Cambridge Environmental Research Consultants

Contract number 257430174: Atmospheric Chemistry Modelling

Variation Order 2: Dispersion sensitivity analysis

Final report

Prepared for

CO_2 Capture Mongstad Project
Gassnova SF

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1. Introduction

The CO_2 capture Mongstad (CCM) project involves the construction of a combined heat and power (CHP) plant at Mongstad refinery in Norway, equipped with large-scale post-combustion carbon capture. 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.

The work reported here was carried out as a Variation Order under Contract number 257430174: Atmospheric Chemistry Modelling. Data regarding the CHP stack parameters, emissions and atmospheric transformation percentages were provided to CERC by CCM Project.

Sensitivity tests were carried out as follows:

- **Task 1:** Additional sensitivity analyses using Scenario 1;
- **Task 2:** Modelling using detection limits;
- **Task 3:** Modelling using simplified chemistry scheme (as used by DNV); and
- **Task 4:** Calculation to estimate concentrations in water bodies.

Full details of the meteorological data, site location, study area and other aspects of the model set-up can be found in the CERC report, *Atmospheric Chemistry Modelling Activity 1: Gaseous Phase Chemistry Modelling (initiated by hydroxyl radical),* which is referred to in the current report as the 'Activity 1 report'.

Emissions of dimethylamine (DMA), monomethylamine (MMA), monoethanolamine (MEA), directly-emitted N-nitrosodimethylamine (NDMA) were considered. Different combinations of these emitted species were considered in each Task. Two different methods of calculating the concentrations of these species were used: a fixed transformation percentage value; and the ADMS amine chemistry scheme. Direct emissions of N-nitromonoethanolamine (nitra-MEA) were also considered in Task 2, for modelling using detection limits.

No official limit values for nitrosamines and nitramines have been set for Norway. For the purposes of this modelling, 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 limit has been recommended by the Norwegian Institute of Public Health (NIPH) as a maximum acceptable level to ensure minimal or negligible risk of cancer for the public from exposure to nitrosamines and nitramines, following their review of existing international risk evaluations and toxicological information in the scientific literature.[1] This guideline limit is assumed to apply to annual average concentrations.

Section 2 gives a description of the stack parameters, emissions data, data used for the fixed transformation calculations and ADMS amine chemistry scheme inputs. Tasks 1 to 4 are described in Sections 3 to 6, along with predicted concentrations and other results.

[1] 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-/

2. Stack, emission and atmospheric transformation data

The model runs described in this report were based on the Baseline runs described in the Activity 1 report, with modifications made for each of the four Tasks. These modifications are described in Sections 3 to 6.

Emissions of DMA MMA, MEA and directly-emitted NDMA were modelled. Data for four scenarios, representing different combinations of emission rates for these species, were originally provided by the CCM Project, along with varying stack parameters. Of these four, only Scenario 1 is considered in this report. For Task 2, directly-emitted nitra-MEA was also modelled. Meteorological data for the year 2008 were used as input to the model for all of the Tasks.

Two different methods of accounting for atmospheric transformations of the emitted species were used in the various Tasks. The ADMS amine chemistry scheme method is described in the Activity 1 report, and all parameters input for the chemistry scheme correspond to the Baseline, or reference, parameters described in that report. The fixed transformation, post-processing method is described in Section 2.2 of the current report.

2.1. CHP source parameters and emissions

The CHP stack parameters used for the modelling for all four Tasks are shown in Table 2.1. As described above, these correspond to the parameters from Scenario 1 of the four Scenarios originally provided.

Table 2.1: 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

Emissions from the CHP absorber stack were provided by CCM Project, comprising several specific amines, plus nitrosamines that might be expected to form within the stack. All emissions were provided as emission concentrations, in volumetric units, which were converted into emission rates for input into ADMS. These values are shown in Table 2.2. For the purposes of the volumetric to mass conversion and the chemical transformations it was assumed that the data for 'nitrosamines' correspond to NDMA.

Other emissions data were provided for Task 2, representing limits of detection of the emitted species; these are described in Section 4.1.

Table 2.2: Scenario 1 emissions data

Species	Emission concentrations as provided (ppmv)	Modelled emission rate (g/s)
Amines:		
Monomethylamine	0.1	0.041
Dimethylamine	0.05	0.030
Monoethanolamine	1.0	0.162
Nitrosamines	0.00025	0.000197
Nitramines	0	0

2.2. Fixed transformation data and methodology

Information on the transformation of amines in the atmosphere was provided by CCM Project, comprising a constant, single percentage value for each conversion, on a volumetric mixing ratio basis. The values used for Tasks 1, 3 and 4 are shown in Table 2.3. Other transformation values were provided for Task 2, as described in Section 4.2.

Note that the production of nitrosamines from MMA and MEA is given as zero.

The calculation method involved outputting concentrations output by ADMS 4, for a model run that considered only dispersion, i.e. the amines and directly-emitted NDMA were treated as chemically-inert substances. Nitrosamine and nitramine concentrations were then calculated by post-processing the ground-level concentrations, based on the percentage transformation values given in Table 2.4, and summing the totals.

No further consideration of the photolysis of the directly-emitted nitrosamines was included in the percentage transformation calculations, as the percentage value takes into account photolysis of the nitrosamines as well as the formation, i.e. the competing production and loss processes.

Schematic diagrams outlining the calculation steps are shown in Figures 2.1 and 2.2, for nitrosamines and nitramines, respectively.

Table 2.3: Percentage transformations applied to each amine for Tasks 1, 3 and 4

Amine	Transformation in the atmosphere (%) to:	
	Nitramine	Nitrosamine
Monomethylamine	0.4	0
Dimethylamine	2.5	0.4
Monoethanolamine	0.3	0

Figure 2.1: Percentage transformation calculation process for nitrosamines

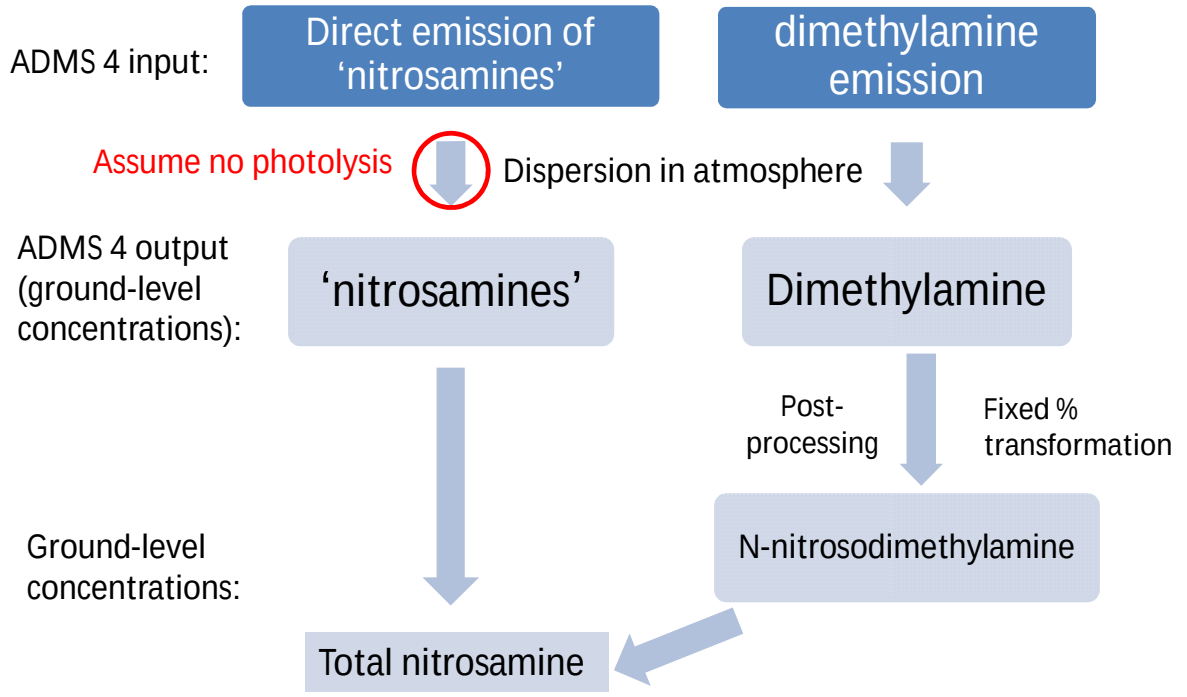
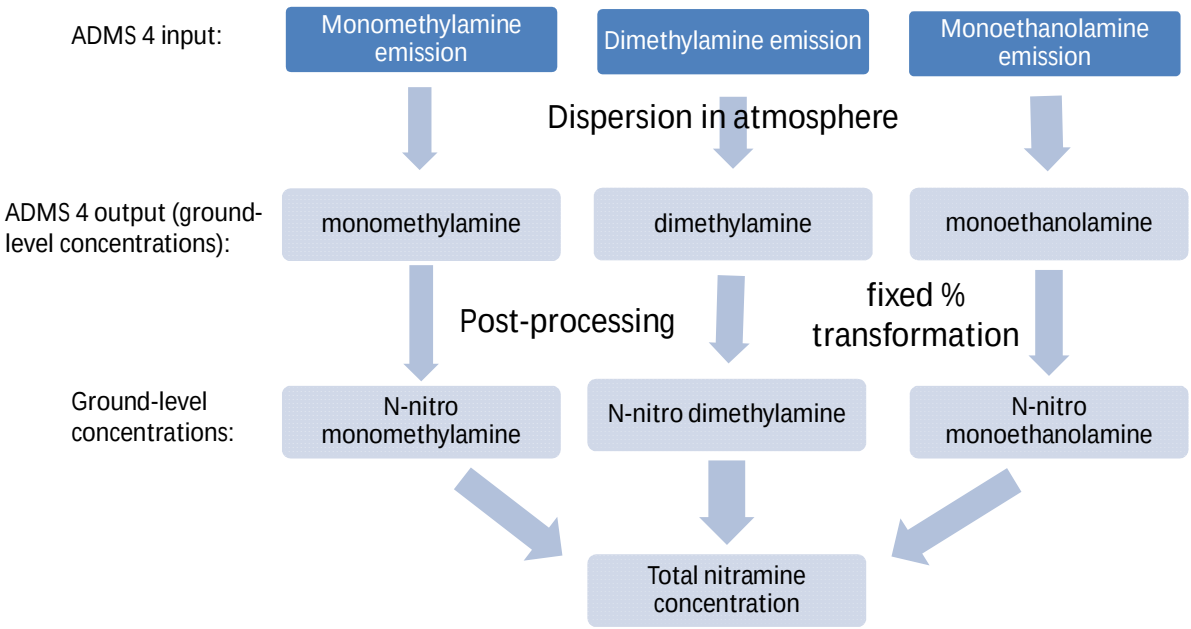


Figure 2.2: Percentage transformation calculation process for nitramines



3. Task 1: Additional sensitivity analyses using Scenario 1

3.1. Overview

Task 1 involved modelling with a range of stack heights and locations, as presented in Table 3.1.

The three cases comprised three different chemistry scenarios:

A. post-processing using a fixed atmospheric transformation percentage;
B. the chemical reaction scheme developed by CERC under Activity 1; and
C. no chemistry, to show the effects of changes to stack height and location in isolation.

The building configuration used for the model runs was the 'multiple-building' scenario, described in the Activity 1 report; this configuration, along with the various stack locations, is shown in Figure 3.1.

Table 3.1: Model runs carried out under Task 1

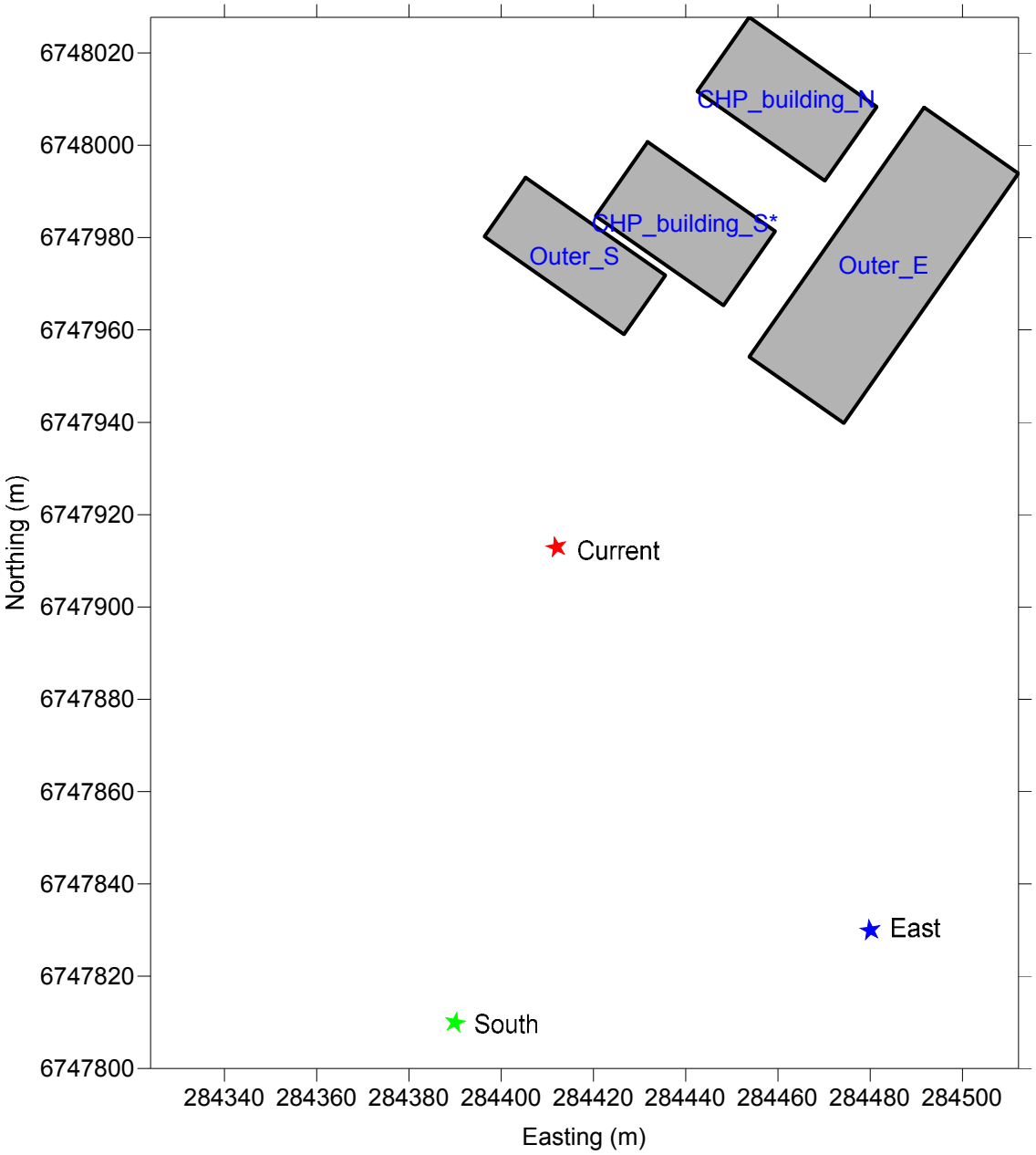
Case	Chemistry scheme	Stack height (m)	Location
A	Post-processing	65	South[2], East[3], Current[4]
		75	Current
		85	South, East, Current
		95	Current
		105	Current
B	Activity 1 chemistry	65	South, East, Current
		75	Current
		85	South, East, Current
		95	Current
		105	Current
C	No chemistry (dispersion only)	65	South, East, Current
		75	Current
		85	South, East, Current
		95	Current
		105	Current

For Cases A and B, emission parameters were based on the emission data described in the previous sections of this report. Case C assumes a representative 1g/s emission rate, so the results do not represent meaningful values but are intended just for intercomparison purposes, to isolate the effects of the dispersion processes.

Ground level concentrations were calculated over a 10km by 10km output grid, at a resolution of 100m.

[2] South = 284390, 6747810
[3] East = 284480, 6747830
[4] Current = 284412, 6747913

Figure 3.1: Stack and building locations



3.2. Results for Case A: Chemistry applied using post-processing

Section 2.2 describes the methodology and data used for the post-processing in Case A.

The maximum predicted annual average concentrations of nitrosamines and nitramines for Case A are shown in Tables 3.2 to 3.10, and a selection of contour plots of annual average concentrations of the sum of (nitrosamines and nitramines) for Case A are shown in Figures 3.2 to 3.4. All concentrations shown in the contour plots have units of ng/m^3.

Table 3.2: Case A - Stack height 65m, current location

Emitted amine	**Maximum concentration (ng/m^3)**		
	Nitrosamines	**Nitramines**	**Sum (nitrosamines and nitramines)**
DMA	0.057	0.432	0.489
MMA	-	0.063	0.063
MEA	-	0.646	0.646
Directly emitted NDMA	0.038	-	0.038
Total	0.095	1.140	1.235

Table 3.3: Case A - Stack height 65m, east location

Emitted amine	**Maximum concentration (ng/m^3)**		
	Nitrosamines	**Nitramines**	**Sum (nitrosamines and nitramines)**
DMA	0.034	0.611	0.644
MMA	-	0.089	0.089
MEA	-	0.913	0.913
Directly emitted NDMA	0.054	-	0.054
Total	0.087	1.612	1.699

Table 3.4: Case A - Stack height 65m, south location

Emitted amine	**Maximum concentration (ng/m^3)**		
	Nitrosamines	**Nitramines**	**Sum (nitrosamines and nitramines)**
DMA	0.051	0.387	0.438
MMA	-	0.056	0.056
MEA	-	0.578	0.578
Directly emitted NDMA	0.034	-	0.034
Total	0.085	1.022	1.106

Table 3.5: Case A - Stack height 75m, current location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.040	0.303	0.343
MMA	-	0.044	0.044
MEA	-	0.452	0.452
Directly emitted NDMA	0.027	-	0.027
Total	0.066	0.799	0.866

Table 3.6: Case A - Stack height 85m, current location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.030	0.239	0.269
MMA	-	0.035	0.035
MEA	-	0.357	0.357
Directly emitted NDMA	0.021	-	0.021
Total	0.051	0.631	0.682

Table 3.7: Case A - Stack height 85m, east location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.014	0.258	0.271
MMA	-	0.037	0.037
MEA	-	0.385	0.385
Directly emitted NDMA	0.023	-	0.023
Total	0.036	0.680	0.716

Table 3.8: Case A - Stack height 85m, south location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.030	0.239	0.269
MMA	-	0.035	0.035
MEA	-	0.357	0.357
Directly emitted NDMA	0.021	-	0.021
Total	0.051	0.630	0.681

Table 3.9: Case A - Stack height 95m, current location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.011	0.193	0.203
MMA	-	0.028	0.028
MEA	-	0.288	0.288
Directly emitted NDMA	0.017	-	0.017
Total	0.028	0.508	0.536

Table 3.10: Case A - Stack height 105m, current location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.008	0.159	0.167
MMA	-	0.023	0.023
MEA	-	0.237	0.237
Directly emitted NDMA	0.014	-	0.014
Total	0.022	0.419	0.441

Figure 3.2: Contour plots for Case A, 65m stack height; current, east and south locations, respectively

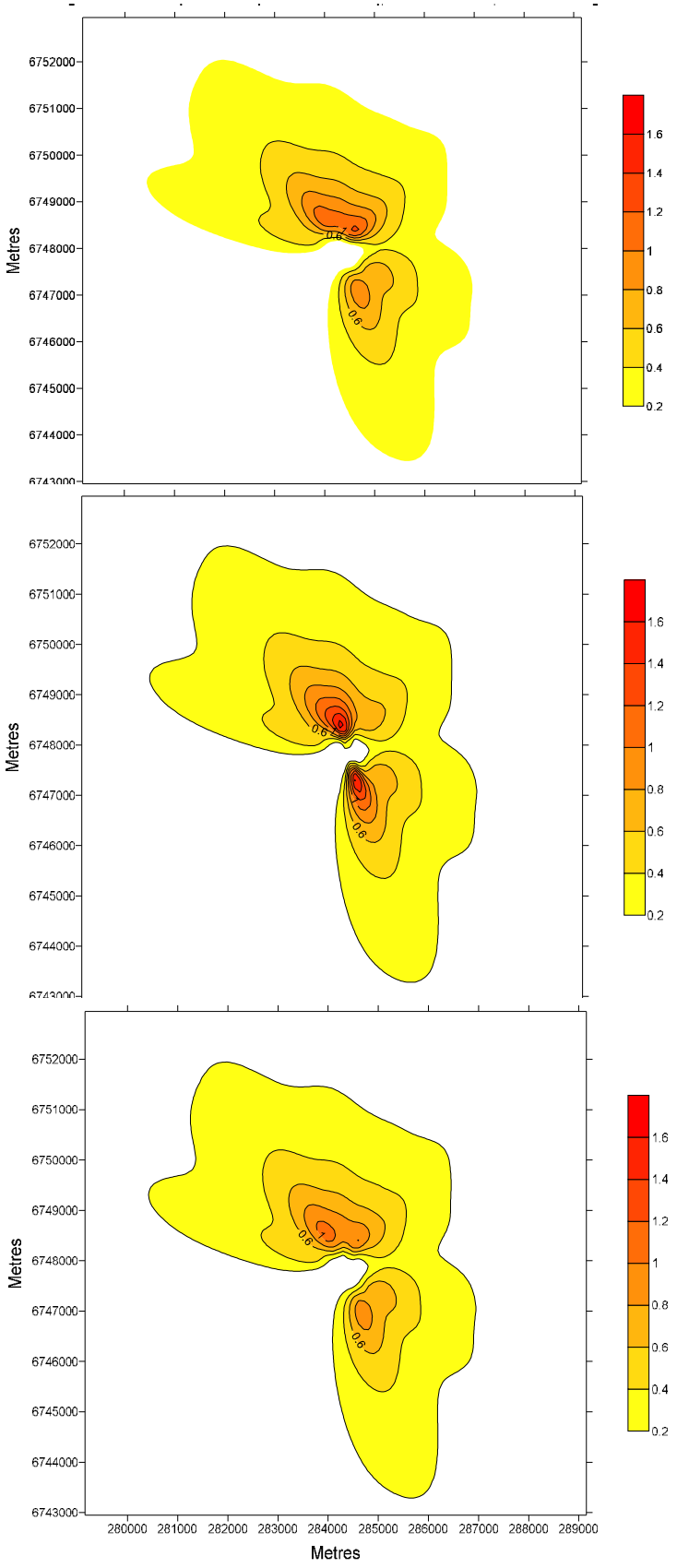


Figure 3.3: Contour plots for Case A, 85m stack height; current, east and south locations, respectively

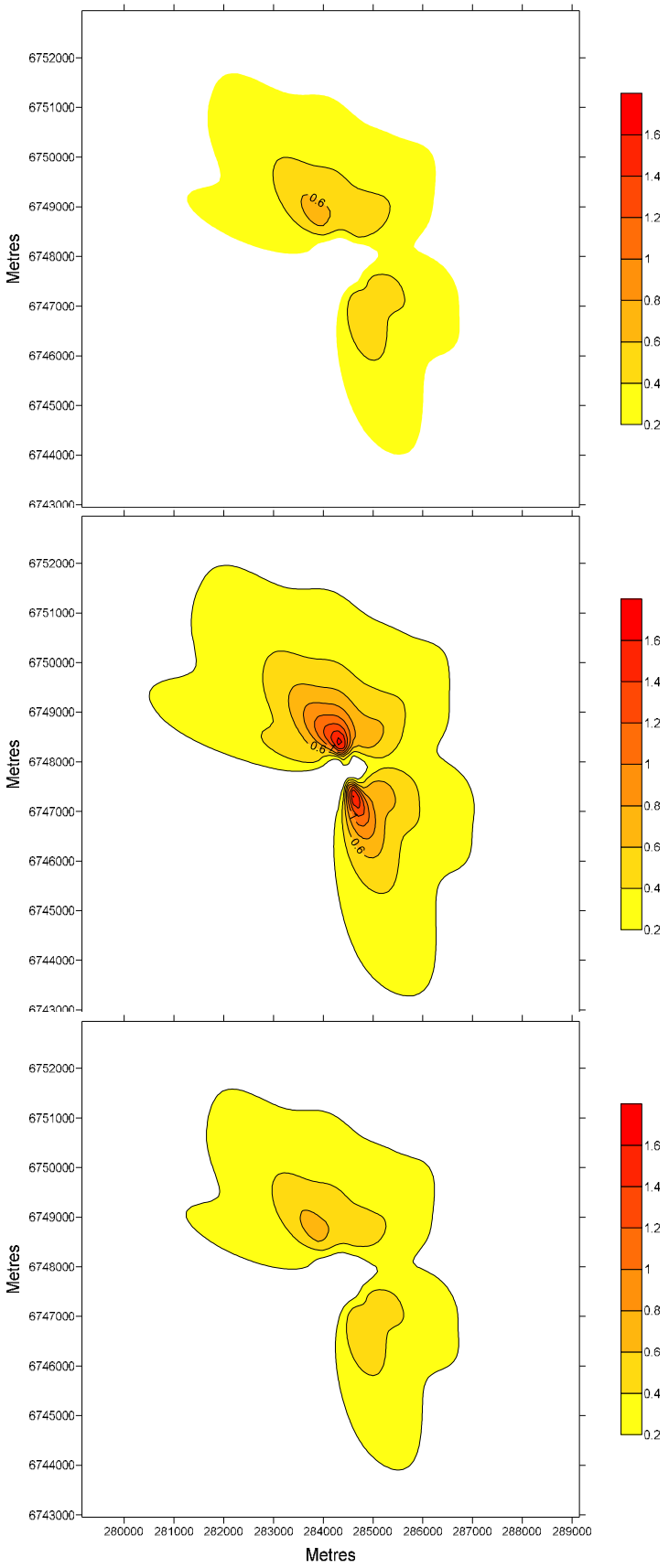
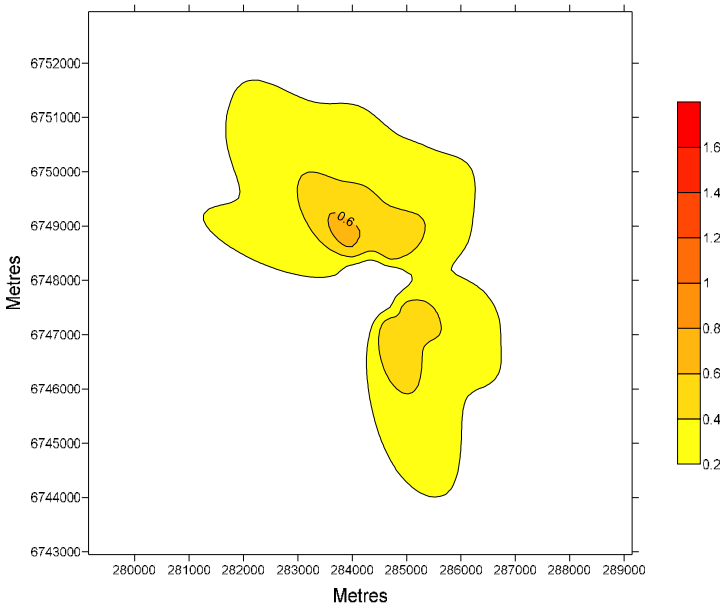


Figure 3.4: Contour plots for Case A, 105m stack height; current, location



3.3. Results for Case B: Activity 1 chemistry scheme

The maximum predicted concentrations of nitrosamines and nitramines for Case B are shown in Tables 3.11 to 3.19. Contour plots of annual average concentrations of the sum of (nitrosamines and nitramines) for Case B are shown in Figures 3.5 to 3.7. Not all results are shown.

Table 3.11: Case B - Stack height 65m, current location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.013	0.023	0.035
MMA	-	0.003	0.003
MEA	-	0.051	0.051
Directly emitted NDMA	0.037	0.0004	0.037
Total	0.042	0.078	0.107

Table 3.12: Case B - Stack height 65m, east location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.013	0.023	0.035
MMA	-	0.003	0.003
MEA	-	0.051	0.051
Directly emitted NDMA	0.053	0.0004	0.053
Total	0.058	0.078	0.107

Table 3.13: Case B - Stack height 65m, south location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.013	0.023	0.035
MMA	-	0.003	0.003
MEA	-	0.051	0.051
Directly emitted NDMA	0.033	0.0004	0.033
Total	0.036	0.078	0.107

Table 3.14: Case B - Stack height 75m, current location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.011	0.021	0.032
MMA	-	0.003	0.003
MEA	-	0.046	0.046
Directly emitted NDMA	0.026	0.0004	0.026
Total	0.028	0.071	0.096

Table 3.15: Case B - Stack height 85m, current location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.010	0.019	0.028
MMA	-	0.003	0.003
MEA	-	0.043	0.043
Directly emitted NDMA	0.020	0.0003	0.020
Total	0.023	0.066	0.086

Table 3.16: Case B - Stack height 85m, east location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.010	0.019	0.029
MMA	-	0.003	0.003
MEA	-	0.043	0.043
Directly emitted NDMA	0.022	0.0003	0.022
Total	0.024	0.066	0.086

Table 3.17: Case B - Stack height 85m, south location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.009	0.019	0.029
MMA	-	0.003	0.003
MEA	-	0.043	0.043
Directly emitted NDMA	0.020	0.0003	0.020
Total	0.023	0.066	0.086

Table 3.18: Case B - Stack height 95m, current location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.008	0.018	0.026
MMA	-	0.003	0.003
MEA	-	0.040	0.040
Directly emitted NDMA	0.016	0.0003	0.016
Total	0.019	0.061	0.078

Table 3.19: Case B - Stack height 105m, current location

Emitted amine	Maximum concentration (ng/m^3)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
DMA	0.007	0.017	0.024
MMA	-	0.002	0.002
MEA	-	0.037	0.037
Directly emitted NDMA	0.013	0.0003	0.013
Total	0.017	0.056	0.071

For Case A, there is a significant difference in the maximum calculated concentrations for different stack locations; for example, see Tables 3.2, 3.3 and 3.4, for a 65m stack. This method is overly sensitive to dispersion processes and hence to the relative locations of the stack and buildings. Where building effects are significant, as in this case, maximum concentrations occur close to the stack.

For Case B, using the Activity 1 chemistry scheme, there is negligible difference in the maximum calculated concentrations for different stack locations; for example, see Tables 3.11, 3.12 and 3.13, for a 65m stack. Given that maximum concentrations occur close to the stack, introducing the time-dependency of the chemical transformations reduces the sensitivity to stack location. The integration of the chemistry scheme with dispersion makes this approach much more realistic.

Figure 3.5: Contour plots for Case B, 65m stack height; current, east and south locations, respectively

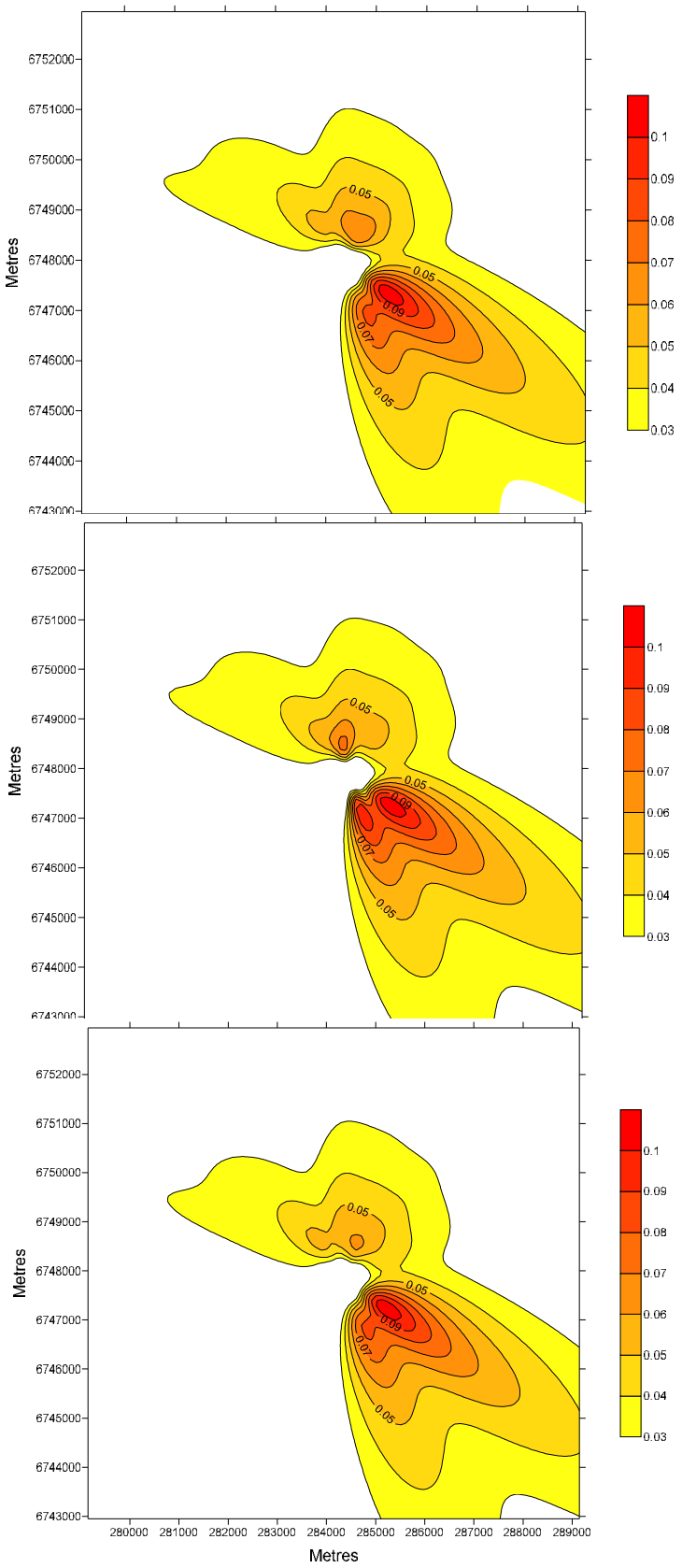


Figure 3.6: Contour plots for Case B, 85m stack height; current location, respectively

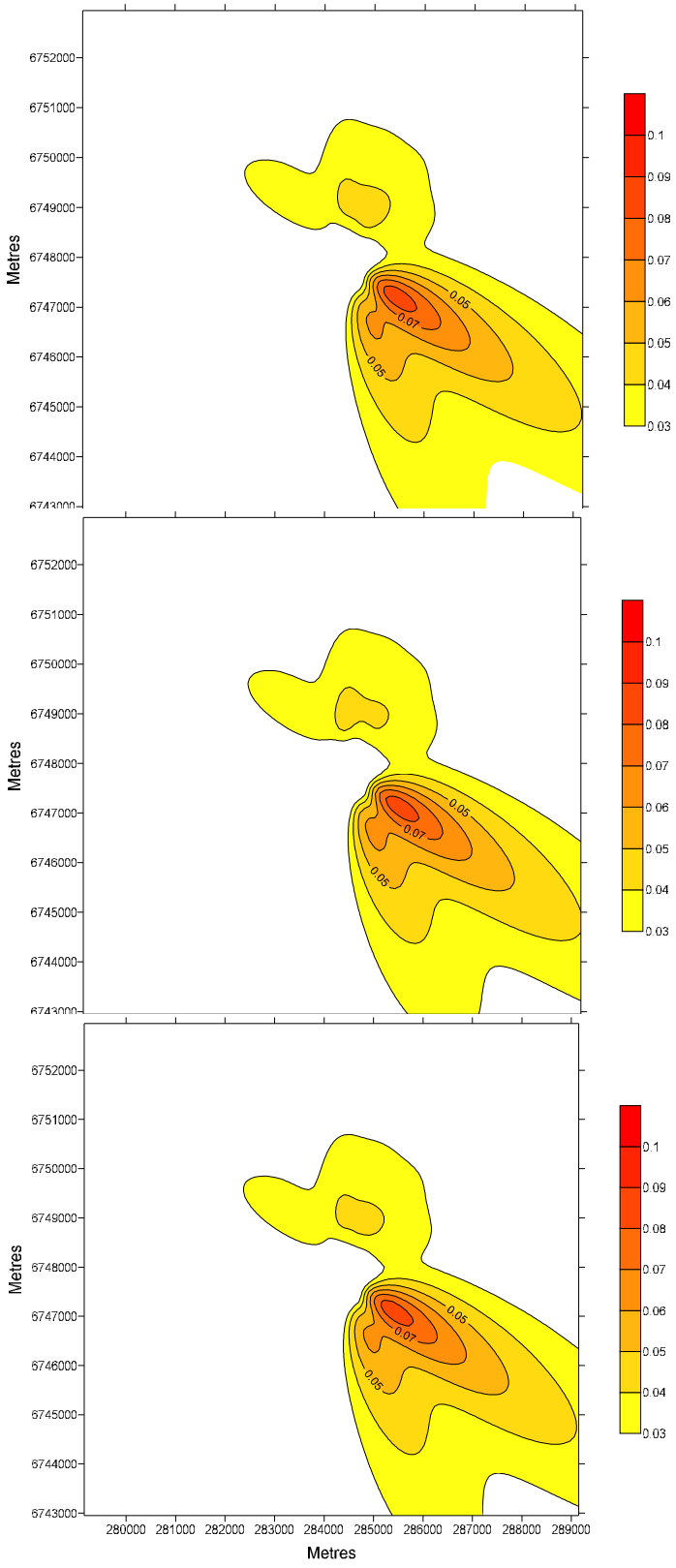
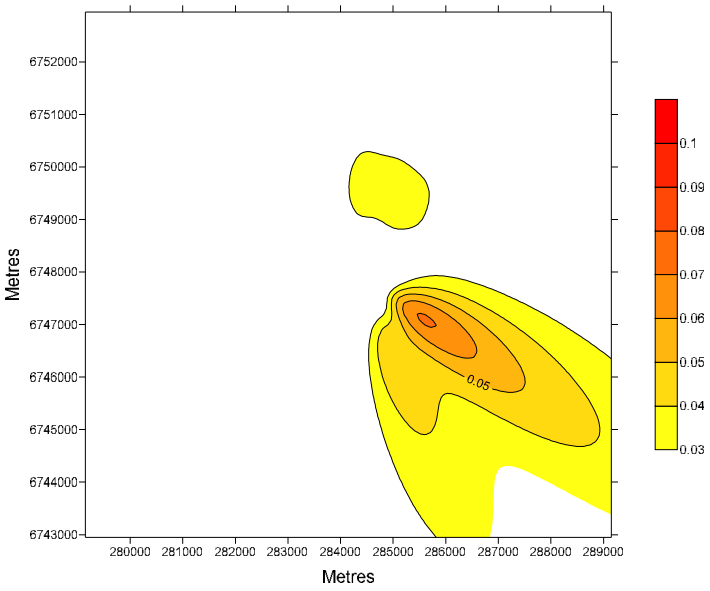


Figure 3.7: Contour plot for Case B, 105m stack height; current location



3.4. Results for Case C: No chemistry (dispersion only)

The maximum predicted concentrations of an arbitrary pollutant, with a unit emission rate, are shown in Table 3.20. Results are given relative to the concentration predicted for a 65m stack at the current location.

Table 3.20: Case C - Maximum predicted annual average concentrations (arbitrary units)

Stack height (m)	Location		
	Current	East	South
65	1.00	1.41	0.90
75	0.70	-	-
85	0.55	0.60	0.55
95	0.45	-	-
105	0.37	-	-

Figures 3.8 to 3.10 show contour plots of the annual average concentration calculated for each of the scenarios, shown on the same scale for comparison purposes.

Note that the results for a 65m stack at the east location are significantly higher than those for a 65m stack at the other two locations. This is due to the alignment of the prevailing wind with the buildings and source in this case, which leads to increased concentrations in the wake of the building.

Figure 3.8: Contour plots for Case C, 65m stack height; current, east and south locations, respectively

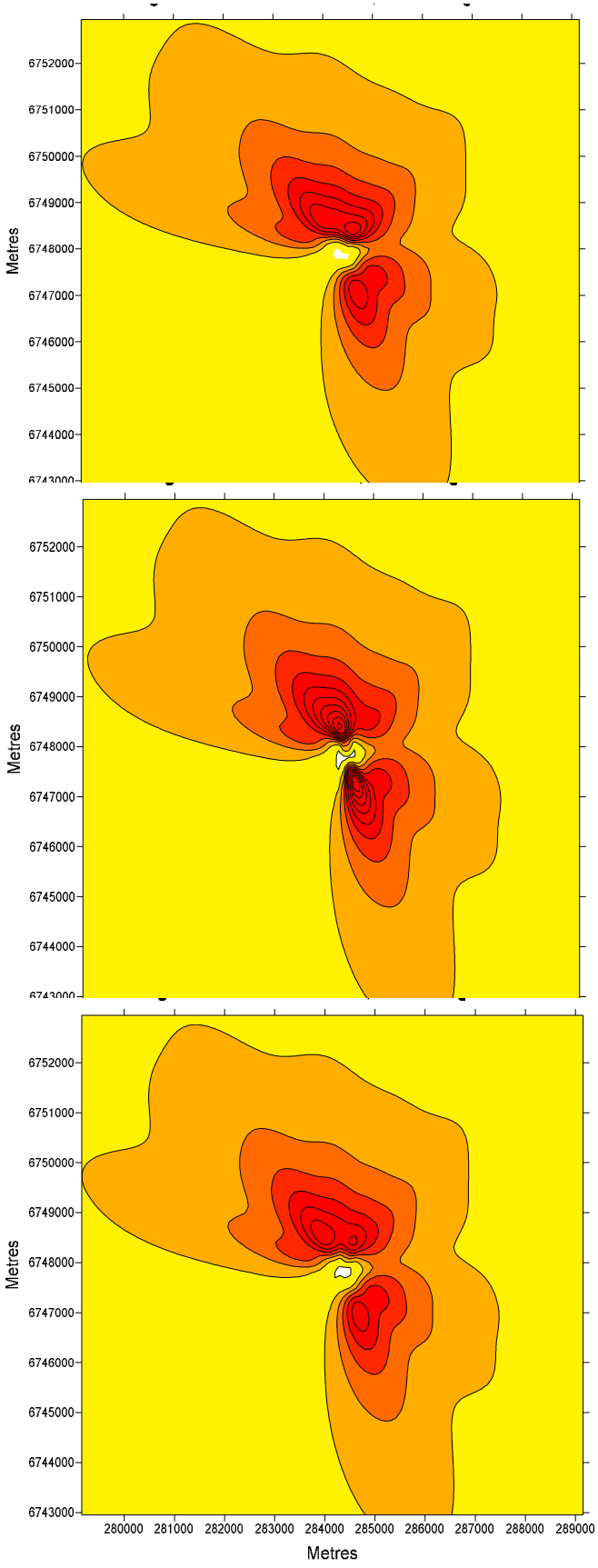


Figure 3.9: Contour plots for Case C, 85m stack height; current, east and south locations, respectively

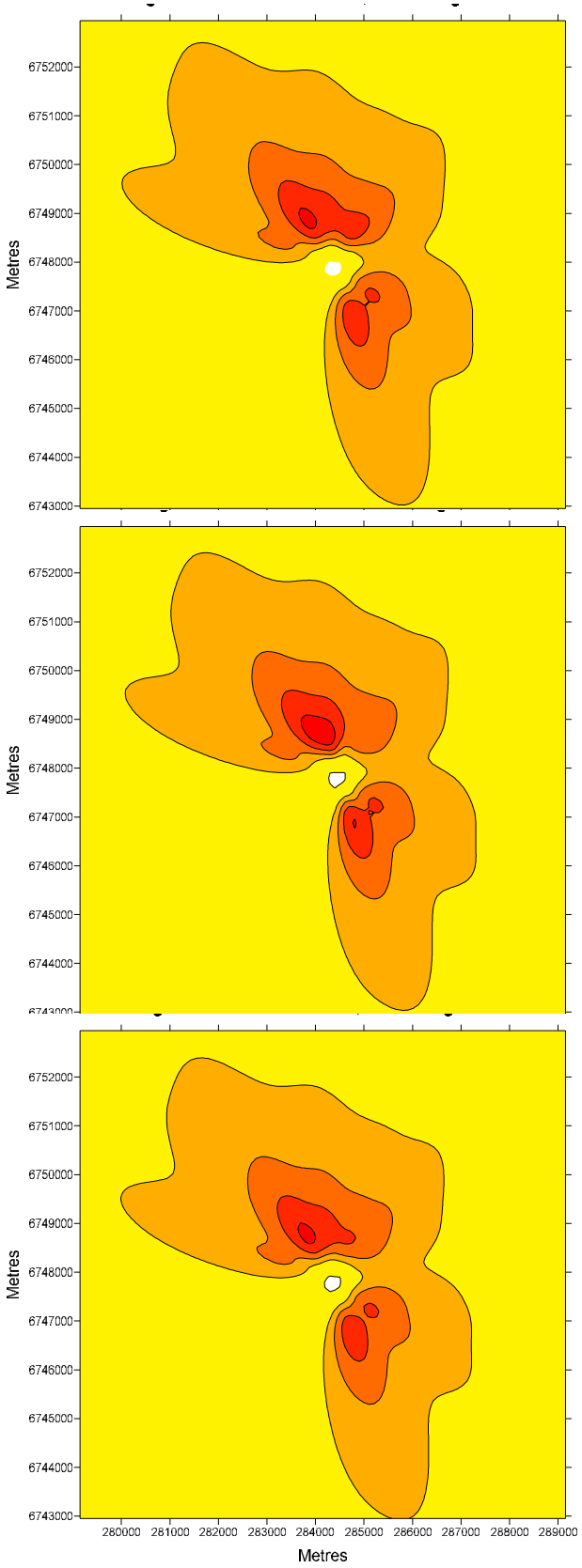
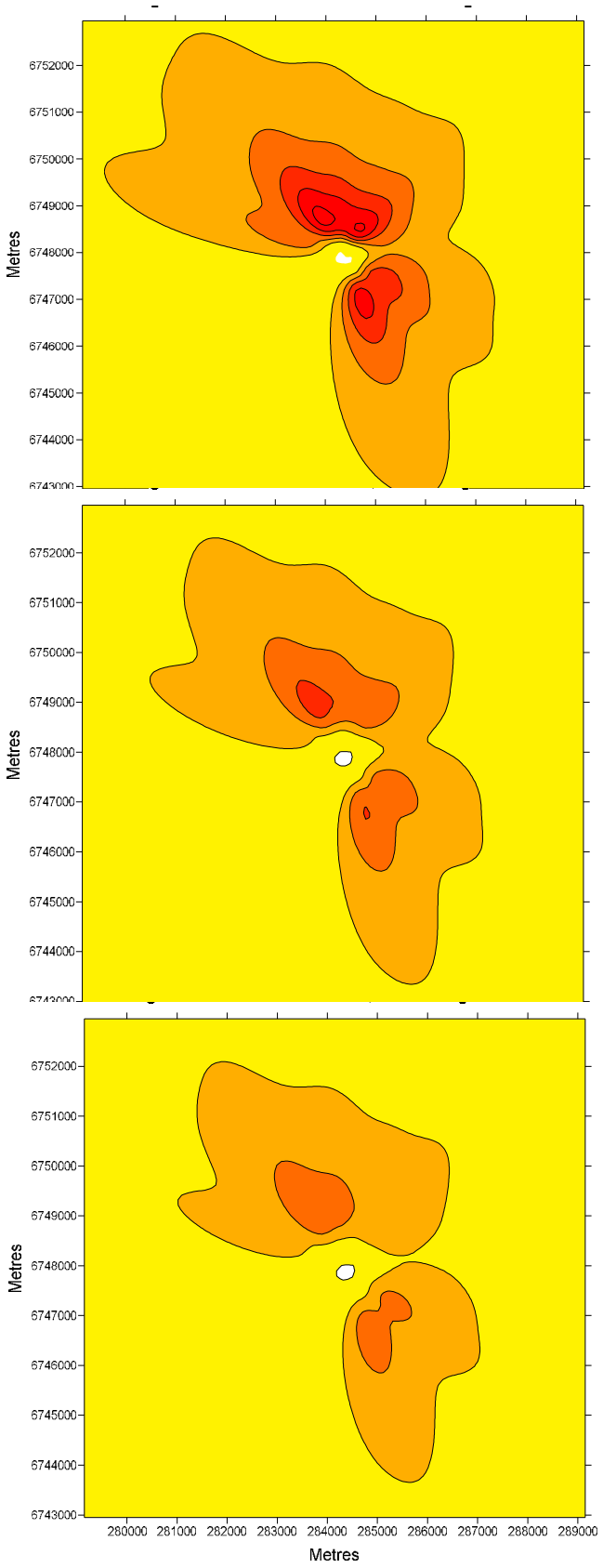


Figure 3.10: Contour plots for Case C, current location, 75, 95 and 105m stack height, respectively



4. Task 2: Modelling using detection limits

4.1. Overview

This modelling task considered emissions based on the lowest detection limits for each emitted species, which are presented in Table 4.1. Nitra-MEA is N-nitromonoethanolamine, a directly-emitted nitramine.

The three cases were modelled using both the ADMS chemical reaction scheme and the post-processing method, as described in Section 2.

Table 4.1: Detection limits and emission rates:

Emitted species	Detection limit (µg/m^3)	Equivalent emission rate (g/s)
MMA	0.80	5.36 x10^{-4}
MEA	8.00	5.36 x10^{-3}
NDMA	0.0008	5.36 x10^{-7}
nitra-MEA	0.60	4.02 x10^{-4}

For all runs under this Task, the same stack location as described in the Activity 1 report model runs was assumed, and stack heights of 65m and 85m were modelled. Ground level concentrations were calculated over a 10km by 10km output grid, at a resolution of 100m. All results represent annual average concentrations in units of ng/m^3.

Model runs were carried out with both the single-building (of height 60m) and multiple-building scenarios (described in the Activity 1 report), for comparison purposes.

4.2. Results for Case A: Chemistry applied using post-processing

Results for Case A were generated by post-processing, using the fixed atmospheric transformation percentages shown in Table 4.2.

Table 4.2: Assumed atmospheric transformation values

Emitted species	Transformation in the atmosphere (%) to:	
	Nitramine	Nitrosamine
Monomethylamine	0.4	0
Monoethanolamine	0.3	0
NDMA	0	100
Nitra-MEA	100	0

The maximum predicted concentrations of nitrosamines and nitramines for Case A are shown in Tables 4.3 to 4.6.

Table 4.3: Case A - multiple building, 65m stack

Emitted species	Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
MMA	-	0.0004	0.0004
MEA	-	0.0021	0.0021
NDMA	4.13×10^{-5}	-	4.13×10^{-5}
nitra-MEA	-	0.031	0.031
Total	4.13×10^{-5}	0.036	**0.036**

Table 4.4: Case A - multiple building, 85m stack

Emitted species	Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
MMA	-	0.0002	0.0002
MEA	-	0.00118	0.00118
NDMA	2.29×10^{-5}	-	2.29×10^{-5}
nitra-MEA	-	0.017	0.017
Total	2.29×10^{-5}	0.019	0.019

Table 4.5: Case A – single building, 65m stack

Emitted species	Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
MMA	-	0.0016	0.0016
MEA	-	0.0084	0.0084
NDMA	0.0002	-	0.0002
nitra-MEA	-	0.122	0.122
Total	0.0002	0.132	**0.132**

Table 4.6: Case A - single building, 85m stack

Emitted species	Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
MMA	-	0.0006	0.0006
MEA	-	0.0029	0.0029
NDMA	5.68×10^{-5}	-	5.68×10^{-5}
nitra-MEA	-	0.043	0.043
Total	5.68×10^{-5}	0.046	**0.046**

4.3. Results for Case B: Activity 1 chemistry scheme

The maximum predicted concentrations of nitrosamines and nitramines for Case B are shown in Tables 4.7 to 4.10.

These results were generated using the ADMS amine chemistry scheme developed under Activity 1. All results are in units of ng/m^3.

Note that the emission rate for NDMA was increased by a factor of 10 (to 0.008 µg/m^3), for these model runs ('with chemistry scheme' runs only). This is because the very low modelled concentrations resulting from the 0.0008 µg/m^3 value fall below the current lower threshold limit specified within the ADMS amine chemistry scheme. This limit can be reduced if appropriate.

Table 4.7: Case B - multiple building, 65m stack

Emitted species	Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
MMA	-	2.25×10^{-5}	2.25×10^{-5}
MEA	-	0.0002	0.0002
NDMA	0.0003	3.56×10^{-5}	0.0003
nitra-MEA	-	0.031	0.031
Total	0.0003	0.031	**0.031**

Table 4.8: Case B - multiple building, 85m stack

Emitted species	Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
MMA	-	1.89×10^{-5}	1.89×10^{-5}
MEA	-	0.0001	0.0001
NDMA	0.0001	2.41×10^{-6}	0.0001
nitra-MEA	-	0.017	0.017
Total	0.0001	0.017	**0.017**

Table 4.9: Case B - single building, 65m stack

Emitted species	Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
MMA	-	2.26×10^{-5}	2.26×10^{-5}
MEA	-	0.0002	0.0002
NDMA	0.0015	3.56×10^{-5}	0.0015
nitra-MEA	-	0.12	0.12
Total	0.0015	0.12	**0.12**

Table 4.10: Case B - single building, 85m stack

Emitted species	Nitrosamine	Nitramine	Sum (nitrosamine plus nitramine)
MMA	-	1.89×10^{-5}	1.89×10^{-5}
MEA	-	0.0001	0.0001
NDMA	0.0005	2.41×10^{-6}	0.0005
nitra-MEA	-	0.043	0.043
Total	0.0005	0.043	**0.043**

5. Task 3: Modelling using simplified chemistry scheme (as used by DNV)

5.1. Overview

In the CERC chemistry routines for the production of nitrosamines and nitramines from amines, rate reactions are used to model the generation of amino radicals by OH radical reaction and the subsequent reaction of the amino radicals with NO and NO_2 to form nitrosamines and nitramines and then, in the case of nitrosamines, subsequent photolysis.

Our understanding of the DNV scheme is that rate reactions are used to calculate amino radical concentrations, and then yields for the transformation of the amines to nitrosamines and nitramines (as given in Table 5.1 below, taken from Table 2.1 of the DNV document) are used to determine concentrations of nitrosamines and nitramines from the amino radicals.

This apparently simplified scheme appears to have a number of issues, as follows:

(i) The yields used are yields for the transformation from the amines to the nitrosamines and nitramines, not yields for the transformation from the amino radicals to the nitrosamines and nitramines (which are unknown). Implicit in this is that the transformation to the amine radical is treated twice in the same scheme, reducing the rate of production of nitrosamines and nitramines;

(ii) There is no variation in the generation of nitrosamines and nitramines with NO and NO_2 concentrations; and

(iii) The k_{OH} values used and presented in Table 5.1 (DNV Table 2.1) should represent OH attack of the amine functional group only and therefore be values of k_{1a} (not k_1) as described in the ADA report. It appears that k_{1a} is used for MEA but that k_1 is used for DMA and MMA, although this is not stated explicitly in the DNV report.

The next section describes the application of the DNV approach in ADMS using the amine chemistry scheme already implemented. This task involves modelling the first of the series of hydroxyl radical-initiated gaseous reactions, to calculate amino radical concentrations, followed by post-processing to calculate concentrations of nitrosamines and nitramines. The post-processing comprises the application of transformation yields similar to those provided for previous studies, as given in Table 5.1.

Table 5.1: Rate coefficient and percentage transformation values used in the DNV calculations

Amine	k_{OH} (cm^3 $molecule^{-1}$ s^{-1})	Transformation in the atmosphere (%) to:	
		Nitramine	Nitrosamine
DMA	$(6.54 \pm 0.66) \times 10^{-11}$	2.5	0.6
MMA	$(2.20 \pm 0.22) \times 10^{-11}$	0.4	0
MEA	2.48×10^{-12}	0.3	0

5.2. Replication of DNV approach using ADMS

In order to try to replicate the DNV approach using the ADMS amine chemistry scheme, all rate parameters were set to zero, except for k_1 and k_{1a}/k_1, which were set to appropriate values for each amine. Since it is not known whether the k_{OH} values used by DNV were used as k_1 or k_{1a} parameters, CERC carried out two sets of model runs (Cases 1 and 2) using each of these approaches, respectively.

Where a range of k_{OH} values is given in Table 5.1, it is not clear which value was used by DNV in the calculation. The values used by CERC for Cases 1 and 2 were the highest in this range; for example, for MMA, a value of 2.42×10^{-11} cm^3 $molecule^{-1}$ s^{-1} was used.

A third set of model runs (Case 3) was carried out, in which k_1 and k_{1a}/k_1 values were set to the reference values used by CERC in the Activity 1 modelling.

The resulting amino radical concentrations for all modelling cases were post-processed by applying the atmospheric transformation percentage values shown in Table 5.1.

5.2.1. Case 1: K_{OH} values assumed to be k_1 values

In this set of model runs, the K_{OH} values in Table 5.1 were assumed to be k_1 values. Each k_{OH} value was therefore assumed for the 'k_1' parameter in the ADMS amine chemistry scheme, and reference parameters used in CERC's Activity 1 modelling were assumed for the '$k1_a/k_1$' parameter. The values used are shown in Table 5.2.

Table 5.2: Rate coefficient values used for the ADMS parameters in Case 1

Emitted amine	**k_1 (cm^3/molecule/s)**	**k_{1a}/k_1**
DMA	7.20×10^{-11}	0.42
MMA	2.42×10^{-11}	0.75
MEA	2.48×10^{-12}	0.08

The maximum predicted concentrations of the amino radical, nitrosamines and nitramines for Case 1 are shown in Table 5.3.

Table 5.3: Case 1 results

Emitted amine	**Maximum concentration (ng/m^3)**			
	Amino radical	**Nitrosamines**	**Nitramines**	**Sum (nitrosamines and nitramines)**
DMA	0.11	0.00064	0.0026	0.0033
MMA	0.10	0	0.00039	0.00039
MEA	0.02	0	0.00006	0.00006
Total	-	0.0006	0.003	0.004

5.2.2. Case 2: K_{OH} values assumed to be k_{1a} values

In this set of model runs, the K_{OH} values in Table 5.1 were assumed to be k_{1a} values. Each k_{OH} value was therefore assumed for the 'k_1' parameter in the ADMS amine chemistry scheme, and the 'k_{1a}/k_1' values were set to 1. The values used are shown in Table 5.4.

Table 5.4: Rate coefficient values used for the ADMS parameters in Case 2

Emitted amine	**k_1 (cm^3/molecule/s)**	**k_{1a}/k_1**
DMA	7.20×10^{-11}	1
MMA	2.42×10^{-11}	1
MEA	2.48×10^{-12}	1

The maximum predicted concentrations of the amino radical, nitrosamines and nitramines for Case 2 are shown in Table 5.5.

Table 5.5: Case 2 results

Emitted amine	**Maximum concentration (ng/m^3)**			
	Amino radical	**Nitrosamines**	**Nitramines**	**Sum (nitrosamines and nitramines)**
DMA	0.25	0.0015	0.0063	0.0078
MMA	0.13	0	0.00051	0.00051
MEA	0.27	0	0.00080	0.00080
Total	-	**0.002**	**0.008**	**0.009**

5.2.3. Case 3: K_{OH} values used as in Activity 1 chemistry scheme

In this set of model runs, the K_{OH} values were those used in CERC's Activity 1 modelling, as shown in Table 5.6. Note that, because the k_{OH} value used by DNV for MEA appears to take into account the branching ratio, the k_{OH} value for MEA in Table 5.4 is around ten times greater than that in Table 5.1.

Table 5.6: Rate coefficient values used for the ADMS parameters in Case 3

Emitted amine	**k_1** (cm^3/molecule/s)	**k_{1a}/k_1**	**k_{1a}** (cm^3/molecule/s)
DMA	6.5×10^{-11}	0.42	2.73×10^{-11}
MMA	1.73×10^{-11}	0.75	1.30×10^{-11}
MEA	3.1×10^{-11}	0.08	2.48×10^{-12}

The maximum predicted concentrations of the amino radical, nitrosamines and nitramines for Case 3 are shown in Table 5.7.

Table 5.7: Case 3 results

Emitted amine	**Maximum concentration (ng/m^3)**			
	Amino radical	**Nitrosamines**	**Nitramines**	**Sum (nitrosamines and nitramines)**
DMA	0.10	0.00058	0.0024	0.0030
MMA	0.07	0	0.00028	0.00028
MEA	0.25	0	0.00076	0.00076
Total	-	**0.0006**	**0.003**	**0.004**

5.3. Previous results for comparison

Tables 5.8 and 5.9 show results from CERC's modelling for the first Variation Order and Activity 1, respectively. The former study used post-processing of output amine concentrations using percentage transformation yields and the latter used the complete ADMS amine chemical scheme.

Note that the results of the calculations using the DNV methodology are significantly lower than even the chemistry scheme results in Table 5.9.

Table 5.8: CERC Variation Order 1 results for comparison (post-processing)

Emitted amine	**Maximum concentration (ng/m^3)**			
	Amino radical	**Nitrosamines**	**Nitramines**	**Sum (nitrosamines and nitramines)**
DMA	-	0.13	0.26	0.39
MMA	-	-	1.0	1.0
MEA	-	-	2.7	2.7
Directly-emitted NDMA	-	0.16	-	0.16
Total (with NDMA)	-	0.29	4.0	4.3
Total (without NDMA)	-	0.13	4.0	4.1

Table 5.9: CERC Activity 1 results for comparison (chemistry scheme)

Emitted amine	**Maximum concentration (ng/m^3)**			
	Amino radical	**Nitrosamines**	**Nitramines**	**Sum (nitrosamines and nitramines)**
DMA	-	0.013	0.023	0.036
MMA	-	-	0.0035	0.0035
MEA	-	0	0.051	0.051
Directly-emitted NDMA	-	0.15	0.00041	0.15
Total (with NDMA)	-	0.15	0.08	0.16
Total (without NDMA)	-	0.013	0.078	0.089

6. Task 4: Calculation to estimate concentrations in water bodies

6.1. Overview

This task involved using the ADMS amine chemistry scheme to predict concentrations in air and deposition of nitrosamines and nitramines, at a selection of locations representing freshwater bodies around Mongstad. As the ADMS deposition module has not been developed alongside the amine chemistry module, it is not yet possible to run amine chemistry and deposition in a single run. The deposition fluxes of the nitrosamines and nitramines were therefore calculated by post-processing the air concentrations, based on ratios of concentrations to deposition fluxes, determined in a second model run. This second run involved an identical model set-up, but with a nominal pollutant emitted, the amine chemistry module switched off and the deposition module switched on. The deposition parameters were estimated, based on the results of sensitivity tests carried out as part of the Case Study for Call Off 1 (H&ETQPAmine2).

The deposition velocity is an important parameter for dry deposition calculations, but this parameter has not been measured for nitrosamines and nitramines. In ADMS, if the deposition velocity value is unknown, the user can specify the nature of the gas: reactive, unreactive or inert. The model then calculates the surface resistance and hence the deposition velocity. For the dry deposition model run, the pollutant was run as a 'reactive gas'.

Wet deposition parameters for nitrosamines and nitramines have not been measured. The washout coefficient, Λ, is an important parameter for wet deposition calculations, and was modelled as a function of the precipitation rate: $\Lambda=AP^B$, where A and B are user-specified constants and P is the precipitation rate in mm/hr. The values of A and B used were 0.0001 and 0.64, respectively; these are ADMS 4 default values. The precipitation rates were derived from the meteorological data.

Following the calculation of the deposition fluxes in air, a rough approximation of the resulting concentration of nitrosamines and nitramines in each water body was made, by post-processing the deposition results described above. This calculation assumes that:

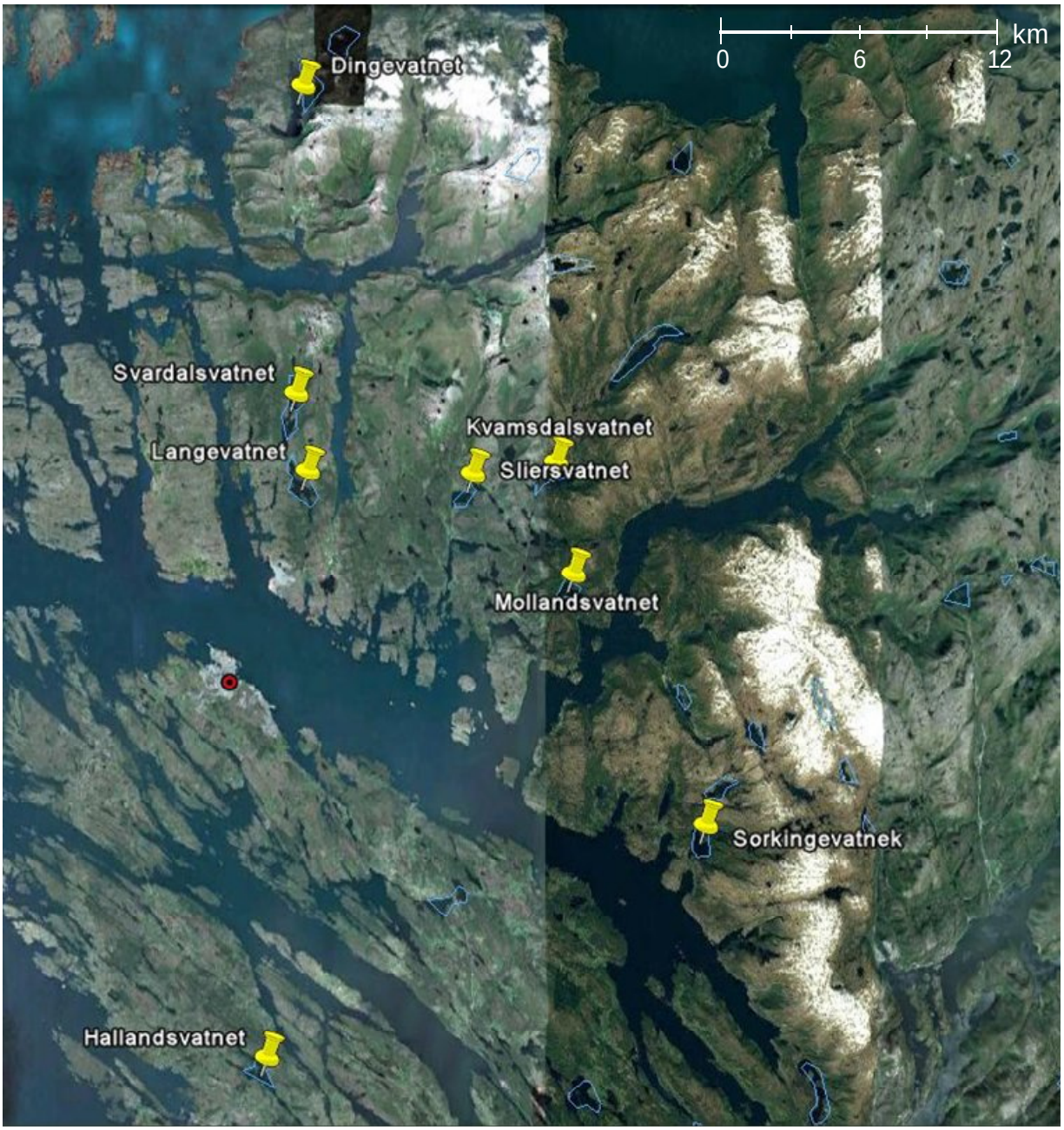
- The nitrosamines and nitramines are completely soluble in water (i.e. all of the mass in the gaseous phase is transferred to the aqueous phase); and
- The nitrosamines and nitramines in the aqueous phase are well-mixed to a depth of 1m below the surface of the water.

Table 6.1 gives the coordinates used for the model receptors, which broadly represent the centre of each water body, and Figure 6.1 shows the location of each of the water bodies.

Table 6.1: Locations of the modelled receptors representing the water bodies

Water body	Coordinates (m)		
	x	y	z
Dingevatnet	288600	6772500	0
Langevatnet	287900	6755900	0
Svardalsvatnet	287600	6759300	0
Sliersvatnet	295000	6755400	0
Kvamsdalsvatnet	298600	6755700	0
Mollandsvatnet	299100	6755900	0
Hallandsvatnet	284800	6730800	0
Sorkingevatnet	304200	6739800	0

Figure 6.1: Locations of the selected water bodies. The red circle represents the stack



6.2. Results of water body calculations

Table 6.2 shows predicted concentrations of the nitrosamines and nitramines in air at 'ground level', i.e. at the water surface level, at each of the receptors.

Tables 6.3 to 6.4 show dry and wet deposition fluxes, respectively, at each receptor. Table 6.5 shows the total deposition, i.e. the sum of the dry and wet deposition fluxes.

Tables 6.6 and 6.7 show approximate concentrations, in ng/dm^3/year (ng/litre/year), within the surface layer of each water body, assuming that the nitrosamines and nitramines are well-mixed to a depth of 1m and 4m, respectively. These mixing depths were chosen to represent possible depths of the epilimnion (the upper layer of a stratified lake) that might be formed in lakes of this size and latitude in summer months.[5] Depths of 1m and 4m were used, giving conservative and best estimate values, respectively, for the concentrations in water. Concentrations can be calculated for other assumed mixing layer depths, by means of a simple linear calculation; note that the concentrations in water for the 1m depth layer are four times those for the 4m depth.

[5] von Einem, J and Granéli, W. Effects of fetch and dissolved organic carbon on epilimnion depth and light climate in small forest lakes in southern Sweden**.** *Limnol. Oceanogr.*, **55**, 2, 920–930. 2010

Table 6.2: Predicted concentrations in air at each receptor point

Water body	Modelled concentration (ng/m^3)						
	DMA		MMA	MEA	NDMA		Sum (nitrosamines and nitramines)
	Nitrosamines	Nitramines	Nitramines	Nitramines	Nitrosamines	Nitramines	
Dingevatnet	0.000017	0.0008	0.00017	0.0025	0.00018	0.000003	0.004
Langevatnet	0.00019	0.0022	0.00044	0.0062	0.00092	0.000027	0.010
Svardalsvatnet	0.00011	0.0017	0.00036	0.0050	0.00061	0.000017	0.008
Sliersvatnet	0.000081	0.0015	0.00032	0.0044	0.0004	0.000013	0.007
Kvamsdalsvatnet	0.000043	0.0011	0.00025	0.0034	0.00027	0.000006	0.005
Mollandsvatnet	0.000040	0.0011	0.00024	0.0033	0.00026	0.000006	0.005
Hallandsvatnet	0.00010	0.0017	0.00031	0.0045	0.00068	0.000014	0.007
Sorkingevatnet	0.000069	0.0024	0.00055	0.0074	0.00016	0.000006	0.011

Table 6.3: Predicted dry deposition rates at each receptor point

Water body	Dry deposition rate (ng/m²/s)							
	DMA		MMA	MEA	NDMA		Totals	
	Nitrosamines	Nitramines	Nitramines	Nitramines	Nitrosamines	Nitramines	Nitrosamines	Nitramines
Dingevatnet	3.87×10^{-7}	1.85×10^{-5}	3.95×10^{-6}	5.63×10^{-5}	4.04×10^{-6}	6.12×10^{-8}	4.43×10^{-6}	7.88×10^{-5}
Langevatnet	4.64×10^{-6}	5.29×10^{-5}	1.06×10^{-5}	1.49×10^{-4}	2.20×10^{-5}	6.53×10^{-7}	2.66×10^{-5}	2.14×10^{-4}
Svardalsvatnet	2.56×10^{-6}	4.12×10^{-5}	8.56×10^{-6}	1.19×10^{-4}	1.44×10^{-5}	3.96×10^{-7}	1.69×10^{-5}	1.69×10^{-4}
Sliersvatnet	1.87×10^{-6}	3.44×10^{-5}	7.44×10^{-6}	1.02×10^{-4}	9.69×10^{-6}	2.94×10^{-7}	1.16×10^{-5}	1.44×10^{-4}
Kvamsdalsvatnet	9.61×10^{-7}	2.53×10^{-5}	5.63×10^{-6}	7.68×10^{-5}	6.17×10^{-6}	1.46×10^{-7}	7.13×10^{-6}	1.08×10^{-4}
Mollandsvatnet	8.96×10^{-7}	2.44×10^{-5}	5.44×10^{-6}	7.42×10^{-5}	5.88×10^{-6}	1.35×10^{-7}	6.78×10^{-6}	1.04×10^{-4}
Hallandsvatnet	2.09×10^{-6}	3.38×10^{-5}	6.24×10^{-6}	9.27×10^{-5}	1.39×10^{-5}	2.81×10^{-7}	1.60×10^{-5}	1.33×10^{-4}
Sorkingevatnet	1.47×10^{-6}	5.05×10^{-5}	1.17×10^{-5}	1.58×10^{-4}	3.30×10^{-6}	1.37×10^{-7}	4.77×10^{-6}	2.20×10^{-4}

Table 6.4: Predicted wet deposition rates at each receptor point

Water body	Wet deposition rate (ng/m²/s)							
	DMA		MMA	MEA	NDMA		Totals	
	Nitrosamines	Nitramines	Nitramines	Nitramines	Nitrosamines	Nitramines	Nitrosamines	Nitramines
Dingevatnet	9.34×10^{-7}	4.47×10^{-5}	9.54×10^{-6}	1.36×10^{-4}	9.77×10^{-6}	1.48×10^{-7}	1.07×10^{-5}	1.91×10^{-4}
Langevatnet	8.42×10^{-6}	9.60×10^{-5}	1.93×10^{-5}	2.71×10^{-4}	3.99×10^{-5}	1.18×10^{-6}	4.83×10^{-5}	3.87×10^{-4}
Svardalsvatnet	5.17×10^{-6}	8.31×10^{-5}	1.73×10^{-5}	2.41×10^{-4}	2.90×10^{-5}	7.99×10^{-7}	3.42×10^{-5}	3.42×10^{-4}
Sliersvatnet	4.46×10^{-6}	8.19×10^{-5}	1.77×10^{-5}	2.43×10^{-4}	2.31×10^{-5}	7.00×10^{-7}	2.75×10^{-5}	3.43×10^{-4}
Kvamsdalsvatnet	2.54×10^{-6}	6.69×10^{-5}	1.49×10^{-5}	2.03×10^{-4}	1.63×10^{-5}	3.86×10^{-7}	1.89×10^{-5}	2.85×10^{-4}
Mollandsvatnet	2.39×10^{-6}	6.52×10^{-5}	1.45×10^{-5}	1.98×10^{-4}	1.57×10^{-5}	3.60×10^{-7}	1.81×10^{-5}	2.78×10^{-4}
Hallandsvatnet	2.09×10^{-6}	3.38×10^{-5}	6.25×10^{-6}	9.29×10^{-5}	1.39×10^{-5}	2.82×10^{-7}	1.60×10^{-5}	1.33×10^{-4}
Sorkingevatnet	2.83×10^{-6}	9.69×10^{-5}	2.25×10^{-5}	3.03×10^{-4}	6.33×10^{-6}	2.63×10^{-7}	9.16×10^{-6}	4.22×10^{-4}

Table 6.5: Predicted (dry plus wet) deposition rates at each receptor point

Water body	Total deposition rate (ng/m²/s)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
Dingevatnet	1.51×10^{-5}	2.69×10^{-4}	2.85×10^{-4}
Langevatnet	7.49×10^{-5}	6.01×10^{-4}	6.76×10^{-4}
Svardalsvatnet	5.11×10^{-5}	5.11×10^{-4}	5.63×10^{-4}
Sliersvatnet	3.91×10^{-5}	4.87×10^{-4}	5.26×10^{-4}
Kvamsdalsvatnet	2.60×10^{-5}	3.93×10^{-4}	4.19×10^{-4}
Mollandsvatnet	2.49×10^{-5}	3.83×10^{-4}	4.07×10^{-4}
Hallandsvatnet	3.20×10^{-5}	2.66×10^{-4}	2.98×10^{-4}
Sorkingevatnet	1.39×10^{-5}	6.43×10^{-4}	6.57×10^{-4}

Table 6.6: Approximate concentrations in water assuming a mixing depth of 1m

Water body	Concentrations in water (ng/dm³/year)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
Dingevatnet	0.5	8.5	9.0
Langevatnet	2.4	18.9	21.3
Svardalsvatnet	1.6	16.1	17.7
Sliersvatnet	1.2	15.4	16.6
Kvamsdalsvatnet	0.8	12.4	13.2
Mollandsvatnet	0.8	12.1	12.9
Hallandsvatnet	1.0	8.4	9.4
Sorkingevatnet	0.4	20.3	20.7

Table 6.7: Approximate concentrations in water assuming a mixing depth of 4m

Water body	Concentrations in water (ng/dm³/year)		
	Nitrosamines	Nitramines	Sum (nitrosamines and nitramines)
Dingevatnet	0.1	2.1	2.2
Langevatnet	0.6	4.7	5.3
Svardalsvatnet	0.4	4.0	4.4
Sliersvatnet	0.3	3.8	4.1
Kvamsdalsvatnet	0.2	3.1	3.3
Mollandsvatnet	0.2	3.0	3.2
Hallandsvatnet	0.3	2.1	2.4
Sorkingevatnet	0.1	5.1	5.2