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Activity 1: Gaseous Phase Chemistry Modelling (initiated by hydroxyl radical)

Final report

Prepared for
CO_2 Capture Mongstad Project
Gassnova SF

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CONTENTS

1. Introduction

The CO_2 capture Mongstad (CCM) project involves the planning and construction of a large-scale post-combustion carbon capture plant downstream the combined heat and power (CHP) plant at the Mongstad refinery in Norway. Cambridge Environmental Research Consultants Ltd (CERC) was commissioned by CCM Project to carry out an assessment, using CERC's industrial dispersion model ADMS 4 (version 4.2.2.0), to investigate the dispersion of the amines and their degradation products, specifically nitrosamines and nitramines.

There is still relatively limited knowledge regarding the behaviour of amines and their degradation products in the atmosphere, but understanding is advancing quickly. As a result, the current dispersion modelling assessment is similar in nature to the Case Study carried out by CERC under H&ETQPAmine2, but incorporates the latest, revised, estimates for possible emissions and transformations in the atmosphere. The work reported here comprises Activity 1 of contract number 257430174: Atmospheric Chemistry Modelling. This Activity considers the gaseous chemistry initiated by OH radicals.

Data regarding the CHP stack parameters and emissions were provided by CCM Project. The results of sensitivity tests carried out by CERC under H&ETQPAmine2, and the additional case study work carried out as a Variation Order under the current contract, were used to inform the model setup for this current assessment.

Emissions of three different amines, dimethylamine, methylamine and monoethanolamine (MEA), were provided, as well as direct emissions of nitrosamines. All four emitted species were investigated as part of the Case Study.

Results of the Case Study are provided as tabulated values of maximum annual average ground level concentrations and contour plots of annual average concentrations.

The amine chemistry considered under Activity 1 is discussed in Section 2, and Section 3 sets out the way in which this has been incorporated into ADMS. Section 4 gives a description of the case study carried out for Activity 1, including the input data and all results. Finally, a brief discussion of the results is given in Section 5.

2. Amine chemistry: General overview of hydroxyl radical-initiated reactions considered in Activity 1

Activity 1 deals with atmospheric dispersion coupled with the amine chemistry initiated by the attack of the amine by a hydroxyl radical ($^{\bullet}OH$), specifically the subsequent formation of nitrosamines and nitramines. The information provided for the CHP stack emissions has been based on the use of monoethanolamine (MEA) as the solvent used for the carbon capture process.

For monoethanolamine (MEA) as the parent solvent, current understanding[1] from recent studies suggests that:

- Nitrosamines and nitramines can be formed when MEA is converted, in the CO_2 absorption process, to other amines, and these amines go on to react with $^{\bullet}OH$ in the atmosphere.
- Nitrosamines can be formed during the capture process, and are therefore emitted directly from the stack.

Therefore the current report and the Case Study deal exclusively with emissions of monoethanolamine (MEA), and also of two other amines, dimethylamine (DMA) and monomethylamine (MMA). In addition, direct emission of nitrosamine has been assumed.

2.1. Basic information regarding DMA, MMA and MEA

MMA and DMA are simple alkyl amines; that is, they comprise an alkyl group and an amino group only. MMA (often called 'methylamine') broadly represents the *primary* amines that could be emitted; that is, amines where one of the hydrogen atoms in ammonia is replaced by an alkyl group. DMA represents the *secondary* amines; that is, amines where two of the hydrogen atoms are replaced by alkyl groups. As their names suggest, all of the alkyl groups in MMA and DMA are methyl (CH_3) groups.

Throughout this report, the nitrosamine produced from DMA, N-nitroso dimethylamine, is shortened to NDMA. The nitramine produced from DMA is commonly called dimethylnitramine, and is shortened to DMN in this report. Note that the name for the nitramine that is analogous to that given for the nitrosamine above is N-nitro dimethylamine. The free radical species that is formed as an intermediate during the conversion is referred to as the amino radical, or rDMA.

For the purposes of this report, analogous shortened names have been designated for the products of MMA and MEA. These names, along with chemical formulae and structures of the amines and their associated species are given in Tables 2.1.1 to 2.1.3. Note that no nitrosamine is given for MMA, or for MEA, as these nitrosamines are highly unstable, and therefore not a viable product of MMA or MEA transformation, as discussed in later sections.

Two reports have been published by the Norwegian Institute for Air Research (NILU) as part of the Climit project. One deals with MEA and its subsequent atmospheric transformations (referred to in the current report as the '2010 ADA report')[2] and the other deals with methylamine, dimethylamine and trimethylamine transformations (referred to as the '2011 ADA report').[3] A useful convention used in the ADA reports is the use of colours to distinguish between different species, which has been adopted in this report for nitrosamines and nitramines, as they can easily be confused, due to their similar structure; nitrosamines are shown in red text and nitramines in pink text wherever this is considered to be useful.

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[1] Unofficial translation of letter submitted from Statoil to the Norwegian Ministry of Oil and Energy. 10th September 2010 http://www.statoil.com/no/NewsAndMedia/News/2011/Downloads/Letter%2010%20feb%202011%20english.pdf

[2] Nielson *et al.* "Atmospheric Degradation of Amines (ADA). Summary Report: Gas phase photo-oxidation of 2-aminoethanol (MEA)". Climit project no. 193438. Norwegian Institute for Air Research. January, 2010.

[3] Nielson *et al*. "Atmospheric Degradation of Amines (ADA). Summary Report: Photo-oxidation of Methylamine, Dimethylamine and Trimethylamine". Climit project no. 201604. Norwegian Institute for Air Research. January, 2011.

Table 2.1.1: Dimethylamine and its products

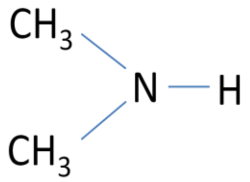
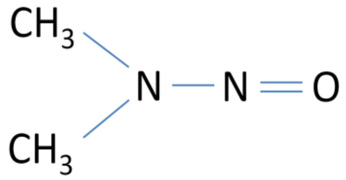
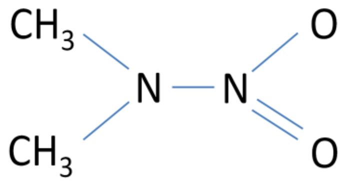
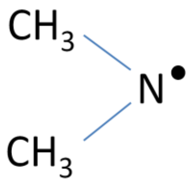
Short name	**Full name**	**Type of compound**	**Chemical formula**	**Structure**
DMA	Dimethylamine	Amine (secondary)	$(CH_3)_2NH$	
NDMA	N-nitroso dimethylamine	Nitrosamine	$(CH_3)_2NN0$	
DMN	N-nitro dimethylamine / dimethylnitramine	Nitramine	$(CH_3)_2NN0_2$	
rDMA	Dimethylamino radical	Free radical (reaction intermediate)	$(CH_3)_2N^{\bullet}$	

Table 2.1.2: Monomethylamine and its products

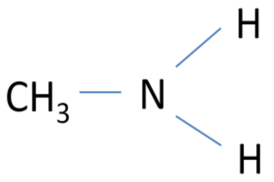
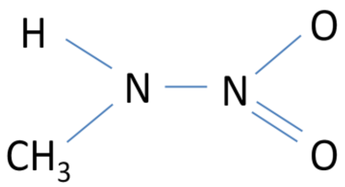
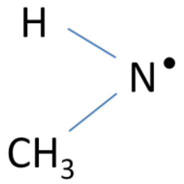
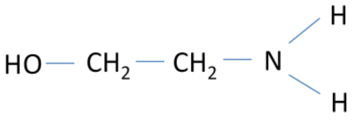
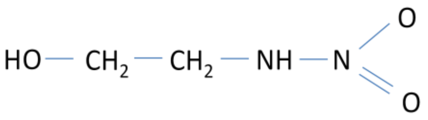
Short name	Full name	Type of compound	Chemical formula	Structure
MMA	(mono) Methylamine	Amine (primary)	CH_3NH_2	
MAN	N-nitro methylamine	Nitramine	CH_3NHN0_2	
rMMA	Methylamino radical	Free radical (reaction intermediate)	$CH_3N^{\bullet}$	

Table 2.1.3: Monoethanolamine and its products

Short name	Full name	Type of compound	Chemical formula	Structure
MEA	Monoethanolamine	Amine (primary, with an alcohol group)	$HOCH_2CH_2NH_2$	
MEN	N-nitro monoethanolamine	Nitramine	$HOCH_2CH_2HNNO_2$	
rMEA	Monoethanolamino radical	Free radical (reaction intermediate)	$HOCH_2CH_2N^{\bullet}H$	

2.2. Reaction schemes

2.2.1. General reaction with OH radicals

Hydroxyl radicals in the atmosphere act to abstract (remove) a hydrogen atom from the amine. The site of initial attack determines the type of species formed, through two separate branches of reactions. For amines in general, the $^{\bullet}OH$ can attack (a) the hydrogen on the N atom (N—**H**) or (b) one of the hydrogen atoms in the methyl groups (C—**H**). Only abstraction of an N—**H** hydrogen atom results in the formation of nitrosamines and nitramines. The ratio between the rate of attack on the C—**H** hydrogen and an N—**H** hydrogen is known as a *branching ratio*.

The product of the attack of the N-H by $^{\bullet}OH$ results in the formation of an amino radical species. For dimethylamine, for example, the radical species is $(CH_3)_2N^{\bullet}$

Once the H atom has been removed from the nitrogen atom of the amine, the next step is the reaction of the resulting species, $(CH_3)_2N{\bullet}$, with nitric oxide (NO) or nitrogen dioxide (NO_2) present in the atmosphere, to form the nitrosamine or nitramine, respectively. The amount of nitrosamine and nitramine formed depends on the amount of NO_x (that is, the total amount of NO_2 plus NO) present, and also on the ratio of NO to NO_2.

2.2.2. Dimethylamine reaction scheme

Of the three amine species considered in this report, DMA is the most studied in terms of its behaviour in the atmosphere, and so the reaction schemes are better understood than those of MMA and MEA. The DMA reaction scheme given in the 2011 ADA report is shown below:

$$(CH_3)_2NH + {}^{\bullet}OH \rightarrow (CH_3)_2N^{\bullet} + H_2O \qquad (1a)$$

$$\rightarrow (CH_3)_2N(H)C^{\bullet}H_2 + H_2O \qquad (1b)$$

$$(CH_3)_2N^{\bullet} + O_2 \rightarrow CH_2{=}N{-}CH_3 + HO_2 \qquad (2)$$

$$(CH_3)_2N^{\bullet} + NO \rightarrow (CH_3)_2N{-}NO \qquad (3)$$

$$(CH_3)_2N^{\bullet} + NO_2 \rightarrow (CH_3)_2N{-}NO_2 \qquad (4a)$$

$$\rightarrow CH_2{=}N{-}CH_3 + HONO \qquad (4b)$$

$$(CH_3)_2N{-}NO \xrightarrow{hv} (CH_3)_2N^{\bullet} \qquad (5)$$

Steps 1a and 1b represent the two possible branching reactions for the initial $^{\bullet}OH$ attack, and Step 5 represents the photolysis of the nitrosamine during daylight hours. Kinetic data for all of the above reactions are presented in the 2011 ADA report. The scheme includes the formation of an imine, $CH_2{=}N{-}CH_3$, but this reaction is only of interest here because it competes with the reaction for the formation of nitrosamines and nitramines.

2.2.3. Monomethylamine reaction scheme

The MMA reaction scheme given in the 2011 ADA report is shown below:

$$CH_3NH_2 + {}^{\bullet}OH \rightarrow C^{\bullet}H_2NH_2 + H_2O \qquad (17a)$$

$$\rightarrow CH_3N^{\bullet}H + H_2O \qquad (17b)$$

$$CH_3NH + O_2 \rightarrow CH_2{=}NH + HO_2 \qquad (18)$$

$$CH_3N^{\bullet}H + NO \rightarrow CH_3NHNO \qquad (19)$$

$$CH_3NHNO \leftrightarrows CH_2NHNOH \qquad (20)$$

$$CH_2NHNOH + O_2 \rightarrow CH_2{=}NH + NO + HO_2 \qquad (21)$$

$$CH_3N^{\bullet}H + NO_2 \rightarrow CH_2{=}NH + HONO \qquad (22)$$

$$\rightarrow CH_3NHNO_2 \qquad (23)$$

The MMA reaction scheme is different to that of DMA after the initial OH attack step in that, on formation, the nitrosamine formed from monomethylamine (a primary amine) isomerises. The product of this very fast isomerisation step then reacts very quickly with O_2 to form an imine. That is, a stable nitrosamine is not formed.

2.2.4. Monoethanolamine reaction scheme

The reaction scheme and rate expressions given in the 2010 ADA report are the same as those presented in the 2011 ADA report for dimethylamine. The rate constants are analogous, but with a different numbering system. Subsequent studies have shown, however, that a stable nitrosamine is not produced.

3. Hydroxyl radical-initiated amine chemistry in ADMS 4

3.1. Overview

The general release version of ADMS 4 contains a reaction scheme for NO_x chemistry. This section of the report discusses how the NO_x chemistry scheme has been developed to include the effects of hydroxyl-initiated amine chemistry in the gaseous phase. The scheme has been used in the Activity 1 Case Study (see Section 4).

As described in the previous section, the three amines of interest are DMA, MEA and MMA. The reaction information for DMA and MMA was taken from the 2011 ADA report, and the information for the reaction of MEA was taken from the 2010 ADA report; these reaction schemes are given in the previous section.

The implementation of the chemistry under the remaining three Activities will be reported in subsequent reports:

- Activity 2: Aqueous phase chemistry modelling;
- Activity 3: Dark / night-time chemistry modelling; and
- Activity 4: Chlorine chemistry modelling.

3.2. General description of the ADMS 4 amine chemistry scheme

The chemical scheme has been set up so that a single model code can generally cover the reactions of DMA, MMA and MEA, based on the information currently available.

In order that other amines can be modelled in the future, the amine chemistry scheme code has been set up so that generic names are used for the various species. These are simply ‘AMINE’, ‘NITROSAMINE’ and ‘NITRAMINE’. The amino radical species is denoted ‘RADICAL’, and can also be output by the model. The reaction scheme also involves NO_x emissions and background concentrations and ozone background concentrations. It uses information from the ADMS meteorological pre-processor to determine photolysis rates on an hourly basis.

Kinetic parameters for the various species are specified by the model user, and each can be varied independently, as well as parameters that the model uses to calculate $^{\bullet}OH$ concentration values. These are described further in the Case Study section of this report.

3.3. Implementation of chemistry scheme in ADMS 4

The values of the kinetic parameters are currently specified using an auxiliary file (.aai file). This simple text file is also used to generally switch on the amine chemistry scheme.

For the kinetic parameters, the reaction numbering system is based on that of the DMA reaction scheme, as outlined in Section 2. Values are required for k_1, k_{1a}/k_1, k_3, k_{4a}, k_2, k_4 and j_5/j_{NO2}, and these are discussed in Sections 4.6.1, 4.7.2 and 4.7.3. Sensitivity tests relating to these values are described in Section 4.8.1, with results given in Section 4.10.4.

The rate expressions used in the model are as follows:

1. Loss of the AMINE

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

2. Production of the amino RADICAL

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

   Note that $[O_2]$ is assumed to be constant.

3. Production of NITRAMINE

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

4. Production of NITROSAMINE

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

The concentration of oxygen in the atmosphere can also be specified, and this is assumed to be constant over time, specifically equal to 209,406,000 ppb.

Various checks are made on the input data to ensure that values are within reasonable ranges. If the requirements are not met, then the model returns an error message explaining this.

The hydroxyl radical concentration [OH] is modelled by the equation

$$[OH] = c[O_3]j_{NO_2}$$

where:

- c is a constant that is specified in the .aai file
  A value for c can be estimated from the known typical average values of $[O_3]$, [OH] and j_{NO2}.
- $[O_3]$ is the ambient ozone concentration
- j_{NO2} is the photochemical rate constant for NO_2 photolysis
  The modelled value for j_{NO2} varies hourly according to the time of day and the time of year.

4. Case Study

4.1. Overview

This Case Study comprises the modelling of the dispersion of amines and their degradation products, using ADMS 4.2 and its newly-developed amine chemistry scheme under Activity 1.

The Case Study includes a Baseline Case, which is used as the basis of comparison for sensitivity studies, to allow investigation of the effects of changing various model parameters and other input data. The modelling for the current Case Study has been designed with a particular emphasis on the parameters that influence the amine chemistry, in order to test the newly-developed amine chemistry scheme.

Section 4.2 discusses the guideline value with which the modelled results will be compared.

Section 4.3 describes the meteorological data used, and Section 4.4 describes the general model set-up and study area. Section 4.5 presents the stack parameters and emissions data provided by CCM Project for this Case Study.

Section 4.6 provides the details of the Baseline Case, which models DMA emissions, and Section 4.7 presents the details of model runs for the other amines. The various sensitivity tests are described in Section 4.8, and other model runs are described in Section 4.9.

The results of the Case Study model runs are given in Section 4.10 and summarised in Section 4.11.

4.2. Guideline value for the protection of human health

No official limit values for nitrosamines and nitramines have been set for Norway. For the purposes of this modelling study, CCM Project provided a value for the guideline limit of 0.3 ng/m^3, representing the total concentration of nitrosamines and nitramines in air. This guideline value is assumed to apply to annual average concentrations.

The value of 0.3 ng/m^3 has been recommended as a maximum acceptable level to ensure minimal or negligible risk of cancer for the public from exposure to nitrosamines and nitramines by the Norwegian Institute of Public Health (NIPH), following their review of existing international risk evaluations and toxicological information in the scientific literature.[4]

4.3. Meteorological data

In ADMS, the meteorological parameters in each line of input data describe the meteorological conditions for one hour, the conditions being assumed to be fixed for any given hour. The meteorology input module reads the data and uses the pre-processing algorithms to estimate values of the various meteorological quantities required for running the dispersion model.

Data are usually provided in the form of a chronological record, termed ‘hourly sequential’. The meteorological data from one surface meteorological observing site is typically input into the dispersion model; this may be supplemented by data from other surface meteorological observing sites and/or from vertical profile data provided by radiosondes.

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[4] Låg *et al*. “Health effects of amines and derivatives associated with CO_2 capture”. Norwegian Institute of Public Health. April, 2011. http://www.klif.no/no/Publikasjoner/Publikasjoner/2011/Mai/Health-effects-of-amines-and-derivatives-associated-withCO2-capture-/

The typical parameters supplied in hourly sequential meteorological data sets and used by ADMS 4 are:

- Day of the year (Julian day,1-365 or 366);
- Hour of the day;
- Wind speed (m/s) at a user-specified height;
- Wind direction (° clockwise from north);
- Near ground surface temperature (°C); and
- Cloud cover (oktas, 0-8).

In the work carried out under H&ETQPAmine2, an analysis of the data available from the eKlima portal of the Norwegian Meteorological Institute[5] resulted in a dataset for input into ADMS 4 that incorporated a combination of the most suitable data from three sites, for the three years 2007 to 2009.

The three sites were Fedje, Bergen Flesland and Takle, as shown in Figure 4.3.1. A summary of the characteristics of these three sites is given in Table 4.3.1. Fedje is the nearest site but is more coastal that Mongstad. The other two sites, Takle and Bergen, are 30km and 60km respectively from Mongstad and both are inland. All the sites are at a low elevation above sea level.

The same meteorological data were used in the current modelling study, although the rainfall data obtained from the Takle site were not required for the current modelling. The data taken from each site are summarised in Table 4.3.2, and Figure 4.3.2 shows wind roses for each of the three years.

Table 4.3.3 shows the statistics of the meteorological data for each year, as summarised by the ADMS 4 meteorological pre-processor. This includes the percentage of hours actually used by ADMS 4 in the model calculations; it can be seen that there is extremely good data capture and usage for all three years. When running ADMS 4, meteorological data may be present but not used if the wind speed measured at 10m, U_{10}, is below 0.75m/s. In this case the model skips the meteorological data for that hour unless the 'calms' option has been selected. The wind speed data for Mongstad shows very few hours with wind speeds at 10m lower than 0.75m/s and so the calms option was not used in this assessment.

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[5] http://sharki.oslo.dnmi.no/portal/page?_pageid=73,39035,73_39049&_dad=portal&_schema=PORTAL

Figure 4.3.1: Google Earth image showing Mongstad (yellow) and the three meteorological sites: Takle, Fedje and Bergen Flesland (red). Fedje is approximately 20km from Mongstad.

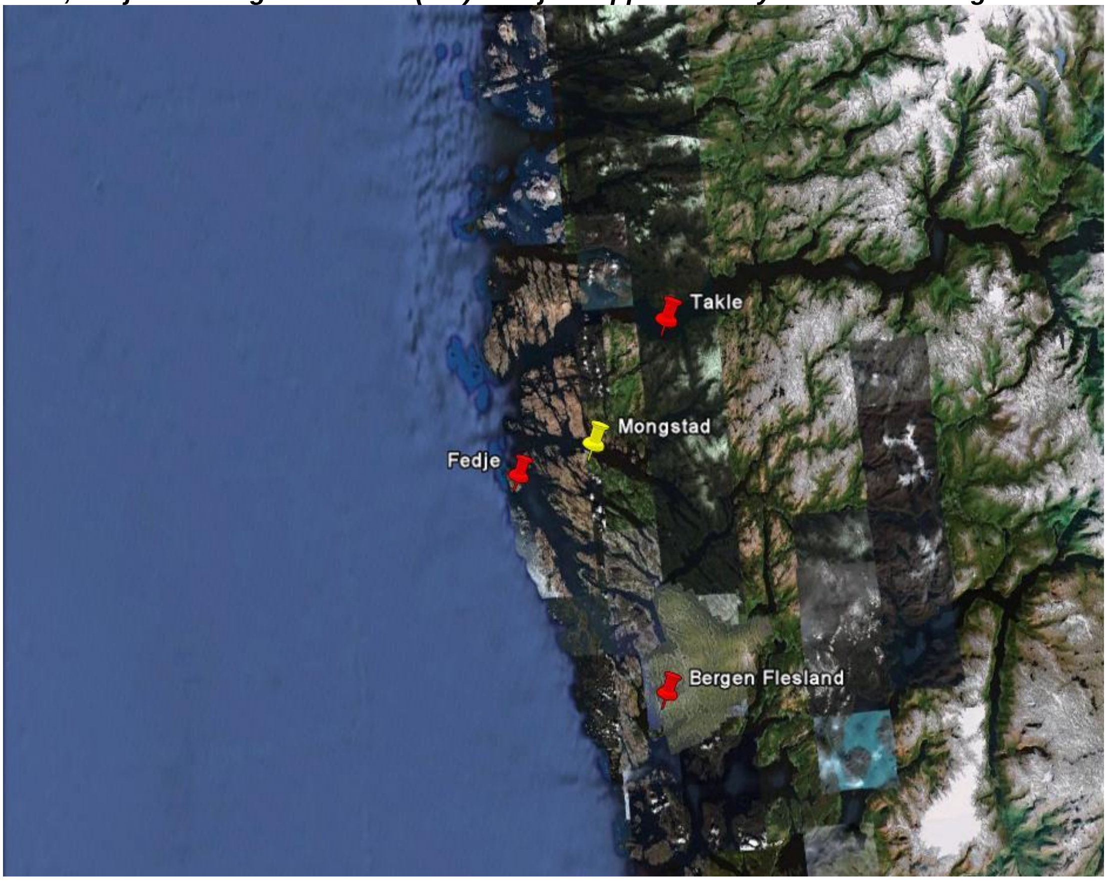


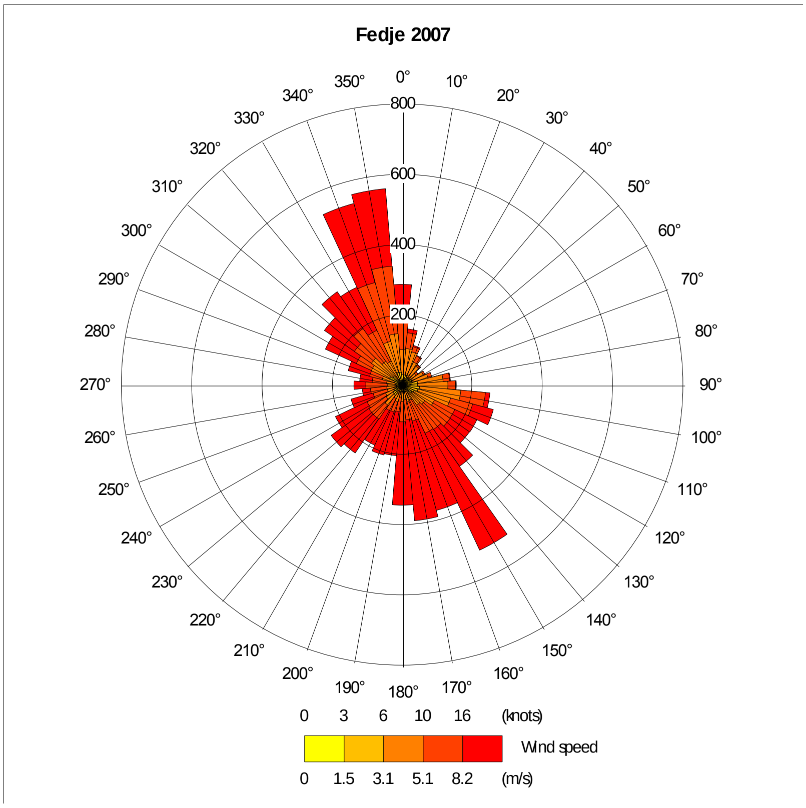
Table 4.3.1: Summary of relevant properties of the meteorological sites

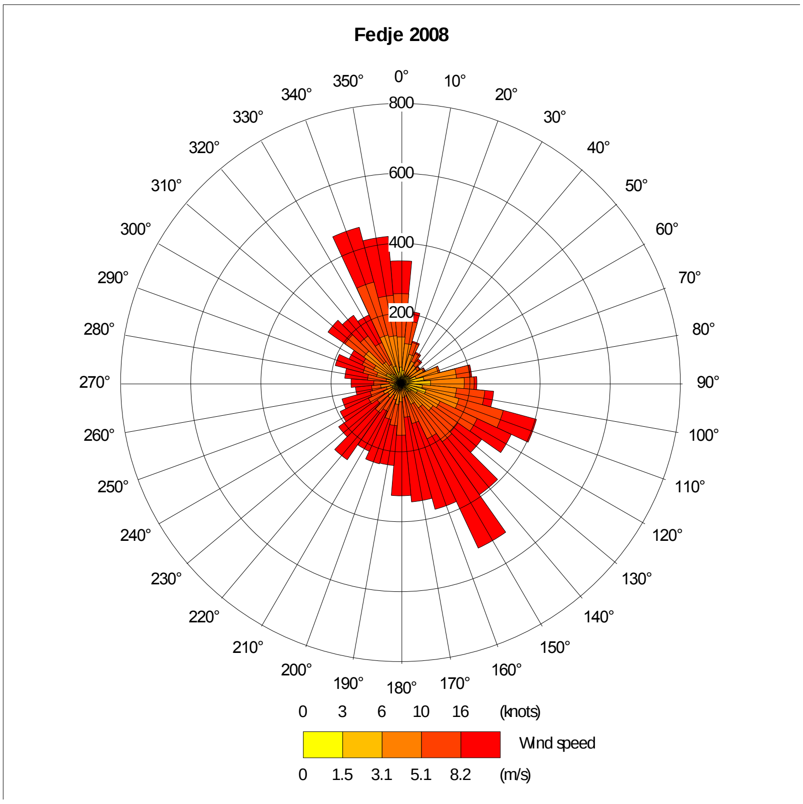
	Site name			Mongstad
	Fedje	**Bergen Flesland**	**Takle**	
Location (Lat, Long)	60.78, 4.72	60.283, 5.233	61.033, 5.383	60.808, 5.036
Relative location	20km west of Mongstad	60km south of Mongstad	30km north east of Mongstad	-
Coastal / inland	Coastal	20km inland	40km inland	15km inland
Height above sea level (m)	19	50	38	20

Table 4.3.2: A summary of meteorological sites used for each parameter

Parameter	**Site used**	**Reasons for choice of site**
Wind speed	Fedje	Closest site to Mongstad
Wind direction		Wind roses very similar to wind roses generated from measurements at Mongstad
Temperature		Closest site to Mongstad
Cloud cover	Bergen Flesland (3-hourly data)	No data at Fedje. The 3-hourly data were applied to the following 2 hours.

Figure 4.3.2: Wind roses for Fedje, 2007 to 2009





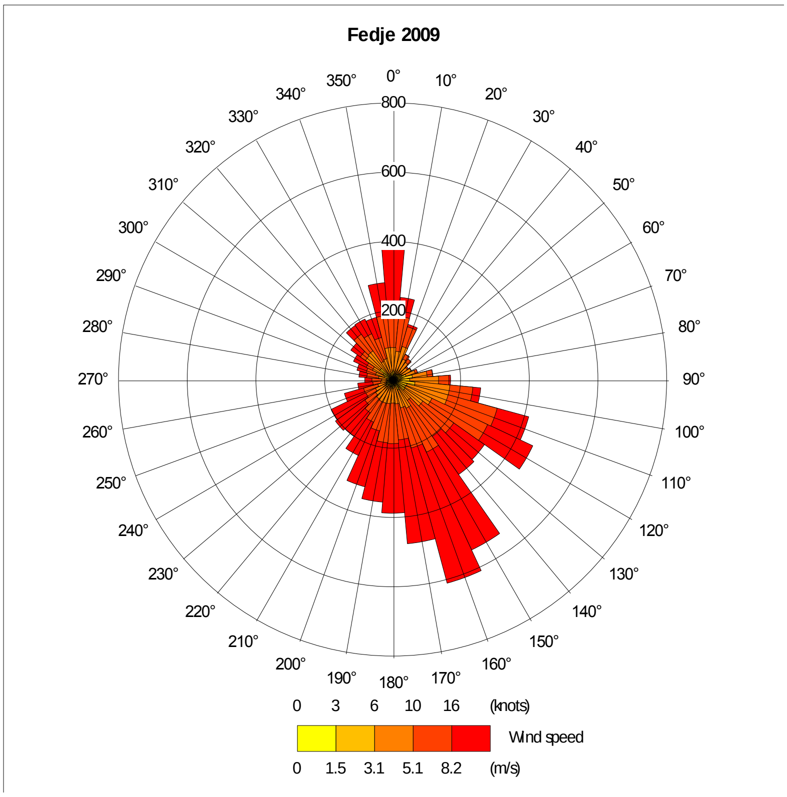


Table 4.3.3: Summary of meteorological parameters used by ADMS 4

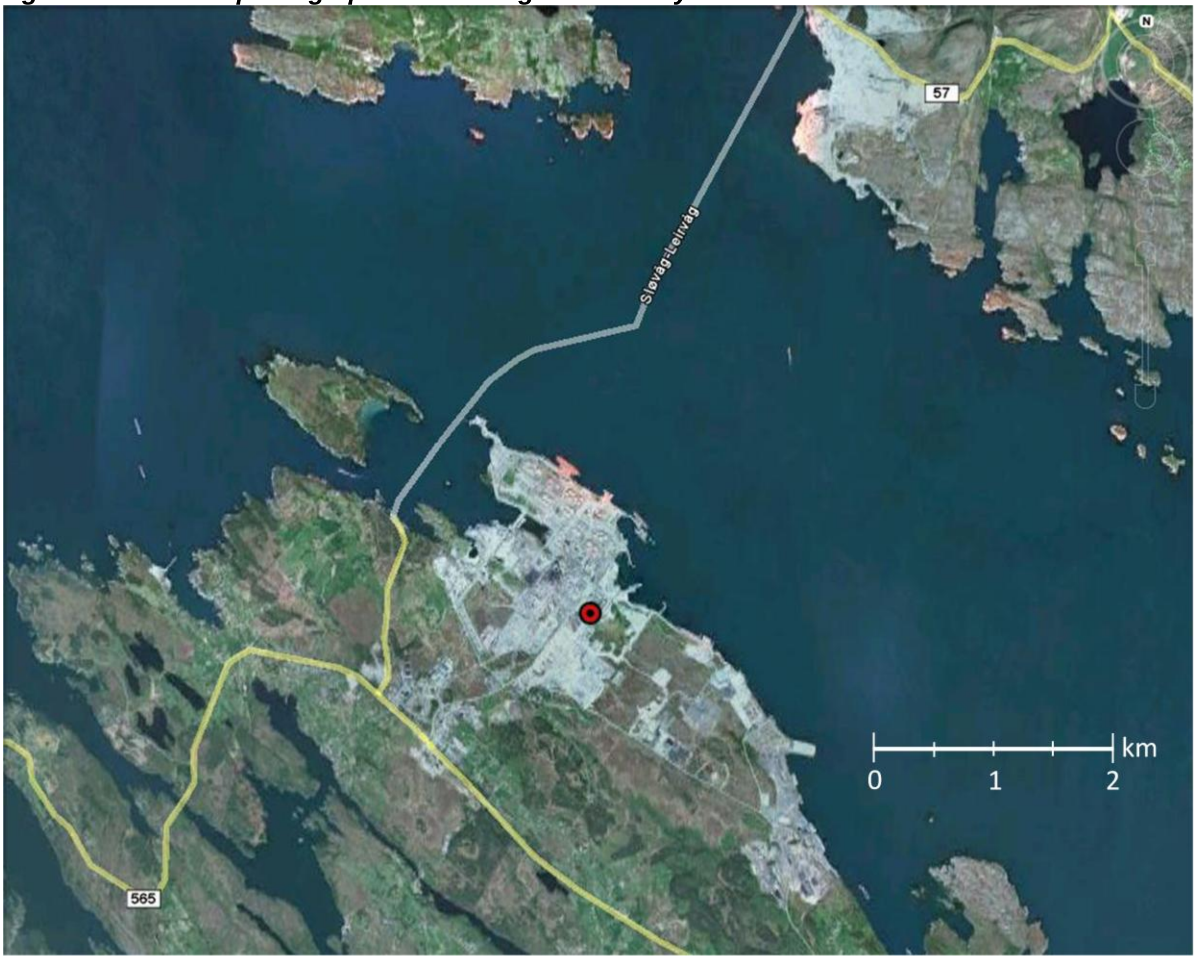
Year	Percentage data that can be used	Parameter	Minimum	Maximum	Mean
2007	95.3 %	Temperature (°C)	-3.9	23.3	8.3
		Wind speed at 10m (m/s)	0	25.2	7.7
		Cloud cover (oktas)	0	8	6
		Relative humidity (%)	21	100	81
		Rainfall (mm, annual)	3933		
2008	98.9 %	Temperature (°C)	-2.9	26.3	8.9
		Wind speed at 10m (m/s)	0	27.3	7.5
		Cloud cover (oktas)	0	8	5
		Relative humidity (%)	23	100	78
		Rainfall (mm, annual)	3377		
2009	95.9 %	Temperature (°C)	-4.8	26.5	8.0
		Wind speed at 10m (m/s)	0	24.3	7.4
		Cloud cover (oktas)	0	8	6
		Relative humidity (%)	19	99	79
		Rainfall (mm, annual)	2887		

4.4. Study Area

4.4.1. Site location and surrounding area

Figure 4.4.1 shows the Mongstad refinery site and its immediate surroundings. The red marker shows the location of the CHP absorber stack.

Figure 4.4.1: Aerial photograph of the Mongstad refinery



4.4.2. Building effects

When a stack is located immediately upwind of or on top of a building, the maximum concentrations can occur very close to the building, because all or part of the plume can be entrained into the building cavity and the plume can be brought towards the ground. Close to a source, when the plume spread is smaller than a representative building dimension, the presence of a building can have a major impact on the plume. The transport of the plume, its spread due to changes in turbulence, and hence the surface concentrations, are modified.

The ADMS 4 building module takes account of these effects. This module is used to calculate the dispersion of pollution from sources near large structures, and has the following features:

- Buildings are defined by the user in terms of their height, length, width and orientation. A main building is defined for each source. Then, for each wind direction the buildings are reduced to a single cuboidal effective wind-aligned building, whose height is a function of the height of the main building.
- The disturbed flow field consists of a re-circulating flow region or cavity in the lee of the building, with a diminishing turbulent wake downwind.
- Concentrations within the well-mixed re-circulating flow region are uniform and based upon the fraction of the release that is entrained.
- The concentration at a point further downwind is the sum of two contributions: a ground level plume from the re-circulating flow region and an elevated plume from the unentrained remainder. The turbulent wake reduces plume height and increases turbulent spread.
- The concentrations are set to zero within the user-defined buildings.

In the Case Study sensitivity tests carried out under H&ETQPAmine2 and as part of the Variation Order under the current contract, modelled concentrations were sensitive to the effect of the modelled building, with a distinct difference in concentration patterns resulting from modelling with and without the building effects included. The maximum concentrations were much higher when the building was included.

For the current runs, a detailed plan of the CHP buildings was provided by CCM Project. The plans do not include a location for the absorber stack, as this has not yet been decided, so an estimate of the absorber stack location with respect to the CHP buildings was made. The estimated stack location and the structure of the nearby CHP buildings are shown in Figure 4.4.2, where the stack is shown by a red marker. Further details of the modelled stack are given in Section 4.5.

The main criteria to be taken into account when deciding whether particular buildings should be included in dispersion modelling are the height with respect to the stack height(s) and the distance from the stack(s). A useful informal rule is to include buildings that are higher than a third of the stack height. In this case, the stack is likely to be situated very close to the CHP plant, and the height of the buildings is greater than a third of the 65m stack height, so the effects of the CHP buildings should be included in the modelling.

For the majority of the model runs carried out in the Case Study, a single, idealised building was modelled in ADMS to represent the CHP plant buildings; this is shown in Figure 4.4.3, and the parameters are given in Table 4.4.1.

Note that the height modelled for the idealised single building is higher than the proposed height of the CHP buildings, and therefore the resulting concentrations will tend to be conservative (overestimating). Sensitivity tests were carried out to investigate the effects of modelling the buildings as a more realistic set-up of separate structures at individual heights. The configuration for this multiple-building building scenario is shown in Figure 4.4.4, and the parameters are shown in Table 4.4.2. A further sensitivity test was carried out to investigate the effects of modelling without any building effects at all.

For all model runs, other on-site buildings were accounted for in a general way by applying a high surface roughness value for the Mongstad site only (see Section 4.4.4).

Note that it is possible that other buildings or structures could be constructed around the absorber stack that would need to be modelled explicitly in future modelling studies, when more information is known; this might include the absorber stack tower, if its dimensions were sufficiently large.

Figure 4.4.2: Estimated location of the absorber stack with respect to the CHP plant buildings

Figure 4.4.3: Modelled building dimensions – single building

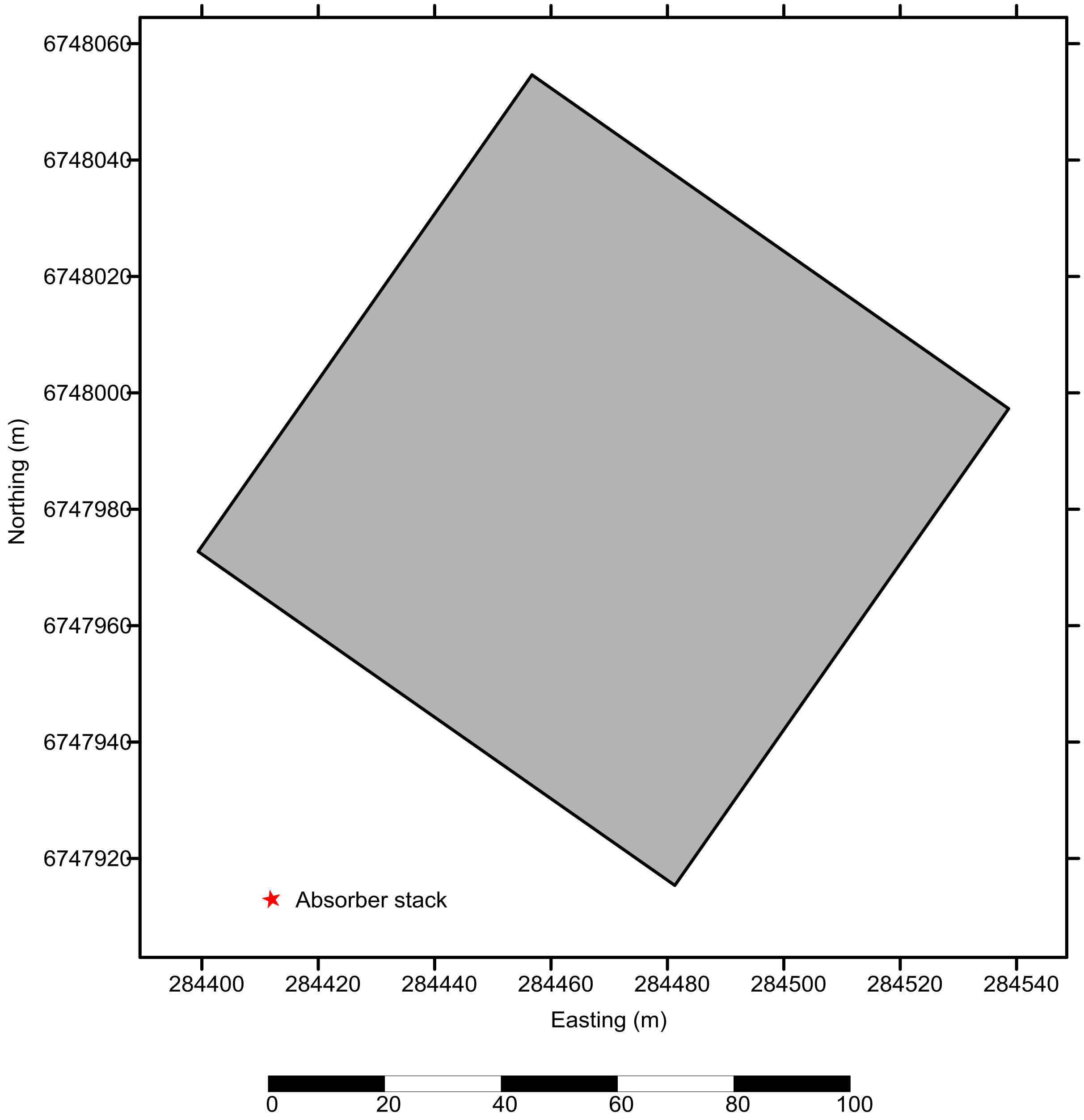


Table 4.4.1: Modelled building parameters – single building

Parameter	**Value**
Location of centre	284469, 6747985
Height (m)	60
Length (m)	100
Width (m)	100
Angle of the length of the building from north (°)	125

Figure 4.4.4: Locations of modelled building and absorber stack – multiple building layouts

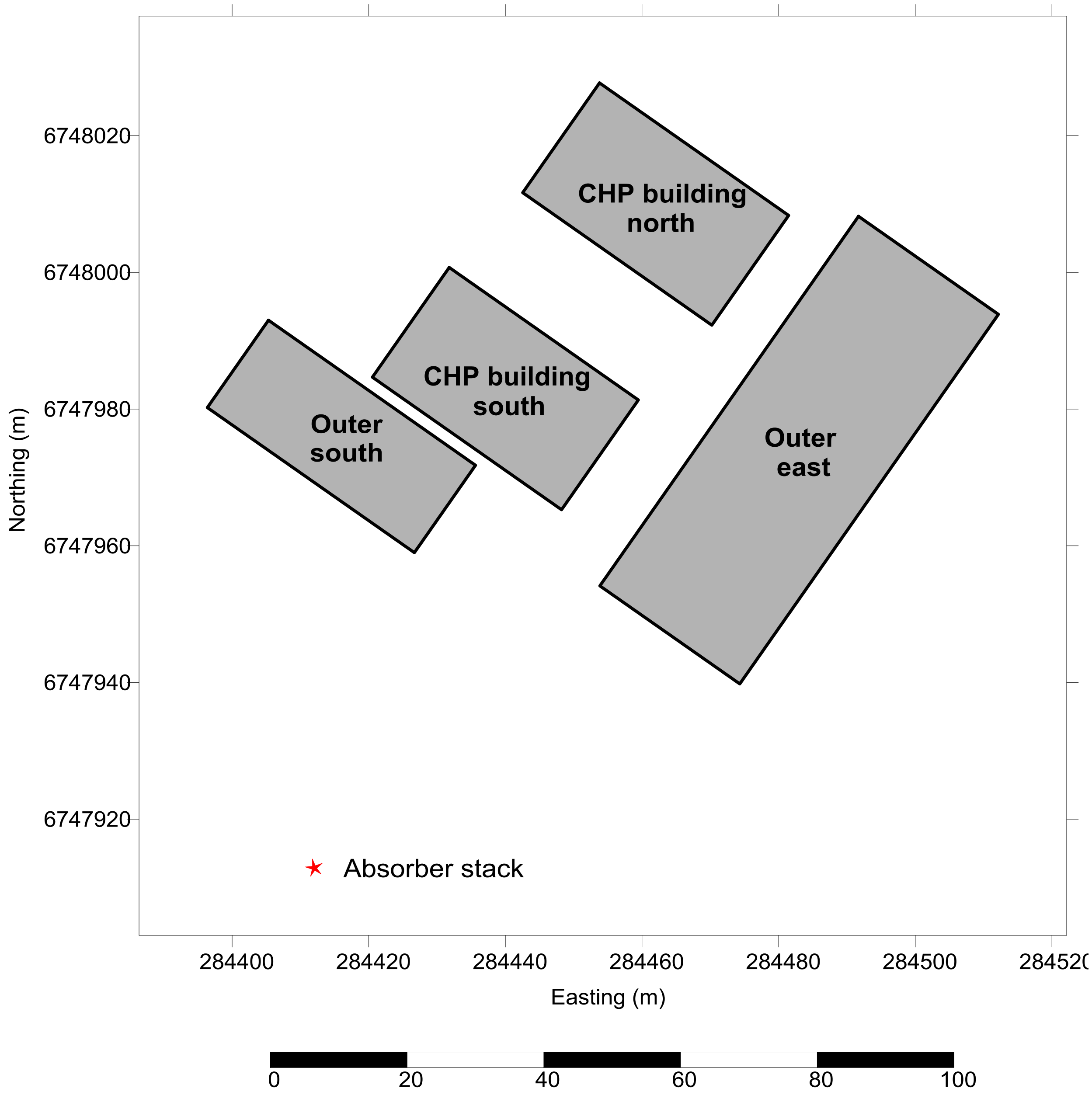


Table 4.4.2: Modelled building parameters – multiple buildings

Building name	**Parameter**	**Value**
CHP building south	Location of centre	284440, 6747983
	Height (m)	34
	Length (m)	34
	Width (m)	20
	Angle of the length of the building from north (°)	125
Outer east	Location of centre	284483, 6747974
	Height (m)	25
	Length (m)	25
	Width (m)	66
	Angle of the length of the building from north (°)	125
CHP building north	Location of centre	284462, 6748010
	Height (m)	34
	Length (m)	34
	Width (m)	20
	Angle of the length of the building from north (°)	125
Outer south	Location of centre	284416, 6747976
	Height (m)	25
	Length (m)	37
	Width (m)	16
	Angle of the length of the building from north (°)	125

4.4.3. Complex terrain effects

The complex terrain model FLOWSTAR, within ADMS 4, is able to take into account the effects of terrain. The baseline model runs were run without these terrain effects, which ensured that model run times were kept to a minimum, and hence many more sensitivity tests could be carried out in the available time. This is unlikely to have a large effect on the modelled results. The area immediately surrounding the Mongstad site is relatively flat, and although there are mountains to the north east of the site, these are relatively far from Mongstad. Effects of this large-scale terrain will partially be taken into account in the meteorological data. Where terrain effects were modelled in previous modelling studies, the effects were relatively small, i.e. seen as a small difference in the modelled concentrations.

Sensitivity tests were carried out to test the effects of the terrain. The details of the terrain data are given in Section 4.8.5, and results are given in Section 4.10.8.

4.4.4. Surface roughness

To account for the effects of surface roughness, a single surface roughness length of 0.5 m was used for the modelling site, and a second value of 0.1 m was used for the meteorological site. These values are likely to be representative of the general area.

The surface roughness length is an important parameter used to determine the impact of the surface features such as buildings, trees and bushes on the mean wind speed and the turbulence near to the surface.

FLOWSTAR, within ADMS 4, is able to take into account spatially-varying roughness. This was included in sensitivity tests, as described in Section 4.8.5. Results of these sensitivity tests are given in Section 4.10.8.

4.4.5. Minimum Monin-Obukhov length

In ADMS 4, the boundary layer structure is characterised by the boundary layer height, h, and the Monin-Obukhov length, L_{MO}, rather than by a Pasquill stability category.

In unstable (convective conditions), L_{MO} is negative, with a magnitude of typically less than 20 metres. For these conditions, the magnitude of L_{MO} is a measure of the height above which convective turbulence (the turbulence caused by heating effects) is more important than mechanical turbulence, the turbulence generated by friction at the Earth's surface.

In near-neutral conditions, the magnitude of L_{MO} is very large, and it can be a positive or negative value, depending on whether the surface is being heated or cooled by the air above it. In stable conditions, L_{MO} has a positive value of between 1 metre and 20 metres. It is then a measure of the height above which vertical turbulent motion is significantly inhibited by the stable stratification.

In urban and suburban areas, a significant amount of heat is emitted by buildings at night time, after absorbing heat during the day. The heat emitted warms the air within and above the urban area. This is known as the urban heat island and its effect is to prevent the atmosphere in a built-up area from becoming very stable. In general, the larger the area the more heat is generated and the stronger the effect becomes. This means that L_{MO} will never fall below some minimum value, and the larger the urban area, the larger the minimum value.

ADMS 4 allows the user to define a minimum value for L_{MO} at the meteorological site as well as at the dispersion site to account for any difference in the nature if the sites. A minimum Monin-Obukhov length of 1m (the model default) was used for the current modelling study, for both met and dispersion sites. The Mongstad site, and the sites from which the meteorological data was sourced are all situated in rural areas, and therefore likely to be well-represented by a value of 1m.

4.4.6. Surface wetness and albedo

Surface wetness refers to the amount of water on the surface or the amount of moisture in vegetation. This is important in determining how much heat from the sun is used for evaporation and therefore not available for heating the surface and generating turbulence. If the surface wetness is high, a significant proportion of heat from the sun is used for evaporation, so less heat is available for turbulence and mixing. The Priestley-Taylor parameter represents the surface moisture available for evaporation; the value must be between 0 and 3 and the model default value is 1, which corresponds to moist grassland.

In ADMS 4, values of Priestley-Taylor parameter for the meteorological site and the dispersion site can be set independently of one another. The sensitivity tests from the Case Study carried out under H&ETQPAmine2 showed that although ADMS results varied significantly for the range of values tested, this range was very extreme; representing very wet and very dry surfaces. The default value of 1, representing moist grassland, is considered to be representative of the area around the Mongstad site and the meteorological site, so this value was used for both areas.

The surface albedo or reflectivity is the fraction of incident radiation from the sun which is reflected by the surface. It is therefore also important in determining how much heat from the sun is available to heat the surface. A value of 0.6 is used for snow-covered surfaces and a value of 0.23 is an average value used for non-snow covered surfaces.

In ADMS 4, values of surface albedo for the meteorological site and the dispersion site can be set independently of one another. The albedo at both sites can be varied hourly via the ADMS 4 *.met* file, allowing real snow cover data to be used to change the value of albedo from hour to hour.

The sensitivity of the modelled results to the presence of snow cover was tested in the Case Study sensitivity tests carried out under H&ETQPAmine2 by setting the albedo for both the meteorological site and the dispersion site to 0.6, representing snow-covered ground, for all of December, January and February. The value for the remainder of the year was set to 0.23, the model default value. These sensitivity tests showed that model results were not very sensitive to these variations, even given the overestimated period for snow coverage assumed. For the current model runs, therefore, the surface albedo at the Mongstad site was set to a constant value of 0.23.

The values of albedo for the meteorological site and the Mongstad site were set to be the same, as the meteorological sites are sufficiently close to the Mongstad site that albedo effects will be very similar.

4.5. Source parameters and emissions data

4.5.1. CHP stack parameters and emissions

Data for the stack parameters and plans for the CHP plant building and other structures were provided by CCM Project, and the resulting modelled stack parameters are shown in Table 4.5.1. The location of the CHP absorber stack was estimated by CERC, from the site plans, in conjunction with digital map data; this is shown in Figure 4.4.2.

Table 4.5.1: Modelled source parameters

Parameters					
Emission velocity (m/s)	**Volume flow rate (m^3/s) at 30°C**	**Source height (m)**	**Source diameter (m)**	**Emission temperature (°C)**	**Location (m)**
20	670	65	6.53	30	284412, 6747913

Data were provided for emissions of specific amines and nitrosamines emitted from the CHP stack. A main emissions scenario was provided, but there are three other scenarios that have been used for sensitivity tests.

The emissions provided for the absorber stack comprise several amines plus an emission rate for nitrosamines that might be expected to form within the stack. All emissions were provided as emission concentrations, in volumetric units (ppmv and ppbv).

Monoethanolamine (MEA) represents the main amine solvent that is assumed to be used for the carbon capture process.

Table 4.5.2 shows the emission concentrations that were provided to CERC by CCM Project for the modelling.

Table 4.5.2: Emissions data provided

Species	**Units**	**Composition**
Amines:		
Monomethylamine	ppmv	0.1
Dimethylamine	ppmv	0.05
Monoethanolamine	ppmv	1.0
Nitrosamines	ppbv	0.25
Nitramines	ppbv	0

4.5.2. Emissions data input to ADMS 4

Emission concentrations in volumetric units (ppmv and ppbv) were converted to emission rates in g/s using the volume flow rate information provided, the relative molecular masses (RMM) and the ideal gas equation. The emission temperature of 30°C was assumed for these conversion calculations.

For the directly emitted nitrosamines, the conversion of the supplied emission rates in volumetric units (ppbv) to a mass-based emission rate (g/s) depends on the mass of the particular nitrosamine emitted from the stack, and therefore requires an assumed relative molecular mass. It was assumed that the directly-emitted nitrosamine was N-nitrosodimethylamine (NDMA).

Table 4.5.3 shows the resulting emission rates, as input into ADMS 4.

Emissions were assumed to be constant throughout each day, and throughout the year, i.e. no time-varying factors were applied to the emission rates.

Table 4.5.3: Calculated emission rates and RMM values

Species	**RMM**	**Emission rate (g/s)**			
		Scenario 1 (Baseline)	**Scenario 2**	**Scenario 3**	**Scenario 4**
Amines:					
Monomethylamine	31	0.082	0.165	0.041	0.025
Dimethylamine	45	0.060	0.120	0.030	0.018
Monoethanolamine	61	1.623	1.623	0.162	0.487
Direct nitrosamine emission (assuming NDMA)	74	4.92×10^{-4}	9.84×10^{-4}	1.97×10^{-4}	1.48×10^{-4}

CCM project provided data for NOx emissions from the CHP stack. This data is important because the formation of nitrosamines and nitramines depends on reactions with NO and NO_2 respectively. Monthly totals were provided, and annual average emission rates were used. The emissions were assumed to be continuous throughout the year. Emissions were also provided for the other refinery stacks that are significant emitters of NOx. These were used to produce background concentrations, as described in Section 4.6.2.

The data input to the model are summarised in Table 4.5.4. The proportion of NO_2 in the emitted NOx is also shown.

Table 4.5.4: Modelled NOx emissions

Source	**NOx emission rate (g/s)**	**Percentage NO_2**
CHP	1.79	10
SK101	7.94	10
SK702	3.75	10
SK4802	15.08	10
Flare	4.17	10

4.6. Baseline Case

The Baseline Case used the model setup described in previous sections, with meteorological data from 2008, and emissions of dimethylamine (DMA) only. Terrain effects were not included in the Baseline Case, and a fixed surface roughness length was used. Annual average output was produced on a 10km by 10km grid with a resolution of 100m. The Baseline Case assumptions are described in this section.

The Baseline Case was kept as simple as possible, to allow model parameters and input data to be varied separately, to allow a straightforward, transparent comparison. A wide range of model parameters and input data was investigated, with the Baseline case as a basis for comparison. These investigations include the modelling of the other emitted amines, other meteorological years, the effects of terrain, roughness and buildings and the effects of varying the input kinetic data for the chemical reaction schemes.

4.6.1. Assumed kinetic parameters for dimethylamine

The kinetic and photochemical parameters for dimethylamine, used for the Baseline Case were specified by means of the .aai file, as described in Section 3.3.

The information used for the DMA chemistry scheme is described in Section 2.2.2. This was taken from the 2011 ADA report, which includes data and information from experimental studies, chemical modelling and literature surveys. The most up-to-date values were chosen for the Baseline Case parameters.

The reaction parameter values used in the Baseline Case are given in Table 4.6.1. Parameters used for investigating other species are given in Section 4.7, and Section 4.10.4 details investigations into the sensitivity of the model results to the various reaction parameters; other values given in the 2011 ADA report were used for these investigations.

Table 4.6.1: Reaction rate constant values for DMA, for the Baseline Case

Parameter	Value	Unit	Description
k_1	6.50×10^{-11}	cm^3/molecule/s	From Atkinson *et al,*[6] and Carl and Crowley[7]
k_2	9.54×10^{-20}	cm^3/molecule/s	Based on ADA experiments
k_3	2.39×10^{-13}	cm^3/molecule/s	Based on ADA experiments
k_{4a}	3.18×10^{-13}	cm^3/molecule/s	from Lazarou *et al*[8]
k_4	3.50×10^{-13}	cm^3/molecule/s	Based on ADA experiments
k_{1a}/k_1	0.42	dimensionless	Based on ADA experiments
j_5 / j_{NO2}	0.25	dimensionless	Based on ADA experiments

The value used for the constant, c, which determines the hourly-varying hydroxyl concentration, was 3.92×10^{-3} s. This was based on estimated typical daytime average values for OH concentration and annual average actinic flux at Mongstad.

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[6] Atkinson, R. *et al.* (1978) Rate constants for the reactions of the hydroxyl radical with dimethylamine, trimethylamine and ethylamine over the temperature range 298-426 K. *J. Chem. Phys*., **68**, 1850-3

[7] Carl, S. A and Crowley, J.N. (1998). Sequential two (blue) photon absorption by NO_2 in the presence of H_2 as a source of OH in pulsed photolysis kinetic studies: Rate constants for reaction of OH with CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, and $C_2H_5NH_2$ at 295 K. *J. Phys. Chem. A*, **102**, 8131-41.

[8] Lazarou, Y.G et al. (1994). Gas-phase reactions of $(CH_3)_2N$ radicals with NO and NO_2. *J. Phys. Chem.* , **98**, 2110-15.

4.6.2. Background data

The chemistry scheme in ADMS requires the input of either single annual average values or hourly sequential values. Hourly background data represent the ambient conditions much more effectively than a single annual value, and are input into ADMS 4 using a .bgd file.

Hourly sequential background data files were generated for the Mongstad site by running ADMS with emissions from the other main refinery stacks, along with a fixed values of NO_2, NO and O_3 to represent the rural ambient concentrations. The refinery stack emissions were provided by CCM project, and are described in Section 4.5.2.

The background files account for the differences in wind direction, so are specific to each year of meteorological data. For the baseline case, the met data was for 2008, so the .bgd file was created using meteorological data for this year.

4.6.3. Summary of Baseline Case assumptions

Table 4.6.2 gives a summary of the various assumptions and parameters that make up the Baseline Case model runs.

Table 4.6.2: Summary of Baseline Case assumptions

Parameters	Description
Amine emitted	Dimethylamine (DMA) only
Amine emission rate	Value for the main emission scenario (Scenario 1)
Stack parameters	Values provided by CCM project
Kinetic parameters	Based mainly on the 2011 ADA report experimental values
Meteorological data	2008
CHP NOx emission rate	Provided by CCM project
Background data	Hourly-varying data, created from model run of refinery stack NOx and rural ambient values of NO_x and O_3
Output	10 km by 10km receptor grid. Resolution100m
Buildings	Included
Complex terrain	Not included
Surface roughness length	Fixed values for dispersion site (0.5 m) and meteorological site (0.1 m)
Minimum Monin-Obukhov length	1m
Surface wetness	Priestley-Taylor parameter value of 1
Albedo	Value of 0.23

4.7. Other amines and directly-emitted nitrosamine

4.7.1. Overview

For this set of model runs, the model was run separately for each amine, and for the directly-emitted nitrosamine. The results were summed to give a total (nitrosamine plus nitramine) concentration.

As well as the specific emission rates, the conversion factor for ppb to $\mu g/m^3$ has to be specified, which depends on relative molecular mass.

For each of the amines and directly emitted NDMA, a set of reference kinetic parameters were established. For DMA these were those used in the Baseline Case. The reference kinetic parameters for the other two amines emitted, and for the directly-emitted nitrosamine, are described in the following sections. These are named 'reference' parameters because they act as a baseline on which to base sensitivity tests.

For MEA, the reaction expressions on which the kinetic parameters are based are from the 2010 ADA MEA report. The reaction scheme given is analogous to that for DMA, so the rate constants are analogous. Subsequent research, however, has shown that no stable nitrosamine is formed from MEA, so this was taken into account in the modelling.

For MMA, no full rate expression was available from the 2011 ADA report. There are rate constant values for the initial OH attack reaction (k1 in the ADMS amine chemistry scheme), and also branching ratios for this reaction (k1a / k1). The subsequent reaction steps shown in the report are very different to those for DMA and MEA, as described below.

4.7.2. Reference kinetic parameters for monomethylamine (MMA)

As previously described, the MMA reaction scheme is generally analogous to the DMA reaction scheme, so the DMA amine scheme in ADMS can be used to model MMA. This scheme is set up so that the numbering system of the DMA reaction scheme (as shown in Section 2.2.2) is used for inputs into the model.

Table 4.7.1 shows the numbering system used for the MMA reaction scheme in the 2011 ADA report (shown in Section 2.2.3), with respect to the numbering system used for the ADMS amine chemistry scheme (and the DMA reaction scheme), given in Section 2.2.2.

Despite the general similarity between the two reaction schemes, there is one important difference in the MMA reaction scheme reported in the 2011 ADA report, compared with that of DMA. After the initial OH attack step, the nitrosamine formed from MMA (a primary amine) isomerises. The product of this very fast isomerisation step then reacts very quickly with O_2 to form an imine. That is, a stable nitrosamine is not formed. There is, therefore, no equivalent photolysis rate coefficient, j_5, for MMA.

Table 4.7.1: Comparison of rate coefficient numbering schemes

MMA numbering	DMA (ADMS scheme) numbering
k_{17}	k_1
k_{17b}	k_{1a}
k_{18}	k_2
k_{19}	k_3
k_{22}	k_{4b}
k_{23}	k_{4a}
n/a	j_5

For MMA, the kinetic expressions for the steps following the initial OH attack are not given explicitly in the 2011 ADA report, but the assumptions made for the chemical modelling are described, and branching ratio values from experimental results are given. The combination of literature values, assumptions (based on DMA values) and experimental results was used to generate the reference kinetic parameters for the ADMS modelling. It is noted that '*Considering the differences in electronic structure between the* CH_3NH *and* $(CH_3)_2N$ *radicals the kinetic parameters of the two systems are remarkably like*' (2011 ADA report, p59), which gives confidence in the use of some of the same kinetic information as for the DMA reaction scheme.

The value for k_3 is not set to zero, as there still needs to be a sink for the amino radical, because it is not regenerated once it reacts with NO. The value for j_5 ***is*** set to zero, because the aforementioned reaction occurs instead of the photolysis. That is the nitrosamine isomerises and reacts to form the imine. It is important to set the generation of the amino radical to be as realistic as possible to avoid the formation of nitramine from the radical. The model will output nitrosamine concentrations, but these are simply ignored.

The reference kinetic parameter values used for MMA are presented in Table 4.7.2.

Table 4.7.2: Reference kinetic parameter values used for MMA

Parameter	Value	Unit	Description
k_1	1.73×10^{-11}	cm^3/molecule/s	From Carl and Crowley [7]
k_2	6.36×10^{-19}	cm^3/molecule/s	Based on ADA experiments
k_3	2.39×10^{-13}	cm^3/molecule/s	Based on ADA experiments
k_{4a}	3.18×10^{-13}	cm^3/molecule/s	From Lazarou *et al* [8]
k_4	1.59×10^{-12}	cm^3/molecule/s	Based on ADA experiments
k_{1a}/k_1	0.75	dimensionless	Based on ADA experiments
j_5 / j_{NO2}	0	dimensionless	Based on ADA experiments

4.7.3. Reference kinetic parameters for monoethanolamine (MEA)

The information for the MEA chemistry scheme was based on that given in the 2010 ADA report, which focuses on MEA reactions. The reaction parameters given in the report are generally the same as that for DMA, with a $k4/k_{tot}$ branching ration value for MEA determined by experiment.

The current understanding, however, is that a stable nitrosamine is not formed in the atmospheric transformation of MEA. This has been taken into account in the MEA kinetic parameters by setting the j_5 value to zero, and keeping a non-zero value for k_3, in a similar way to the MMA reaction parameters, as described in the previous section.

The reference kinetic parameter values used for MEA are presented in Table 4.7.3.

Table 4.7.3: Reference kinetic parameter values used for MEA

Parameter	Value	Unit	Description
k_1	3.10×10^{-11}	cm^3/molecule/s	Estimated in ADA report
k_2	9.54×10^{-20}	cm^3/molecule/s	Same as DMA value
k_3	2.39×10^{-13}	cm^3/molecule/s	Same as DMA value
k_{4a}	3.18×10^{-13}	cm^3/molecule/s	Same as DMA value
k_4	3.50×10^{-13}	cm^3/molecule/s	Same as DMA value
k_{1a}/k_1	0.08	dimensionless	Based on ADA experiments (average value)
j_5 / j_{NO2}	0	dimensionless	Based on current knowledge

4.8. Sensitivity test descriptions

4.8.1. Amine-specific reaction parameters

This section describes tests carried out to investigate the sensitivity of the modelled results to the various kinetic parameters in the amine reaction scheme. The following parameters were varied:

- the rate coefficients;
- the photochemical rate coefficient for nitrosamine photolysis j_5 ; and
- the branching ratio for the initial reaction step, k_1/k_{1a}.

4.8.1.1. DMA parameters

Table 4.8.1 describes the parameters used in each of the sensitivity tests for DMA, and Table 4.8.2 gives the values of these parameters, with the Baseline Case parameters shown for comparison purposes. For ease of reference, those values that differ from Baseline values are shown in blue font. The Lindley *et al.* values used for Test 2, and the Tuazon *et al.* values used in Tests 2 and 3, are those values given in Table 5.15 of the 2011 ADA report.

Note that the value for j_{NDMA} / j_{NO2} obtained by Nielson *et al* is almost half that of Tuazon *et al*. The experimental set-up of Tuazon *et al.* means that their value for j_{NDMA} / j_{NO2} is likely to be an upper limit for the nitrosamine relative photolysis rate. Therefore, higher values of j_5 were not tested here.

Table 4.8.1: Description of the DMA parameter sensitivity tests

Test	**Description**
1	Lindley *et al*[9] values plus j_5 value from Tuazon *et al*[10]
2	Baseline plus j_5 value from Tuazon *et al*
3	Doubled k_1
4	Halved k_1
5	Higher k_{1a}/k_1
6	Lower k_{1a}/k_1
7	Higher k_3/k_{4a} (Increasing k_3)
8	Higher k_3/k_{4a} (Decreasing k_{4a})
9	Lower k_3/k_{4a} (Decreasing k_3)
10	Higher k_2/k_{4a} (Increasing k_2)
11	Lower k_2/k_{4a} (Decreasing k_2)
12	Lower j_5

Table 4.8.2: Parameters used for the DMA sensitivity tests

Test	**k_1**	**k_2**	**k_3**	**k_{4a}**	**k_4**	**K_{1a}/k_1**	**J_5 /j_{NO2}**
Baseline	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
1	6.5×10^{-11}	1.24×10^{-19}	8.53×10^{-14}	3.18×10^{-13}	3.9×10^{-13}	0.37	0.53
2	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	$3.18 \text{ X } 10^{-13}$	3.5×10^{-13}	0.42	0.53
3	1.3×10^{-10}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
4	3.25×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
5	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.7	0.25
6	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.2	0.25
7	6.5×10^{-11}	9.54×10^{-20}	3.18×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
8	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	2.39×10^{-13}	3.5×10^{-13}	0.42	0.25
9	6.5×10^{-11}	9.54×10^{-20}	3.18×10^{-14}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
10	6.5×10^{-11}	1.59×10^{-19}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
11	6.5×10^{-11}	6.37×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.25
12	6.5×10^{-11}	9.54×10^{-20}	2.39×10^{-13}	3.18×10^{-13}	3.5×10^{-13}	0.42	0.1

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[9] Lindley *et al.* "Rate studies of the reactions of the $(CH_3)_2N$ radical with O_2, NO and NO_2". *Chem. Phys. Lett.*, **67**, 57-62. 1979.
[10] Tuazon *et al.* "Atmospheric reactions of n-nitrosodimethylamine and dimethylnitramine". Environ. Sci Technol., **18**, 49-54.

4.8.1.2. MMA

Table 4.8.3 describes the parameters used in each of the sensitivity tests for MMA, and Table 4.8.4 gives the values of these parameters, with the Baseline Case parameters shown for comparison purposes. For ease of reference, those values that differ from Baseline values are shown in blue font.

Table 4.8.3: Description of the MMA parameter sensitivity tests

Test	**Description**
1	DMA values, with the Carl and Crowley [7] k1 value and the Rudic *et al*[11] k_{1a}/k_1 branching ratio
2	Doubled k_1
3	Halved k_1
4	Lower k_1/k_{1a}

Table 4.8.4: Parameters used for the MMA kinetic parameter sensitivity tests

Test	k_1	k_2	k_3	k_{4a}	k_4	K_{1a}/k_1	J_5/j_{NO2}
Baseline	1.73×10^{-11}	6.36×10^{-19}	2.39×10^{-13}	3.18×10^{-13}	1.59×10^{-12}	0.75	0
1	1.73×10^{-11}	1.24×10^{-19}	8.27×10^{-14}	3.18×10^{-13}	3.88×10^{-13}	0.52	0
2	3.46×10^{-11}	6.36×10^{-19}	2.39×10^{-13}	3.18×10^{-13}	1.59×10^{-12}	0.75	0
3	8.65×10^{-12}	6.36×10^{-19}	2.39×10^{-13}	3.18×10^{-13}	1.59×10^{-12}	0.75	0
4	1.73×10^{-11}	6.36×10^{-19}	2.39×10^{-13}	3.18×10^{-13}	1.59×10^{-12}	0.20	0

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[11] Rudic *et al*. (2003). The product branching and dynamics of the reaction of chlorine atoms with methylamine. *Phys. Chem. Chem Phys.*, **5**, 1205-12.

4.8.1.3. MEA

Table 4.8.6 describes the parameters used in each of the sensitivity tests for MEA, and Table 4.8.7 gives the values of these parameters, with the Baseline Case parameters shown for comparison purposes. For ease of reference, those values that differ from Baseline values are shown in blue font. The Lindley *et al.* values used for Test 1 are those values given in Table 5.15 of the 2011 ADA report.

Table 4.8.6: Description of the MEA parameter sensitivity tests

Test	**Description**
1	Lindley *et al.*[9] DMA values
2	Doubled k_1
3	Halved k_1
4	Lowest k_{1a}/k_1
5	Middle k_{1a}/k_1
6	Highest k_{1a}/k_1

Table 4.8.7: Parameters used for the MEA kinetic parameter sensitivity tests

Test	k_1	k_2	k_3	k_{4a}	k_4	K_{1a}/k_1	J_5 / j_{NO2}
Baseline	3.1 x 10^{-11}	9.54 x 10^{-20}	2.39 x 10^{-13}	3.18 x 10^{-13}	3.5 x 10^{-13}	0.08	0
1	3.1 x 10^{-11}	1.24 x 10^{-19}	8.53 x 10^{-14}	3.18 x 10^{-13}	3.88 x 10^{-13}	0.08	0
2	6.2 x 10^{-11}	9.54 x 10^{-20}	2.39 x 10^{-13}	3.18 x 10^{-13}	3.5 x 10^{-13}	0.08	0
3	1.55 x 10^{-11}	9.54 x 10^{-20}	2.39 x 10^{-13}	3.18 x 10^{-13}	3.5 x 10^{-13}	0.08	0
4	3.1 x 10^{-11}	9.54 x 10^{-20}	2.39 x 10^{-13}	3.18 x 10^{-13}	3.5 x 10^{-13}	0.01	0
5	3.1 x 10^{-11}	9.54 x 10^{-20}	2.39 x 10^{-13}	3.18 x 10^{-13}	3.5 x 10^{-13}	0.04	0
6	3.1 x 10^{-11}	9.54 x 10^{-20}	2.39 x 10^{-13}	3.18 x 10^{-13}	3.5 x 10^{-13}	0.12	0

4.8.2. Other reaction parameters

Tests were carried out to test sensitivity to the following parameters:

- The emission of NO_x from the CHP plume;
- The NO_2: NO ratio in the CHP plume emissions;
- The refinery NO_x emissions;
- The background (rural) NO_x concentration;
- The background (rural) ozone concentration; and
- The value of c, the constant that determines hourly OH concentrations.

Table 4.8.8 shows descriptions of the sensitivity tests in which the effects of NOx and ozone parameters were investigated.

Table 4.8.8: Descriptions of sensitivity test parameter changes with respect to the Baseline Case - varying NO_x and ozone

Parameter	Action	Value
Refinery NO_x emissions	doubled	Various values (four sources)
	halved	
CHP NO_x emissions	doubled	3.58 g/s
	halved	0.89 g/s
	Decreased proportion of NO_x that is NO_2	5%
	Increased proportion of NO_x that is NO_2	20%
Rural background NOx concentration	doubled	20 µg/m^3
	halved	5 µg/m^3
Rural background O_3 concentrations	decreased	40 µg/m^3
	increased	80 µg/m^3

Tables 4.8.9 and 4.8.10 show the values of c that were input for sensitivity tests, calculated by varying the typical OH concentrations and j_{NO2}, respectively.

Table 4.8.9: Values of c – varying OH

	Change to OH		
	Halved	Baseline	Doubled
c value (s)	0.00196	0.00392	0.00785

Table 4.8.10: Values of c – varying j_{NO2}

	Change to j_{NO2}		
	Halved	Baseline	Doubled
c value (s)	0.00785	0.00392	0.00196

4.8.3. Alternative emission scenarios

Although the main focus of this Case Study is a Baseline emissions scenario, a total of four scenarios were provided by CCM project, each representing different emissions combinations: Scenarios 1 to 3 represent a CHP absorber overhead of 2 x 100%, and Scenario 4 represents a CHP absorber overhead of 1 x 60%.

Table 4.8.11 shows the source parameters for the three alternative scenarios (2 to 4), shown alongside the main emissions scenario (1) for comparison. Table 4.8.12 shows the emissions data provided.

Note that, although Scenarios 1 and 4 appear to be identical based on these emission concentration values, different modelled concentrations will result from each of them, as they have different emission parameters. The lower volume flow rate and velocity in Scenario 4 will result in greater ground level concentrations than those in Scenarios 1 to 3, as the initial momentum of the plume will be lower.

Table 4.8.11: Modelled source parameters for the four scenarios

Scenario	Parameters					
	Emission velocity (m/s)	**Volume flow rate (m^3/s) at 30°C**	**Source height (m)**	**Source diameter (m)**	**Emission temperature (°C)**	**Location (m)**
1 (Main)	20	670	65	6.53	30	284412, 6747913
2						
3						
4	6	201				

Table 4.8.12: Emissions data provided for Scenarios 1 to 4

Species	Units	Composition			
		Scenario 1 (Baseline)	**Scenario 2**	**Scenario 3**	**Scenario 4**
Amines:					
Monomethylamine	ppmv	0.1	0.2	0.05	0.1
Dimethylamine	ppmv	0.05	0.1	0.025	0.05
Monoethanolamine	ppmv	1.0	1.0	0.1	1.0
Nitrosamines	ppbv	0.25	0.5	0.1	0.25
Nitramines	ppbv	0	0	0	0

4.8.4. Other meteorological data

Model runs were carried out with meteorological data for 2007 and 2009, to investigate the effect of inter-annual variations on predicted concentrations. Results of these investigations are shown in Section 4.10.7.

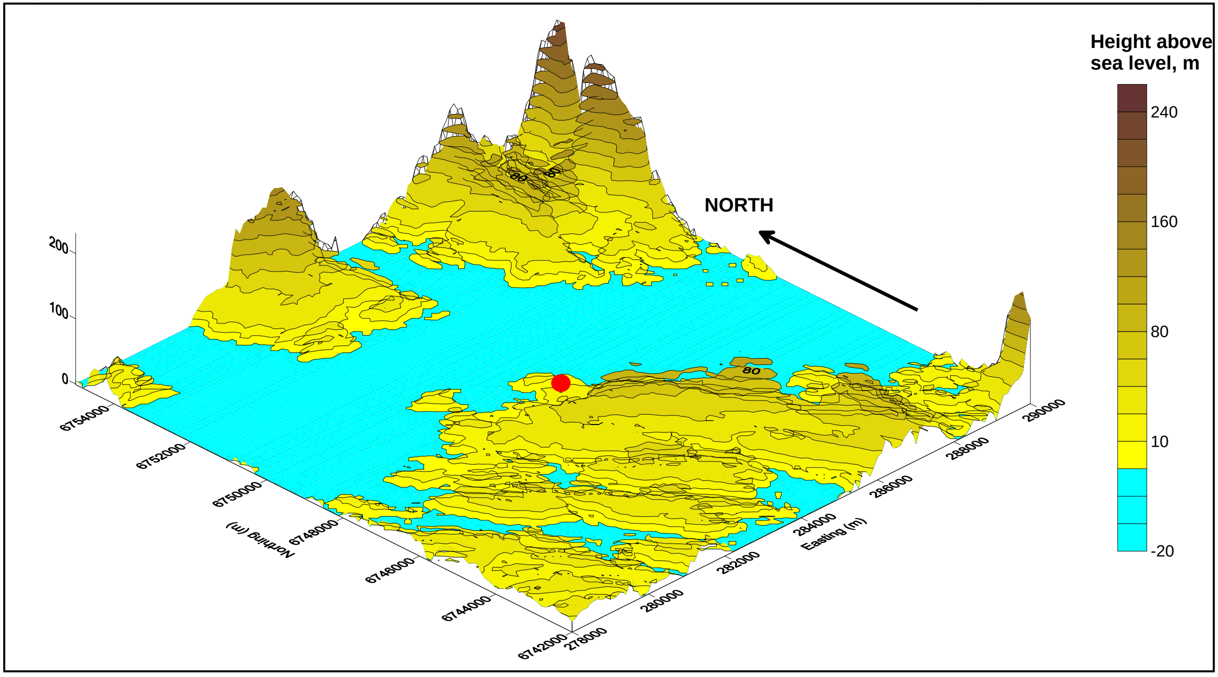
A .bgd file for the hourly sequential background concentrations was produced for each year, using the same method as for the Baseline .bgd file, as described in Section 4.6.2.

4.8.5. With terrain and variable roughness

Tests were carried out to investigate the sensitivity of the modelled results to modelling with terrain and spatially-varying roughness lengths. This section describes the input data used for these tests, and the results of the tests are given in Section 4.10.8.

The extent of the terrain data input to ADMS 4 must be larger than that of the receptor grid in order to avoid edge effects in the modelling. The terrain data used has an extent of 12km, with a resolution of 50m. Figure 4.8.1 shows a 3-dimensional plot of the terrain data. Note that the vertical scale in this plot is exaggerated.

Figure 4.8.1: Plot of local terrain. The red marker indicates the location of Mongstad

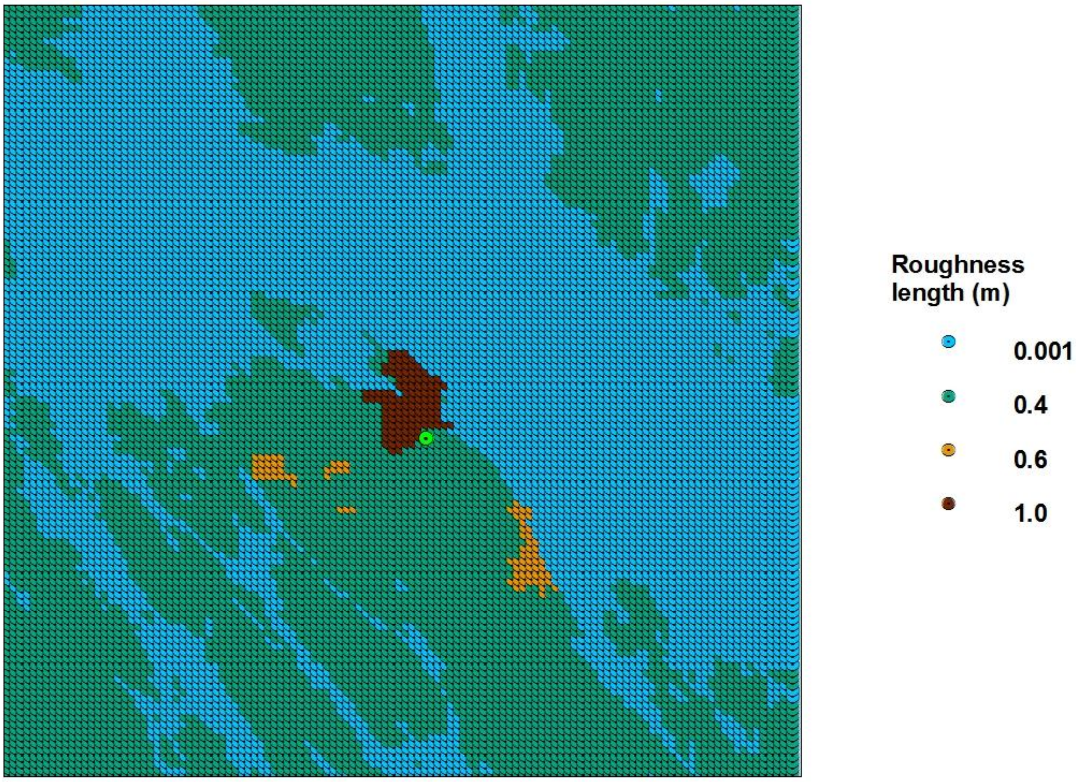


Effects of spatial changes in surface roughness were considered in the modelling using FLOWSTAR, with spatially varying surface roughness entered via the ADMS 4 *.ruf* file.

Four different values of roughness length were used: 0.001m for the sea and other water, 0.4m for the majority of the land, 0.6m for areas with a relatively high density of buildings and 1m for the Mongstad site. Figure 4.8.2 shows how these roughness points were distributed. The extent and resolution of the roughness data is the same as that of the terrain data.

A roughness value of 0.1m was input for the surface roughness length at the meteorological site, to account for the difference in land use at the meteorological site compared to the modelled area.

Figure 4.8.2: Visualisation of the spatially-varying roughness file. The light green marker represents the absorber stack



4.8.6. Building effects

These sensitivity tests were carried out to investigate the effect of the modelled building on the predicted concentrations.

Model runs were carried out for a no-building case, and a multiple-building case, for comparison with the Baseline Case building setup (single-building case). Runs were carried out for all three meteorological years (2007 to 2009).

The no-building case was carried out with the ADMS buildings module switched off. Details of the building parameters specified for the multiple-building and single-building cases are given in Section 4.4.2.

The results are shown in Section 4.10.9.

4.9. Other model runs

4.9.1. Amine concentration output

Amine concentrations were output for Scenario 1 emissions, with the Baseline Case setup. These are model runs to show the residual amine concentrations, with the chemistry scheme switched on.

The results are given in Section 4.10.10.

4.9.2. Amine concentration output with no chemistry modelling

Amine concentrations were output for Scenario 1 emissions, with the Baseline Case setup, but with the chemical reaction scheme switched off.

The results are presented in Section 4.10.11.

4.9.3. Unit emission rate

Runs were carried out with a unit emission rate (1g/s) of a generic pollutant, and no chemistry effects modelled, to isolate the effects of dispersion. The runs were based on the Baseline Case, for the meteorological years 2007, 2008 and 2009.

As described previously, Scenarios 1 to 3 share the same emission characteristics in terms of volume flow rate, velocity and temperature, a single model run can be used to demonstrate the dispersion pattern for these. Scenario 4 has a different volume flow rate (and hence a different velocity) to the other three scenarios, and the resulting plume will therefore disperse differently; a second model run was therefore carried out to demonstrate the dispersion pattern for Scenario 4.

These results are presented in Section 4.10.12.

4.10. Results

4.10.1. Overview

All of the concentrations presented in this section are ground level concentrations, calculated over a 100m resolution output grid with an extent of 10km by 10km, centred on the Mongstad site. All concentrations were calculated using 2008 meteorological data, unless otherwise stated.

The results are all annual average values, as this is the relevant statistic with which to compare the guideline value. All concentrations presented are in units of ng/m^3, unless otherwise stated.

4.10.2. Baseline case

These model runs were carried out for the Baseline Case, which includes emissions of DMA and its products only.

Table 4.10.1 shows the maximum annual average concentrations of nitrosamine and nitramine predicted over the output grid.

Table 4.10.1: Maximum predicted concentrations for the Baseline Case

Emitted species	**Maximum annual average concentration (ng/m^3)**		
	Nitrosamine	**Nitramine**	**Sum (nitrosamine plus nitramine)**
DMA	0.013	0.023	0.036

Figures 4.10.1 and 4.10.2 show a contour plot of the Baseline Case nitrosamine concentration, with and without the base map.

Figures 4.10.3 and 4.10.4 show a contour plot of the Baseline Case nitramine concentration, with and without the base map.

Figure 4.10.5 shows a contour plot of the Baseline Case sum of (nitrosamine and nitramine) concentration, without the base map.

Figure 4.10.1: Baseline Case; Nitrosamine concentrations

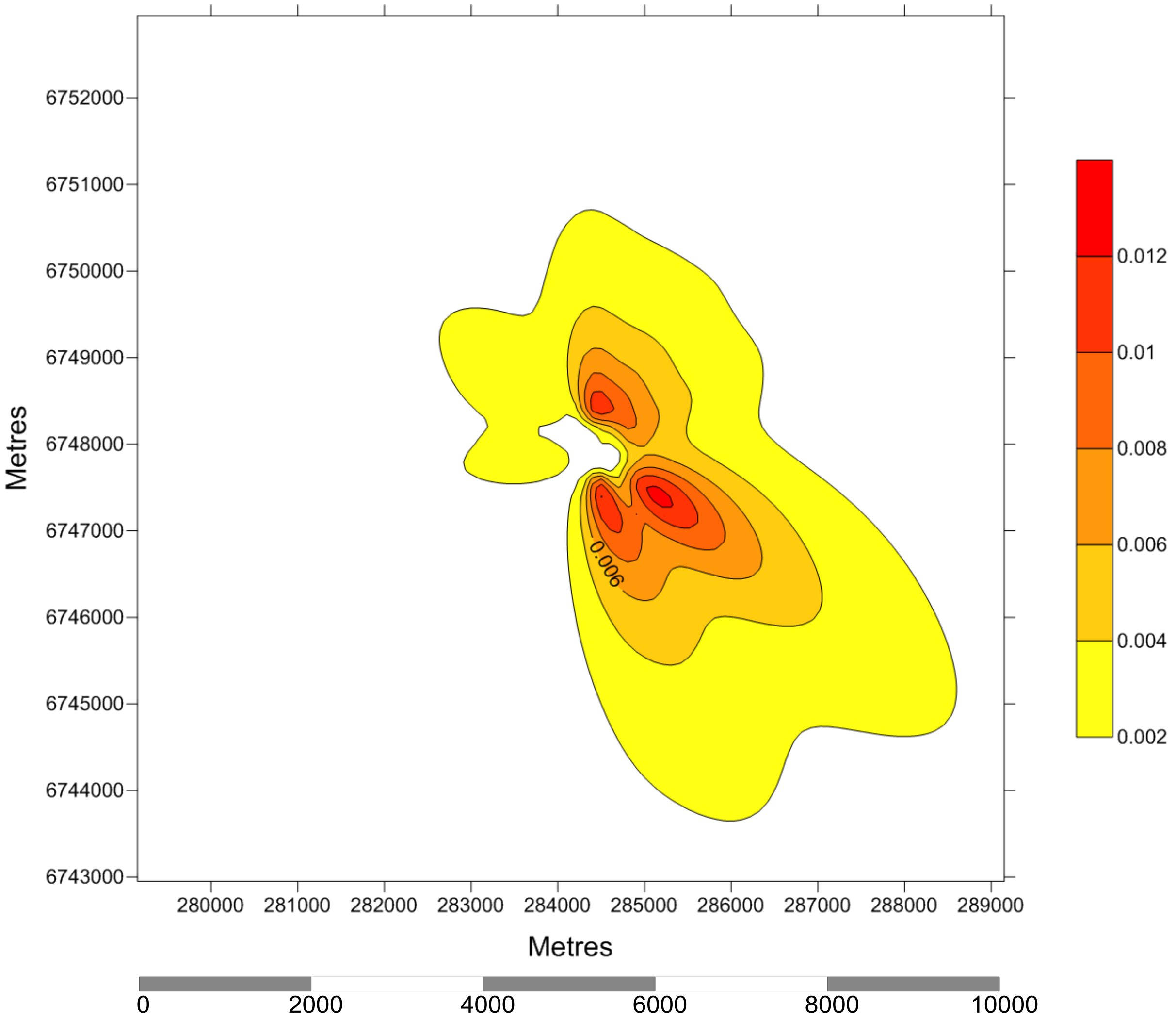


Figure 4.10.2: Nitrosamine concentrations for the Baseline Case, showing background map and stack location (black circle)

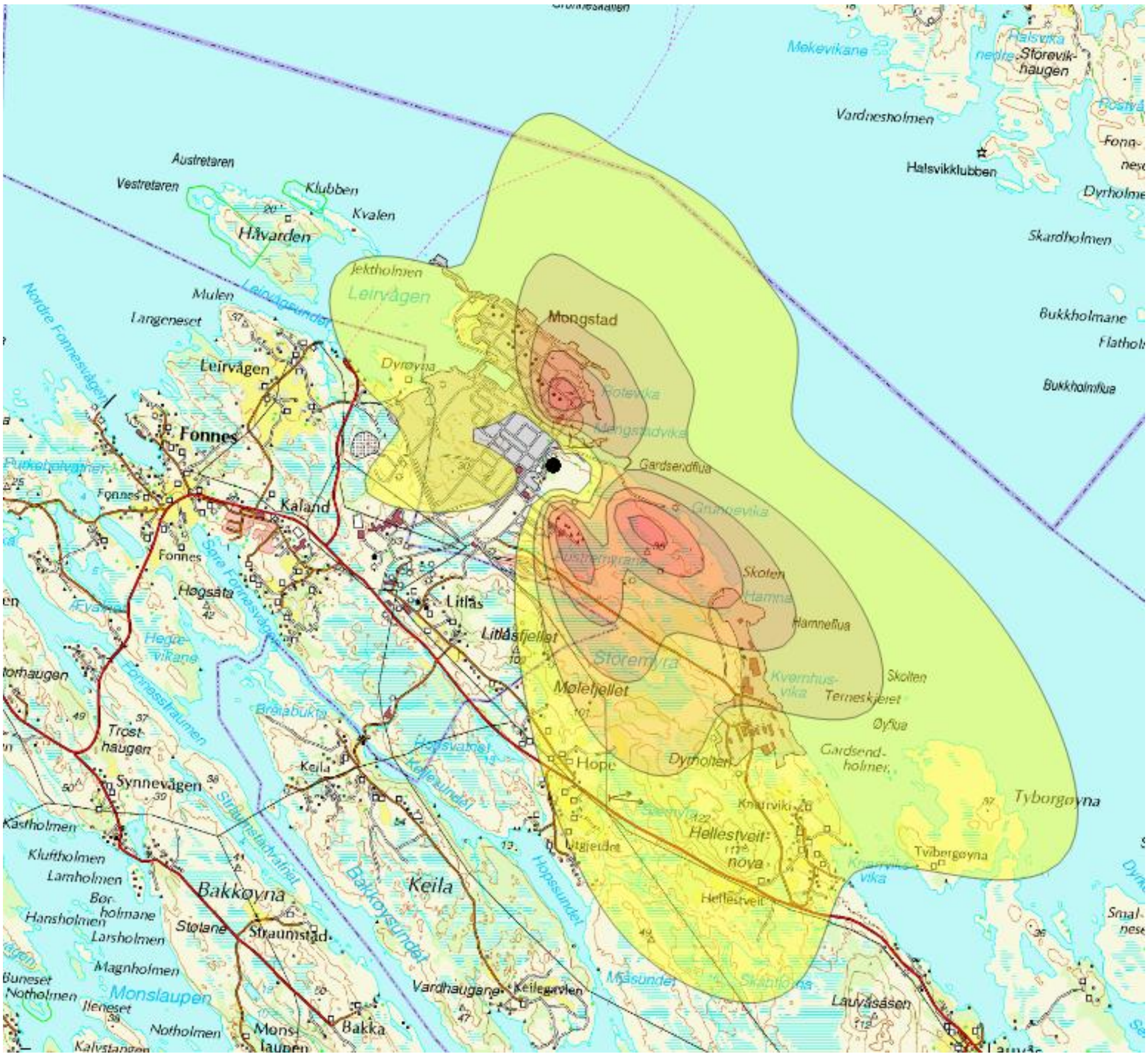


Figure 4.10.3: Baseline Case; Nitramine concentrations

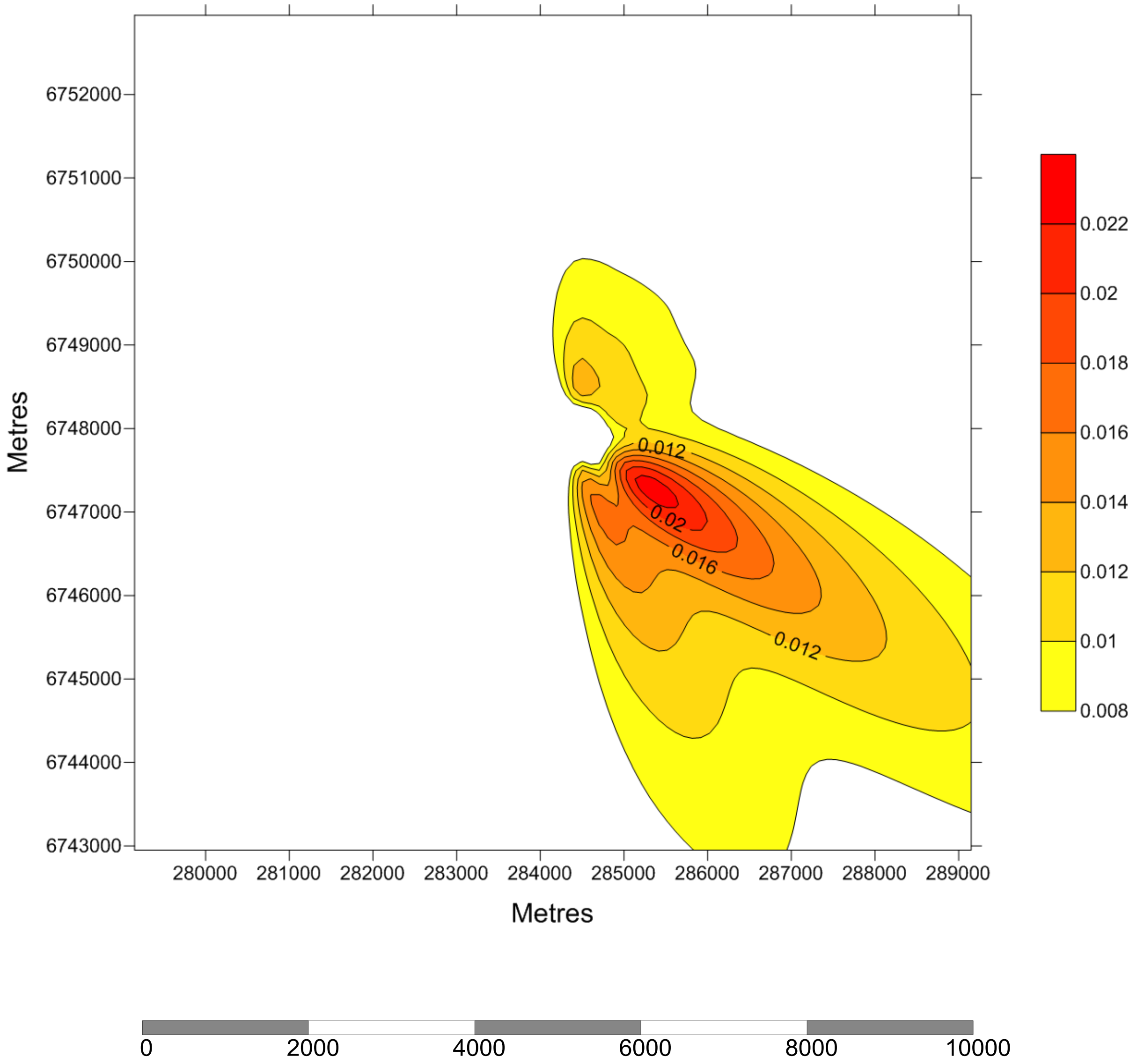


Figure 4.10.4: Nitramine concentrations for the Baseline Case, showing background map and stack location (black circle)

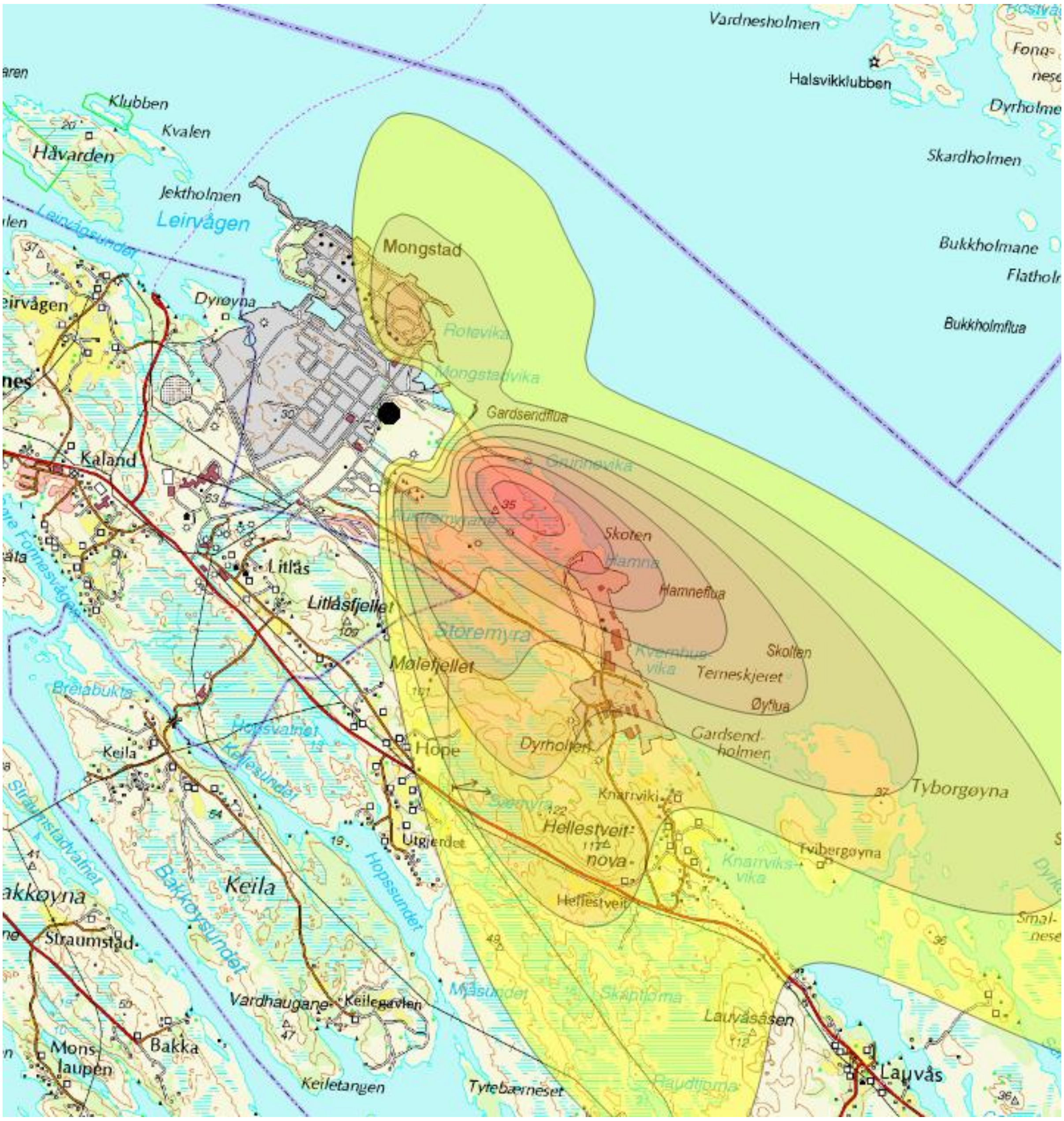
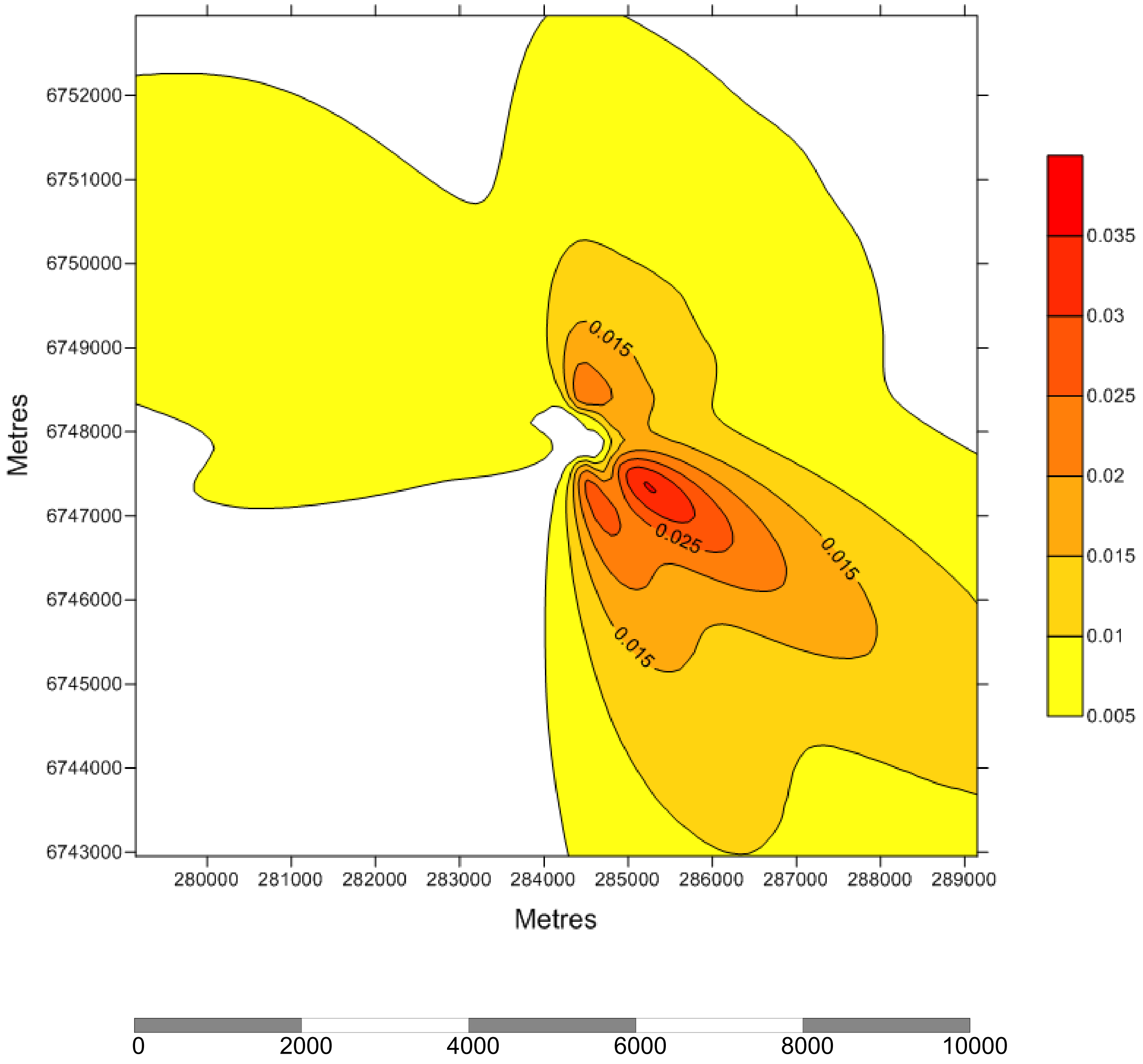


Figure 4.10.5: Sum of (nitrosamine and nitrosamine)



4.10.3. Emissions of other amines and directly-emitted nitrosamine

Scenario 1 comprises simultaneous emissions of DMA, MMA, MEA and NDMA. Model runs were carried out for these species.

Table 4.10.2 shows the maximum concentrations of these species predicted over the output grid.

Note that the maximum values occurring over the grid are not additive, so the values in the **Total** row are not a simple sum of the maximum values from each of the constituent species. This is because the different chemistry parameters result in the maximum concentrations occurring in different locations for different species. Adding together the maximum concentrations from all of the constituent species would be over-conservative.

Similarly, the **sum** column represents the maximum of the (nitramine + nitrosamine), as opposed to the (maximum nitrosamine plus the maximum nitramine). For the pie charts, the breakdown reflects the maximum concentrations of each species at the location of each maximum.

Table 4.10.2: Maximum concentrations predicted over the output grid

Emitted species	**Maximum annual average concentration (ng/m^3)**		
	Nitrosamine	**Nitramine**	**Sum (nitrosamine plus nitramine)**
DMA (Baseline)	0.013	0.023	0.036
MMA	-	0.0035	0.0035
MEA	-	0.051	0.051
Directly-emitted NDMA	0.15	0.00041	0.15
Total	0.15	0.08	**0.16**

Figure 4.10.6 and 4.10.7 show pie charts to illustrate the breakdown of each of the emitted species to the maximum nitrosamine and nitramine concentrations, respectively.

Figure 4.10.8 shows a contour plot of the nitramine concentrations from MMA emissions.

Figure 4.10.9 shows a contour plot of the nitramine concentrations from MEA emissions.

Figure 4.10.10 a) b) and c) show contour plots of the nitrosamine, nitramine and sum of (nitrosamine and nitramine) concentrations from NDMA emissions.

Figure 4.10.11 a) b) and c) show contour plots of the nitrosamine, nitramine and sum of (nitrosamine and nitramine) concentrations from all emissions.

Note that the scale for the plot of nitramine formed from the NDMA emissions, shown in Figure 4.10.10 (b) is much lower so as to clearly show the concentration pattern.

Figure 4.10.6: Maximum contributions to nitrosamines

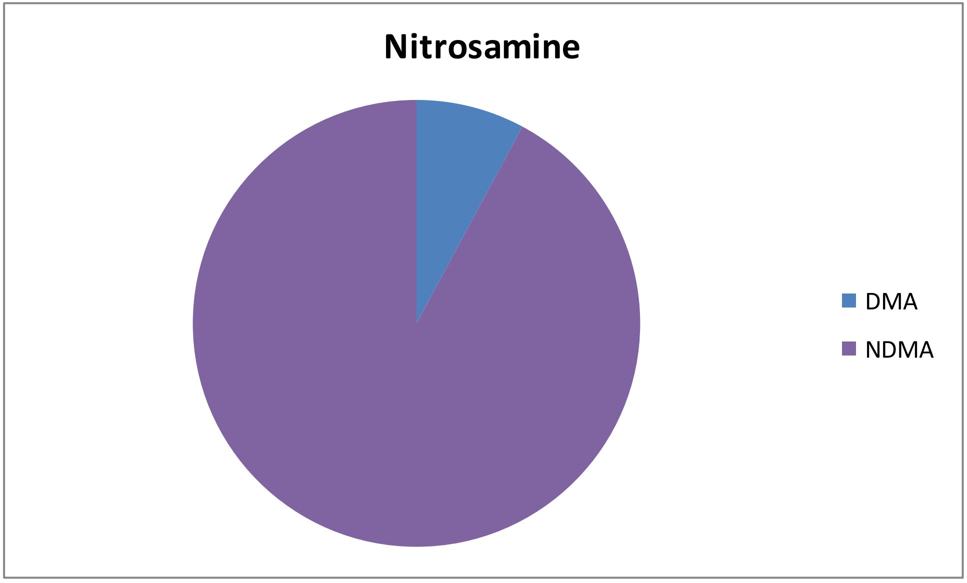


Figure 4.10.7: Maximum contributions to nitramines

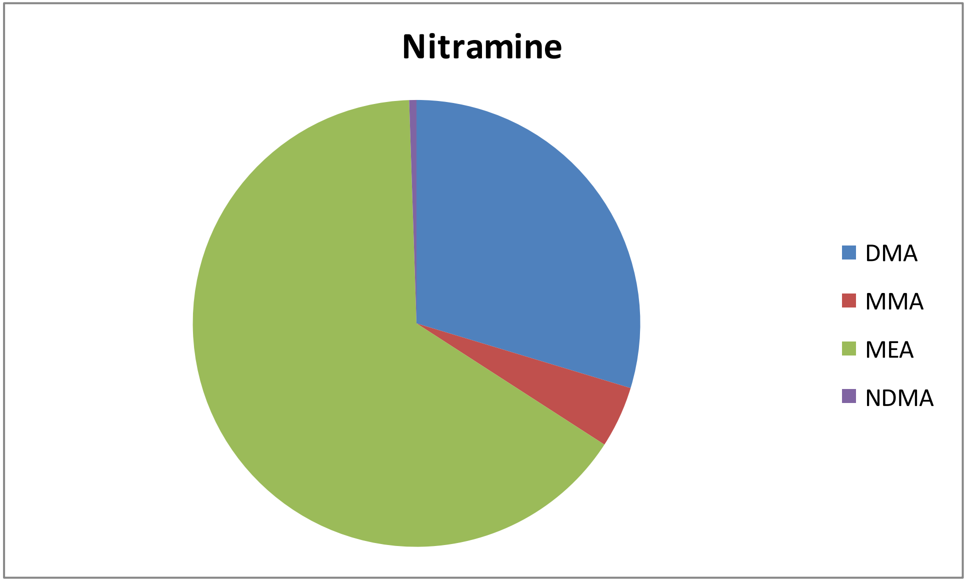


Figure 4.10.8: Nitramine concentrations from MMA emissions

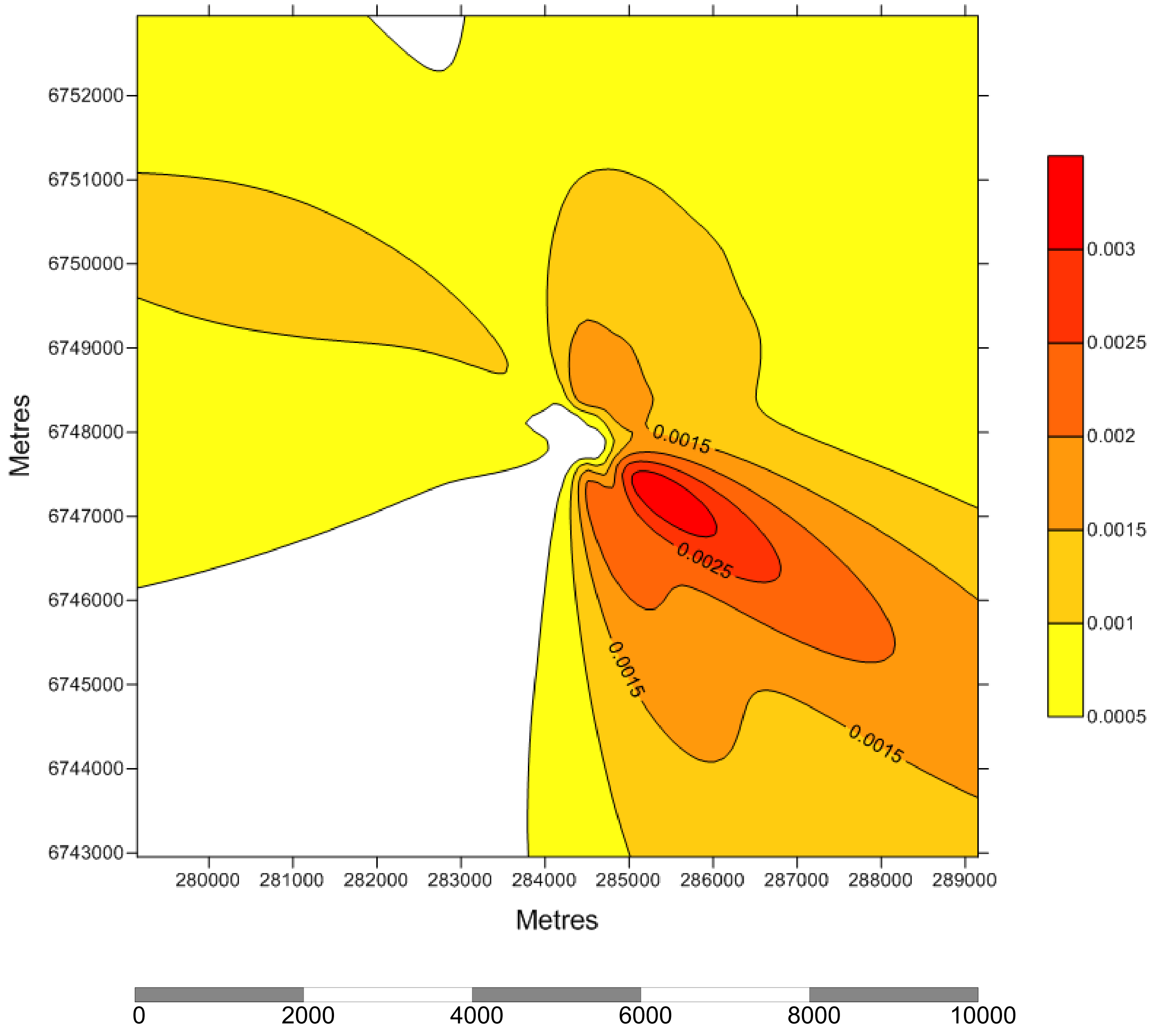


Figure 4.10.9: Nitramine concentrations from MEA emissions

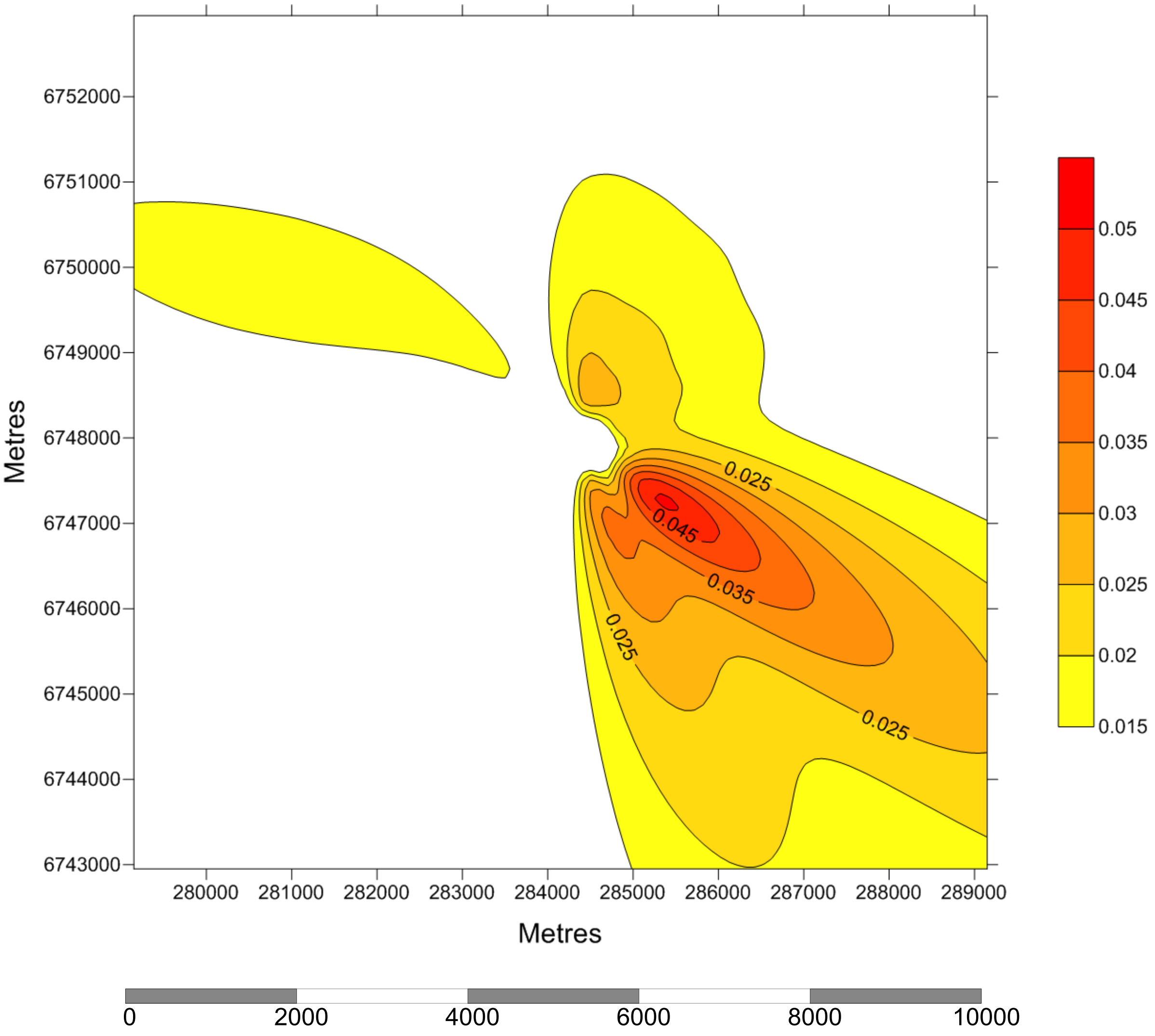


Figure 4.10.10: (a), (b) and (c): Nitrosamine, nitramine and (nitrosamine plus nitramine) concentrations, respectively, from NDMA emissions

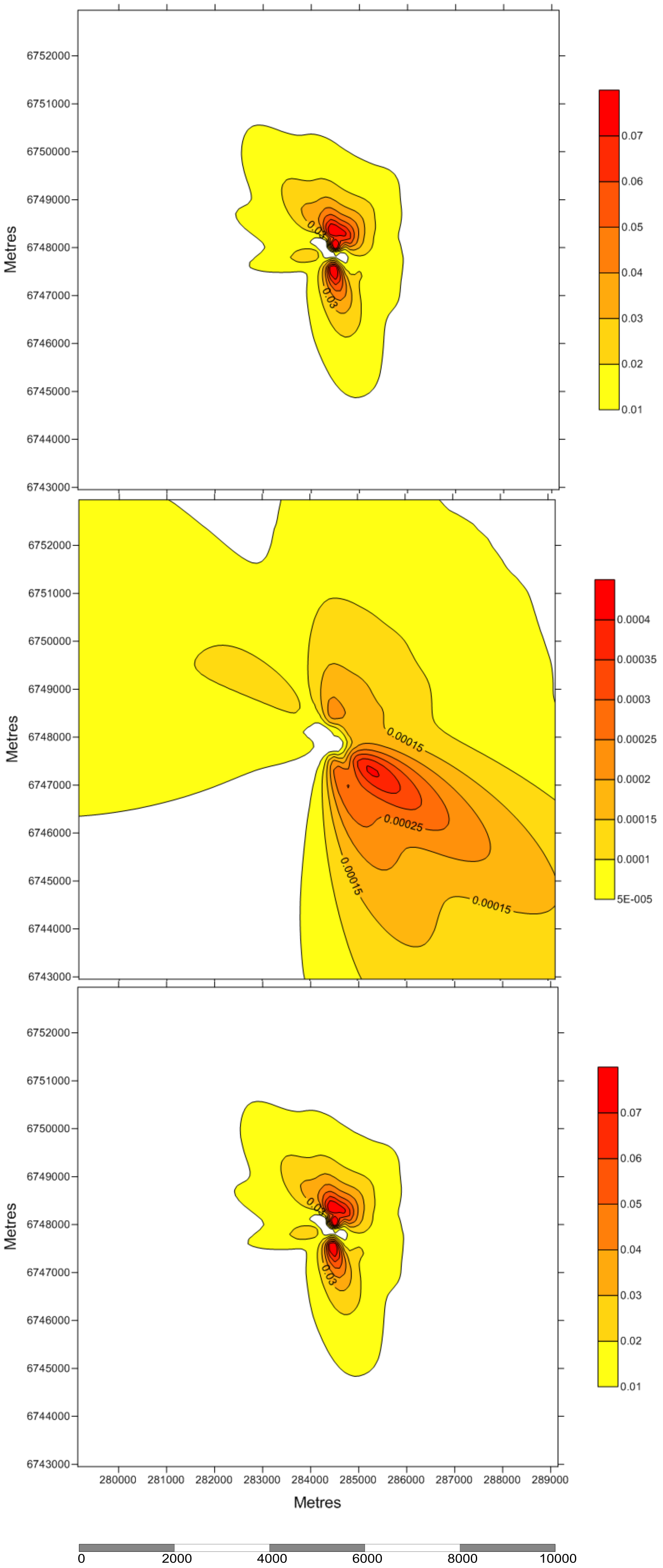
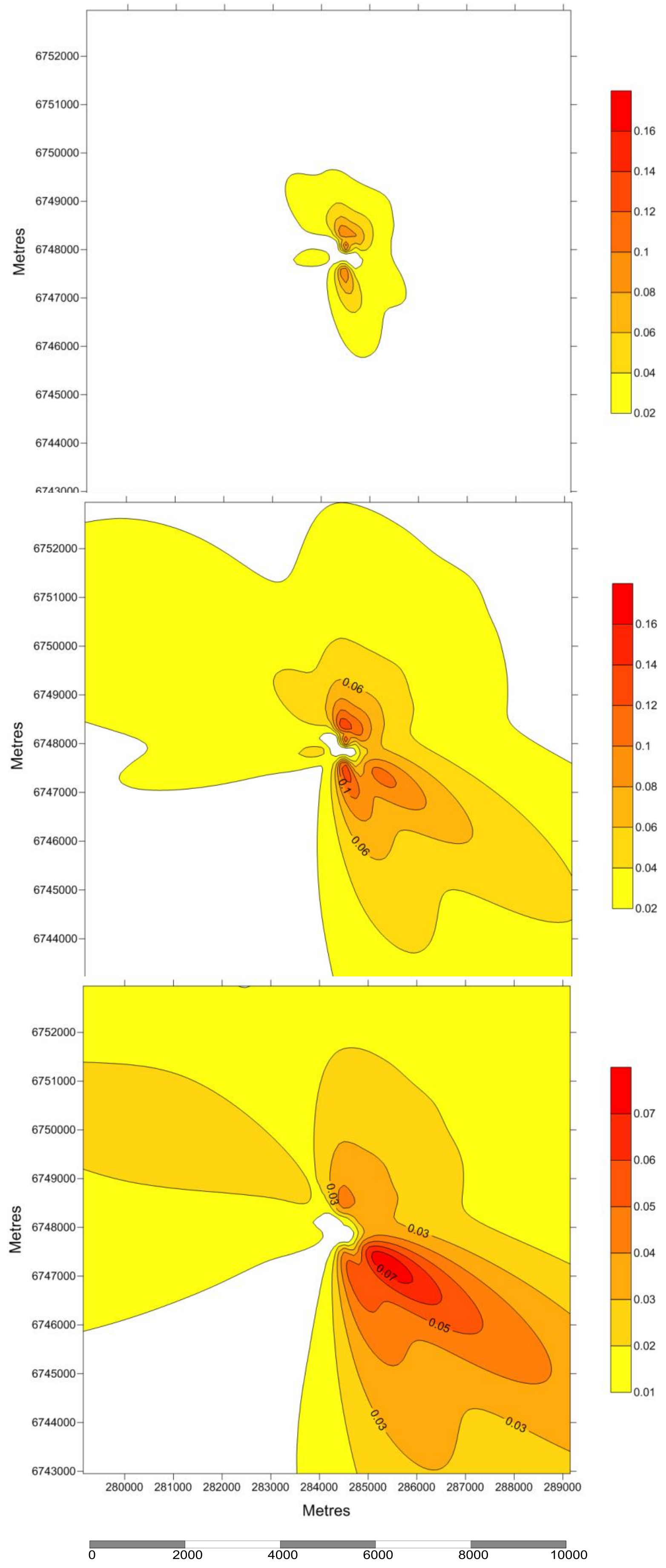


Figure 4.10.11: (a), (b) and (c): Nitrosamine, nitramine and (nitrosamine plus nitramine) concentrations, respectively, from all emissions



4.10.4. Sensitivity tests: Amine-specific reaction parameters

Tables 4.10.3 to 4.10.5 show maximum predicted concentrations for sensitivity tests investigating kinetic parameters, for DMA, MMA and MEA, respectively. For each of the tests, only those parameter values that are different to the baseline values are shown; for a full list and description of the parameters used in each case, see Sections 4.7 and 4.8.1.

Table 4.10.3: Maximum predicted concentrations for the amine-specific reaction parameter tests: DMA

Test	**Description**	**Parameter**	**Value***	**Maximum annual average concentration (ng/m^3)**	
				Nitrosamine	**Nitramine**
Baseline	-	k_1	6.50×10^{-11}	0.013	0.023
		k_2	9.54×10^{-20}		
		k_3	2.39×10^{-13}		
		k_{4a}	3.18×10^{-13}		
		k_4	3.50×10^{-13}		
		k_{1a}/k_1	0.42		
		j_5 / j_{NO2}	0.25		
1	Lindley *et al* values plus j_5 value from Tuazon *et al*	k_2	1.24×10^{-19}	0.004	0.017
		k_3	8.53×10^{-14}		
		k_4	3.18×10^{-13}		
		k_{1a}/k_1	0.37		
		j_5 / j_{NO2}	0.53		
2	Baseline plus j_5 ratio value from Tuazon *et al*	j_5 / j_{NO2}	0.53	0.011	0.023
3	Doubled k_1	k_1	1.3×10^{-10}	0.024	0.042
4	Halved k_1	k_1	3.25×10^{-11}	0.006	0.012
5	Higher k_{1a}/k_1	k_{1a}/k_1	0.7	0.021	0.039
6	Lower k_{1a}/k_1	k_{1a}/k_1	0.2	0.006	0.011
7	Higher k_3/k_{4a} (Increasing k_3)	k_3	3.18×10^{-13}	0.016	0.023
8	Higher k_3/k_{4a} (Decreasing k_{4a})	k_{4a}	2.39×10^{-13}	0.013	0.017
9	Lower k_3/k_{4a} (Decreasing k_3)	k_3	3.18×10^{-14}	0.002	0.026
10	Higher k_2/k_{4a} (Increasing k_2)	k_2	1.59×10^{-19}	0.009	0.015
11	Lower k_2/k_{4a} (Decreasing k_2)	k_2	6.37×10^{-20}	0.016	0.031
12	Lower j_5 / j_{NO2}	j_5 / j_{NO2}	0.1	0.014	0.023

* k_1 to k_4 *have units of molecules* cm^{-3} s^{-1} *and* k_{1a}/k_1 *and* j_5 / j_{NO2} *are dimensionless*

Table 4.10.4: Maximum predicted concentrations for the amine-specific reaction parameter tests: MMA

Test	Description	Parameter	Value*	Maximum annual average concentration (ng/m^3)	
				Nitrosamine	Nitramine
Baseline	-	k_1	1.73×10^{-11}	-	0.0035
		k_2	6.36×10^{-19}		
		k_3	2.39×10^{-13}		
		k_{4a}	3.18×10^{-13}		
		k_4	1.59×10^{-12}		
		k_{1a}/k_1	0.75		
		j_5 / j_{NO2}	0		
1	Lindley *et al.* DMA values, with Carl and Crowley k_1 value and Rudic *et al* k_{1a}/k_1 branching ratio	k_2	1.24×10^{-19}	-	0.0054
		k_3	8.27×10^{-14}		
		k_4	3.88×10^{-13}		
		k_{1a}/k_1	0.52		
2	Doubled k_1	k_1	3.46×10^{-11}	-	0.0069
3	Halved k_1	k_1	8.65×10^{-12}	-	0.0018
4	Lower k_1/k_{1a}	k_{1a}/k_1	0.20	-	0.00048

* *k_1 to k_4 have units of molecules cm^{-3} s^{-1} and k_{1a}/k_1 and j_5 / j_{NO2} are dimensionless*

Table 4.10.5: Maximum predicted concentrations for the amine-specific reaction parameter tests: MEA

Test	**Description**	**Parameter**	**Value***	**Maximum annual average concentration (ng/m^3)**	
				Nitrosamine	**Nitramine**
Baseline	-	k_1	3.10×10^{-11}	-	0.051
		k_2	9.54×10^{-20}		
		k_3	2.39×10^{-13}		
		k_{4a}	3.18×10^{-13}		
		k_4	3.50×10^{-13}		
		k_{1a}/k_1	0.08		
		j_5 / j_{NO2}	0		
1	Lindley *et al.* DMA values	k_2	1.24×10^{-19}	-	0.044
		k_3	8.53×10^{-14}		
		k_4	3.18×10^{-13}		
2	Doubled k_1	k_1	6.2×10^{-11}	-	0.097
3	Halved k_1	k_1	1.55×10^{-11}	-	0.026
4	Lowest k_{1a}/k_1	k_{1a}/k_1	0.01	-	0.006
5	Middle k_{1a}/k_1	k_{1a}/k_1	0.04	-	0.025
6	Highest k_{1a}/k_1	k_{1a}/k_1	0.12	-	0.076

** k_1 to k_4 have units of molecules cm^{-3} s^{-1} and k_{1a}/k_1 and j_5 / j_{NO2} are dimensionless*

Figures 4.10.12 to 4.10.17 show contour plots for nitrosamines from DMA emissions for the various sensitivity tests.

Figures 4.10.18 to 4.10.23 show contour plots for nitramines from DMA emissions.

Figures 4.10.24 to 4.10.26 show contour plots for nitramines from MMA emissions.

Figures 4.10.27 to 4.10.29 show contour plots for nitramines from MEA emissions.

Figure 4.10.12: DMA Baseline, Test 1 and Test 2 (various parameters) - nitrosamine

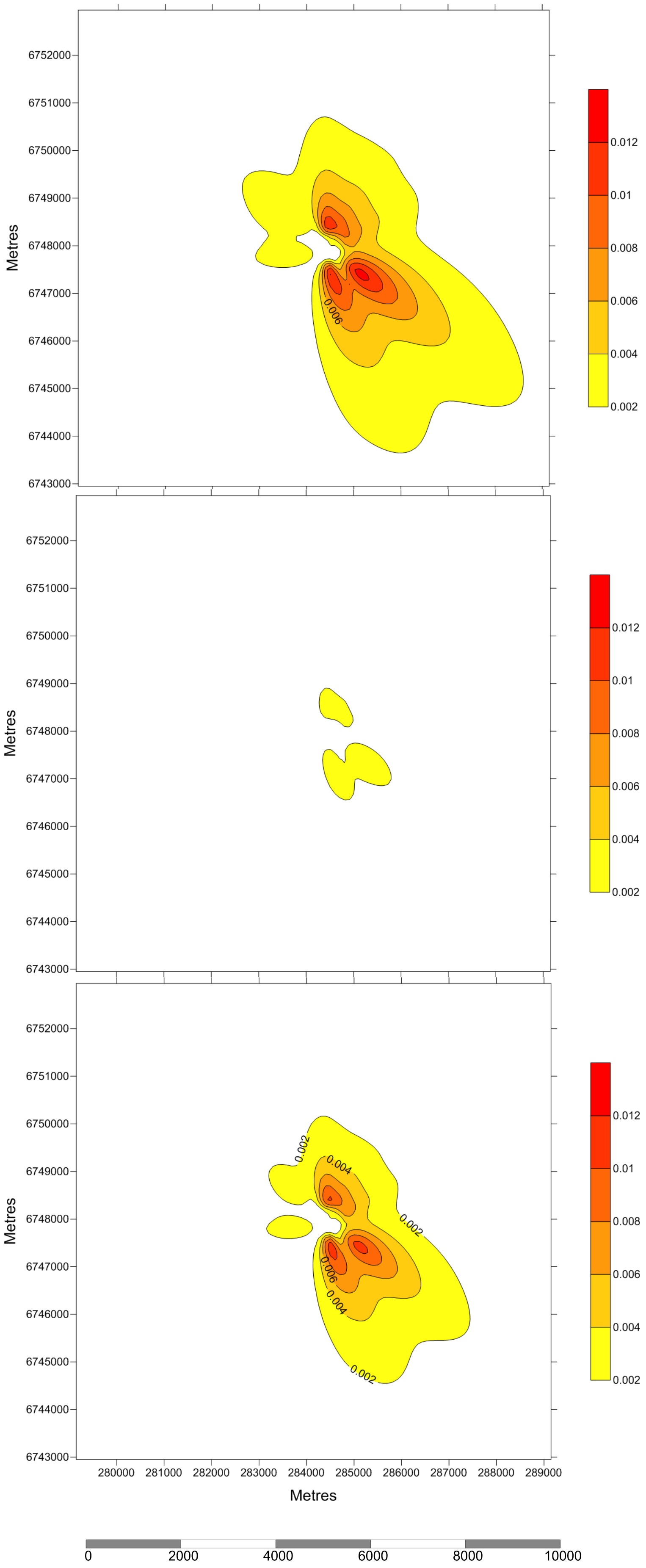


Figure 4.10.13: DMA Tests 3 and 4 (Doubled and halved k_1, respectively) - nitrosamine

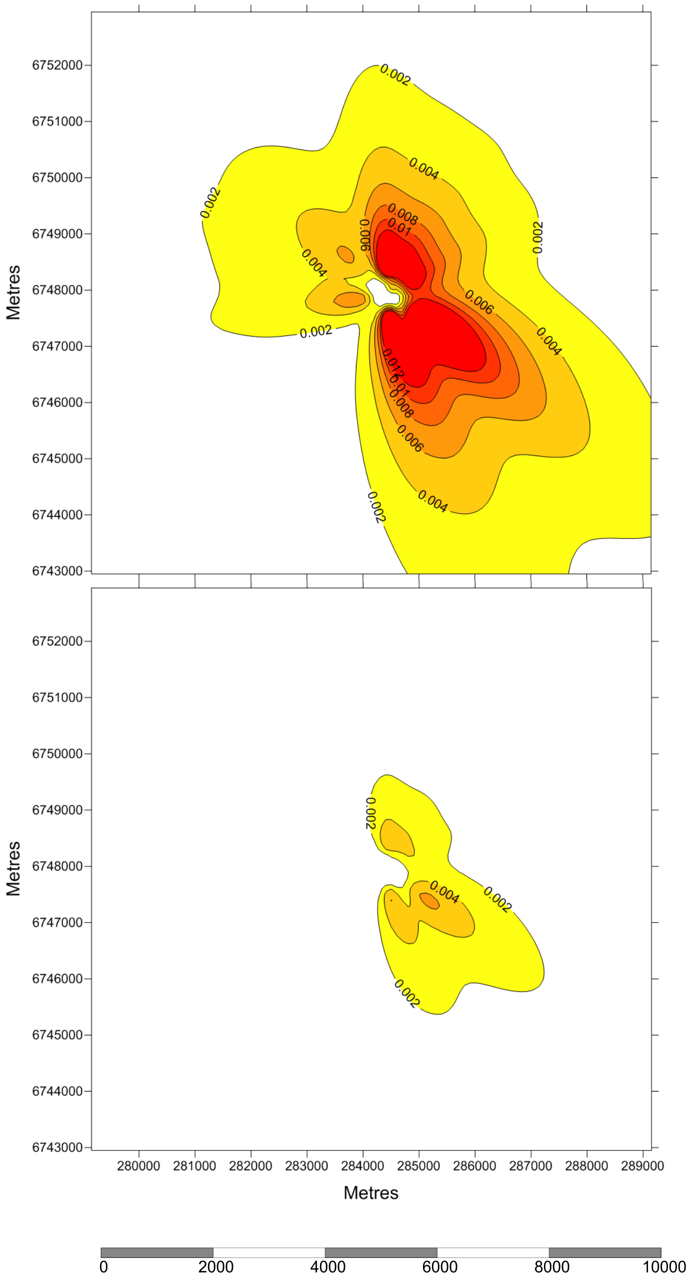


Figure 4.10.14: DMA Tests 5 and 6 (Higher and lower k_{1a}/k_1, respectively) - nitrosamine

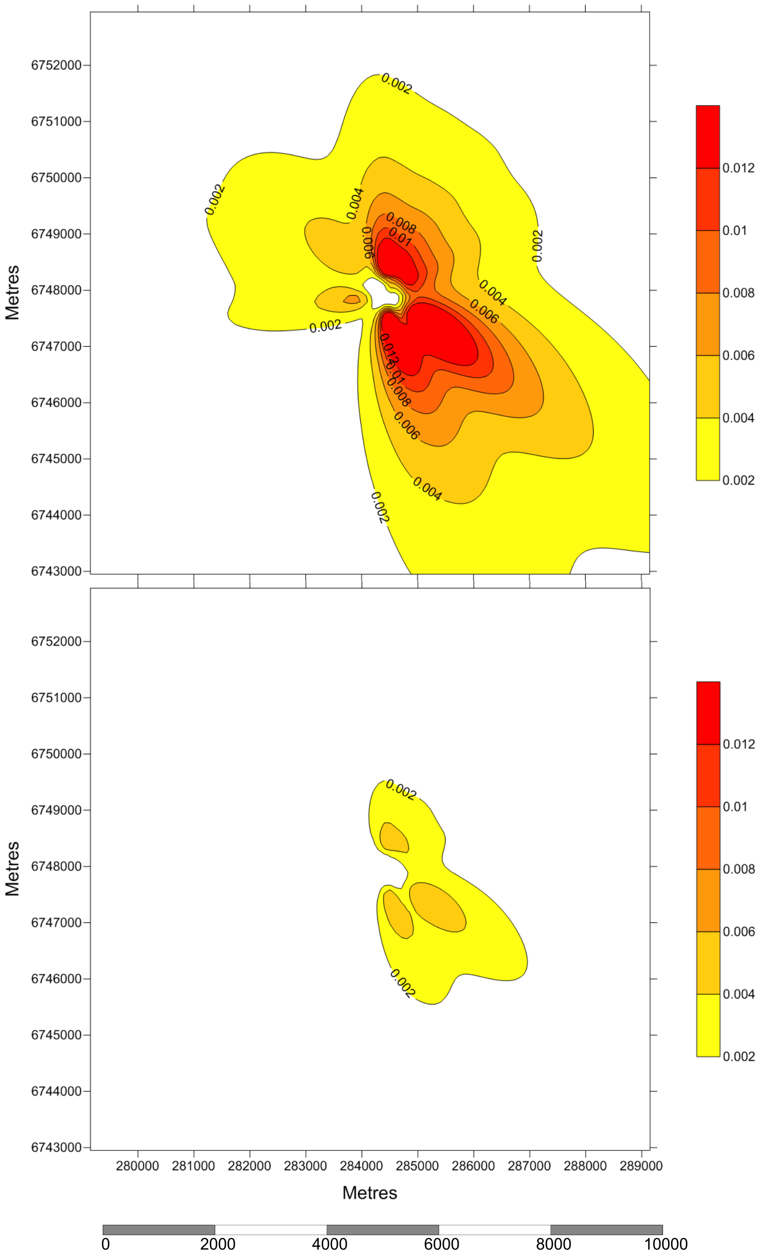


Figure 4.10.15: DMA Tests 8 and 9 (Varying k_3/k_{4a}) - nitrosamine

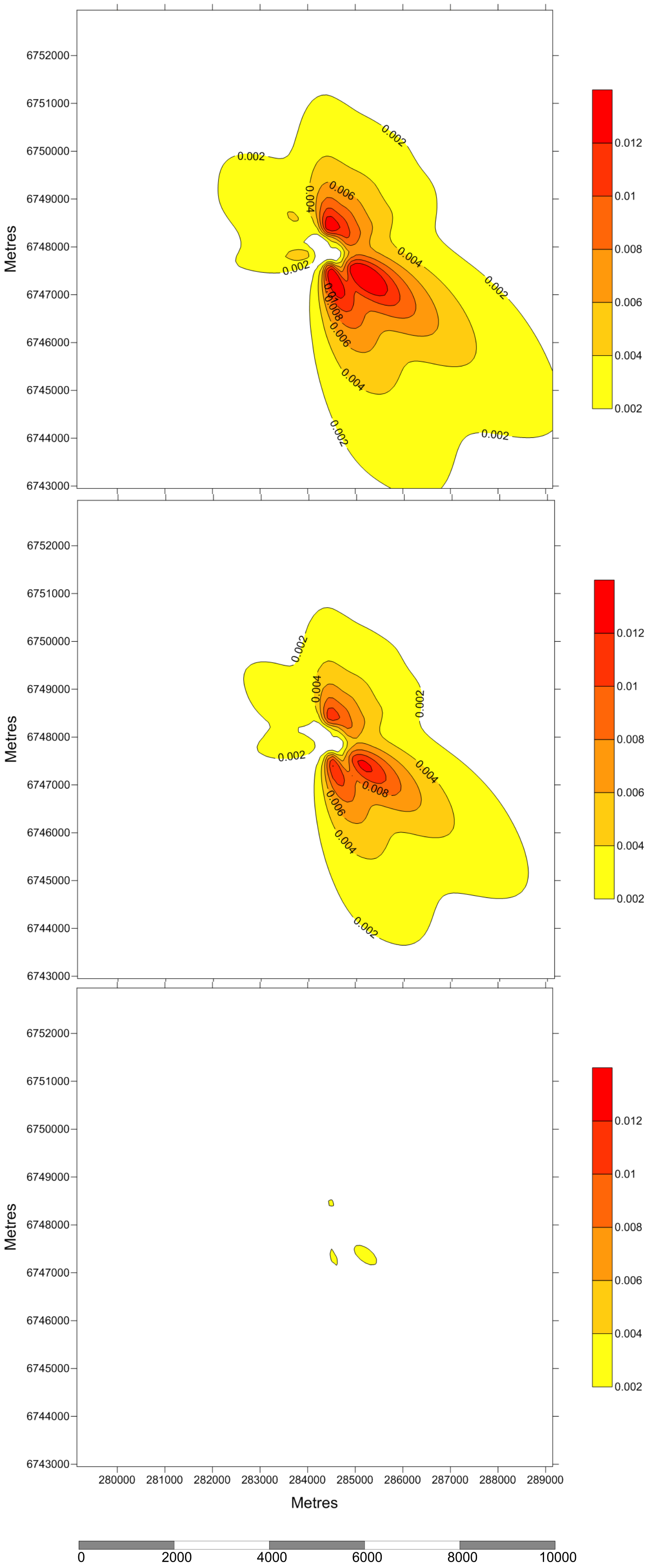


Figure 4.10.16: DMA Tests 5 and 6 (Higher and lower k_2/k_3, respectively) - nitrosamine

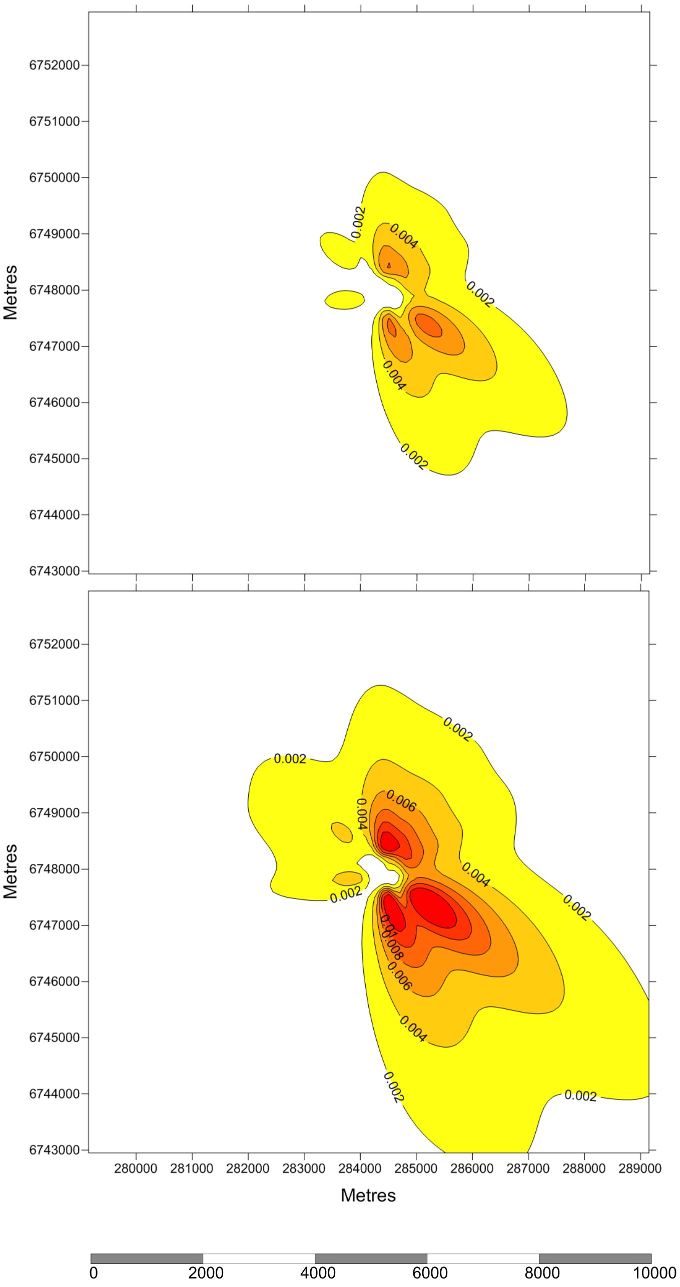


Figure 4.10.17: DMA Tests 8 (Lower j) – nitrosamine

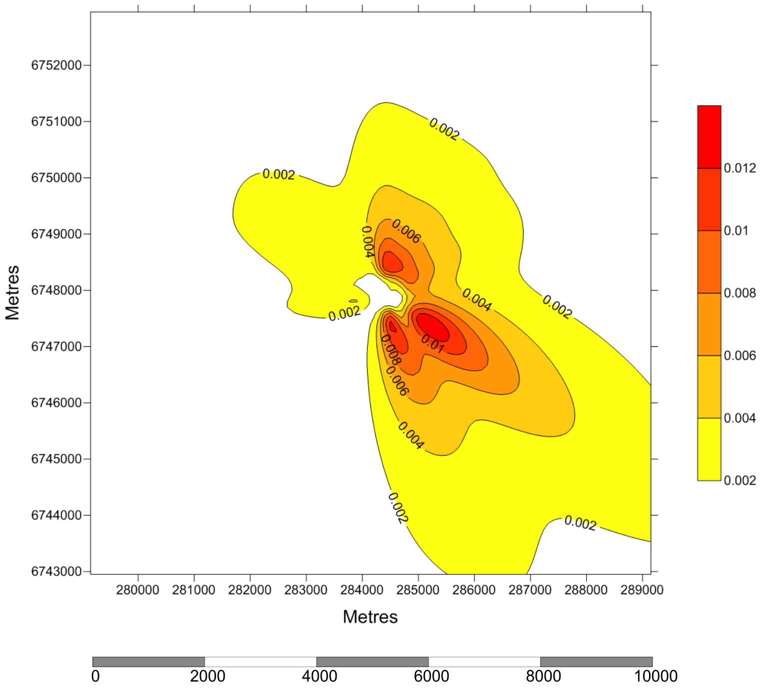


Figure 4.10.18: DMA Baseline, Test 1 and Test 2 (various parameters) - nitramine

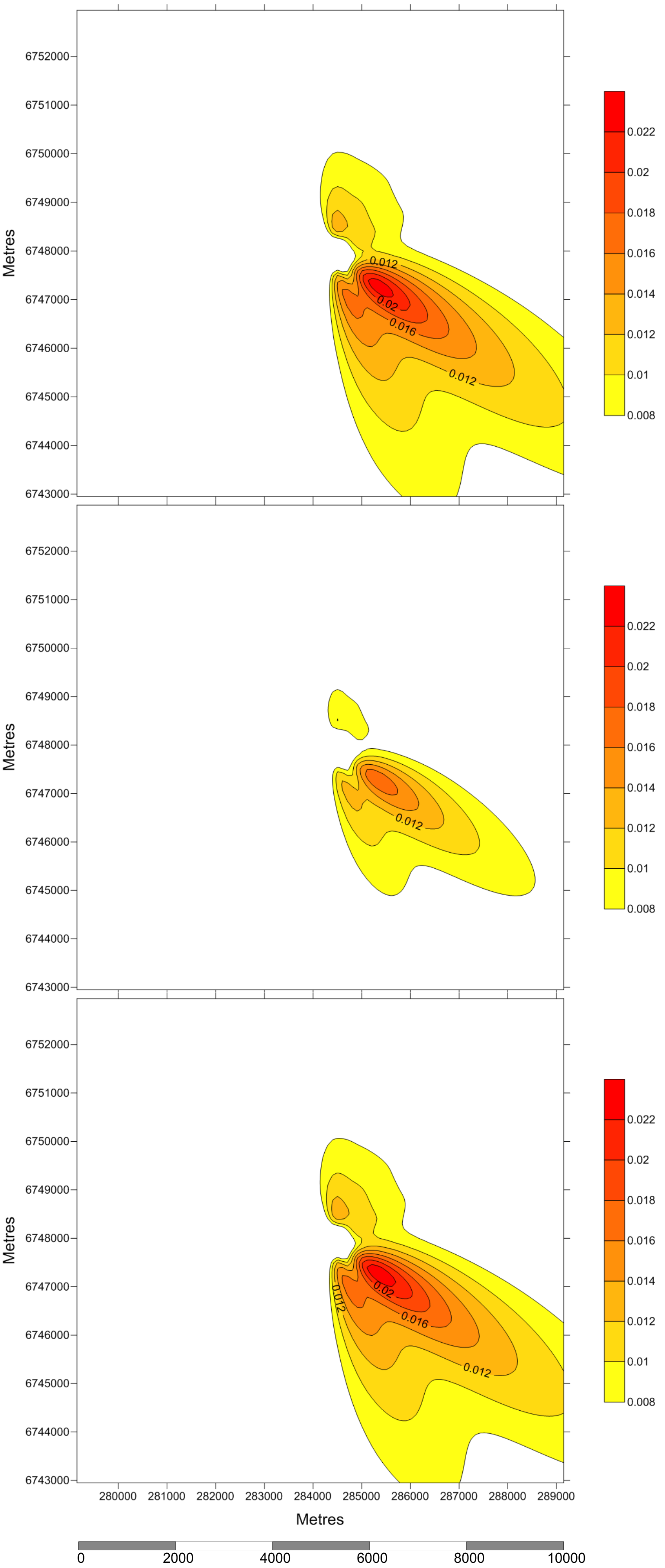


Figure 4.10.19: DMA Tests 3 and 4 (Doubled and halved k_1, respectively) - nitramine

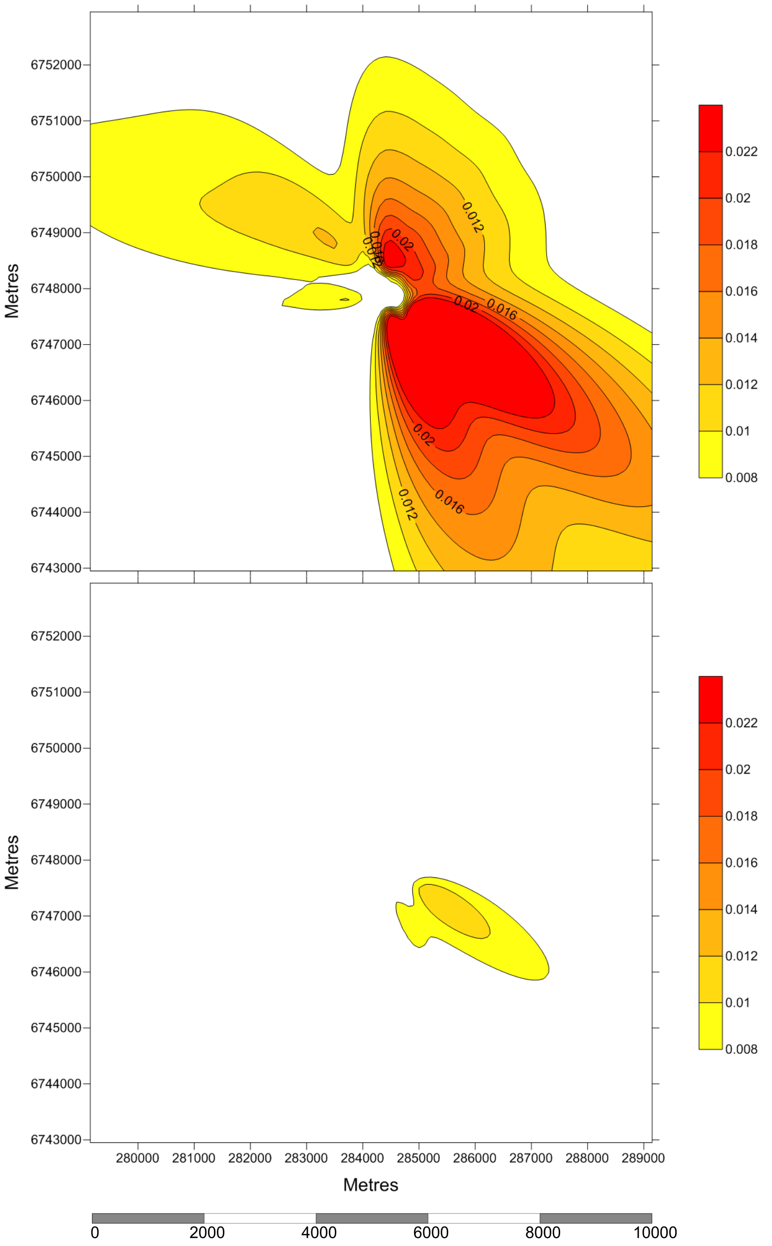


Figure 4.10.20: DMA Tests 5 and 6 (Higher and lower k_{1a}/k_1, respectively) - nitramine

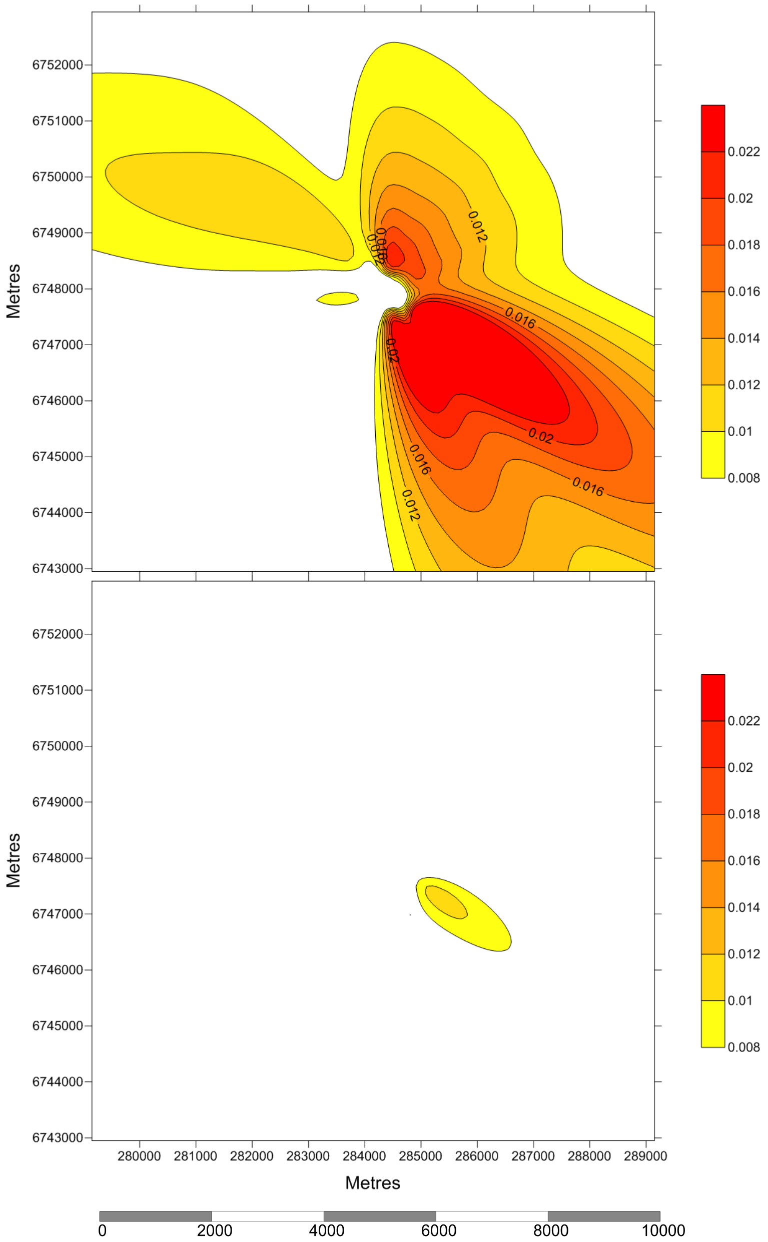


Figure 4.10.21: DMA Tests 8 and 9 (Varying k_3/k_{4a}) - nitramine

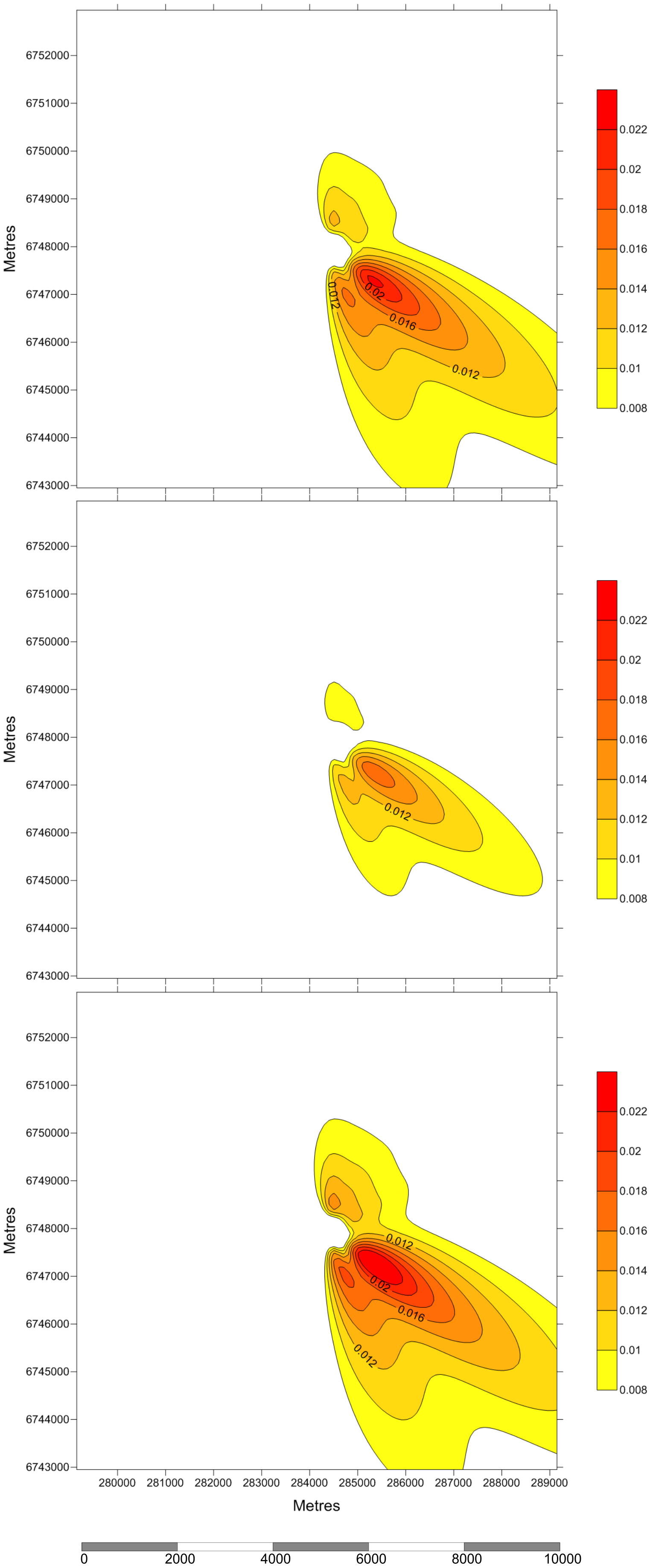


Figure 4.10.22: DMA Tests 5 and 6 (Higher and lower k_2/k_3, respectively) - nitramine

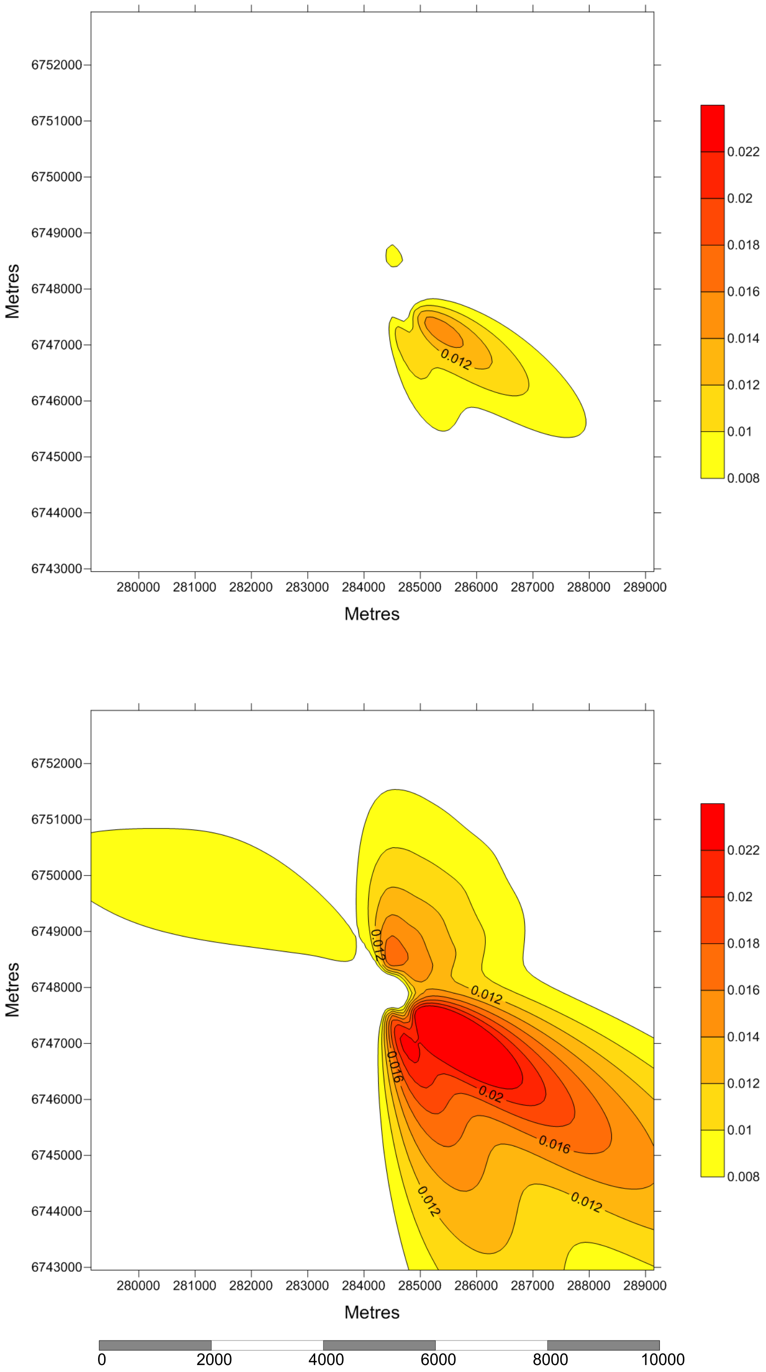


Figure 4.10.23: DMA Tests 8 (Lower j) – nitramine

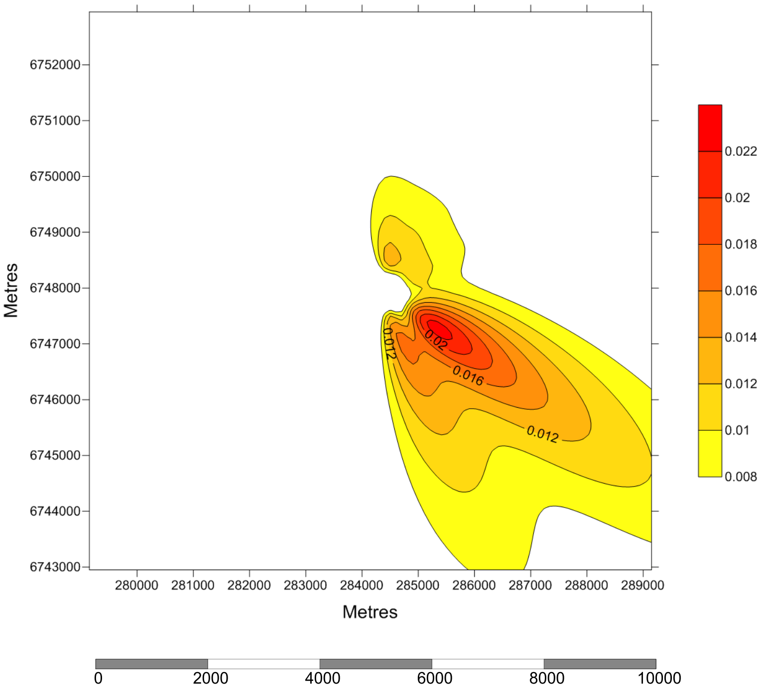


Figure 4.10.24: MMA Baseline and Test 1 (various parameters) - nitramine

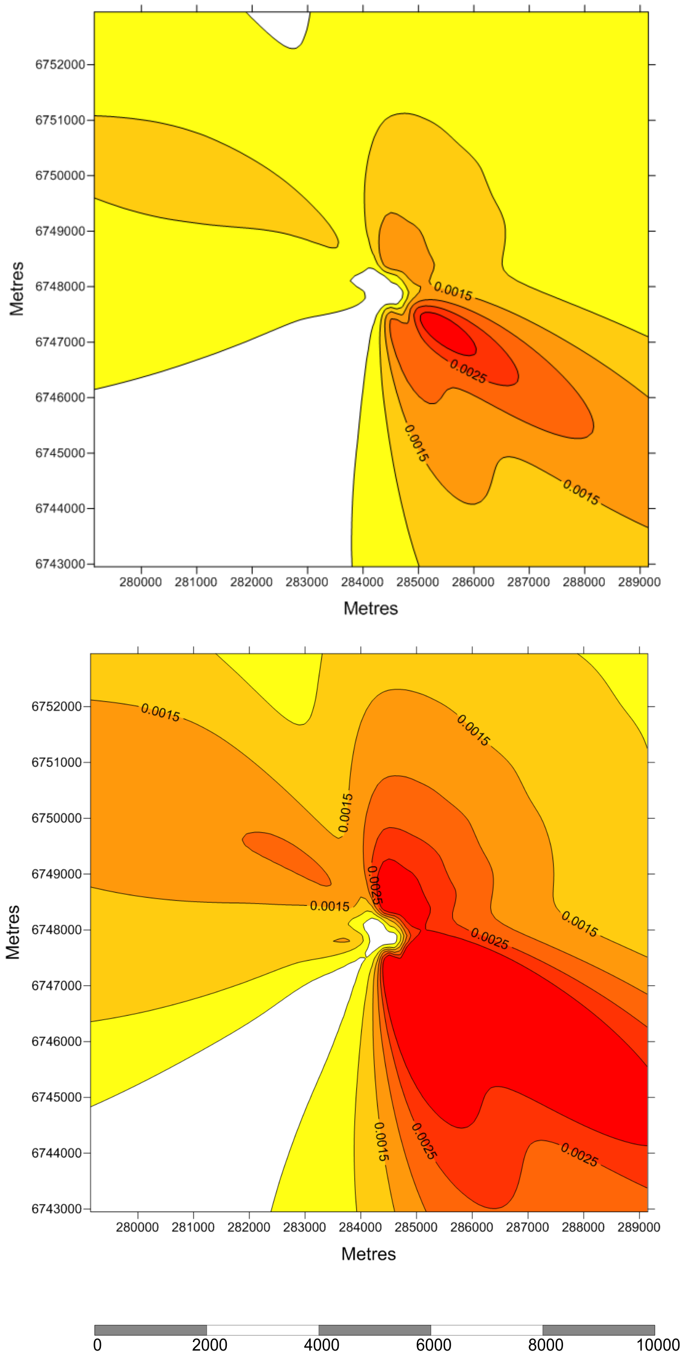


Figure 4.10.25: MMA Tests 2 and 3 (Doubled and halved k_1, respectively) - nitramine

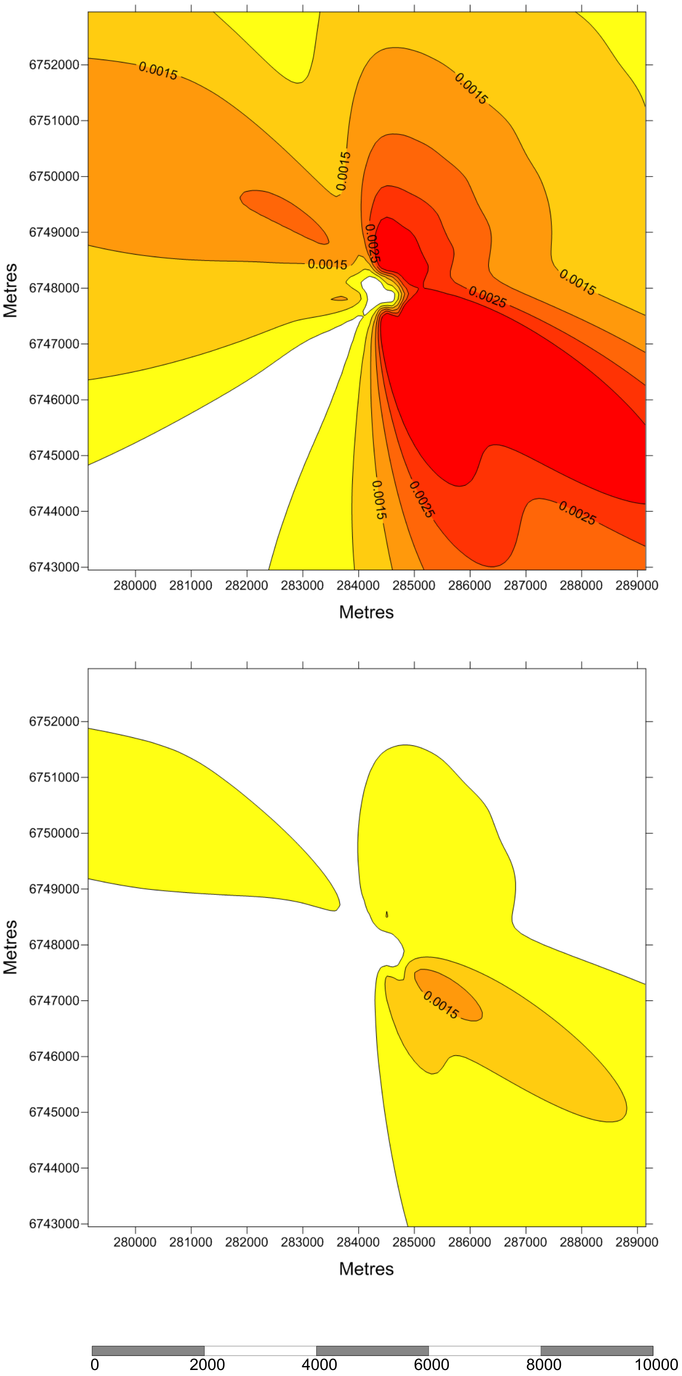


Figure 4.10.26: MMA Test 4 (Lower k_{1a} / k_1) - nitramine

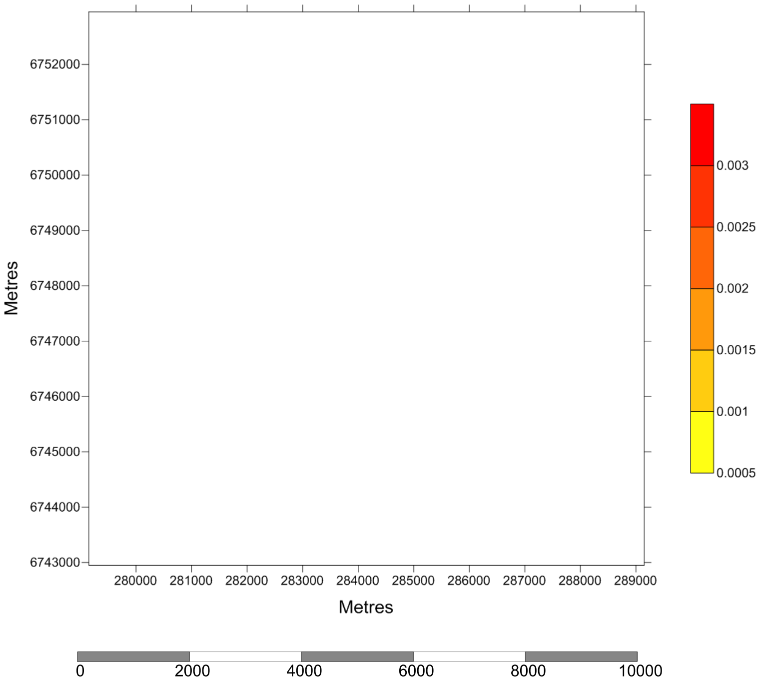


Figure 4.10.27: MEA Baseline and Test 1 (various parameters) - nitramine

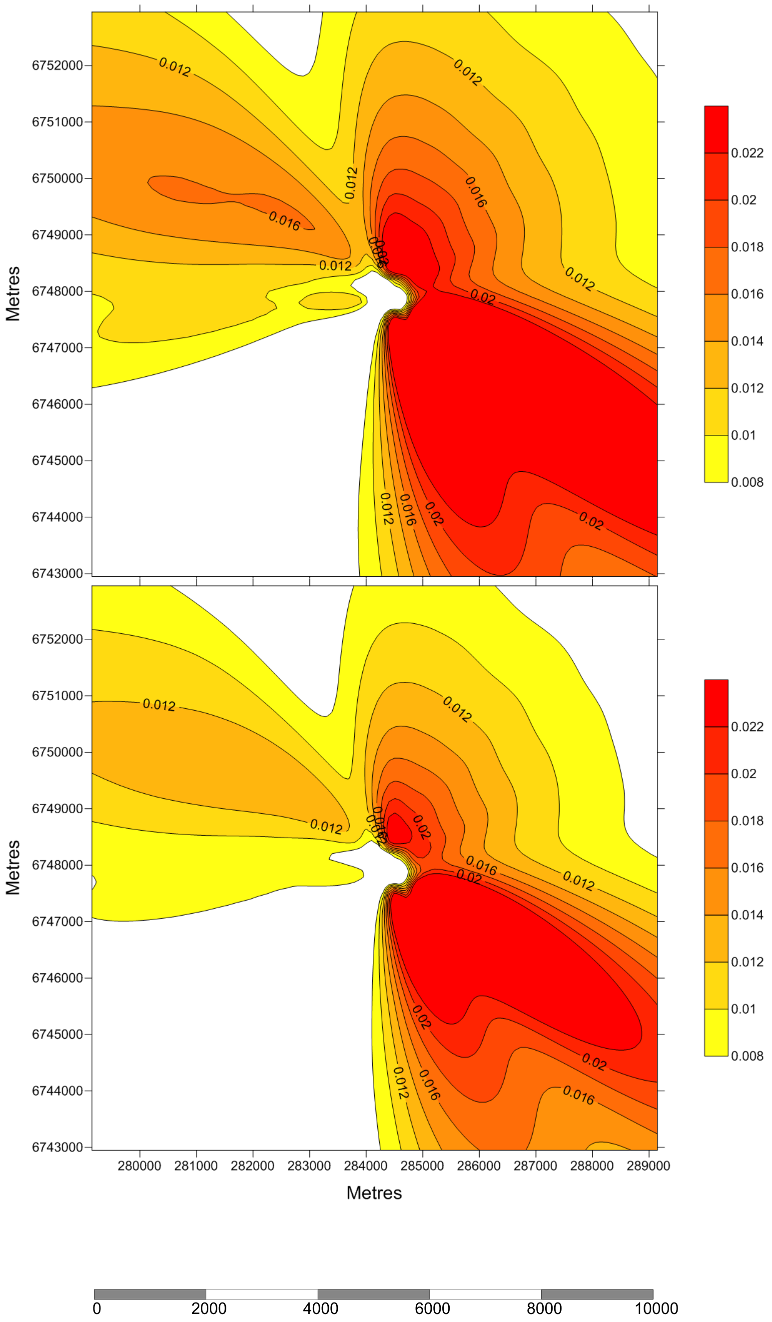


Figure 4.10.28: MEA Tests 2 and 3 (Higher and lower k_1, respectively) – nitramine

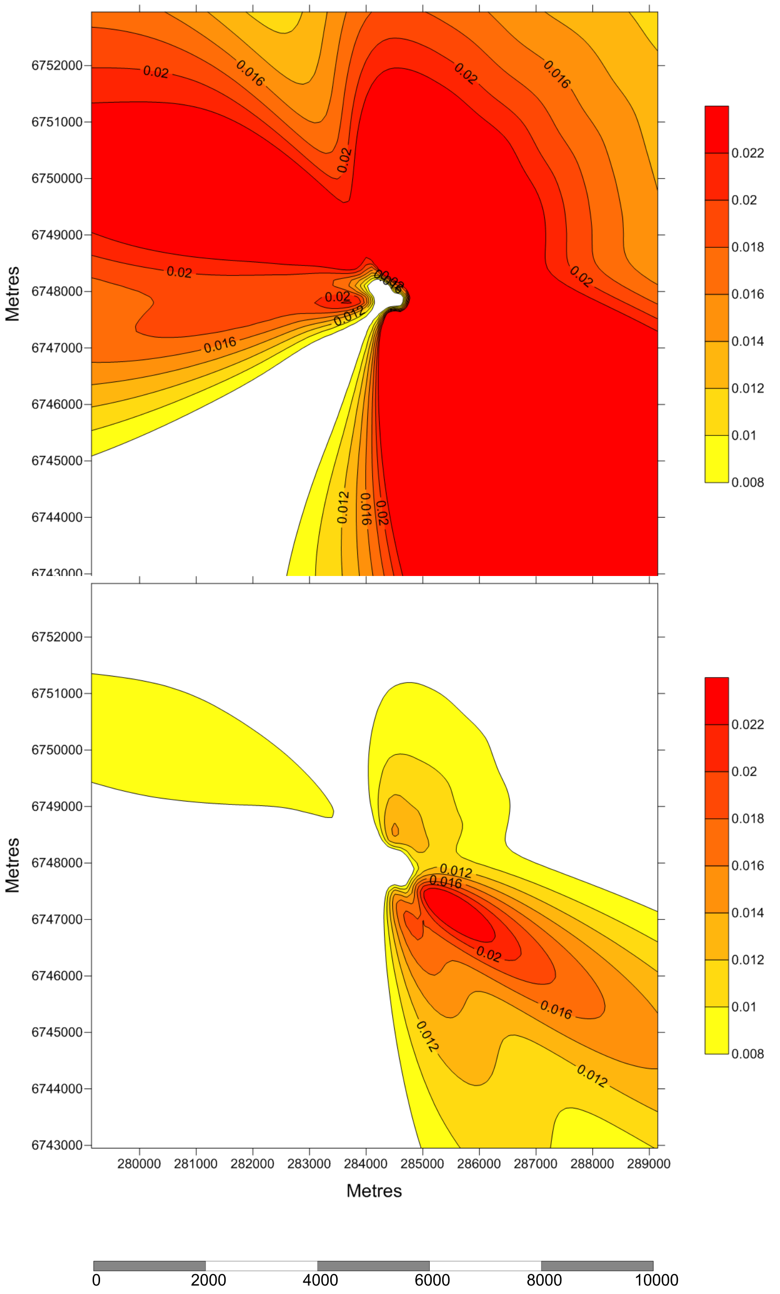
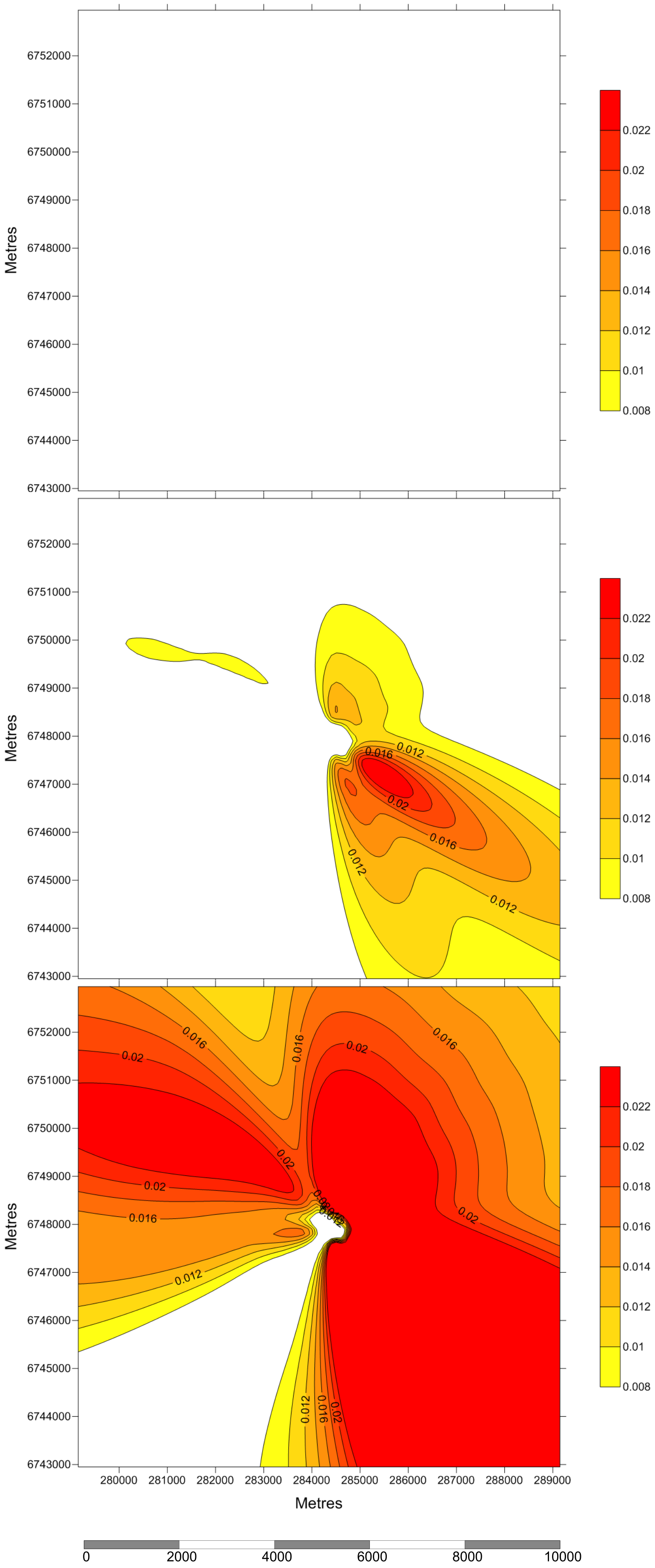


Figure 4.10.29: MEA Tests 4, 5 and 6 (Low, middle and high k_{1a}/k_1, respectively) – nitramine



4.10.5. Sensitivity tests: Other reaction parameters

Tests were carried out to test sensitivity to the following parameters:

- The emission of NO_x from the CHP;
- The NO_2: NO ratio in the CHP emissions;
- The refinery NO_x emissions;
- The background (rural) NO_x concentration;
- The background (rural) ozone concentration; and
- The value of c, the constant that determines hourly OH concentrations.

Table 4.10.6 shows the maximum concentrations for each of these tests.

Table 4.10.6 Maximum predicted concentrations for the other reaction parameters

Parameter	Action	Nitrosamine	Nitramine	Sum
Baseline	-	0.013	0.023	0.036
CHP NOx emissions	doubled	0.016	0.024	0.039
	halved	0.010	0.022	0.032
	5% NO_2	0.013	0.022	0.035
	20% NO_2	0.012	0.025	0.037
Refinery NOx emissions	doubled	0.013	0.027	0.040
	halved	0.012	0.020	0.032
Rural background NOx concentration	doubled	0.014	0.030	0.044
	halved	0.012	0.019	0.031
Rural background O_3 concentrations	40 µg/m^3	0.010	0.014	0.023
	80 µg/m^3	0.015	0.034	0.048
c value	doubled [OH]	0.024	0.043	0.067
	halved [OH]	0.006	0.012	0.018

Figures 4.10.30 to 4.10.43 show the resulting maximum nitrosamine and nitramine concentrations for the above sensitivity tests.

Figure 4.10.30 (a), (b) and (c): Baseline Case with halved, baseline and doubled CHP NO_x emission rate, respectively; nitrosamine

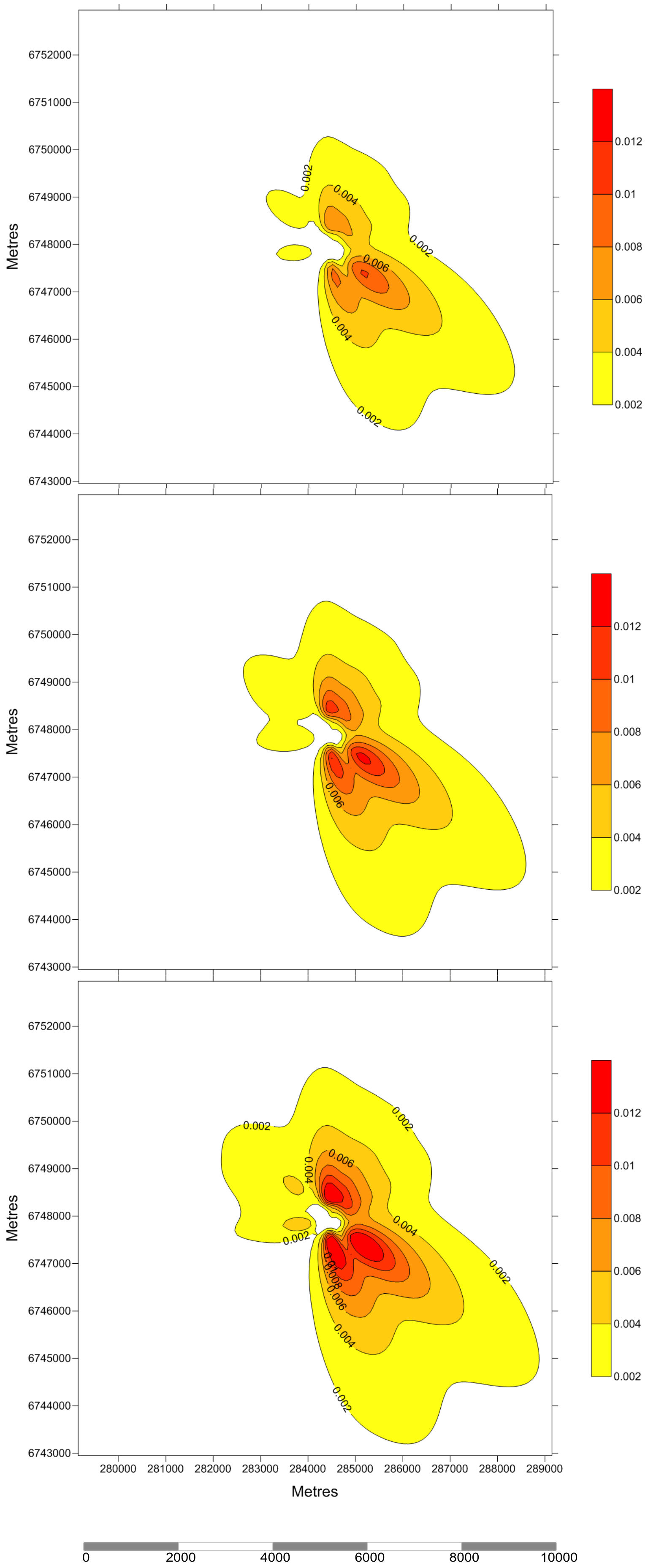


Figure 4.10.31 (a), (b) and (c): Baseline Case with halved, actual (Baseline) and doubled CHP NO$_x$ emission rate, respectively; nitramine

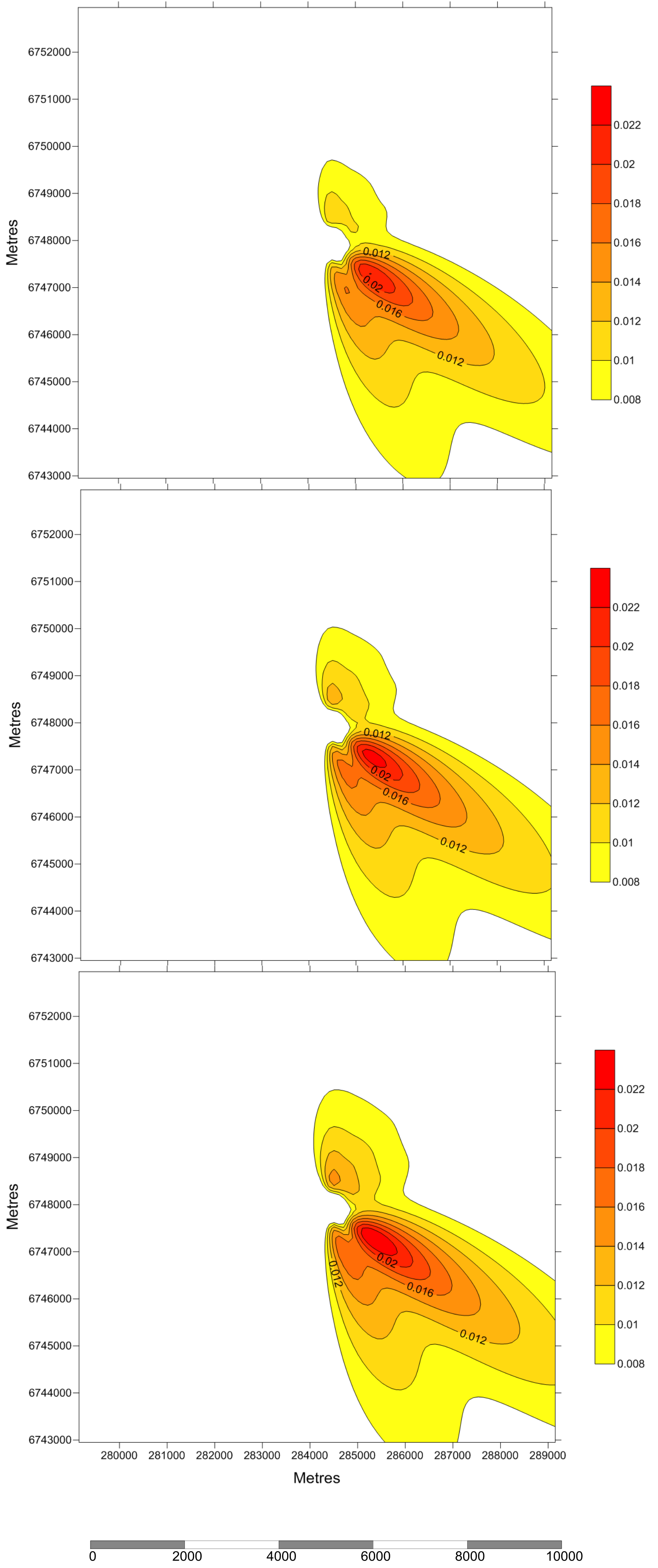


Figure 4.10.32 (a), (b) and (c): Baseline Case with 5%, 10% (Baseline) and 20% CHP NO_2 emission, respectively; nitrosamine

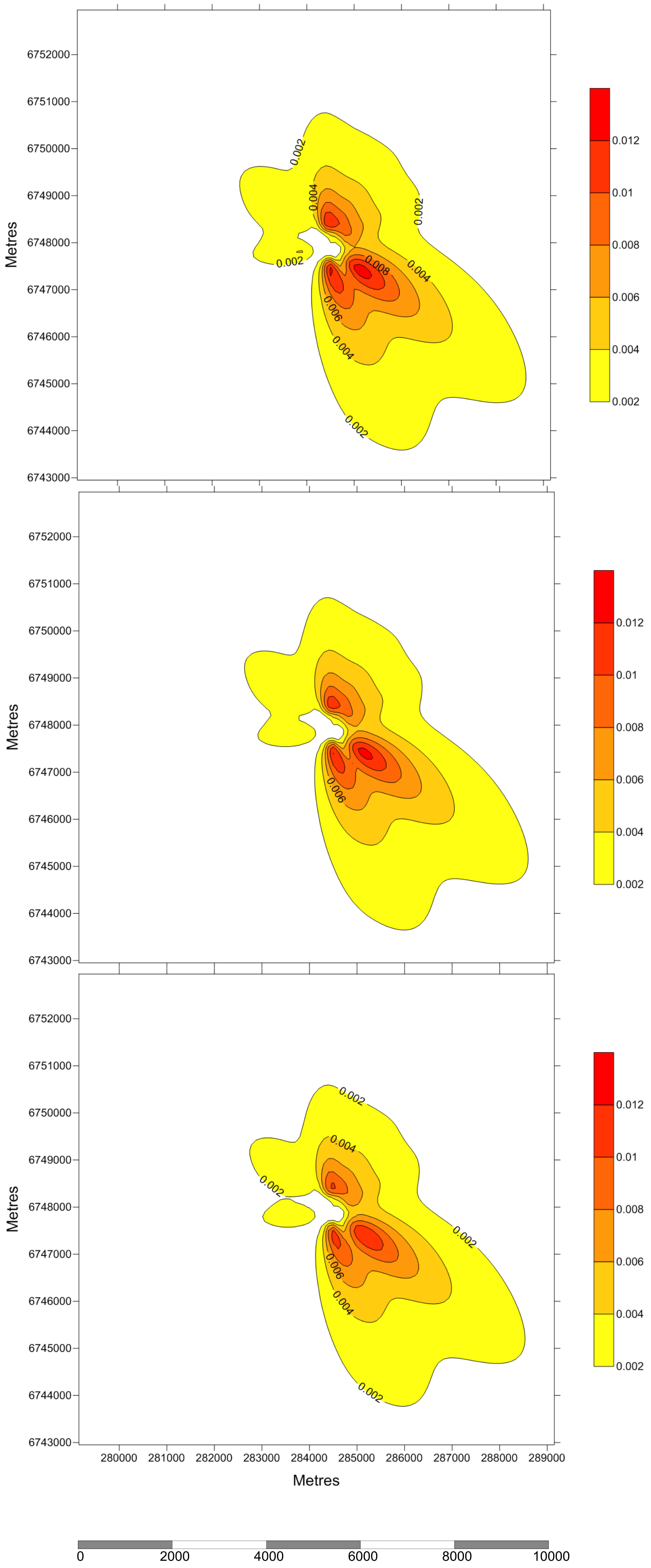


Figure 4.10.33 (a), (b) and (c): Baseline Case with 5%, 10% (Baseline) and 20% CHP NO_2 emission, respectively; nitramine

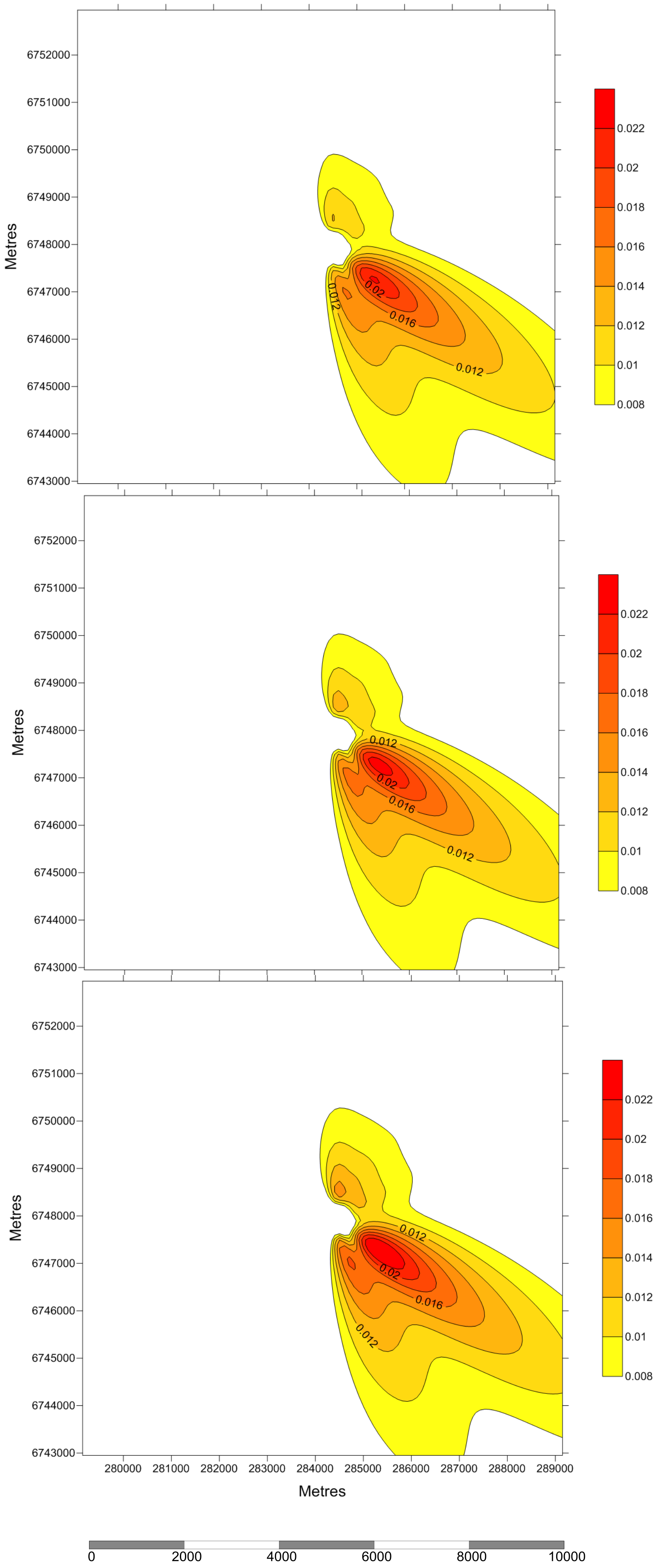


Figure 4.10.34 (a), (b) and (c): Baseline Case with halved, baseline and doubled refinery sources NO_x emission, respectively; nitrosamine

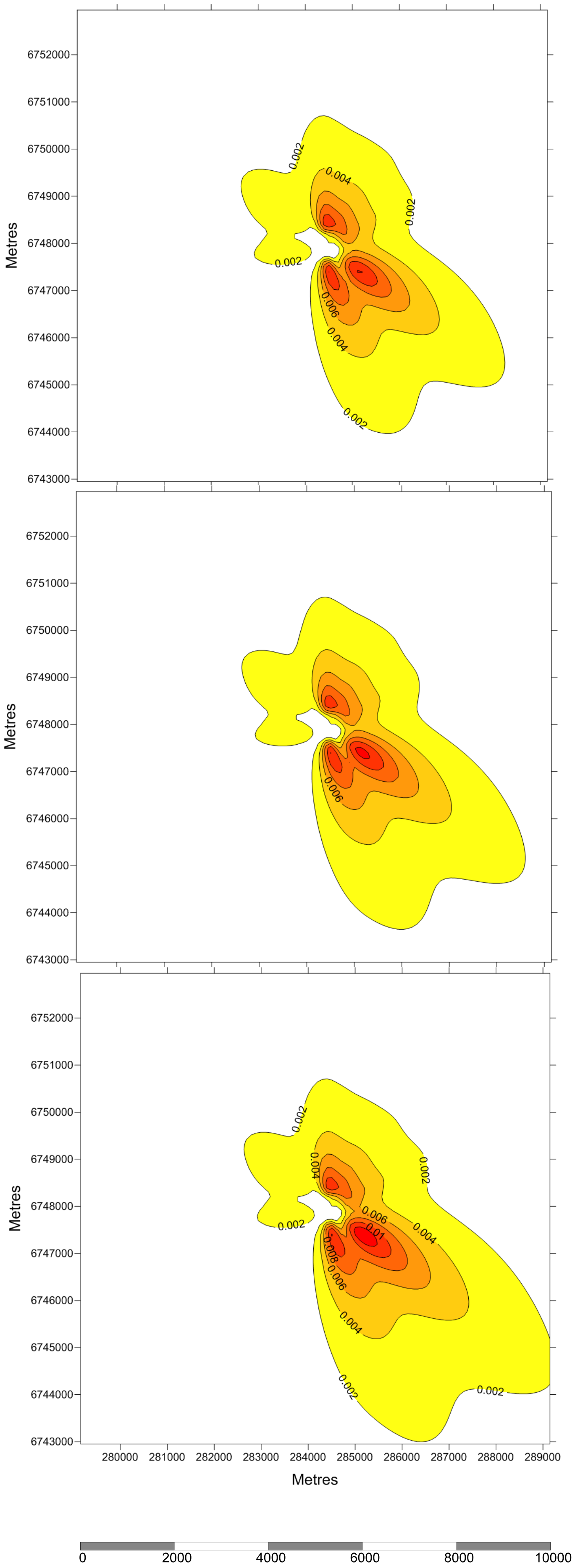


Figure 4.10.35 (a), (b) and (c): Baseline Case with halved, baseline and doubled refinery sources NO_x emission, respectively; nitramine

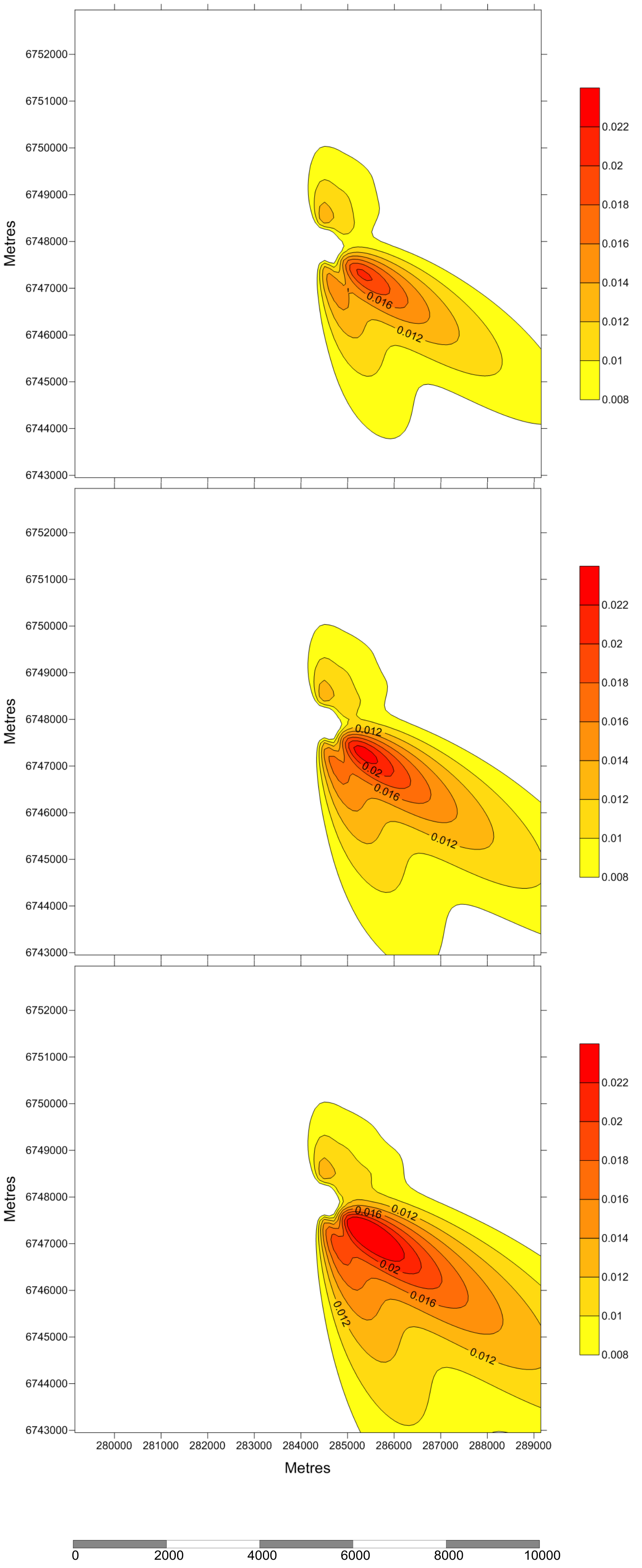


Figure 4.10.36 (a), (b) and (c): Baseline Case with halved, baseline and doubled rural NO_x concentration, respectively; nitrosamine

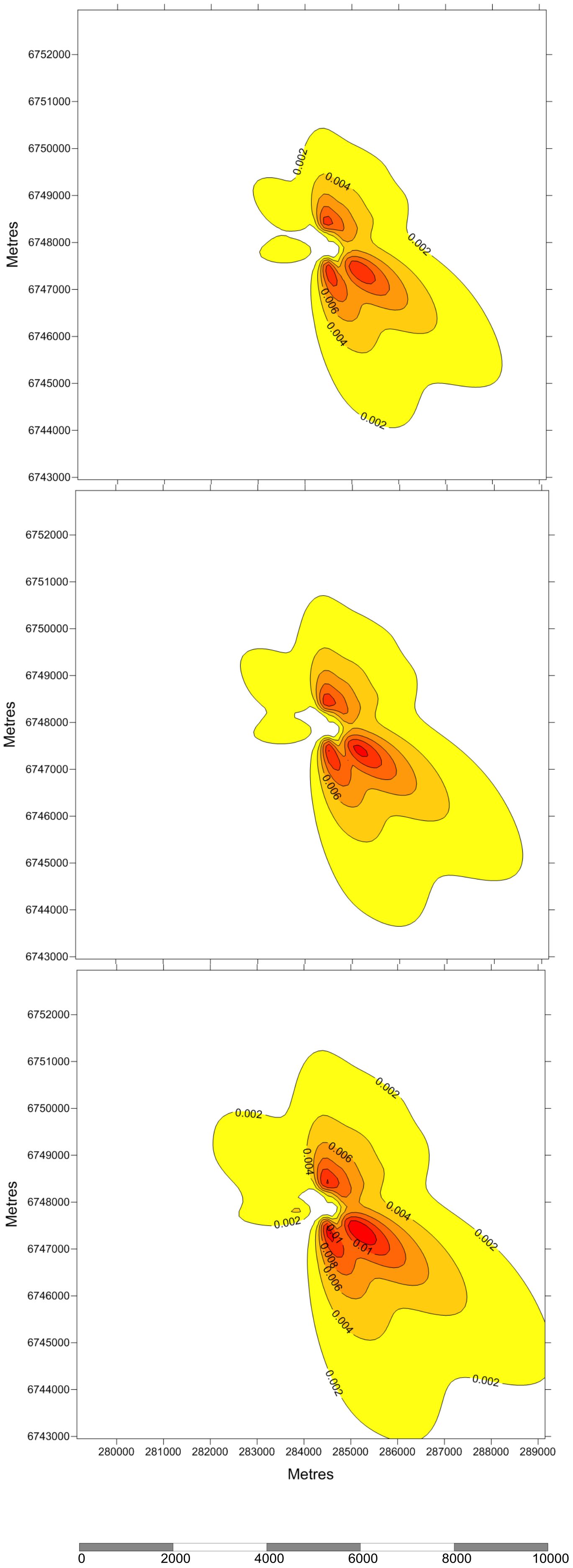


Figure 4.10.37 (a), (b) and (c): Baseline Case with halved, actual and doubled rural NO_x concentration, respectively; nitramine

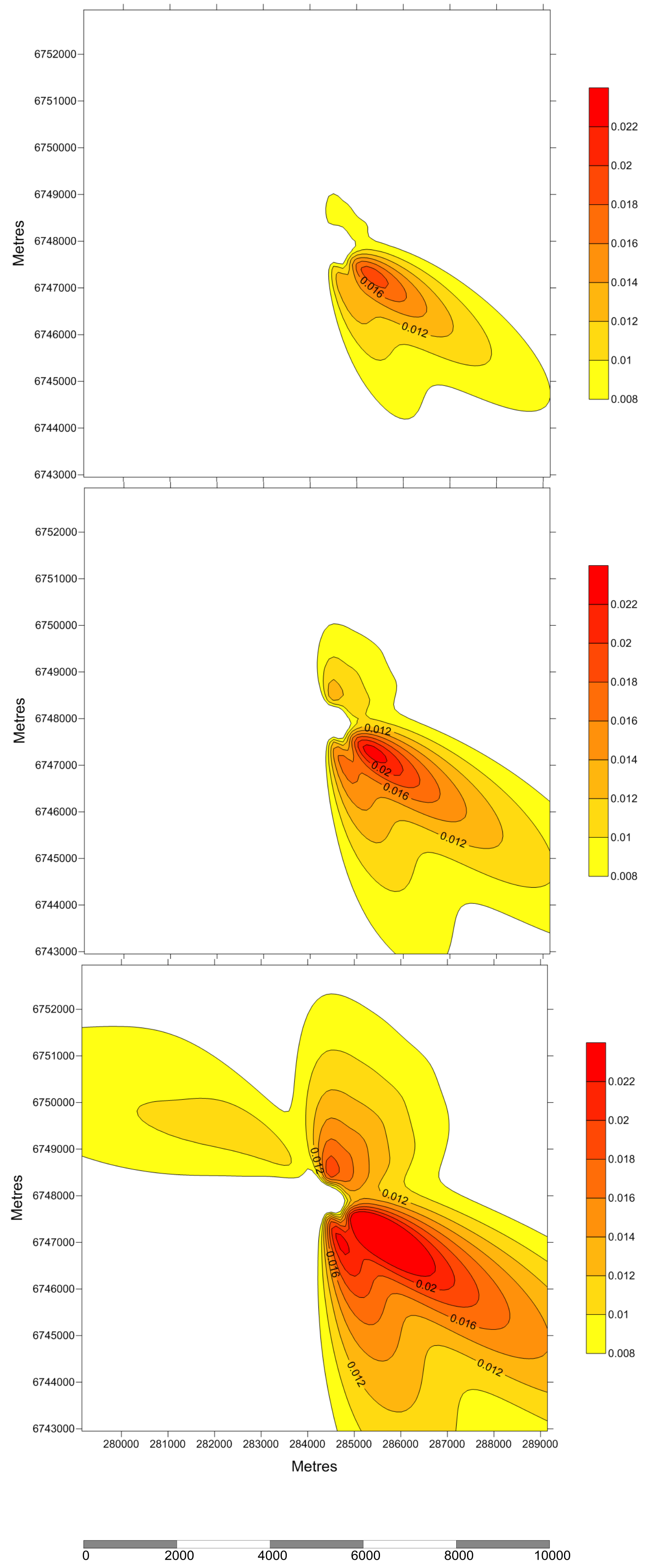


Figure 4.10.38 (a), (b) and (c): Baseline Case with 40, 60 (Baseline) and 80 µg/m^3 rural O$_3$ concentration, respectively; nitrosamine

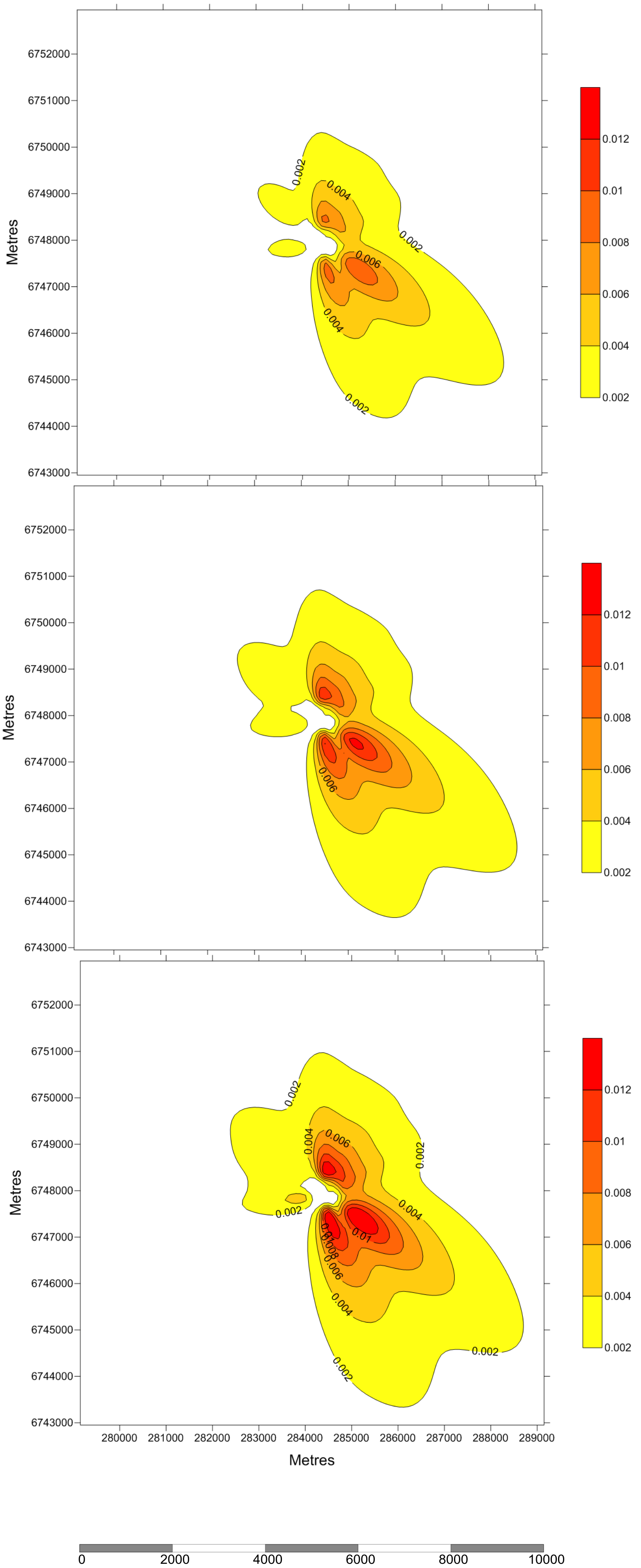


Figure 4.10.39 (a), (b) and (c): Baseline Case with 40, 60 (Baseline) and 80 µg/m^3 rural O_3 concentration, respectively; nitramine

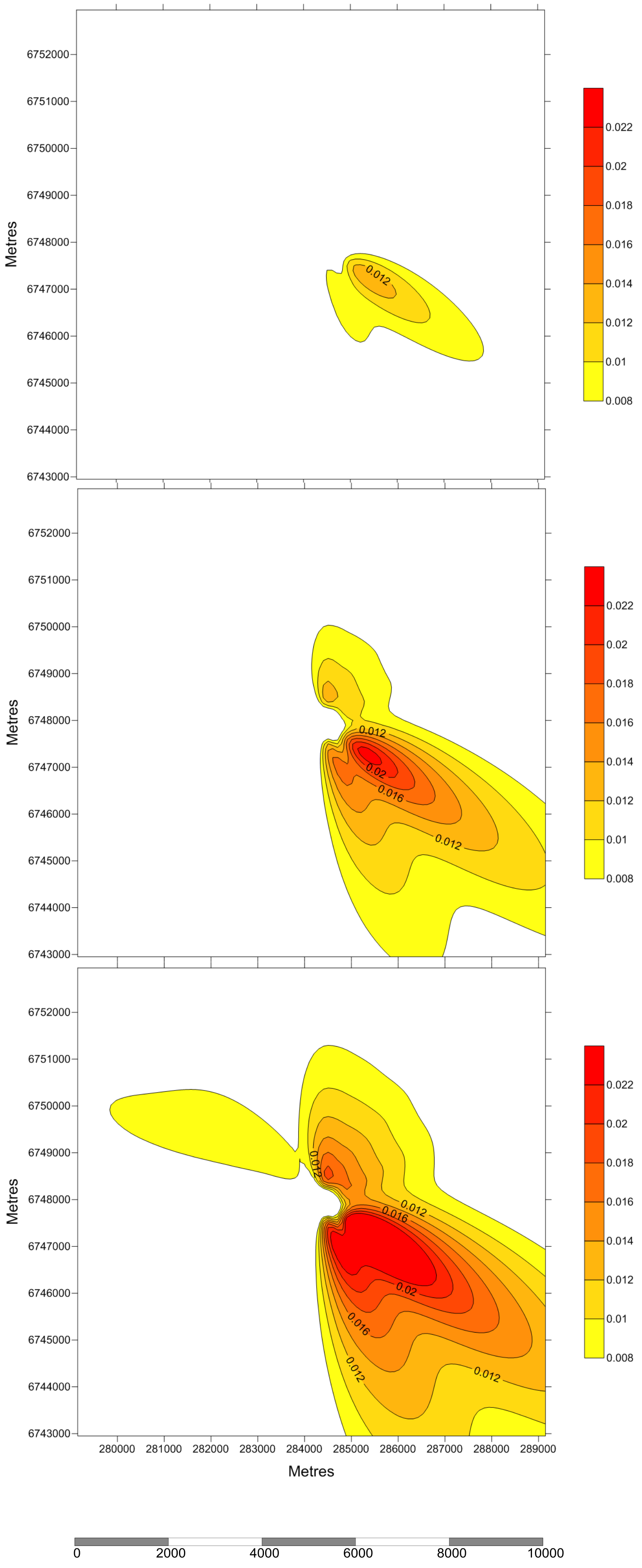


Figure 4.10.40 (a), (b) and (c): Baseline Case with c value derived from halved, baseline and doubled OH concentration, respectively; nitrosamine

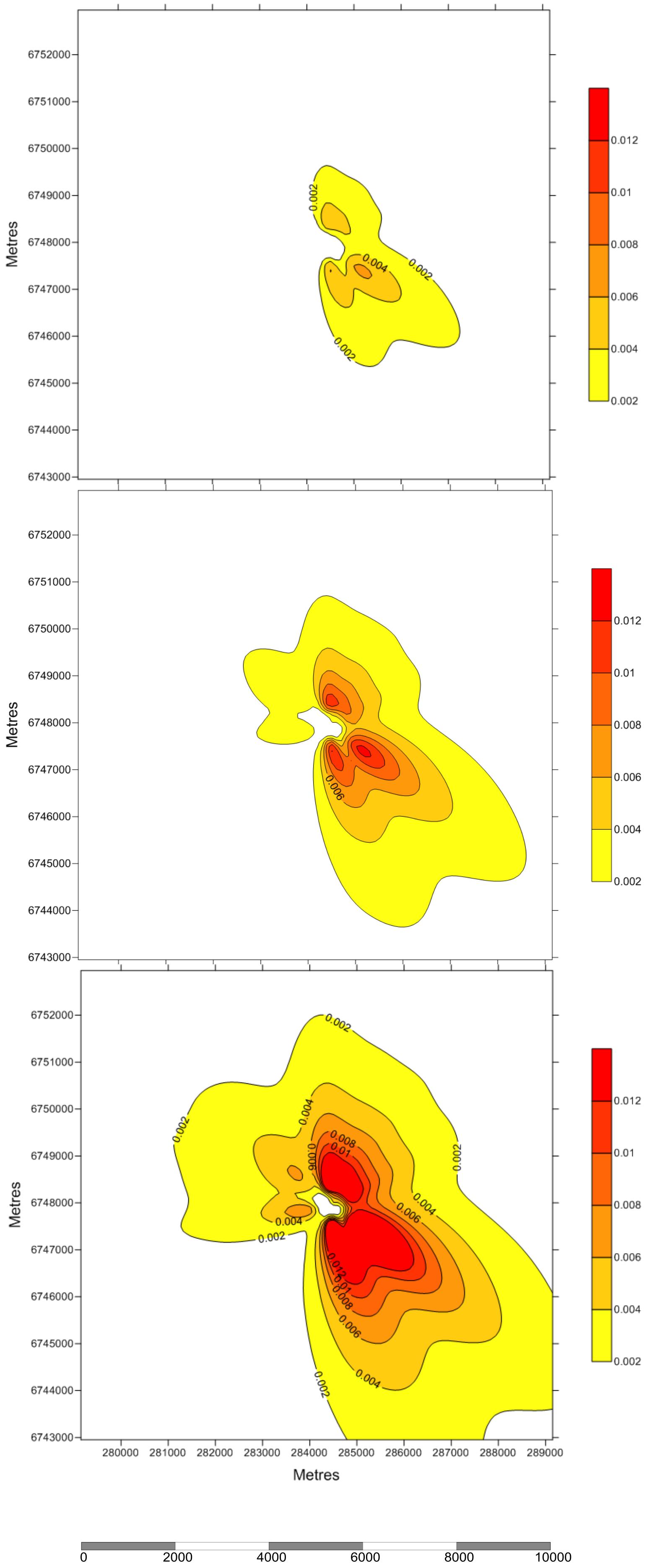


Figure 4.10.41 (a), (b) and (c): Baseline Case with c value derived from halved, baseline and doubled OH concentration, respectively; nitramine

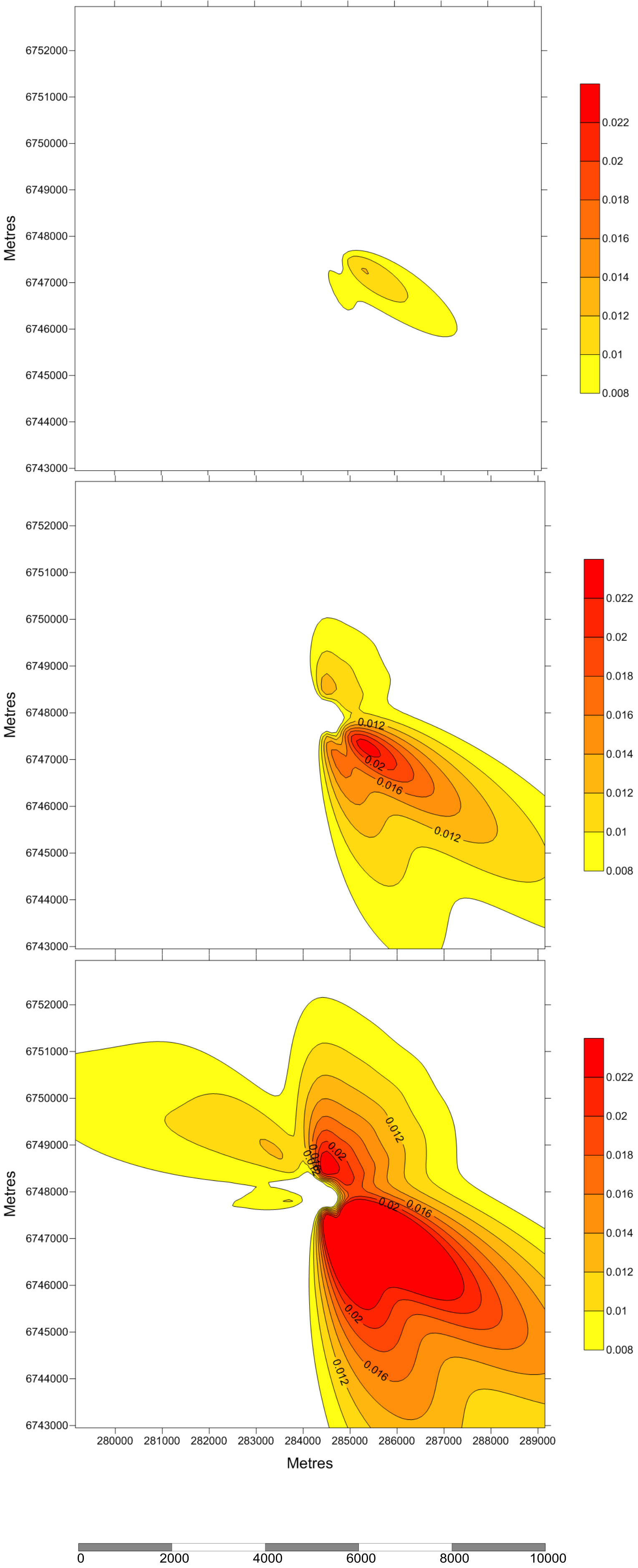


Figure 4.10.42 (a), (b) and (c): Baseline Case with c value derived from halved, baseline and doubled values of j_{NO2} , respectively; nitrosamine

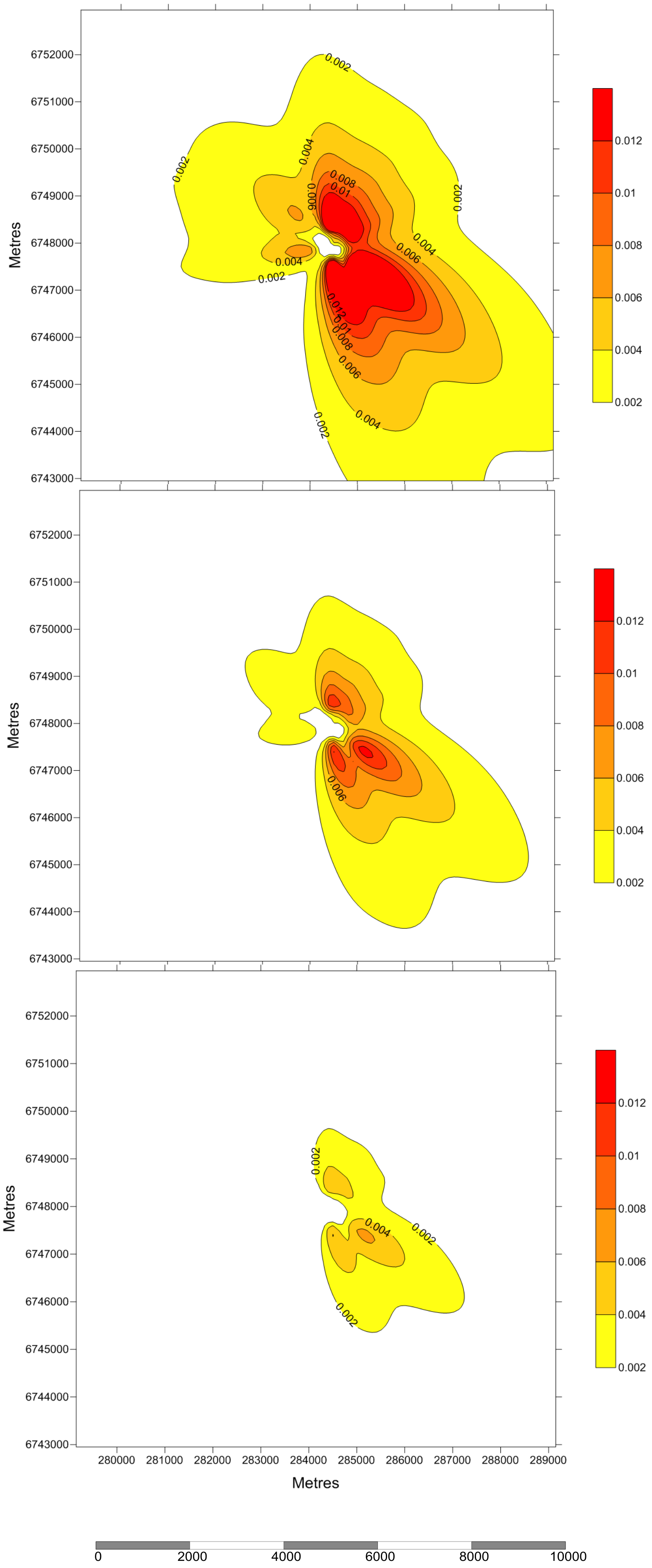
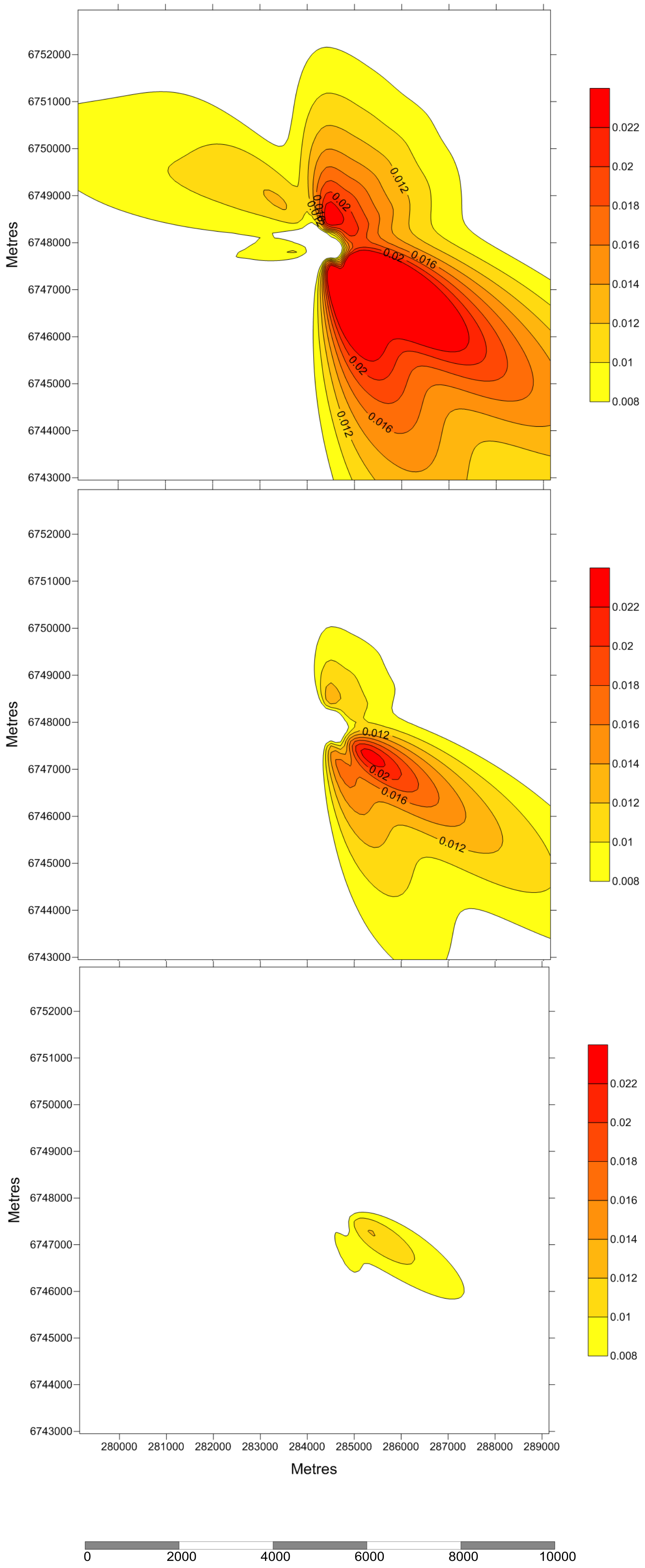


Figure 4.10.43 (a), (b) and (c): Baseline Case with c value derived from halved, baseline and doubled values of j_{NO2} , respectively; nitramine



4.10.6. Sensitivity tests: Alternative emission scenarios

Table 4.10.7 shows the emissions data provided for the four scenarios, as a reminder of the different proportions of each species. Also, note that Scenario 4 has different emission parameters, with a velocity of 6 m/s (as opposed to 20 m/s for the other Scenarios), and different emission rates for each species as a result.

Tables 4.10.8 to 4.10.10 show the maximum predicted concentrations of each species for Scenarios 2 to 4, respectively.

Figures 4.10.44 to 4.10.49 show pie charts to illustrate the breakdown of the contribution of each of the emitted species to the maximum nitrosamine and nitramine concentrations, respectively, for each of the Scenarios.

Figures 4.10.50, 4.10.51 and 4.10.52 shows contour plots of nitrosamines, nitramines and sum of (nitrosamines plus nitramines) for Scenarios 2 to 4, respectively.

Table 4.10.7: Emissions data provided for Scenarios 1 to 4

Species	Units	Composition			
		Scenario 1 (Baseline)	Scenario 2	Scenario 3	Scenario 4
Amines:					
Monomethylamine	ppmv	0.1	0.2	0.05	0.1
Dimethylamine	ppmv	0.05	0.1	0.025	0.05
Monoethanolamine	ppmv	1.0	1.0	0.1	1.0
Nitrosamines	ppbv	0.25	0.5	0.1	0.25
Nitramines	ppbv	0	0	0	0

Table 4.10.8: Maximum concentrations predicted over the output grid – Scenario 2

Emitted species	Maximum annual average concentration (ng/m^3)		
	Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
DMA	0.025	0.046	0.071
MMA	-	0.007	0.007
MEA	-	0.051	0.051
Directly-emitted NDMA	0.30	0.0008	0.30
Total	**0.35**	**0.10**	**0.45**

Table 4.10.9: Maximum concentrations predicted over the output grid – Scenario 3

Emitted species	Maximum annual average concentration (ng/m^3)		
	Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
DMA	0.006	0.012	0.018
MMA	-	0.0017	0.0031
MEA	-	0.0051	0.0051
Directly-emitted NDMA	0.06	0.0002	0.059
Total	**0.07**	**0.02**	**0.09**

Table 4.10.10: Maximum concentrations predicted over the output grid – Scenario 4

Emitted species	Maximum annual average concentration (ng/m^3)		
	Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
DMA	0.015	0.014	0.025
MMA	-	0.0022	0.0049
MEA	-	0.030	0.030
Directly-emitted NDMA	0.22	0.0003	0.22
Total	**0.27**	**0.02**	**0.29**

Figure 4.10.44: Scenario 2 - Maximum contributions to nitrosamines

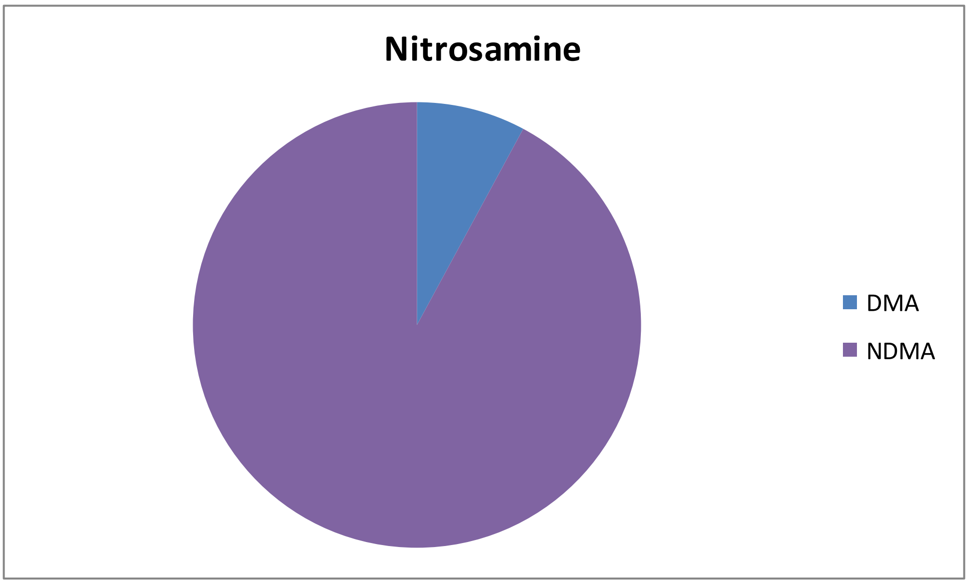


Figure 4.10.45: Scenario 2 - Maximum contributions to nitramines

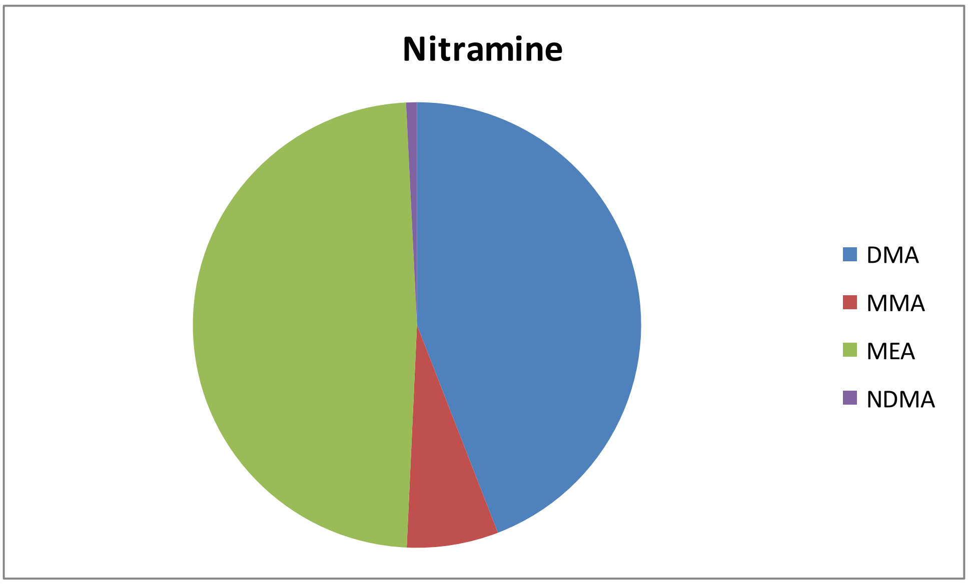


Figure 4.10.46: Scenario 3 - Maximum contributions to nitrosamines

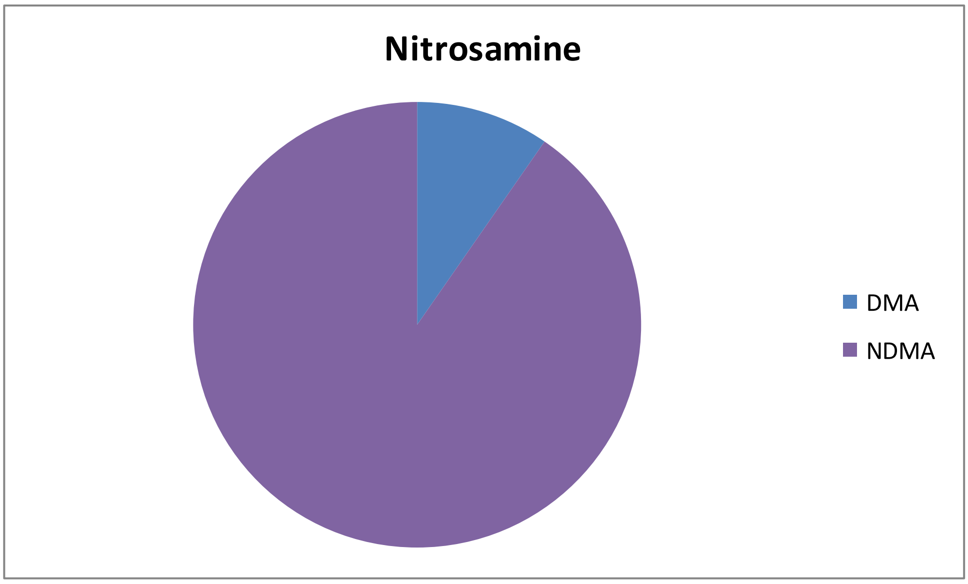


Figure 4.10.47: Scenario 3 - Maximum contributions to nitramines

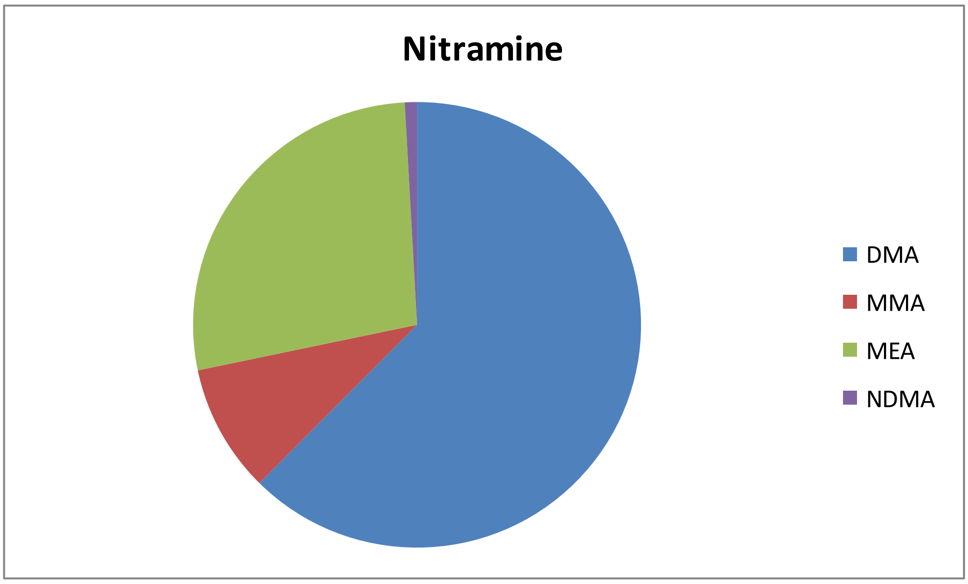


Figure 4.10.48: Scenario 4 - Maximum contributions to nitrosamines

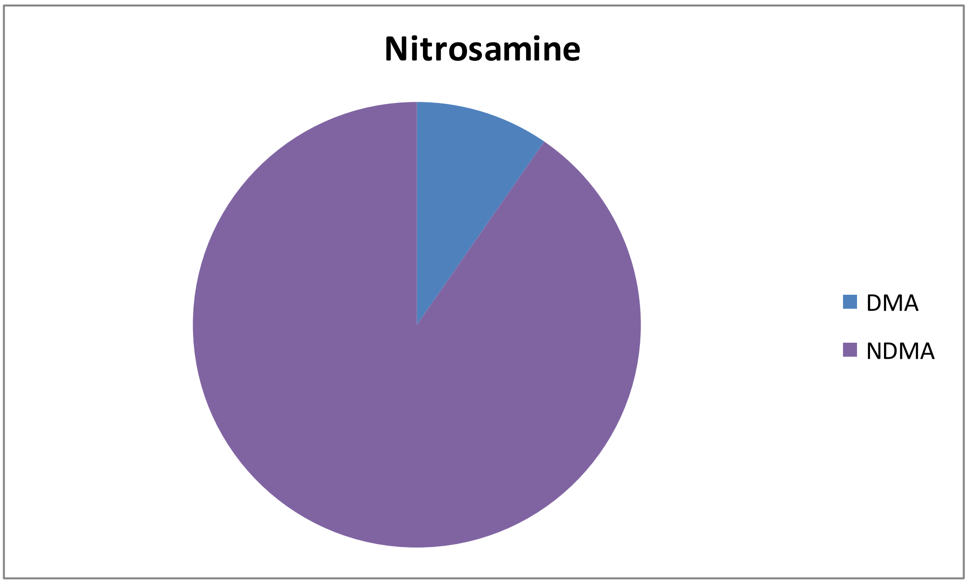


Figure 4.10.49: Scenario 4 - Maximum contributions to nitramines

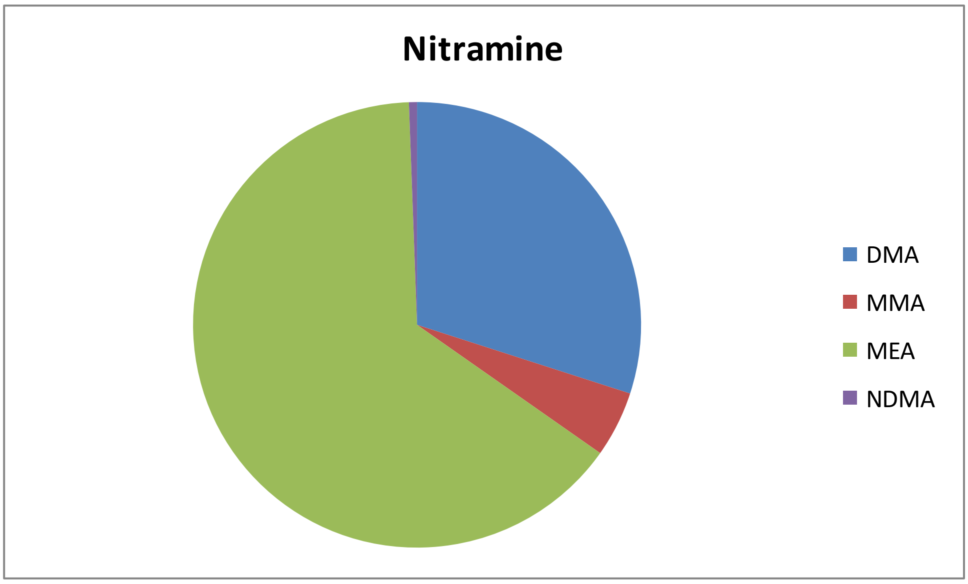


Figure 4.10.50 (a) Nitrosamine (b) Nitramine and (c) (Nitrosamine plus nitramine) concentrations from all emissions - Scenario 2

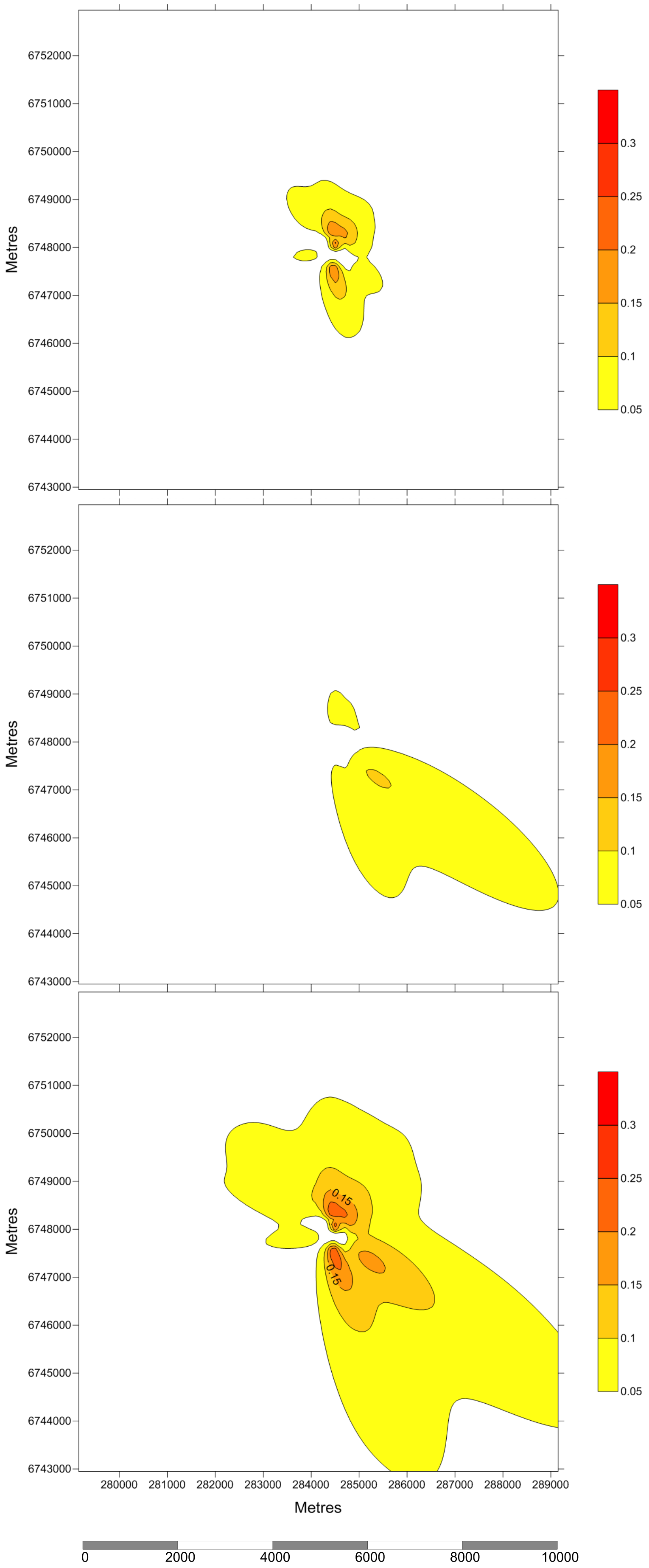


Figure 4.10.51 (a) Nitrosamine (b) Nitramine and (c) (Nitrosamine plus nitramine) concentrations from all emissions - Scenario 3

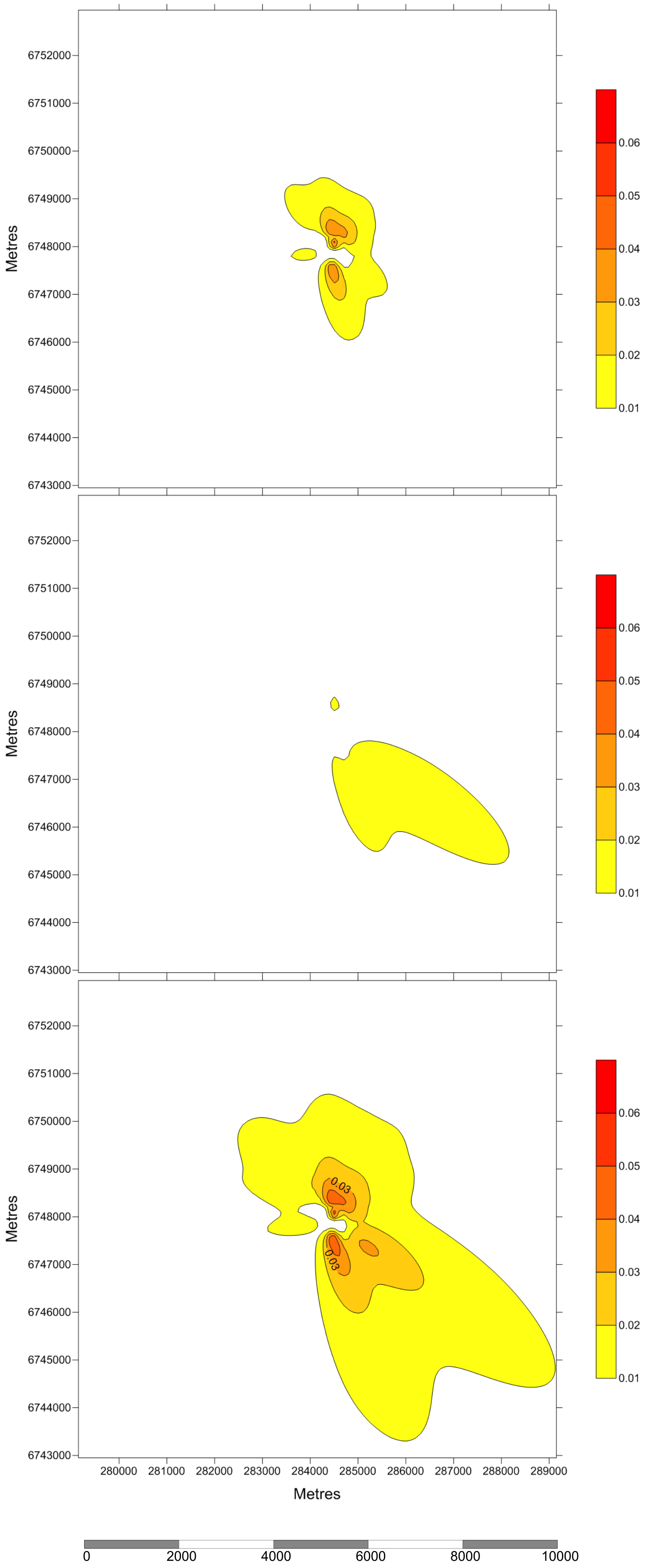
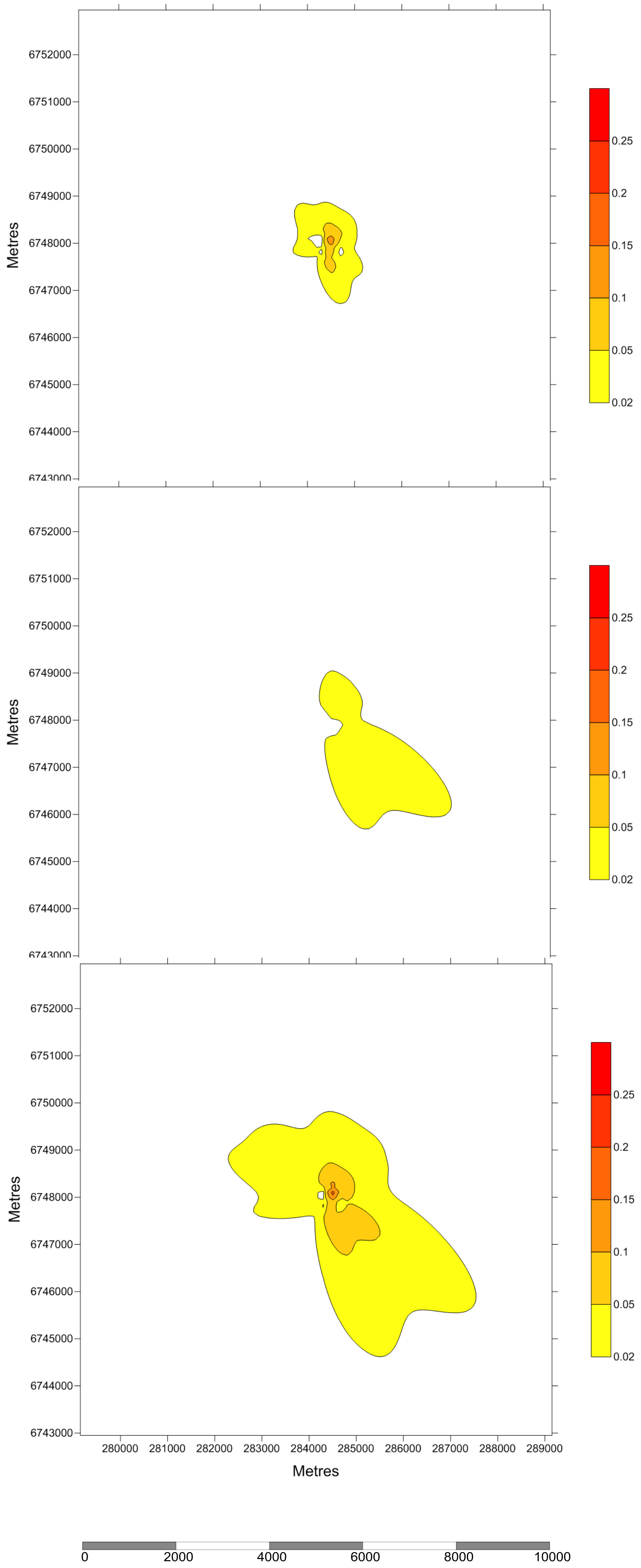


Figure 4.10.52 (a) Nitrosamine (b) Nitramine and (c) (Nitrosamine plus nitramine) concentrations from all emissions - Scenario 4



4.10.7. Sensitivity tests: Other meteorological data

Table 4.10.11 shows the maximum predicted concentrations for the Baseline Case with other years of meteorological data.

Figure 4.10.52 (a) and (b) show annual mean concentrations of nitrosamine (NDMA) for the Baseline Case, run with meteorological data for 2007 and 2009, respectively.

Figure 4.10.53 (a) and (b) show annual mean concentrations of nitramine for the Baseline Case, run with meteorological data for 2007 and 2009, respectively.

Table 4.10.11: Maximum predicted concentrations for the Baseline Case with other years of meteorological data

Meteorological year	**Maximum annual average concentration (ng/m^3)**		
	Nitrosamine	**Nitramine**	**Sum (nitrosamine plus nitramine)**
2007	0.012	0.021	0.032
2008 (Baseline)	0.013	0.023	0.036
2009	0.016	0.018	0.032

Figure 4.10.53 (a) and (b): Baseline Case with 2007, 2008 and 2009 meteorological data, respectively; nitrosamine concentrations

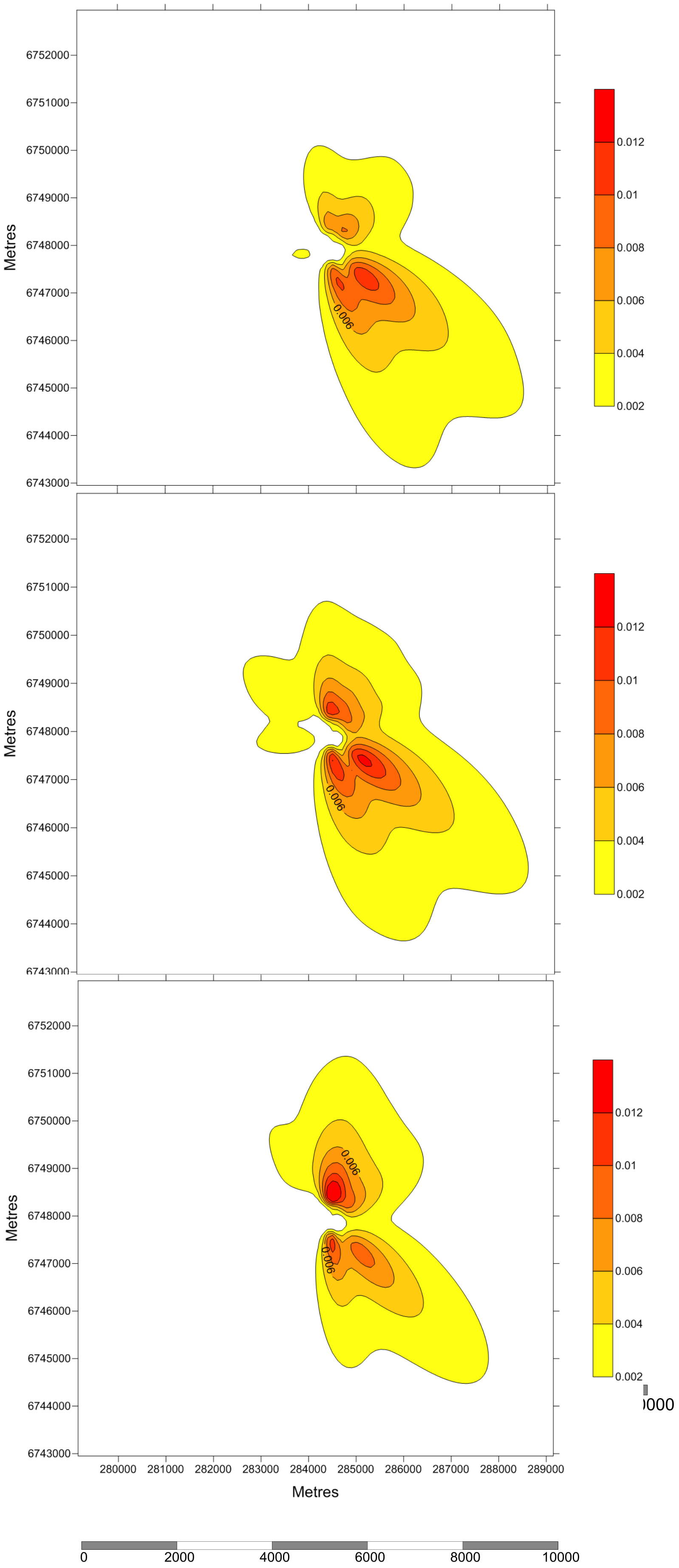
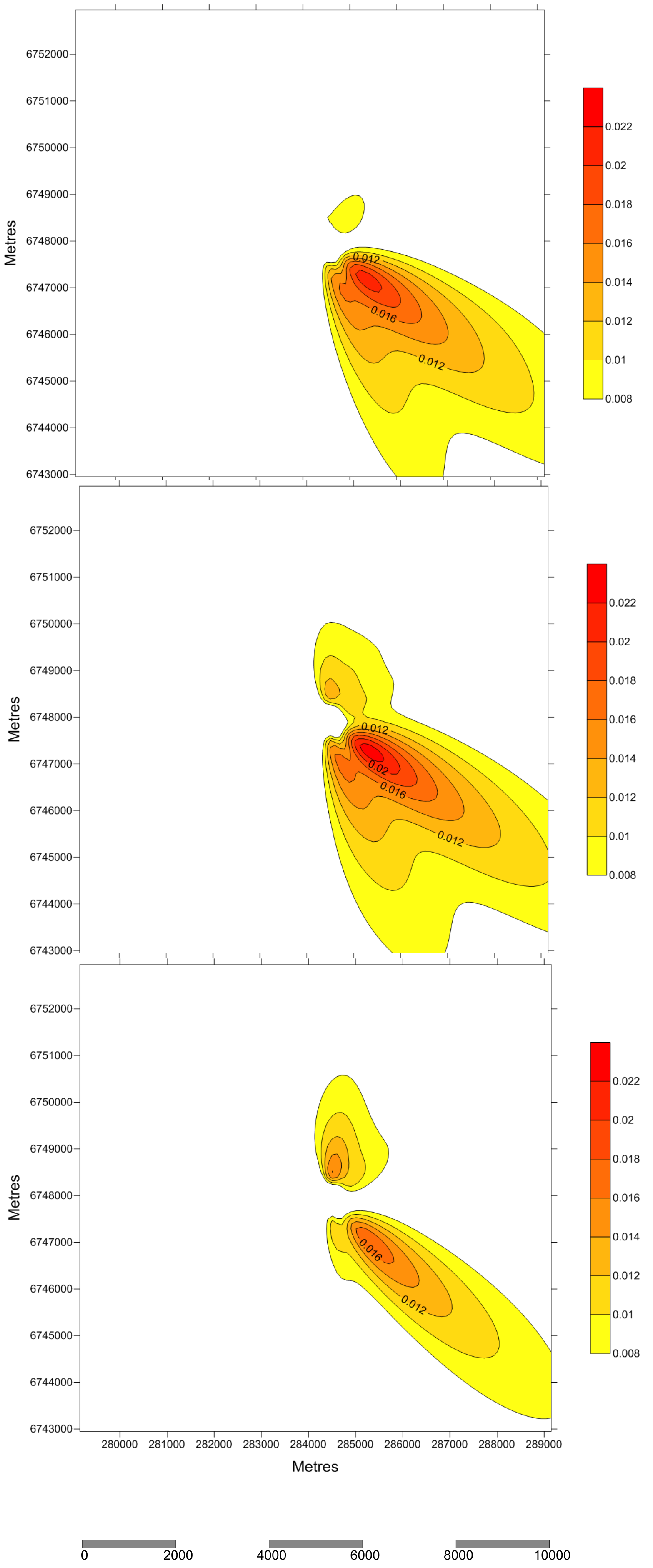


Figure 4.10.54 (a) and (b): Baseline Case with 2007 and 2009 meteorological data, respectively; nitramine concentrations



4.10.8. Sensitivity tests: With terrain and variable roughness

Table 4.10.12 shows the maximum predicted concentrations for the Baseline Case with terrain and spatially-variable roughness modelled

Figures 4.10.55 and 4.10 56 show contour plots for these results, for all three years of meteorological data.

Table 4.10.12: Maximum predicted concentrations for the Baseline Case with terrain and variable roughness modelled

With / without terrain and variable roughness	Meteorological year	Maximum annual average concentration (ng/m^3)		
		Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
Without (Baseline)	2007	0.012	0.021	0.032
	2008	0.013	0.023	0.036
	2009	0.016	0.018	0.032
With	2007	0.009	0.017	0.025
	2008	0.010	0.019	0.028
	2009	0.014	0.015	0.028

Figure 4.10.55 (a), (b) and (c): Baseline Case with terrain and variable roughness effects, 2007, 2008 and 2009 meteorological data, respectively; nitrosamine concentrations

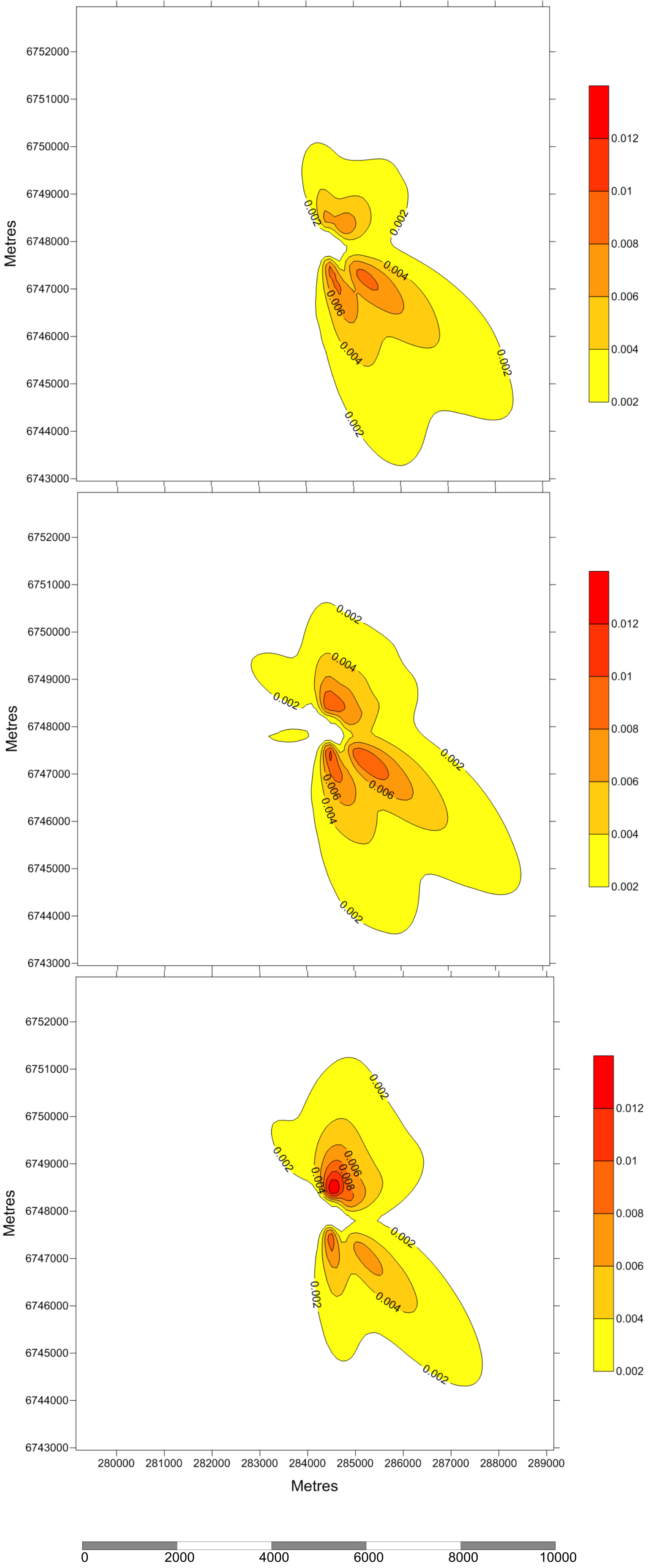
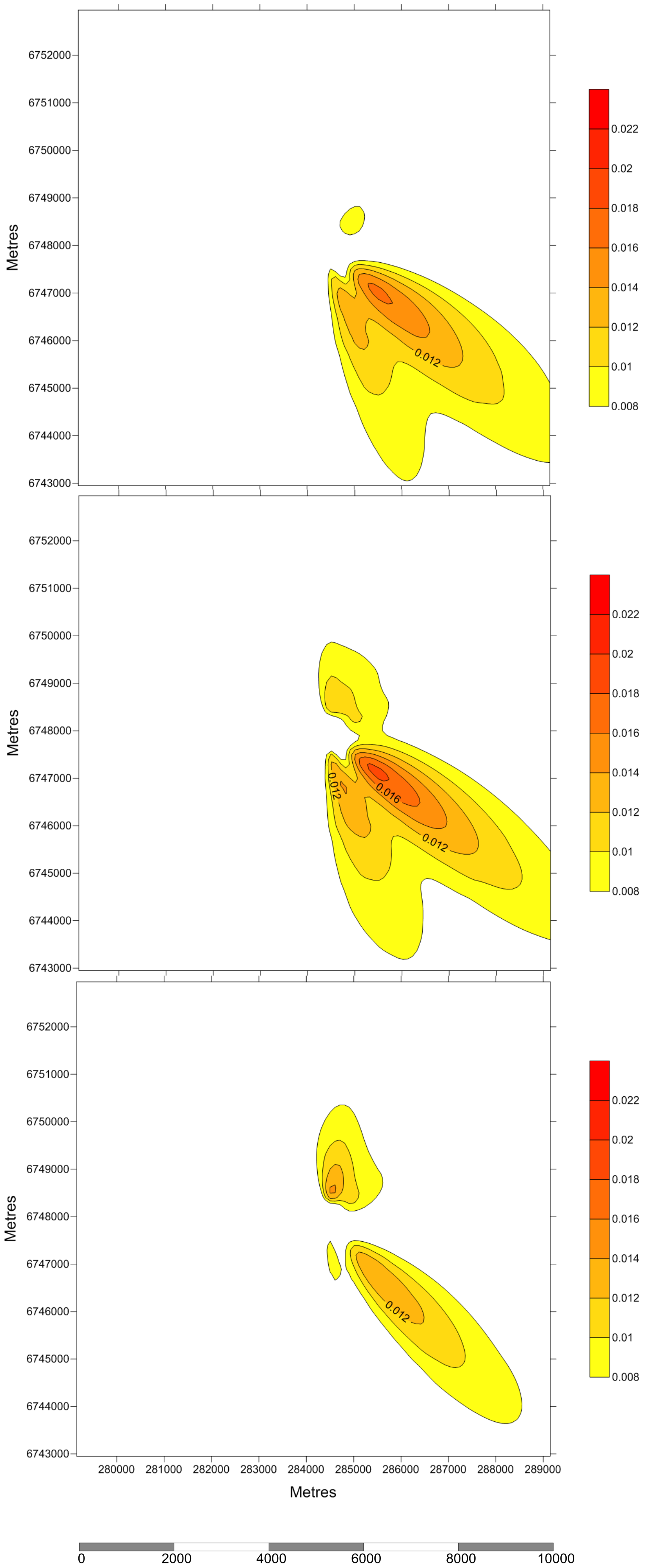


Figure 4.10.56 (a), (b) and (c): Baseline Case with terrain and variable roughness effects, 2007, 2008 and 2009 meteorological data, respectively; nitramine concentrations



4.10.9. Sensitivity tests: Building effects

Tables 4.10.13 to 4.10.16 show the maximum predicted concentrations for three different modelled building scenarios, for each of the emitted species, respectively. Values are given for all three years of meteorological data. All runs are based on the Baseline Case model set-up.

A brief summary of the three scenarios is given in Section 4.4.2, and full details of the building parameters modelled for the single-building and multiple-building scenarios are given in Section 4.8.6. The overall (nitrosamine plus nitramine) concentration, for all emitted species is 0.11 ng/m^3, for both the multiple-building case and the no-building case.

Figures 4.10.57 to 4.10.62 show contour plots for these building scenarios; plots for 2009 meteorological data are shown, as this is the year that generally shows the most pronounced differences in concentration patterns between the three building scenarios.

Table 4.10.13: Maximum predicted DMA concentrations with different buildings

Meteorological year	**Building scenario**	**Maximum annual average concentration (ng/m^3)**		
		Nitrosamine	**Nitramine**	**Sum (nitrosamine plus nitramine)**
2007	Single-building (Baseline)	0.012	0.021	0.032
	Multiple-building	0.012	0.021	0.032
	No building	0.012	0.021	0.032
2008	Single-building (Baseline)	0.013	0.023	0.036
	Multiple-building	0.013	0.023	0.035
	No building	0.013	0.023	0.035
2009	Single-building (Baseline)	0.016	0.018	0.032
	Multiple-building	0.009	0.018	0.026
	No building	0.009	0.018	0.026

Table 4.10.14: Maximum predicted MMA concentrations with different modelled buildings

Meteorological year	**Modelled building**	**Maximum annual average concentration (ng/m^3)**		
		Nitrosamine	**Nitramine**	**Sum (nitrosamine plus nitramine)**
2007	Single-building (Baseline)	-	0.0031	0.0031
	Multiple-building	-	0.0031	0.0031
	No building	-	0.0031	0.0031
2008	Single-building (Baseline)	-	0.0035	0.0035
	Multiple-building	-	0.0035	0.0035
	No building	-	0.0035	0.0035
2009	Single-building (Baseline)	-	0.0026	0.0026
	Multiple-building	-	0.0026	0.0026
	No building	-	0.0026	0.0026

Table 4.10.15: Maximum predicted MEA concentrations with different modelled buildings

Meteorological year	Modelled building	Maximum annual average concentration (ng/m^3)		
		Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
2007	Single-building (Baseline)	-	0.046	0.046
	Multiple-building	-	0.046	0.046
	No building	-	0.046	0.046
2008	Single-building (Baseline)	-	0.051	0.051
	Multiple-building	-	0.051	0.051
	No building	-	0.051	0.051
2009	Single-building (Baseline)	-	0.039	0.039
	Multiple-building	-	0.039	0.039
	No building	-	0.039	0.039

Table 4.10.16: Maximum predicted NDMA concentrations with different modelled buildings

Meteorological year	Modelled building	Maximum annual average concentration (ng/m^3)		
		Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
2007	Single-building (Baseline)	0.14	0.0004	0.14
	Multiple-building	0.035	0.0004	0.035
	No building	0.034	0.0004	0.035
2008	Single-building (Baseline)	0.15	0.0004	0.15
	Multiple-building	0.037	0.0004	0.037
	No building	0.033	0.0004	0.033
2009	Single-building (Baseline)	0.16	0.0003	0.16
	Multiple-building	0.047	0.0003	0.047
	No building	0.042	0.0003	0.042

Figure 4.10.57 a) b) and c): DMA Baseline Case, multiple-building and no-building scenarios respectively; nitrosamine concentrations, 2009 meteorological data.

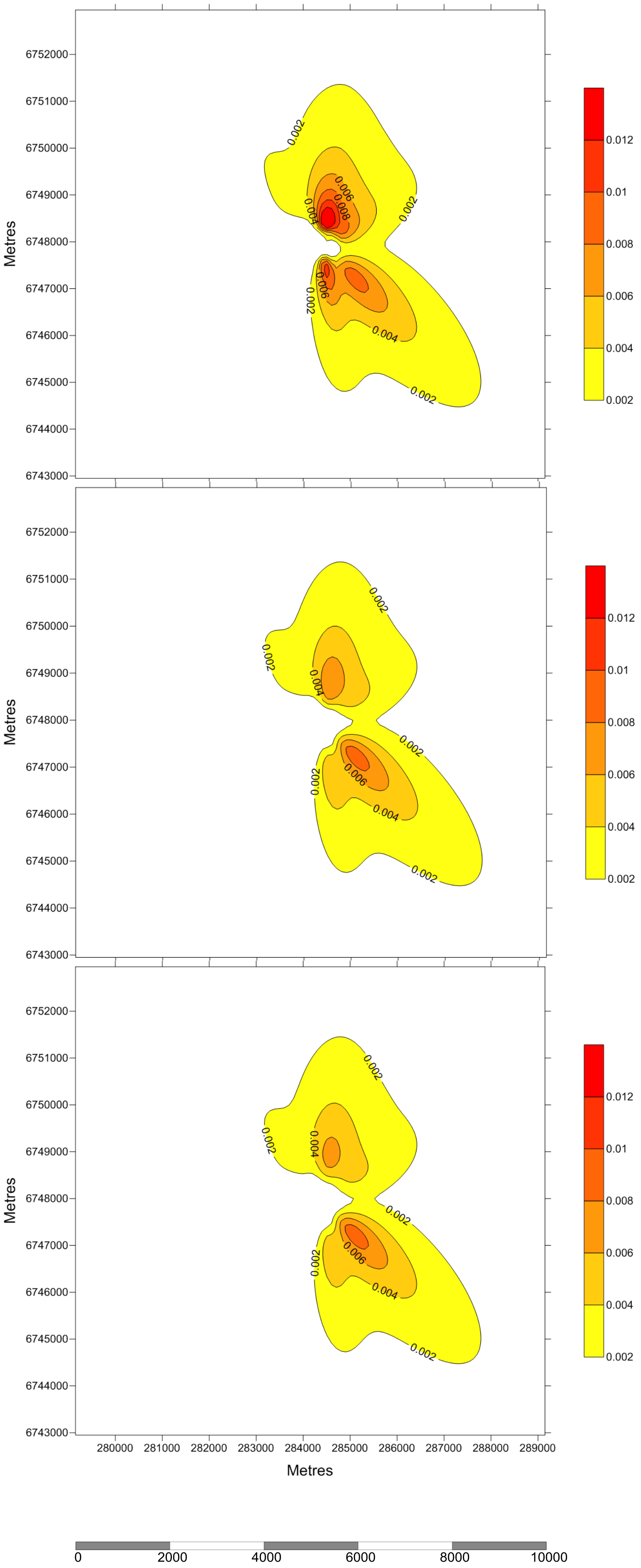


Figure 4.10.58 a) b) and c): DMA Baseline Case, multiple-building and no-building scenarios respectively; nitramine concentrations, 2009 meteorological data.

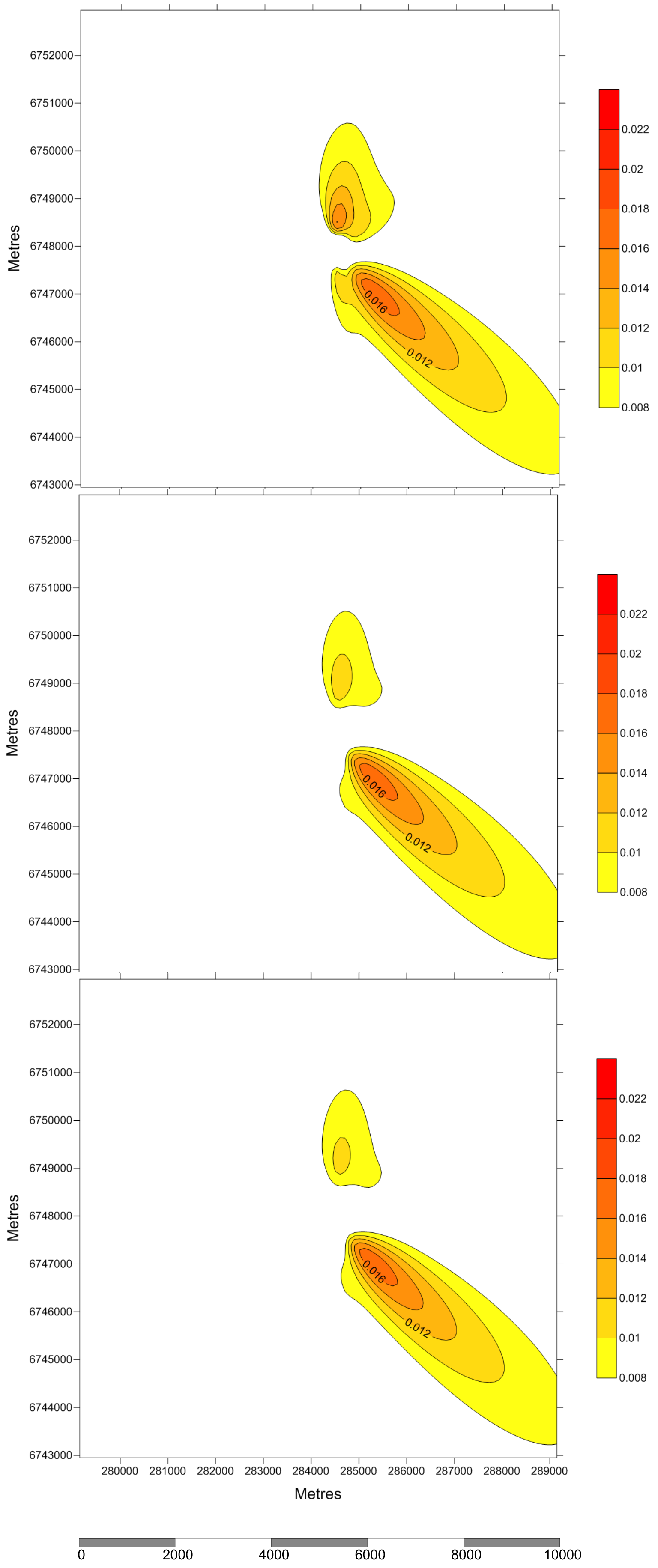


Figure 4.10.59 a) b) and c): MMA Baseline Case, multiple-building and no-building scenarios respectively; nitramine concentrations, 2009 meteorological data.

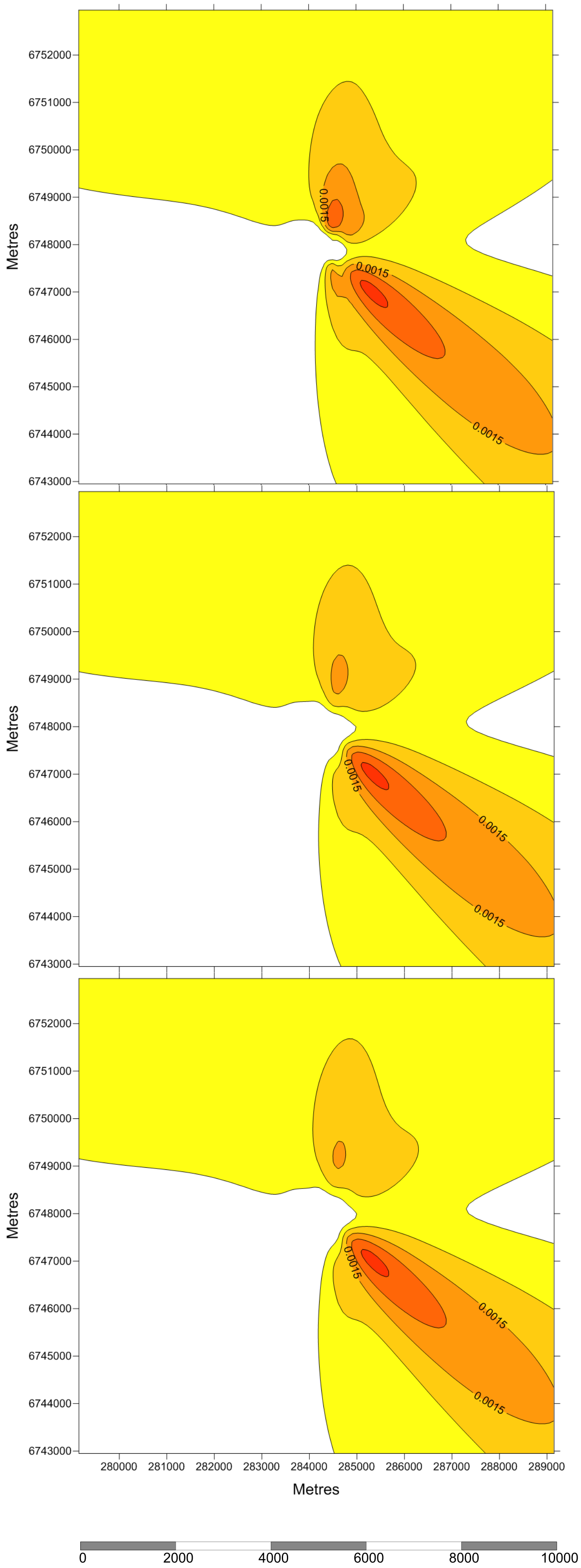


Figure 4.10.60 a) b) and c): MEA Baseline Case, multiple-building and no-building scenarios respectively; nitramine concentrations, 2009 meteorological data.

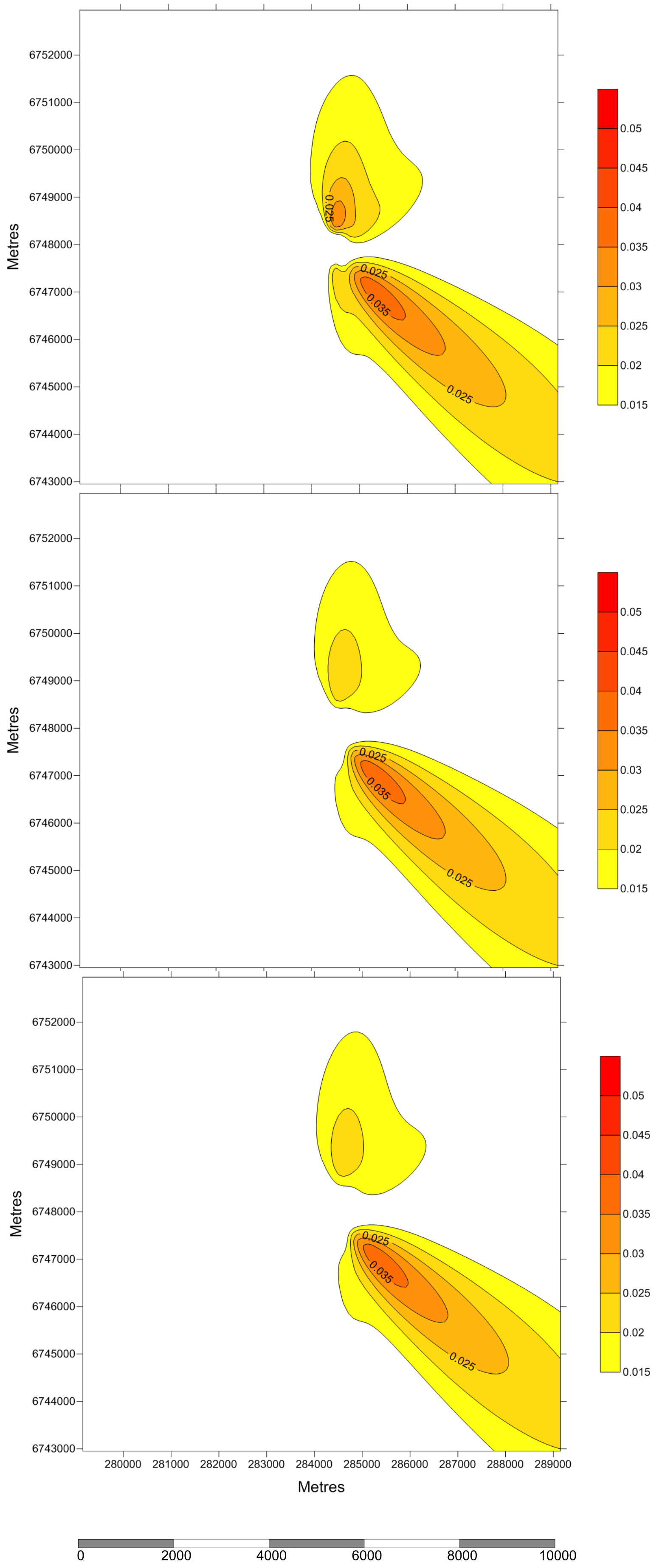


Figure 4.10.61 a) b) and c): NDMA Baseline Case, multiple-building and no-building scenarios respectively; nitrosamine concentrations, 2009 meteorological data.

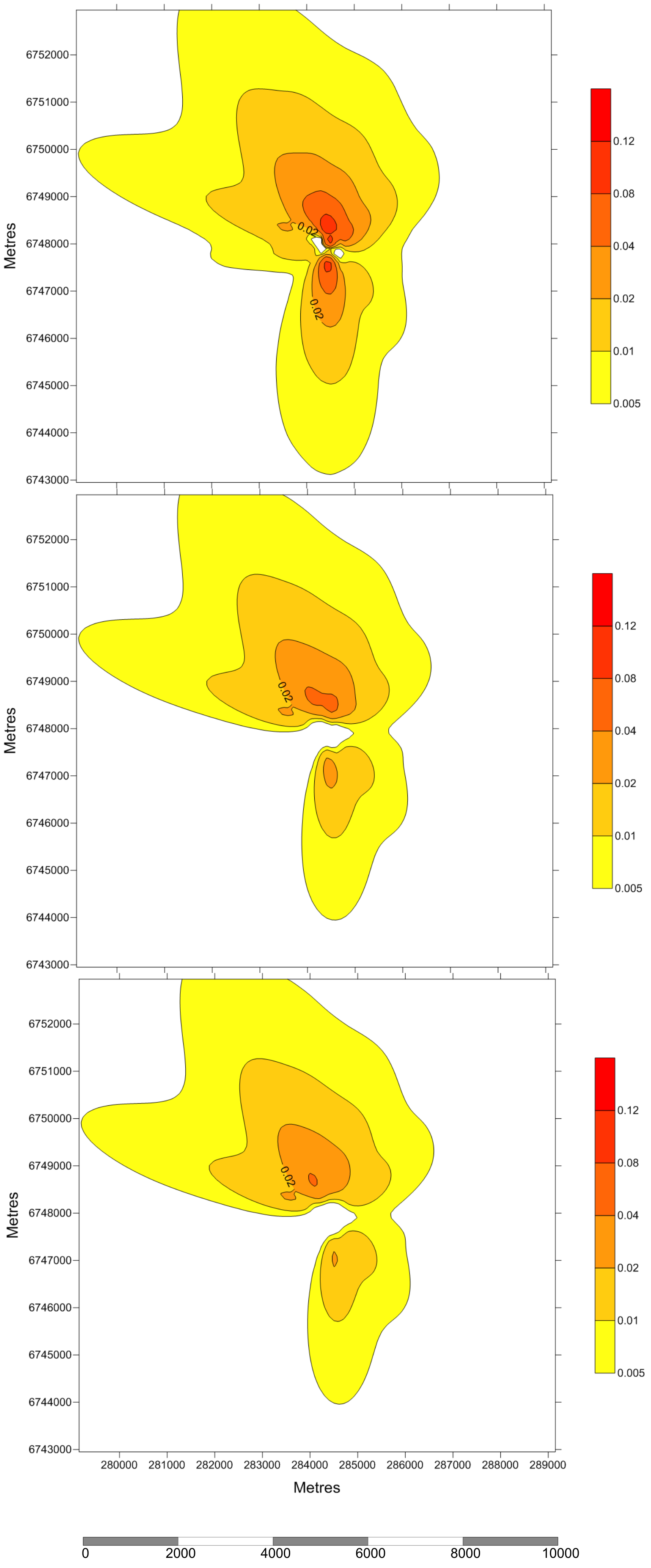
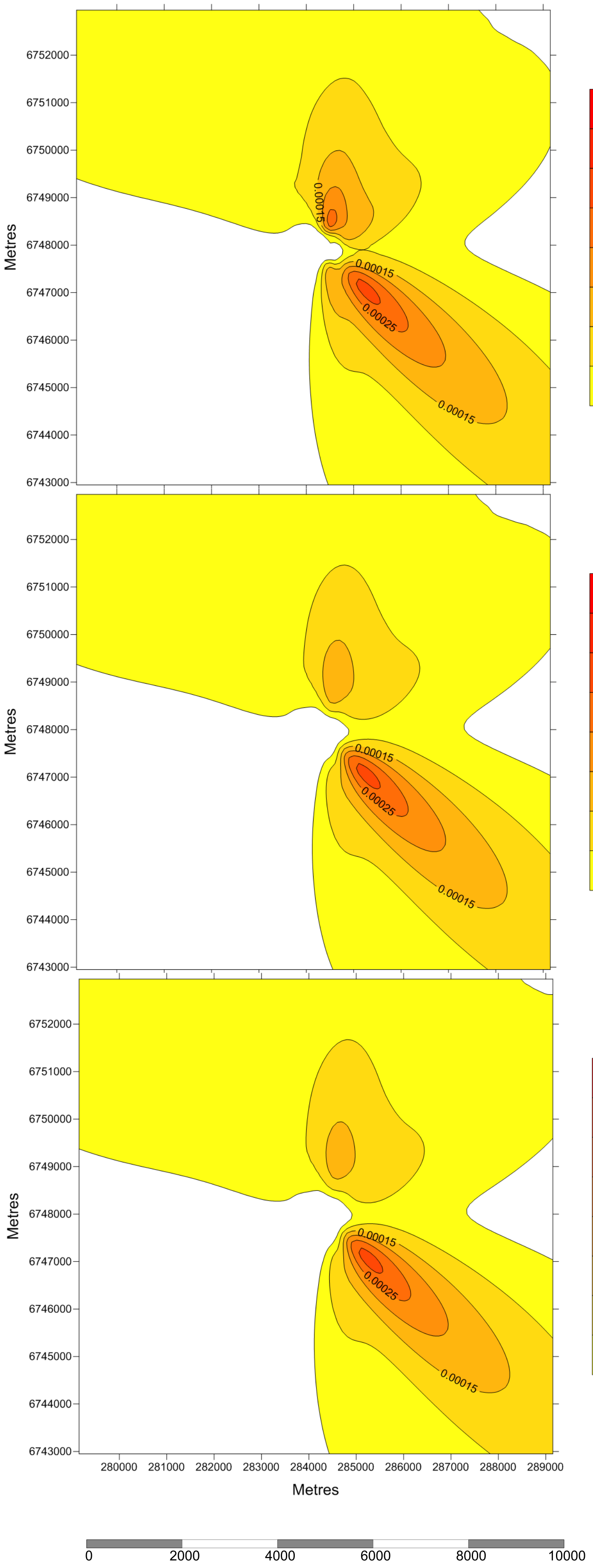


Figure 4.10.62 a) b) and c): NDMA Baseline Case, multiple-building and no-building scenarios respectively; nitramine concentrations, 2009 meteorological data



4.10.10. Other runs: Amine concentration output

Table 4.10.17 shows the maximum residual amine concentrations from DMA, MMA and MEA emissions. Note that these results are from model runs that included the amine chemical reaction scheme calculations.

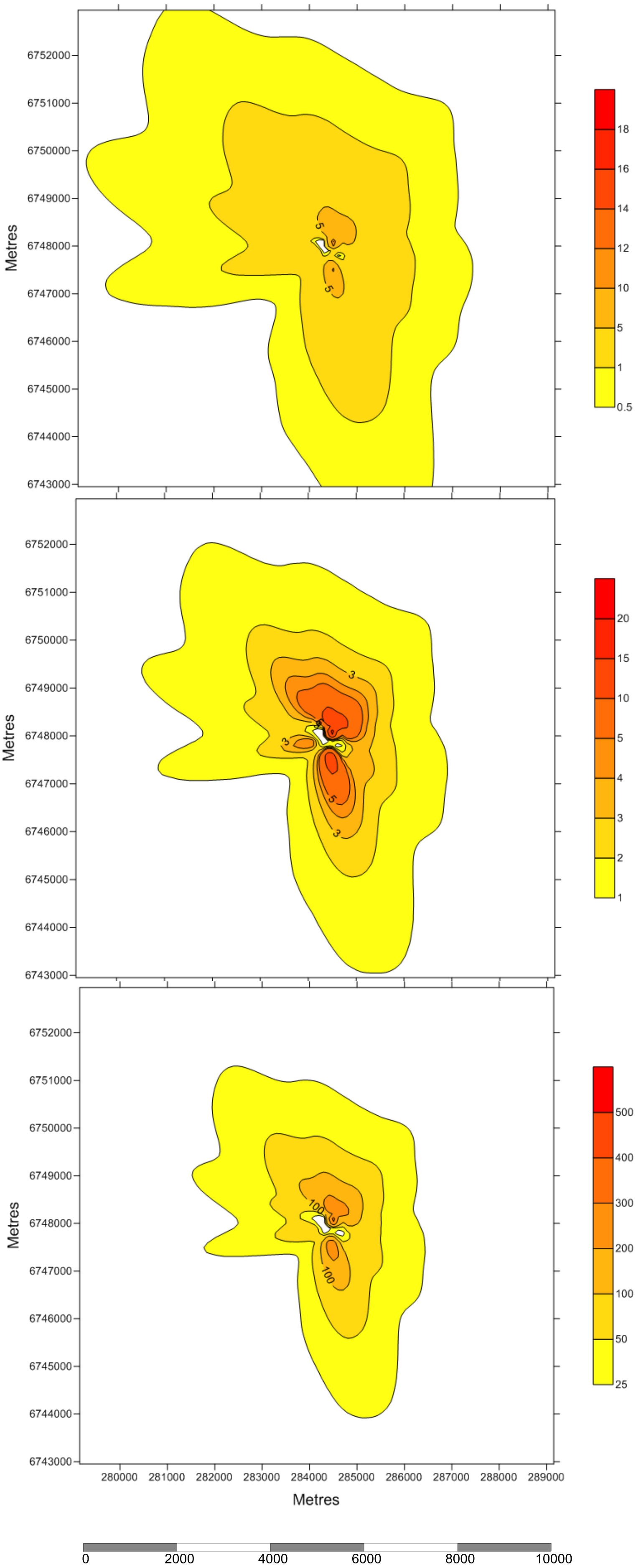
Table 4.10.17: Residual amine concentrations for each emitted amine

Emitted species	Maximum annual average concentration ($\mu g/m^3$)
DMA (Baseline)	18.1
MMA	24.9
MEA	491.0

Figure 4.10.63 a) b) and c) show the residual amine concentrations from DMA, MMA and MEA emissions, respectively, for the Baseline Case, with the model chemistry scheme included.

Note that all contour plots showing output amine concentrations have units of $\mu g/m^3$, as the values are much larger than those of the nitrosamine and nitramine concentrations.

Figure 4.10.63 a) b) and c): Baseline Case, amine concentrations from DMA,MMA and MEA emissions, respectively



4.10.11. Other runs: Amine concentration output with no chemistry modelling

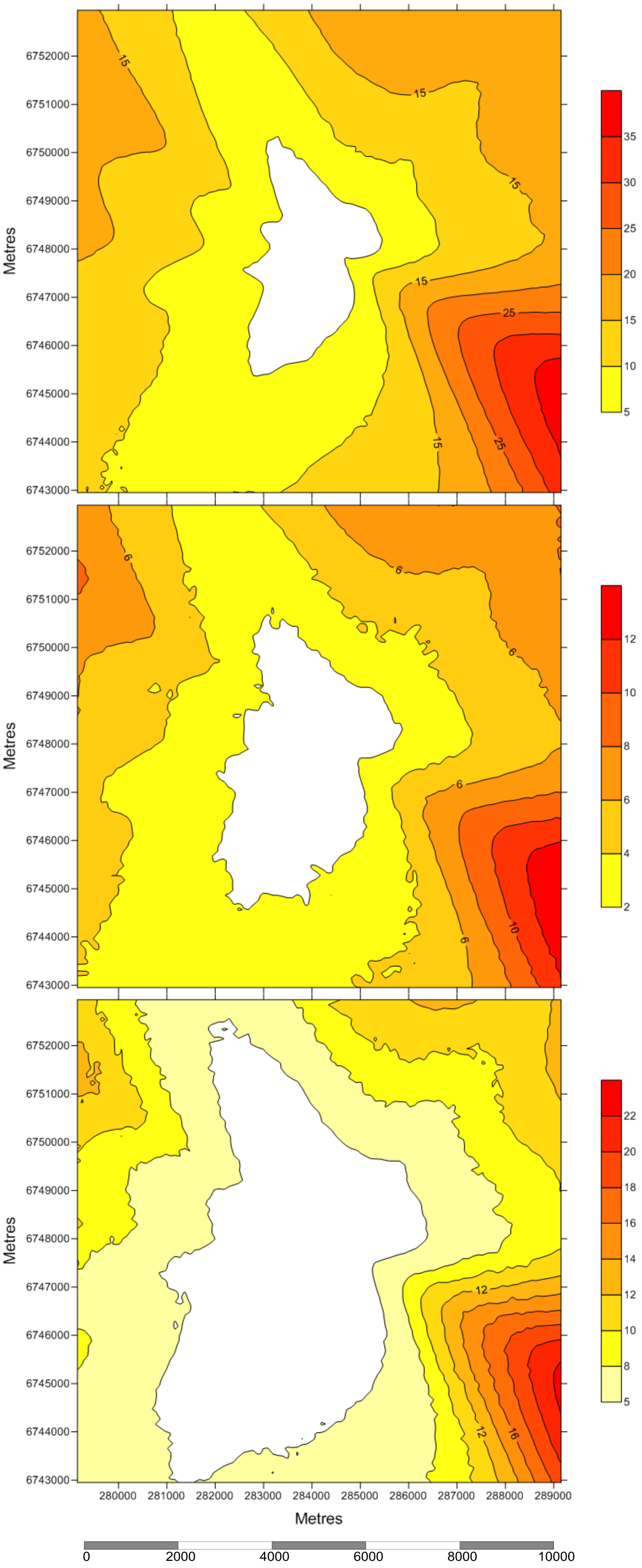
Table 4.10.18 shows the maximum residual amine concentrations from DMA, MMA and MEA emissions. These results are from model runs that did not include the amine chemical reaction scheme calculations. Note that these maximum results are very similar to the values given for those runs with the chemistry scheme included, which is why the contour plots below show percentage differences instead of absolute values.

Table 4.10.18: Residual amine concentrations for each emitted amine

Emitted species	Maximum annual average concentration (ng/m^3)
DMA (Baseline)	18.1
MMA	25.0
MEA	491.0

Figure 4.10.64 a) b) and c) show the percentage difference in residual amine concentrations from DMA, MMA and MEA emissions, respectively, for the Baseline Case, with and without out the model chemistry scheme included.

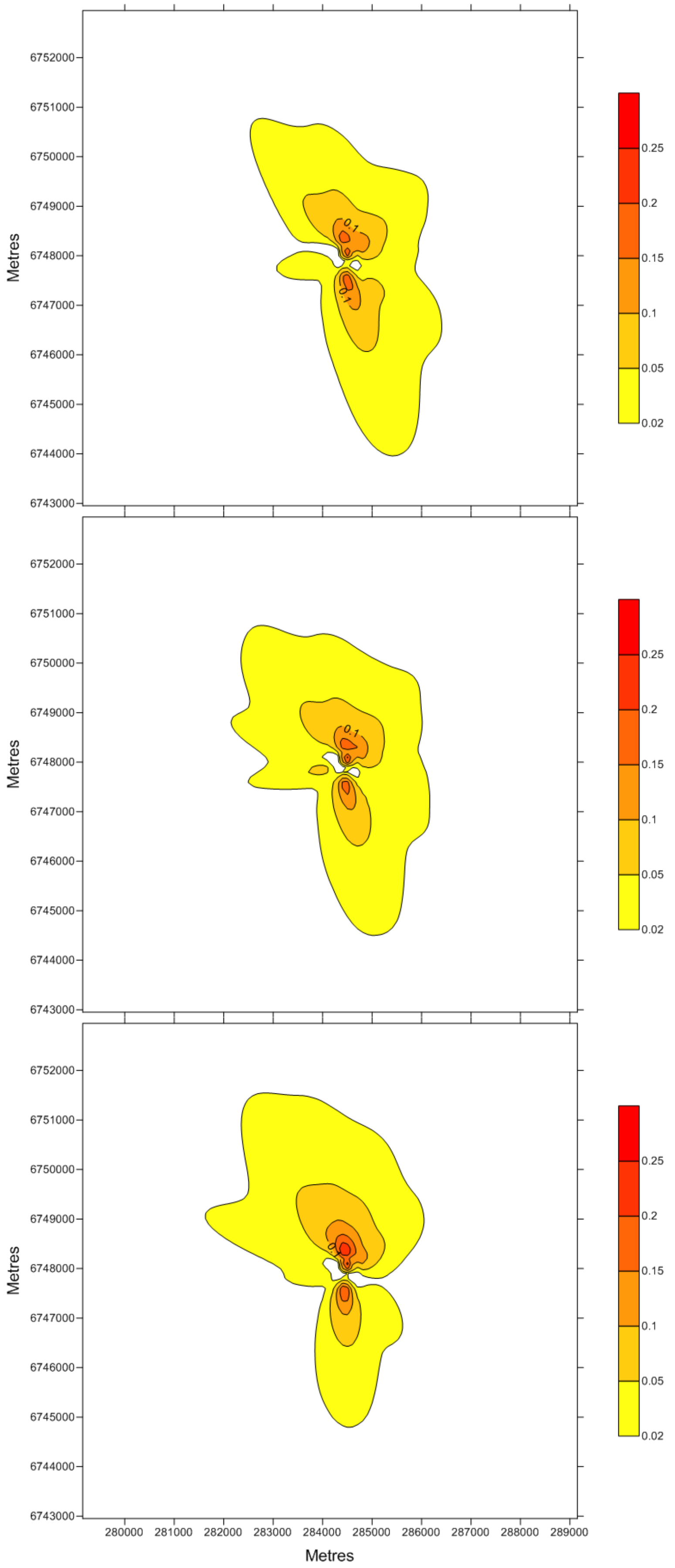
Figure 4.10.64 a) b) and c): Percentage difference between amine concentrations - with and without chemistry



4.10.12. Other runs: Unit emission rate

Figures 4.10.65 a) b) and c) show contour plots of the Baseline Case with a nominal 1g/s emission rate, for the three years of meteorological data.

Figure 4.10.65 a) b) and c): Baseline Case with unit emission rate, 2007, 2008 and 2009 meteorological data, respectively



5. Discussion

This section comprises a brief discussion of the main findings of the modelling study and areas of uncertainty. It is extremely difficult to give a quantitative assessment of the overall uncertainty in the modelled results, due to the large number of different input data types and their respective uncertainties. Sensitivity tests, however, provide a means of isolating and investigating the effect of changing a single parameter at a time, including varying the parameter values within and beyond expected uncertainty ranges.

Discussion of the results of the sensitivity tests are given in the following sections.

5.1.1. Total concentrations from emissions of all amines and directly-emitted nitrosamine

Modelling all emitted species allowed total concentrations of nitrosamines and nitramines to be calculated for the baseline emissions scenario, for comparison with the guideline limit value. The maximum annual average concentrations, in µg/m^3, are as follows:

Nitrosamines	0.15
Nitramines	0.08
Sum	0.16

The guideline limit value considered for the purposes of this modelling study is 0.3 ng/m^3, which represents the total concentration of nitrosamines plus the total concentration of nitramines in air. The total modelled value for the sum of nitrosamines and nitramines is around half that of the guideline limit value for this emissions scenario. The nitrosamine concentrations dominate the total value, and these are, in turn, dominated by direct NDMA emissions.

The modelled concentrations are based on reasonable estimates of rate parameters and other input data, so this is a relevant comparison. A notable exception to this is building effects, where modelling with a multiple-building setup is likely to be more realistic, and would result in a lower impact due to NDMA. The equivalent maximum total (for 2008) with the multiple-building scenario is 0.11 ng/m3, approximately a third of the guideline limit value. Further discussion of the effects of buildings is given in Section 5.1.7.

5.1.2. Sensitivity tests: Amine-specific reaction parameters

These sensitivity tests involved varying the values of the rate coefficients and other parameters directly relating to the amine chemistry scheme. Some of the tests were based on values within realistic ranges, while others involved larger, less realistic ranges for certain parameters.

Those tests that involved realistic parameters present a way of assessing the sensitivity of the modelled concentrations to different values in the literature. For DMA, comparing the Baseline (reference values) results with those of Test 2 shows that using the j_5 value of Tuazon *et al.* gives only a slight decrease in the resulting nitrosamine concentrations; the fact that this difference is small is notable, as Tuazon *et al.* reported that their value represents a predicted upper limit for the j_5 parameter.

A comparison of DMA Tests 1 and 2 allows an assessment of the effect of using the Lindley *et al*. values for several of the parameters. The main differences are in the values specified for k_2, k_3 and k_{1a}/k_1, and these differences all tend towards producing lower concentrations. The k_3 values show a particular difference, with the value for Test 1 being around three times lower than that for Test 2; this parameter determines the rate of the reaction of the amino radical with NO, which leads to formation of the nitrosamine.

In addition, the value for k_2 in Test 1 is greater than the value in Test 2. The k_2 parameter determines the rate of the reaction of the amino radical with oxygen, to form the imine, which is a reaction in direct competition with the reactions that form the nitrosamines and nitramines. These effects, along with the fact that the k1a/k1 branching ratio value is slightly lower for Test 1, explain why the differences in concentrations are significant, particularly for nitrosamines (for which concentrations are almost three times lower for Test 1). These two tests illustrate how the application of different rate coefficient values from the literature can significant affect modelled concentrations, especially when these act in combination.

For MMA, comparing the Baseline (reference values) results with those of Test 1 shows the effect of using alternative parameters for k_1 (from Carl and Crowley *et al*.) and the k_1/k_{1a} branching ratio (from Rudic *et al*.). The resulting nitramine concentration is greater for Test 1 than for the Baseline run. Test 1 shows how applying different rate coefficients from the literature can affect the resulting nitramine concentrations; varying these parameters independently could give rise to even larger differences in concentrations, as some of the differences between the Baseline and Test 1 values act in favour of nitramine production, and others against it.

For MEA, comparing the Baseline (reference values) results with those of Test 1 shows the effect of using the Lindley *et al*. values for several of the parameters. The resulting concentrations are lower for Test 1 than for the Baseline case, mainly due to the differences in values for k_2 and k_3, for the same reasons as given above for DMA (the parameters used for MEA are the same as those used for DMA).

Those tests that involve values over an unrealistic range were included to demonstrate the effects of these large changes, and to check that the amine chemistry scheme behaves as expected. To put these results into context, the ranges employed in these tests are likely to be significantly larger than the ranges corresponding to uncertainties in the values for these parameters. For example, the estimated error quoted in the 2011 ADA report for k_{1a}/k_1 is around 15% for DMA, whereas the tested range represents an increase and decrease of around 100% compared with the reported value.

The concentrations modelled in these tests generally do behave as expected from the reported reactions and rate expressions.

5.1.3. Sensitivity tests: Other reaction parameters

The sensitivity to the following parameters was tested; these are parameters that are not directly related to the amines but are important for the amine chemistry scheme:

- The emission of NO_x from the CHP plume;
- The NO_2: NO ratio in the CHP emissions;
- The refinery NO_x emissions;
- The background (rural) NO_x concentration;
- The background (rural) ozone concentration; and
- The value of c, the constant that determines hourly OH concentrations.

When the CHP NO_x emissions are varied, the modelled concentrations of nitrosamines are significantly affected. The nitrosamine concentrations are far more sensitive to this than the nitramine concentrations because the NO_x emissions at the stack exit are likely to comprise around 90% NO, which is the component of NO_x that leads to nitrosamine formation.

Changing the refinery NO_x emissions and the rural background NO_x concentrations, on the other hand, affects the nitramine concentrations much more than the nitrosamine concentrations (with a significant change in the predicted values); this is because the proportion of NO_2 is much greater than that of NO for ambient levels of NO_x (i.e. away from the point of emission).

There is some sensitivity to changing the NO_2: NO ratio of the CHP emissions, but less so than in the other tests involving NO_x emissions.

Varying the rural background O_3 concentrations has a large effect on both the nitrosamine and nitramine concentrations. Similarly, changing the c value, whether by doubling/halving the hydroxyl radical concentration or by doubling/halving the j_{NO2} value, has a considerable effect on modelled concentrations.

There is considerable uncertainty in the values for many, if not all, of these parameters, so the tested ranges are likely to be within uncertainty ranges, and therefore represent realistic values.

5.1.4. Sensitivity tests: Alternative emission scenarios

For Scenarios 1 to 3, the differences in modelled concentrations reflect the relative proportions of the various species. For Scenario 4, however, the lower volume flow rate, and hence lower exit velocity, lead to significantly larger concentrations than Scenario 1 (with equivalent emissions) due to reduced dispersion effects.

5.1.5. Sensitivity tests: Other meteorological data

The meteorological year that gives the highest total concentrations is 2008, the year on which the Baseline case is based. The results show that, although there are differences in both the maximum concentrations and the concentration patterns, these inter-annual differences are relatively small.

In addition to these sensitivity tests, the contour plots from the model runs carried out with a unit emission rate (Section 4.10.12) show the effects of varying the meteorological year on dispersion only (i.e. not including the effects of the year on chemical reactions). These plots mainly reflect the differences in wind speed and direction between the three years.

5.1.6. Sensitivity tests: With terrain and variable roughness

The model runs carried out with terrain and variable roughness effects included generally result in lower concentrations than those carried out without terrain effects and with a fixed roughness length (i.e. the Baseline case runs). These differences are relatively small.

5.1.7. Sensitivity tests: Building effects

The effects of the different modelled building scenarios on the maximum modelled concentrations deriving from the amines (DMA, MMA and MEA) are negligible or small. For the directly-released nitrosamine, NDMA, there is a significant difference in the maximum modelled concentrations for the different building scenarios.

It is likely that these differences can be attributed to the time required for formation of nitrosamines and nitramines in the plume. When NDMA is emitted directly, this nitrosamine is already present in the plume at the emission point, whereas emissions of amines need time to react with OH and NO_x before nitrosamines and nitramines are formed in the plume. A major effect of buildings is to rapidly bring the plume towards the ground, so the reaction time effects are amplified where buildings are present. The maximum concentrations occur close to the stack and/or buildings, so these values can show extreme differences.

While comparing the maximum concentrations is useful, these values do not give the full picture of the differences in concentrations; contour plots show the differences in patterns across the whole modelled output grid.

The contour plots given in Section 4.10.9 are for the year 2009, as this year generally shows the most pronounced differences in concentration patterns for the three scenarios. See, for example, the values for nitrosamines formed from DMA.

The differences seen for 2009 are likely to be due to differences in the prevailing wind directions, which can be seen in the wind roses. For 2007 and 2008, there is a clear NW / SE prevailing wind, which suggests little interaction of the wind (and hence the plume) with the building; for 2009, however, there is more of an influence from northerly and southerly winds, which would tend to give rise to more interaction of the winds with the building, thus affecting the plume.

For most of the emitted species the contour plots do not show much sensitivity to the building scenarios. There is a significant difference for the DMA plots (particularly the nitrosamines), probably due to the 2009 meteorology effects described above; plots for the years 2007 and 2008 show much less variation. The significant sensitivity of concentrations from NDMA emissions to the different building scenarios is apparent in the contour plots; note that there is a striking north / south alignment of these plots.