references (Sander et al. 2021, Sander 2015) and the general information and unit conversion tool available at the following website: www.henrys-law.org. The main function of the website is to provide a searchable database of Henry's Law constant values of thousands of species in water, including many amines (and some nitrosamines). Note that the units of M/atm available as one of the options in the articles and the online unit converter tool is equivalent to the units required by ADMS (moles/litre/atm), since M represents the molar concentration, which equates to moles/litre.

3.2.5.2 Henry's Law constant values

Henry's Law values for the selected group of amines (see Section 3.1) were derived from the Sander website, and are shown in Table 3.12. Note that the values are provided in units of moles/(m^3.Pa) on the website, and have been converted to moles/(litre.atm) inputs to the ADMS aqueous partitioning scheme (using a conversion factor of 101.325). Where there are multiple values given for a given amine species, each value refers to a different reference, and the method used to determine the value is denoted in each case (presented in the footnote).

Figure 3.10 shows a plot of the mean of the Henry's Law values given in Table 3.12 for each amine. The colours of the columns denote the presence of key functional groups in the amine species, namely the number of alcohol groups (OH) and the presence of a carboxylic acid (carboxyl) group, COOH. Note that the y axis has a logarithmic scale, which is indicative of the wide variation in values among amine species, with the high value for glycine skewing this representation quite significantly. Table 3.13 shows a summary of the basic solubility statistics and properties of the amines.

As these are Henry's Law *solubility* constant values, the higher the values, the more soluble the amine is in water. Note the comparatively high values for some amine species, such as triethanolamine and glycine. The former owes its solubility to its three alcohol functional groups, and the latter to the fact that it is the simplest amino acid, and so has a hydrophilic carboxylic acid functional group and only a small hydrophobic alkyl group (See Section 1.2.2.2 for an introduction to the hydrophobic properties of different functional groups).

As shown in Table 3.12, some of the selected amines do not have values within the Sander et al. database. As there is increased attention on many amines for carbon capture solvents, there is increased research on their key parameters, including Henry's Law constants. Nguyen et al., 2011, for example, present Henry's Law values for a range of amines relevant to carbon capture, including 2-amino-2-methyl-propanol (*AMP*) (though note that, as their interest relates to processes within the carbon capture unit, rather than atmospheric processes, the values are presented as Henry's Law volatility constants and for a temperature of 40 °C).

Other potential sources of Henry's Law constant information include the websites of: the US National Institute of Standards and Technology (NIST); the open chemistry database at the National Institutes of Health, PubChem; and the European Chemicals Agency (ECHA).

Table 3.12: Henry's Law constants for the selected amine species, retrieved from Sander et al., 2015

Amine name	Abbr.	Henry's Law constant, H_s^{cp} (mol/(litre.atm))	Type*
Dimethylamine	DMA	3.0×10^1	L
		5.7×10^1	M
		5.9×10^1	T
		6.1×10^1	Q
		5.5×10^1	Q
		5.7×10^1	?
		5.8×10^1	?
Piperazine	PZ	1.0×10^4	T
2-amino-2-methyl-propanol	AMP	Not found in database	
Diethanolamine	DEA	2.5×10^7	V
Diethylamine/ethylethanamine	DiEA	4.0×10^1	M
		4.2×10^1	T
		1.8×10^1	Q
		3.9×10^1	?
		1.5×10^1	?
		4.0×10^1	?
Ethylamine	EA	3.5×10^1	L
		8.1×10^1	M
		1.0×10^2	M
		3.0×10^1	V
		8.0×10^1	Q
		4.7×10^1	Q
		1.0×10^2	?
		8.1×10^1	?
Trimethylamine	TMA	7.7	M
		9.6	M
		9.9	V
		3.7	Q
		4.8×10^1	Q
		1.5×10^1	?
		9.1	?
Methylamine	MMA/MA	3.5×10^1	L
		9.0×10^1	M
		1.2×10^2	Q
		5.7×10^1	Q
		9.0×10^1	?
		8.9×10^1	?
		1.4×10^2	?
N-(2-hydroxyethyl) ethylenediamine (dihydrochloride)	HEEDA	9.1×10^9	Q

CERC

Amine name	Abbr.	Henry's Law constant, H_s^{cp} (mol/(litre.atm))	Type*
Morpholine	MOR	8.3×10^2	V
		7.4×10^3	T
		1.6×10^4	Q
		1.0×10^3	Q
Ethylenediamine	EDA	5.9×10^5	M
		1.5×10^4	T
		5.7×10^5	Q
Methyldiethanolamine	MDEA	3.2×10^7	**V**
2-(diethylamino)ethanol	DEELA	Not found in database	
N-ethyldiethanolamine	EDELA	9.1×10^6	Q
Glycine	GLY	1.2×10^{13}	V
		9.0×10^7	E
N-(2-hydroxyethyl) glycine	HEGLY	Not found in database	
Methylethanolamine/monomethylethanolamine	MMEA	9.1×10^3	V
Triethylamine	TEA	6.7	M
		7.2	V
		7.2	V
		8.7	Q
		3.3×10^1	Q
		9.3	?
Triethanolamine	TELA	1.4×10^9	V
Tris(hydroxymethyl)aminomethane	TRIS	Not found in database	
Monoethanolamine	MEA	6.1×10^6	M
3-aminopropanol	–	Not found in database	
2-(Ethylamine) ethanol or monoethylaminoethanol	EAE	Not found in database	

*Key for 'type' from www.henrys-law.org website: L) literature review, M) measured, V) VP/AS = vapour pressure/aqueous solubility, R) recalculation, T) thermodynamic calculation, X) original paper not available, C) citation, Q) quantitative structure-property relationships (QSPR), E) estimate, ?) unknown. See section of Sander (2015) for further details.
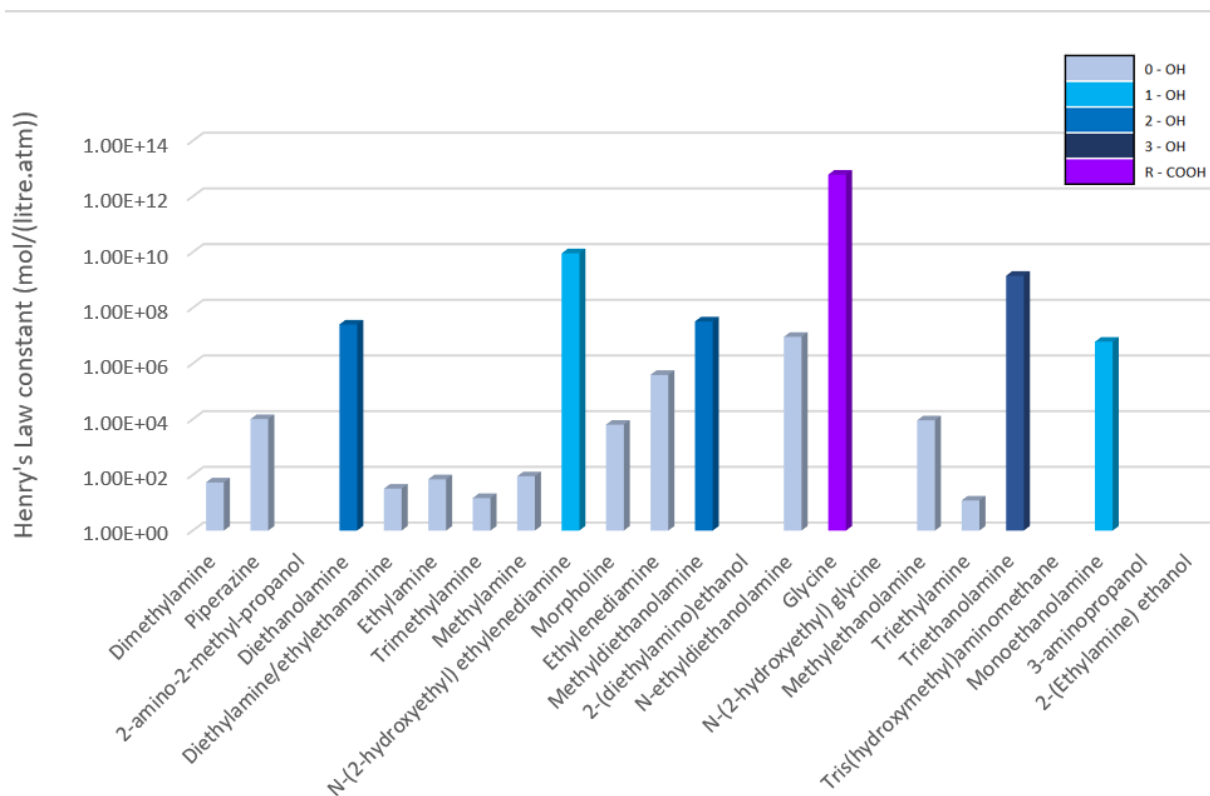
Figure 3.10: Plot of Henry's Law constants depicting the relative difference in Henry's constants. Note that the y axis has a logarithmic scale. The colours of the columns denote key functional groups (i.e., number of alcohol groups (OH) and the presence of a carboxylic acid group, -COOH).

Table 3.13: Summary of Henry's Law value basic statistics, molecular mass and functional groups

Amine name	Abbr.	Molecular mass	No. of hydroxyl groups	Arithmetic Mean of H_s^{cp}	Standard deviation
				mol/(litre.atm)	
Dimethylamine	DMA	45.1	0	5.37×10^1	1.79×10^1
Piperazine	PZ	86.1	0	1.01×10^4	0
2-amino-2-methyl-propanol	AMP	89.1	1	–	–
Diethanolamine	DEA	105.1	2	2.53×10^7	0
Diethylamine / ethylethanamine	DiEA	73.1	0	3.21×10^1	1.36×10^1
Ethylamine	EA	45.1	0	6.94×10^1	3.13×10^1
Trimethylamine	TMA	59.1	0	1.47×10^1	1.32×10^1
Methylamine	MMA/ MA	31.1	0	8.93×10^1	4.14×10^1
N-(2-hydroxyethyl) ethylenediamine	HEEDA	104.1	1	9.12×10^9	0
Morpholine	MOR	87.1	0	6.36×10^3	6.16×10^3
Ethylenediamine	EDA	60	0	3.90×10^5	2.85×10^4

Amine name	Abbr.	Molecular mass	No. of hydroxyl groups	Arithmetic Mean of H_s^{cp}	Standard deviation
Methyldiethanolamine	MDEA	119.2	2	3.24×10^7	0
2-(diethylamino)ethanol	DEELA	117.2	1	–	–
N-ethyldiethanolamine	EDELA	133.2	2	9.12×10^6	0
Glycine	GLY	75.1	0 * (–COOH group drives solubility)	6.08×10^{12}	5.73×10^{12}
N-(2-hydroxyethyl) glycine	HEGLY	119.1	1	–	–
Methylethanolamine	MMEA	75.1	1	9.12×10^3	0
Triethylamine	TEA	101.2	0	1.21×10^1	9.13
Triethanolamine	TELA	149.2	3	1.42×10^9	0
Tris(hydroxymethyl) aminomethane	TRIS	121.1	3	–	–
Monoethanolamine	MEA	61.1	1	6.08×10^6	0
3-aminopropanol	–	75.1	1	–	–
2-(Ethylamine) ethanol	EAE	89.1	1	–	–

*The carboxylic acid functional group (–COOH) drives the solubility

Data for nitrosamines is more limited. Table 3.14 shows those Henry' Law constant values that are available from the Sander database website for the nitrosamines relating to the selected group of amines for this project. Nielsen et al. (2012b) note that the values for nitrosamines are generally an order of magnitude smaller than those of the corresponding amine. They caution that, for nitrosamines "*the agreement between models and experiment is unsatisfactory. It is likely that there are large errors in the experimental data and therefore also large uncertainties in the model predictions. Naive use of existing theoretical programs for estimation of nitrosamine partitioning is discouraged*.".

Although some reported modelled values for nitramines are in the literature (e.g. Karl et al., 2012b), it is generally reported that there are essentially no reliable data available for Henry's Law constants for nitramines, but that the values for nitramines are likely to be similar to those of the corresponding nitrosamines (Tan et al., 2021b, Nielsen et al., 2012b). For modelling the partitioning of nitramines, Nielsen et al. (2012b) offer a similar caution to that for nitrosamines, this time stating that it is "*strongly discouraged*".

Table 3.14: Henry's Law constants for nitrosamine species, retrieved from Sander et al., 2015

Nitrosamine name	Abbr.	Henry's Law constant H_s^{cp} (moles/ (litre.atm))	Type*
N-nitrosodimethylamine	NDMA	6.2×10^2	M
		5.3×10^2	M
		3.0×10^1	C
		9.6×10^2	Q
		3.0×10^1	?
Dinitrosopiperazine	NPZ	1.9×10^4	M
N-nitrosodiethanolamine	NDELA	2.0×10^8	Q
N-nitrosodiethylamine	NDEA	5.7×10^2	M
		1.4×10^2	M
		3.9×10^2	Q
4-nitrosomorpholine	NMOR	3.9×10^4	M
		9.1×10^4	Q
N-nitroso-(2-hydroxyethyl)glycine	NHEGLY	Not found in database	
N-nitrosopiperidine	NPIP	1.1×10^3	M
		2.9×10^3	Q

*Key for 'type' from www.henrys-law.org website: L) literature review, M) measured, V) VP/AS = vapour pressure/aqueous solubility, R) recalculation, T) thermodynamic calculation, X) original paper not available, C) citation, Q) quantitative structure-property relationships (QSPR), E) estimate, ?) unknown. See section of Sander (2015) for further details.

Table 3.15 shows Henry's Law constant values for a range of other common pollutants and analogous species, for comparison purposes. The values are typical values, derived from the Sander database website.

Table 3.15: Henry's Law constants for other species, for reference

Species	Henry's Law constant H_s^{cp} (moles/ (litre.atm))
Ammonia	5.98×10^1
Methanol	2.10×10^2
Ethanoic acid (acetic acid)	4.26×10^1
Nitrogen dioxide (NO_2)	1.21×10^{-2}
Nitric oxide (NO)	1.93×10^{-3}
Butane	1.22×10^{-3}
Cyclohexane	5.67×10^{-3}

3.2.6 Reactions with other radicals

Amines can also react with other radicals in the atmosphere, including nitrate ($NO_3^\cdot$, or simply NO_3) and chlorine ($^\cdot Cl$, or simply Cl) radicals.

3.2.6.1 Reactions with NO₃

The effect of night-time reaction of amines with NO_3 radicals was investigated by CERC during the CCM project using a version of ADMS that extended the amine chemistry scheme to include initiation by NO_3 radicals. A summary can be found in Price, 2012c, and more details can be found in Price, 2012b. Dispersion modelling was carried out for the Mongstad site for *DMA* and *MEA*. The key findings of the modelling were that the NO_3 radical modelling gave much lower maximum annual average ground level concentrations of both nitrosamines and nitramines than the OH radical modelling, and that the NO_3 model runs gave maximum nitramine concentrations at a much larger distance from the source than the equivalent OH radical chemistry runs.

Sensitivity tests were carried out to investigate key areas of uncertainty in the input data, and the conclusions were that the reactions of amines with NO_3 radicals need not form a major part of future dispersion modelling studies at the Mongstad site, unless any information arose which suggested that ambient nitrate concentrations at Mongstad are significantly higher than those modelled, and/or that rate constants are significantly higher than those used. The modelling was carried out using a constant night-time NO_3 concentration of 3.2×10^7 radicals cm^{-3} (1.3ppbt). Measurements and modelling of NO_3 reported in the literature (e.g. Khan et al., 2008; Khan et al., 2015) suggest that this is broadly typical of UK average concentrations.

To the best of our knowledge, there has been no subsequent research published on this topic that changes the general consensus that the reaction of amines with NO_3 radicals is much less important than the reaction with OH radicals, and can therefore be omitted from air emission assessments.

3.2.6.2 Reactions with Cl

As described previously, amines in the gas phase can react in the atmosphere with the chlorine radical ($^\cdot Cl$, or simply Cl). Research on the formation of nitrosamines and nitramines in the atmosphere has historically tended to give relatively little attention to the potential impact of this reaction pathway, and to instead focus attention on the OH reactions. This is understandable, as the limited information available on the reaction kinetics and the ambient concentrations of Cl suggested that, despite high reaction rates, the contribution of the Cl radical reactions would be much lower than the equivalent OH radical reactions, due to low expected Cl concentrations in ambient air.

Nielsen et al. (2012), for example, suggested the following, regarding the Mongstad area: "*Cl atom reactions with amines are extremely fast… Assuming [Cl]$_{12 h}$ = 2 x 10^3 cm^{-3}, the characteristic time for atmospheric removal of amines by reaction with Cl atoms will be around 30 days, and amine–Cl chemistry will therefore only be important in areas with substantially higher Cl atom concentrations*."

A combination of recent findings has sparked renewed interest in the reaction of Cl with amines, as noted by reviewers such as Shen et al. (2023). These findings include evidence for high rate constants and branching ratios for certain amine/Cl reactions and advances in the understanding of Cl formation in the atmosphere. Xie et al. (2015), for example, state "*Recent findings on the formation of ˙Cl in continental urban areas necessitate the consideration of ˙Cl initiated degradation when assessing the fate of volatile organic pollutants*" and Bhattacharyya et al. (2023) describe how "*atmospheric Cl radical concentrations have been historically underestimated and consequently understudied*". For further information on Cl concentrations, see, for example, Wang et al. (2019), who discuss global concentrations, and for a discussion of Cl concentrations relevant to the UK, see, for example, Priestley et al. (2018), and Bannan et al (2015), who calculate Cl concentrations based on measurement campaigns carried out in Manchester and London, respectively.

Regarding rate constants, Nicovich et al. (2015) carried out experiments to determine rate constants for the reaction of chlorine radicals with simple amines. In this publication, they highlighted the lack of any previous kinetic experiments for reactions of amines with chlorine, citing the work of Rudić et al. (2003), in which the k_{Cl} branching ratio of methylamine was measured, as an exception.

Table 3.16 shows the values of Nicovich et al., and other reaction rates of the initial hydrogen abstraction reaction of Cl with amines (k_{Cl}) for the selected list of amines and other relevant amines. Table 3.17 shows collated branching ratios of this reaction (the Cl equivalent of k_{1a}/k_1 in ADMS notation). Note that these are not exhaustive lists of values, but intended to give an indication of the values for key species.

The values in Tables 3.16 and 3.17 show that the k_{Cl} values are significantly greater than the corresponding k_{OH} values, and the k_{Cl} branching ratios are also generally greater than the corresponding OH branching ratio values.

Table 3.16: Collated values of k_{Cl} for the selected amines

Amine	Abbr.	k_{Cl} (cm^3 molecule^{-1} s^{-1})	Reference	Type
Dimethylamine	DMA	3.90 x 10^{-10}	Nicovich et al., 2015	E
Piperazine	PZ	4.70 x 10^{-10}	Ma et al., 2018	P
Diethanolamine	DEA	4.7 x 10^{-11}	Feilburg, 2011	
Trimethylamine	TMA	3.70 x 10^{-10}	Nicovich et al., 2015	E
Methylamine	MMA/MA	2.90 x 10^{-10}	Nicovich et al., 2015	E
Methyldiethanolamine	MDEA	9.7 x 10^{-11}	Feilburg, 2011	
Monoethanolamine	MEA	3.60 x 10^{-10}	Xie et al., 2015	P
		3.60 x 10^{-11}	Feilburg, 2011	E

Table 3.17: Collated values of k_{Cl} branching ratio (k_{1a}/k_1) for the selected amines

Amine	Abbr.	k_{1a}/k_1 (Cl)	Reference	Type
Dimethylamine	DMA	1.00	Nicovich et al, 2015	P
Piperazine	PZ	0.54	Feilburg, 2011	P
		0.998	Ma et al., 2018	P
Methylamine	MMA/MA	0.52	Rudić et al., 2003	E
		0.49	Feilburg, 2011	P
		0.98	Nicovich et al, 2015	P
Monoethanolamine	MEA	0.72	Xie et al., 2015	P

3.3   User Input Tool

Prior to this project, it was recognised that the preparation of the various input data for modelling amines has substantial potential for error. This includes the conversion of units and the calculation of the 'c' parameter (as described in Section 3.2.2.1). In response to this, as part of this project and its Framework, CERC have developed a standalone tool for use in conjunction with ADMS, to improve usability of the amine chemistry scheme, help to reduce potential user error and facilitate the transparency of the input data and assumptions.

The tool is focused on helping the model/framework user to calculate and document key input data regarding:
- the kinetic information required for the amine species
- other amine-specific conversion factors required by the model
- the local environment data – essentially automating the calculation of the constant, c (which determines the hourly ambient concentrations of the hydroxyl radical).

The appropriate format and requirements for the tool were determined following the literature reviews, development and with consultation with the Environment Agency Air Quality Modelling and Assessment Unit (AQMAU).

The ADMS amine chemistry scheme requires a value for c, which is calculated from typical values of local ambient ozone concentrations and J_{NO2}. Previously, in the absence of an additional tool, the value for J_{NO2} would need to be manually calculated by the model user by running ADMS and using the hourly incoming solar radiation (K) values obtained from the meteorological pre-processor output from ADMS (which in turn uses the input local meteorological data). There is potential for user error at several stages of a manual calculation, and automating this process should eliminate much of this.

It is anticipated that the use of this tool will make the process much more reproducible and transparent, helping users to carry out checks, and allow regulators to make these inputs and assumptions auditable.

The tool should also facilitate the process of user sensitivity testing of the parameters involved in the calculation of the 'c' parameter.

3.4 Framework summary

The preliminary assessment Framework for the ADMS amine chemistry resulting from this project comprises the following:

- A database of collated kinetic parameter values and interpretation for their use in the ADMS chemistry scheme:
    - k_1 to k_4 rate constants
    - Branching ratios
    - Photolysis constants

- A database of collated aqueous partitioning parameters and interpretation for their use in the ADMS aqueous partitioning scheme:
    - Henry's Law constants

- A User Input Tool, for the preparation of model input data for the ADMS amine chemistry scheme:
    - Unit conversion
    - Calculation of the constant, 'c' based on input background and meteorology data

This framework has been tested and used for sensitivity testing, as described in the following section.

4 Sensitivity testing

This section outlines sensitivity tests, carried out using ADMS 6, to investigate the effect of various input parameters and assumptions on model output. It considers various aspects reviewed and presented in the development of the framework section, aiming at testing their significance and their relative degree of change in the resultant concentrations (i.e., amine species, kinetic parameter data, solubility parameters, etc.).

The focus for these sensitivity tests is on amine-specific parameters, and those over which site operators have some level of control, and those over which model users have an element of choice. The focus of the sensitivity tests here are not general parameters such as meteorological data or local terrain data. These are usually subject to minimum decision-making on the part of the model user, as the location of the site dictates the data to be used. An exception is a test to compare the effect of using background data from an urban background site, for comparison against that from a rural site.

Parameters and inputs solely related to dispersion were not investigated in these sensitivity tests, as these have been addressed in detail elsewhere; see for example, the ADMS validation documents (CERC, 2023d).

It was intended that these sensitivity tests should build on sensitivity tests carried out previously under the CCM project (Price, 2012a). The base case was set up with many of the same parameters and assumptions as the base case for those tests, with only the UK-specific data and parameters changed for the current tests.

4.1 Standard (gaseous phase) amine chemistry

4.1.1 Base case inputs and assumptions

A base case modelling scenario was set up, representing emissions of dimethylamine (*DMA*). A single point source was modelled, and the modelled parameters are given in Table 4.1. The emitted species and their emission rates are given in Table 4.2. The percentage of emitted NO_x that is NO_2 was assumed to be 10%, representative of a typical combustion process. Tables 4.3 and 4.4 show the reaction rate constant values, and other parameters relating to the amine chemistry scheme, respectively. These are the same source and reaction rate parameter values used in the previous CCM sensitivity tests (Price, 2012a), with the exception of the amine and NO_x emission rates, and the 'c' parameter, which was calculated from the meteorological and background data described below.

Note that the amine emission rate was set to a large unit value (1 g/s), for ease of scaling; this does not represent a realistic amine emission rate.

For the base case, a single, square building was modelled in ADMS, with the stack located at the centre of the building; the configuration is shown in Figure 4.1, and the parameters are given in Table 4.5.

A year of meteorological data measured at Manchester Airport, for 2018, was used for the modelling, and a wind rose for the site is given in Figure 4.2. This site was chosen because it represents the approximate mid-point for the locations of the major carbon capture projects likely to be developed in the near future in England and the rest of the UK. The latitude was set to 53.5, to represent the location of the meteorological data measurements.

Terrain effects were not included in the base case, and a fixed surface roughness length of 0.7 m was used, representative of a typical industrial area in the UK.

Hourly sequential measured ambient concentrations of ozone, NO_2 and NO from the Glazebury monitoring site were used for the base case modelling. This is a rural background site around 10 km to the west of Manchester.

The outputs generated were the annual average concentrations of amine, nitrosamine, nitramine and the inert tracer. The concentrations were generated over a regular output grid at ground level, extending 8 km by 8 km, with a resolution of 40 m.

Note that no directly emitted nitrosamines or nitramines were included in the dispersion modelling, as this was outside the scope of the project.

Table 4.1: Modelled source parameters

Source parameters					
Height (m)	Diameter (m)	Emission velocity (m/s)	Volume flow rate (m³/s)	Temperature (°C)	Location (m)
65	6.53	20	670	30	0,0

Table 4.2: Emitted species and emission rates (g/s)

Amine	NOₓ	Tracer
1	5	1

Table 4.3: Reaction rate constant values used for the base case

Parameter	Value	
	cm^3 molecule^{-1} s^{-1}	ppb^{-1} s^{-1}
k_1	6.50×10^{-11}	1.63
k_2	9.54×10^{-20}	2.39×10^{-9}
k_3	2.39×10^{-13}	0.060
k_{4a}	3.18×10^{-13}	0.080
k_4	3.50×10^{-13}	0.088

Table 4.4: Other amine-related values used for the base case

Parameter		Value (dimensionless)
k_{1a}/k_1		0.42
$J_{nitrosamine} / J_{NO2}$		0.25
c		0.044*
μg/m³ to ppb conversion factor†	Amine	0.54
	Nitrosamine	0.33
	Nitramine	0.27

*Based on an average OH concentration of 5×10^6

†Values correspond to the relative molecular mass values of 45, 74 and 90, for the amine (*DMA*), and its nitrosamine and nitramine, respectively

Table 4.5: Modelled building parameters

Parameter	Value
Location of centre	0,0
Height (m)	60
Length (m)	50
Width (m)	50
Angle of the length of the building from north (°)	0

Figure 4.1: Modelled stack and building configuration
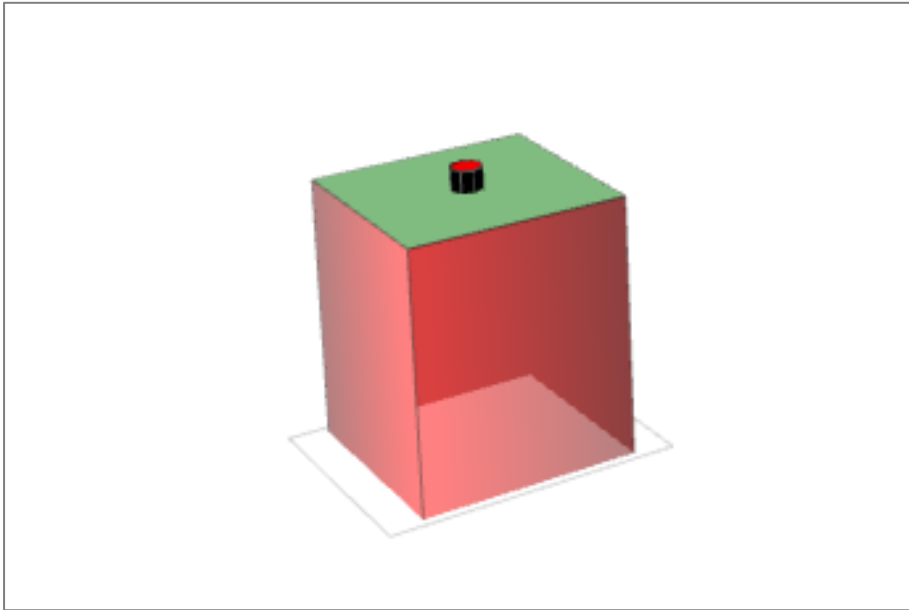
Figure 4.2: Wind rose, Manchester Airport, 2018
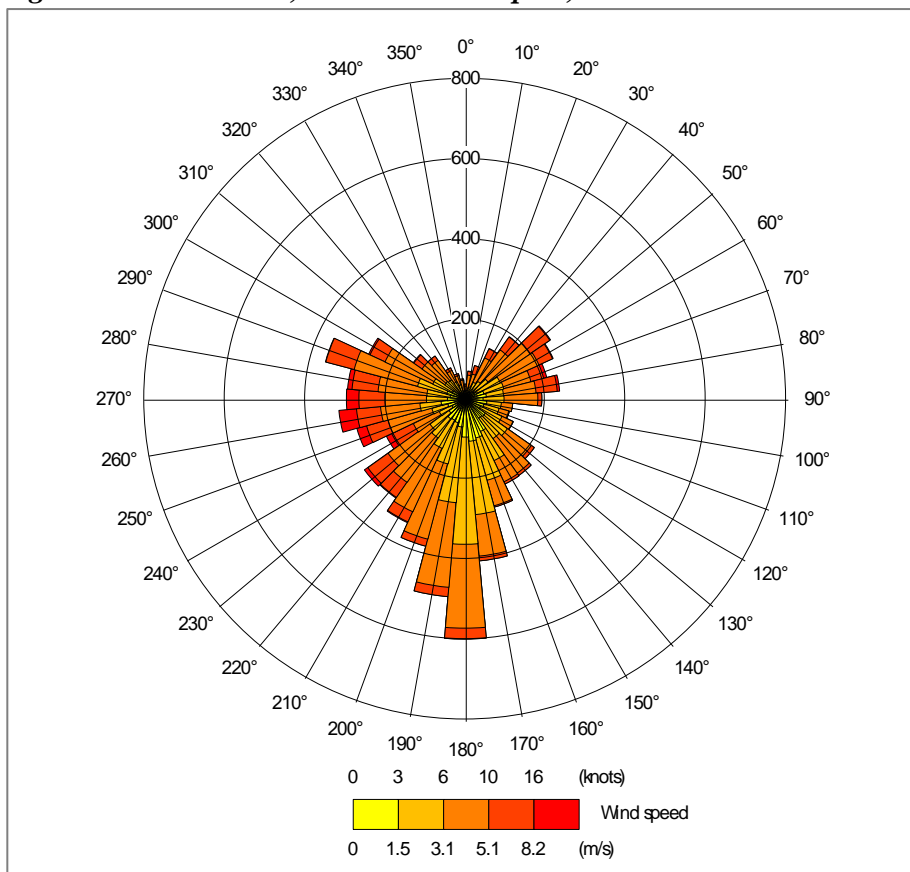
4.1.2 Sensitivity test descriptions

Sensitivity tests were carried out by modifying the base case model run summarised in the previous section, with the purpose of showing the relative change in output concentrations on varying model input parameters. Table 4.6 describes the parameters and modelling assumptions varied for each of the sensitivity tests.

Table 4.7 gives the values of the parameters used for those sensitivity tests involving reaction parameters, with the base case parameters shown for comparison purposes. For ease of reference, those values that differ from base case values are shown in shaded cells.

For run no. 5, the value used as a maximum value of k_2 was chosen to represent a realistic maximum value, excluding the outliers in Table 3.4. As such, the value used in this test is representative of the maximum of the values shown in Figure 3.4(b).

For the piperazine and *MEA* runs (runs no. 11 and 12, respectively), the reaction rate parameter values used were the average of the most appropriate values shown in Section 3.2.1 (e.g. values from structure activity relationship (SAR) estimations were excluded). In addition to the values shown in Table 4.7, '$\mu g/m^3$ to ppb' conversion factors were also changed for the relevant species, to represent the respective molecular mass values. Note that, although *MEA* is a primary amine, it was allowed to form nitrosamines in the model runs (i.e. carried out without the 'creation of unstable nitrosamines' option selected), for ease of comparison, and to maximise the output information.

Table 4.8 shows the average values of the ambient OH radical and ozone concentrations used for the base case and sensitivity tests 23 to 26, and the corresponding 'c' values input for the model runs.

Table 4.6: Names and descriptions of the sensitivity tests

Test	Name	Description
1	k_1 max	Maximum value of k_1 found for selected amines (relates to piperazine)
2	k_1 min	Minimum value of k_1 found for selected amines (relates to tert-butylamine)
3	k_{1a}/k_1 max	Maximum value of k_{1a}/k_1 found for selected amines (relates to piperazine)
4	k_{1a}/k_1 min	Minimum value of k_{1a} found for selected amines (relates to 3-aminopropanol)
5	k_2 max	100 x Base case value
6	k_2 min	Minimum value of k_2 found for selected amines (relates to piperazine)
7	k_3 max	Higher k3 value (relates to piperazine)
8	k_3 min	Minimum value of k_3 found for selected amines (relates to piperazine)
9	k_{4a} and k_4 max	Maximum values of k4 and k4a found for selected amines (relates to methylamine)
10	k_{4a} and k_4 min	Minimum value of k4 and k4a found for selected amines (relates to MEA)
11	Piperazine	Run with all amine-related parameter values set to those of piperazine
12	MEA average values	Run with all amine-related parameter values set to those of MEA, using average of values found
13	MEA CCSA values	Run with all amine-related parameter values set to those of MEA, using CCSA recommended values (all experiment-derived values)*
14	Photolysis 0	Varying values for the '$J_{nitrosamine}/J_{NO2}$' parameter (which determines the photolysis rate of the nitrosamine)
15	Photolysis 0.1	
16	Photolysis 0.5	
17	Photolysis 0.75	
18	Photolysis 1	
19	Mr 31.1	Varying values for the molecular mass of the amine (from which 'µg/m^3 to ppb' conversion values for the amine, nitrosamine and nitramine species were calculated and input)
20	Mr 50	
21	Mr 100	
22	Mr 150	
23	Mr 200	
24	Ambient OH 1 x 10^5	Varying values for the typical ambient concentrations of hydroxyl radical (OH) assumed for the calculation of the 'c' parameter
25	Ambient OH 1 x 10^6	
26	Ambient OH 1 x 10^7	
27	Urban background site	Using ambient background data (and associated value of the 'c' constant) from an urban background measurement site (Manchester Piccadilly))
28	No buildings	Building downwash effects excluded

*Values from Hazell-Marshall & Nielsen, 2022

Table 4.7: Values used for the reaction parameter sensitivity tests (the shaded cells show the parameter value(s) changed in each case)

	k_1	k_2	k_3	k_{4a}	k_4	k_{1a}/k_1	$J_{nitrosamine}/J_{NO2}$
Test	cm^3 molecule^{-1} s^{-1}					Dimensionless	
Base case	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
1	2.86×10^{-10}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
2	8.4×10^{-12}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
3	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.96	0.25
4	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.011	0.25
5	6.5×10^{-11}	9.54×10^{-18}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
6	6.5×10^{-11}	1.30×10^{-21}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
7	6.5×10^{-11}	9.54×10^{-20}	7.20×10^{-11}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
8	6.5×10^{-11}	9.54×10^{-20}	5.20×10^{-14}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
9	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	9.70×10^{-13}	3.5×10^{-12}	0.42	0.25
10	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	8.40×10^{-15}	1.25×10^{-14}	0.42	0.25
11	2.86×10^{-10}	1.30×10^{-21}	5.20×10^{-14}	3.18×10^{-13}	3.5×10^{-13}	0.09	0.34
12	8.00×10^{-11}	2.00×10^{-18}	7.00×10^{-14}	3.18×10^{-13}	3.5×10^{-13}	0.10	0.53
13	7.6×10^{-11}	1.24×10^{-19}	8.53×10^{-14}	3.18×10^{-13}	3.88×10^{-13}	0.08	0.53
14	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0
15	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.1
16	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.5
17	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.75
18	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	1

Table 4.8: Values used for the 'c' constant for the base case and sensitivity tests 24 to 27

Test	Typical OH concentration (molecules/cm^3)	Mean O$_3$ concentration	Value of c (dimensionless)
Base case	5×10^6		4.4×10^{-3}
24	1×10^5		8.8×10^{-5}
25	1×10^6	48	8.8×10^{-4}
26	1×10^7		8.8×10^{-3}
27	5×10^6	30	1.5×10^{-3}

4.1.3 Results

Table 4.9 shows the results of the standard (gaseous phase) amine chemistry sensitivity tests, and Figure 4.3 presents the output concentrations of nitramine, nitrosamine and the sum of these two species, for comparison. Contour plots for these results are given in Appendix A. Note that, although stable nitrosamines would not be expected to be formed from primary amines, nitrosamine output has been generated and reported here for primary amines, to maximise the information generated.

Table 4.9: Maximum gridded annual average output concentration of amine secondary products (ng/m³)

	Test	Name	Nitramine	Nitrosamine	Sum (nitramine and nitrosamine)
	0	Base case	0.623	2.48	3.01
	1	k_1 max	1.70	9.01	10.5
	2	k_1 min	0.105	0.341	0.424
	3	k_{1a}/k_1 max	1.42	5.66	6.87
	4	k_{1a}/k_1 min	0.0163	0.0651	0.0790
	5	k_2 max	0.017	0.195	0.209
	6	k_2 min	2.09	4.67	6.25
	7	k_3 max	0.103	5.86	5.93
	8	k_3 min	1.17	0.226	1.37
	9	k_{4a} and k_4 max	1.55	2.17	3.53
	10	k_{4a} and k_4 min	0.0181	2.64	2.66
	11	Piperazine	2.53	0.41	2.89
	12	MEA average values	0.0222	0.00792	0.0295
	13	MEA CCSA values	0.175	0.0491	0.217
	14	Photolysis 0	0.575	2.70	3.24
	15	Photolysis 0.1	0.595	2.61	3.14
	16	Photolysis 0.5	0.623	2.48	3.01
	17	Photolysis 0.75	0.696	2.14	2.68
	18	Photolysis 1	0.723	2.01	2.55
	19	Mr 31.1	0.762	2.92	3.57
	20	Mr 50	0.592	2.38	2.88
	21	Mr 100	0.452	1.95	2.33
	22	Mr 150	0.405	1.80	2.14
	23	Mr 200	0.381	1.73	2.05
	24	Ambient OH 1 x 10^5	0.0177	0.0534	0.0667
	25	Ambient OH 1 x 10^6	0.157	0.535	0.654
	26	Ambient OH 1 x 10^7	1.05	4.67	5.53
	27	Urban background site	0.219	0.785	0.964
	28	No buildings	0.562	1.76	2.26

Figure 4.3: Maximum annual average output concentrations of nitrosamine and nitramine for each sensitivity test
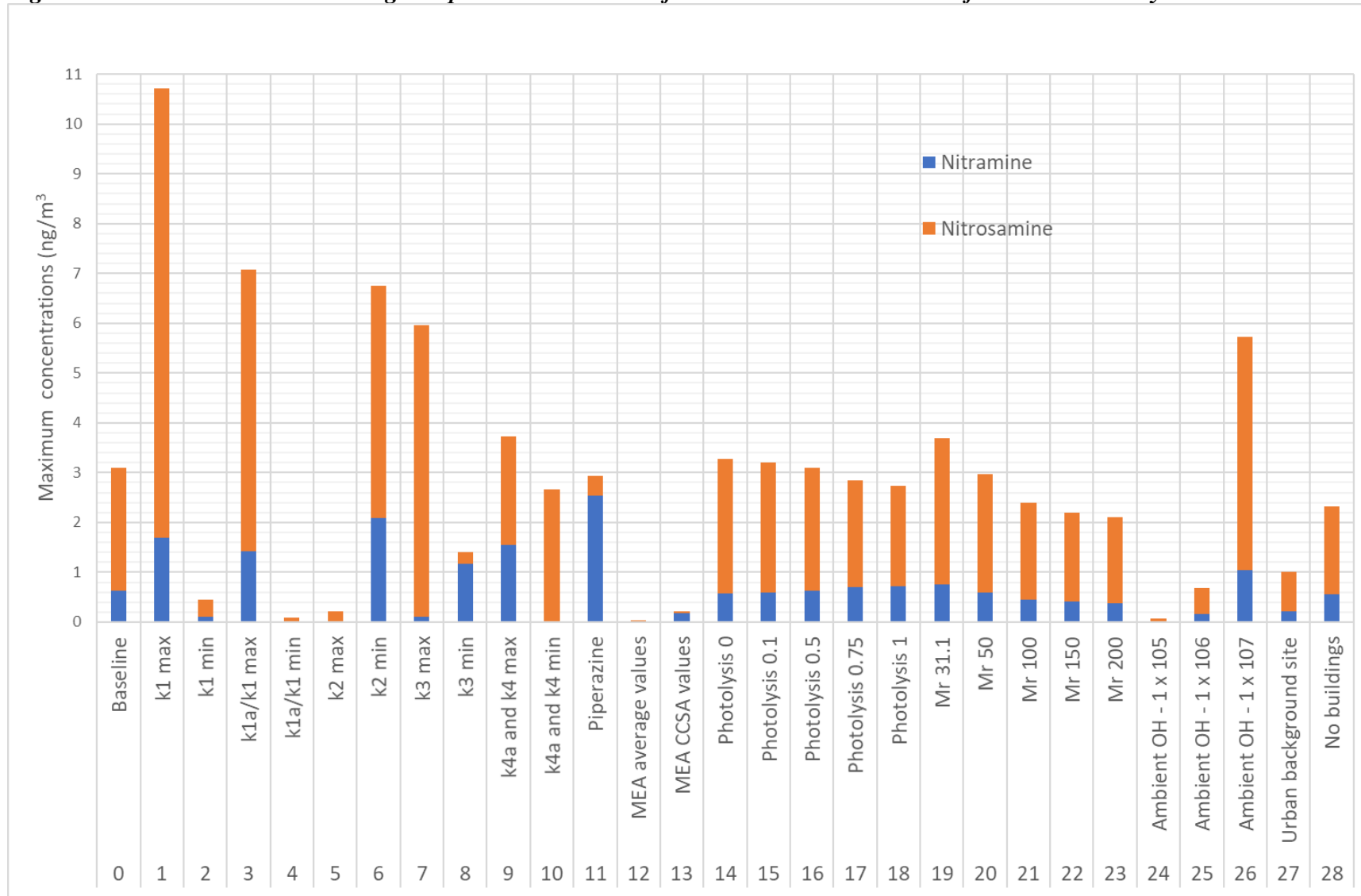
4.1.4 Discussion

1 and 2: Variation in k_1 (k_{OH} – the overall rate of H abstraction from the amine)

The effect of the k_1 parameter is significant and the relationship of k_1 to the output concentrations of nitrosamines and nitramines is approximately linear. This is as expected, as this relationship is derived from the fundamental chemistry, and has been demonstrated in previous sensitivity tests (Price, 2012a). Note that the value used for the 'k_1 max' test (corresponding to piperazine) is much higher than those of the other amines.

3 and 4: k_{1a}/k_1 (branching ratio for the H abstraction from the amine)

As expected, the variation in output concentrations follows a similar (approximately linear) pattern to that of Tests 1 and 2 (k_1 values), as the branching ratio acts to limit the initial hydrogen abstraction from the nitrogen atom of the amine, and hence the formation of the amino radical.

5 and 6: Variation in k_2 (Amino radical + O_2 → imine)

This reaction acts as a sink for the amino radical, and the very large value of k_2 for the '*k_2 max*' test gives an increase in the resulting nitrosamine and nitramine concentrations compared with the baseline. This highlights the significance of the wide variation and uncertainty in the k_2 values in the literature (as described in Section 3.2.1) and the need for further research in this area.

7 and 8: Variation in k_3 (Amino radical + NO → nitrosamine)

The total (nitrosamine + nitramine) concentration for *k_3 max* is nearly double that of the base case, and for *k_3 min* is around half that of the base case. But note that the total is almost all in the form of nitrosamine for *k_3 max* and almost all in the form of nitramine for *k_3 min*. As with k_2, this highlights the wide variation and uncertainty in the k_3 values in the literature and the need for further research and clarity in this area.

9 and 10: Variation in k4a and k4 (Amino radical + NO_2 → nitramine) and (Amino radical + NO_2 → nitramine and imine)

These tests involved the simultaneous change of k_{4a} and k_4 (an increase of both for Test 9 and a decrease of both for Test 10). These results show a less dramatic variation than those seen for the k_2 and k_3 tests. Note, however, that total concentrations for the '*k_{4a} and k_4 min*' test are almost entirely in the form of nitrosamine.

11: Piperazine values

While there is very little effect on the total nitrosamine and nitramine concentrations, the output is mainly in the form of nitramine for this test (in contrast to the base case, where the output is mostly in the form of nitrosamine). Note that the values of k_2 and k_3 used for this test were both taken from the Liu et al. (2019) paper. Note also that the k_4 and k_{4a} values were kept the same as the values in the base case run.

12 and 13: *MEA* values
There is a large reduction in the output total concentrations for both the '*MEA average values*' and '*MEA CCSA* values' tests, compared with the base case. Note that these results are not generated with the 'formation of unstable nitrosamine' option selected, so the domination of the nitramine in the CCSA value test is due to the rate constant values alone.

14 to 18: Photolysis rate tests
The variation of the $J_{nitrosamine}/J_{NO2}$ values has very little effect on the output concentrations. This, and the fact that there is much smaller range in the reported values for different amines species than was tested here, suggests that there is very little sensitivity to this parameter in a realistic setting.

19 to 23: Molecular mass tests
There is relatively little variation in the output for these tests, although the variation is more substantial for the lower values of molecular mass. This suggests that an approximation of the molecular mass of a given amine solvent species in the event of amine solvent confidentiality may be acceptable, providing this approximation is reasonable (rounding to the nearest 10, for example). For comparison, note that the variation in molecular mass for the selected amines is between 31 and 139 (and the base case value is 45).

24 to 26: Ambient OH tests
The effect of varying the average ambient OH concentration is significant. As with the k_1 parameter, this is a fundamental aspect of the chemistry, as the initial attack of the OH radical on the amine species is an important step. This highlights the importance of determining a representative value for the typical (average) ambient OH value in the model region.

27: Urban background data
The effect of using this urban background measuring site instead of a rural site has a relatively large effect. The fact that the output nitrosamine and nitramine concentrations reduce for this scenario, with respect to the base case, indicates that the reduced ambient O_3 concentrations (characteristic of urban atmospheres) have the dominant effect; note, though, that there is also an increase in the ambient NO_x concentrations, the general effect of which is to increase the nitrosamine and nitramine concentrations. This highlights the likely importance of determining a representative monitoring site, and also a representative value for the typical ambient OH value in the model region. That is, not just representing the general location, but also the local conditions.

28: Buildings
Although this is a very specific test, as building dimensions and locations are highly site-specific, the results give an indication of the general effects of buildings. Table 4.10 shows the distance of the maximum ground level concentrations from the source, for the base case (which includes building downwash effects), and the equivalent run without building effects modelled.

While there is relatively little effect on the maximum output concentrations the distances of the maximum concentrations from the source demonstrate how buildings often bring the maximum ground level concentrations closer to the source.

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Table 4.10: Approximate distance of maximum ground level concentration from source (m)

Species	Base case (with buildings)	No buildings
Nitrosamine	600	800
Nitramine	900	1200
Tracer	400	750

4.1.4.1 Summary

Based on these sensitivity tests, the following are the key conditions that result in the lowest sum of concentrations of nitrosamines and nitramines:

- Low k_1 (k_{OH})
- Low k_{1a}/k_1 branching ratio
- Lower ambient ozone concentrations
- Low typical (average) ambient OH

4.2 Aqueous partitioning

4.2.1 Base case inputs and assumptions

The base case modelling scenario set up for the gaseous chemistry runs, (as described in Section 4.1.1), was modified to set up a base case scenario for sensitivity testing of the aqueous partitioning scheme. The aqueous partitioning and plume visibility modules were activated, and a value of 58 mol/L/atm used for the Henry's Law solubility constant of the amine, which represents the value for *DMA*, as given in Section 3.2.5. Henry's Law constant values for the nitrosamine and nitramine species were set to zero, which essentially means that they are treated as insoluble species in the model runs.

A source water content of 0.027 kg of water / kg of dry air was used, which represents a saturated plume at the modelled source temperature of 30 °C (that is, the plume air contains as much water vapour as it is possible to contain at this temperature without condensation occurring). This was chosen to be representative of a typical amine carbon capture process emission. Ellison et al. (2022), for example, describe how the amine carbon capture process requires the: "*...temperature of waste gas stream to be around 30°C – 40°C to work optimally. The low temperature alongside the presence of moisture will likely result in a water saturated flue gas.*"

Droplet nucleation and washout were not included in the aqueous partitioning base case run. Annual average concentrations of amines partitioned into the aqueous phase were added to the model outputs.

The outputs generated were the annual average concentrations of the amine partitioned into the gas phase and into the aqueous phase, nitrosamine and nitramine. The concentrations were generated over a regular output grid at ground level, extending 8 km by 8 km, with a resolution of 40 m.

4.2.2 Sensitivity test descriptions

Sensitivity tests were carried out by modifying the base case model run. Table 4.11 describes the parameters and modelling assumptions varied for each of the sensitivity tests.

Table 4.11: Names and descriptions of the sensitivity tests

Test	Name	Description
A1	40 °C saturated	Source temperature 40 °C, water content 0.048 kg/kg (to represent a saturated plume)
A2	40 °C	Source temperature 40 °C, water content same as base case (0.027 kg/kg)
A3	50 °C saturated	Source temperature 50 °C, water content 0.087 kg/kg (to represent a saturated plume)
A4	50 °C	Source temperature 50 °C, water content same as base case (0.027 kg/kg)
A5	PZ H	Aqueous base case with Henry's Law constant set to that of piperazine (1 x 10^4 mol/L/atm)
A6	PZ H, 40 °C	Aqueous base case with Henry's Law constant set to that of piperazine and source temperature 40 °C
A7	PZ H, 40 °C, saturated	Aqueous base case with Henry's Law constant set to that of piperazine; source temperature 40 °C; water content 0.048 kg/kg (to represent a saturated plume)
A8	PZ H, 50 °C	Aqueous base case with Henry's Law constant set to that of piperazine and source temperature 50 °C
A9	PZ H, 50 °C, saturated	Aqueous base case with Henry's Law constant set to that of piperazine; source temperature 50 °C; water content 0.087 kg/kg (to represent a saturated plume)
A10	MEA H	Aqueous base case with Henry's Law constant set to that of MEA (6.1 x 10^6 mol/L/atm)
A11	MEA H, 40 °C	Aqueous base case with Henry's Law constant set to that of MEA and source temperature 40 °C
A12	MEA H, 40 °C, saturated	Aqueous base case with Henry's Law constant set to that of MEA; source temperature 40 °C; water content 0.048 kg/kg (to represent a saturated plume)
A13	MEA H, 50 °C	Aqueous base case with Henry's Law constant set to that of MEA and source temperature 40 °C
A14	MEA H, 50 °C, saturated	Aqueous base case with Henry's Law constant set to that of MEA; source temperature 50 °C; water content 0.087 kg/kg (to represent a saturated plume)
A15	PZ	Run with all amine-related parameter values set to those of piperazine, including the Henry's Law constant
A16	MEA	Run with all amine-related parameter values set to those of MEA, including the Henry's Law constant
A17	No reactions, MEA H	Run with no gaseous reactions, and Henry's Law constant set to that of MEA

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Test	Name	Description
A18	Droplets base case	Aqueous base case with Droplet scheme on, with: - Number of ions in dissociation for the salt = 2 - Concentration of salt particles = 10 µg/m^3 - Molecular mass of salt = 100 - Number of salt particles per cubic centimetre = 1000
A19	Droplets 1	As droplet base case, with: Number of ions in dissociation for the salt = 2
A20	Droplets 2	As droplet base case, with: Concentration of salt particles = 5 µg/m^3
A21	Droplets 3	As droplet base case, with: Concentration of salt particles = 20 µg/m^3
A22	Droplets 4	As droplet base case, with: Molecular mass of salt = 50
A23	Droplets 5	As droplet base case, with: Molecular mass of salt = 150
A24	Droplets 6	As droplet base case, with: Number of salt particles per cubic centimetre = 500
A25	Droplets 7	As droplet base case, with: Number of salt particles per cubic centimetre = 2000
A26	No building	As base case, but with no building downwash effects

4.2.3 Results

Table 4.12 shows the results for the aqueous partitioning sensitivity tests. The concentrations for each species are the maximum gridded output concentrations.

Figure 4.4 shows a plot of the maximum gridded total (nitrosamine + nitramine) concentrations for each of the sensitivity tests.

Figure 4.5 shows the variation of the gaseous concentrations of nitrosamine and nitramine with increasing plume temperature. The plume temperature results shown here are those representing the saturated plumes; i.e. plumes with the maximum water content corresponding to each emission temperature.

Figure 4.6 shows a plot of the maximum gridded output amine concentrations. These represent the concentration of the amines partitioned into the gaseous and aqueous phases, and the total amine concentrations (the sum of the gaseous and aqueous phase amine concentrations).

Contour plots for the sensitivity test results are given in Appendix A.

Table 4.12: Annual average output concentrations for each species, for the aqueous partitioning sensitivity tests

Test		Concentration ($\mu g/m^3$)			Concentration (ng/m^3)		
		Amine (aqueous phase)	Amine (gas phase)	Amine (total)	Nitramine (gas phase)	Nitrosamine (gas phase)	Sum nitramine and nitrosamine
Base case	30 °C saturated	9.18×10^{-7}	0.114	0.114	0.556	2.17	2.59
A1	40 °C saturated	9.75×10^{-6}	0.0859	0.0859	0.424	1.44	1.72
A2	40 °C	2.89×10^{-7}	0.0943	0.0943	0.454	1.59	1.90
A3	50 °C saturated	3.92×10^{-5}	0.0624	0.0624	0.352	0.970	1.17
A4	50 °C	2.34×10^{-7}	0.0805	0.0805	0.399	1.24	1.49
A5	PZ H	1.49×10^{-4}	0.114	0.114	0.556	2.17	2.59
A6	PZ H, 40 °C saturated	1.47×10^{-3}	0.0859	0.0859	0.424	1.43	1.71
A7	PZ H, 40 °C	4.74×10^{-5}	0.0943	0.0943	0.454	1.59	1.90
A8	PZ H, 50 °C saturated	4.94×10^{-3}	0.0624	0.0625	0.352	0.948	1.15
A9	PZ H, 50 °C	3.77×10^{-5}	0.0805	0.0805	0.399	1.24	1.49
A10	MEA H	3.41×10^{-3}	0.113	0.114	0.553	2.15	2.57
A11	MEA H, 40 °C saturated	1.48×10^{-2}	0.0849	0.0860	0.419	1.38	1.66
A12	MEA H, 40 °C	1.41×10^{-3}	0.0934	0.0943	0.449	1.59	1.90

Test		Concentration (µg/m³)			Concentration (ng/m³)		
		Amine (aqueous phase)	Amine (gas phase)	Amine (total)	Nitramine (gas phase)	Nitrosamine (gas phase)	Sum nitramine and nitrosamine
A13	MEA H, 50 °C	2.05×10^{-2}	0.0614	0.0626	0.345	0.875	1.07
A14	MEA H, 50 °C saturated	9.63×10^{-4}	0.0798	0.0805	0.345	1.24	1.49
A15	PZ	1.48×10^{-4}	0.102	0.102	2.27	0.36	2.60
A16	MEA	3.41×10^{-3}	0.112	0.113	0.0183	0.00638	0.0240
A17	No reactions, MEA H	3.41×10^{-3}	0.118	0.119	0.00	0.00	0.00
A18	Droplets base case	9.07×10^{-7}	0.114	0.114	0.555	2.17	2.58
A19	Droplets 1	9.09×10^{-7}	0.114	0.114	0.555	2.17	2.58
A20	Droplets 2	9.16×10^{-7}	0.114	0.114	0.555	2.17	2.58
A21	Droplets 3	9.45×10^{-7}	0.114	0.114	0.555	2.17	2.58
A22	Droplets 4	9.10×10^{-7}	0.114	0.114	0.555	2.17	2.58
A23	Droplets 5	9.07×10^{-7}	0.114	0.114	0.555	2.17	2.58
A24	Droplets 6	9.08×10^{-7}	0.114	0.114	0.555	2.17	2.58
A25	Droplets 7	9.07×10^{-7}	0.114	0.114	0.555	2.17	2.58
A26	No buildings	1.54×10^{-7}	0.0399	0.0399	0.487	1.55	1.94

Figure 4.4: Maximum annual average gaseous (nitrosamine + nitramine) concentrations over the output grid for each sensitivity test
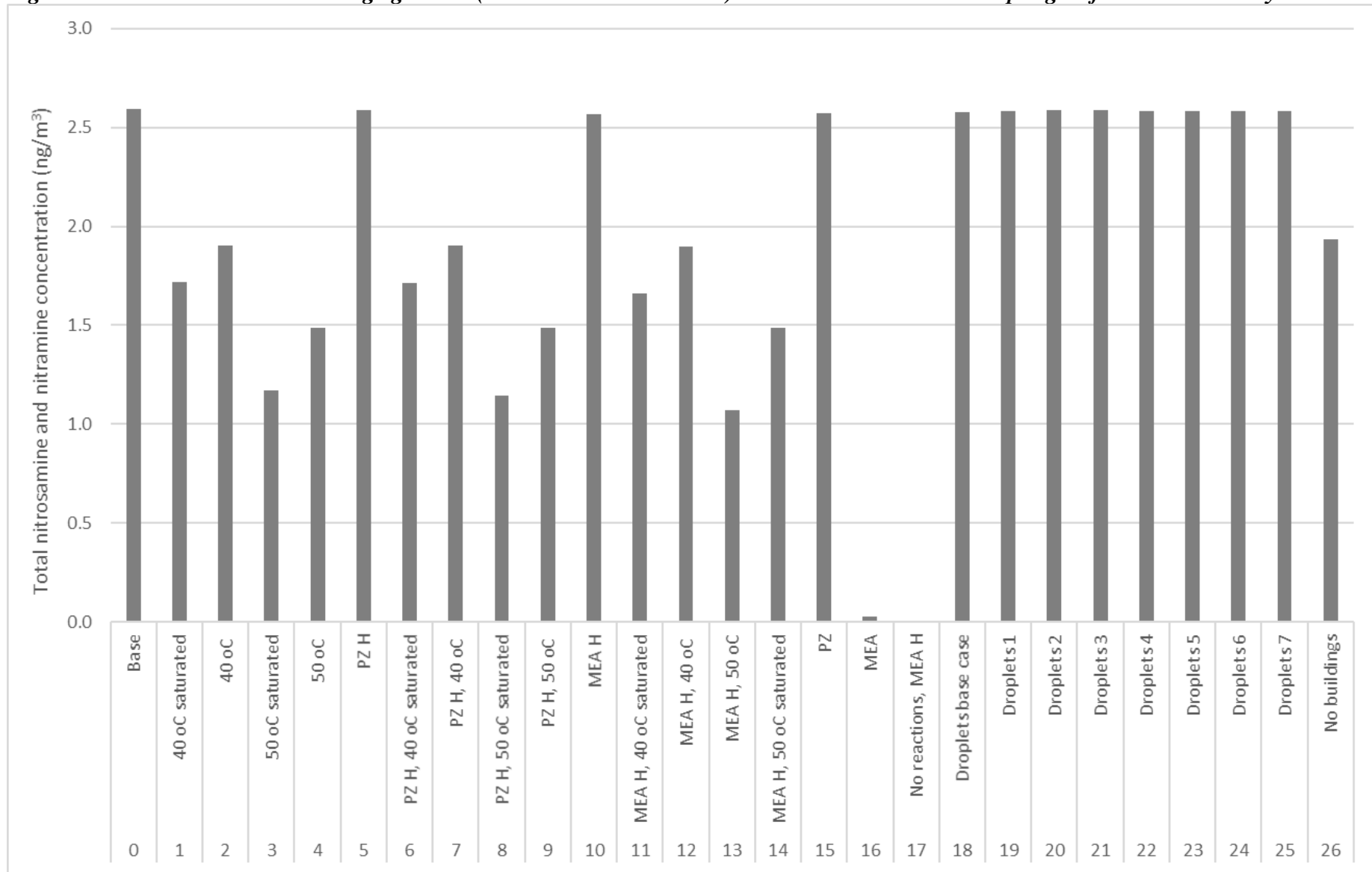
Figure 4.5: Summary plot of the maximum amine concentrations. Here 'g' refers to amines in the gaseous phase, 'Aq' to amines in the aqueous phase, and 'Tot' refers to the total (aqueous phase + gaseous phase).
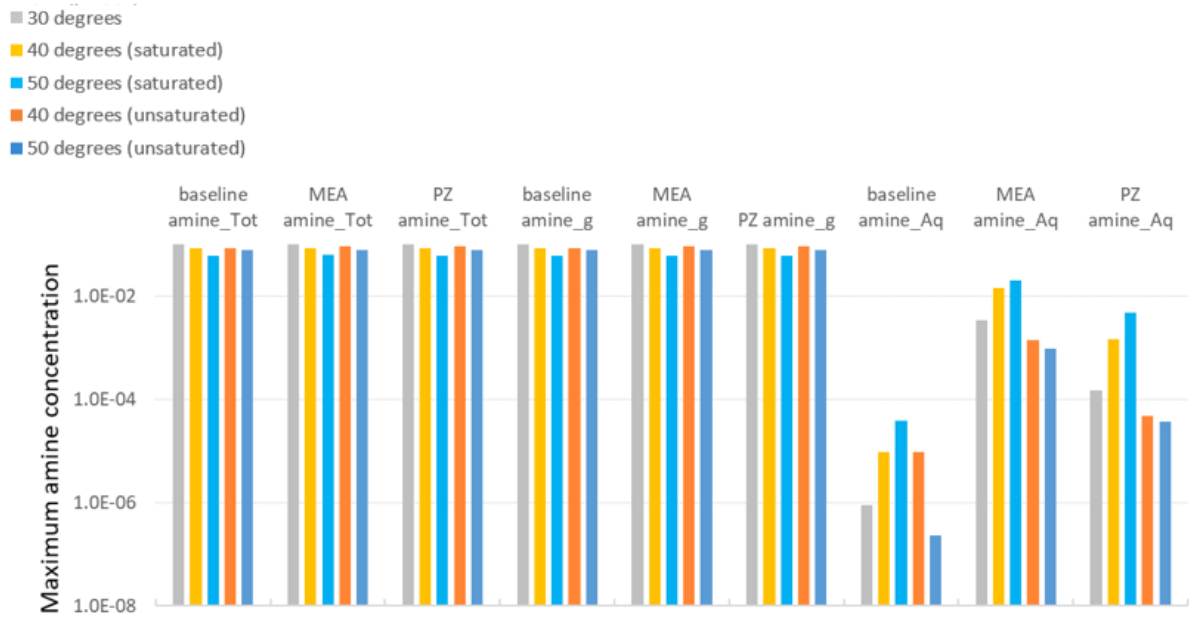
Figure 4.6: Variation of the maximum gaseous nitrosamine and nitramine concentrations with plume temperature (saturated plumes)
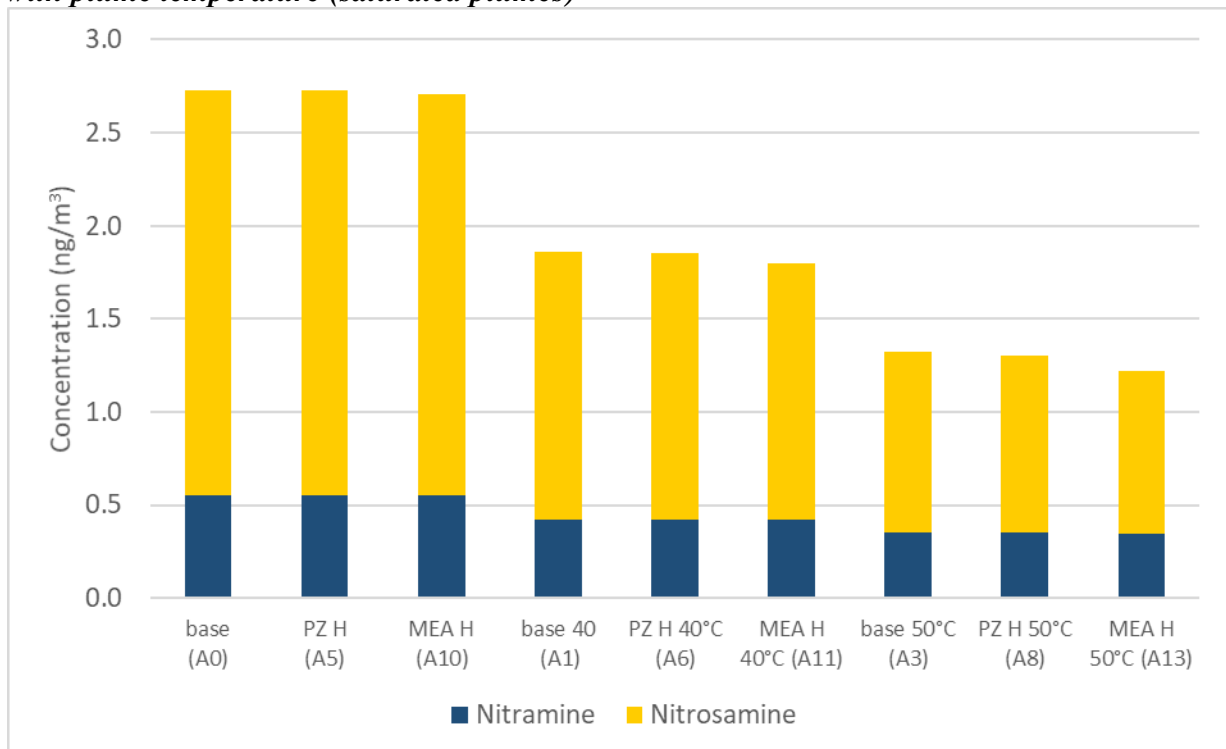
4.2.4 Discussion

Figure 4.4 illustrates the results of the aqueous sensitivity tests, specifically the effect on the total reaction products (the sum of nitrosamine and nitramine) in the gaseous phase. This shows that there is little difference in those results for which the Henry's Law solubility constant is the only parameter varied (tests 5, 10 and 15), even though this variation in solubility among amines is substantial.

Figure 4.5 illustrates the direct effect of the solubility of the amines on the partitioning of the amine to the aqueous phase. The solubility of the amines increases in the order *DMA < PZ < MEA* (with Henry's Law solubility constants of 5.8 x 10^1, 1.0 x 10^4 and 5.8 x 10^1 mol/L/atm, respectively). This is clearly reflected in the partitioning of the amines to the aqueous phase.

The two plots (Figure 4.4 and 4.5) together show that, while there is evidence that some partitioning to the aqueous phase does occur, this is not translated to a large impact on the reaction products for those model runs (tests 5, 10 and 15). The model runs that test the effect of temperature and the associated initial plume water content shed some light on the likely reason for this.

Figure 4.6 compares the results of those tests that vary the emission temperature. There is a clear reduction in the concentration of nitrosamines and nitramines with the increasing plume water content that is associated with increasing plume temperature (i.e. saturated plumes at different temperatures). This indicates increased partitioning of the amines to the aqueous phase as the plume water content increases, leading to reduced gas phase reactions of the amines. It suggests that the dispersing plume in the base case run (and other runs with the same initial water content) does not contain enough water for the partitioning to have a significant effect on the maximum nitrosamine and nitramine concentrations.

The sensitivity tests relating to the droplet parameters show very little variation in results; this demonstrates that enhanced nucleation has little effect if the amine is of low solubility and the plume has a low water content (the properties of the base case run on which these tests are based). This nucleation could be more important if emission temperatures are higher (and hence there is potential for more water in the plume).

Summary

Based on these sensitivity tests, the following are the key conditions that result in the lowest sum of concentrations of nitrosamines and nitramines:

- Higher emission temperature (at a constant water content)
- Saturated conditions

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5 Recommendations based on project findings

5.1 Kinetic parameters

The data collation and comparisons carried out in this project have identified significant gaps and areas of uncertainty in the available kinetic parameter values. It is therefore recommended that further focused research on the amine scheme rate constants is carried out, with an emphasis on the following areas:

- Research into the identification of the likely types of amines and degradation products that will be released from full-scale carbon capture facilities. This should be informed by communication with carbon capture plant operators, solvent providers, researchers and other key organisations. This should include consideration of the amines that can form within the carbon capture process and subsequent treatment steps, prior to release to ambient air.

    ♦ Recommendation 1: Identify the likely amines/degradation amine products emitted

- The development of methods/frameworks to identify and select representative proxy amine species for modelling emissions and transformations. These can be used to give a reasonable conservative prediction of likely air quality impacts, to offset uncertainty and complexity, and inform sound risk-based decisions. These should be based on robust justifications, on the best available scientific knowledge, and on proxy species that are representative of behaviour source-pathway-receptor and environmental fate.

    ♦ Recommendation 2: Identify potential proxy species and sound methods for proxies for air emissions risk assessments considering source-pathway-receptor and environmental fate.

- Further measurements and/or calculations of key atmospheric reaction rate constant data, specifically:

    o The research should be targeted towards the most relevant types of amine, as per the preceding point. It should also be targeted towards species and parameters where the gaps and uncertainty, and hence the need for additional data, is the greatest.

    o It should include a range of different types of relevant amines, with a range of structures and functional groups, such as:
        - Sterically-hindered amines
        - Primary, secondary and tertiary amines
        - Amines with alcohol, carboxylic acid, and other functional groups
        - Diamines

    o Sensitivity tests have shown that the k_1 and k_{1a} values are the most important values to consider; these are the rate constants that have the greatest impact on the concentrations of nitrosamines and nitramines produced in the atmosphere.

o The research should also include measurements and/or calculations of the k_2 to k_4 values, relating to the reaction of the amino radical. There is a lack of robust data for these parameters, for all amine solvent species.

♦ Recommendation 3: More research to quantify relevant kinetic parameters

- The creation and ongoing development of a central database of rate constant values. This should be hosted and managed to facilitate the addition of new data, with appropriate quality assurance and control measures put in place.

♦ Recommendation 4: Creation of a central database of rate constant values for modelling

- Although this work has provided data collation and interpretation of k values, and the significance for amine chemistry modelling, a detailed analysis of the accuracy and uncertainty of the rate constant values and recommendations for their use is beyond the scope of the current project. A high-level review of the different parameters is required to enable recommendations of which values are more reliable, and to further understand the uncertainty range in the values. This should be carried out by specialists in the use of both computational and experimental methods of atmospheric kinetics, ideally those with experience in reactions of hydroxyl radicals with organic compounds.

♦ Recommendation 5: Consolidation of kinetic parameter data and uncertainty

- Structure activity relationships (SARs) are valuable tools used to calculate rate constants for a wide range of different species important in atmospheric chemistry. The research in this project suggests that they show potential to be useful tools for calculating rate constants specific to amine chemistry, but that more work is needed to extend existing SARs to amine reactions. The data from existing and future measurements and/or calculations for kinetic parameters should be used to improve the accuracy and reliability of existing SAR methods, and expand their applicability to a wide range of amine species with a range of functional groups and structures. The k_1 and k_{1a} values are the most important values to consider, but the research should also include the k_2 to k_4 values, relating to the reaction of the amino radical.

♦ Recommendation 6: Consolidation of SAR methods as tools to estimate amine kinetic parameters

5.2 Ambient measurements and model validation

As previously noted, it is not possible to directly validate modelled nitrosamine and nitramine concentrations, as routine gaseous measurement techniques are not yet widely available with the very low detection limits required to measure the very low ambient concentrations. As a reminder of the concentrations in question, the UK Environmental Assessment Level (EAL) for *NDMA* is 0.2 ng/m^3, or 0.0002 µg/m^3.

A review by the Scottish Environmental Protection Agency (SEPA, 2015) gives a thorough review of ambient measurements of nitrosamines and nitramines, and Zhang (2016) also reviews sampling and measurement techniques for *NDMA* in air.

Zhang (2016) reports a measurement methodology with a detection limit for *NDMA* in ambient air as low as 0.003 ng/m^3, in work carried out at Arizona State University. The demonstration of this methodology appears to be a considerable step forwards in the development of routine atmospheric measurements of nitrosamines, with much lower detection limits and a robust sampling method suitable for practical deployment. Although the research group is not currently actively working on developing or applying this methodology, it is understood that the group is in a position to resume this research if there is sufficient interest (Herckes, 2023).

It is recommended that further research is carried out to develop such measurement methods for nitrosamines and nitramines in ambient air. It is also recommended that developments in other fields of research are closely followed; one example is the analysis of nitrosamine impurities in pharmaceutical products, in which there has been significant development in recent years (e.g. Wichitnithad et al, 2023).

5.3   Reaction with chlorine radicals

As discussed in Section 3.2.6, there has been recent renewed interest in the reaction of amines with the chlorine radical (Cl), due to research findings regarding relatively high rate constants and ambient Cl concentrations. Further research is recommended in the following areas:

- Investigation of the potential impact on modelled nitrosamine and nitramine concentrations, based on the best currently available knowledge of amine and chlorine reaction rates and ambient chlorine concentrations.

- Further measurements and/or calculations of the rate constants, for more amine species.

- Research on typical atmospheric Cl radical concentrations in different areas (urban, rural, industrial, marine), and other spatial variation considerations.

- Research on the time variation of Cl radicals in the atmosphere, including diurnal profiles and seasonal changes, and the key drivers of these temporal patterns.

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Appendix A: Contour plots for sensitivity tests

A.1. Standard (gaseous phase) amine chemistry

Nitramine (ng/m^3)

■	0.01
■	0.02
■	0.03
■	0.04
■	0.05
■	0.06
■	0.07
■	0.08
■	0.09
■	0.1
■	0.2
■	0.3
■	0.4
■	0.5
■	0.6
■	0.7
■	0.8
■	0.9
■	1
■	2
■	3
■	4
■	5
■	6
■	7
■	8
■	9
■	10
■	>10

Nitrosamine (ng/m^3)

■	0.01
■	0.02
■	0.03
■	0.04
■	0.05
■	0.06
■	0.07
■	0.08
■	0.09
■	0.1
■	0.2
■	0.3
■	0.4
■	0.5
■	0.6
■	0.7
■	0.8
■	0.9
■	1
■	2
■	3
■	4
■	5
■	6
■	7
■	8
■	9
■	10
■	>10

Test	Nitramine	Nitrosamine
0		
1		
2		

9		
10		
11		

12		
13		
14		

18		
19		
20		

| 27 | | |
| 28 | | |
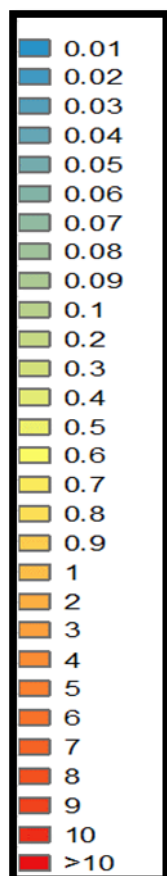
A.2 Aqueous partitioning

Amine Aqueous (µg/m³)	Amine Aqueous (µg/m³) (droplet resolution)	Amine gaseous (µg/m³)	Amine total (µg/m³)
<1E-10	1E-11	< 1E-5	< 1E-5
1E-09	1E-10	1E-4	1E-4
1E-08	1E-9	0.0010	0.0010
2E-08	1E-8	0.0025	0.0025
4E-08	2E-8	0.0050	0.0050
5E-08	3E-8	0.0075	0.0075
6E-08	4E-8	0.01	0.01
8E-08	5E-8	0.02	0.02
1E-07	6E-8	0.025	0.025
2E-07	7E-8	0.03	0.03
4E-07	8E-8	0.04	0.04
5E-07	9E-8	0.05	0.05
6E-07	1E-7	0.06	0.06
8E-07	1.05E-7	0.07	0.07
1E-06	1.1E-7	0.075	0.075
2E-06	1.5E-7	0.08	0.08
4E-06	2E-7	0.09	0.09
5E-06	2.5E-7	0.10	0.10
6E-06	3E-7	0.11	0.11
8E-08	4E-7	0.12	0.12
1E-05	5E-7		
2E-05	6E-7		
4E-05	7E-7		
5E-05	8E-7		
6E-05	9E-7		
8E-05	1E-6		
1E-04	1E-5		
2E-04			
4E-04			
5E-04			
6E-04			
8E-04			
1E-03			
2E-03			

Test	Amine (aqueous phase)	Amine (gaseous phase)	Amine (total)
A0			

| A7 | | |
| A8 | | |

A11

A12

A15

A16

A17		
Amine aqueous phase	Amine aqueous phase (increased resolution)	**Amine (total)*** * contours for total (below) and gaseous (not shown) amines are indistinguishable from the basecase.

A19

A20

A21

A22

A23			
A24			
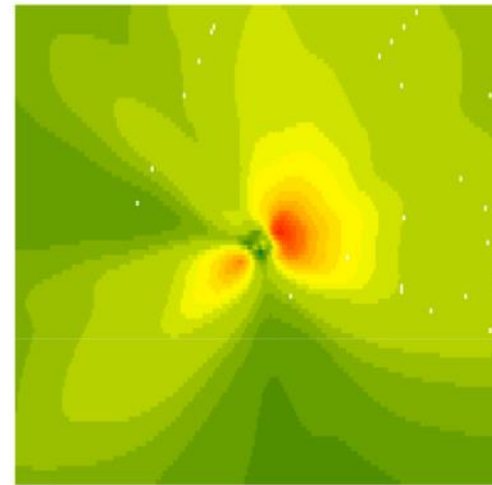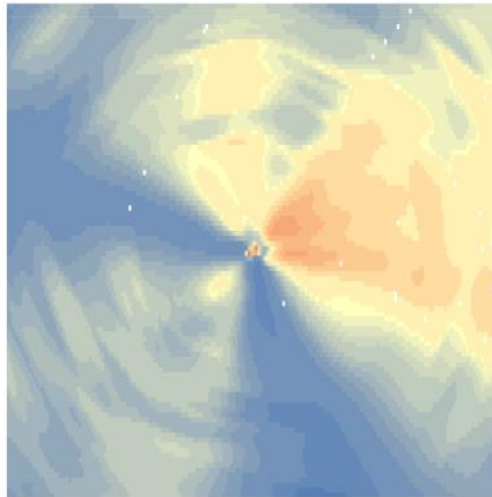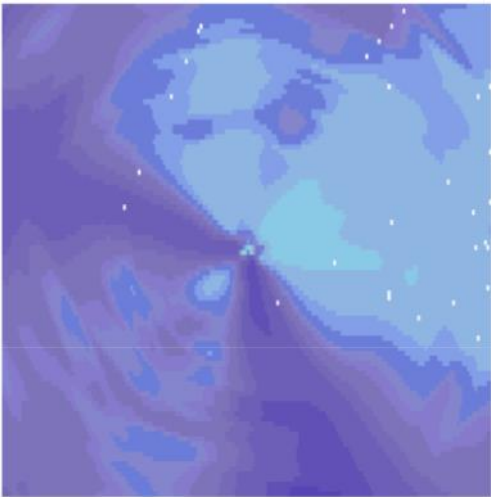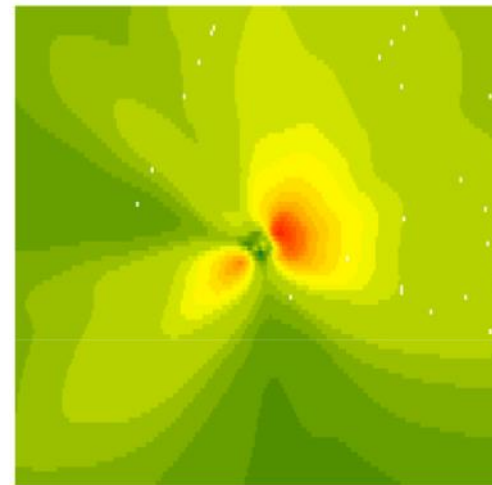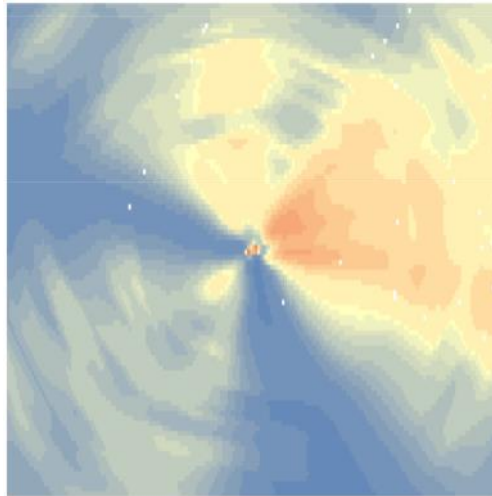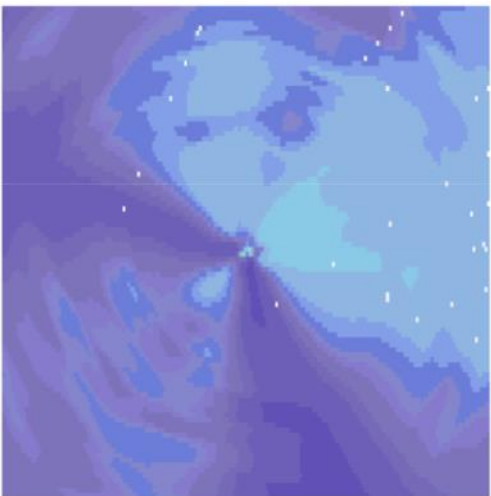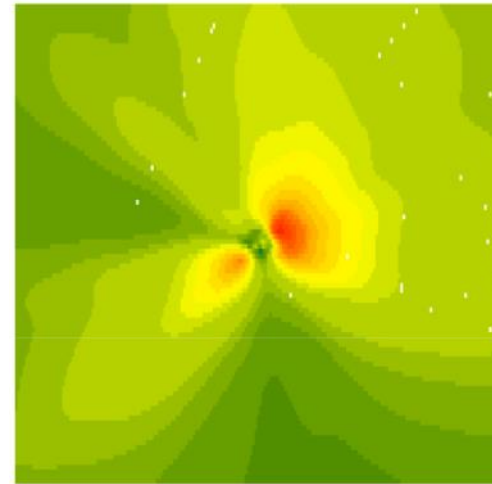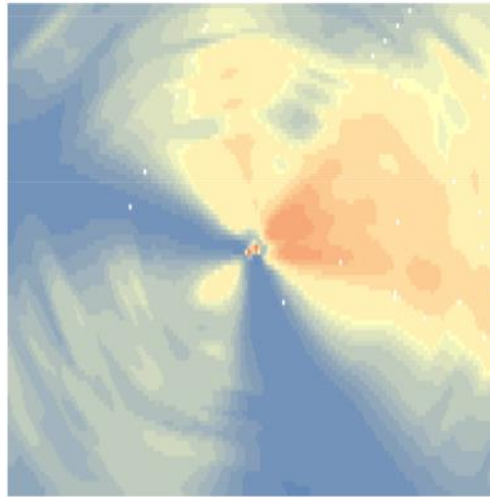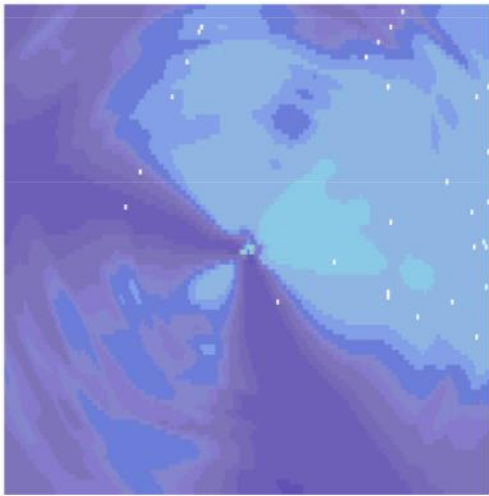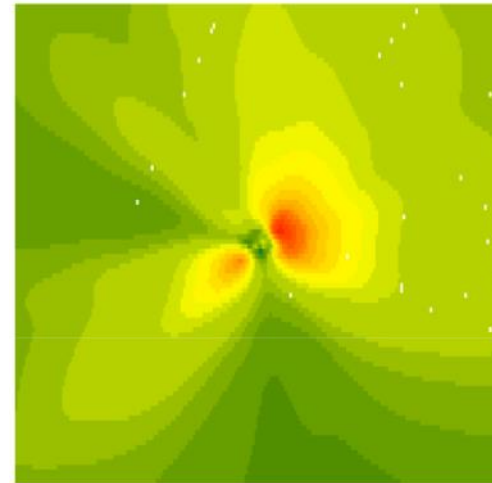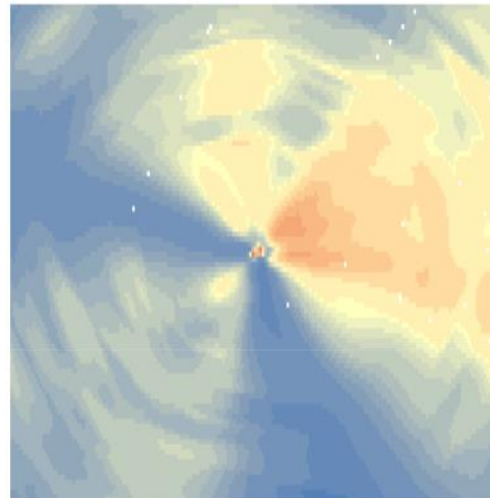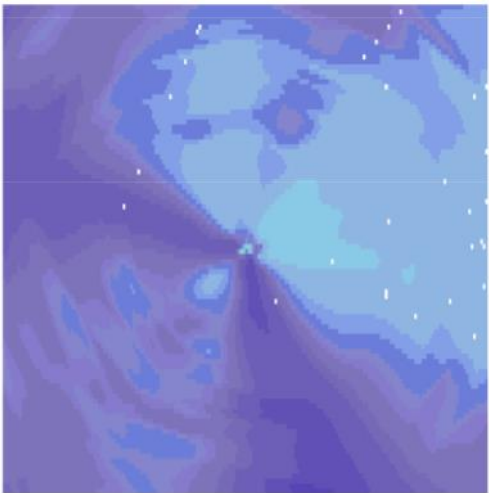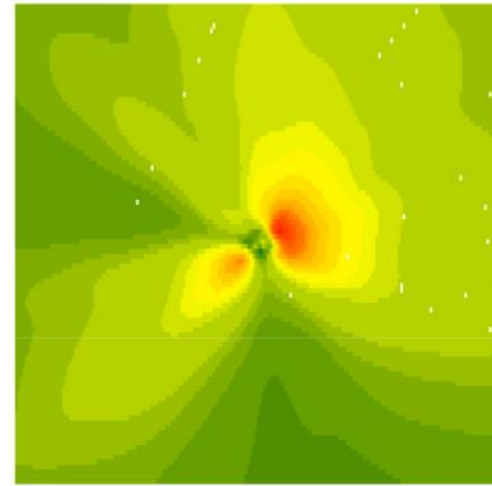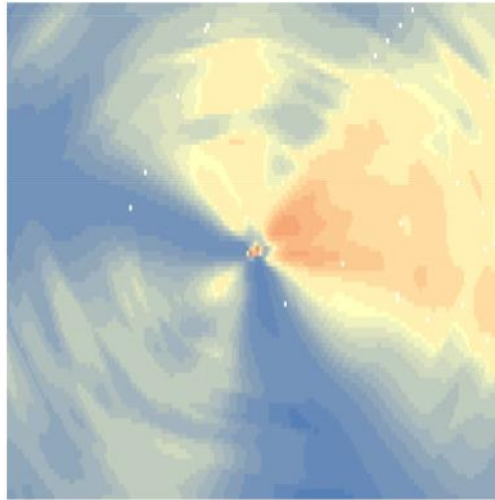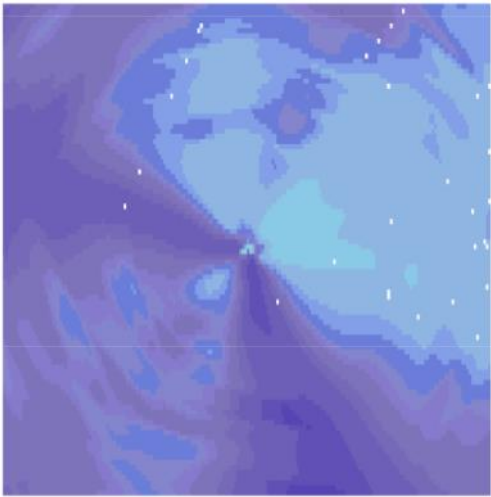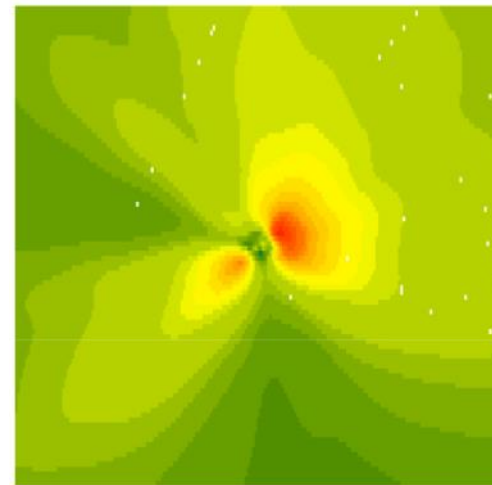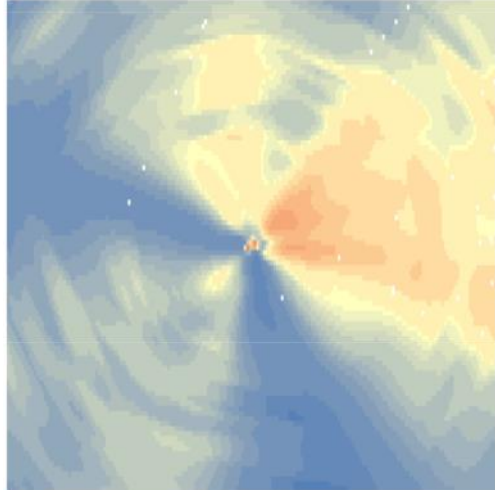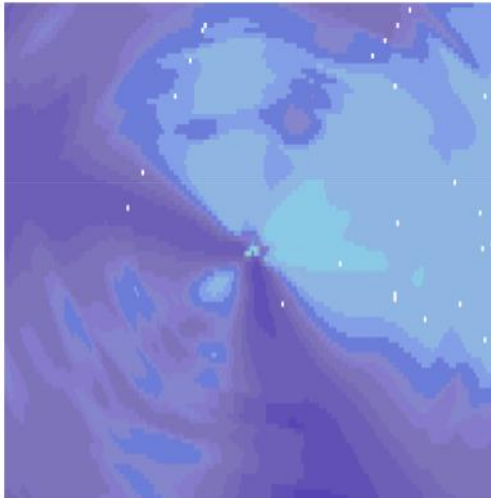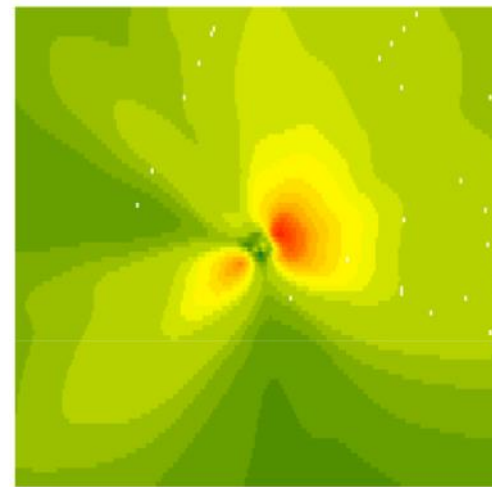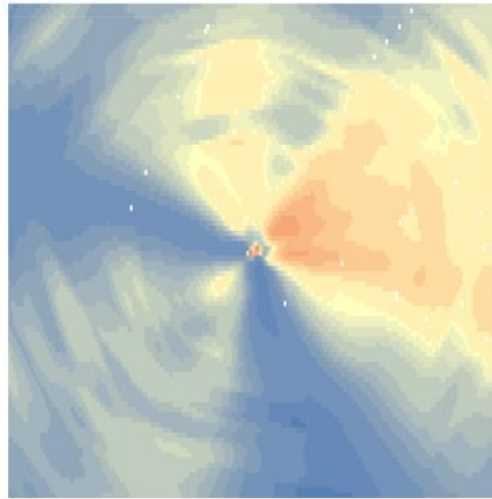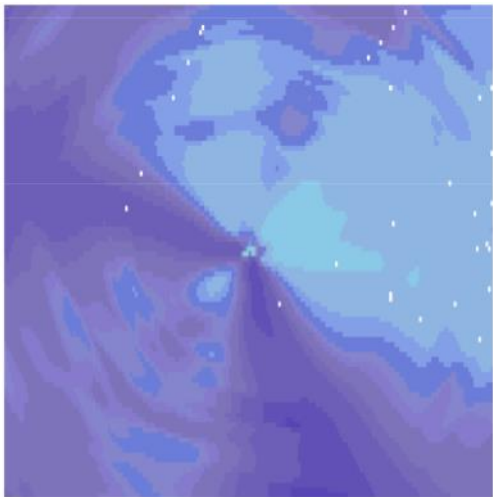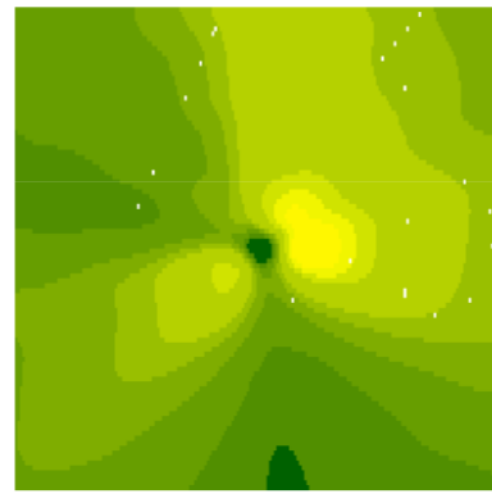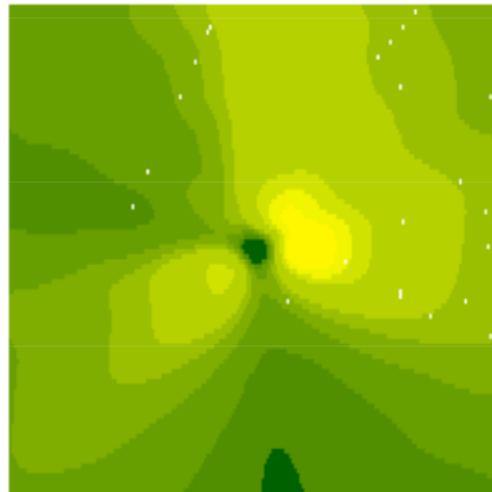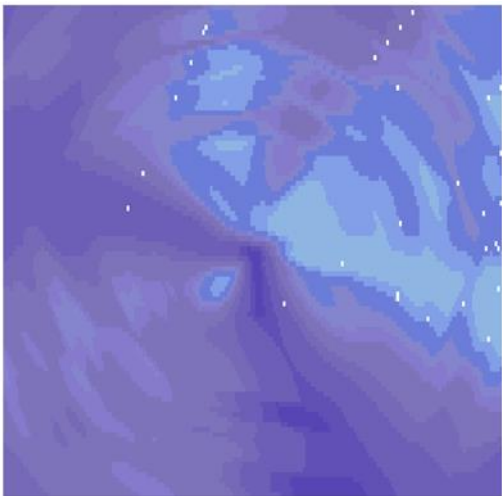
Nitramine (ng/m³)   **Nitrosamine (ng/m³)**   **Sum (ng/m³)**

CERC

Improving post-combustion carbon capture air quality risk assessment techniques

Test	Nitramine	Nitrosamine	Sum
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A1			
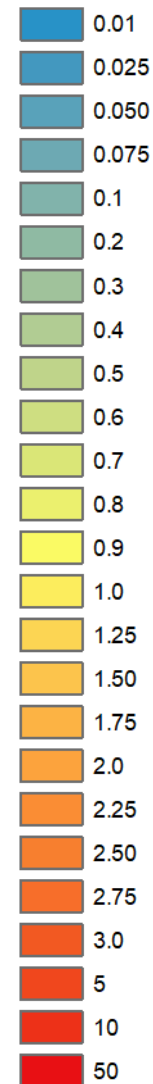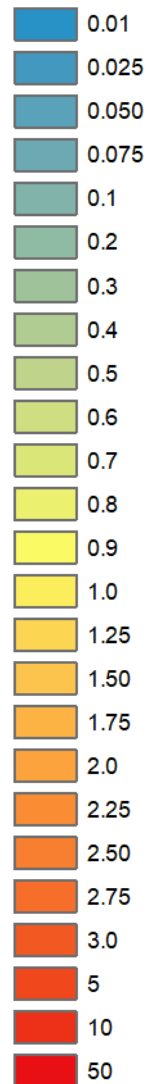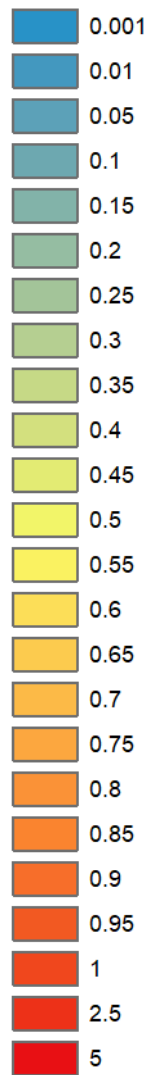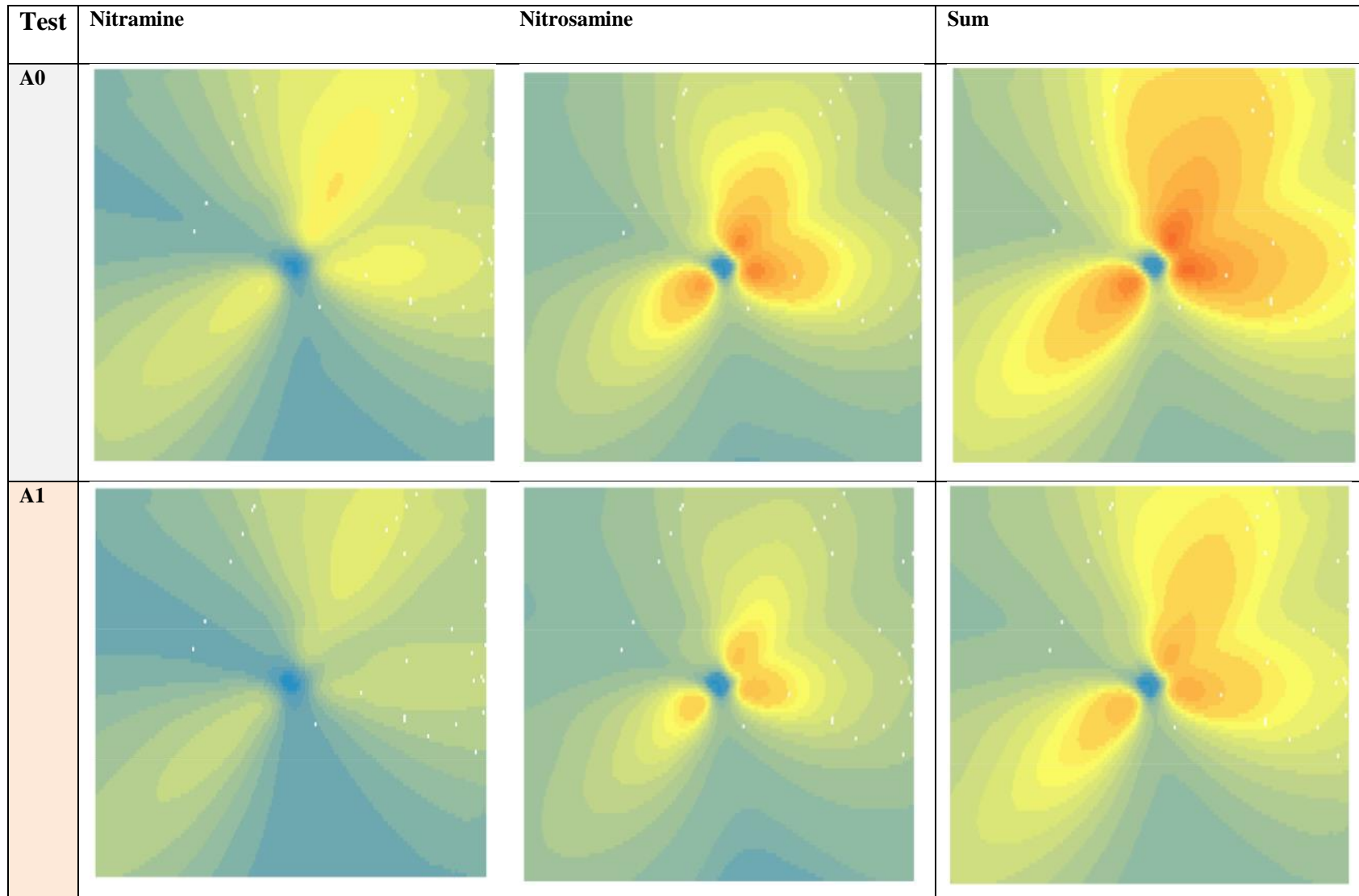
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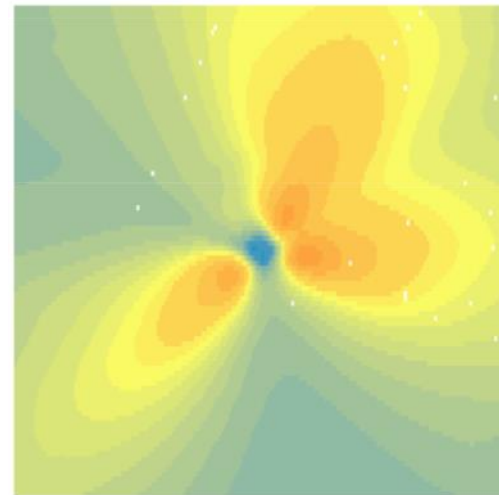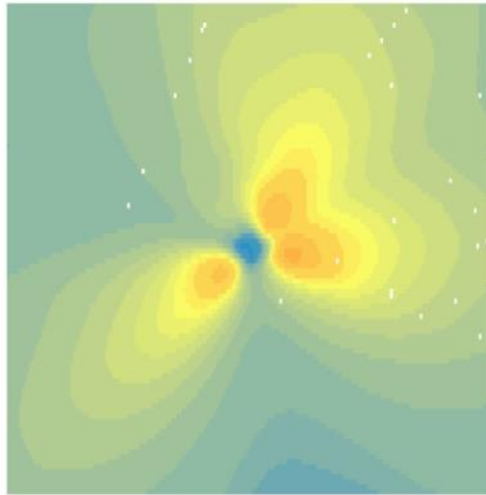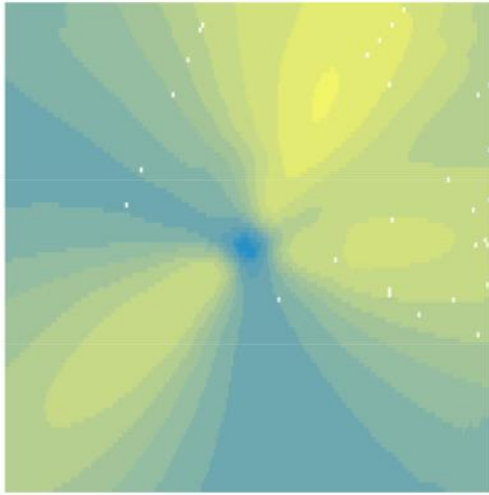
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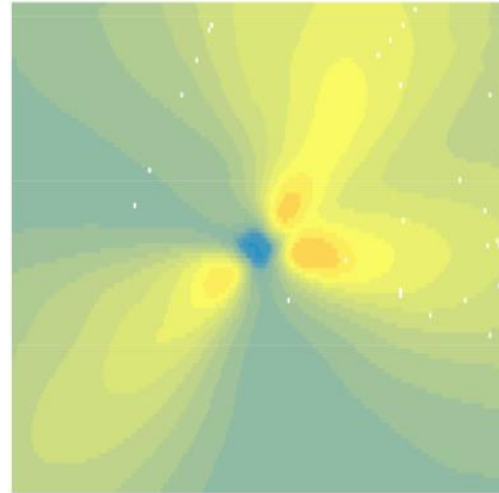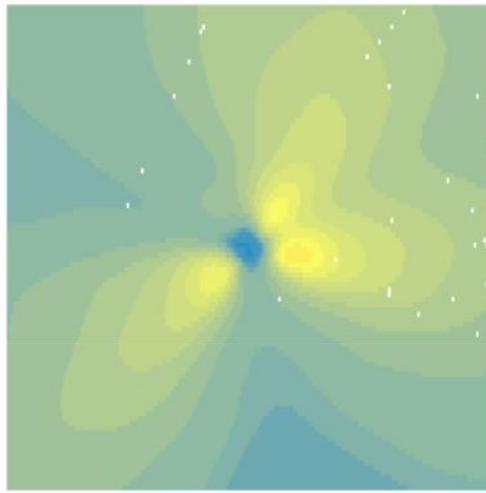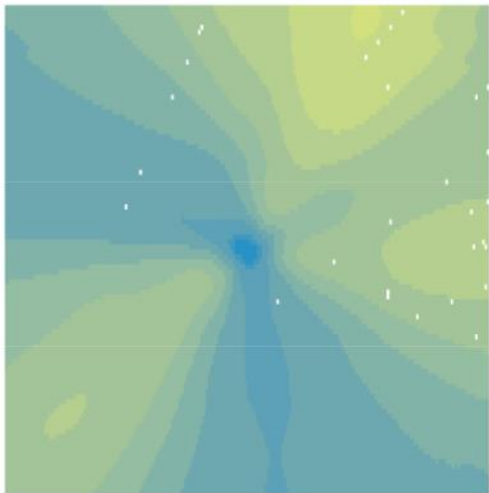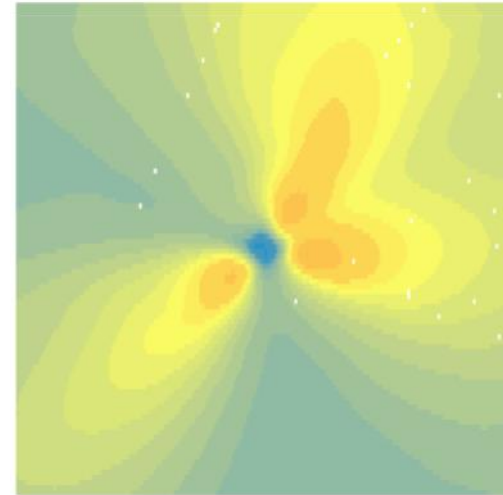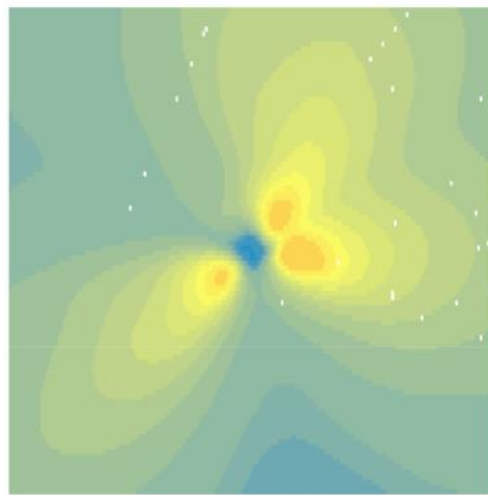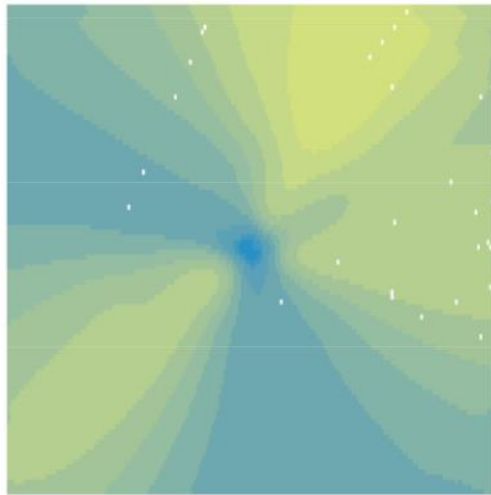
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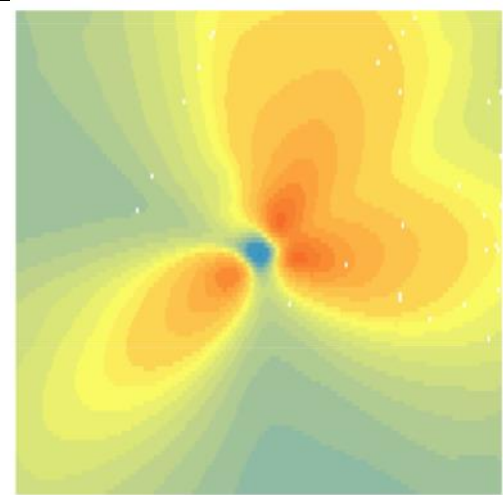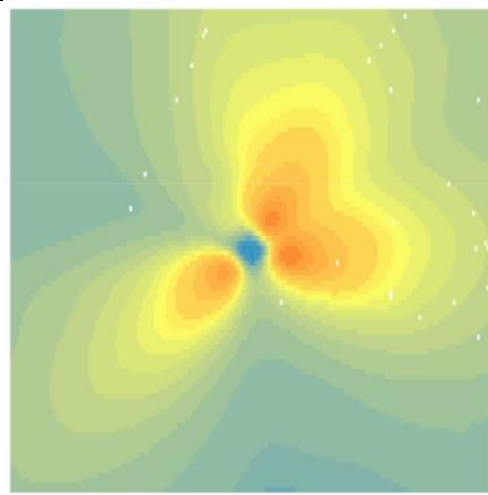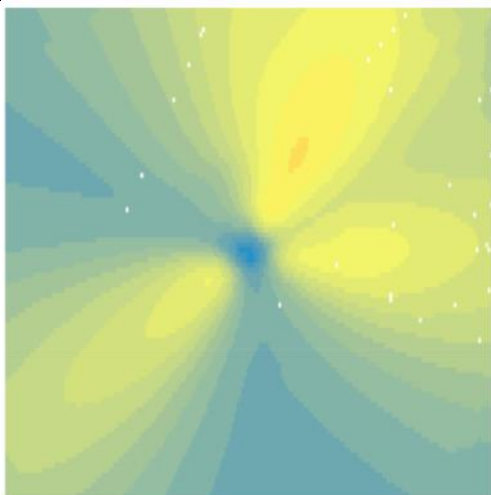
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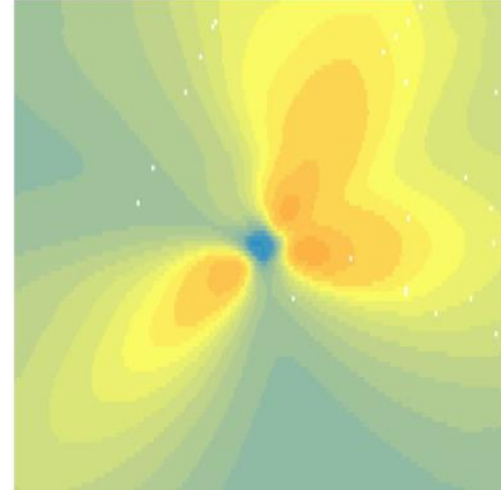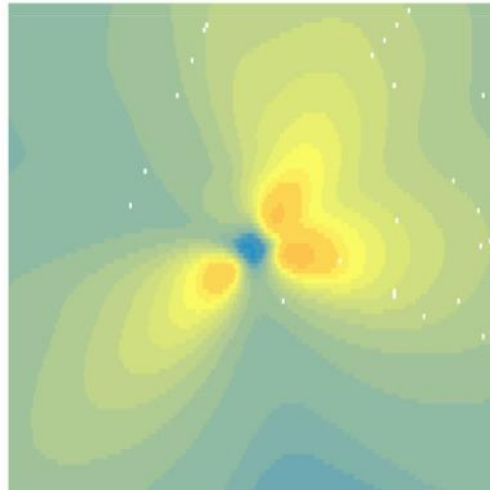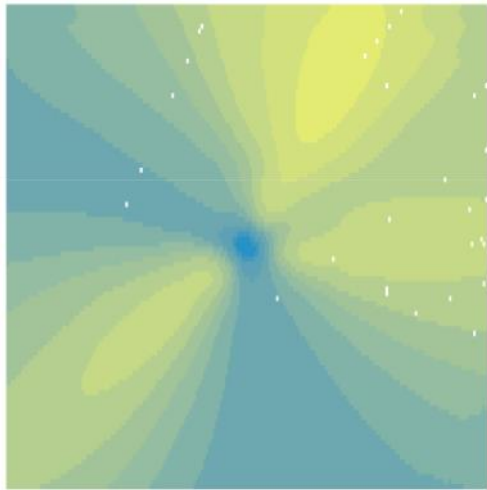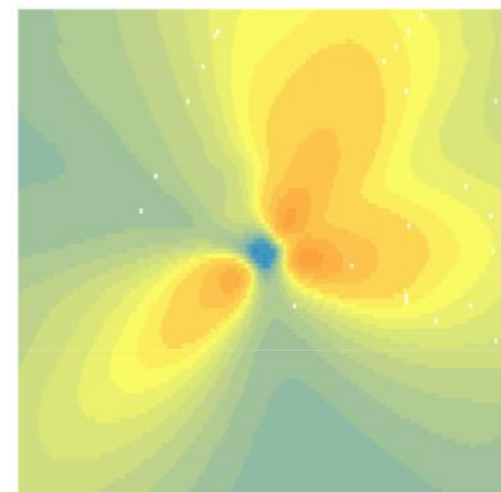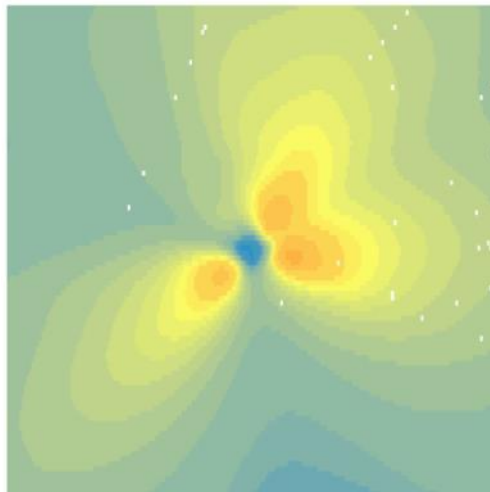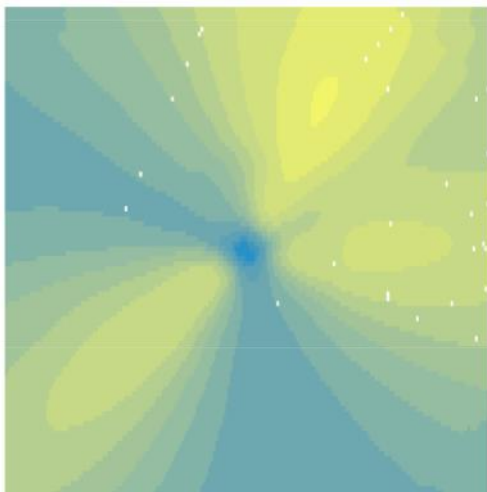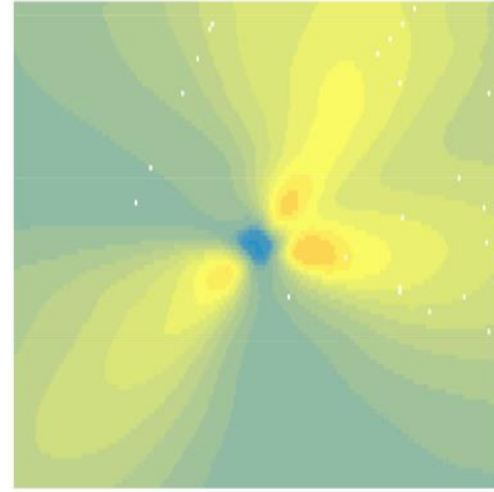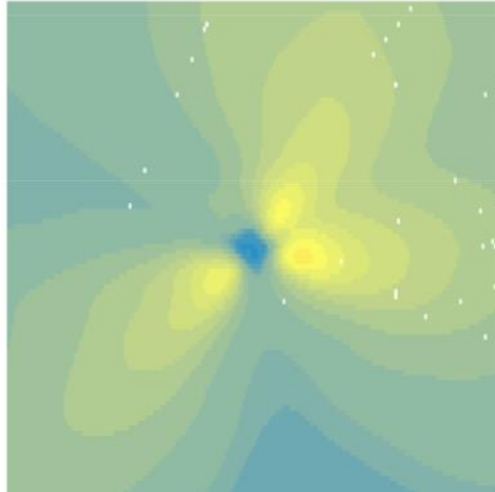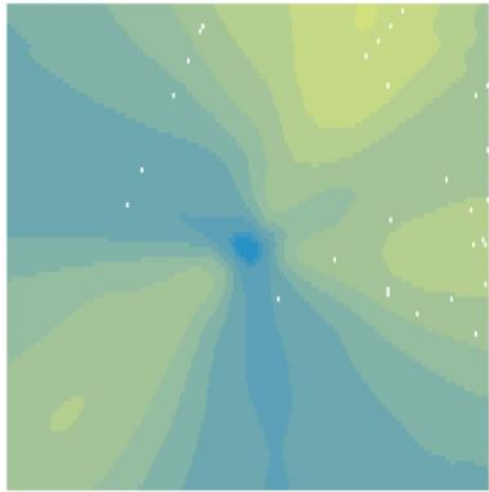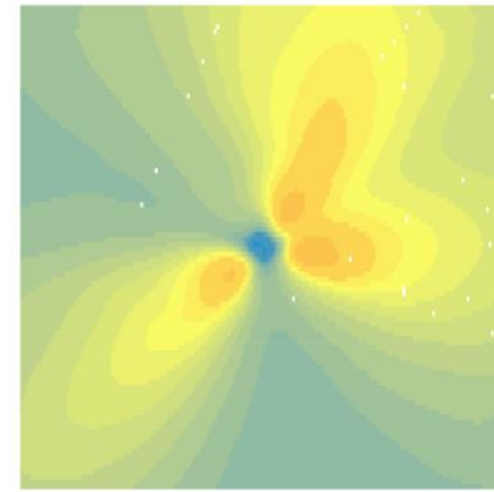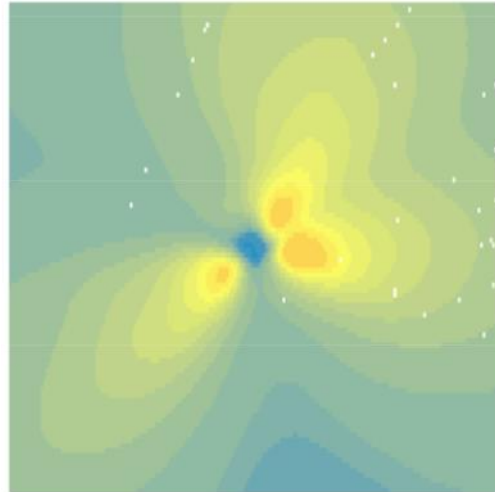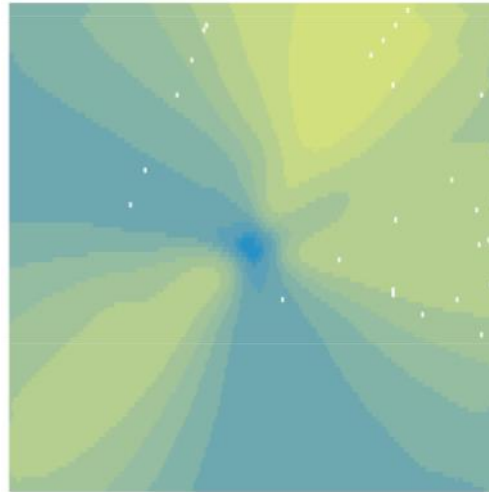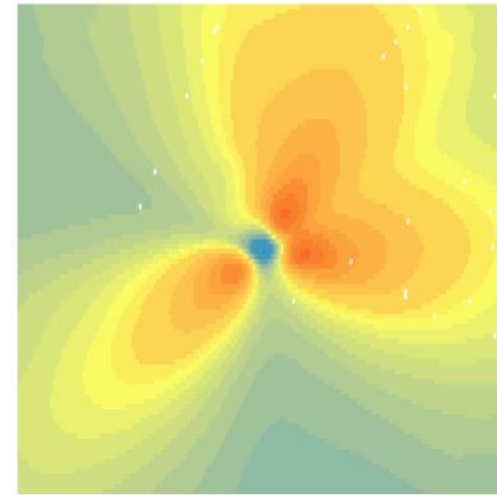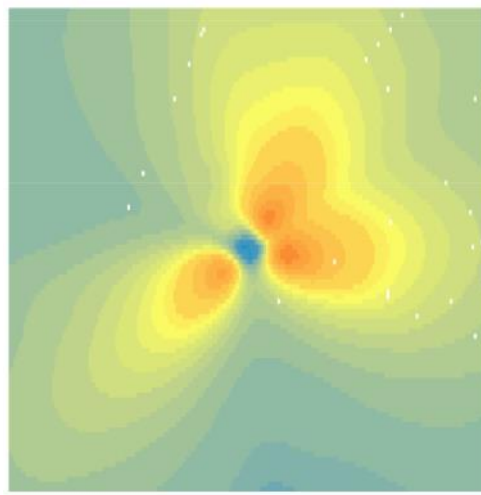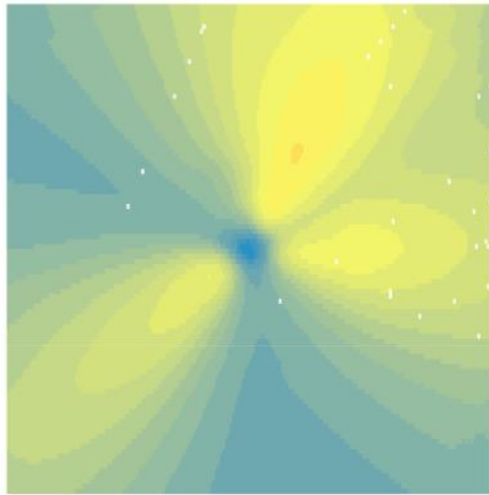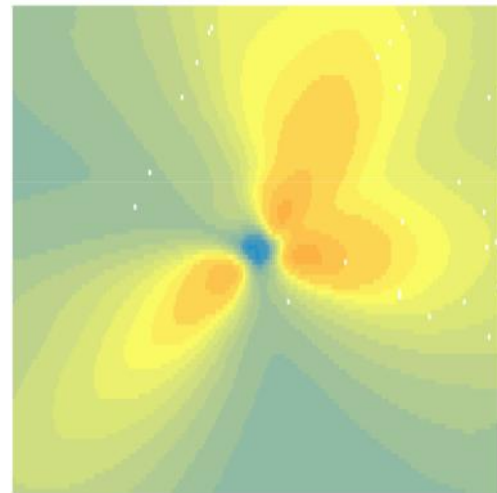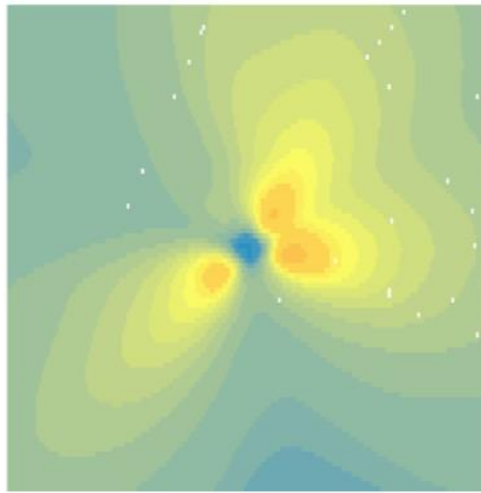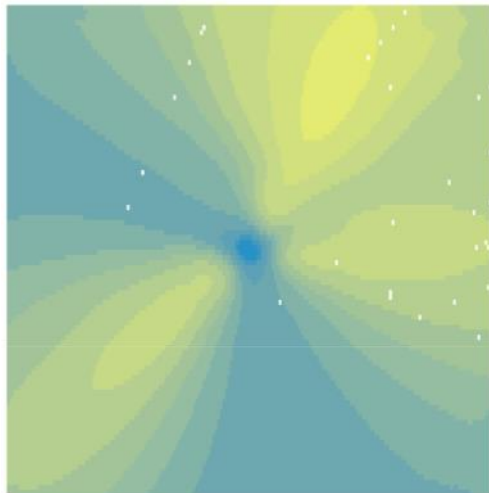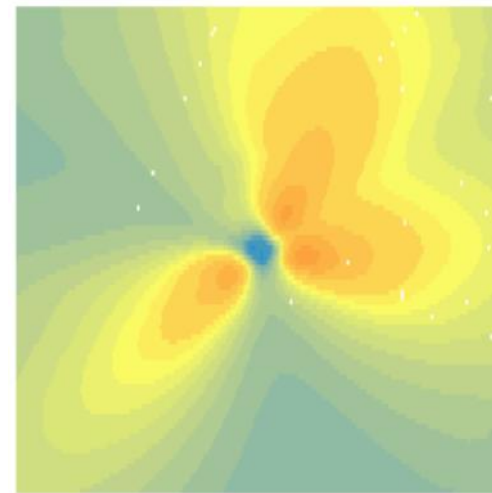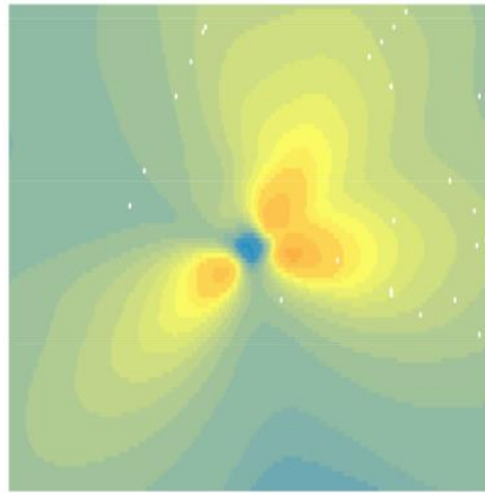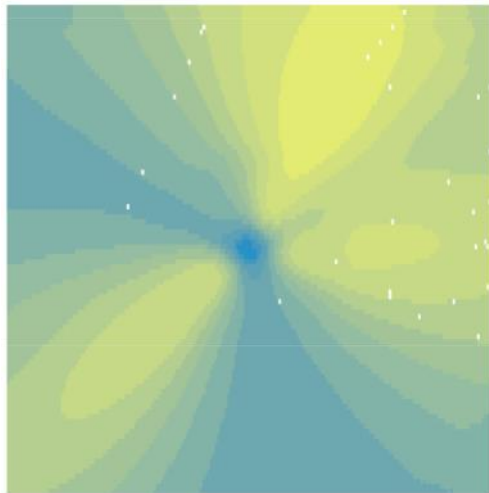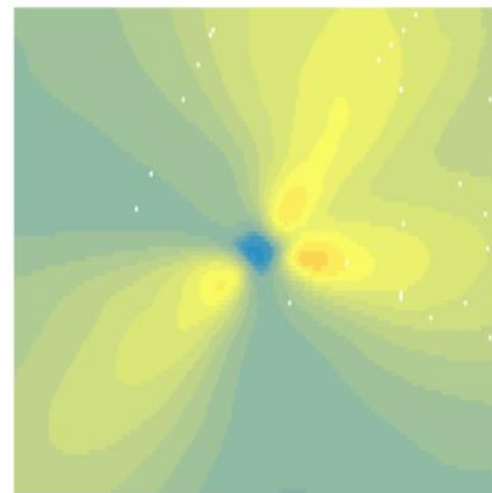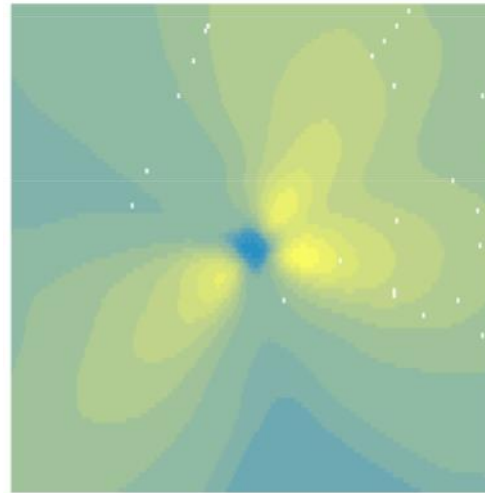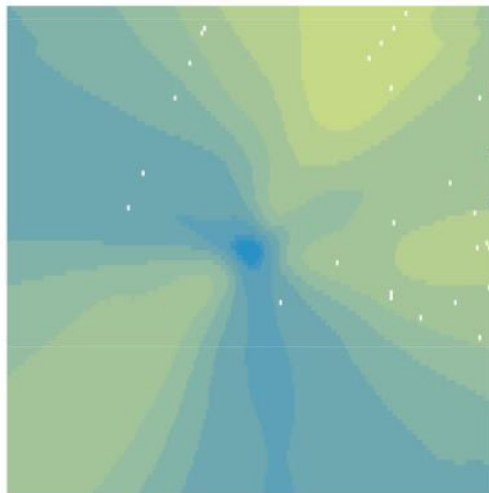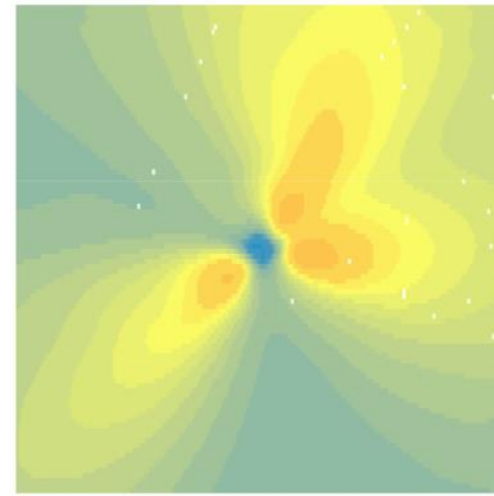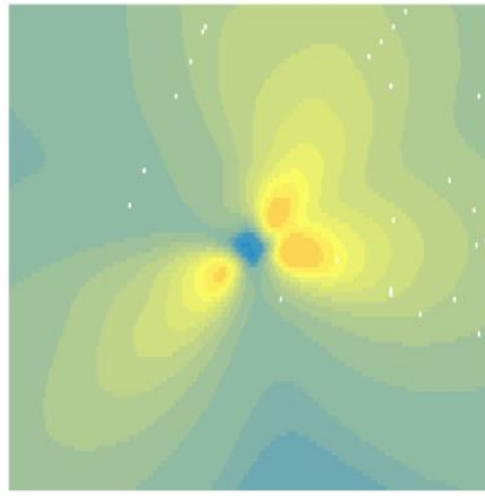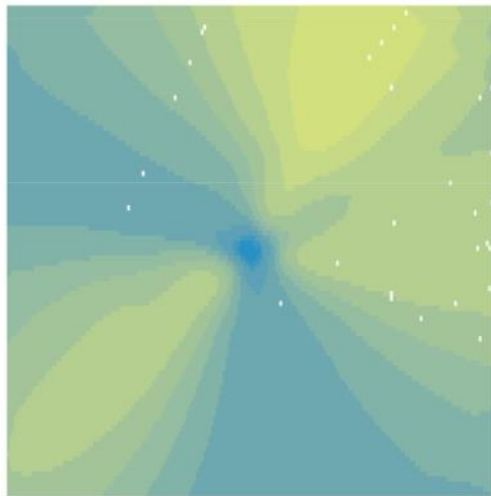
A14			
A15			
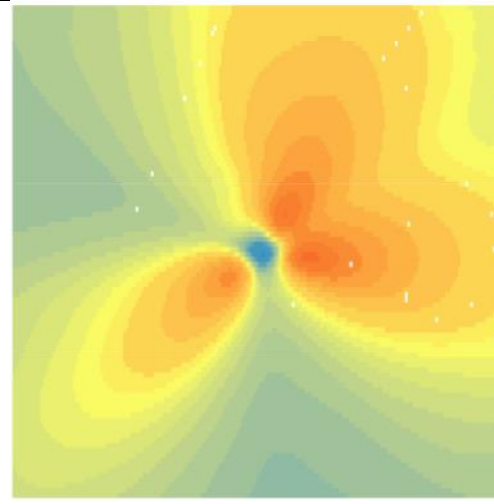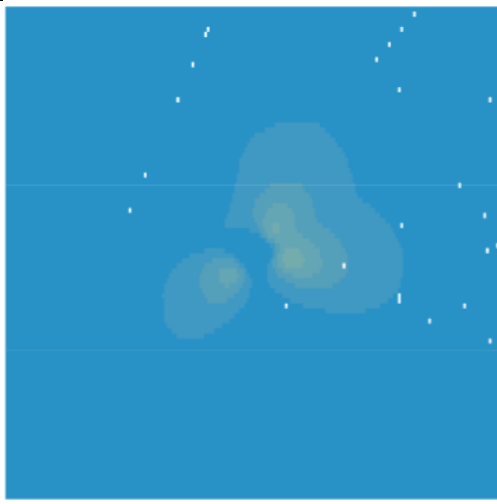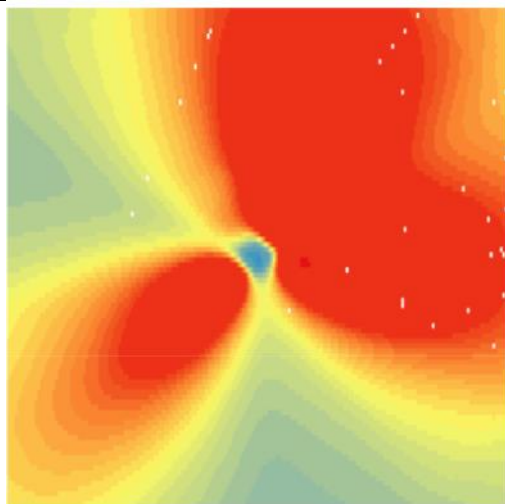
A16		\n*Nitramine scale	\n*Nitramine scale
A26			