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Atmospheric chemistry modelling of amine emissions from post combustion CO_2 capture technology

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Abstract

Emissions from post combustion CO_2 capture plants using amine solvents are of concern due to their adverse impacts on the human health and environment. Potent carcinogens such as nitrosamines and nitramines resulting from the degradation of the amine emissions in the atmosphere have not been fully investigated. It is, therefore, imperative to determine the atmospheric fate of these amine emissions, such as their chemical transformation, deposition and transport pathways away from the emitting facility so as to perform essential risk assessments. More importantly, there is a lack of integration of amine atmospheric chemistry with dispersion studies. In this work, the atmospheric chemistry of the reference solvent for CO_2 capture, monoethanolamine, and the most common degradation amines, methylamine and dimethylamine, formed as part of the post combustion capture process are considered along with dispersion calculations. Rate constants describing the atmospheric chemistry reactions of the amines of interest are obtained using theoretical quantum chemistry methods and kinetic modeling. The dispersion of these amines in the atmosphere is modeled using an air-dispersion model, ADMS 5. A worst case study on the UK's largest CO_2 capture pilot plant, Ferrybridge, is carried out to estimate the maximum tolerable emissions of these amines into the atmosphere so that the calculated concentrations do not exceed guideline values and that the risk is acceptable.

Keywords: Post combustion CO_2 capture; monoethanol amine; nitrosamine; nitramine; atmospheric chemistry modelling; atmospheric dispersion.

1. Introduction

There are growing concerns over the adverse impacts of amine degradation products, such as nitrosamines (NS) and nitramines (NA) present in the emissions from amine-based solvent post combustion CO_2 capture (PCCC) plants

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on human health and the natural environment [1]. The resulting degradation products, NS and NA, formed as a consequence of the PCCC process in the atmosphere are suspected potent carcinogens [2-4]. It is, therefore, crucial to assess the atmospheric fate and impacts of amines emitted from CO_2 capture plants so as to identify the environments most at risk. In order to achieve this, an in-depth understanding of the complex atmospheric chemistry of the amines is essential. Hence, it is of interest to investigate the mechanisms of all the atmospheric degradation pathways, degradation yields and atmospheric lifetimes of the degradation products [5, 6]. The aim of the work presented here is to consider the atmospheric chemistry along with the dispersion of monoethanolamine (MEA), the most commonly used solvent for capturing CO_2, away from the emitting PCCC facility.

Owing to the high volatility of amines it is challenging to carry out experimental studies to gain an understanding of the reactions they undergo in the atmosphere. As a consequence, the amine atmospheric chemistry remains a knowledge gap. To assist with this, theoretical calculations can be performed instead to help comprehend the convoluted chemistry. For the purposes of this study, the mechanisms of the radical atmospheric chemistry reactions of the most common amine emissions, namely MEA, dimethylamine (DMA) and methylamine (MA) are examined. A simplified amine atmospheric chemistry scheme is illustrated in Fig. 1 which considers gas phase radical reaction of the amine with the OH radical in the atmosphere to form the amino radical. The amino radical is highly unstable and therefore reacts with NO to form NS, with NO_2 to form NA and with O_2 to form imine. The NS undergoes photolysis back to the amino radical in the presence of sunlight. If the amine is a primary amine, it forms a primary NS that is unstable (unlike the stable secondary NS) and dissociates to an imine.

Previous studies have not considered the detailed atmospheric chemistry of the amines but rather assumed experimentally determined fixed chemistry formation yields to account for the NA and NS concentrations [7-9]. However, with such an approach, the concentrations of the NS and NA do not change with the distance from the source and estimates depend on sparse experimental values, which constitutes a major knowledge gap in identifying the risks posed by amine-based PCCC technology. This limitation has been addressed in this study where the atmospheric chemistry of each amine is integrated into a general-purpose advanced Gaussian dispersion model, ADMS 5 [10]. ADMS is a regulatory standard in Europe and has been extensively used for air quality modeling of impacts from industrial facilities [11]. Such a methodology enables both gas dispersion and chemical transformation calculations to be performed simultaneously, hence, assisting in determining the concentration of the released amines into the air, their dispersion and deposition away from the emitting source. A more accurate determination of the fate of the amine degradation products in the industrial emissions can therefore be established. The Norwegian Institute for Air Research [12] has reported that the maximum concentration of these chemicals in air and in wet and dry deposition that will not have a harmful impact on the human health and the environment are 0.3 ng m^{-3} and 4 ng L^{-1} in drinking water [13].

A worst case scenario on the UK's largest CO_2 capture pilot plant, CCPilot 100+ in Ferrybridge which operated between 2012 and 2013 capturing 100 t of CO_2 per day, is carried out in this study. The model estimations are used to establish the maximum tolerable emissions of amines from CO_2 capture, which result in concentrations of the NS and NA that do not exceed the pre-defined safety limits. This would imply that even in the worst case scenario the risk is acceptable. With such an approach accurate estimate of the amine and amine degradation product concentrations in time and space can be established to assess the risk these discharges possess.

2. Methodology

2.1. Amine emissions and chemistry

The atmospheric chemistry scheme investigated (Fig. 1a) is described as a set of ordinary differential equations (Fig. 1b). Here k_1 is the rate of amino radical and OH reaction, k_{1b} is the rate of alkyl radical and OH reaction, k_2 is the rate of amino radical and O_2 reaction, k_3 is the rate of amino radical and NO reaction, k_{4a} is the rate of amino radical and NO_2 reaction, k_{4b} is the rate of nitramine dissociation to imine, $j_5 h\upsilon$ is the nitrosamine photolysis rate, C_{max} is the maximum concentration of amine and E_{max} is the maximum tolerable emission rate of amine.
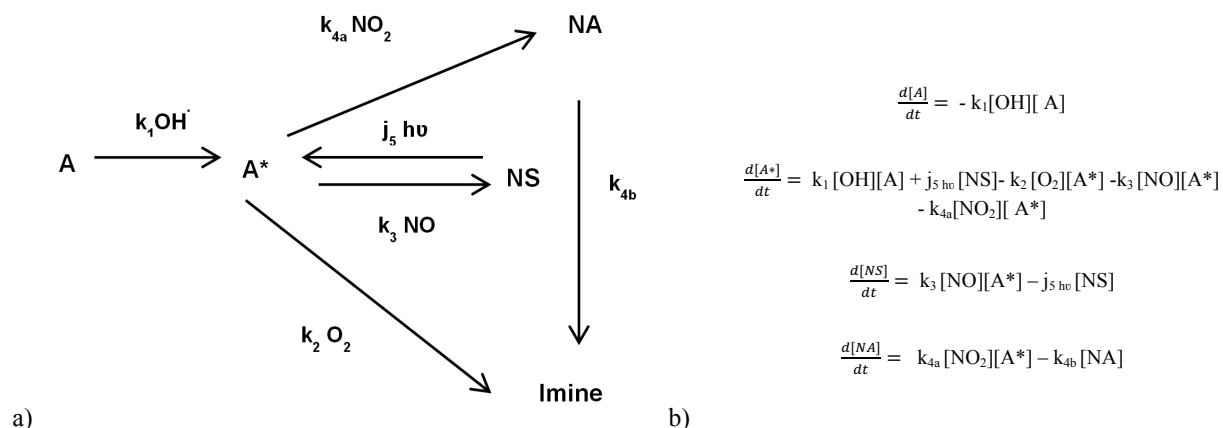
Fig. 1. (a) A simplified amine atmospheric chemistry scheme where A is amine, NS is nitrosamine, NA is nitramine, Imine is a non-toxic product, A* is a reactive intermediate species and each 'k' represents the rate constant describing the kinetics of a specific reaction step in the scheme; (b) The full system of differential equations corresponding to the amine chemistry scheme.

The amine chemistry scheme can be solved to determine the change in concentration with time of each of the chemicals of interest. For this, the rate constants describing the kinetics of each of these reaction steps in the scheme need to be established. Therefore, theoretical investigations of the reaction mechanisms to obtain reliable rate constants have been performed.

Three types of reactions were considered: (i) reactions with a barrier (ii) reactions without a barrier and (iii) a photolysis reaction. This approach required geometric, energetic and thermodynamic data to be obtained with Gaussian 09 [14] using the M062X functional [15-17] and 6-31G (2d, p) basis set [18].

Transition state theory was employed to determine k_1 via ΔG as the difference between the free energy of the reactant and the transition state. It is then used in Eyring-Polanyi's equation (Eq.1) [19] to calculate the rate constant (k_1).

$$k\,(T) = \Gamma(T)\frac{k_B T}{h}\,e^{(-\frac{\Delta G^{\neq}}{RT})} \qquad (1)$$

where $\Delta G^{\neq}$ is the Gibbs energy of activation, k_B is Boltzmann's constant, h is Planck's constant and T is absolute temperature. The Wigner tunnelling correction factor (Γ) [20] is used to correct the rate constants in order to obtain a more accurate value.

Transition states were located with the QST2 method [21-22] by starting from the reactant and product geometries. Then intrinsic reaction coordinate (IRC) calculations were performed to confirm the corresponding reactants and products. Stationary points such as minima and transition states on the minimum energy path of these potential energy surfaces were characterised with frequency calculations.

Rice-Ramsperger-Kassel-Marcus (RRKM) theory [23] was used to determine k_2, k_3, k_{4a} and k_{4b} using ChemRate 1.5.8 [24], which contains a master equation solver. The rate constants for the reactions in the energy transfer region under non-steady state conditions are determined by calculating the density and sum of states for the M062X optimised geometries using the thermochemical data produced by the quantum chemical calculations. The bath gas considered for the calculations was Argon.

To determine the rate of the nitrosamine photolysis ($j_5h\upsilon$ pathway) in the atmosphere, Time-Dependent Density Functional Theory, TD-DFT, with the B3LYP density functional and the aug-ccpVTZ basis set, was employed to calculate the UV-Vis spectra of the target nitrosamines [25-26]. The photolysis rate ($j_5h\upsilon$) is a function of solar actinic flux (at a specified latitude, longitude and time of the year), the molar extinction coefficient (at the wavelength and temperature of the chemical substance) and the quantum yield of the photolysis reaction (value of

1). The photolysis rate, $j_5h\upsilon$, was evaluated by numerically integrating the intersection area between the simulated UV spectra for all the NS and solar actinic flux at Ferrybridge. The calculated rate constants are listed in Table 1.

Table 1. The calculated rate constants (cm^3 molecule $^{-1}$ s^{-1}) describing the atmospheric chemistry of the amines of interest (where J / J(NO$_2$) is the nitrosamine photolysis rate constant (j$_5$hυ) relative to that of NO$_2$ and k$_{OH}$ represents the sum of rates for H abstraction from an amine group (k$_1$) and from the non-amine group (k$_{1b}$) therefore the branching ratio for the OH attack is a ratio of k$_1$/(k$_1$+ k$_{1b}$) = k$_1$/k$_{OH}$).

Amine	k_{OH}	Branching ratio, k_1/k_{OH}	k_2	k_3	k_{4a}	k_{4b}	J / J(NO$_2$)
MA	2.18×10^{-11}	0.35	3.64×10^{-18}	1.70×10^{-12}	9.70×10^{-11}	2.02×10^{-13}	0.53
Experimental	2.22×10^{-11} [27]	0.25 [28]					
DMA	6.26×10^{-11}	0.38	3.64×10^{-18}	8.37×10^{-14}	3.15×10^{-13}	1.10×10^{-14}	1.24
Experimental	6.49×10^{-11} [29]	0.37 [30]	1.24×10^{-19} [30]	8.53×10^{-14} [31]	3.18×10^{-13} [31]	1×10^{-14} [3-]	0.53 [30]
MEA	9.20×10^{-11}	0.05	2.49×10^{-16}	5.62×10^{-14}	8.40×10^{-15}	4.14×10^{-15}	0.58
Experimental	9.31×10^{-11} [8]	0.08 [28]					

N.B The experimental k$_2$ and k$_{4b}$ for the DMA are the calculated rates from the ratios reported by Lindley et al. [30].

2.2. Atmospheric dispersion model

Following the release of the amine emissions into the atmosphere, the amine and the resulting NS and NA undergo atmospheric processes such as dispersion, chemical transformation and deposition. Consequently, this results in a decrease in the concentration of these species with respect to distance from the PCCC plant. To calculate the change in concentration of the dispersing species in air, dispersion calculations along with the atmospheric chemistry was performed using ADMS 5 [10]. The model is applicable up to 60 km from the source. Being a new generation Gaussian plume air dispersion model, two parameters such as the boundary layer depth and the Monin-Obukhov length are used to describe the atmospheric boundary layer. The model has atmospheric chemistry integrated such that it can perform calculations to consider chemical transformation, deposition and transport of the emitted species in the environment. The chemistry scheme of each of the amines of interest is described by the rate constants listed in Table 1. These parameters are used in solving the advection-dispersion equation using ADMS 5 where the concentrations and age of the primary pollutants are calculated at each receptor point using the standard ADMS dispersion algorithms. This process of calculating the dispersion and then the chemistry is carried out hourly. For the chemistry calculations, there needs to be the consideration of timescales. After each hourly dispersion calculation, the 'age' of the pollutants is calculated by considering the plume travel time. The reaction equations are applied over time δt to the background and then to the pollutants from the source. In addition, the dilution and entrainment calculations account for the fact that the pollutants in the plume are diluted as they travel [10].

The emission source of interest for the purposes of this study is assumed to be the absorber stack of the Ferrybridge power station, since amine emissions are usually from the absorber [32]. Maximum long-term average concentrations and annual deposition flux of amines, NS and NA for the mentioned scenarios are obtained from the model output. Wet deposition is treated using a wash out coefficient method [10]. Annual average output is produced on a 30 km × 30 km grid with a resolution of 300 m centred on the power station. Each cell is assigned terrain elevation based on UK OS Profile DTM dataset (Fig. 2a). The meteorological model has been initialised with the meteorological data from the UK Met office and National Oceanic and Atmospheric Administration (NOAA). Since the Ferrybridge CCPilot 100+ started operation in 2012, the surface meteorological data and precipitation data for 2012 was obtained from the Castleford weather station. The wind rose for Ferrybridge is illustrated in Fig. 2b. The emission source parameters used for this case study are listed in Table 2.

Table 2. Modeled source parameters for Ferrybridge power station.

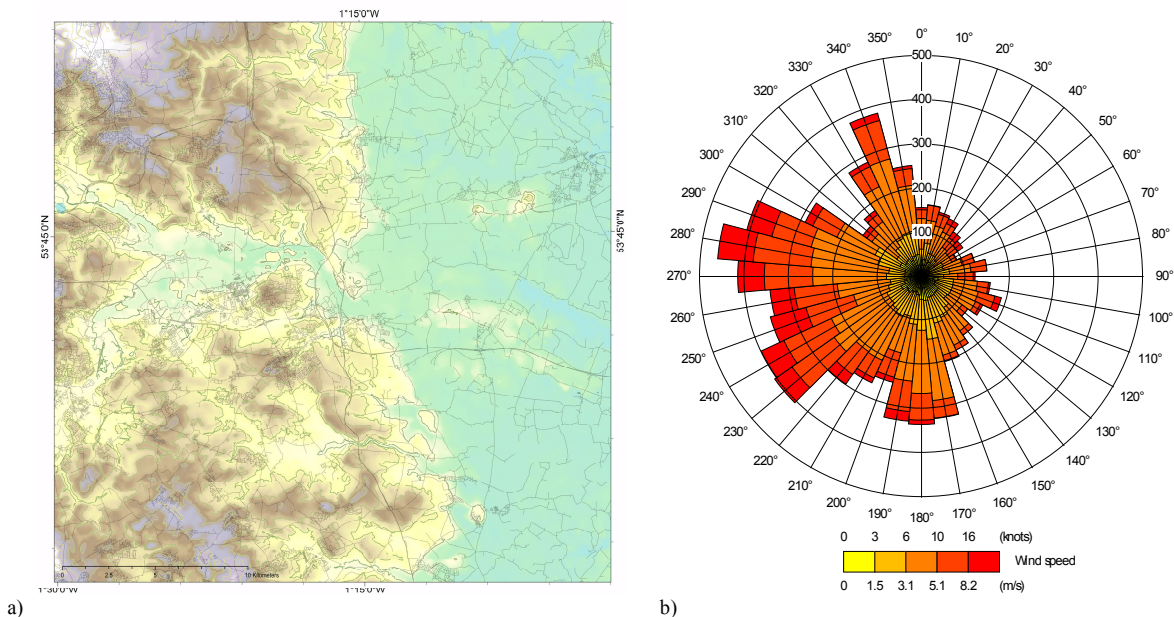| Stack height (m)	Stack diameter (m)	Plume velocity (m/s)	Emission temperature (°C)	Volume flow rate (m^3/s) at 90 °C
198	9.74	20	90	1490.2

Fig. 2 (a) Local features and terrain elevation around the Ferybridge CCPilot 100+; (b) Wind rose for Ferrybridge for 2012.

Owing to data confidentiality, no amine emission rates are reported for the CCPilot 100+, therefore, the dispersion model simulations were initially carried out with a unity emission rate (1 g/s) for each amine for a year (Table 3) and the results used to establish the emission rates for the worst case scenario. NO_x emissions from the stack were also considered since the formation of the NS and NA depends on the reactions with NO and NO_2 (Table 2). Based on data from Ferrybridge, 0.49 % of NO_2 in the NO_x emissions is used for all the calculations.

Results (C_{max} of emitted amine) from the unity emissions are used to establish the maximum tolerable emission rates, E_{max}, for each of the amines emitted for the worst case study. The same approach as Karl et al. [12] was used but also accounting for the chemical transformation of the parent amine to NS and NA, which was determined (Table 3) using the established chemistry scheme (Fig 1a) as opposed to fixed formation yields used by Karl et al. [12]. The sum of NS and NA resulting from all the considered amines for the worst case scenario is compared to pre-established safety limits of the respective toxic compounds.

For comparison, conservative dispersion was also modeled by deselecting the amine chemistry module in ADMS 5. Fixed formation yields from experimental data [7] were applied to the results from conservative dispersion so as to estimate the resulting concentrations of NS and NA.

Table 3. Percentage transformations applied to each amine and the maximum concentration of amine at unity emission and the calculated maximum tolerable emission for the worst case scenario.

Emitted species	[Amine] (ng m^{-3})	Sum of NS + NA (ng m^{-3})	Transformation of amine to NS+NA (%)	C_{max} (ng m^{-3})	E_{max} (g s^{-1})
MA	0.84	7.82×10^{-4}	0.09	2.58	125
DMA	0.91	7.82×10^{-4}	0.09	2.52	138
MEA	1.36	4.85×10^{-3}	0.36	4.03	20.8
NO_x					1.79

3. Results and discussion

3.1. Chemical transformation, dispersion, deposition calculations

As can be seen from Table 1, the calculated rate constants for DMA are in very good agreement with those determined experimentally as they are within the same order of magnitude. It is therefore assumed that, in the absence of experimentally reported rate constants, the method used for the case of DMA is appropriate for MA and MEA. Upon comparison of the estimated rate constants, it is apparent that the fastest reaction is the reactions of the amine with the OH radical. The reaction of amino radical with O_2, k_2, is the slowest step.

The established rate constants were used to carry out atmospheric chemistry dispersion modeling of MA, DMA and MEA for one year (2012) at the Ferrybridge CCPilot 100+ for unity and maximum tolerable emission rates. As the emissions are not known, it was assumed that 1 g/s of each of the amine was emitted into the atmosphere from the capture plant. The results obtained from the unity emission rate estimations were utilised to establish the maximum tolerable emissions of each of these amines (Table 3). The maximum long-term average concentrations of the target amines and the corresponding maximum tolerable emission levels calculated are listed in Table 4.

Table 4. Maximum long term average concentrations of total nitrosamines and nitramines for assumed maximum emissions of MA, DMA and MEA at Ferrybridge.

	NIPH guideline value	Maximum annual concentration of total NS and NA considering atmospheric chemistry
Air (ng/m^3)	0.3	0.29
Water (ng/L)	4	3.43

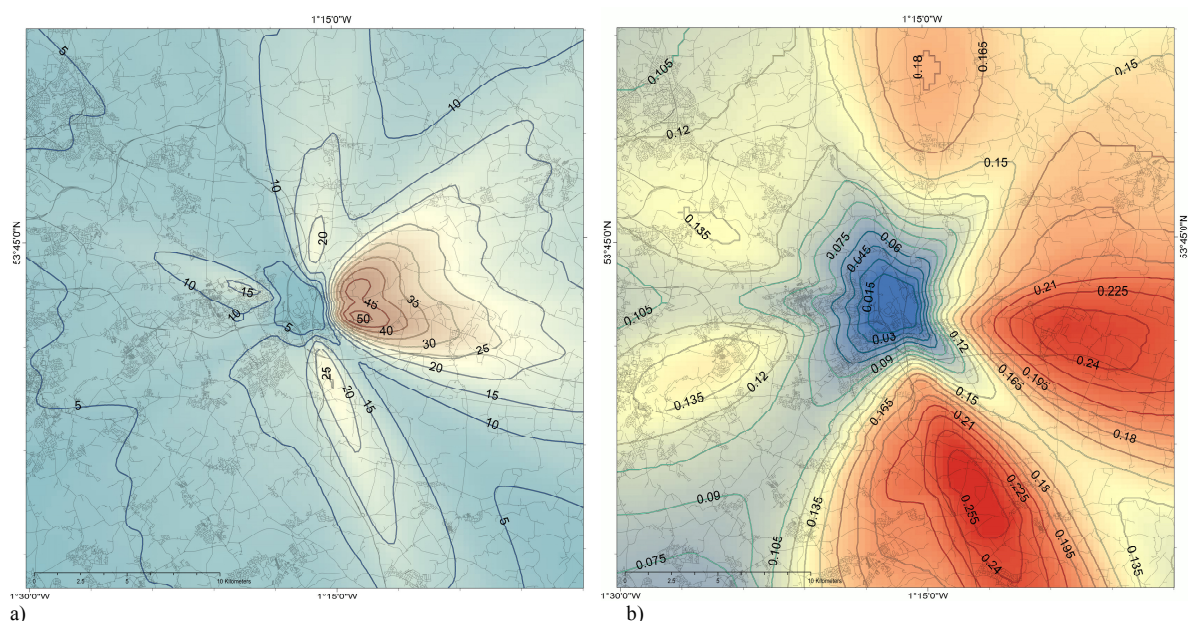a)   b)

Fig. 3 Contoured distributions of maximum annual concentration of amines in air for the worst case scenario in 2012: (a) MEA (ng/m^3) and (b) total NS and NA (ng/m^3) resulting from MA, DMA and MEA emissions.

A contour map showing the concentration of the emitted MEA and the total (sum of) NS and NA resulting from the three amines (MA, DM and MEA) considered for 2012 is illustrated in Fig. 3 over an area of 30 km × 30 km centered on the Ferrybridge site for a 300 m resolution square grid. The results are in annual average values, which are the relevant statistics to compare with the threshold values.

The results demonstrate that the highest concentration of the emitted amine species are found in close proximity of the emission source (within 2-3 km) owing to the dispersive effect of the atmosphere (Fig. 3a). The concentrations then decrease with increasing distance from the PCCC facility. The resulting concentrations of NS and NA increases further away from the source as they are produced from the emitted amine which reacts with the radicals in the atmosphere to form the degradation products (Fig. 3b). The dispersion of the species is influenced by the terrain surrounding the site and the meteorological conditions in year 2012 (Fig. 2). The maximum annual concentration of total NS and NA in air for the worst case scenario for the meteorological year 2012 is 0.29 ng m^{-3} (Table 4), which is below the critical concentration of 0.30 ng m^{-3} by 1%. Therefore, the level of risk posed by these chemicals is acceptable. The total maximum deposition flux of the chemicals is calculated to be 3.43 ng L^{-1} (Table 4) which does not exceed the critical annual deposition flux of 4 ng L^{-1}. At such deposition fluxes, the aquatic and drinking water concentrations of these chemicals will not reach levels which may have adverse impacts on human beings and aquatic species.

To observe the effect of chemistry on dispersion (or vice versa), conservative dispersion of these amines was performed. Resulting amine concentrations for the worst case scenario were 1, 4 and 5% higher than that obtained when both dispersion and chemistry were considered for MA, DMA and MEA respectively. This is in agreement with the fact that dispersion processes reduce concentrations of reactive species a lot faster than chemical transformation processes. This is due to dependency of the rate constants on the absolute concentration of amine; therefore, reduced chemical transformation occurs. Hence, simultaneous dispersion and chemical transformation slows down the formation of the NS and NA, which is estimated 58.9 times lower than the estimates made using formation yields by Nielsen et al. [28].

Conservative dispersion neglects the reactions of the amine emissions occurring in the atmosphere, therefore, does not evaluate reliably the concentrations of the resulting NS and NA that influence human health and environment. For an accurate risk assessment it is of paramount importance to calculate concentrations of these species from the emitting facility in time and within the area of interest. Applying fixed formation yields to conservative dispersion was one of the first approaches which included experimentally determined fixed formation yields [7] to account for NA and NS concentrations [9, 13]. The limitation of this approach is that the concentrations remain constant with distance from the source. Additionally, this approach relies on the use of experimental data which is very limited.

The results from the implementation of the chemistry to the advection-diffusion reaction solved by the dispersion model accounts for the detailed atmospheric fate of the amines emissions. Such an approach provides a more accurate estimate of the amine concentrations over time and space. The methodology described here can be applied to any amine as it is independent of experimentally determined formation yields.

4. Conclusions

The research described in this paper coupled a detailed atmospheric chemistry modelling scheme with an atmospheric dispersion model and developed a reliable and universal methodology to assess the fate of amines emitted from a PCCC facility. The methodology can be used to assess the risk these emissions pose to the natural environment and human health.

Acknowledgements

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