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Abstract

Post combustion using amine solvents is the most mature technology for the capture of CO2 from coal-fired power plants. Yet, amines atmospheric fate and their environmental and human health impacts, after their release by evaporation and solvent degradation from post combustion CO2 capture (PCCC) plants to the surrounding air, remains a key area to address in view of the worldwide installation of large-scale carbon capture and storage facilities. It is therefore crucial to test potential industrial applications with respect to plant design parameters influencing the fate of the amine degradation products. In this work, a method is developed to propose ideal PCCC plant parameters with respect to its design and operation. A risk limiting scenario was modelled on the UK's largest CO2 capture pilot plant (CCPilot100+) in Ferrybridge using the air dispersion model ADMS, such that the total nitrosamines and nitramines from the amines realised did not exceed the reported atmospheric safety limits of 0.3 ng /m3 with respect to human health in the local environment. A parametric sensitivity study was performed to determine the plant design parameters that most influenced the fate of the nitrosamines and nitramines. It was found that stack height and diameter, exit flue gas temperature and velocity are parameters of the PCCC plant can influence the total sum of nitrosamine (NS) and nitramine (NA) from +58 % to -42% compared to the baseline parameterization. Environmental parameters, such as the site specific background meteorology and the background photochemistry were also inspected. Meteorology, i.e. mainly wind speed and wind flow field, affected the total NS and NA baseline concentrations from +28 % to -10 %, and background photochemistry from +165 % -65 %. In conclusion, if a PCCC plant is constructed with advantageous exhaust geometry, environmentally optimized operation conditions, and placed in an area with low background pollution, the risk associated with employing amines for capturing CO2 emissions might be reduced to a minimum.

Keywords	Amine, nitrosamine; nitramine; methylamine; monoethanolamine; dimethylamine; degradation; atmospheric chemistry; photolysis; dispersion; advection; ADMS; human health; photochemistry; worst case scenario; risk limiting scenario; meteorology; gas phase; amine emissions; plant design parameters; PCCC
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Cover letter

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09-01-2017

Dear Dr. John J. Gale,

I wish to submit a new manuscript entitled “Model Study on the influence of plant design, photochemistry, and meteorology on atmospheric concentrations of nitrosamines and nitramines in vicinity of an amine-based CO_2 capture facility” for consideration by the International Journal of Greenhouse Gas Control.

I confirm that this work is original and has not been published elsewhere nor is it currently under consideration for publication elsewhere.

In this paper, we report on post combustion using amine solvents, which is the most mature technology for the capture of CO_2 from coal-fired power plants. Yet, amines atmospheric fate and their environmental and human health impacts, after their release by evaporation and solvent degradation from post combustion CO_2 capture (PCCC) plants to the surrounding air, remains a key area to address in view of the worldwide installation of large-scale carbon capture and storage facilities. It is therefore crucial to test potential industrial applications with respect to plant design parameters influencing the fate of the amine degradation products. In this work, a method is developed to propose ideal PCCC plant parameters with respect to its design and operation. It was established that if a PCCC plant is constructed with advantageous exhaust geometry, environmentally optimized operation conditions, and placed in an area with low background pollution, the risk associated with employing amines for capturing CO_2 emissions might be reduced to a minimum.

The paper should be of interest to readers in the areas of environmental chemistry, public health, chemical engineering etc as well as industries dealing with post combustion CO_2 capture technologies. The manuscript belongs in this journal since; IJGGC has long been interested in the area of carbon capture using amine solvent. It has in the past-published work that has studied the fate of amines in the environment and their impact on the human health and the environment.

Please address all correspondence concerning this manuscript to me at saba.manzoor08@imperial.ac.uk

Thank you for your consideration of this manuscript.

Sincerely,

Dr. Saba Manzoor

Model Study on the influence of plant design, photochemistry and meteorology on atmospheric concentrations of nitrosamines and nitramines in vicinity of an amine-based CO_2 capture facility

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Abstract

Post combustion using amine solvents is the most mature technology for the capture of CO_2 from coal-fired power plants. Yet, amines atmospheric fate and their environmental and human health impacts, after their release by evaporation and solvent degradation from post combustion CO_2 capture (PCCC) plants to the surrounding air, remains a key area to address in view of the worldwide installation of large-scale carbon capture and storage facilities. It is therefore crucial to test potential industrial applications with respect to plant design parameters influencing the fate of the amine degradation products. In this work, a method is developed to propose ideal PCCC plant parameters with respect to its design and operation. A risk limiting scenario was modelled on the UK's largest CO_2 capture pilot plant (CCPilot100+) in Ferrybridge using the air dispersion model ADMS, such that the total nitrosamines and nitramines from the amines realised did not exceed the reported atmospheric safety limits of 0.3 ng /m^3 with respect to human health in the local environment. A parametric sensitivity study was performed to determine the plant design parameters that most influenced the fate of the nitrosamines and nitramines. It was found that stack height and diameter, exit flue gas temperature and velocity are parameters of the PCCC plant can influence the total sum of nitrosamine (NS) and nitramine (NA) from +58 % to -42% compared to the baseline parameterization. Environmental parameters, such as the site specific background meteorology and the background photochemistry were also inspected. Meteorology, i.e. mainly wind speed and wind flow field, affected the total NS and NA baseline concentrations from +28 % to -10 %, and background photochemistry from +165 % -65 %. In conclusion, if a PCCC plant is constructed with advantageous exhaust geometry, environmentally optimized operation conditions, and placed in an area with low background pollution, the risk associated with employing amines for capturing CO_2 emissions might be reduced to a minimum.

Key words: **Amine**, **nitrosamine**; nitramine; methylamine; **monoethanolamine**; dimethylamine; degradation; **atmospheric chemistry**; photolysis; dispersion; advection; ADMS; **human health**; photochemistry; worst case scenario; **risk limiting scenario**; meteorology; gas phase; amine emissions; **plant design parameters**; **PCCC**

1. Introduction

According to the latest report by the Intergovernmental Panel on Climate Change (IPCC), the planet is experiencing the impacts of human-induced climate change such as accelerating sea level rise, melting glaciers, extreme weather conditions and extinction of species (IPCC 2014). Human influence on warming is primarily from the burning of fossil fuels which has caused greenhouse gas (GHG) emissions to increase in the same manner as the GHG concentrations in the atmosphere (IPCC 2014). Increasing emissions of greenhouse gases (GHG) in the atmosphere, in particular CO_2, will further trigger global warming and climate change. By the end of this century, it is anticipated that the impacts from warming will be widespread, severe and irreversible (IPCC 2014). To prevent the global warming from rising by the anticipated 2°C, GHG emissions have to be reduced by 40-70 % by 2050 and 100% by 2100 (IPCC 2014). To meet this reduction target, CO_2 capture and storage (CCS) technology is a proposed and promising way forward (IPCC 2013).

The technologically most progressed mitigation technology for coal-fired power plants is post combustion CO_2 capture (PCCC) using amine solvents for large scale CO_2 capture. However, as part of the capture process there is an inevitable leakage of the amine solvent into the atmosphere that forms as part of the CO_2-free flue gas (Eide-Haugmo et al. 2009, Booth et al, 2012a, Booth et al. 2012b). The fate of the released amines is determined by atmospheric processes such as chemical transformation, dispersion and deposition processes. Subsequently, the release of amines leads to the production of substances such as nitrosamines, nitramines (Nielsen *et al.* 2010, Nielsen et al. 2011a and Nielsen et al. 2011b), imines and isocyanic acid (Bunkan et al., 2014). The atmospheric ground-level concentrations of these emitted substances vary as a function of distance from the emitting PCCC facility (e.g. Karl *et al.* 2015). Nitrosamines and nitramines have been documented to possess mutagenic and carcinogenic properties in animal testing (Lag *et al*. 2009 and Lag *et al*. 2011). Therefore, it is imperative to study these products to determine their impact on human health and environment.

The atmospheric chemistry of amines is highly complex and due to their high volatility, polarity, hygroscopic nature and great affinity to surfaces, there are challenges in performing experiments representative of environmental conditions. As a consequence, only a limited number of experimental investigations on amine degradation have been carried out in the laboratory and in pilot plant studies. Due to the lack of such studies, theoretical chemistry and dispersion modelling studies have attempted to fill the knowledge gaps. Initially, impact assessment studies only considered the atmospheric dispersion of the amines as passive tracers following their emissions from the PCCC plant into the atmosphere. Chemical transformation of amines in the atmosphere was accounted for by performing a post-processing step following the dispersion calculations, assuming instantaneous formation of the degradation products, such as nitrosamines and nitramines, from the parent amine at the stack of the emitting facility. The respective concentrations of the by-products was then determined as fraction of the parent amine concentration, where these specific fractions were acquired from experimentally determined fixed formation yields (FFY) (Karl *et al.* 2011, de Koeijer *et al.* 2013). Such an approach could not take into account the detailed atmospheric degradation of the amine during transport by advection and diffusion. Consequently, the spatial distribution of the concentrations of the reaction products showed the same dispersion pattern as the parent amine, with the highest impact of air concentrations near the plant. Clearly, this approach does not realistically represent the change in the concentration with increasing distance from the plant. Hence, the impact of nitrosamines and nitramines from PCCC emissions has not been evaluated accurately.

To overcome the caveats of the FFY approach, some recent studies have considered amine gas-phase chemistry reactions along with dispersion and deposition (CERC 2012d, Fowler and Vernon 2012, Emmerson *et al.* 2013, Karl *et al.* 2014, Wu and Nelson 2014, Karl *et al.* 2015). However, except for studies by Karl *et al.* (2014) and Karl *et al.* (2015), they have all adopted rate constants from literature and used estimated values in the absence of experimentally determined rate constants. Manzoor *et al.* (2015) recently developed a theoretical method capable of investigating the reaction mechanisms and evaluating reaction kinetics of any generic amine with atmospheric radicals, therefore, making it comprehensive and versatile. It has been validated against existing experiment data sets (Atkinson *et al*. 1977, Atkinson *et al* 1978, Lindley *et al*. 1979, Lazarou *et al*. 1994, Nielsen *et al*. 2011a, Onel *et al*. 2012, Karl *et al*. 2012, Borduas *et al*. 2013 and Xie *et al*. 2014). Since the method does not require any experimental data as input, it is possible to study amines that have previously not been investigated experimentally.

In this study, the atmospheric dispersion model, ADMS 5 (CERC 2012a, CERC 2012b) was utilized to quantify the photochemical production of nitrosamines and nitramines from emitted amines when atmospheric chemistry of amines is considered in addition to their dispersion in the region around the PCCC plant, in the same manner as demonstrated by Manzoor *et al.* 2015. To illustrate the implementation of the above approach, a case study for UK's largest CO_2 capture pilot plant (CCPilot100+) in Ferrybridge was conducted. Due to the lack of reliable amine emission data, risk-limit scenario cases were created based on modelling experience such that the chemical discharges of the most common leakages of amine (such as monoethanolamine, MEA) and degradation products formed as part of the amine-based PCCC capture process (such as methylamine, MA and dimethylamine, DMA) from the emitting source had the highest rate for which the associated risk was still acceptable with respect to the health of the general public and the local environment. To determine the parameters (such as meteorology, background chemistry, rate constants, plant design and operation) that are most influential on the fate of the resulting ambient concentrations of nitrosamines and nitramines from PCCC process emissions, parametric sensitivity analysis was performed on the risk-limit case.

The application of amine-based solvent PCCC technology for CO_2 capture on a full-scale commercial plant is still in its early stages, with the Boundary Dam CCS project in Canada being the first in operation (MIT, 2016). It is proposed that the risk associated with solvent discharge issues from amine-based solvent PCCC plant can be made negligible. This can be achieved if the sensitivity analysis technique applied in this work is utilized to propose ideal plant design parameters and an ideal geographical location for a proposed industrial application. Therefore, the findings of this research are expected to result in useful data to the CO_2 capture industry especially for compliance with air quality regulations.

2. Materials and methods

2.1 Atmospheric dispersion model ADMS 5

An advanced Gaussian dispersion model, ADMS 5 with its amine chemistry module (CERC 2012a) was used for quantifying the atmospheric chemistry, dispersion and deposition atmospheric processes of the amine emissions of interest. ADMS 5 has been employed for modelling air quality impact of pollutants from industrial sources (McHugh *et al.* 1997, Carruthers *et al.* 2000, Colgan *et al.* 2003, Leksmono *et al.* 2006, Hodgson *et al.* 2007, CERC 2010, CERC 2012d). ADMS 5 is a new generation Gaussian plume air dispersion model, capable of describing the in-plume process and the distinct nature of the plume by directly linking the characteristic of the atmospheric turbulence to the plume spread. Therefore, the atmospheric boundary layer properties and atmospheric stability are characterised by the boundary layer depth and the Monin-Obukhov length, L_{MO}, in contrast to other Gaussian models which typically use the Pasquill-Gifford or other stability classifications. Under stable conditions, L_{MO}, is positive, whereas, it is negative under unstable or convection conditions. The model is limited to a distance of up to 60 km from the source and it possesses various advanced features, making it a suitable candidate for accessing the fate of pollutants from industrial installations.

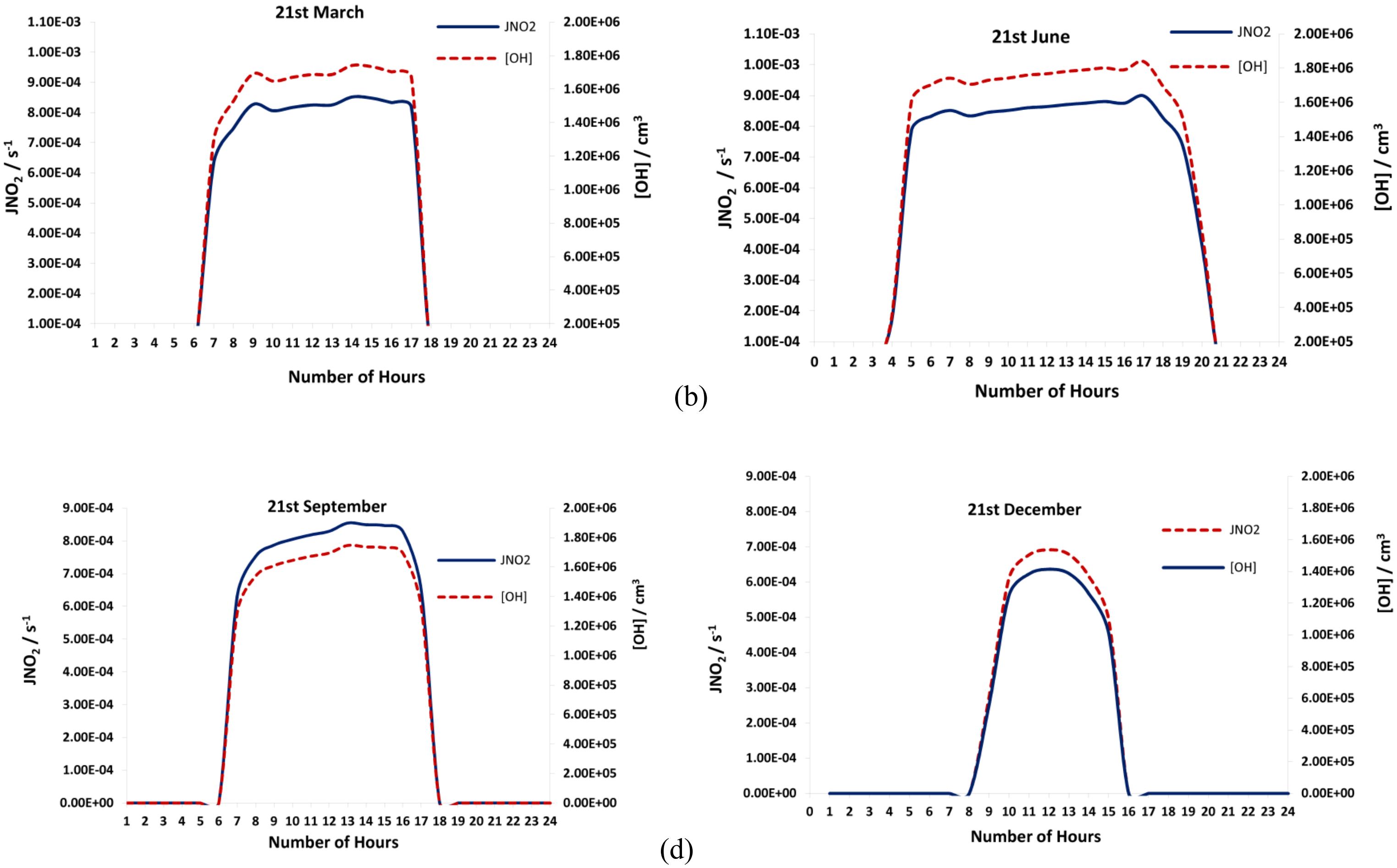
ADMS 5 was used to estimate the atmospheric concentration levels of the emitted amines over distance and time from the source. Dispersion modelling requires information on emission rates of amine and nitrogen oxides from the source, characteristics of the emission source i.e. stack height and stack diameter, stack exit velocity, exhaust gas emission temperature at stack exit, geographic location, local topography, meteorology (such as wind speed and direction, ground surface temperature and cloud cover) of the site and background concentrations of NO_x (i.e the sum of nitric oxide (NO) and nitrogen dioxide (NO_2)) and ozone (O_3). The model's meteorological pre-processor was employed to calculate the hourly photolysis rate of nitrogen dioxide, J_{NO2} (CERC 2012a):

$$J_{NO2} = 8x10^{-4}\exp\left(-\frac{10}{K}\right) + 7.4x10^{-6}K \qquad (1)$$

The evaluated hourly J_{NO2} along with ambient hourly O_3 concentrations were then used for the determination of the hourly hydroxyl radical (OH) concentration using the relationship defined in Eq. 2. This equation also accounts for a site-specific parameter c (CERC 2012a).

$$[OH] = c\, x\, [O_3]\, x\, J_{NO2} \qquad (2)$$

Where, J_{NO2} is the hourly photolysis rate of NO_2, K is the solar radiation (in W/m^2) at the considered latitude. Ambient background concentrations of O_3 and OH are used in Eq. (2) . Diurnal profiles of OH concentration and J_{NO2} for equinox and solstice days are displayed in Figure 1.



(a) (b)

(c) (d)

Figure 1: Typical diurnal profiles for OH and photolysis rate J_{NO2} for (a) 21st March (b) 21st June (c) 21st September and (d) 21st December, for Ferrybridge.

ADMS 5 initially computes pollutant dispersion using advanced advection-dispersion algorithms for the determination of the concentration distribution profile of the species of interest within the boundary layer described by a Gaussian plume (accounting for reflections at the ground level and at the inversion layer). Details are given in the Supplementary Materials, section S1. Subsequently, ADMS evaluates the concentrations of the emitted amine at each receptor point for every hour (Figure 2). Following the hourly dispersion calculations, it then considers the plume time travel to determine the plume age.

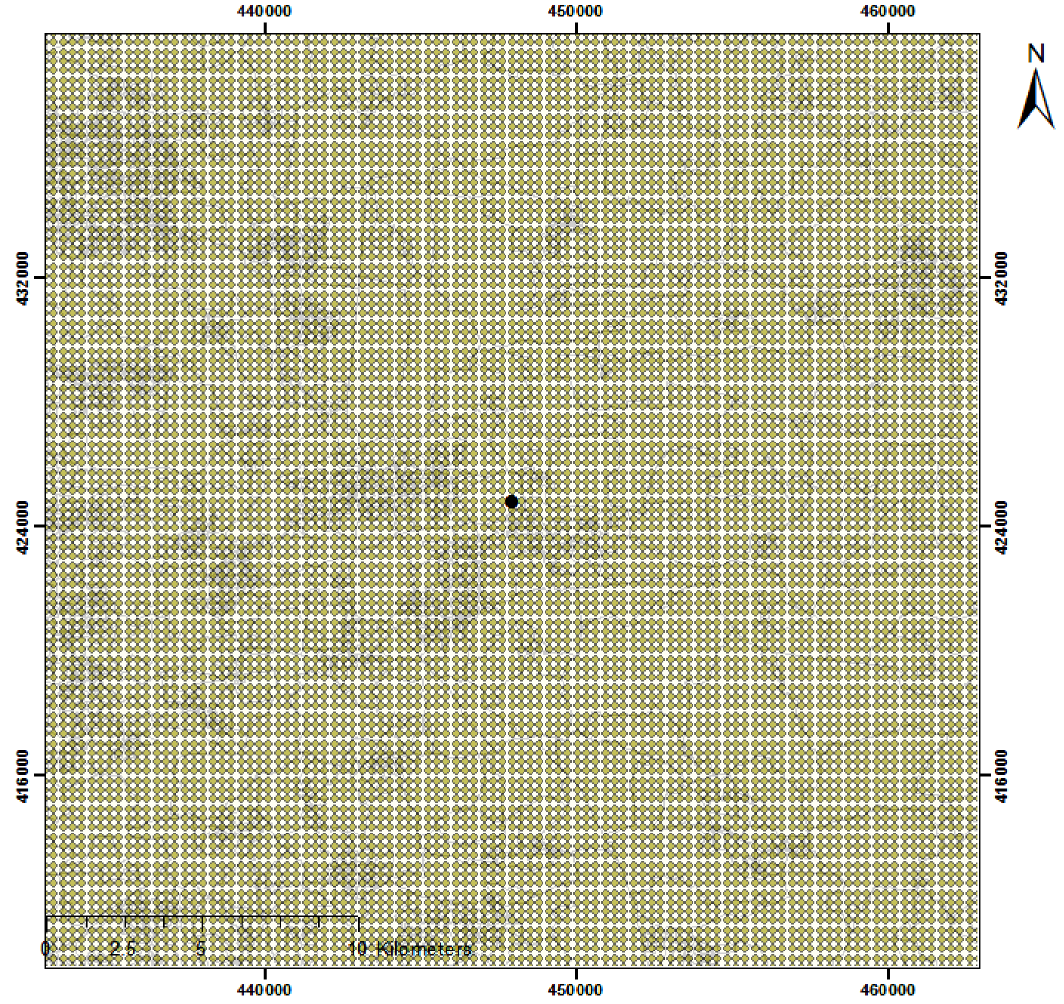


Figure 2: 101x101 Gridded receptors over 30 km x 30 km domain centered on Ferrybridge

An adaptive time-stepping method is employed for the numerical integration of the ordinary differential equation (ODE) system (Table S1) describing the atmospheric chemistry (CERC 2012e). After solving the system, the resulting solution is applied over time to the background and to the emissions from the source for every time step until plume travel time becomes equal to the life time of the parent amine. Dilution and entrainment of the amines as they travel in the plume are also accounted for.

2.2. The amine chemistry module in ADMS 5

ADMS 5 has an in-plume chemistry model for consideration of chemical reactions to form harmful chemicals from amines such as nitrosamines and nitramines. The amine specific rate constants and the other parameters mentioned in section 2.1 are then used to compute the atmospheric chemistry of the amines. A generic amine chemistry scheme (Table 1) based on experimentally evaluated chemistry scheme for MEA by Nielsen *et al.* (2011) (as presented in Manzoor *et al.* (2015)) has been integrated with the dispersion algorithms in ADMS 5 by its developers.

Table 1: A generic amine chemistry scheme incorporated in ADMS 5 (CERC 2012a).

Amine + OH → Amino radical + H_2O	k_{1a}
→ $RN(H)CH_2 + H_2O$	k_{1b}
Amino radical + O_2 → Imine + HO_2	k_2
Amino radical + NO → Nitrosamine	k_3
Nitrosamine + hυ → Amino radical + NO	J
Amino radical + NO_2 → Nitramine	k_{4a}
→ Imine +HONO	k_{4b}

Manzoor *et al.* (2015) studied the atmospheric chemistry schemes for MA, DMA and MEA employing quantum chemistry theoretical methods and kinetic modelling to develop a reaction scheme with reaction rate constants, as specified in Table 2. The atmospheric chemistry schemes for MA, DMA and MEA and their corresponding ODE systems are summarized in Table S1 and Figure S1 (Supplementary materials).

Table 2: A summary of the rate constants (cm^3 $molecule^{-1}$ s^{-1}) describing the atmospheric chemistry scheme for Monomethylamine (MA), dimethylamine (DMA) and monoethanolamine (MEA) studied using quantum chemistry theoretical methods and kinetic modelling established in Manzoor et al., 2015.

k / cm^3 $molecule^{-1}$ s^{-1}	**MA**	**DMA**	**MEA**
k_{1a}	7.63×10^{-12}	2.38×10^{-11}	4.60×10^{-12}
k_{1b}	1.42×10^{-11}	3.88×10^{-11}	8.74×10^{-11}
k_2	3.64×10^{-18}	3.64×10^{-18}	2.49×10^{-16}
k_3	1.70×10^{-12}	8.37×10^{-14}	5.62×10^{-14}
k_{4a}	9.70×10^{-13}	3.15×10^{-13}	8.40×10^{-15}

k_{4b}	2.02×10^{-13}	1.10×10^{-14}	4.14×10^{-15}
J /s^{-1}	4.34×10^{-3}	7.51×10^{-3}	3.48×10^{-3}

2.3. Study sites

To demonstrate the application of the developed methodology, case studies on the PCCC plant at Ferrybridge (give latitude; longitude coordinates of the plant) was conducted to quantify the change in concentration of the amine discharges in time and space with respect to the emitting facility. Ferrybridge CCPilot 100+ is UK's largest CO_2 capture coal-fired pilot plant in Ferrybridge, CCPilot 100+. It was operational in 2012 and 2013 capturing 100 tonnes of CO_2 per day with a 90 % capture rate (Fitzgerald *et al.* 2014).

It is assumed that the absorber stack is the emission source of amines (CERC 2012c, CERC 2012d). The stack exhaust geometry is circular. The source parameters of each emitting facility are shown in Table 3.

Table 3: Source parameters for carbon capture facilities included in this study

PCCC plant	Stack height (m)	Stack diameter (m)	Stack exit velocity (m/s)	Exhaust emissions temperature at stack exit (°C)	Volume flow rate (m^3) at emission temperature	NO_x emission rate (g/s)
Ferrybridge	198	9.74	20.0	90.0	1490	$5.06\text{x}10^2$

Atmospheric chemistry and dispersion modelling for each of the amines mentioned is performed for a particular meteorological year. Meteorological data for Ferrybridge is from the UK Met office and National Oceanic and Atmospheric Administration (NOAA). The meteorological year modelled for Ferrybridge is 2012, which was the starting year of operation, and the relevant data was obtained from Castleford weather station. The wind rose for Ferrybridge is shown in Figure 3.

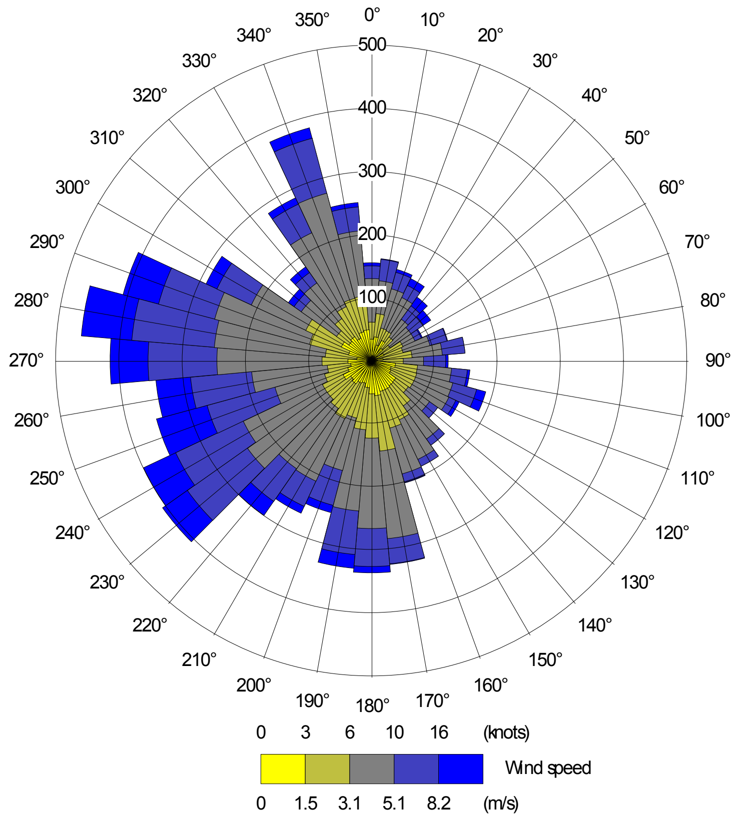


Figure 3: Wind rose plot for depicting the downwind flow vector (direction towards which the wind was blowing) in m/s for Ferrybridge (2012). In this polar plot, the angle of an element represents wind direction whereas the radial distance from the centre represents the frequency of wind speed occurrence. The frequency of each wind record is taken as 1 (CERC (2012b)).

The background concentrations of pollutant gases in the vicinity of the plant were used to represent ambient concentrations of pollutants in the atmosphere in the meteorological year of interest. These were obtained from the Department of Environment Food and Rural Affairs (DEFRA) for the UK sites (Table 4).

Table 4: Background concentrations of pollutant gases around the Ferrybridge capture plant for the particular meteorological year studied.

Pollutant	**unit**	**Ferrybridge 2012**
NO_x	µg / m^3	25.1
NO_2	µg / m^3	16.2
NO	µg / m^3	4.61
O_3	µg / m^3	65.0
PM_{10}	µg / m^3	16.9

$PM_{2.5}$	µg / m^3	10.9

Terrain elevation data for Ferrybride was obtained from the UK OS Profile DTM dataset for Ferrybridge. The terrain features for the site are shown in (Figure S2) along with its geographic location.

Emissions of amine and other by-products from the capture facility are in most cases confidential. There are no publicly available amine emissions rates reported for Ferrybridge CCPilot100+ due to confidentiality reasons. However, Fitzgerald *et al.* (2014) reported nitrosamine emissions from Ferrybridge pilot plant to be very low throughout its operation. In October 2013, three individual nitrosamines were characterised with the highest concentration nitrosamine recorded as 10 µg/m^3 and the total as 20 µg/m^3 at process exhaust. Similarly, three months later, three nitrosamines were again identified but with concentrations below 1 µg/m^3. Only one of the reported nitrosamines was identical during the measurements in October and December 2013.

2.4. Worst-case and risk-limit scenario

Usually in the absence of reliable emission rates for amines, a hypothetical worst-case scenario is considered for the plants. The worst-case scenario follows the precautionary principle to avoid risks for the environment and public health in a situation where the data basis (emission totals, chemical kinetics and branching ratios, meteorological variables, etc.) is relatively weak. Since the (original) worst-case scenario (Karl et al., 2011) neglects chemistry, only atmospheric processes that act linearly on the concentration of amines are considered. As a result, predicted air concentrations have a linear dependency on emissions of the amines.

The environmental concentrations of nitrosamines and nitramines resulting from a PCCC process should be within the safety limits proposed by various scientists and regulatory authorities, to keep the risk for human health and the environment at a minimum. Unfortunately, no environmental assessment levels or environmental quality standards for the nitrosamines and nitramines have been enforced in the European Union or in UK until now. For the Technology Centre Mongstad (TCM) capture facility, the Norwegian Climate and Pollution Agency has issued a discharge permit allowing for maximum concentrations of 0.3 ng/m^3 for total nitrosamines and nitramines in the air (at a cancer lifetime risk < 10^{-5}) and 4 ng/L in water in the surrounding environment during its operation (Låg *et al.* 2011). The safety thresholds for TCM may serve as a benchmark since they have been calculated based on the methods used under the EU regulations on registration, evaluation, authorisation and restriction of chemicals (REACH). The safety thresholds for TCM were applied in the present study.

The dispersion results acquired for unity emission, $E_{unit,amine}$, (i.e. 1 g/s) are used to estimate the maximum tolerable emission of amines, $E_{max,\ amine}$ (in g/s) (Karl *et al.* 2011). It is assumed that the emissions are constant throughout each day and throughout the year i.e. no time variation factors are applied to the emission rates. The maximum concentration output, $C_{max,\ amine}$, (i.e. the maximum yearly-averaged ground concentration of the model grid area) at unity emission is scaled until the critical concentration (or safety threshold) of the amine in air (or deposition),

$C_{safe,\ amine}$, is reached. By doing so, the exceedance factor, e, of the emission source strength is acquired:

$$e = \frac{C_{max,amine}}{C_{safe,amine}} \tag{3}$$

If the unity emission is divided by e, then the amine maximum tolerable emission, $E_{max,amine}$, from the PCCC facility with respect to the $C_{safe,amine}$ in air, is obtained:

$$E_{max,amine} = E_{unit,amine} * \frac{C_{safe,amine}}{C_{max,amine}} \tag{4}$$

The maximum tolerable emission, $E_{max,\ amine}$, is calculated as follows:

1. The percentage transformation of the amine to the corresponding nitrosamine and nitramine is calculated at a specific point as follows:

$$\%\ transformation\ of\ amine\ to\ NS + NA = \frac{[NS] + [NA]}{[Amine]} * 100 \tag{5}$$

Where [NS] + [NA] is the maximum total concentration of nitrosamine (NS) and nitramine (NA) in the study domain and [Amine] is the amine concentration at the particular point in the domain where the maximum sum of NS and NA occurs.

2. The $C_{safe,amine}$ in air for the emitted amine is determined as shown:

$$C_{safe,amine} = \left(\frac{C_{safe,\ NS+NA}}{\%\ transformation} * 100\right) \tag{6}$$

where $C_{safe,\ NS+NA}$ in air for nitrosamines and nitramines is around 0.3 ng/m^3 (Låg *et al.* 2011).

3. Hence, after determining $C_{safe,amine}$ and $C_{max,amine}$, of amine at unity emission, Eq 4 for the maximum tolerable emission of the amine, $E_{max,\ amine}$, can be rewritten as:

$$E_{max,amine} = E_{unit,amine} * \frac{C_{safe,amine}}{C_{max,amine}} = E_{unit,amine} * \frac{\left(\frac{C_{safe,\ NS+NA}}{\%\ transformation} * 100\right)}{C_{max,amine}} \tag{7}$$

For Ferrybridge, the dispersion model simulatons for the worst-case scenario were performed assuming that 1 g/s of amine was emitted constantly for one meterological year.

Dispersion calculations with ADMS 5 for the Ferrybridge capture plant was conducted using the outlined worst-case scenario method. The original worst-case scenario (Karl et al., 2011) was designed without taking into account chemical transformation, which ensured that the resulting maximum amine concentration follows a linear dependency on the amine emission rate. In this study, however, in modification of the original worst-case scenario, the degradation of gas-phase amines in the atmosphere was considered. Introducing chemical transformation in the calculation of the maximum tolerable amine emission rates will certainly affect the linearity of the relationship. However, preliminary calculations revealed that despite introducing chemical transformations in the calculation of the maximum tolerable emission rates, the relationship still behaved linear as shown in Figure 4.

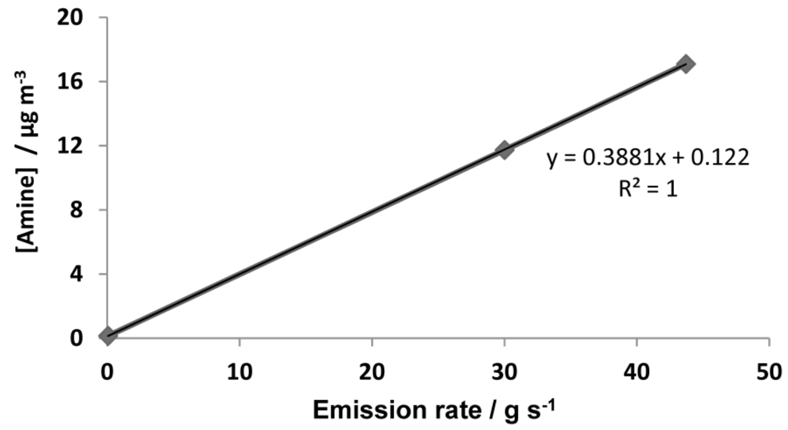


Figure 4: Amine emission rate versus amine concentration for Ferrybridge (2012).

NO_x emissions from the capture plant were considered in the scenario calculations because the production of NA and NS from the parent amine critically depends on the ambient level of NO_x and the ratio of NO to NO_2. 0.49 % of NO_2 in NO_x emissions from the stack was used in all the calculation for Ferrybridge.

Table 5 lists the maximum of the long term averaged concentration of the emitted amine $C_{max,amine}$ calculated according to Eq. (7) at unity emission in the Ferrybridge study domain. The maximum sum of the nitrosamines and nitramines from each of the amine and the amine concentration at that particular point in the grid are shown. The percentage transformation of the amine into its corresponding nitrosamine and nitramine is calculated as well. These results establish the maximum tolerable amine emission rates ($E_{max,amine}$) which are in the next step used for the risk-limit case study. By definition, the application of maximum tolerable emission rates of the three amines will result in nitrosamine and nitramines concentration (as sum from all the three amines) that are below the safety threshold limit, which results in an acceptable risk. Within the range of the acceptable risk the applied amine emission rates are at the maximum, hence, the scenario is referred to as risk-limit case in the remainder of the manuscript.

Table 5: Results from the worst-case simulations. Maximum amine concentrations ($C_{max,amine}$), maximum sum NS and NA concentrations and the amine concentration at the location of the maximum, percentage transformation of the parent amine to NS and NA at the unity emissions for Ferrybridge and their corresponding maximum tolerable amine emission rate estimates ($E_{max,amine}$). Note that $C_{max,amine}$ refers to the maximum yearly-averaged ground air concentration in the model grid area (30 km × 30 km).

PCCC plant	Emitted species	[Amine] (ng m^{-3})	Sum of NS+NA (ng m^{-3})	Transformation of amine to NS+NA (%)	$C_{max,amine}$ (ng m^{-3})	$E_{max,amine}$ (g/s)
Ferrybridge	MA	0.84	7.82x10^{-4}	0.09	2.58	125
	DMA	0.91	7.82x10^{-4}	0.09	2.52	138
	MEA	1.36	4.85x10^{-3}	0.36	4.03	20.8
	NO_x					5.06x10^{2}

2.5. Sensitivity analysis method

A parametric sensitivity analysis was carried out to determine the influence of individual parameters (such as meteorology, background chemistry, rate constants, plant design and operation) on the resulting environmental concentrations of nitrosamines and nitramines. Parametric sensitivity analysis was performed with the risk-limit case scenario for the Ferrybridge plant during 2012 for the three amines. The risk-limit case was defined as the baseline case of this study since the dispersion calculations in the risk-limit case were performed with the basic parameter values before any variation (baseline values).

Table 6 provides an overview of the investigated parameters and their respective value ranges. Each parameter value was doubled and halved compared to its baseline value as listed in Table 6. The considered ranges are assumed to be considerably larger than the presumed uncertainty ranges associated with the parameters.

Meteorological parameters. Meteorological data was taken from the UK Met office and National Oceanic and Atmospheric Administration (NOAA) for Ferrybridge. The meteorological parameters included hourly means of wind speed, wind direction, ambient temperature, precipitation and cloud cover. The effect of meteorology from 2004 to 2013 on the baseline NS and NA concentrations was studied.

Gas-phase kinetic parameters (rate constants and branching ratios). The sensitivity study performed investigates how the concentration of the resulting NS and NA from the three amines is influenced by changing the rate constants describing the chemistry. The respective baseline values and tested values of the rate constants $\boldsymbol{k}_{\mathrm{OH}}$, $\boldsymbol{k}_2$, $\boldsymbol{k}_3$, $\boldsymbol{k}_{\mathbf{4a}}$, $\boldsymbol{k}_{\mathbf{4b}}$, branching ratio ($\boldsymbol{k}_{1a}/\boldsymbol{k}_{\mathrm{OH}}$) and nitrosamine photolysis ratio, $\boldsymbol{J}/\boldsymbol{J}(NO_2)$, for MA, DMA and MEA, respectively, considered in this work were those reported in Manzoor et al., 2015.

Background photochemistry parameters (background concentration of O_3, NO_x/NO_2 ratio). The effect of changing the background concentrations of NO_x, O_3, OH and NO_x/NO_2 ratio was investigated. The background concentrations of NO_x and O_3 in the vicinity of the Ferrybridge plant were used to represent ambient concentrations of pollutants in the atmosphere in the meteorological year of 2012. These baseline values were obtained from the Department of Environment Food and Rural Affairs (DEFRA) for Ferrybridge. The OH concentration was evaluated from modelled $\boldsymbol{J}(NO_2)$ using equations (1) and (2). The NO_x/NO_2 ratio was obtained from the Ferrybridge operators.

Stack and exit flue parameters and NO_x emissions. Plant design parameters such as stack height, stack diameter, stack exit velocity and stack exit gas temperature along with NO_x emissions from the stack are also varied. These baseline values were obtained from the Scottish and Southern Energy operators of the CCPilot 100+ plant in Ferrybridge.

Table 6: The values of the selected model parameters doubled and halved of its true value for consideration in sensitivity analysis conducted on the baseline risk-limit case on Ferrybridge.

	MA			DMA			MEA		
	Halved	**Baseline**	**Doubled**	**Halved**	**Baseline**	**Doubled**	**Halved**	**Baseline**	**Doubled**
k_{OH} / cm^3 molecule^{-1} s^{-1}	1.09×10^{-11}	2.18×10^{-11}	4.36×10^{-11}	3.13×10^{-11}	6.26×10^{-11}	1.25×10^{-10}	4.60×10^{-11}	9.20×10^{-11}	1.84×10^{-10}
k_2	1.82×10^{-18}	3.64×10^{-18}	7.28×10^{-18}	1.82×10^{-18}	3.64×10^{-18}	7.28×10^{-18}	1.25×10^{-16}	2.49×10^{-16}	4.98×10^{-16}
k_3	8.50×10^{-13}	1.70×10^{-12}	3.40×10^{-12}	4.19×10^{-14}	8.37×10^{-14}	1.67×10^{-13}	2.81×10^{-14}	5.62×10^{-14}	1.12×10^{-13}
k_{4a}	4.85×10^{-13}	9.70×10^{-13}	1.94×10^{-12}	1.58×10^{-13}	3.15×10^{-13}	6.30×10^{-13}	4.20×10^{-15}	8.40×10^{-15}	1.68×10^{-14}
k_{4b}	1.01×10^{-13}	2.02×10^{-13}	4.04×10^{-13}	5.50×10^{-15}	1.10×10^{-14}	2.20×10^{-14}	2.07×10^{-15}	4.14×10^{-15}	8.28×10^{-15}
Branching ratio ($??_{1a}/??_{OH}$)	0.175	0.35	0.70	0.19	0.38	0.76	0.025	0.05	0.1
$J/J(NO_2)$	0.265	0.53	1.06	0.62	1.24	2.48	0.29	0.58	1.16
Stack height / m	99	198	396						
Stack diameter / m	4.87	9.74	19.48						
Velocity / m s^{-1}	25	50	100						
Temperature / °C	45	90	180						
O_3 / µg m^{-3}	32.5	65	130						
NO_x	12.55	25.1	50.2						
NO_x/NO_2	0.245	0.49	0.98						
NO_x emissions / µg m^{-3}	8.1	16.2	32.4						
c for OH	1.19×10^{-3}	2.38×10^{-3}	4.75×10^{-3}						

3. Results

3.1 Baseline case

For the baseline case study dispersion calculations were performed with the risk-limit case scenario using the baseline values of the relevant model parameters (Table 6) without any prior variation. Emissions and meteorological year are defined in section 2.3. The atmospheric chemistry of MA, DMA and MEA was introduced in the ADMS 5 model using the rate constants and branching ratios determined by Manzoor *et al.* (2015). In addition to the simulations of the risk-limit case scenario considering amine chemistry, an Inert Dispersion Model (IDM) calculation, in which the emitted amines are treated as inert tracers, has been performed with ADMS 5 for comparison purposes.

3.1.1 Spatial concentration distributions

The model was used to simulate the yearly average concentrations for the amines of interest at the maximum tolerable emission rates. The resulting maximum long-term average concentrations of the target amines and their corresponding nitrosamine (NS) and nitramine (NA) from calculations using the maximum tolerable emission rate of the amines ($E_{max,\ amine}$ in Table 6) are listed in Table 7. Results are in annual average values, which can be used to compare with the safety guideline values.

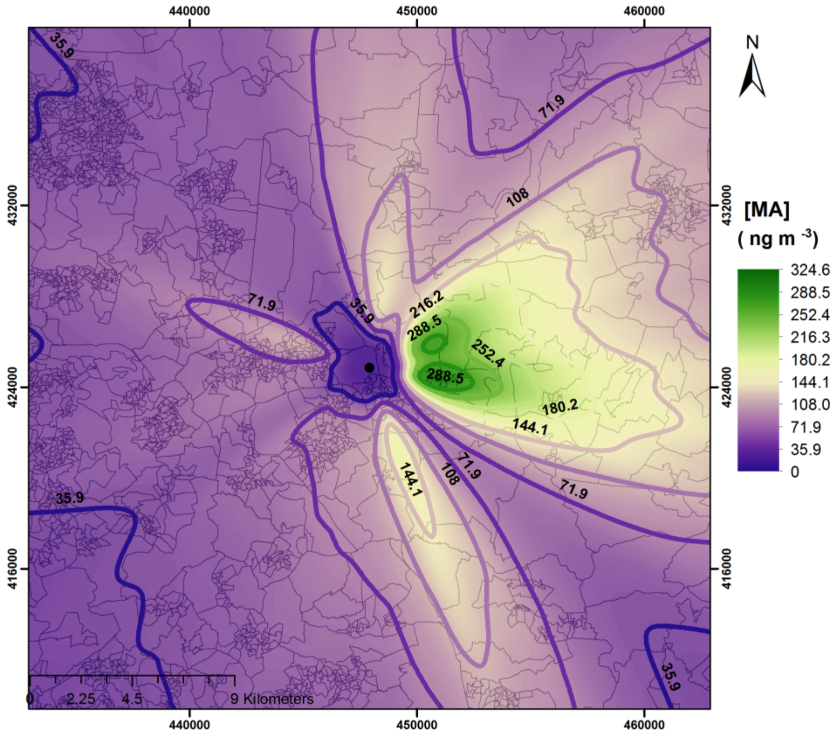
Table 7: Maximum long-term average air concentrations of amines, nitrosamines and nitramines for the risk-limit scenario (baseline case) modelled for each site, where A represents Amine, NS is nitrosamine and NA is nitramine. Concentrations shown in brackets are from Inert Dispersion modeling (IDM) where chemistry is not considered. [A] is reported at the maximum sum of NS and NA location in the study domain.

PCCC	Amine	E_{max} (g/s)	[A] / ng m^{-3}	[NS] / ng m^{-3}	[NA] / ng m^{-3}	[NS+NA] / ng m^{-3}
Ferrybridge	MA	125	323 (327)	0	9.77×10^{-2}	
	DMA	138	348 (361)	2.38×10^{-2}	1.05×10^{-1}	
	MEA	20.8	51.6 (54.4)	9.87×10^{-3}	5.87×10^{-2}	
						0.29

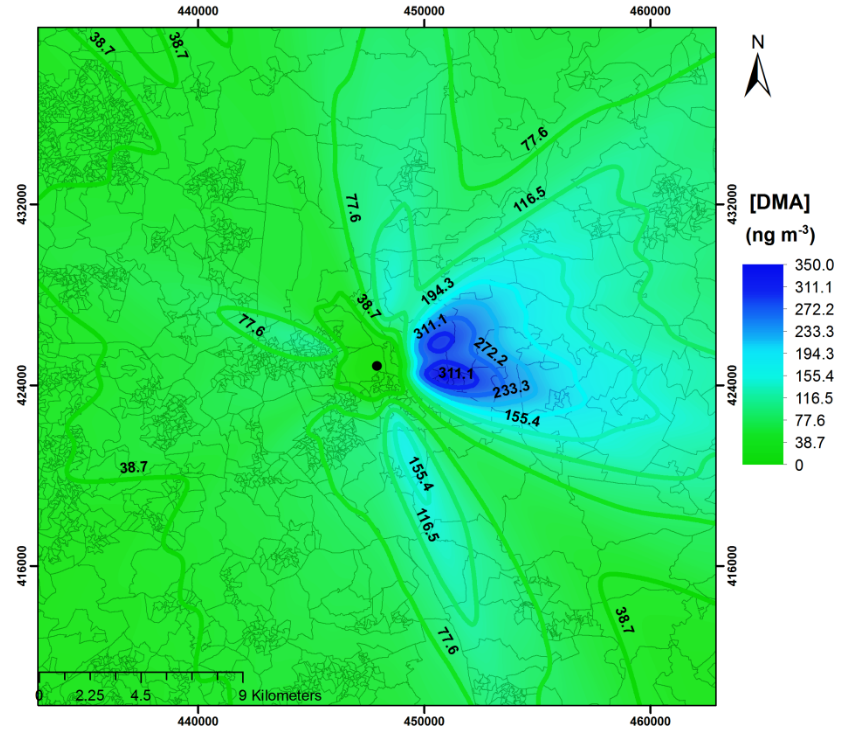
Contour maps illustrating the annual average concentrations of the amine emissions and the total NS and NA from all the three amines (MA, DMA and MEA) for the modelled meteorological year specific to each site, over an area of 900 km^2 centred on Ferrybridge for a grid resolution of 300 m × 300 m are shown in Figure 5 a-d. Highest concentrations of the emitted amines are found in a distance of 2-3 km from the emission source as has been expected due to plume rise and the applied Gaussian plume dispersion scheme. Clearly, a reduction in concentration of the amines with increasing distance from the PCCC plant is found. However, the opposite is true for the total NS and NA concentrations, since they form along the travel path as the amine reacts with the atmospheric oxidants (Figure 5d). Terrain and the local wind field strongly modulate the pattern of dispersion of these species in the atmosphere.

The calculated maximum long term calculated average concentrations for the sum of nitrosamine and nitramine for the worst case modelled on Ferrybridge is 0.29 ng m^{-3}, which is only slightly lower than the critical concentration of 0.3 ng/m^3. The close agreement of the maximum concentrations with the critical concentration confirms the robustness of the worst-case method to derive maximum tolerable amine emissions. The small deviation from the critical concentration is probably due to non-linear effects of the amine chemistry, as discussed in section 2.4 (Figure 4); while the original worst-case did not include degradation of amines in air.

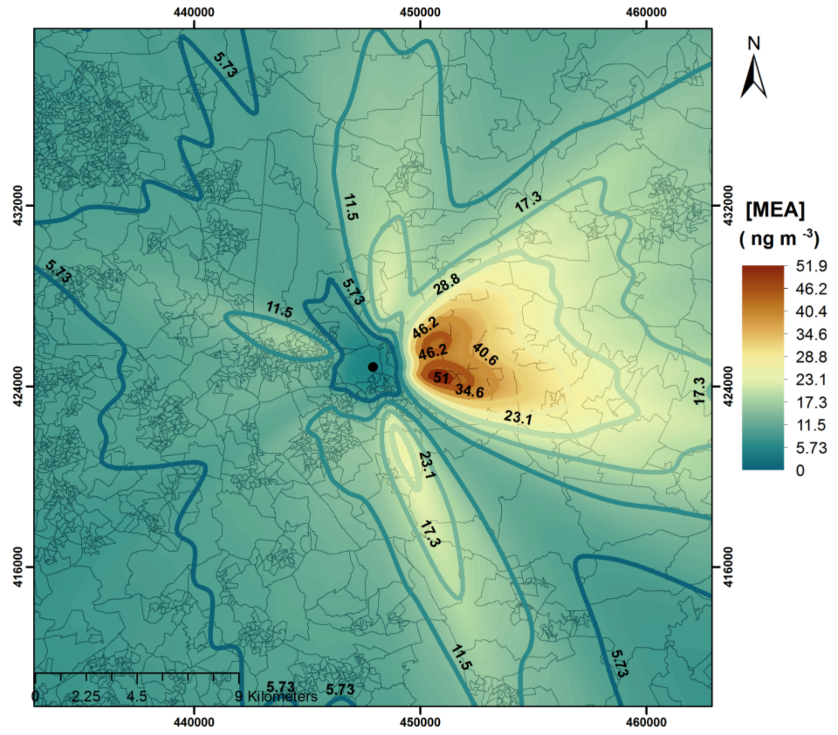
(a)



(b)


440000
450000
460000
432000
424000
416000
N
[DMA]
(ng m-3)
350.0
311.1
272.2
233.3
194.3
155.4
116.5
77.6
38.7
0
0
2.25
4.5
9 Kilometers

(c)


440000
450000
460000
432000
424000
416000
N
[MEA]
(ng m-3)
51.9
46.2
40.4
34.6
28.8
23.1
17.3
11.5
5.73
0
0
2.25
4.5
9 Kilometers

(d)

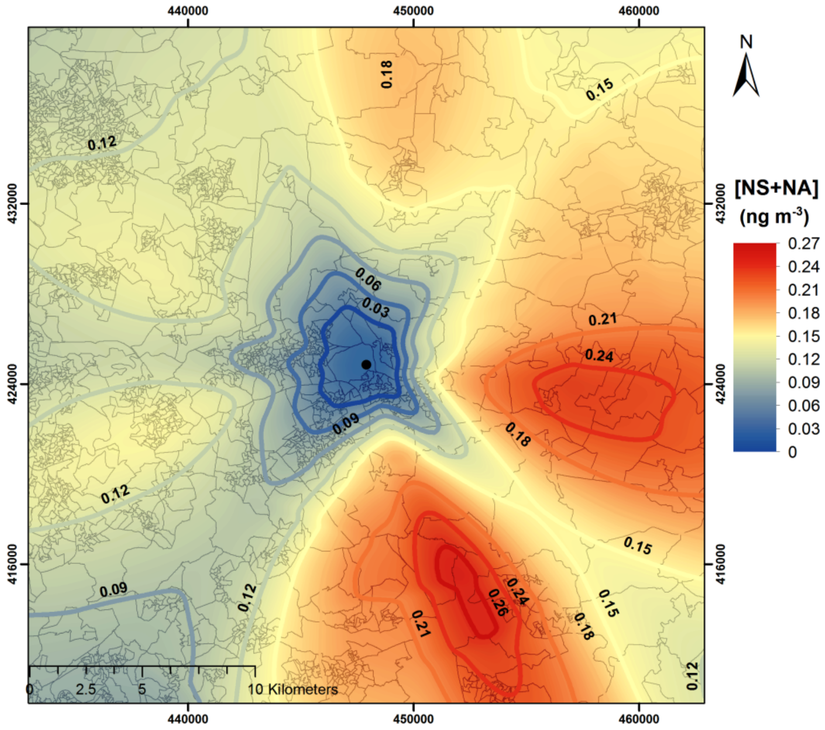


Figure 5: Contoured distributions of maximum annual concentration of amines in air for the risk-limit case in 2008: (a) MA (b) DMA (c) MEA at the amine emission rates reported in Table 7 and (d) the total NS and NA (ng/m^3) resulting from MA, DMA and MEA emissions for Ferrybridge. To estimate a surface from the set of scattered concentration points evaluated at 101 × 101 gridded receptor points over 30 km × 30 km domain centred on Ferrybridge (Figure 2), interpolation using a Krigging approach in Arc-GIS software is employed.

3.1.2 Chemical conversion to nitrosamines and nitramines

For Ferrybridge, the calculated concentration sum of nitrosamines and nitramines of 0.29 ng m^{-3}, based on Table 7, consists of 89 % NA, which is formed from the three parent amines that are MA, DMA and MEA (Figure S3), and of 11 % NS, which is formed from MEA and DMA, but not from MA. NS originates from 29 % of MEA and 71 % DMA, whereas, NA originates from 22 % of MEA, 40% of DMA and 37% of MA.

The higher percentage contribution of NA to the concentration sum is due to the fact that NS undergoes photolysis in the presence of sunlight, leading to its rapid decay in the atmosphere at daytime. Only MEA and DMA contribute to NS. A secondary alkyl amino radical (such as DMA radical) forms a stable nitrosamine that does not further dissociate. The same has been observed for MEA radical, which despite being a primary alkyl amino radical, forms a thermally stable nitrosamine (Manzoor et al., 2015). However, this is not the case for MA radical which forms a primary nitrosamine (represented by the fastest k_3 rate of nitrosamine formation in Table 2), that is highly unstable and dissociates to its corresponding imine (Nielsen et al., 2011a).

The fate of both the stable and unstable nitrosamines from the three amines, is also influenced by photolysis in the presence of sunlight; leading to their rapid decay in the atmosphere at daytime. The secondary nitrosamine, DMA-NO, photolysis fastest (highest ***J*** /s in Table 2) in comparsion to the two other primary nitrosamines. Photolysis of the nitrosamine leads to the amino radical, which, with increasing distance from the plant, rather reacts with NO_2 than with NO due to the greater NO_2/NO farther away from the plant, forming the nitamine. As consequence of this, in comparison to nitrosamines a much higher percentage formation exists for nitramines.

The atmospheric lifetime of nitramines is on the order of one or two days, since its only removal reaction is the thermal reaction with OH to its corresponding imine, which is a rather slow reaction.

There are various factors that can play a role in influencing the production of nitrosamines and nitramines from the parent amines at the location of a PCCC plant. These factors include different meteorological conditions, insolation (availability of sunlight), background concentrations of NO_x and O_3, terrain features, as well as the stack characteristics, considered for a particular modelling study and emitting facility.

3.1.3 Monthly variability of MEA and oxidation products

Additionally, monthly MEA concentrations were obtained from ADMS for every month of the 2012 meteorological year using the maximum tolerable emission rate. Safety limits established in literature indicate that the monthly average concentration of MEA should be below 10 µg/m^3 (Låg *et al.* 2009) in order to prevent health risks for the general public. Therefore, maximum monthly concentrations of MEA and its corresponding NS and NA, for the risk-limit scenario case for each month of the year were modelled to inspect the change in concentrations over time and to determine whether the obtained values exceeded the safety limit. The results for MEA and the degradation products are shown in Table S2. Additionally, Figure 6 a-b, shows the graphical representation of the monthly variation in the MEA and the NS and NA concentrations along with their respective box and whisker plots outlining their respective lowest, lowest quartile, median, upper quartile and highest concentration values.

Figure 6a shows that the monthly concentration for MEA ranges from 37 – 134 ng/m^3 with the maximum occurring in January. The maximum MEA concentration is then observed to decrease from January onwards only to increase in September and decrease afterwards. The box and whisker plot for MEA monthly concentration indicates the lowest (37 ng/m^3), the lowest quartile (52.2 ng/m^3), median (72.3 ng/m^3), upper quartile (89.3 ng/m^3) and highest (134 ng/m^3) values, respectively. An interquartile range of 37.1 ng/m^3 is calculated which shows the spread of the values, whereas, the highest value of 134 ng/m^3 laying outside the box and whisker plot is considered to be an outlier by the analysis.

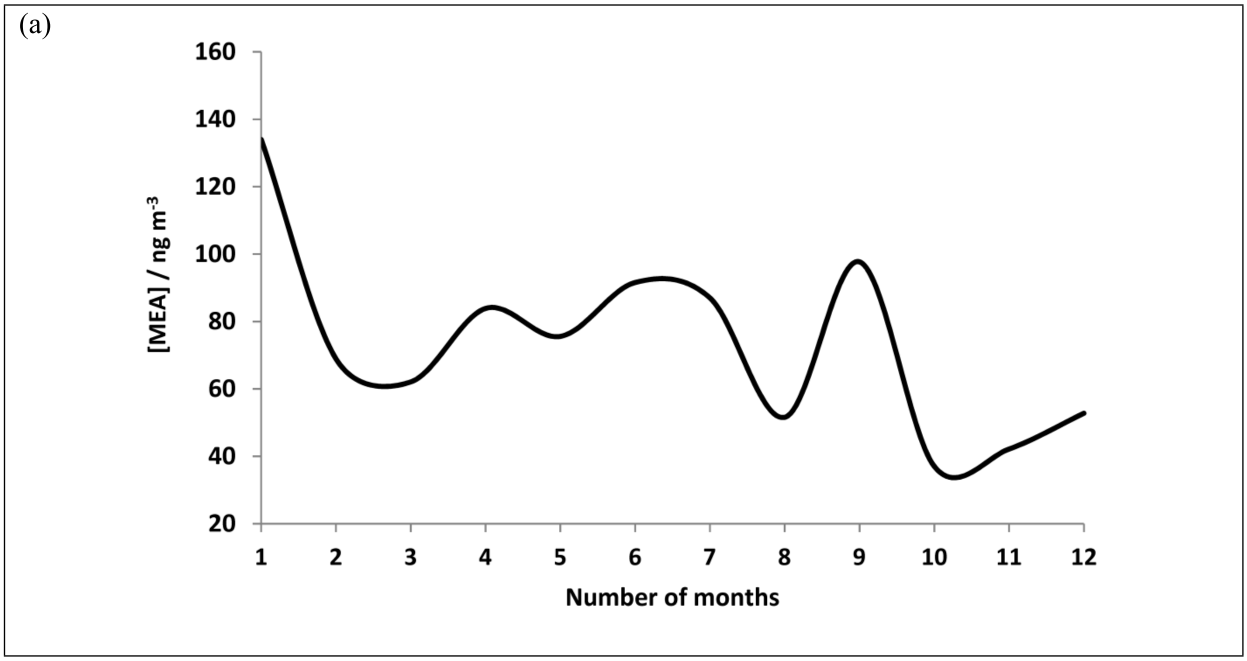
The monthly concentrations for NS and NA resulting from MEA were in the range of 0.02 – 0.22 ng /m^3, with the maximum monthly concentrations occurring in May (Figure 6b). The box and whisker plot for their monthly concentration indicates the lowest (0.02 ng/m^3), the lowest quartile (0.04 ng/m^3), median (0.12 ng/m^3), upper quartile (0.14 ng/m^3) and highest (0.22 ng/m^3)

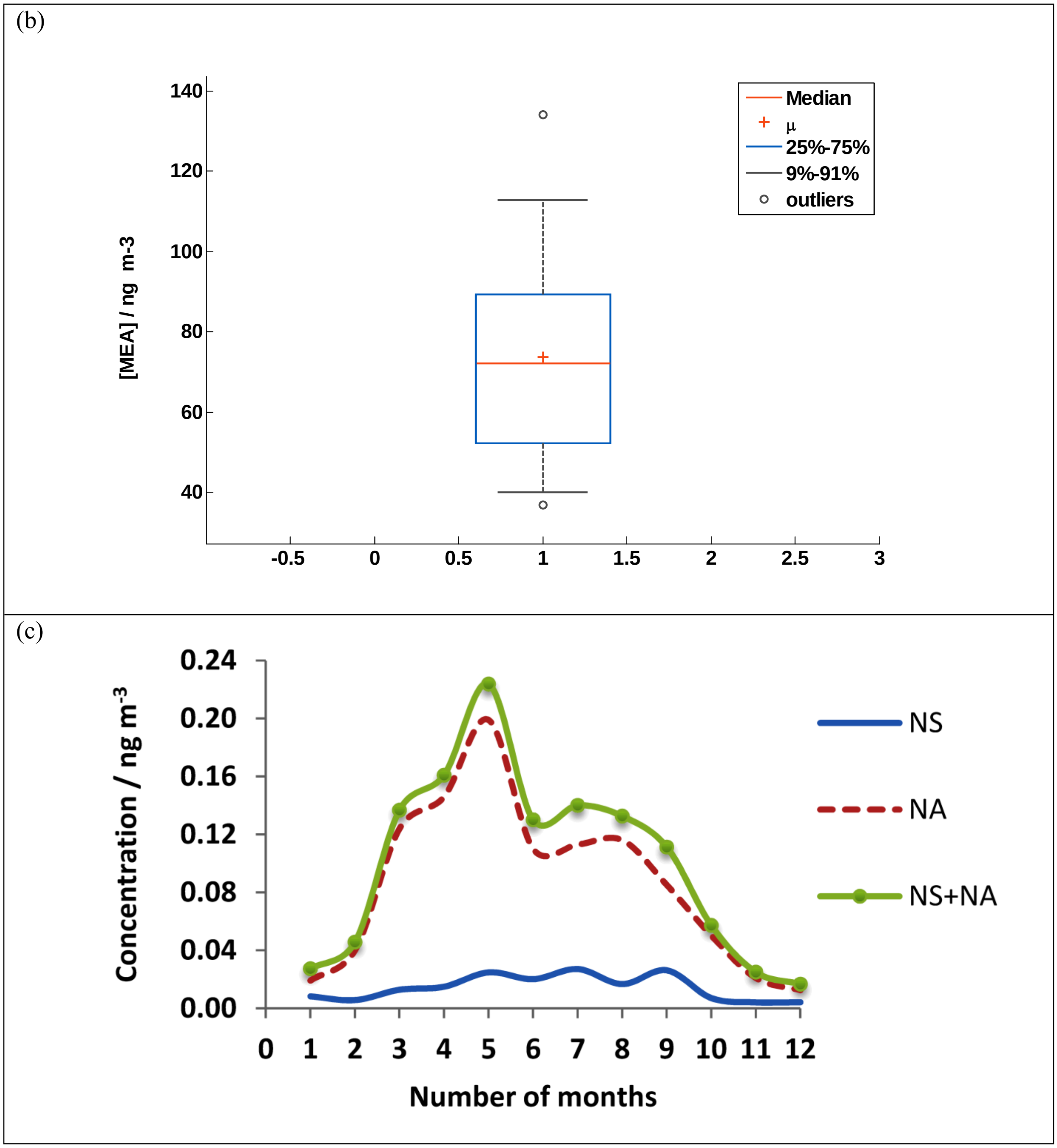
values, respectively. An interquartile range of 0.10 ng/m^3 is calculated and the highest value of 0.22 ng/m^3 is considered as an outlier.

In January when there is little photochemical activity, MEA concentration was highest (134 ng/m^3) and did not form the degradation products; therefore, these had their lowest concentration (0.02 ng/m^3) during this period. Conversely, as the MEA concentration decreased until August, an increase in NS and NA concentration was found. This is in cognisant with the fact that the parent amine determines the fate of its products. The maximum MEA concentration of 134 ng/m^3 (i.e. 0.134 µg/m^3) is 75 times lower than the safety limit of 10 µg/m^3. Hence, no risk is posed to the environment or humans during any of the months of the meteorological year 2012, at Ferrybridge with respect to MEA even at the maximum tolerable emission rate of 20.8 g/s.

The obtained maximum NS and NA concentration of 0.22 ng/m^3 does not exceed the 0.3 ng/m^3 annual average safety limit, in line with the design of the risk-limit case. From Figure 6c, it can be seen that the total sum of NS and NA concentrations is dominated by the nitramines which are relatively stable in the atmosphere.

When comparing NS monthly air concentrations to the monthly average NS concentration safety limit of 0.02 ng/m^3 corresponding to a 10^{-6} lifetime cancer risk, as defined by the U.S: EPA (US EPA, IRIS database: http://www.epa.gov/IRIS/subst/0042.htm last accessed June 2015), this threshold was exceeded in May, July and September by factors of 1.2, 1.4 and 1.3, respectively.




(b)
140
120
100
80
60
40
[MEA] / ng m-3
-0.5
0
0.5
1
1.5
2
2.5
3
Median
μ
25%-75%
9%-91%
outliers
(c)
0.24
0.20
0.16
0.12
0.08
0.04
0.00
Concentration / ng m^{-3}
0
1
2
3
4
5
6
7
8
9
10
11
12
Number of months
NS
NA
NS+NA

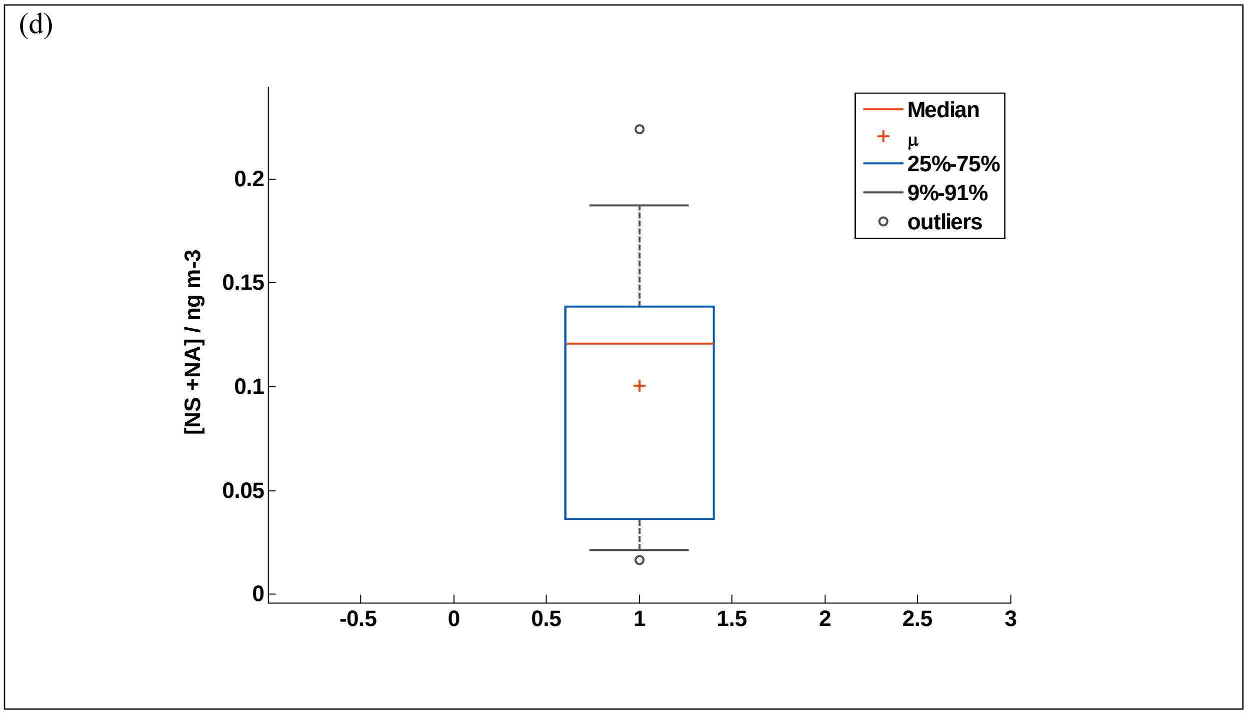


Figure 6: Monthly maximum average concentrations (ng/m^3) for 2012: (a) time series of MEA and (b) a box and whiskers plot showing the lowest (37 ng/m^3), lower quartile (52.2 ng/m^3), median (72.3 ng/m^3), upper quartile (89.3 ng/m^3) and highest value (134 ng/m^3) of the MEA concentration for every month of the year 2012 and (c) time series of NS and NA (d) together with their box and whisker plot showing lowest (0.02ng/m^3), lower quartile (0.04 ng/m^3), median (0.12 ng/m^3), upper quartile (0.14 ng/m^3) and highest value (0.22 ng/m^3) of the sum of NS and NA concentrations resulting from the oxidation of MEA for the sensitivity testing on the risk-limit case on Ferrybridge. See text for more details.

3.2 Sensitivity analysis

3.2.1 Meteorology

To investigate the effect of year-to-year variances on expected concentrations, model runs with meteorological years from 2004 to 2013 were performed for MA, DMA and MEA (Figure 7). The variation of meteorological conditions from year to year can potentially lead to situations where the limit values of the risk-limit case are exceeded, with negative consequences for human health. The meteorological year that gives the highest long-term annual concentration of the sum of NS and NA is 2004, with a risk to the human health. In the years 2010 and 2011, the safety limit value of 0.3 ng m^{-3} is slightly exceeded, by 7% and 3%, respectively. From the results (Table S3), the changes in the maximum concentrations and concentration patterns are apparent but the inter-annual variations are not that significant except from 2004 to 2005.

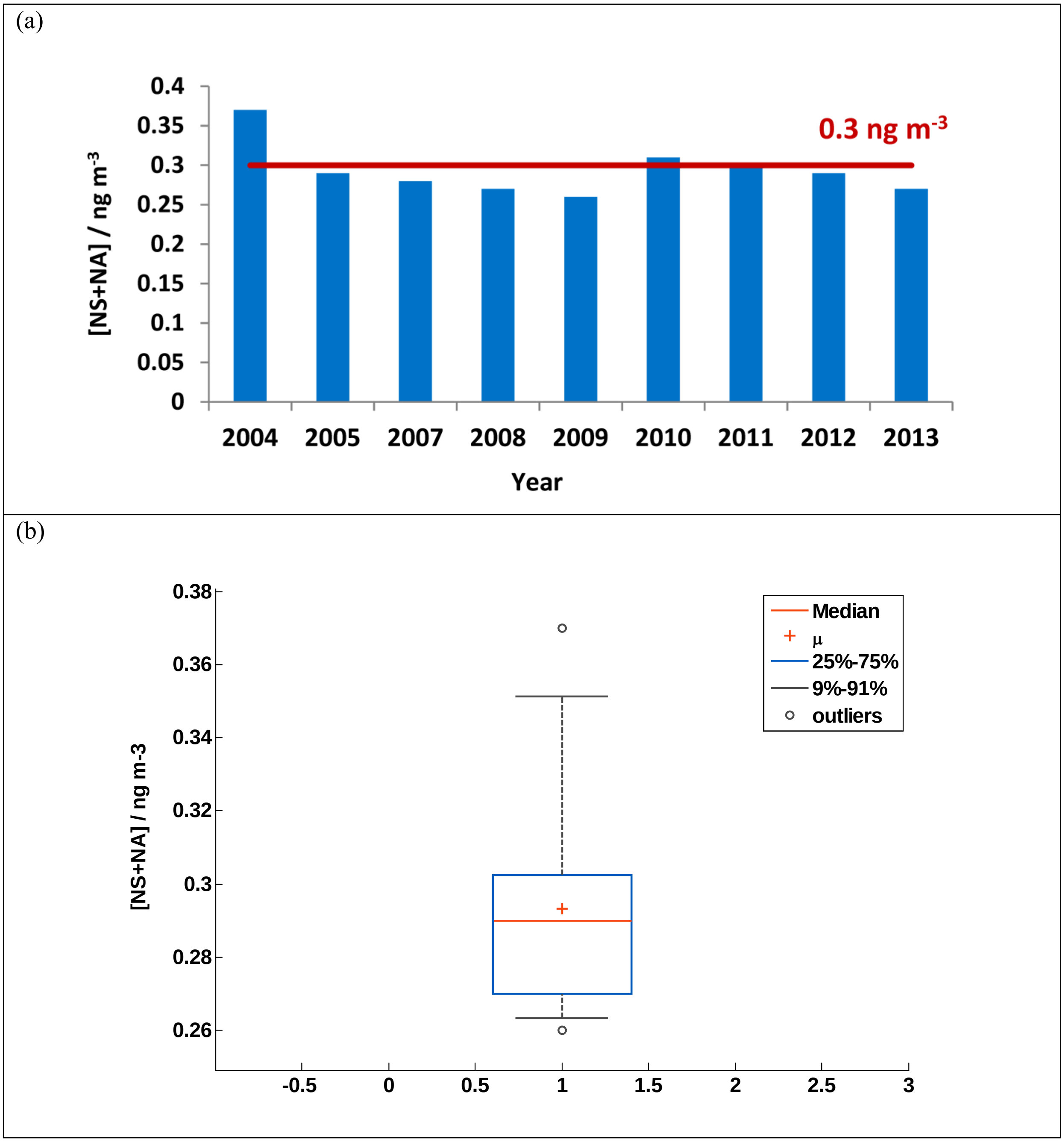


Figure 7: A graphical representation of the sensitivity analysis on the meteorological years from 2004 to 2013 with a box and whiskers plot showing the lowest (0.26 ng/m^3), lower quartile (0.27 ng/m^3), median (0.29 ng/m^3), upper quartile (0.30 ng/m^3) and highest value (0.37 ng/m^3) of the sum of NS and NA concentrations resulting from the three amines for the sensitivity testing on the risk limit scenario on Ferrybridge. One outlier was also obtained at a value 0.37 ng/m^3. The red straight line corresponds to the safety limit of 0.3 ng m^{-3}.

For the meteorological year 2004, the maximum long term annual concentration of the total NS and NA (0.37 ng m^{-3}) is relatively higher than those determined for the rest of the years. This difference could be due to variation of wind speed, wind direction, or cloud cover. The differences between 2004 and the average meteorology of the years 2004-2013 has been inspected in more detail. In Figure 8, the windrose for 2004 is compared to the windrose for the multiannual average. While the 2004-2013 average has a prevailing downwind wind direction towards the southwest (frequency of 49 % for winds towards 190°−240° with wind speed > 3.0 m/s), the year 2004 has a prevailing downwind wind direction towards northwest (frequency of 29 % for winds towards 270°−350° with wind speed > 3.0 m/s). This major change in wind direction in 2004 is responsible for increased dispersion of amine emissions towards the area west of the PCCC plant. More importantly, the histogram of the wind speed distribution was inspected for 2004 and the 2004-2013 average (Figure S4), revealing that 2004 had an exceptional high proportion of situation with calm winds. In 2004 calm situations with wind speed < 1.5 m/s, occurred during 8 % of the time while no occurrence of calm situations (wind speed < 1.5 m/s) were found for the 2004-2013 average.

Calm situations with low or non-existent winds are typically related to stable conditions, most commonly found at night. These conditions prevent the usual plume travel and diffusion out of the region (Stern, 1976). If in addition the plume has insufficient rise, the emitted amines will remain with the region and accumulate. Only large plumes with sufficient buoyancy may rise to higher elevations, where they escape the restricted movement of the calm conditions (Stern, 1976). However, the plumes from carbon capture with amine solvent are usually cold plumes with low buoyancy. Hence, calm situations will be associated with higher ground concentrations of amines and its oxidation products due to accumulation of pollutants in the region around the PCCC facility. By default, ADMS 5 does not model meteorological data for which the wind speed at 10 m is less than 0.75 m/s. Consequently, the effect of calm conditions on modelled nitrosamine and nitramine concentration would be even more pronounced if the treatment of calm conditions (wind speed < 0.75 m/s) was enabled in ADMS 5. The option for specific treatment of calm conditions in ADMS 5 calculates the concentration as a weighted average of a normal Gaussian type plume and a radially symmetric plume, where the weighting depends on the wind speed at 10 m. The radially symmetric plume in this case is modelled as a passive source that has a source height equal to the maximum plume height from the standard plume rise calculations, and assumes equal probability of all wind directions.

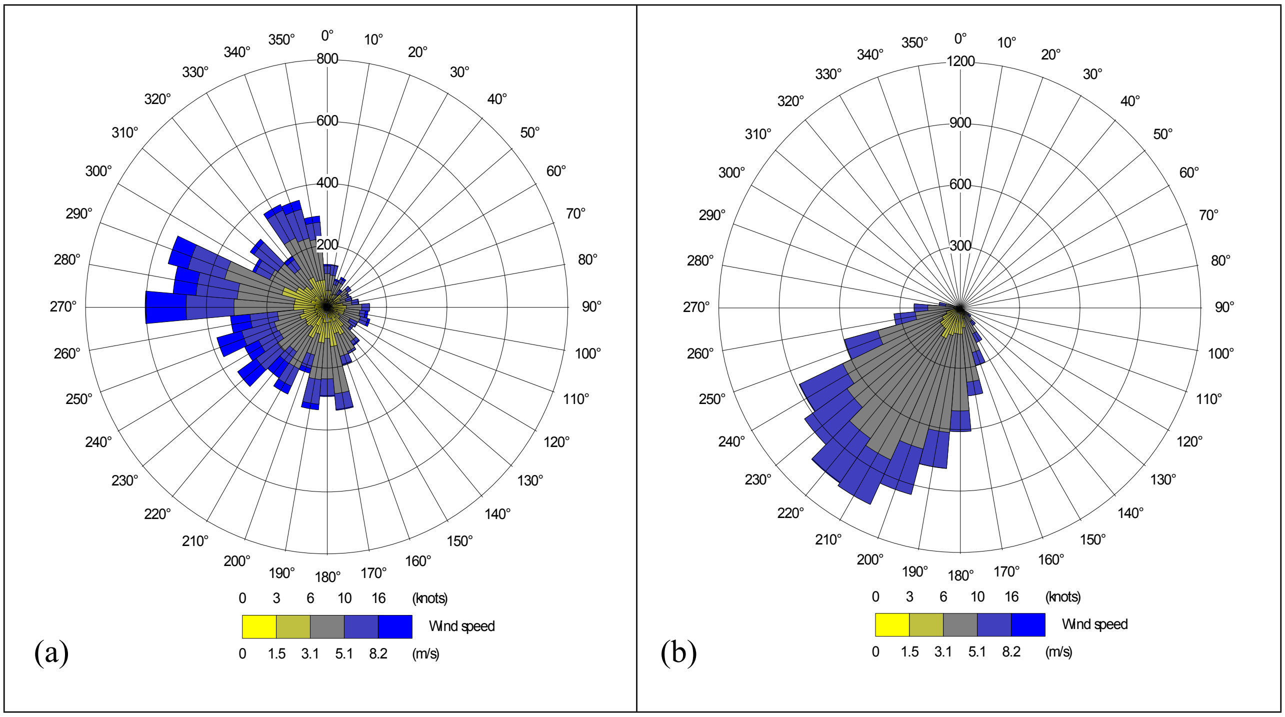


Figure 8: Wind rose plot for depicting the downwind flow vector in m/s for Ferrybridge (a) 2004 and (b) average windrose from all the years. In this polar plot, the angle of an element represents wind direction whereas the radial distance from the centre represents the frequency of wind speed occurrence. The frequency of each wind record is taken as 1 (CERC (2012b)).

3.2.2 Background photochemistry

Changes of the background concentrations of NO_x, O_3, and OH as well as the background air NO_x/NO_2 ratio strongly affected the concentration sum of NS and NA in the study domain of Ferrybridge. Doubling the NO_x/NO_2 ratio caused the baseline case NS and NA concentration to increase by a 3% whereas halving it led to an increase of 1 %. Therefore, it is deduced that varying this parameter has a negligible effect on the final output value. Varying NO_x background concentration affected the concentration of nitrosamines and nitramines by up to 11 %. Changing the concentration of OH radical also affected the baseline case NS and NA concentration. Doubling it, led to an 8 % increase of the baseline value whereas, halving it brought about a 65 % reduction. OH is the precursor to the atmospheric chemistry of the amines and it will therefore influence the fate of the resulting degradation products.

Ozone is a source of OH radicals; therefore, doubling O_3 background concentration increases the rate of amine and OH reaction, resulting in a decrease in the amine concentration. Subsequently, more of the amino radical is formed to react with NO and NO_2 to produce the corresponding nitrosamine and nitramine, exceeding the baseline case value of the total NS and NA by 165 %. Halving O_3 concentration had the opposite effect, resulting in a 59 % reduction. As shown in Fig. 9, the NS and NA concentration sum exhibits an almost linear dependency on the O_3 background concentration.

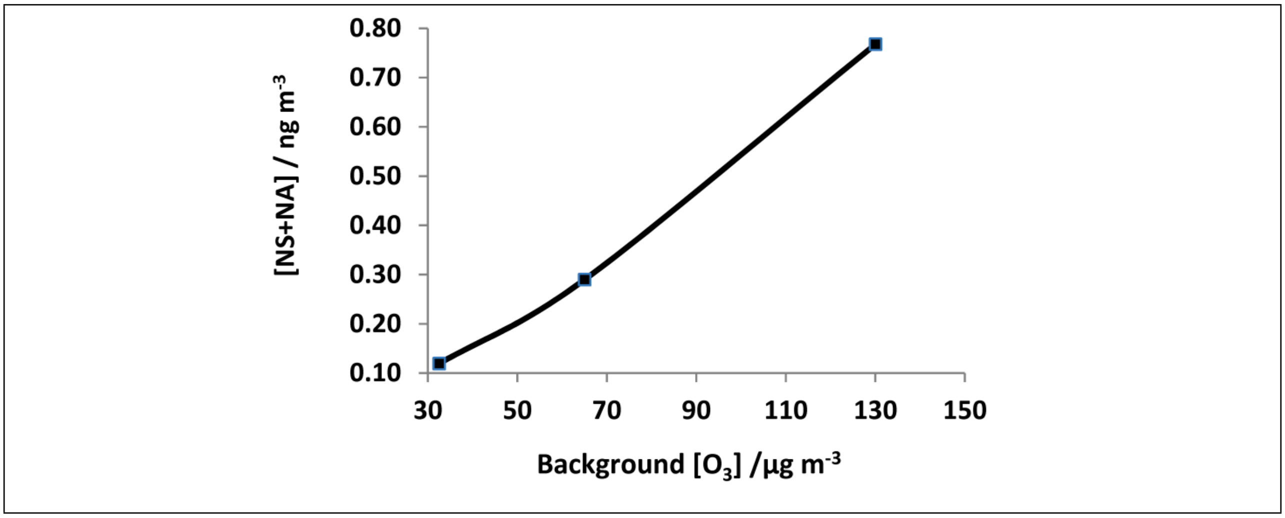


Figure 9: Plot showing a linear dependency of the NS and NA concentrations with $[O_3]$ / µg m^{-3}.

3.2.3 Gas-phase kinetic parameters

Gas-phase kinetic parameters of the amine chemistry reaction scheme, i.e. its reaction rate constants, branching ratios and nitrosamine photolysis rates are parameters associated with high uncertainty and changing them has the potential to affect the concentration sum of NS and NA in the study domain of Ferrybridge. Rate constants describing the amine chemistry and parameters directly related to the amine chemistry were varied up to a factor of 2 to study how these particular parameters influence the fate of the total NS and NA formation from the three parent amines.

The rate constant k_1 determines the rate of the reaction of the amine with OH radical to form the amino radical and water. Therefore, doubling the rate of this reaction causes the amine concentration to decrease as the amine converts to the amino radical. The amino radical which is higher in concentration then reacts with NO and NO_2 to form the nitrosamine and nitramine, resulting in an increase in their concentration which exceeds the baseline case value of 0.29 ng/m^3 by 80 %. Halving k_1 has the opposite effect and reduces the concentration by up to 45 % of the baseline value.

The rate constant k_2 determines the rate of the reaction of the alkyl amino radical with O_2 to form imine. This reaction competes with those forming nitrosamines and nitramines. Therefore, doubling k_2 results in a decrease in the concentrations of nitrosamines and nitramines by up to 45 %, as it causes an increase in the imine concentration. The concentration of the amine is unaffected by this, therefore, it stays the same as the baseline amine concentration. Halving k_2 has the opposite effect and the concentration of the NS and NA exceeds the baseline value by 84 %.

The rate constant k_3 determines the rate of the reaction of the alkyl amino radical with NO to form the nitrosamine. Therefore, doubling k_3 increases the formation of the nitrosamines i.e. its concentration. The concentrations of the amine and nitramine remain unaffected. The overall concentration nevertheless exceeds the baseline value by 8 %. Halving k_3 has the opposite effect, resulting reduction of 2 % of the baseline value.

The rate constant k_4 determines the rate of the reaction of the alkyl amino radical with NO_2 to form the nitramine. Therefore, doubling k_4 increases the formation of the nitramines i.e. its concentration doubles. The concentrations of the amine and nitrosamine are unaffected by this. Halving k_4 has the opposite effect. However, in both the cases the total NS and NA concentrations remain much below baseline value i.e. by 43 and 5 %.

The ratio J/J_{NO2} determines the rate of photolysis of the nitrosamine. Therefore, doubling it increases this rate and results in a decrease in the concentration of the nitrosamine. The concentrations of the amine and nitramine remain unaffected. The total NS and NA concentration is 2 % lower than the baseline value. Halving J/J_{NO2} has the opposite effect, resulting in an increase of 5 % of the baseline.

Doubling the branching ratio ($k_{1\mathrm{a}}/k_{\mathrm{OH}}$) causes a higher fraction of the amino radical to be formed, which subsequently reacts with NO and NO_2, resulting in the production of nitrosamine and nitramine exceeding the baseline value by 36 %. Halving the branching ratio has the opposite effect and the resulting concentration is 49 % lower than the baseline value.

Hence, it is found that increasing k_1, k_3, k_4 and branching ratio ($k_{1\mathrm{a}}/k_{\mathrm{OH}}$) values, and, reducing k_2 and J/J_{NO2} values, will overall lead to an increase in the NS and NA concentrations. Yet, the most influential kinetic parameters in determining the fate of the NS and NA are k_1, k_2 and branching ratio ($k_{1\mathrm{a}}/k_{\mathrm{OH}}$), affecting the concentration total NS and NA by up to 80, 84 and 49 %, respectively.

3.2.4 Plant design and operation

In this part of the sensitivity analysis, the influence of the design of the PCCC plant and the properties of the flue gas exit was studied. The amount of NO_x emissions from the plant stack are also seen as a design component since they can be reduced by installation of emission reduction devices.

With an increase in temperature of the exit flue gas, the density of the exhaust gas is decreased which causes them to be lifted to upper layers of the atmospheric boundary layer, consequently reducing ground level concentrations. Additionally, the involved chemical reactions are exothermic reactions and therefore doubling the temperature (from baseline temperature), shift the reaction to the reactants, decreasing the concentration of the nitrosamines and nitramines by 35% of the baseline value. Halving the temperature, results in an increase of 4% of the NS and NA concentration in comparison to the baseline value. Doubling the velocity of the exit flue gas results in a decrease of NS and NA concentration by 20% of the baseline value, whereas, upon considering half the value of the velocity, the resulting concentrations rises by 32%.

Doubling the stack height, results in a decrease in total NS and NA concentration by 42 % of the baseline value. The decrease in the concentration suggests that the NS and NA can disperse farther from the source, therefore, having a reduced effect on the environment. An increase in total NS and NA concentration by 58 % is observed with halving the stack height, suggesting that the emissions cannot disperse further from the source as well as go to the upper layers of the atmospheric boundary. A power law dependence of the NS and NA concentration on the stack height is observed, as illustrated in Figure 10a. The same power law dependence of the total NS and NA concentration with stack height was observed when the simulations were performed with a one-dimensional Gaussian plume model for neutral stability (Figure 10 b).

The same relationship extends to the total NS and NA concentration with stack diameter, where doubling the diameter causes the total NS and NA concentration to increase by 45 % of the baseline and halving this parameter causes a decrease by 51 %.

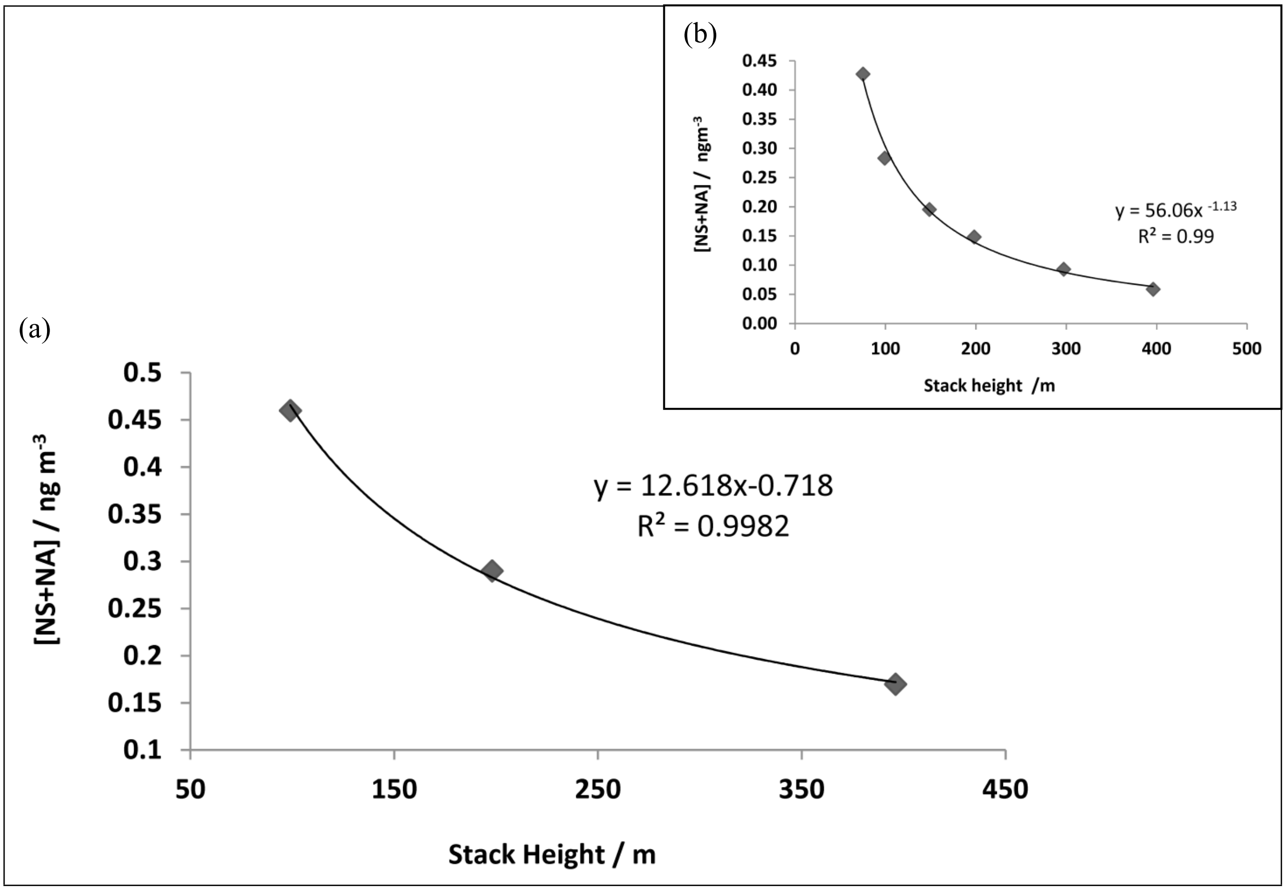


Figure 10: Plots showing a power law dependency of the NS and NA concentrations with (a) stack height from ADMS model results, which is further confirmed from (b) results a one-dimensional Gaussian plume model for neutral stability in flat terrain at an average wind speed of 4 m/s.

NO_x emission at the stack comprises around 99.5 % of NO, which is a component of NO_x that leads to the formation of nitrosamine. Therefore, doubling the NO_x emissions results in an increase in the formation of the nitrosamine and subsequently a decrease in the nitramine concentration owing to the fact that there is more NO to compete with NO_2, for the amino radical. Overall it results in a decrease of the baseline value by 9 %. Halving NO_x decreases the concentration of the nitrosamine, causing the baseline value to increase by 8%.

3.2.5 Summary

The total maximum NS and NA concentrations from all the three amines for the baseline case is a value of 0.29 ng/m^3, which is shown along with the results from the sensitivity tests, are summarized in Table 8. A graphical representation of the sensitivity analysis on the most influential parameters is presented in Figure 11a. A box and whisper plot is illustrated in Fig. 11b, outlining the lowest (0.1 ng/m^3), lower quartile (0.23 ng/m^3), median (0.29 ng/m^3), upper quartile (0.31 ng/m^3) and highest value (0.77 ng/m^3) of the sum of NS and NA concentrations resulting from the three amines for the sensitivity testing on the risk-limit case scenario on Ferrybridge.

Table 8: Sensitivity analysis for different model parameters: Maximum long term average concentrations of the total NS and NA from the three amines at the maximum tolerable emissions from Ferrybridge.

Variation	**Baseline value**	k_1 doubled	k_1 halved	Branching ratio doubled	Branching ratio halved
NS+NA (ng m^{-3})	**0.29**	0.52	0.16	0.39	0.15
k_2 doubled	k_2 halved	k_3 doubled	k_3 halved	k_{4a} halved	k_{4b} doubled
0.16	0.53	0.31	0.28	0.16	0.28
J / J (NO_2) doubled	J / J (NO_2) halved	NO_x/NO_2 doubled	NO_x/NO_2 halved	NO_x emissions doubled	NO_x emissions halved
0.28	0.30	0.30	0.29	0.26	0.31
Stack exit temperature doubled	Stack exit temperature halved	Stack exit velocity doubled	Stack exit velocity halved	Stack height doubled	Stack height halved
0.19	0.30	0.23	0.38	0.17	0.46
Stack diameter doubled	Stack diameter halved	Background O_3 doubled	Background O_3 halved	Background NO_x doubled	[OH] doubled
0.16	0.44	0.77	0.12	0.26	0.31
[OH] halved		Met 04	Met 05	Met 07	Met 08
0.10		0.37	0.29	0.28	0.27
Met 09	Met 10	Met 11	Met 13		
0.26	0.31	0.30	0.27		

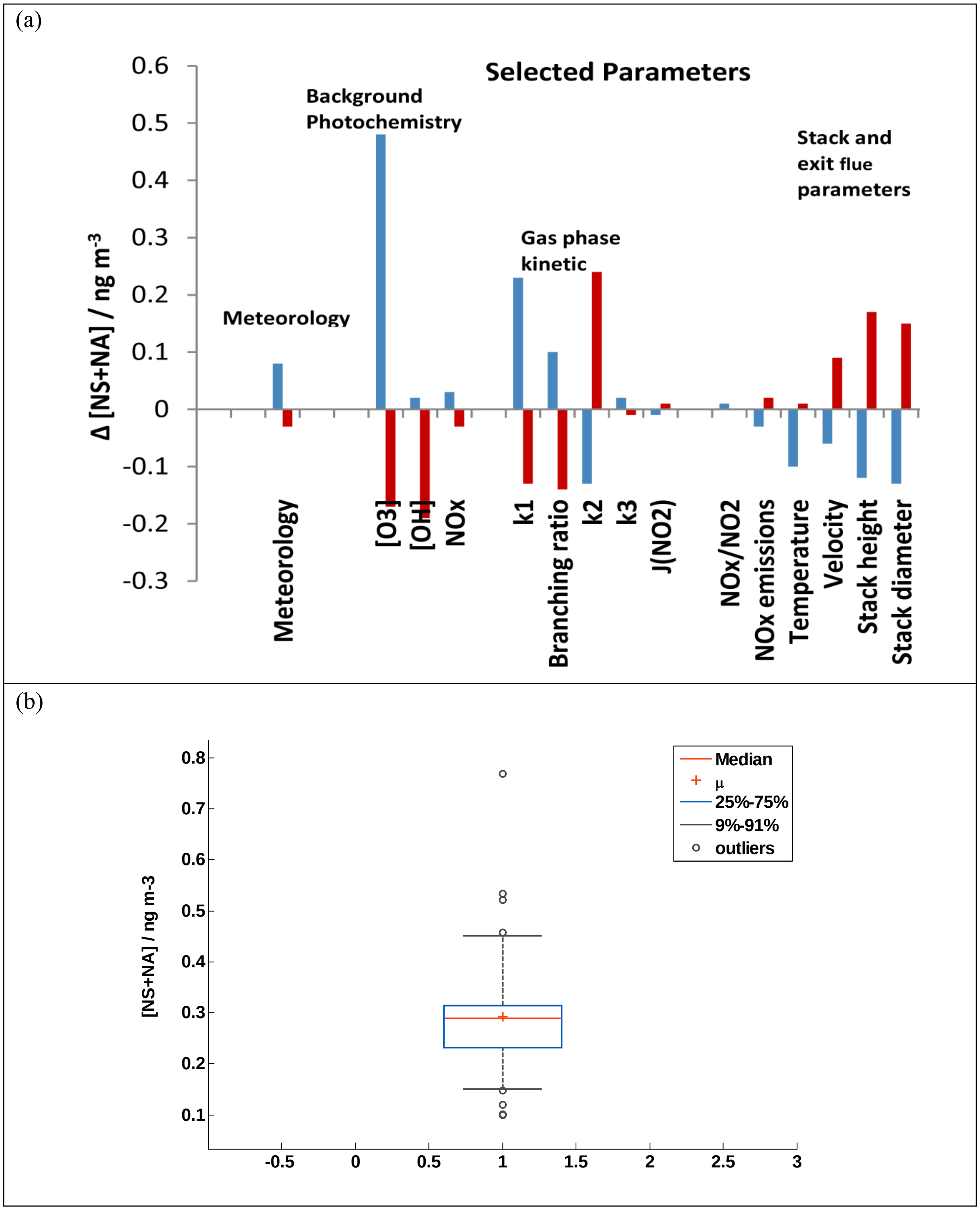


Figure 11: (a) A graphical representation of the sensitivity analysis on parameters selected from meteorology, background photochemistry, gas phase kinetic parameters, stack and exit flue parameters, associated with high uncertainty (b) along with a box and whiskers plot showing the lowest (0.1 ng/m^3), lower quartile (0.23 ng/m^3), median (0.29 ng/m^3), upper quartile (0.31 ng/m^3) and highest value (0.77 ng/m^3) of the sum of NS and NA concentrations resulting

from the three amines for the sensitivity testing on the risk limit scenario on Ferrybridge. Five outliers were also obtained at values 0.10, 0.46, 0.52, 0.53 and 0.77 ng/m^3.

Figure 11a, shows the change in nitrosamine and nitramine concentration as a range of selected parameters varied by up to a factor of 2. The selected parameters represent the variability of meteorology, the variability of background photochemistry, the uncertainty of gas phase kinetic parameters and controlling parameters of the plant design and operation.

The sensitivity of the baseline NS+NA concentration to the inter-annual variability of meteorology was observed to change between +28 % and -10 %. Overall, the parameter that most influences that fate of NS and NA, is the background concentration of ozone, since, it acts as the main source of OH radicals. This suggests that an increase in O_3 concentration leads to an increase in OH concentrations. Reaction of OH radicals with amine forms the amino radical which in turn reacts with NO and NO_2 to produce the corresponding NS and NA. Varying O_3 by a factor of two caused the baseline NS+NA concentration to change between +165 % and – 59 %.

Many parameters of the amine gas-phase oxidation scheme are associated with high uncertainty. Varying the gas-phase kinetic parameters influences the entire chemistry scheme and thus the production of nitrosamines and nitramines. Increasing the rate constant values of k_1, k_3, k_4 and the branching ratio value of ($\boldsymbol{k}_{1a}/\boldsymbol{k}_{OH}$), or on the other hand, reducing the values of k_2 or J/J_{NO2}, causes an increase in the formation of NS and NA. With respect to gas-phase kinetic parameters, the fate of the NS and NA was shown to be most sensitive to changes of k_2 and k_1, which increased the total NS and NA concentration by up to +84 and +80 % respectively and decreased by - 45 %.

Changes of the stack height, stack diameter, stack exit flue gas velocity and stack exit flue gas temperature affect plume rise. Hence, affecting the injection height of the amines, results in a change of the dispersion pattern and of the location and magnitude of the maximum annual average concentrations of amines and the corresponding nitrosamine and nitramine in ground air. Increasing the mentioned stack parameters and exit flue gas parameters causes a decrease in concentrations, indicating that the emitted amines can disperse farther from the source and due to dilution of their concentration in air, have a reduced adverse effect on the environment. Decreasing the mentioned parameters causes an increase in the concentration of these species; suggesting that the distance of dispersion of amine emissions is comparatively shorter, and the maximum ground air concentration is closer to the PCCC plant. The single most significant factor in determining dispersion is the stack height; varying it by a factor of two leads to a change of the baseline case maximum concentration sum of nitrosamines and nitramines between –42 % and +58 %. On the other hand, reducing the amount of NO_x emissions or changing the ratio NO_x/NO_2 in the emissions to air from the PCCC plant, within a factor of two, has a marginal influence on the maximum concentration sum.

4. Discussion

In this study, chemical transformation reactions of the amines were considered along with the dispersion and deposition processes in the atmosphere using an air dispersion model, ADMS 5. By doing so, it was possible to determine the fate of these amine emissions in time and space within 30 km distance from the emitting PCCC facility. The methodology developed in this work combines the estimation of reliable reaction rates derived from quantum chemistry and kinetic modelling (as the theoretical values are within experimental accuracy as discussed in Manzoor *et al.* (2015)) with chemical transport modelling. This allows to consider the entire atmospheric fate of the involved amines including their growth and decay in a given study area. This results in more accurate estimation of amine and amine degradation product concentrations over time and space. The methodology can be applied to any amines used in CO_2 capture as it is independent from experimental parameters. It is expected that application of this approach provides valuable input to studies assessing the environmental and human health risks associated with amine emissions from any PCCC facility irrespective of its geographic location and size.

4.1. Critical evaluation of ADMS model results

For the inert dispersion model (IDM) approach, where chemistry is not considered, the emitted amines are only dispersed and removed by deposition. With respect to such a method, i.e. the dispersion of a passive tracer, in dispersion models like AMDS 5, the models have then been validated with measurement data in tracer experiments by CERC (see http://www.cerc.co.uk/environmental-software/model-validation.html). Therefore, the dispersion of pollutants in ADMS 5 has been regarded as being validated with respect to observations. Modelled amine concentrations from reactive dispersion simulations were compared against results from the IDM implementation in ADMS 5 to determine the influence of photo-chemical degradation on the dispersion of amines and their oxidation products. It was found that for the risk-limit case for Ferrybridge, modelled annual average concentrations (at the location of the maximum) were 17.4, 3.68 and 31.6 ng m^{-3} for MA, DMA and MEA, respectively, in the IDM simulation. These concentrations are 1, 4 and 5 % higher for MA, DMA and MEA, respectively, compared to the reactive dispersion simulation. Overall the comparison indicates that chemical transformation has only a small influence on the average amine concentrations in the surroundings of a PCCC plant (at least in Northern Europe), in agreement with the health risk assessment study by Karl et al. (2015). In other words, dilution of the emitted amines due to atmospheric turbulence and advection changes the average amine concentration much faster than chemical reaction with the OH radical.

From the Table 9 below, the percentage production yield nitrosamines and nitramines from MEA-oxidation at Ferrybridge is 2 %. The percentage production yield of MEA-nitramine from MEA-oxidation is 2 %. This is 10 times higher than the 0.1% reported for Mongstad by Karl et al. (2015), using very detailed MEA chemistry in a simulation with WRF-Chem, but comparable to the value of 0.87 % given by Karl et al. (2014) based on the coupled WRF-EMEP model. The difference can be attributed to various factors such as different chemical schemes, meteorological years, background NO_x and NO_x emissions, background O_3, OH concentrations, as well as model domain and resolution.

Table 9. A comparison of the percentage production yields of NS and NA from MEA-oxidation at the risk-limit case emissions at Ferrybridge.

PCCC plant	Emitted species	$[\text{Amine}]_{\text{reacted}}$ $=[\text{Amine}]_{\text{IDM}}$ – $[\text{Amine}]_{\text{reactive}}$ (ng m^{-3})	Sum of NS+NA (ng m^{-3})	Production yield NS+NA (%)	Production yield of MEA-nitramine (%)
Ferrybridge	MEA	2.8	6.86×10^{-2}	2	2

While the comparison with the IDM approach is useful to evaluate the relative importance of the chemical transformation of amines and to determine the production yield in the amine oxidation, it cannot be used to validate modelled nitrosamine and nitramine concentrations. However, obtaining reliable concentration sums of NS and NA within the area affected by the amine emissions around a facility is vital to establish a realistic assessment of the related human health risk.

One part of the model validation is the check of the mass balance consistency as a possibility to check the plausibility of the model results. That means that the total amount of losses through all processes (chemistry, deposition, advection and turbulent transport out of the study domain) should be equal to the total amount of emission of the amine.

The mass balance consistency for the purposes of this work was analysed using the IDM simulation run for MEA emission at the risk-limit case for Ferrybridge and the MEA reactive dispersion simulation run. The total NS and NA annual average concentration at all the grid points was 0.31μg/m^3. To perform a mass balance consistency check a theoretical sum of NS and NA was calculated using the equation below based on the amine chemistry defined in Table 1 and rate constant parameters in Table 2 (converted to ppb^{-1} s^{-1}). In order to maintain the mass balance, the difference between the modelled concentrations from the inert MEA run, $[\text{MEA}_{\text{IDM}}]$ and the reactive chemistry and dispersion run, [MEA r_{eactive}] multiplied by the branching ratio of the formation of NS and NA must equal the theoretical sum of NS and NA produced from MEA, according to:

$$[\text{NS} + \text{NA}] = ([\text{MEA}_{\text{IDM}}] - [\text{MEA}_{\text{reactive}}]) \times \frac{k_{1a}/k_{\text{OH}} + k_{4a}[\text{NO}_2] + k_3[\text{NO}]}{k_2[\text{NO}_2] + k_3[\text{NO}] + (k_{4a} + k_{4b})[\text{NO}_2]} \tag{8}$$

where, $k_2 = 2.2 \times 10^{-9}$ ppb^{-1} s^{-1}, $k_3 = 1.46 \times 10^{-3}$ ppb^{-1} s^{-1}, $k_{4a} = 1.24 \times 10^{-3}$ ppb^{-1} s^{-1}..

Using the RHS of Equation (8), the total theoretical sum of NS and NA over all the grid points in the study domain was calculated to be 0.31μg/m^3. The obtained value is exactly the same as that obtained for model run with MEA chemistry and dispersion, hence, it is confirmed that the mass is conserved in these model calculations.

4.2. Limitations of the risk-limit method

Due to lack of reliable published emission data from PCCC technology a risk-limit scenario was simulated. Hence, the obtained results refer to a hypothetical case. Furthermore, no ambient measurements exist to which modelled concentrations can be compared, for the purpose of verification. In addition to issues with confidentiality of the specific amine blend used in the PCCC facility, ambient measurements are also hampered by numerous practical challenges when measuring concentrations of nitrosamines and nitramines on the order of pg/m^3 levels around an emitting facility, close to the detection levels of the analytical instruments. Only few studies reported measurements of environmental concentrations of MEA. Measured concentration values of MEA in air, collected on a weekly base, were below 0.01 ng m^{-3} around Mongstad before start of the operation of the TCM plant (Tønnesen 2011). Poste *et al.* (2014) measured MEA concentrations of 0.2 – 1.86 µg L^{-1} in the water of Norwegian lakes.

The remaining uncertainty of the modelling is in the dry and wet deposition of amines and the other emitted compounds. There have been no experimental investigations of the deposition rates. However, the uncertainty due to deposition can be quantified and it would still be possible to come up with a concentration range (lower and upper limit), which could in principle be compared, to measurements. In the risk-limit scenario, yearly averages for the health impacts are mainly considered. Therefore, a measurement series covering one year or at least some parts of the year would be needed.

In the absence of reliable emission data on amines, risk-limit scenario cases were created such that the discharge of amines from the PCCC had the highest rate for which the risk was still acceptable with respect to the health of the general public and the local environment. However, for a complete environmental risk assessment, detailed and reliable emission data for PCCC plants is essential. Such data is the basis for developing accurate risk assessment as it provides the necessary atmospheric input quantity which can then be assessed for the environmental fate processes.

There is an immediate need to perform field experiments to measure the ambient concentrations of the products of interest such as amines, NS and NA in the study domain around the emitting facility. The experimental data can be used to validate the results from modelling studies. This will increase the confidence in using modelling results for drawing conclusions with regards to the maximum tolerable emissions of amines and the corresponding degradation products from PCCC plants.

4.3. Transfer to other geographic locations

Sensitivity studies were performed on parameters selected from meteorology, background photochemistry, gas phase kinetic parameters, stack and exit flue parameters, to determine which of these significantly influenced the fate of the resulting NS and NA from the PCCC process. The parameters were varied by 100 % of the true value to see if the atmospheric chemistry and dispersion processes behaved as expected. The considered ranges are assumed to be considerably larger in comparison to the uncertainty ranges associated with the selected parameters.

Fundamentally, from the sensitivity study it was deduced that the NS and NA concentrations exhibited power law dependence dependency on stack height and stack diameter, whereas, there was a linear dependency with O_3 background concentration. Plume velocity, plume temperature, background photochemistry parameters such as, OH and NO_x concentrations also influence the fate of the total NS and NA from the three amines. However, the relationship between these parameters and the concentrations shows a more complex and non-linear dependence. Overall, the sensitivity study uncovered the factors, which need to be taken into account in the plant design phase and later on during operation to keep the amount of the amine degradation products as small as possible.

The knowledge gained from the sensitivity testing on the base line case study on Ferrybridge can be generalised in terms of gas phase kinetic parameters (for the same atmospheric amine chemistry scheme) and background photochemistry (linear dependency of NS and NA concentration on background ozone), but to a lesser extent in terms of inter-annual variability of meteorology (site specific) and plant design parameters. The found power law dependency for stack height and stack diameter is to a certain degree site-specific, depending on terrain variability as well as on insolation (sunlight) and the prevailing atmospheric stability.

5. Conclusions

In conclusion, the outcome from this work strongly supports that the developed methodology is reliable in influencing and controlling the environmental concentrations of the amine emissions and their corresponding products such as, NS and NA through optimised plant design and operating conditions. In plant design, the parameters that can be controlled are stack height and diameter, which individually influence the total NS and NA baseline concentrations from +58 % to -42 %. Other plant operation parameters such as, exit flue gas temperature and velocity can also be controlled as they can influence the total NS and NA baseline concentrations from +32 % to -35%. On the other hand are the parameters that cannot be controlled, such as the site specific background meteorology, background photochemistry and gas phase kinetic parameters. Meteorology, i.e. mainly wind speed and wind flow field, affected the total NS and NA baseline concentrations from +28 % to -10 %. Background photochemistry from +165 % -65 %, of which O_3 and OH were the key parameters. Gas phase kinetic parameters from 84 % to -49 %, of which $k_2$and $(\boldsymbol{k}_{1a}/\boldsymbol{k}_{OH})$ were influential parameters.

The assessment of the atmospheric fate of these crucial substances and their associated risk to the human health and the environment remains a key area to address for the large-scale carbon capture and storage implementation. Henceforth, it is important to take account of the most influential parameters during the design and consent phase of potential industrial applications. The developed method in this work can in fact be used to propose ideal plant parameters with respect to its design. Therefore, if a PCCC plant is carefully planned, placed and operated, the risk associated with employing amines for capturing CO_2 emissions can be reduced to a minimum.

Commercial scale implementation of the PCCC technology using amine solvents is not as extensive because is in its early stages. The world's first commercial scale PCCC the installation has been to a current Boundary Dam power station in Canada, which began operation in October 2014. It is essential to make sure that the PCCC process is associated with an overall positive human health and environmental impact. Therefore, with the developed methodology in this work, one can ensure that a proposed facility complies with the safety regulatory limits, essential for obtaining its chemical discharge permit. Additionally, the approach can establish maximum tolerable amine emissions for an emitting facility such that the risk is acceptable with regards to human health and the immediate environment. Therefore, the findings of this research are aimed at delivering crucial and useful data to the CO_2 capture industry especially for industries to comply with air quality regulations.

There is a need to perform atmospheric experiments, which could involve using real samples from the emissions to completely characterise these chemical discharges using analytical techniques. This would assist in addressing the uncertainty associated with the formation, accumulation and lifetimes of NS and NA in the atmosphere. The atmospheric chemistry scheme can then be extended to account for the mechanisms for the newly identified products.

Toxicity and ecotoxicity studies are also required to assist with the understanding of the impacts of amine-based solvent PCCC technology on humans and the environment (Karl et al. 2011) a lot more realistically. For this the toxicity exposure limits would require further improvement to develop the current regulatory limits. Both experimental and laboratory approaches are needed to study the impact of amines, NS and NA on humans and the environment such as terrestrial and aquatic ecology. Additionally, due to the carcinogenic nature of these chemical discharges, there is a need to perform vigorous sensitivity studies to assist with the development of the regulatory limits for PCCC and their consideration for full-scale plants.

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Model Study on the influence of plant design, photochemistry and meteorology on atmospheric concentrations of nitrosamines and nitramines in vicinity of an amine-based CO_2 capture facility

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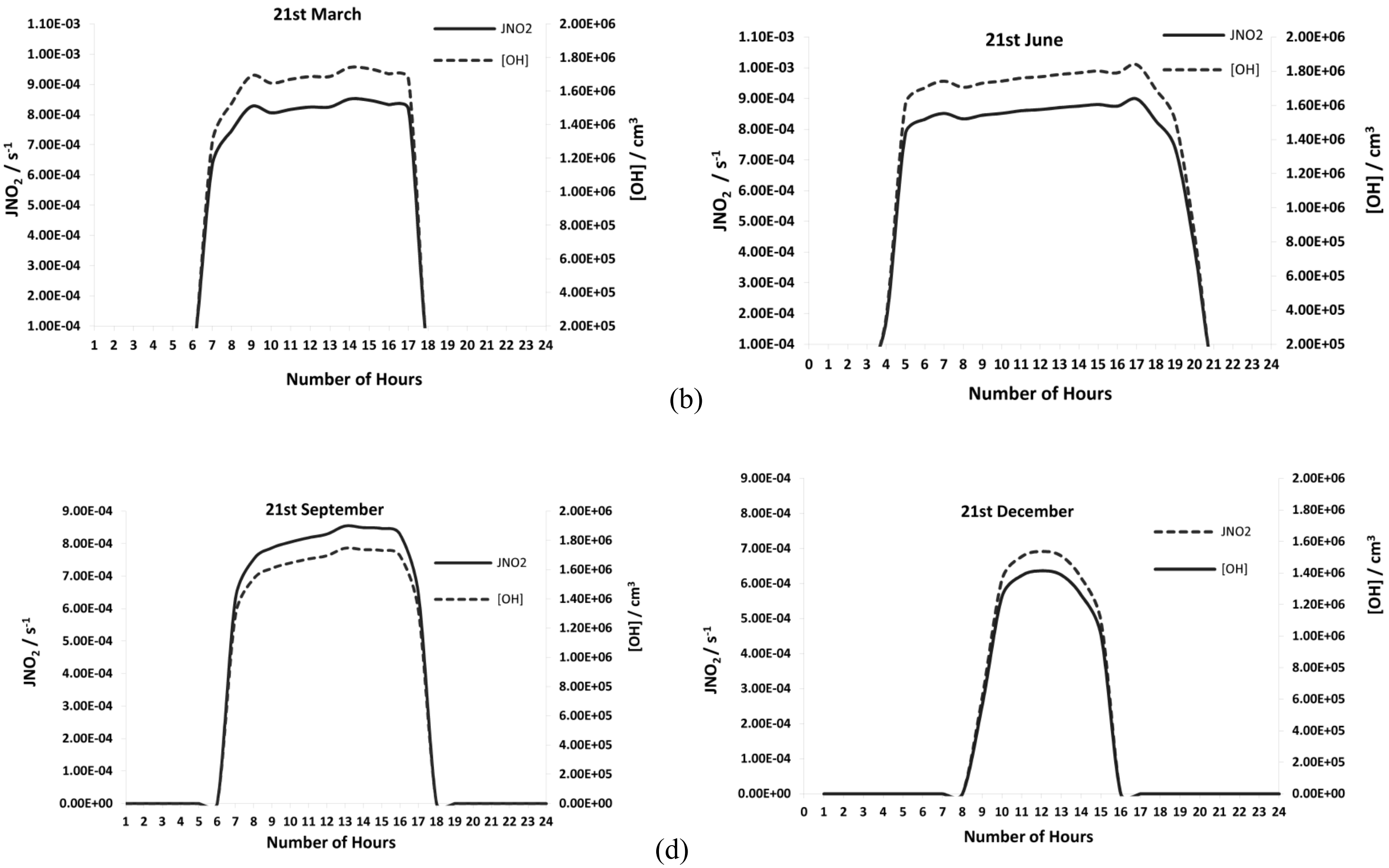


(a) (b)

(c) (d)

Figure 1: Typical diurnal profiles for OH and photolysis rate J_{NO2} for (a) 21st March (b) 21st June (c) 21st September and (d) 21st December, for Ferrybridge.

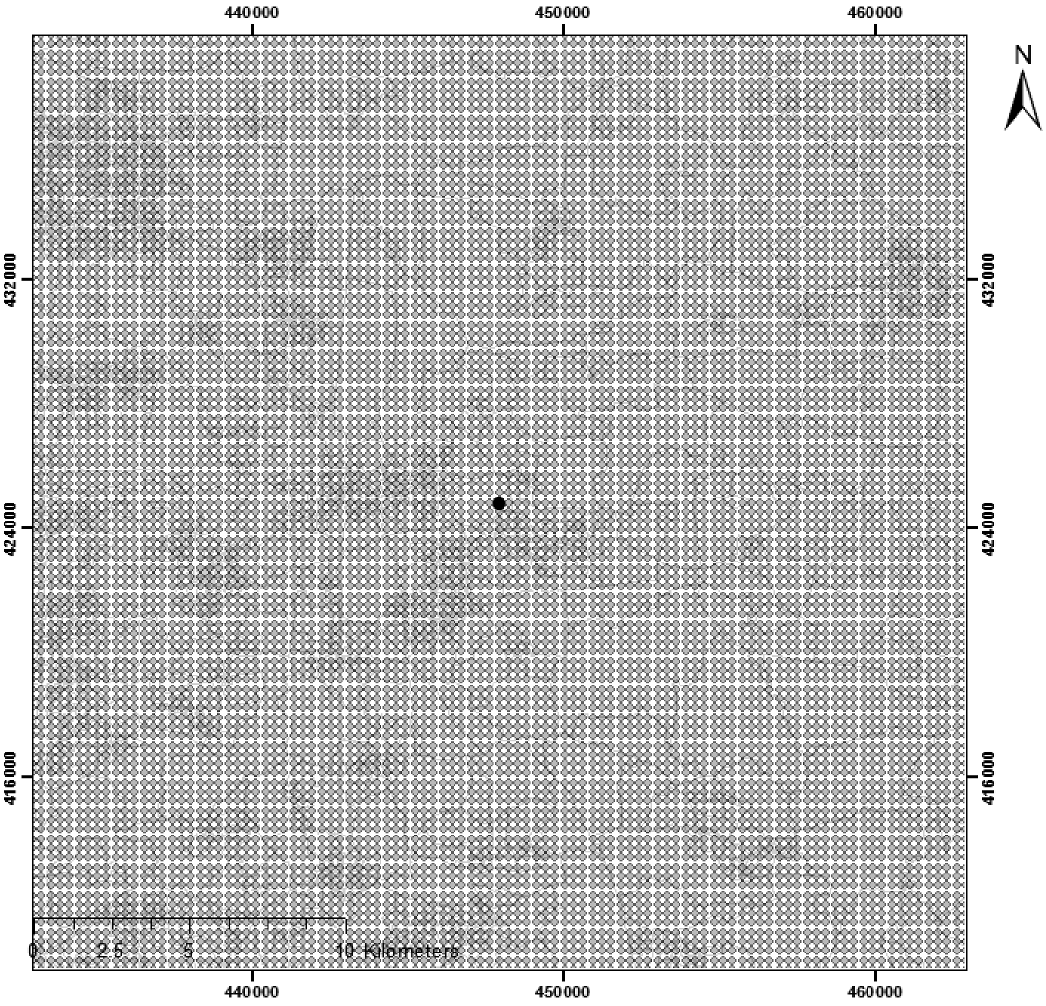


Figure 2: 101x101 Gridded receptors over 30 km x 30 km domain centered on Ferrybridge

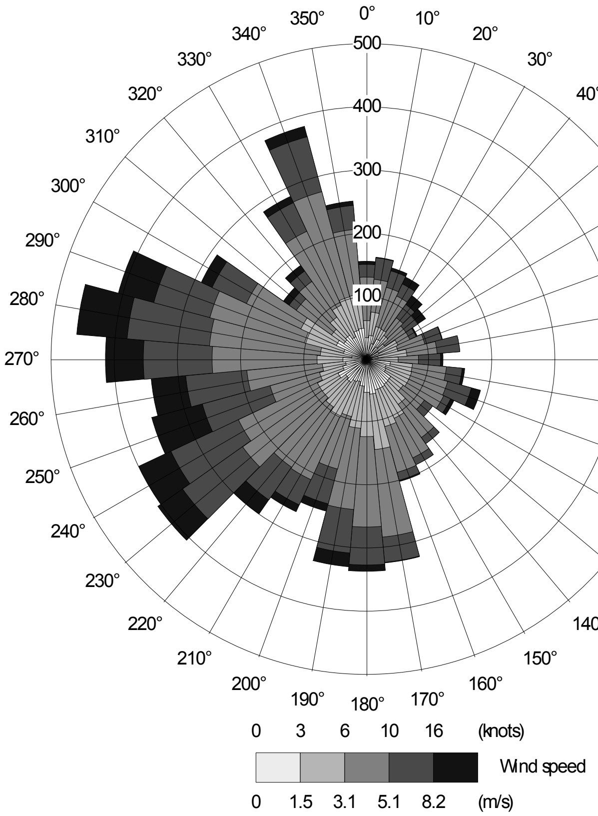


Figure 3: Wind rose plot for depicting the downwind flow vector (direction towards which the wind was blowing) in m/s for Ferrybridge (2012). In this polar plot, the angle of an element represents wind direction whereas the radial distance from the centre represents the frequency of wind speed occurrence. The frequency of each wind record is taken as 1 (CERC (2012b)).

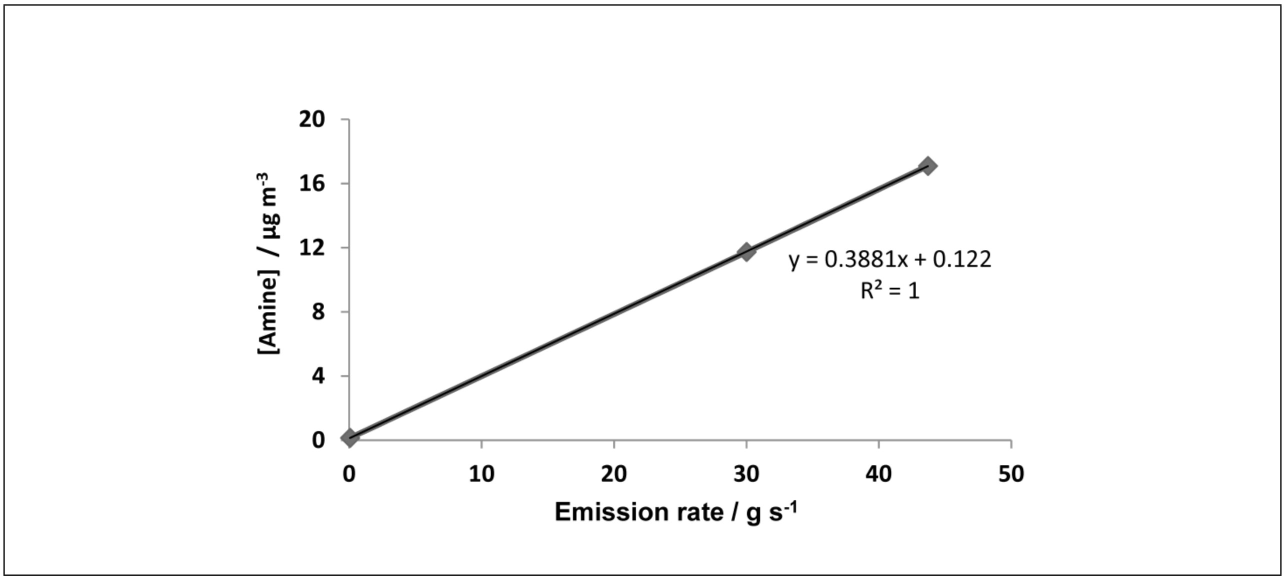
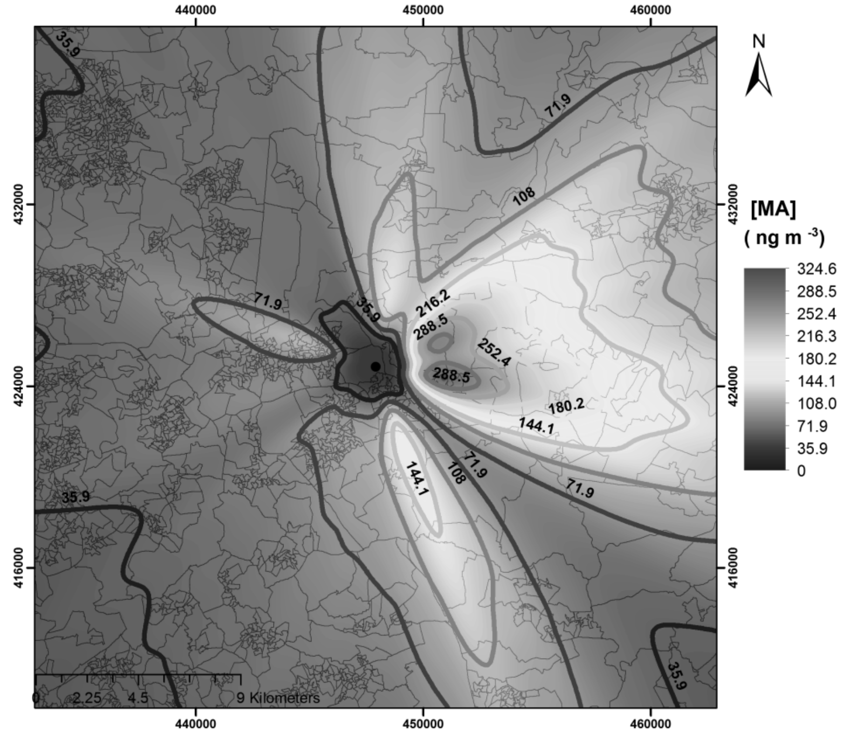
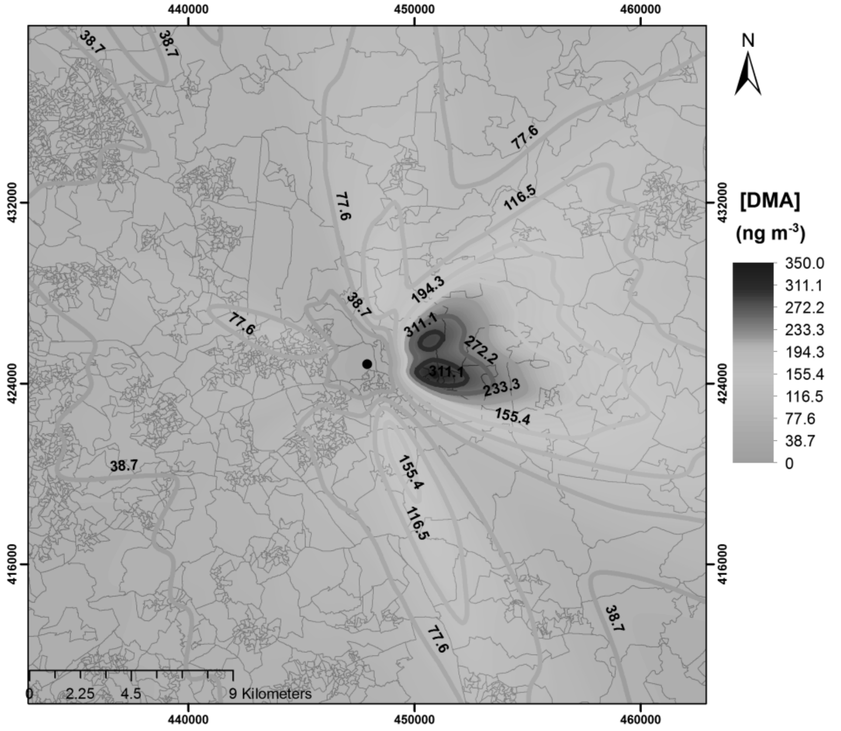


Figure 4: Amine emission rate versus amine concentration for Ferrybridge (2012).

(a)



(b)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460000
432000
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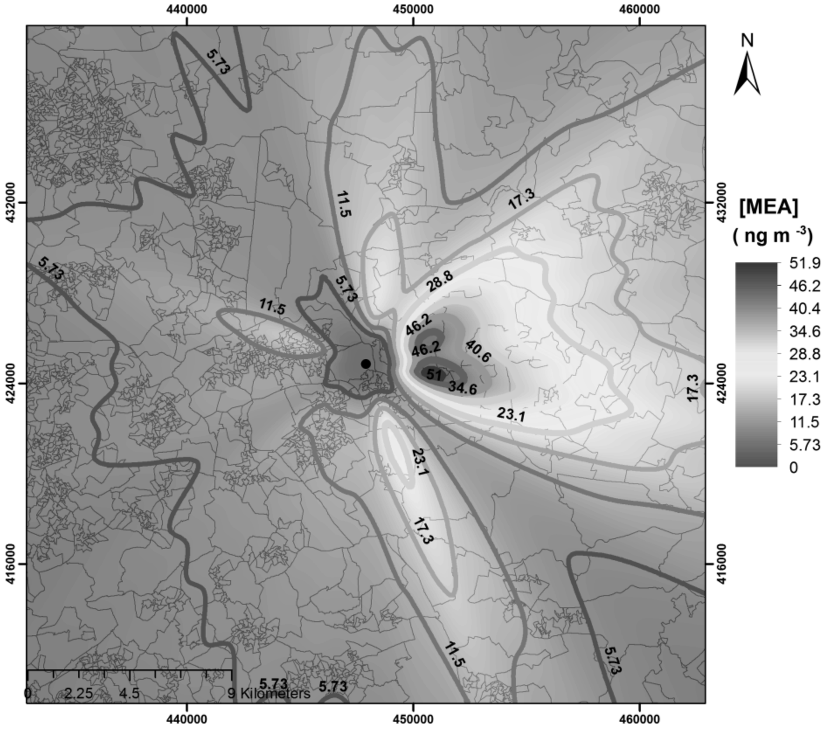
311.1
233.3
155.4
38.7
155.4
116.5
77.6
38.7
0
2.25
4.5
9 Kilometers

(c)


440000
450000
460000
432000
424000
416000
N
[MEA]
(ng m -3)
51.9
46.2
40.4
34.6
28.8
23.1
17.3
11.5
5.73
0
5.73
11.5
17.3
5.73
11.5
5.73
28.8
46.2
46.2
40.6
51
34.6
23.1
17.3
23.1
17.3
11.5
5.73
5.73
5.73
0
2.25
4.5
9 Kilometers

(d)

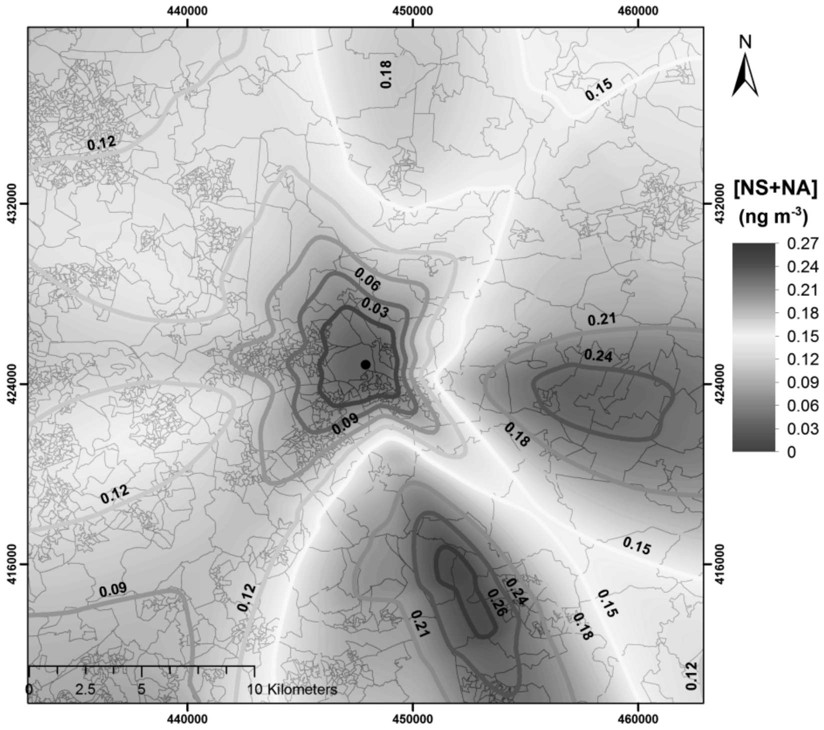
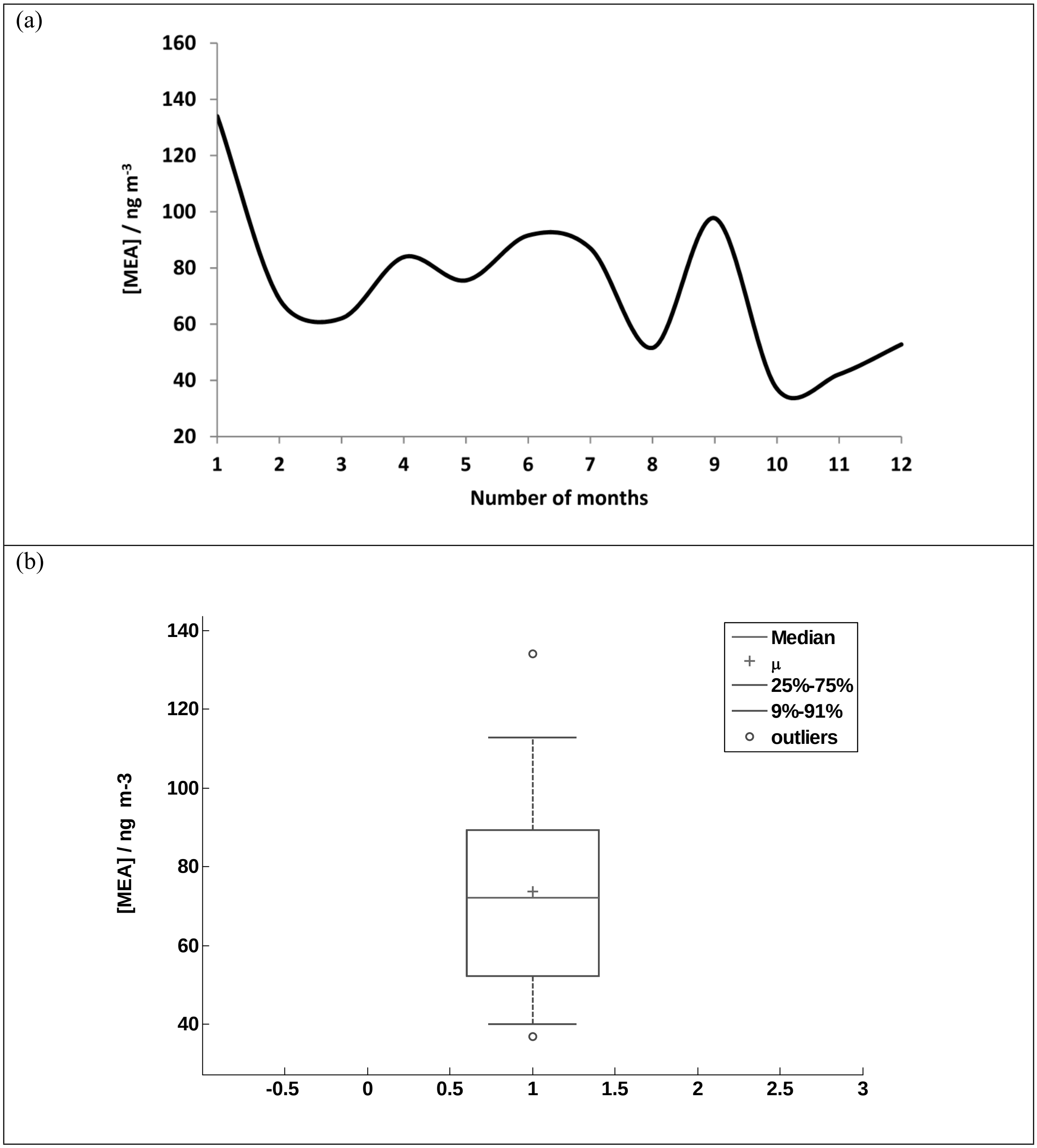
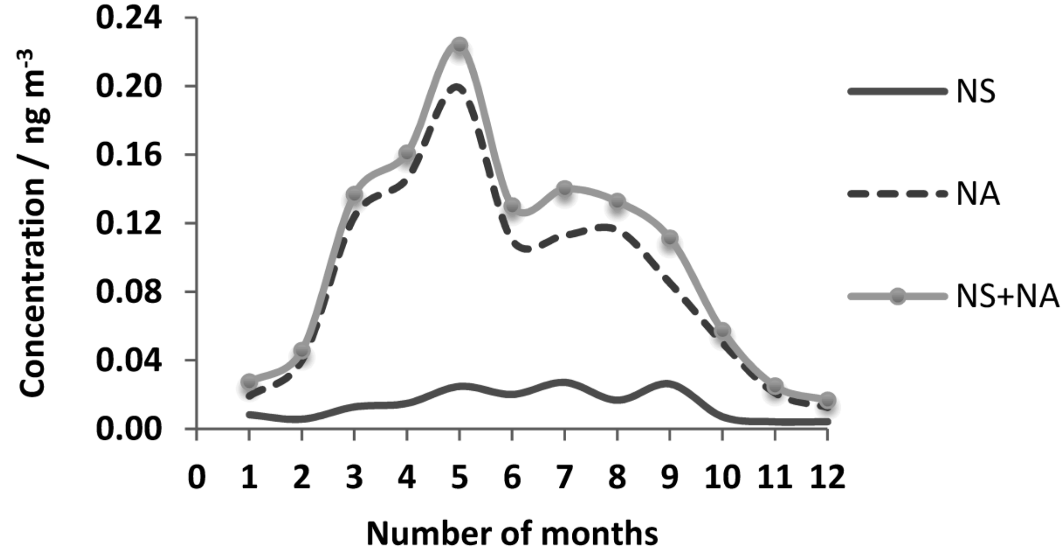


Figure 5: Contoured distributions of maximum annual concentration of amines in air for the risk-limit case in 2008: (a) MA (b) DMA (c) MEA at the amine emission rates reported in Table 7 and (d) the total NS and NA (ng/m^3) resulting from MA, DMA and MEA emissions for Ferrybridge. To estimate a surface from the set of scattered concentration points evaluated at 101 × 101 gridded receptor points over 30 km × 30 km domain centered on Ferrybridge (Figure 2), interpolation using a Krigging approach in Arc-GIS software is employed.


(a)
[MEA] / ng m-3
160
140
120
100
80
60
40
20
1
2
3
4
5
6
7
8
9
10
11
12
Number of months
(b)
[MEA] / ng m-3
140
120
100
80
60
40
-0.5
0
0.5
1
1.5
2
2.5
3
Median
μ
25%-75%
9%-91%
outliers

(c)



(d)

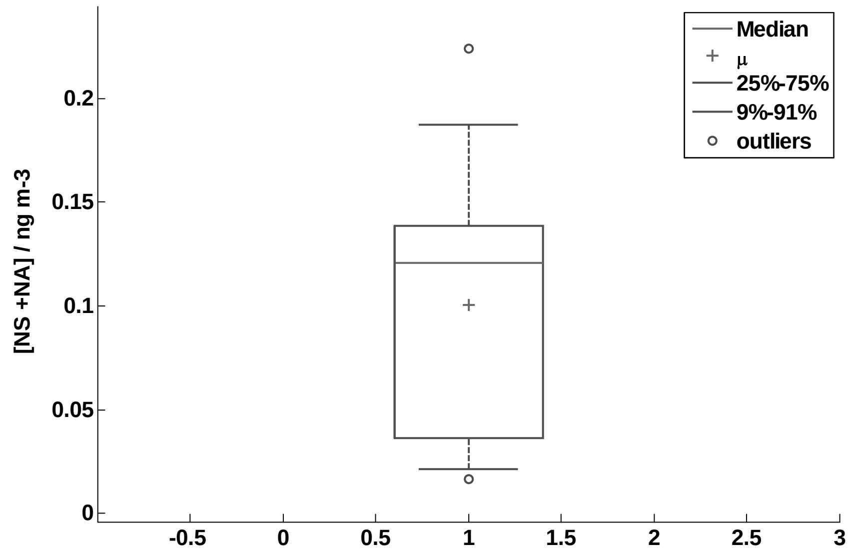


Figure 6: Monthly maximum average concentrations (ng/m^3) for 2012: (a) time series of MEA and (b) a box and whiskers plot showing the lowest (37 ng/m^3), lower quartile (52.2 ng/m^3), median (72.3 ng/m^3), upper quartile (89.3 ng/m^3) and highest value (134 ng/m^3) of the MEA concentration for every month of the year 2012 and (c) time series of NS and NA (d) together with their box and whisker plot showing lowest (0.02ng/m^3), lower quartile (0.04 ng/m^3), median (0.12 ng/m^3), upper quartile (0.14 ng/m^3) and highest value (0.22 ng/m^3) of the sum of NS and NA concentrations resulting from the oxidation of MEA for the sensitivity testing on the risk-limit case on Ferrybridge. See text for more details.

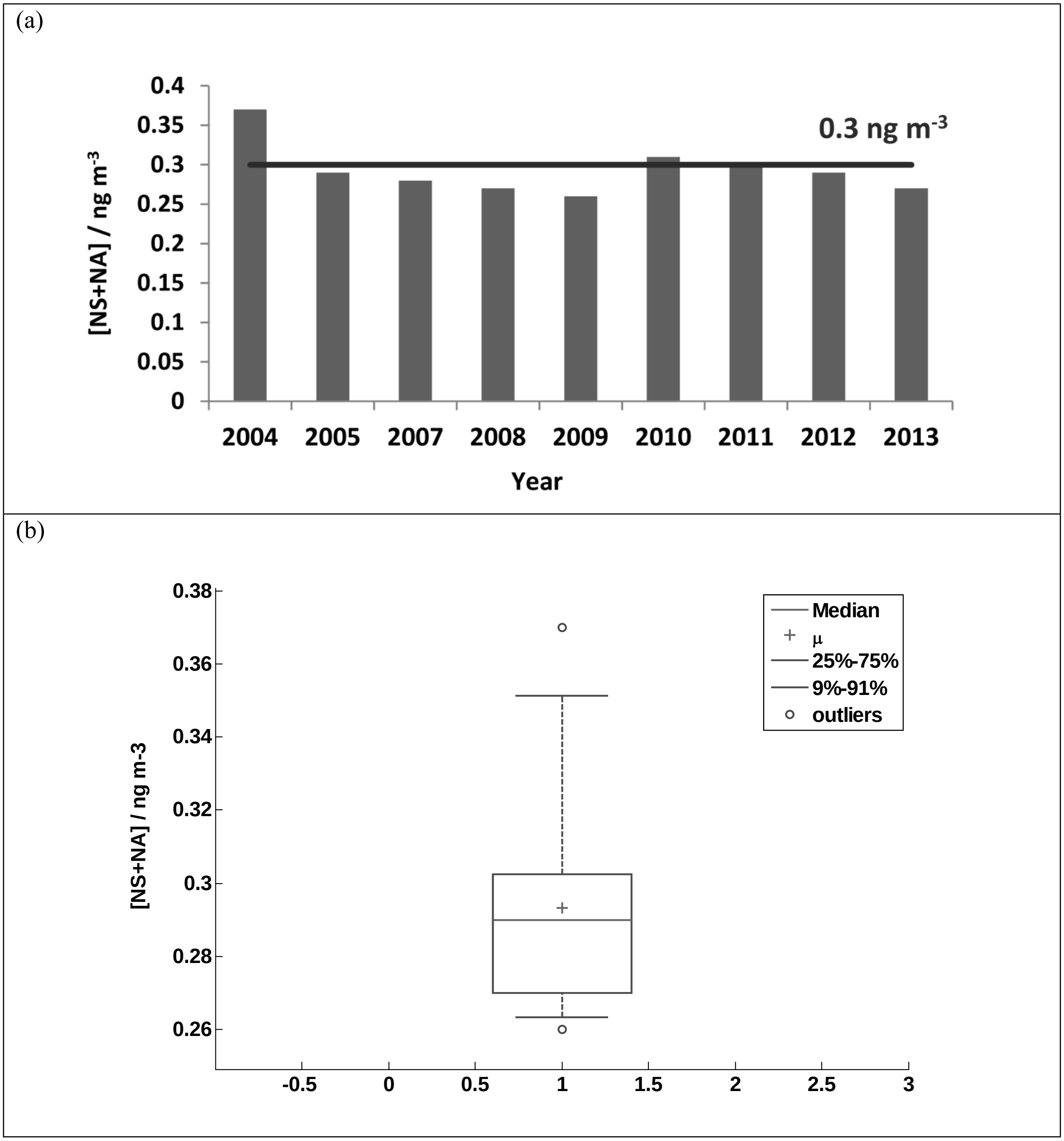


Figure 7: A graphical representation of the sensitivity analysis on the meteorological years from 2004 to 2013 with a box and whiskers plot showing the lowest (0.26 ng/m^3), lower quartile (0.27 ng/m^3), median (0.29 ng/m^3), upper quartile (0.30 ng/m^3) and highest value (0.37 ng/m^3) of the sum of NS and NA concentrations resulting from the three amines for the sensitivity testing on the risk limit scenario on Ferrybridge. One outlier was also obtained at a value 0.37 ng/m^3. The red straight line corresponds to the safety limit of 0.3 ng m^{-3}.

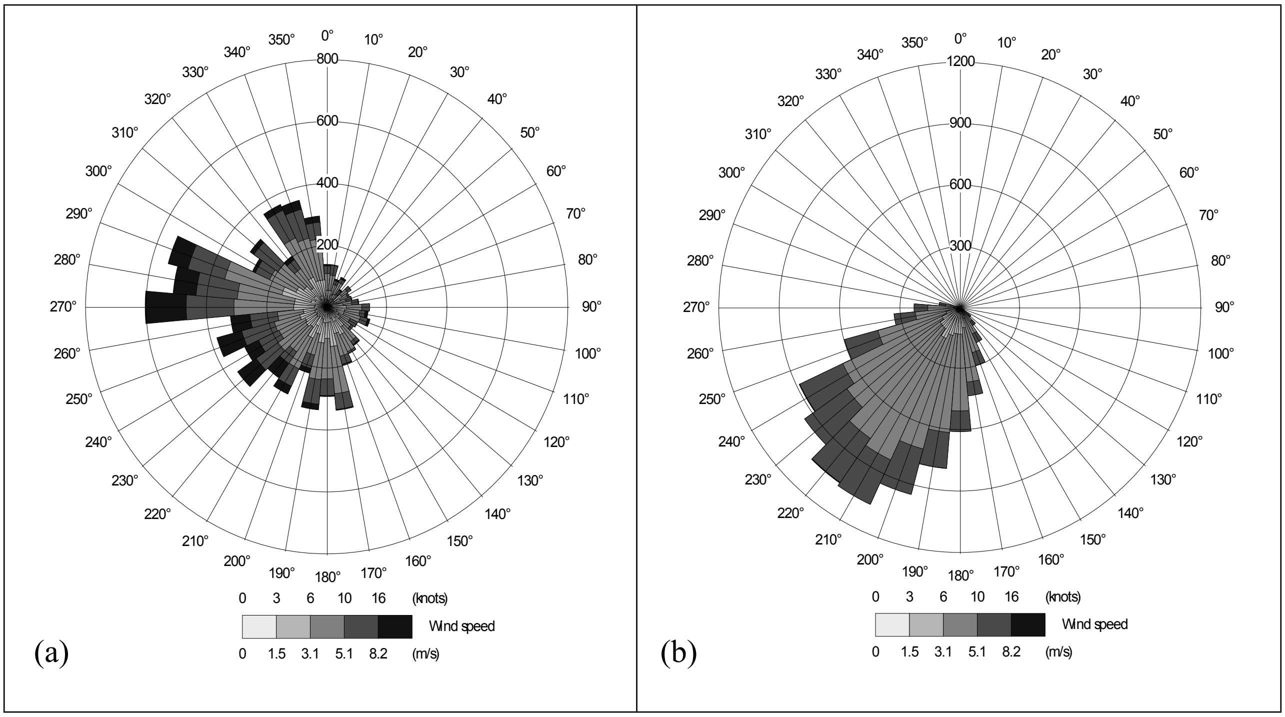


Figure 8: Wind rose plot for depicting the downwind flow vector in m/s for Ferrybridge (a) 2004 and (b) average windrose from all the years. In this polar plot, the angle of an element represents wind direction whereas the radial distance from the centre represents the frequency of wind speed occurrence. The frequency of each wind record is taken as 1 (CERC (2012b)).

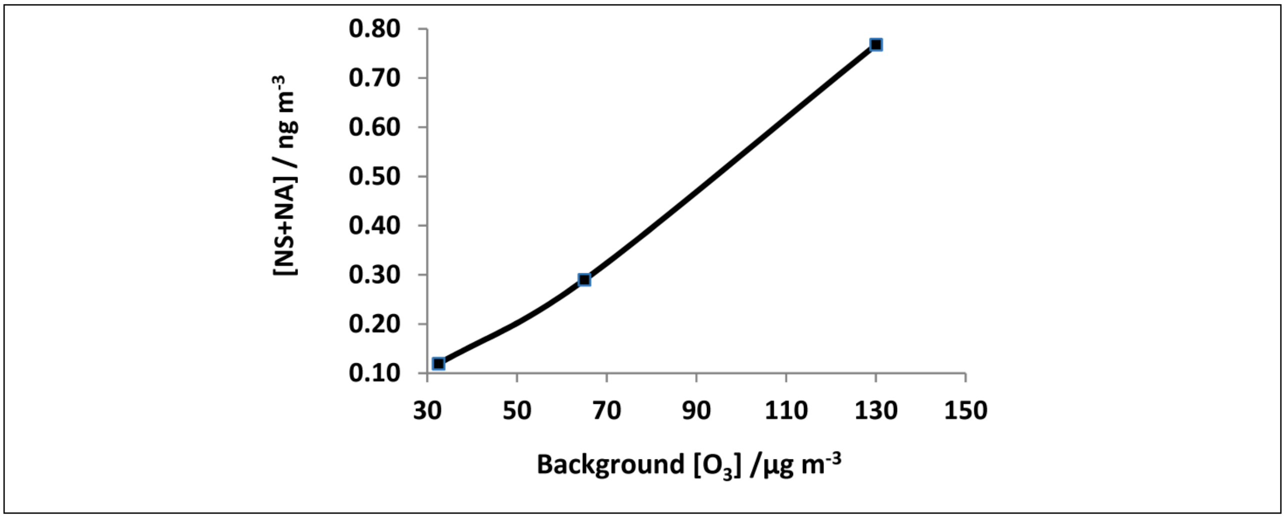


Figure 9: Plot showing a linear dependency of the NS and NA concentrations with $[O_3]$ / µg m^{-3}.

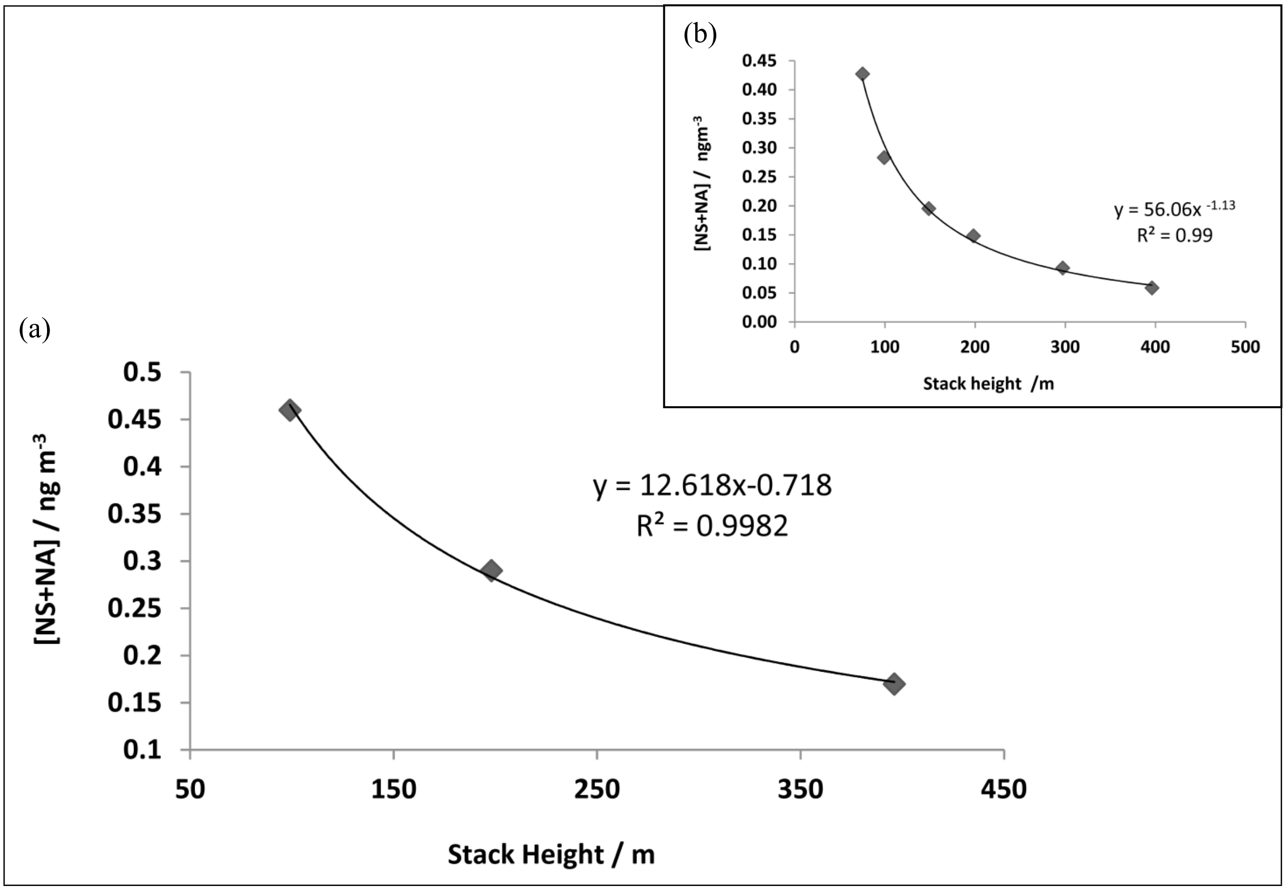


Figure 10: Plots showing a power law dependency of the NS and NA concentrations with (a) stack height from ADMS model results, which is further confirmed from (b) results a one-dimensional Gaussian plume model for neutral stability in flat terrain at an average wind speed of 4 m/s.

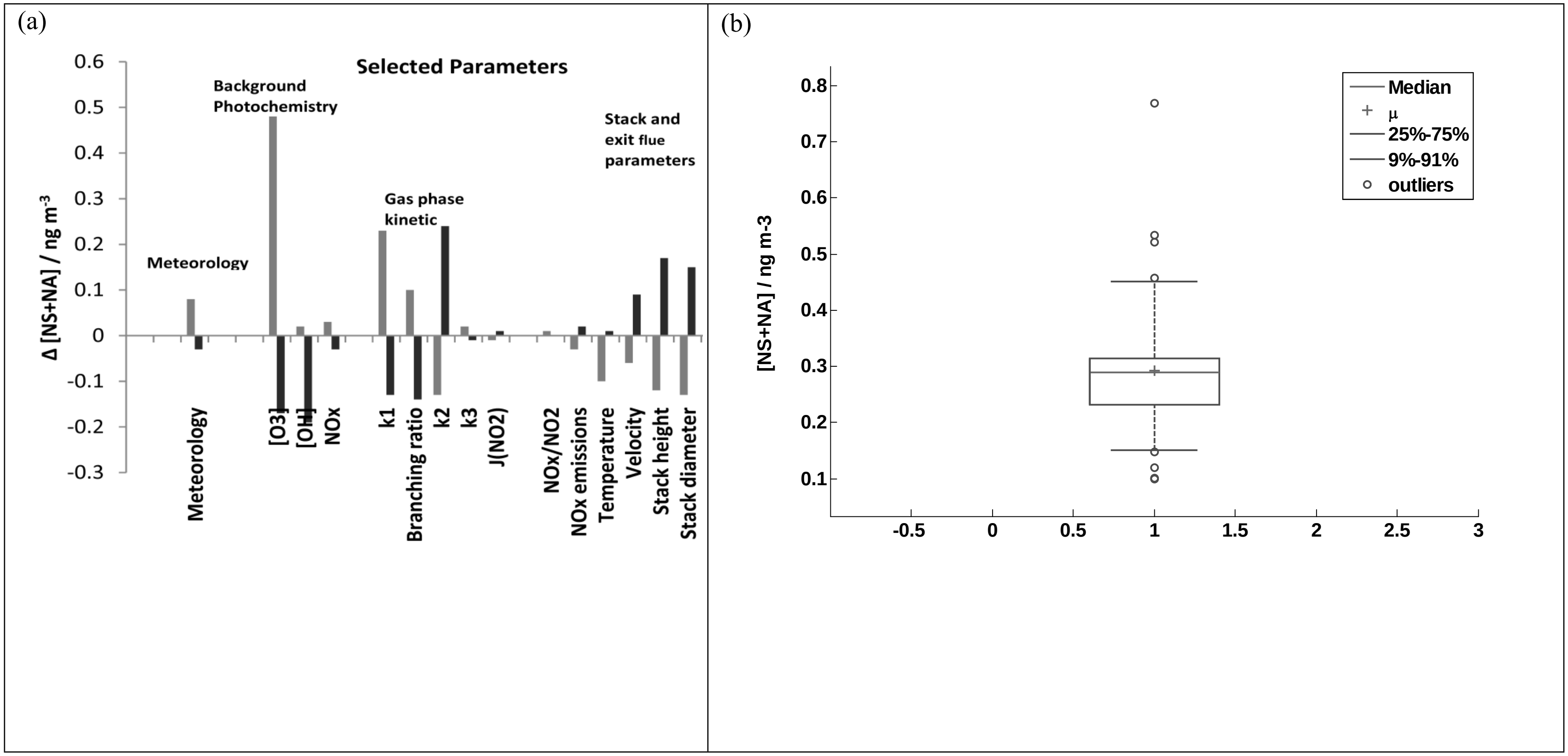


Figure 11: (a) A graphical representation of the sensitivity analysis on parameters selected from meteorology, background photochemistry, gas phase kinetic parameters, stack and exit flue parameters, associated with high uncertainty (b) along with a box and whiskers plot showing the lowest (0.1 ng/m^3), lower quartile (0.23 ng/m^3), median (0.29 ng/m^3), upper quartile (0.31 ng/m^3) and highest value (0.77 ng/m^3) of the sum of NS and NA concentrations resulting from the three amines for the sensitivity testing on the risk limit scenario on Ferrybridge. Five outliers were also obtained at values 0.10, 0.46, 0.52, 0.53 and 0.77 ng/m^3.

Supplementary

Model Study on the influence of plant design, photochemistry and meteorology on atmospheric concentrations of nitrosamines and nitramines in vicinity of an amine-based CO_2 capture facility

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S1 Advection-dispersion equations of ADMS 5

ADMS 5 includes a plume rise model for point sources which uses a Runge-Kutta method to solve conservation equations to determine plume rise. It also accounts for the effect of plume buoyancy, momentum and penetration through a boundary layer inversion. The built-in dry deposition model accounts for spatially varying deposition velocity by assuming that dry deposition is proportional to the near-surface concentration. Wet deposition model uses the washout coefficient method, asuming irreversible uptake. The total rate of wet deposition per unit plane area per interval of time is determined by employing integration over a vertical column of air. A complex terrain model was used to calculate the 3D flow and turbulence field over the study domain to account for the effects of terrain elevation and surface roughness on the dispersion.

The simplistic form of the standard ADMS mathematical advection-dispersion equation governing the concentration distribution profile within the boundary layer is described by a Gaussian plume, accounting for reflections at the ground level and at the inversion layer: (CERC 2012b).

$$C = \frac{Q}{2\pi\sigma_y\sigma_z U} exp\left(-\frac{y^2}{2{\sigma_y}^2}\right)\left\{exp\left(-\frac{(z-H)^2}{2{\sigma_z}^2}\right) + exp\left(-\frac{(z+H)^2}{2{\sigma_z}^2}\right) + exp\left(-\frac{(z-2H_i-H)^2}{2{\sigma_z}^2}\right) + \right. \tag{1}$$

where $C(x,y,z,H)$ is the pollutant concentration as a function of downwind position (x,y,z); Q is the mass emissions rate; the height, $H = 2H_i - H$ (Škraba *et al.* 2012) and is the effective stack height including rise of the hot plume near the source, where H_i is the inversion height or atmospheric boundary layer.

The first exponential term of the E.q (5) is the distribution of the mass in cross-wind dimension (y) at a given downwind distance x and the last two exponential terms of the equation are the distribution of mass in vertical dimension (z) at a given downwind distance x (includes the effect of surface reflection).
The dispersion parameter,σ_y, is defined as the following:

$$\sigma_y{}^2 = \frac{\int_{-\infty}^{\infty}\int_{0}^{\infty} y^2 C dz dy}{\int_{-\infty}^{\infty}\int_{0}^{\infty} C dz dy} \tag{2}$$

When considering the reflections of the Gaussian plume, the vertical dispersion parameter, σ_z, is defined as the following when it is much less than z_s , and therefore the turbulence close to the emitting source defines σ_z:

$$\sigma_z{}^2 = \frac{\int_{-\infty}^{\infty}\int_{0}^{\infty} (z-H)^2 C dz dy}{\int_{-\infty}^{\infty}\int_{0}^{\infty} C dz dy} \tag{3}$$

Obviously, Eq.5 becomes more complex and takes different forms when various other parameters, situations etc. are considered (CERC 2012a).

S2 Amine atmospheric chemistry scheme ADMS 5

The amine atmospheric chemistry scheme can be described by a set of ordinary differential equations as shown in Table S1.

Table S1: The differential equations used in ADMS 5 to solve the amine atmospheric scheme (after CERC (2012a)) .

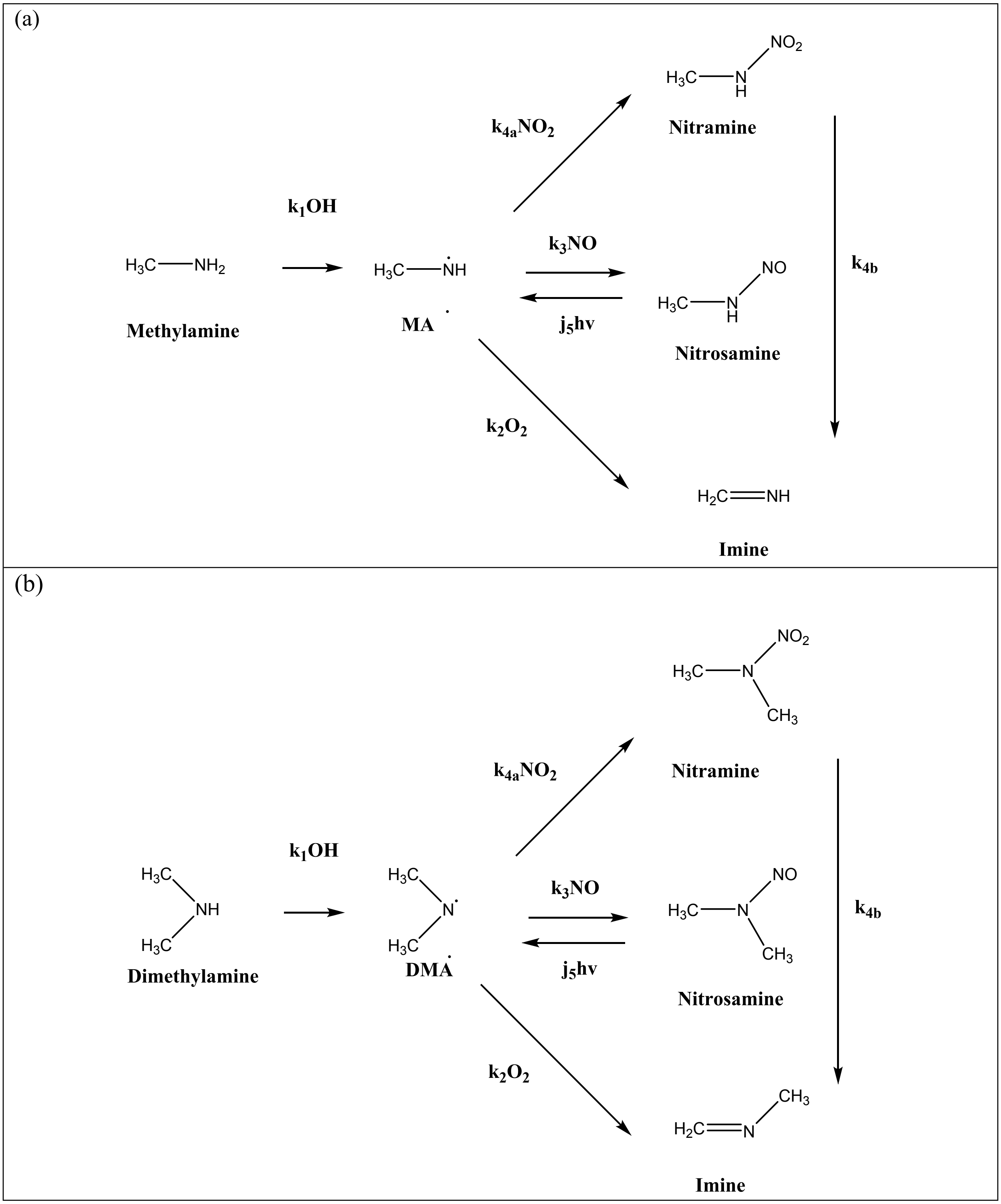
$$\frac{d[Amine]}{dt} = -k_{1a}[\mathrm{OH}]\,[\mathrm{Amine}]$$

$$\frac{d[Radical]}{dt} = k_{1a}\,[\mathrm{OH}]\,[\mathrm{Amine}] + J_5\,\mathrm{h}\upsilon\,[\mathrm{Nitrosamine}] - k_2\,[\mathrm{Radical}][\mathrm{O_2}] - k_3\,[\mathrm{Radical}][\mathrm{NO}] - k_{4a}[\mathrm{Radical}][\mathrm{NO_2}]$$

$$\frac{d[Nitrosamine]}{dt} = k_3\,[\mathrm{Radical}][\mathrm{NO}] - J_5\,\mathrm{h}\upsilon\,[\mathrm{Nitrosamine}]$$

$$\frac{d[Nitramine]}{dt} = k_{4a}\,[\mathrm{Radical}][\mathrm{NO_2}] - k_{4b}\,[\mathrm{Nitramine}]$$

Figures


(a)
Methylamine
k_1OH
MA
$k_{4a}NO_2$
Nitramine
k_3NO
$j_5$hv
Nitrosamine
k_2O_2
Imine
k_{4b}
(b)
Dimethylamine
k_1OH
DMA
$k_{4a}NO_2$
Nitramine
k_3NO
$j_5$hv
Nitrosamine
k_2O_2
Imine
k_{4b}

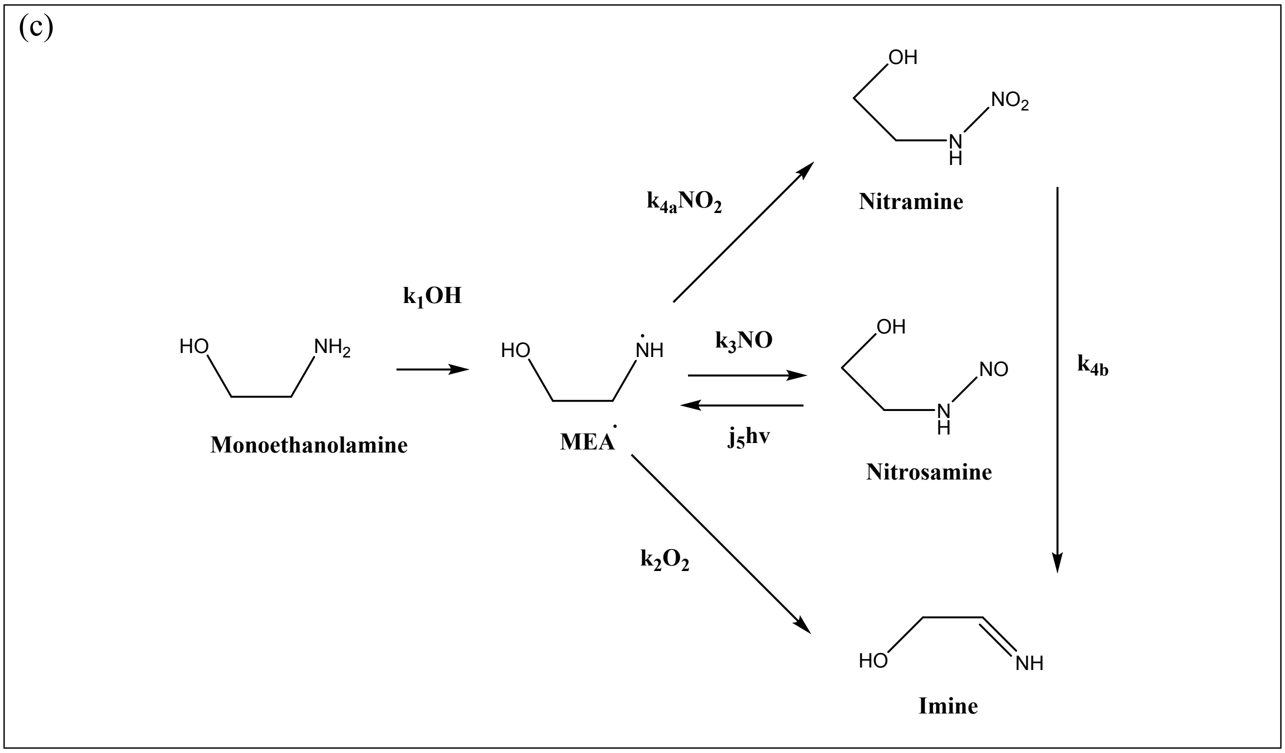


Figure S1: Atmospheric chemistry schemes with rate constants, k, describing the kinetics of each of the reaction describing the atmospheric chemistry scheme for (a) MA (b) DMA and (c) MEA.

(a)

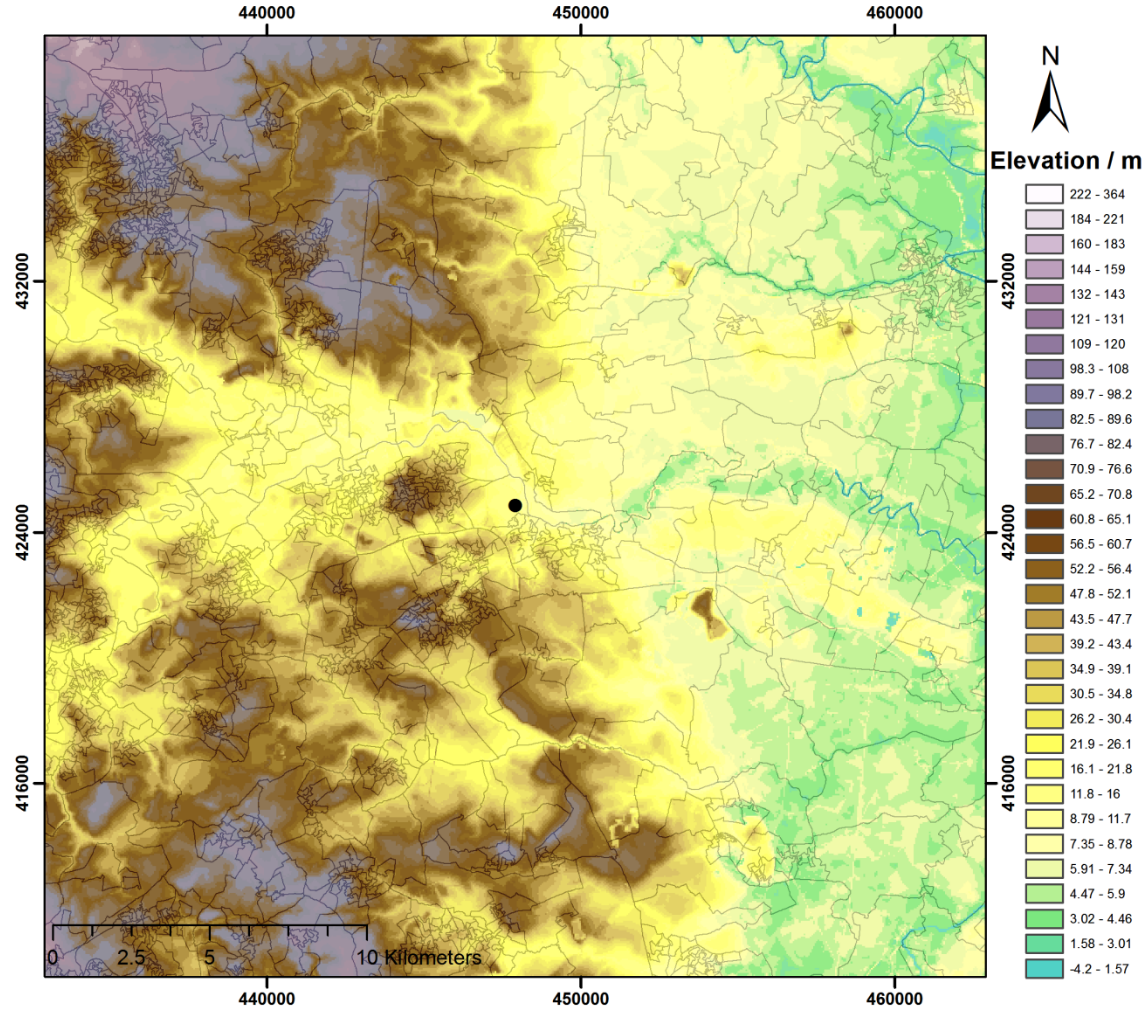


Figure S2: Terrain elevation centred on Ferrybridge CCPilot 100+ on a 30 km by 30 km domain.

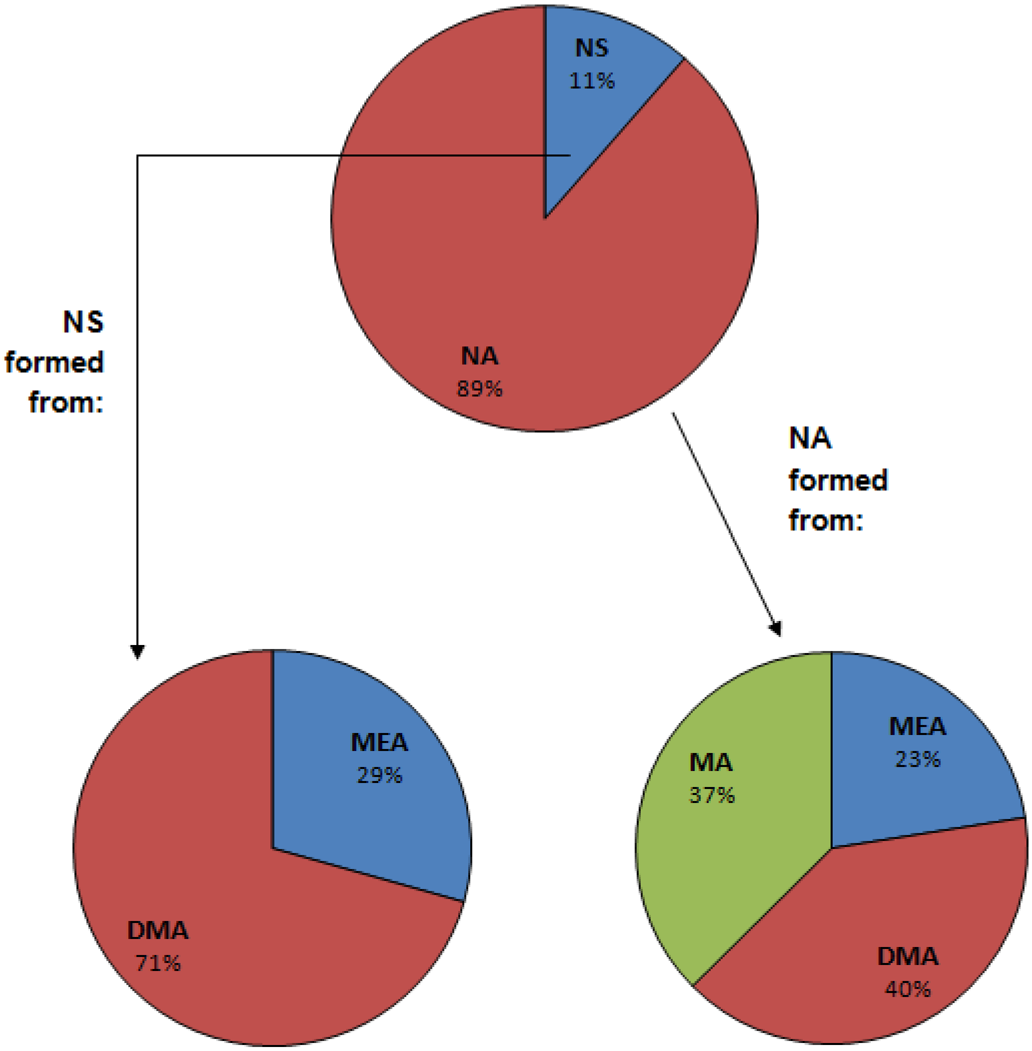


Figure S3: Pie charts showing the maximum contribution to NS and NA from the three amines MA, DMA and MEA for the baseline scenario modelled at Ferrybridge.

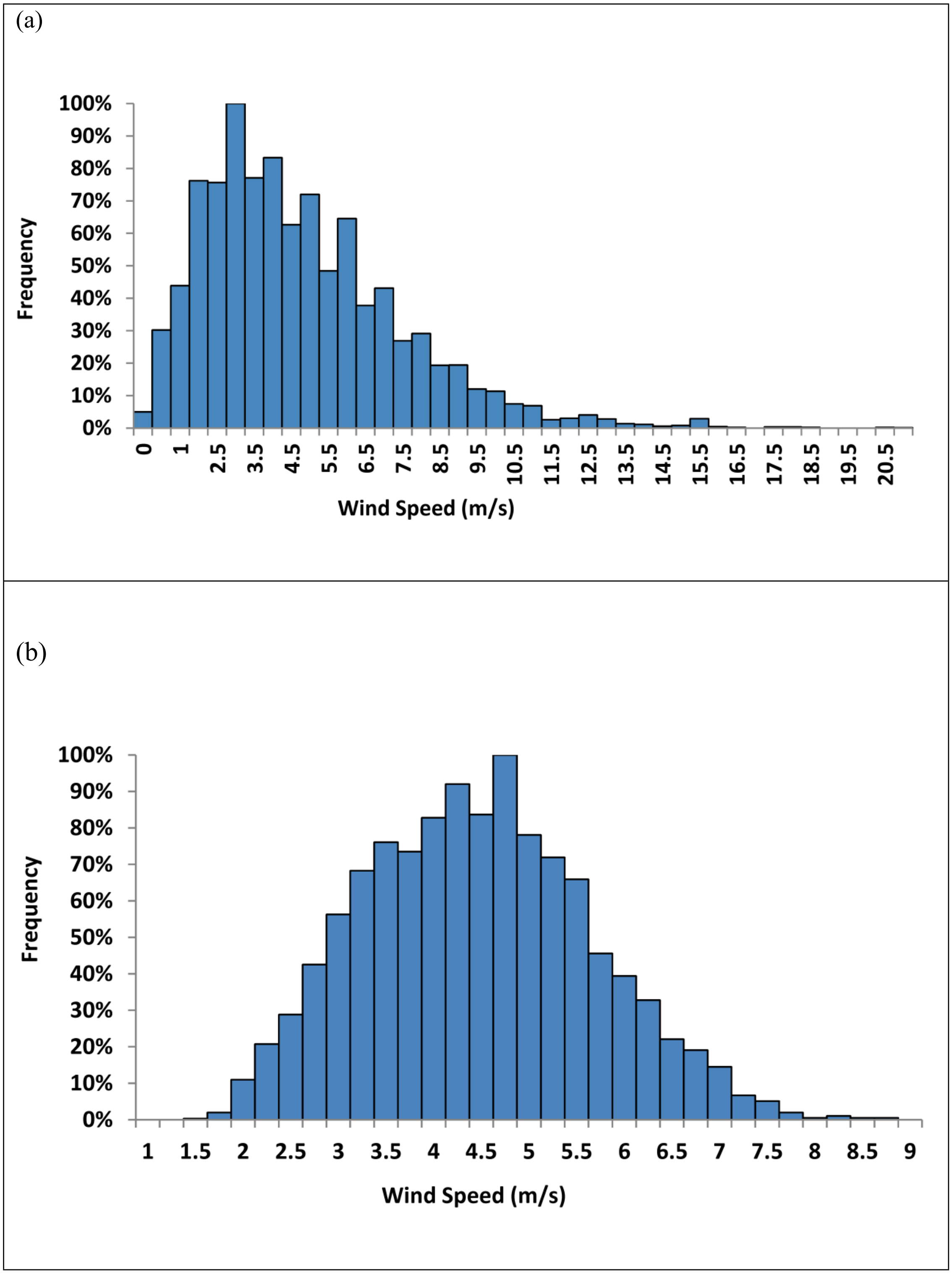


Figure S4 Histogram showing the frequency of wind speeds for (a) 2004 and (b) all the average years from 2004 to 2013

Tables

Table S2: Monthly maximum long term average concentrations of MEA, NS and NA (ng/m^3) for the worst case emissions scenario for the meteorological year 2012.

Month	Monthly [MEA] / ng m^{-3}	Monthly [NS] / ng m^{-3}	Monthly [NA] / ng m^{-3}	[NS+NA] / ng m^{-3}
January	134	8.26×10^{-3}	1.91×10^{-2}	2.74×10^{-2}
February	68.9	5.63×10^{-3}	4.01×10^{-2}	4.57×10^{-2}
March	62.1	1.28×10^{-2}	1.24×10^{-1}	1.37×10^{-1}
April	83.9	1.49×10^{-2}	1.46×10^{-1}	1.61×10^{-1}
May	75.6	2.48×10^{-2}	1.99×10^{-1}	2.24×10^{-1}
June	91.6	2.01×10^{-2}	1.10×10^{-1}	1.30×10^{-1}
July	87.0	2.71×10^{-2}	1.13×10^{-1}	1.40×10^{-1}
August	51.6	1.67×10^{-2}	1.16×10^{-1}	1.33×10^{-1}
September	97.7	2.62×10^{-2}	8.51×10^{-2}	1.11×10^{-1}
October	37.0	7.06×10^{-3}	5.02×10^{-2}	5.73×10^{-2}
November	42.2	4.06×10^{-3}	2.09×10^{-2}	2.50×10^{-2}
December	52.8	4.23×10^{-3}	1.25×10^{-2}	1.67×10^{-2}

Table S3: Sensitivity analysis for different meteorological years: Maximum long term average concentrations of the total NS and NA from the three amines at the maximum tolerable emissions and the percentage change (%Δ) from the baseline value of 0.29 ng m^{-3} in 2012.

Year	NS+NA (ng/m^3)	%Δ
2004	0.37	28
2005	0.29	0
2007	0.28	-3
2008	0.27	-7
2009	0.26	-10
2010	0.31	7

2011	0.30	3
2012	0.29	0
2013	0.27	-7

Reference:

1. CERC (2012b). ADMS 5 Atmospheric Dispersion Modelling System, User Guide version 5. Cambridge. **2013**.
2. Skraba, A., et al. (2012). Integrating Air-Pollution Dispersion Simulation Models and GIS for Urban Air-Pollution Emergency Management. Proceedings of International Conference, MATHMOD.
3. CERC (2012a). ADMS 5 Amine Chemistry Supplement.