
Update and Improvement of Dispersion Calculations for Emissions to Air from TCM's Amine Plant

Part I-Worst case Nitrosamines and Nitramines

Dag Tønnesen



Scientific report

Preface

Two different capture technologies will be tested at the CO₂ Technology Centre Mongstad (TCM) - the chilled ammonia based technology developed by Alstom and the amine based technology developed by Aker Clean Carbon (ACC). The facility will capture CO₂ from two separate flue gas sources: the residue fluid catalytic cracker (RFCC) and the combined heat and power plant (CHP). The TCM facility is designed to capture 100.000 tonnes CO₂ per year.

NILU (The Norwegian Institute for Air Research) carried out dispersion calculation studies for emissions to air from TCM in 2008 and 2010, resulting in two reports (NILU-OR 12/2008 and NILU-OR 41/2010). Based on the availability of new knowledge and updated data for emissions to air from the amine plant, the dispersion calculations have been updated and improved for the amine plant. For the Chilled ammonia technology plant report NILU-OR 41/2010 still applies.

The current update of emission dispersion calculations is divided in two parts. The first part, which is documented in the present report, establishes current knowledge on a worst case study for emissions of nitrosamines and nitramines for amine capture technology. In a second report, a current knowledge likely case study will be described in detail.

Contents

	Page
Preface	1
Summary	5
Sammendrag	7
1 Introduction	9
2 Study definitions	11
2.1 Emission estimates	12
2.2 Topography of the area	12
2.3 Chemical reactions, photolysis and deposition mechanisms	13
2.4 Guideline values for health and environmental impact.....	13
3 Unitary inert emission dispersion	13
4 Nitrosamines and nitramines in air	18
4.1 Worst case for nitrosamines	18
4.2 Worst case assumptions and results for nitramines.....	22
4.3 Total worst case air concentrations of nitramines and nitrosamines.....	24
4.4 Likely case.....	26
5 Nitrosamines and nitramines in fresh water	26
5.1 Worst case estimate	26
5.2 Likely case estimate	28
6 Back calculation of total amount of emission for reaching guideline value	28
7 Discussion	29
7.1 Processes not included in calculations	29
7.1.1 Influence of NO _x concentration	29
7.1.2 Influence of Cl atoms	29
7.1.3 Other reaction products of amines.....	29
7.2 Main uncertainties	29
7.3 Usefulness of CONCX vs TAPM	30
7.4 Comparison of assumptions between 2008, 2010 and 2011	31
8 Conclusions and recommendations	32
9 Abbreviations	33
10 References	33
Appendix A Setup for TAPM model runs	35
Appendix B Data for wind and precipitation in 2007 versus average	41
Appendix C Detailed emission estimate from ACC	45

Summary

NILU has carried out updated dispersion calculations for emissions from amine based CO₂ capture technology at the CO₂ Technology Centre Mongstad (TCM). The update include the latest available knowledge on air chemistry and degradation in water for nitrosamines and nitramines. The sum of concentrations of nitramines and nitrosamines in air and water is below newly recommended guideline values in the worst case study. A preliminary analysis of the current knowledge (likely case) indicates a factor 3 lower sum of concentrations for air and a factor 10 to 20 lower values for water than in the worst case study.

This report includes a detailed modelling of a worst case study of the dispersion of nitrosamines and nitramines and a discussion on a current knowledge likely case. A detailed description of the current knowledge likely case study comes in a separate report. The purpose of the so-called “worst case” study is to include worst estimates on the different aspects of formation and transformation of nitrosamines and nitramines for the same set of emission scenarios. In case the guideline values for air and water quality are not exceeded in the worst case calculations, we expect that these emissions will not pose an environmental risk since the worst case assumptions include large margins. By contrast, the purpose of the so-called current knowledge “likely case” study is to include the current best knowledge estimates regarding the same processes in order to calculate the most likely impact regarding air and water quality. This case will not involve the uncertainty margins from the worst case. By comparing “worst” and “likely” case it is possible to identify the effect of the margins introduced in the worst case. This study includes a first discussion regarding a current knowledge likely case.

This report uses new relevant literature made available after summer 2010. The most important new literature results concern worst case assumptions in the atmospheric chemistry, biodegradation of nitrosamines, atmospheric chemistry of 2-aminoethanol and health effects of amines and their derivatives associated with CO₂ capture, including recommended guideline values from the Norwegian Institute of Public Health (NIPH). In addition to improved knowledge on the atmospheric chemistry and the effects of amines on health, the emissions from the absorber are also updated in this report.

The calculations have been carried out for 4 combinations of flue gas source and solvent used in the absorber. The two flue gas sources are the residue fluid catalytic cracker (RFCC) and the combined heat and power plant (CHP). The two solvents are “MEA” and “Solvent 2”. The 4 combinations of absorbent and flue gas are:

- MEA absorbent with CHP flue gas
- Solvent 2 absorbent with CHP flue gas
- MEA absorbent with RFCC flue gas
- Solvent 2 absorbent with RFCC flue gas

Results from worst case calculations of impact of the sum of nitrosamines and nitramines for air and water are given in the table below along with the

recommended guideline values for air and water. The table shows the maximum impact from the 4 emission scenarios.

	NIPH guideline value ¹	MEA CHP	Solvent 2 CHP	MEA RFCC	Solvent 2 RFCC
Air (ng/m ³)	0.3	0.009	0.013	0.008	0.010
Water (ng/l)	4	0.52	2.1	0.63	1.59

¹ Guideline value is covers the combined concentrations of nitrosamines and nitramines

For air concentrations the contribution to the sum is about equal for nitrosamines and nitramines, whereas for water, the sum is dominated by the contribution from the nitramines. In the treatment of nitrosamines, separation has been made between chemical reactions during day and during night. This separation has not been made for nitramines due to lack of knowledge. Photolysis was the most important degradation mechanism for nitrosamines in water. Biodegradation was less important. No degradation mechanisms for nitramines in water have yet been documented. Furthermore, this report discusses briefly several other likely but not yet quantifiable physical-chemical phenomena that are not included yet, e.g. the reactions of amines with chloride atoms in the atmosphere.

An assessment of the impact for the current knowledge likely case based on the differences in emission, air chemistry and wet deposition show that air concentrations may be more than 3 times lower than in the worst case. The likely case maximum water concentrations may be 10 times lower than the worst case for solvent 2 and 20 times lower for MEA.

These results are TCM specific and cannot be scaled or used for other locations.

Sammendrag

NILU har utført oppdaterte spredningsberegninger av utslipp fra aminbasert teknologi for CO₂-fangst for CO₂ Technology Centre Mongstad (TCM). Denne oppdateringen er basert på den nyeste tilgjengelige kunnskapen om kjemisk omdannelse i luft og nedbrytningsprosesser i vann for nitrosaminer og nitraminer. Samlet belastning fra utslippet av nitrosaminer og nitraminer er under anbefalt retningslinje fra Folkehelseinstituttet for summen av disse to komponentene for et "worst case" studie. Et "likely case" studie basert på nåværende kunnskap tyder på at belastning i luft blir 3 ganger lavere enn "worst case" og at belastningen i vann blir fra 10 til 20 ganger lavere enn "worst case".

Denne modellen inneholder en detaljert beregning av et "worst case" studie og en diskusjon av en "likely case" for nåværende kunnskap i forhold til "worst case". Hensikten med "worst case" studien er å beregne effekt av forholdene for maksimal dannelse og minimal omdannelse av nitrosaminer og nitraminer under gitte utslippsforhold. Dersom beregningene da viser at retningslinjene for luft- og vannkvalitet overholdes, vil utslippene ikke medføre risiko for helse og miljø, fordi forutsetningen i "worst case" scenarioet inneholder store marginer i antagelsene. Hensikten med et "likely case" scenario er å anvende de nåværende beste anslag for de samme prosessene for å beregne den sannsynlige belastningen i luft og vann. Dette scenarioet vil ikke ha usikkerhetsmarginer på samme måte som "worst case". En sammenligning av "worst case" og "likely case" vil gi et anslag for størrelsen av marginene i "worst case".

Denne rapporten anvender bakgrunnsmateriale fra ny litteratur framkommet siden sommeren 2010. Det viktigste materialet gjelder atmosfærekjemi i "worst case" situasjoner, biodegradering av nitrosaminer, atmosfærekjemi for 2-aminoethanol samt helseeffekter fra aminer og nedbrytningsprodukter, inkludert anbefalte retningslinjer fra Folkehelseinstituttet (FHI). I tillegg til forbedret kunnskap om atmosfærekjemi og helseeffekter av aminer er utslippsdata fra absorberer også oppdatert.

Beregningene er utført for 4 kombinasjoner av avgasskilder og anvendt absorbent. De to avgasskildene er RFCC og CHP. De to absorbentene er "MEA" og "Solvent 2". De 4 kombinasjonene er:

- MEA absorbent og CHP avgass
- Solvent 2 absorbent og CHP avgass
- MEA absorbent og RFCC avgass
- Solvent 2 absorbent og RFCC avgass

Resultatene fra "worst case" beregninger av summen av nitrosaminer og nitraminer i luft og vann er vist i tabellen nedenfor sammen med anbefalte retningslinjer for konsentrasjoner i luft og drikkevann. Tabellen viser belastningen fra de 4 ulike utslippsituasjonene.

	FHIs anbefalte retningslinje	MEA CHP	Solvent 2 CHP	MEA RFCC	Solvent 2 RFCC
Luft (ng/m ³)	0.3	0.009	0.013	0.008	0.010
Vann(ng/l)	4	0.52	2.1	0.63	1.59

Bidraget til konsentrasjoner i luft er av samme størrelsesorden fra nitrosaminer og nitraminer, mens bidraget til konsentrasjoner i vann i stor grad er bestemt av bidraget fra nitraminer. For beregning av nitrosaminer er det tatt hensyn til forskjell i reaksjoner om dagen og om natten. For nitraminer har denne oppdelingen ikke blitt utført idet det mangler kunnskap om reaksjoner i mørket. Fotolyse er den viktigste nedbrytningsprosess for nitrosaminer i vann. Biodegradering har vist seg til å være mindre viktig. Det er ikke dokumentert noen nedbrytningsprosesser for nitraminer i vann på det nåværende tidspunkt. I tillegg diskuterer rapporten kort fysisk-kjemiske fenomener som er sannsynlig men ikke kan kvantifiseres ennå. Et eksempel er reaksjoner av aminer med klorid-atomer i atmosfæren.

En vurdering belastning for "likely case" studien i forhold til "worst case" studien, basert på nåværende kunnskap og forskjellene for luftkjemi, utslippsmengde og våtavsetning viser at konsentrasjonene i luft blir mer enn 3 ganger lavere. For konsentrasjoner i vann blir "likely case" 10 ganger lavere enn "worst case" for solvent 2 og 20 ganger lavere for MEA.

Disse resultatene er bare gyldige for TCM, og kan ikke skaleres ellers brukes for andre geografiske steder.

Update and Improvement of Dispersion Calculations for Emissions to Air from TCM's Amine Plant

Part I-Worst case Nitrosamines and Nitramines

1 Introduction

Two different capture technologies will be tested at the CO₂ Technology Centre Mongstad (TCM) - the chilled ammonia based technology developed by Alstom and the amine based technology developed by Aker Clean Carbon (ACC). The facility will capture CO₂ from two separate flue gas sources: the residue fluid catalytic cracker (RFCC) and the combined heat and power plant (CHP). The TCM facility is designed to capture 100.000 tonnes CO₂ per year.

Norwegian Institute for Air Research (NILU) performed in 2008 and 2010 dispersion calculation studies for emissions to air from TCM resulting in two reports (NILU-OR 12/2008 and NILU-OR 41/2010). In the work performed in 2010 it was demonstrated that the environmental impact from chilled ammonia technology was limited, and that the mechanisms leading to impact were well known. The conclusions for the amine technology pointed out the need for more knowledge regarding air chemistry and degradation patterns of nitrosamines and nitramines in water. For a few sets of worst case assumptions, conservative air and water guideline values in the environment were exceeded.

Based on the availability of new knowledge and updated data for emissions to air by ACC, the dispersion calculations have been updated and improved for the amine plant.

This report focus on new relevant literature available since summer 2010, and the impact the information has on the modelling of environmental impact from the amine absorber emissions. The most important new litterature are:

- Claus Jørgen Nielsen, Dirk Hoffmann, Hartmut Herrmann, Evaluation of worst case assumptions – atmospheric chemistry, Report for TCM DA, March 2011
- Odd Gunnar Brakstad, Andy Booth, Kolbjørn Zahlse, Biodegradation of Nitrosamines, SINTEF report A18258 for TCM, Feb 2011
- Noelle E. Selin, Environmental Guidelines and Regulations for Nitrosamines: A Policy Summary, Report by MIT for TCM DA, March 2011
- Claus Jørgen Nielsen et al, Atmospheric Degradation of Amines, ADA 2010 report, Feb 2011
- Claus Jørgen Nielsen et al, Atmospheric chemistry of 2-aminoethanol (MEA), Paper presented at GHGT-10 Amsterdam, Sept 2010
- Folkehelseinstituttet (NIPH), Health effects of amines and derivatives associated with CO₂ capture: Nitrosamines and nitramines, March 2011

- Matthias Karl, Richard F. Wright, Tore F. Berglen, Bruce Denby, Worst case scenario study to assess the environmental impact of amine emissions from a CO₂ capture plant, International Journal of Greenhouse Gas Control, In Press, Corrected Proof, Available online 26 November 2010
- latest version of “Environmental budget” from ACC, April 2011
- Atmospheric Amines. Part I. A review. (Ge et. Al,2011)

The emission scenarios in this report cover the use of two different solvents in the absorber (MEA and Solvent 2) and the use of two different flue gas sources to be treated (CHP and RFCC). TCM has provided updated emission data and information for the definition of two different studies, worst case and likely case.

The purpose of a so-called worst case study is to include worst estimates on the different aspects of formation and transformation of nitrosamines and nitramines. In case the guideline values for air and water quality are not exceeded the emissions do very likely not pose a risk since the worst case assumptions include large margins. In case the health and environmental guideline values are exceeded no conclusion can be made other than there is a need for more knowledge.

The purpose of a so-called likely case study is to include the current best estimates regarding the same processes in order to calculate the most likely impact regarding air and water quality. This case will not have the margins from the worst case. By comparing worst and likely case one can get an idea the effect of the margins introduced in the worst case. This study will include the first attempt to do such a likely case since the new knowledge seems to have obtained a good enough quality in the spring of 2011. NILU-OR 12/2008 and NILU-OR 41/2010 did not include such a likely case, only worst cases.

In NILU-OR 12/2008, the only amine included in the emission inventory was MEA. No transformation was considered. Yearly average concentrations and wet depositions were calculated based on on-site measurements of wind frequencies and precipitation.

In NILU-OR 41/2010, an improved dispersion model (TAPM) was applied, giving a much better description of the impact from the topography on the wind field and precipitation field although the model overestimates the precipitation amount (M. Karl et al, 2011). Due to updated emission inventories with the introduction of several new amines, and also direct emissions of nitrosamines, a very conservative calculation of nitrosamine total impact was made. The calculations contained no degradation of nitrosamines, and an instant formation assumption. Nitramines were not included yet since very little was known and they seemed to be less carcinogenic than nitrosamines.

The 2011 modelling updates the 2010 modelling results by including primary limiting factors towards formation as well as degradation rates of nitrosamines and nitramines. Some of the background material for these processes is summarized by Nielsen, Hoffmann and Hermann (2011). Time dependant calculations with ambient air characteristics from Mongstad based on existing monitoring results for wind conditions and concentrations of NO_x have been run separately, and the results is linked to the dispersion model results by the

advection air speed from the emission to the areas of maximum ground level impact and maximum yearly wet deposition.

2 Study definitions

In Table 1 the differences in assumptions between the worst case and likely case studies are shown.

Table 1: Worst case and likely case studies, defined in “Scope of Work” by TCM.

Aspect	Worst case	Likely case	Common
Emission estimate from absorber by ACC	MEA: 3 ppm – worst case Solvent 2: 3 ppm - worst case Multiply direct nitrosamine emissions with factor 6	MEA: 0.5 ppm – expected case Solvent 2: 1 ppm - design case No factor on direct nitrosamine emissions	Upset cases not to be used
Components	Same for both likely and worst case	Same for both likely and worst case	Dispersion of all amines, formaldehyde, and nitrosamines to be modelled Discuss formamide, O ₃ , imines, particulates, aerosols, amides and isocyanates Nitrosamines as a group
Dispersion models	Same for both likely and worst case	Same for both likely and worst case	The same as 2010 for comparison Discuss CONCX vs TAPM Simple chemistry to be included Improvements from UiO to be included(1)
Atmospheric chemistry	Reaction constant k_{OH} : $6.5 \cdot 10^{-11}$ cm ³ /mol.s OH concentration: $10.0 \cdot 10^5$ molecules/cm ³ Max nitrosamine steady state concentration: 1% Negative corrections for liquid and dark chemistry with NO ₃ radicals	Reaction constant k_{OH} : $4.0 \cdot 10^{-11}$ cm ³ /molecules.s OH concentration: $5 \cdot 10^5$ molecules/cm ³ Max nitrosamine steady state concentration: 0.4% Corrections for day/night and winter/summer No liquid and dark chemistry correction	Improvements from UiO and ADA to be included (1),(2) To be discussed explicitly: <ul style="list-style-type: none"> • Influence of NO_x concentration • Influence of Cl atoms • difference 1^{ary}, 2^{ary}, 3^{ary} amines • degradation of nitramines in air from MEA • formation and degradation of nitramines in air from solvent 2 • competition for NO_x with other components than amines
Deposition	Worst rain and wind frequencies, patterns and quantities	Likely case rain and wind frequencies, patterns and quantities	Nitrosamines and MEA nitramines (option) are 100% water soluble Landscape parameters
Degradation in water	Nitrosamines: <ul style="list-style-type: none"> • Biodegradation half life time: 40 days • Inhibition concentration: 5 µg/l • Photolysis lifetime: 3 weeks 	Nitrosamines: <ul style="list-style-type: none"> • Biodegradation half life time: 15 days • inhibition concentration: 50 µg/l • Photolysis lifetime: 1 week 	Include findings from SINTEF (3) To be discussed explicitly: <ul style="list-style-type: none"> • effects of different soils formation and degradation of nitramines in air from solvent 2
Guideline values air and water	Discussion only - Cannot be defined by TCM	Discussion only - Cannot be defined by TCM	Discuss relative to findings from NIPH and MIT reports (4),(5) Discuss differences between nitrosamines and nitramines

(1):Nielsen, Hoffmann and Hermann, March 2011

(2):Nielsen et. Al, February 2011

(3):Brakstad, Booth and Zahlsen, February 2011

(4):Folkehelseinstituttet (NIPH), March 2011

(5):Selin, March 2011

For deposition of amine reaction products, the conclusion drawn regarding wet deposition model results in TAPM by Karl et.al, 2011 have been used to separate the worst case and likely case. The paper states that the overestimate of wet deposition by the model is 30 %. The worst case study uses the deposition model

results without any adjustment. The likely case takes the overestimate into account by reducing the wet deposition by 30 %. By this approach, the wet deposition for the worst case study represent cases with yearly precipitation of more than 1.5 times the average yearly precipitation in western Norway.

2.1 Emission estimates

The emission from the absorber for the different solvents, feed gases and emission scenarios has been provided to NILU by TCM. Emissions are grouped according to type of amines, and separate emission figures given for formaldehyde and nitrosamines. The emissions are shown in Table 2 .

Table 2: Emissions from the absorber (in g/s) for different cases.

Absorber emissions in g/s - Input for dispersion modelling		
	Feed gas	
	CHP	RFCC
Likely case MEA		
MEA - primary amine	2,1E-02	1,6E-02
Other primary amines	8,7E-04	1,4E-03
Secondary amines	3,5E-03	5,4E-03
Tertiary amines	7,5E-05	5,7E-05
Formaldehyde	2,6E-02	1,3E-02
Nitrosamines	9,1E-05	6,9E-05
Worst case MEA		
MEA - primary amine	1,2E-01	9,4E-02
Other primary amines	2,1E-03	4,5E-03
Secondary amines	7,9E-03	1,7E-02
Tertiary amines	1,5E-04	1,1E-04
Formaldehyde	1,0E-01	5,0E-02
Nitrosamines	3,6E-04	2,8E-04
Likely case solvent 2		
Primary amines	6,3E-02	4,8E-02
Secondary amines	2,8E-02	2,1E-02
Tertiary amines	3,4E-04	2,6E-04
Formaldehyde	4,0E-03	3,1E-03
Nitrosamines	1,8E-04	1,4E-04
Worst case solvent 2		
Primary amines	1,5E-01	1,2E-01
Secondary amines	6,7E-02	5,1E-02
Tertiary amines	4,0E-03	3,1E-03
Formaldehyde	4,0E-03	3,1E-03
Nitrosamines	1,8E-04	1,4E-04

Emissions from the CO₂ stack are not included since they are insignificant relative to the ones from the absorber.

2.2 Topography of the area

The model area is 60 x 60 km centred at Mongstad. The topography can roughly be divided in 3 zones, in the west the North Sea (20 km wide in the model domain), the middle 20 km with low to medium high landmass cut up by fjords in varying directions, and in the east 20 km with mountain terrain. The Sognefjord

cut through the two latter features from west to east in the northern part of the model domain. In the vicinity of Mongstad, the dominant terrain features are Fensfjorden-Austfjorden which runs roughly from southeast to northwest immediately north of Mongstad, with steeper terrain and higher hills / mountains on the north side than the south side. At Lindås and Radøy south of Mongstad the hills and ridges all run in a southeast to northwest direction. The closest population centres are Lindås, Austrheim and Leirvåg. The northern suburbs of Bergen are located on the south edge of the model domain. The two catchment areas of Nordgulelva and Dingja, are located in the northeast part of the model area.

2.3 Chemical reactions, photolysis and deposition mechanisms

The most important overall assumptions are:

- Secondary and tertiary amines form nitrosamines in the atmosphere with NO_x through OH-radicals and NO_3 radicals.
- Primary amines do not form nitrosamines in the atmosphere with NO_x
- All amines form nitramines in the atmosphere with NO_x

2.4 Guideline values for health and environmental impact

The Norwegian Institute for Public Health (NIHP) has recently published a report proposing guideline values for the combined total of nitrosamines and nitramines in air and water (Låg et al. 2011). The proposed guideline values are for long time exposure:

- 0.3 ng/m^3 in air
- 4 ng/l in drinking water

These values are recommendations and are not yet endorsed by the Norwegian authorities. Selin, March 2011, list the same existing regulations and experimental data as is given in the NIHP report. Regarding differences between nitrosamines and nitramines, NIHP conclude that as groups, nitrosamines have higher carcinogenic potential than nitramines. Applying the guideline as a value for the sum of both groups will increase the level of safety. For the other components in the emission inventory, no revision of guideline values has taken place since the previous report.

3 Unitary inert emission dispersion

The dispersion model and dispersion conditions have not been changed since the previous update (Berglen et. al, 2010). This provides a reliable basis for comparison of the new results presented here with those previously presented. The meteorological input to the dispersion model is thus the year of 2007. Model setup files for TAPM are shown in Appendix A. From January to November 2007, monitoring of meteorological parameters and air quality was carried out at Mongstad (Tønnesen, 2008). The results from unitary emission (1g/s) inert dispersion and wet deposition (sulphur chemistry) are shown in Figure 1 and Figure 2. In the previous report, these calculations were scaled uniformly to give the values for the specific emission components. In addition, an 8-hour maximum

value, corresponding to the time span for air quality limit values for working conditions, was extracted from the model runs, resulting in a value of $2.4 \mu\text{g}/\text{m}^3$ for a unitary emission calculated by TAPM (RFC case).

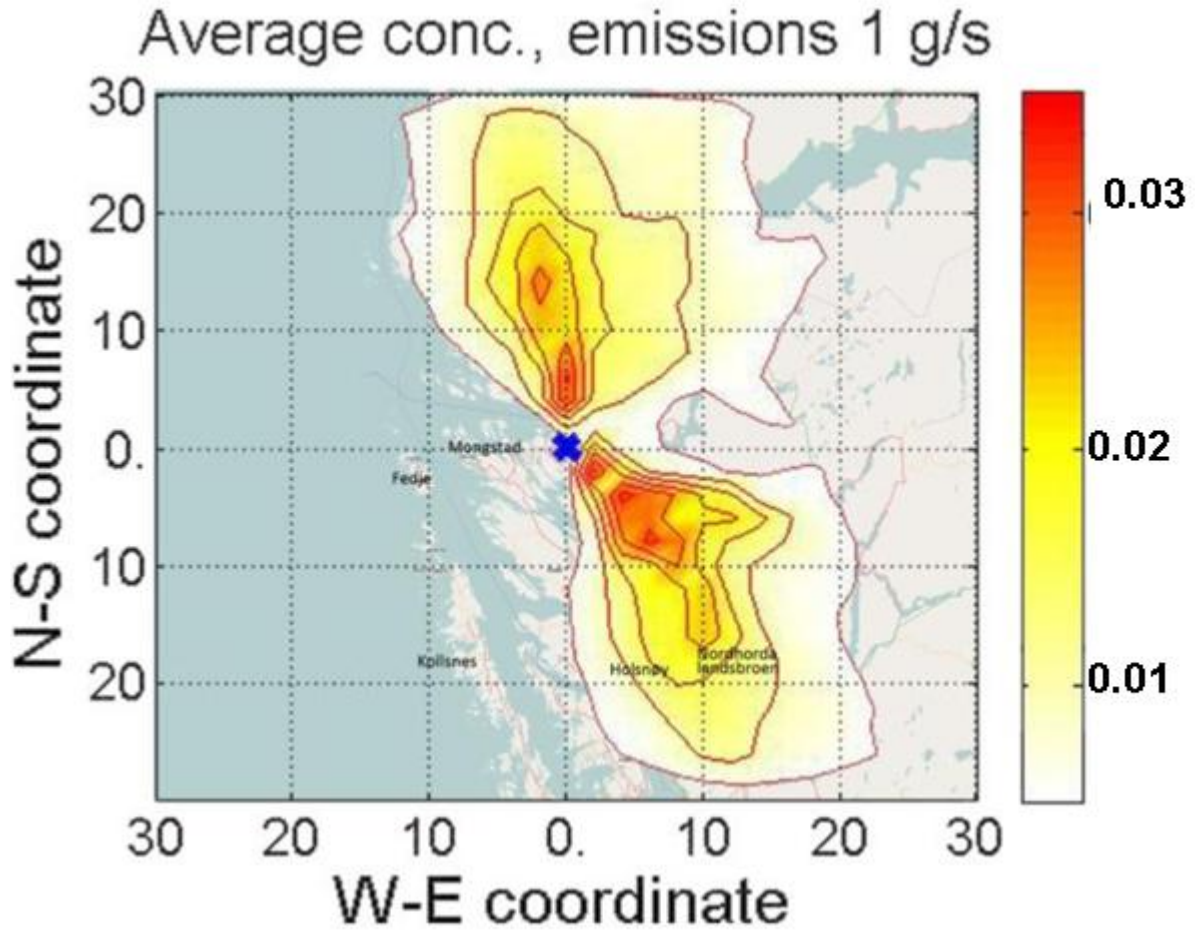


Figure 1: Yearly average concentrations ($\mu\text{g}/\text{m}^3$) from a unitary inert emission of 1 g/s from the TCM absorber (CHP case). Maximum ground level impact is $0.03 \mu\text{g}/\text{m}^3$.

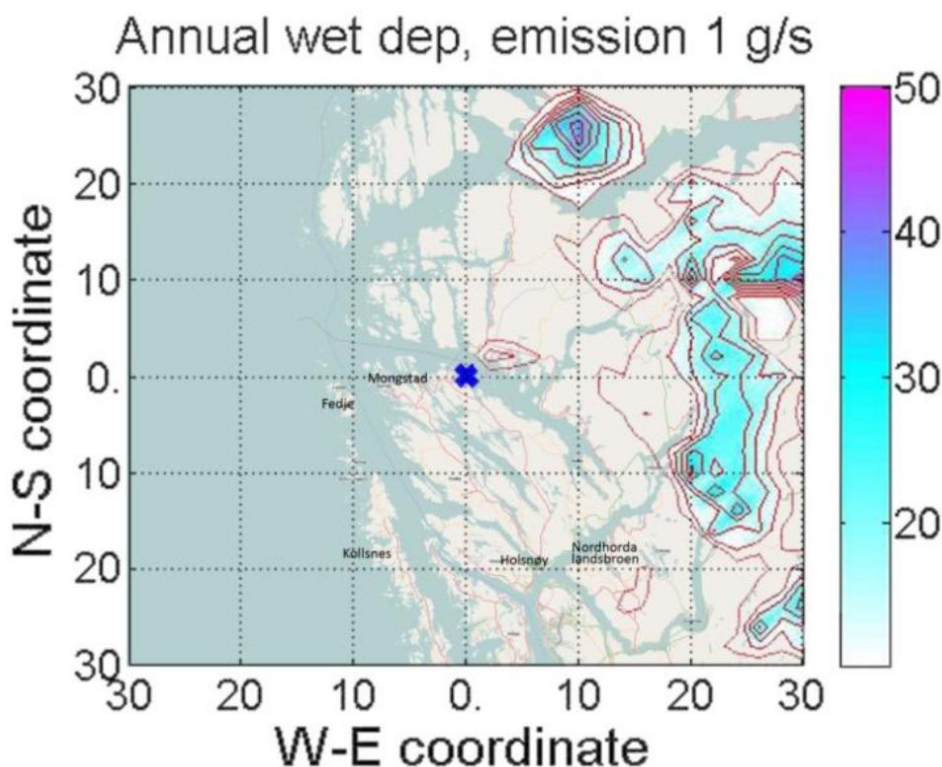


Figure 2: Yearly wet deposition ($\text{mg}/\text{m}^2/\text{yr}$) from a unitary emission of 1 g/s through the TCM absorber (CHP-case), applying sulphur chemistry. Maximum deposition $39 \text{ mg}/\text{m}^2/\text{yr}$.

The results from the unitary inert dispersion modelling have been used to provide the background for calculation of formation and degradation of the reaction products of nitramines and nitrosamines. From the TAPM model, we have extracted the dilution of air along the pathways from the emission to the edge of the model area along the two paths with minimum dispersion. The paths with minimum dispersion are defined by the location of maximum ground level concentration at increasing distance from the emissions. The pathways are shown in Figure 3.

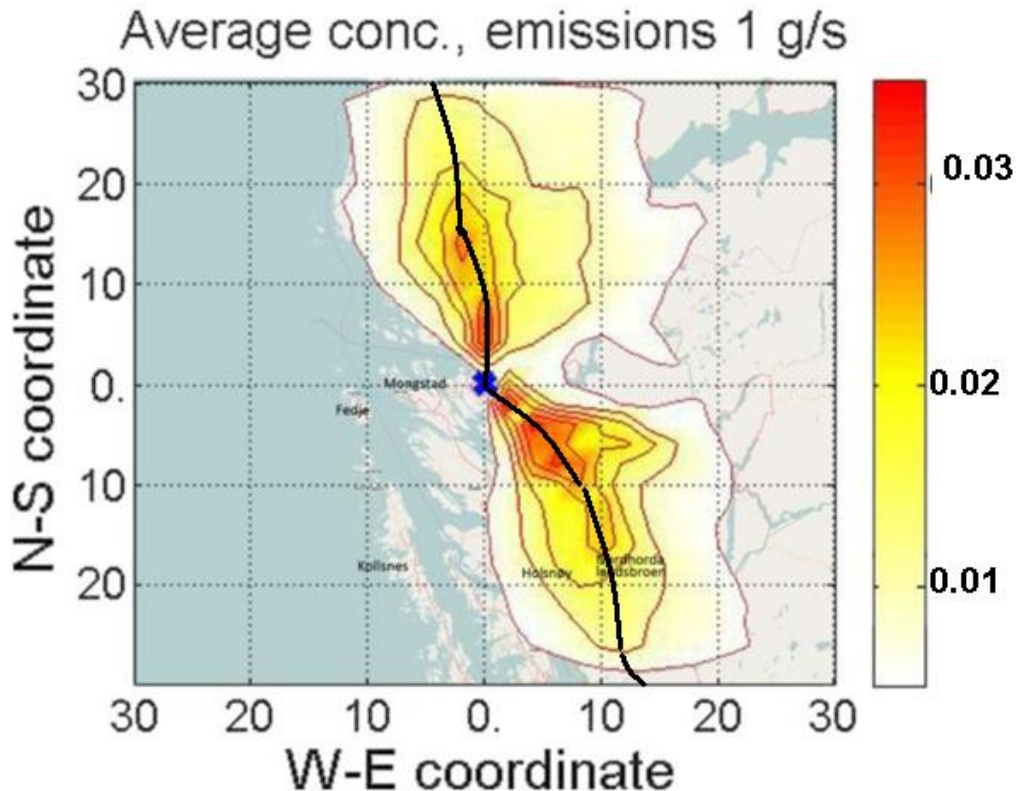


Figure 3: Pathways of minimum dispersion towards north and southeast.

For the emission source, the two areas with maximum ground level impact (at Sande and around Sundsbø/Kolås), and near the model edge in the two main advection directions, the model wind data have been extracted and compared to observations (Tønnesen, 2008) in order to estimate the average travel time from the emission to these areas. The area with maximum wet deposition has been treated likewise. The agreement between the model wind data and the observations is within 2 % at the emission point and within 20 % at the model area edge. The model wind data show that compared to the centre (emission) location, there is an increase in wind speed towards the north and a decrease in wind speed towards the southeast for yearly average values (the two main directions of transport). For the estimation of travel times from the emission point to the three maximum impact areas, the model wind speed has been used. The wind data show that the maximum yearly average travel time for the air from the centre to the model border along the path of minimum dispersion is 2 hours. The dilution of air for the two paths from the emission to the model area edge for the highest concentration is shown in Figure 4. It is expressed as an inert unitary emission impact, and the distance from the emission point have been substituted by time as the ordinate.

The extracted wind data used to transform distance into time is shown in Table 3. The level of 10 ng/m^3 was chosen as locations for extraction because it would represent the wind field at a convenient point between the emission and the model domain edge.

Table 3: Model wind speed (m/s) used to calculate travel times (minutes). The travel times are also shown.

Points	Departure speed	Arrival speed	Travel speed	Travel time
North Max	(from centre) 5.2	5.4	5.3	17,3
South east Max	(from centre) 5.4	4.4	4.9	8.3
North , 10 ng/m ³	(from max) 5.4	6	5.7	80.6
Southeast 10 ng/m ³	(from max) 4.4	3.9	4.15	111
Wet Deposition Max	(from centre) 4.6	4.6	4.6	115

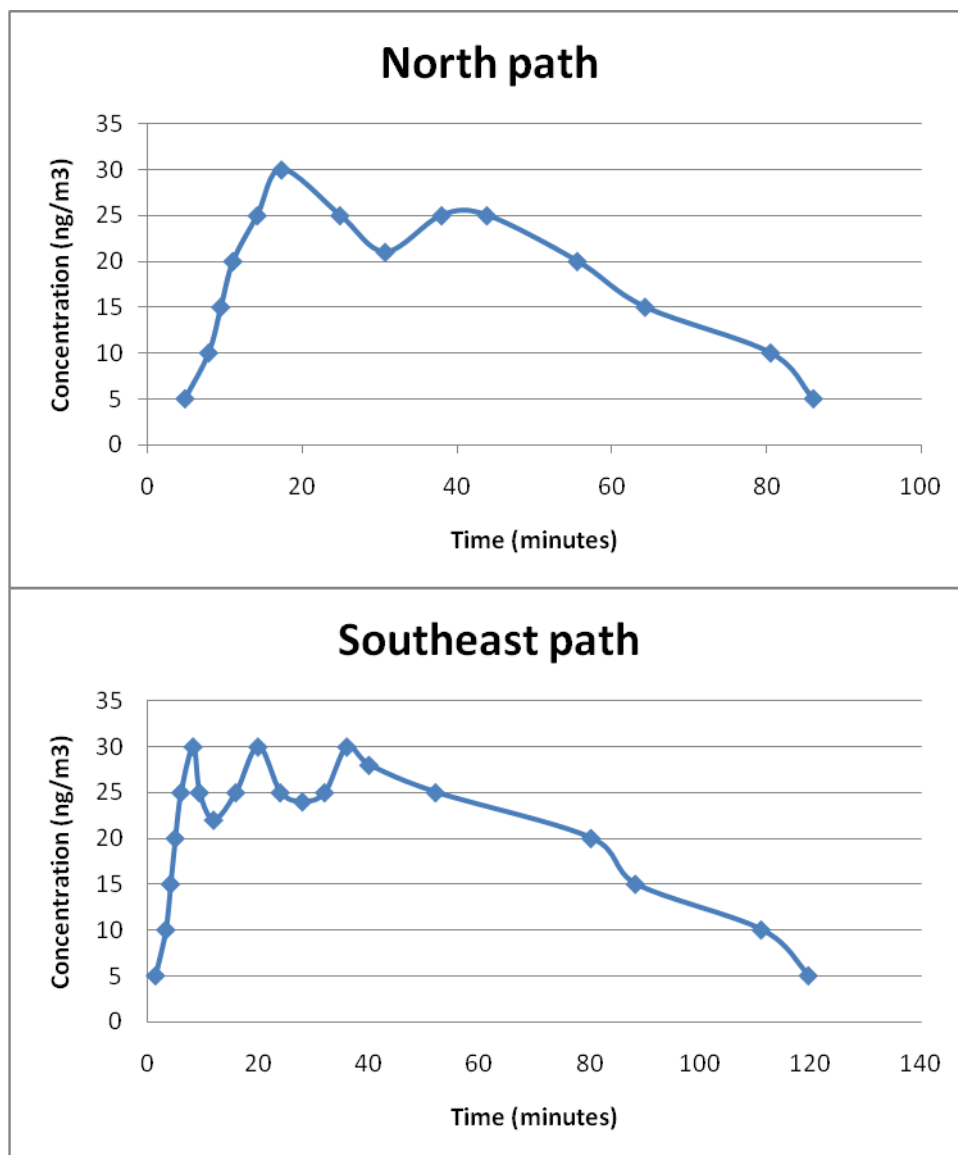


Figure 4: Concentration in north and south east paths of a unitary inert emission of 1 g/s as function of time spent after emission. The paths are along the minimum dispersion.

Due to variations in the dispersion over the year, the concentration does not change uniformly with time. These average yearly concentrations as a function of time from the emission point enables the use of simplified chemical reactions to quantify formation and degradation of the emitted amines (and the emitted nitrosamines).

4 Nitrosamines and nitramines in air

Based on the evaluation of worst case assumptions for atmospheric chemistry (Nielsen, Hoffmann and Hermann, 2011), the ADA 2010 report (Atmospheric degradation of amines (ADA) Summary Report: Photo-Oxidation of Methylamine, Dimethylamine and Trimethylamine CLIMIT project no. 201604.), and the worst case and likely case definitions in the scope of work, impact of nitrosamines and nitramines have been calculated as a function of elapsed time since the emission into the air from the absorber.

4.1 Worst case for nitrosamines

The ADA 2010 report clearly recommends the use of steady state calculations for nitrosamines in air, with a maximum concentration of 1 % of the concentration of amines with potential of forming nitrosamines. However, because of the combination of model area size and wind speed, the average time needed for air passing the emission point to exit the model area is less than 2 hours. The time spent by the moving air from the emission to the maximum ground level impact area is even shorter, approximately 40 minutes, so no steady state will have been established in the model area. The yield for nitrosamine as a reaction product from the OH reaction is not specified in the ADA 2010 report. However, the yields of the other OH reaction products sum up to 98 %. These calculations are based upon an assumption that the remaining 2% of the reaction products are nitrosamines.

The degradation and formation of nitrosamines will be distinctly different for night conditions and day conditions. During the day, reaction by amines with the OH radical will form nitrosamines from the secondary and tertiary amines, while photolysis will destroy nitrosamines. Should there be water droplets present in the air, they can act as a delaying function for both processes, but this process will be of minor importance (Nielsen, Hoffmann and Herrmann, 2011). During night, there will be no (yet known) degradation of nitrosamines, and the amines can react to nitrosamines by the NO₃ radical. For a yearly average value, the duration of night-time and day-time conditions will be equal.

The Eurotrac TOR program (Dubois et al., 1997) contains quantification of NO₃ concentrations. For clean marine air, the level before sunrise is given as 10 ppt. In Ge et al. (2010), reaction constants for NO₃ towards trimethylamine and two amides are given, the constants range from 5×10^{-16} to 5×10^{-14} . Comparing the reaction constants and the concentration levels of OH and NO₃ indicate that the NO₃ reaction would be at least 10 times less efficient in forming nitrosamines than the OH reaction. In the worst case calculations, a formation of nitrosamines by NO₃ during night has been set arbitrarily at 1/5 of the formation by OH during day.

In Table 4 the treatment of the emissions during day and night for the purpose of calculating worst case impact of nitrosamines are shown. The applied reaction constant and OH concentration during day is shown in Table 1.

Table 4: Treatment of emissions during day and night conditions for worst case yearly average impact of nitrosamines.

Emission group	Day	Night
Primary amines (incl. MEA)	No contribution to nitrosamines	No contribution to nitrosamines
Secondary and tertiary amines	Formation by OH-reaction, no photolysis reduction of those formed	Formation by NO ₃ reaction at 1/5 of OH formation rate
Nitrosamines	Reduced by photolysis, at average equinox conditions	No reduction

After calculation of the time dependent conversions for day and night conditions, the two conditions have been averaged. The calculations have been made with the emission rates as basis, this gives the fraction of the primary emissions that have transformed from amines to nitrosamines, and the fraction of nitrosamines that remain as nitrosamines as a function of time since the emission.

Two known effects have been omitted from these calculations, in order to simplify the calculation and because the concentration level at the initial plume height is unknown:

1. The reactions with OH will not start immediately after emissions due to the presence of NO in the plume after release. Approximately 2 to 4 minutes will pass before the NO is oxidized to NO₂ and no OH would be present in the plume until that has happened.
2. The nitrosamines formed by OH reaction during day will immediately start to be reduced by photolysis at the same rate of reduction as the primary emission of nitrosamines.

Both of these effects would reduce the calculated impact of nitrosamines.

The results of the calculations of transformation and reduction are shown in Table 5 in the unit mg/s, and Figure 5 as the average percentage nitrosamines of the total emission of secondary and tertiary amines and nitrosamines. Note that the percentage of nitrosamines for the two flue gases with solvent 2 is nearly identical.

From Table 5 it can be seen that the most important contribution to the total average comes from the nitrosamines directly emitted during the night.

Table 5: Time dependent part of the emissions that remain as or have reacted to nitrosamines for night and day conditions (Unit mg/s). No shade: day, dark shade: night, light shade: average night and day.

Emission scenario	Component	at time 0	20 min	40 min	60 min	100 min	115 min
MEA CHP	Amines ¹	0	0.0024	0.0033	0.0042	0.0059	0.0065
	Nitrosamines	0.363	0.363	0.363	0.363	0.363	0.363
	Sum	0.363	0.3654	0.3663	0.3672	0.3689	0.3695
	Amines ¹	0	0.0121	0.0166	0.0211	0.0295	0.0326
	Nitrosamines	0.363	0.1093	0.0329	0.0099	0.0009	0.0004
	Sum	0.363	0.1214	0.0496	0.0310	0.0304	0.0329
Solvent 2 CHP	Amines ¹	0	0.0215	0.0297	0.0376	0.0527	0.0581
	Nitrosamines	0.181	0.181	0.181	0.181	0.181	0.181
	Sum	0.181	0.2025	0.2107	0.2186	0.2337	0.2391
	Amines ¹	0	0.1076	0.1484	0.1879	0.2633	0.2905
	Nitrosamines	0.181	0.0545	0.0164	0.0049	0.0004	0.0002
	Sum	0.181	0.1621	0.1648	0.1929	0.2638	0.2906
MEA RFCC	Amines ¹	0	0.0051	0.0071	0.0090	0.0126	0.0138
	Nitrosamines	0.276	0.276	0.276	0.276	0.276	0.276
	Sum	0.276	0.2811	0.2831	0.2850	0.2886	0.2898
	Amines ¹	0	0.0257	0.0354	0.0448	0.0628	0.0692
	Nitrosamines	0.276	0.0831	0.0250	0.0075	0.0007	0.0003
	Sum	0.276	0.1088	0.0604	0.0523	0.0635	0.0695
Solvent 2 RFCC	Amines ¹	0	0.0163	0.0225	0.0285	0.0400	0.0441
	Nitrosamines	0.138	0.138	0.138	0.138	0.138	0.138
	Sum	0.138	0.1543	0.1605	0.1665	0.1780	0.1821
	Amines ¹	0	0.0817	0.1127	0.1427	0.2000	0.2206
	Nitrosamines	0.138	0.0416	0.0125	0.0038	0.0003	0.0001
	Sum	0.138	0.1233	0.1252	0.1465	0.2004	0.2207
	Average sum	0.138	0.1388	0.1429	0.1565	0.1892	0.2014

1: sum of secondary and tertiary amines

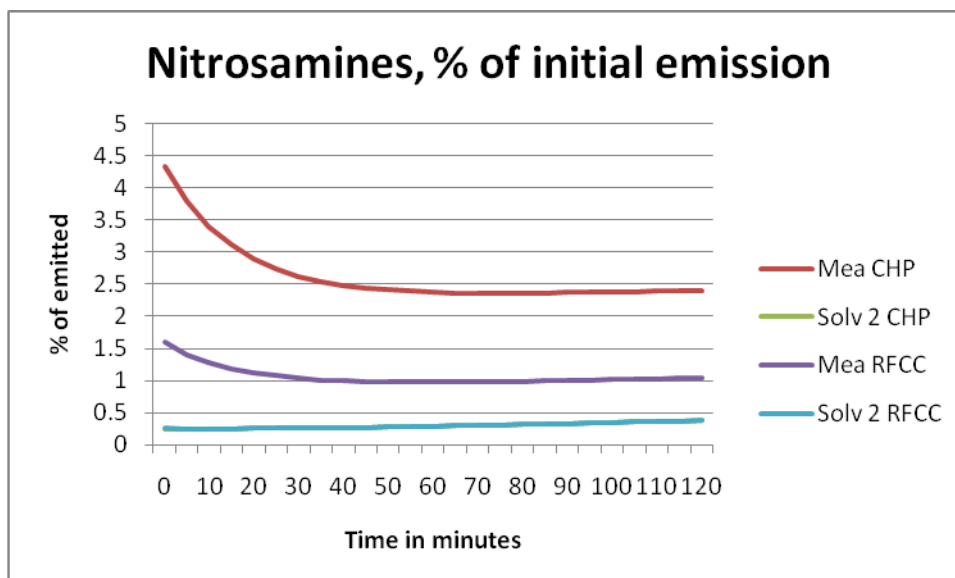


Figure 5: Time dependent part of the emissions that remain as or have reacted to nitrosamines for night and day conditions. Unit % of amines(secondary and tertiary) and nitrosamines emitted. The curve for solvent 2 CHP is covered by the curve for solvent 2 RFCC.

The combined effect of atmospheric dispersion and chemical reactions for the two paths of minimum dispersion is shown in Figure 6. The maximum impact as a yearly average value (the highest concentration from Figure 6) is 0.0089 ng/m^3 , occurring along the southeast path with MEA used together with CHP flue gas. Figure 6 show the combination of dispersion and the time dependent reactions, scaled with the scenario emissions. The local minima and maxima along the curves come from the corresponding variations in the dispersion curves for time dependent concentrations for unitary emissions.

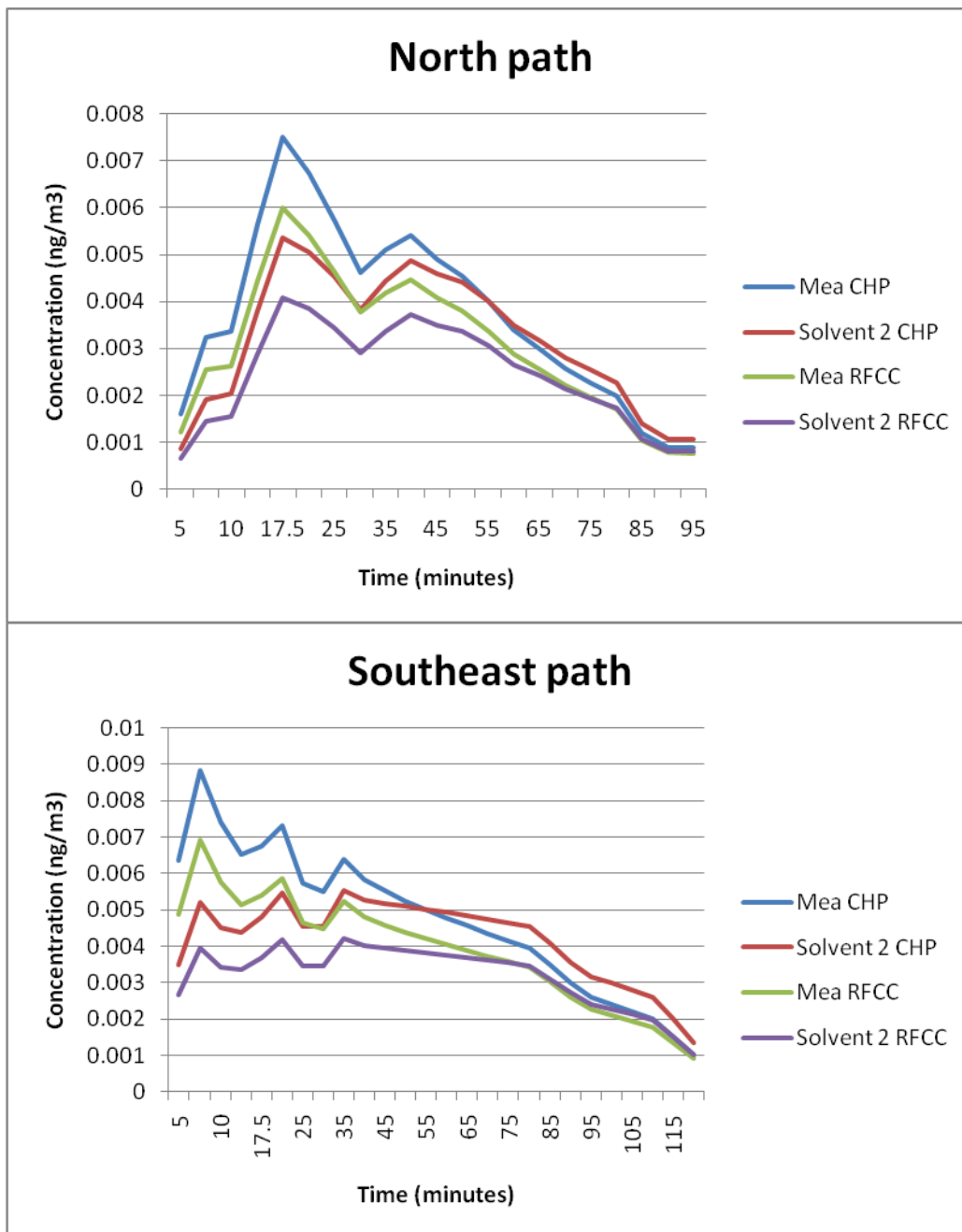


Figure 6: Nitrosamine concentration along the two paths of minimum dispersion as function of time spent after emission for the 4 emission scenarios.

4.2 Worst case assumptions and results for nitramines

No direct emissions of nitramines have been detected in the test measurements. The environmental impact from the emissions will come from degradation of amines in the air. The formation processes will be through OH reaction during day and reaction with other radicals (NO₃) during night. The yields of nitramines from different amines are given in the ADA 2010 report, and for MEA in Nielsen et. al. (2010) Gas phase photo-oxidation of 2-aminoethanol (MEA) (NILU OR 08/2010). The results for rural conditions, which are applicable to the Mongstad

area, are shown in Table 6, together with the emission component group the yields have been applied for.

Table 6: Estimated yields of nitramines from photo oxidation in the atmosphere under rural conditions, and emission component groups the yield has been applied for.

Component	Yield	Applied to emission group
MEA	Less than 0,3 %	MEA
Methylamine	Less than 0.4 %	Other primary amines
Dimethylamine	Less than 2.5 %	Secondary amines
Trimethylamine	Less than 5 %	Tertiary amines

For nitramines there are more groups of components that might cause their formation, and the yields for the different components vary considerably. In these calculations, no attempt has been made to separate day reactions and night reactions, the basic assumption being that the formation during day is higher than at night. Since no primary emissions of nitramines have been measured, the separation between day and night conditions is less critical than for nitrosamines. Thus, applying constant day conditions for formation will not underestimate the impact. The part of the emission formed to nitramines at different travel times from the emission point is shown in Table 7 . The calculation is based on the separate yields given in Table 6. Comparing the nitramine formation to the nitrosamine formation (and non-reduced emission) in Table 5 show that for the MEA scenarios, the nitrosamine fraction is larger than the nitramine fraction, while for the Solvent 2 scenarios the opposite is the case.

Table 7: Nitramine formation from the original emissions, given as mg/s, for different travel times from the emission.

Scenario	Emission	20 min	40 min	60 min	100 min	115 min
MEA CHP	133.2 ¹	0.0438	0.0604	0.0756	0.1071	0.1181
Solvent 2 CHP	226.0	0.1886	0.2601	0.3294	0.4616	0.5091
MEA RFCC	115.0 ¹	0.0547	0.0755	0.0956	0.1340	0.1477
Solvent 2 RFCC	171.6	0.1433	0.1976	0.2502	0.3506	0.3867

1: Sum of amines including MEA

The combination of dispersion and chemistry for the paths of minimum dispersion, corresponding to those previously shown for nitrosamines, are shown in Figure 7 . The curves have been made by scaling the unitary emission concentration by the formation rates in Table 7. Comparing the nitramine concentrations with the unitary emission concentration show that the gradual formation has a large impact on the shape of the curve, much larger than for the nitrosamines, where the component is more dominated by the direct emissions. The maximum ground level impact for nitramines occurs further from the absorber for nitramines than it does for nitrosamines.

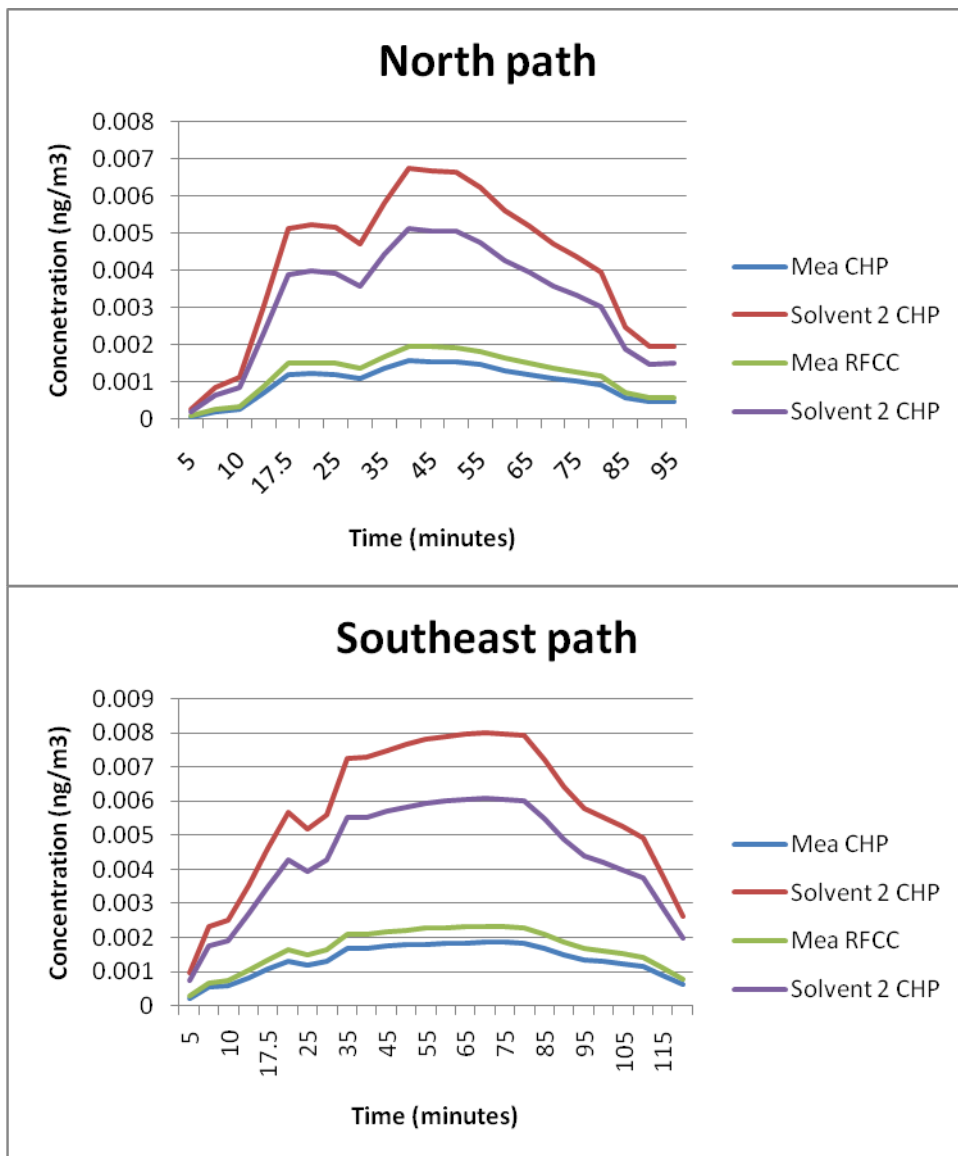


Figure 7: Nitramine concentrations along the paths of minimum dispersion as function of time spent after emission

4.3 Total worst case air concentrations of nitramines and nitrosamines

In order to compare the maximum impact from the emissions with the air quality guideline value (0.3 ng/m^3 for the sum of both nitrosamines and nitramines), the time-dependent impact of both components have been added together for the paths of minimum dispersion. The results are shown in Figure 8. The worst case concentrations in air are just below 0.013 ng/m^3 for the sum of the two components. This is less than 5 % of the proposed guideline value from NIPH. The maximum concentration of the sum of nitrosamines and nitramines for each of the emission scenarios is shown in Table 8.

Table 8: Maximum air concentration (ng/m^3) of nitrosamines and nitramines for the four emission scenarios.

Scenario	MEA CHP	Solvent 2 CHP	MEA RFCC	Solvent 2 RFCC
Nitrosamines	0.0089	0.0055	0.0069	0.0042
Nitramines	0.0019	0.0080	0.0023	0.0061
Sum concentration	0.009	0.013	0.008	0.010

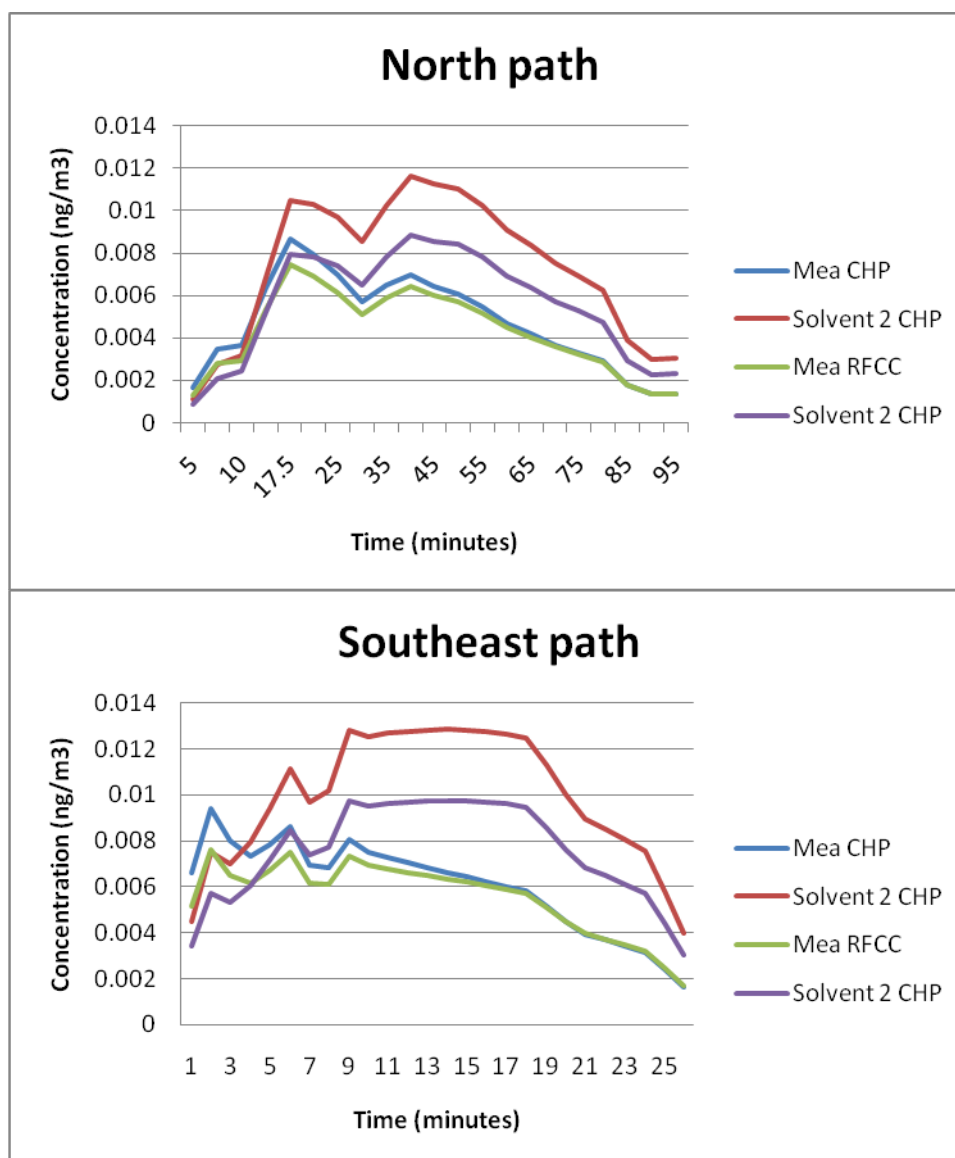


Figure 8: Sum of nitrosamine and nitramine concentrations for the paths of minimum dispersion as function of time spent after emission.

To illustrate the effect of air chemistry versus inert dispersion, the solvent 2 CHP emission with chemistry is shown in Figure 9 together with a dispersion curve for inert dispersion of primary and secondary amines in the same emission scenario.

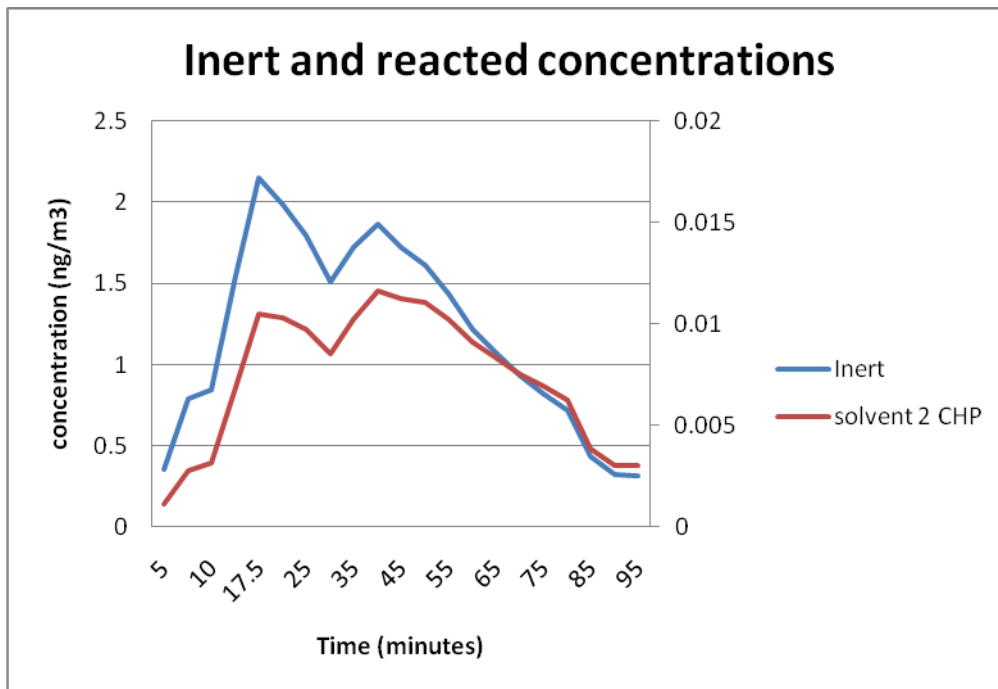


Figure 9: Inert dispersion (left axis) and concentrations of nitramines and nitrosamines after air chemistry is applied (right axis) along the North path for minimum dispersion

4.4 Likely case

For air concentrations from the MEA emission scenarios the nitrosamine concentration is mainly determined by the direct emissions of nitrosamines. The likely case emissions of nitrosamines are a factor of 4 lower than the worst case. For the nitramines, lower OH-concentration and slower reaction rate may reduce the impact by a factor of 3.5. Likely case maximum air concentrations of the sum of the two components may be between 3.5 and 4 times lower than the worst case.

For air concentrations from the Solvent 2 emission scenario, the largest contribution to the sum of the components come from the nitramines, which may be reduced by a factor of 3.5 due to reduced formation rate and a factor of at least 2 due to reduction of emitted amines. The reduction of the contribution from nitrosamines may be much less, around 1.5. The maximum impact of the sum of the components may be more than 3 times lower than the worst case.

5 Nitrosamines and nitramines in fresh water

5.1 Worst case estimate

The calculated maximum impact of wet deposition in the model area is located to the northeast of the emission, covering two catchment areas in Gulen, Nordgulelva and Dingja. The size (21 km² and 28 km²) and runoff (83.1 Mm³/yr and 79.9 Mm³/yr) for these catchment areas can be found at www.nve.no. The model wet deposition maximum from a unitary emission is 39 mg/m²/year, using solubility for sulphur dioxide. Since the water chemistry is an integrated part of

the dispersion model, the sulphur chemistry is the most conservative of the options available.

The annual rainfall (average) is 1890 mm year. Taking into account the size of the catchment areas and the gradients in the wet deposition field, gives an average rainwater concentration of 4 µg/l over the catchment areas from a unitary emission (1 g/s). The extracted travel speed for the air from the emission to the deposition area is 4.6 m/s, giving a minimum time of 101 minutes for the emissions to reach the deposition area. Due to the curvature of the airflow, especially under conditions giving rain, the advection time has been increased to 115 minutes in these calculations.

Applying the same emission conversion factors as shown Table 5 for nitrosamines and Table 6 for nitramines give converted emission figures as shown in Table 9. These reflect the total average emission that remains as or has reacted to nitrosamines, and how much that has reacted to nitramines. The table also show what the resulting average rainwater concentration of nitrosamines and nitramines will be.

Table 9: Part of emissions that have reacted to form or remain as nitrosamines and nitramines after 115 minutes elapsed time since the emission, and the resulting average rainwater concentration over the catchment area.

Scenario	Mass flow in emissions that has reacted		Average rainwater concentration	
	Nitrosamines mg/s	Nitramines mg/s	Nitrosamines ng/l	Nitramines ng/l
MEA CHP	0.2012	0.1181	0.8048	0.4724
Solvent 2 CHP	0.2649	0.5090	1.0596	2.036
MEA RFCC	0.1797	0.1477	0.7188	0.5908
Solvent 2 RFCC	0.2014	0.3867	0.8056	1.5468

For nitramines, there is as yet no documented degradation process for fresh water. For nitrosamines, definitely photolysis (life-time 3 weeks) and possibly biodegradation (half-life 40 days to 400 days) (Brakstad et al., 2011) will reduce the concentrations. The effect of photolysis will result in a reduction of the rainwater concentration of nitrosamines to 5.9 % of its initial value as a contribution to the yearly average fresh water concentrations. Biodegradation might reduce the nitrosamine concentration further, down towards 4 % of the rainwater concentration.

The worst case concentrations in fresh water for nitrosamines and nitramines are then largely decided by the nitramine contribution. All the scenarios are below the guideline value of 4 ng/l proposed by NIPH. The results are shown in Table 10.

Table 10: Worst case concentrations of nitrosamines and nitramines in the most exposed fresh water reservoir around Mongstad (ng/l).

Scenario	MEA CHP	Solv 2 CHP	MEA RFCC	Solv 2 RFCC
Total load (ng/l)	0.52	2.1	0.63	1.59

Any (natural) background concentration of nitramines and nitrosamines will come as an addition to the levels shown in the table.

5.2 Likely case estimate

According to the definitions given for worst case and likely case scenarios, a first order estimate of the most exposed fresh water for the total contribution from TCM can be made. For all 4 emission scenarios, more than 90 % of the total load in water is determined by the contribution from nitramines. Expressed relative to the worst case, the effect of slower formation may be a reduction of 3.5, the effect of lower wet deposition may be a reduction of 1.3, and the effect of emission reduction maybe 5 for MEA scenarios and 2.4 for Solvent 2 scenarios. The likely case maximum water concentrations may be approximately 10 times lower than for the worst case for solvent 2 and 20 times lower for MEA.

6 Back calculation of total amount of emission for reaching guideline value

A calculation of how much the emissions in the different scenarios in Table 2 can increase before the concentration of nitrosamines and nitramines in air reach 0.3 ng/m³ have been made. The calculation is valid if the properties of the emitted gas flow remains the same (volume, temperature) and the different components in the emission scenarios maintain their relative values to each other (all concentrations of components in the emission forming nitramines and nitrosamines increase by the same factor). A back calculation for contribution to fresh water concentrations based on the same simplified approach has also been made. Since the uncertainties regarding dark phase chemistry and degradation for the main contributing component (nitramines) are large, the factor for water has a larger inherent uncertainty than for air. In addition, the treatment of air phase chemistry and water phase chemistry is simplified by applying air chemistry in rain droplets. The results are shown in Table 11.

Table 11: Factor of increase in emission concentration to reach the air quality guideline value.

Scenario	MEA CHP	Solv 2 CHP	MEA RFCC	Solv 2 RFCC
Factor to reach 0.3 ng/m ³	31.9	23.3	39.4	30.7
Factor to reach 4 ng/l	7.6	1.9	6.3	2.5

The factors given in Table 11 would not be applicable if an increase in emissions is caused by an increase in the exhaust gas flow, because this would also affect the

dispersion process. Neither would they be applicable towards changes in emission concentration for one component group, because the nitramine calculation is based on separate yields for the separate groups. They would be applicable towards a reduction in cleaning efficiency of amines from the emission, if this would change all the emission components with the same relative amount.

7 Discussion

7.1 Processes not included in calculations

7.1.1 Influence of NO_x concentration

According to the conclusions in ADA 2010 (Nielsen et. al. 2011) the level of NO_x and the balance between NO and NO_2 strongly influence the formation of nitrosamines and nitramines from amines. The estimates made for yields and steady state show that an urban scenario (20 – 50 ppb NO_x) would give from 3 to 5 times more nitrosamines and nitramines than a rural scenario (0.2 – 10 ppb NO_x). The formations for rural conditions have been applied here because they are the predominant conditions around TCM.

7.1.2 Influence of Cl atoms

The recent review by Ge et al., 2011, does not specifically list chlorine as an active radical towards formation of nitrosamines. Rudolph et al. (1996) have used the global budgets of ethane and tetrachloroethene to calculate the global budget for Cl atoms in the troposphere. They report values for 1×10^3 and 2×10^3 atom cm^{-3} in the northern hemisphere and southern hemisphere, respectively. Chlorine will probably contribute to decay of MEA, and its relative importance will be higher during night than day. There is little evidence at current that Chlorine will contribute to formation of nitrosamines.

7.1.3 Other reaction products of amines

From the ADA 2010 report (Nielsen et. al. 2011), methylamine, dimethylamine and trimethylamine reactions with OH will all produce formamides and imines, which again will react to isocyanatic acid, isocyanat and formaldehyde. The (intermediate) reaction product of formamide has an estimated lifetime of more than one day in the Mongstad area, and secondary reaction products from formamide will occur more than 100 km from Mongstad. Therefore, the concentration level of the secondary reaction products is expected to be relatively low due to higher dispersion than the initial emissions and the primary reaction products.

7.2 Main uncertainties

The combination of inert dispersion and wet deposition of a 100 % soluble component has been combined with gas phase reactions to provide estimates for air and water concentrations of nitrosamines and nitramines. This method is a rough simplification and has inherent limitations, in particular with respect to the

processes mentioned in 7.1.1. An integrated model for dispersion and air chemistry will be more accurate than this simplified method.

The resulting total load in air has contributions of approximately the same size from nitrosamines and nitramines, while the total load in water is dominated by the contribution from nitramines. The air and water chemistry for nitrosamines are better documented than for nitramines. This means that the contribution to total load from nitramines has a higher uncertainty than for nitrosamines, and that the estimated total load for water is more uncertain than for air. No information on night-time reactions of amines toward nitramines has been currently available for the purpose of these calculations.

7.3 Usefulness of CONCX vs TAPM

The 8-hour maximum value of $2.4 \mu\text{g}/\text{m}^3$ calculated by the TAPM model (at 3-4 km distance from the source) and the 1-hour maximum value of nearly $12 \mu\text{g}/\text{m}^3$ calculated by the CONCX model (at 0.5 km from the source) are generally consistent. Several facts must be considered when comparing the results. One aspect is the actual dispersion conditions in the area. CONCX models theoretical dispersion conditions while TAPM consider the actual meteorological conditions. The combination of 1 m/s wind speed and unstable conditions is hardly present in the dispersion data processed through TAPM. As a first order estimate the concentration is inversely proportional to the wind speed. With a yearly average wind speed of 3- 4 m/s, this largely explains most of the difference in the results. Another aspect is that the horizontal resolution in the TAPM model is 2 x 2 km and the concentration from CONCX represents an occurrence within an area of approximately 20 x 50 m.

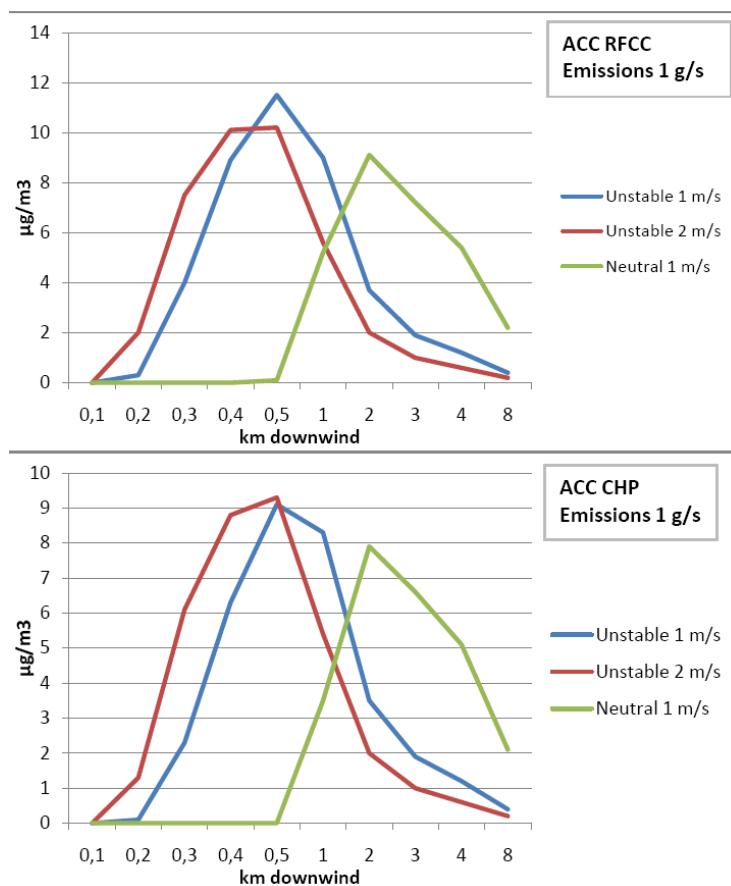


Figure 10: Maximum one hour ground level concentrations from a unitary emission through the TCM absorber from CONCX. Maximum ground level impact, $\mu\text{g}/\text{m}^3$.

Combining unitary emission inert dispersion results and emission totals of the different amine groups show (as in the previous report) that the guideline values of air concentrations for MEA and formaldehyde is upheld with very good margin. Although formaldehyde will be formed as a reaction product (primarily from MEA), the maximum air concentration of formaldehyde will be less than 1% of the air quality guideline.

7.4 Comparison of assumptions between 2008, 2010 and 2011

An overall comparison of the differences in the three dispersion calculations made by NILU for TCM is shown in Table 12. It shows the gradual improvement in the underlying information and the calculations and models and results over the years.

Table 12: Comparison of different aspects in dispersion calculations made by NILU for TCM.

	2008	2010	2011
Emission estimate	Chilled ammonia, MEA	Chilled ammonia, MEA, worst case, base case	MEA worst case and likely
Components	CO ₂ , NH ₃ , NO _x , MEA	CO ₂ , NH ₃ , NO _x , and specific component lists of 25, 31 and 15 species, including nitrosamines	Nitrosamines and nitramines
Dispersion models	CONCX, CONDEP, INPUFF	CONCX, TAPM (2007 dispersion data)	CONCX, TAPM (2007 dispersion data)
Atmospheric chemistry	None	No degradation, instant yield of 10 % for nitrosamines	OH-reaction, NO ₃ reaction, photolytic reduction for air with minimum dispersion
Deposition	Wet deposition of MEA	Wet deposition of nitrosamines	Wet deposition of nitrosamines and nitramines
Degradation in water	None	No degradation and 10 day lifetime	None for nitramines, photolytic for nitrosamines
Guideline values air and water	Water: None Air: None for MEA, AQ limit for NO ₂ , Norms for working environment for the other components	limit value for NO ₂ , Norms for working environment, Guidelines from NIPH and EPA IRIS for nitrosamines	Recommended guideline from NIPH for combined load of both components

8 Conclusions and recommendations

Dispersion and wet deposition of inert species have been combined with air chemistry to estimate maximum ground level concentrations and maximum contribution to fresh water for the sum of nitrosamines and nitramines from the amine technology absorber. The results have been compared to the recommended guidelines from NIPH (in air and water) for the sum of nitrosamines and nitramines. Time dependent calculations have been made for worst case assumptions regarding emissions, chemistry and deposition. In addition to the worst case study, an estimate of how likely conditions derived from current knowledge may reduce the concentrations has been made.

The worst case calculations have been performed for 4 combinations of absorbents and flue gas sources: MEA absorbent with CHP flue gas, Solvent 2 absorbent with CHP flue gas, MEA absorbent with RFCC flue gas and Solvent 2 absorbent with RFCC flue gas. The results, summarised in Table 13 below show that the guideline for air concentrations of 0.3 ng/m³ is upheld with very good margin, while the guideline for drinking water of 4 ng/l is upheld with margin of a factor of at least 1,9 and up to 7.6.

Estimations of how much current knowledge likely case conditions for emission, chemistry and deposition would reduce the worst case impact, show that the air concentrations would be reduced by more than a factor of 3. The water concentrations would be reduced by a factor of 20 for the MEA scenarios and a factor of 10 for the solvent 2 scenarios.

Table 13: Recommended guidelines and maximum impact from the 4 investigated combinations of solvent and flue gas.

	Guideline	MEA CHP	Solvent 2 CHP	MEA RFCC	Solvent RFCC	2
Air (ng/m ³)	0.3	0.009	0.013	0.008	0.010	
Water (ng/l)	4	0.52	2.1	0.63	1.59	

These results are TCM specific and cannot be scaled or used for other locations

9 Abbreviations

ACC: Aker Clean Carbon

CHP: Combined Heat and Power plant

FHI: Folkehelseinstituttet

MEA: 2-aminoethanol

MIT: Massachusetts Institute of Technology

NILU: Norwegian institute for air research

NIPH: Norwegian Institute for Public Health (Folkehelseinstituttet)

NO_x: Nitrogen oxides

OH: Hydroxyl radical

RFCC: Residue Fluid Catalytic Cracker

TAPM: The Air Pollution Model

TCM: Technology Centre Mongstad

TOR: Tropospheric Ozone Research

10 References

T.F. Berglen, Gjerstad, K.I., Knudsen, S., Mc Innes, H., Tønnesen, D.A. (2008) Dispersion calculations of emissions to air from Test Center Mongstad. Kjeller (NILU OR 12/2008). (In Norwegian).

Berglen, T.F., Tønnesen, D., Dye C., Karl, M., Knudsen, S., Tarrason, L. (2010) CO₂ Technology Centre Mongstad – updated air dispersion calculations. Update of OR 12/2008. Kjeller (NILU OR 41/2010).

Brakstad, O.G., Booth, A., Zahlsen, K. (2011) Biodegradation of nitrosamines in water. Trondheim (SINTEF A18258).

Dubois, R., Flentje, H., Heintz, F., Karbach, H.J., Platt, U. (1997) Fig. 8.8.4: Sector-classified diurnal variations in clean maritime (20°-120°) and polluted continental (160°-230°) air for summer 93 and 94. In: *Tropospheric ozone research*. Ed. by Ø. Hov. Berlin, Springer-Verlag. p. 266.

Ge, X., Wexler, A.S., Clegg, S.L. (2011) Atmospheric amines- Part I. A review. *Atmos. Environ.*, 45, 524-546.

- Karl, M., Wright R. F., Berglen, T. F., Denby, B. (2011) Worst case scenario study to assess the environmental impact of amine emissions from a CO₂ capture plant. *Internat. J. Greenhouse Gas Control.*, 5, 439-447.
- Låg, M., Lindeman, B., Instanes, C., Brunborg, G., Schwarze, P. (2011) Health effects of amines and derivatives associated with CO₂ capture. Oslo, The Norwegian Institute of Public Health.
URL: <http://www.fhi.no/dokumenter/5fa8589ddf.pdf> [accessed 09.08.2011]
- Nielsen, C.J., D'Anna, B., Dye, C., George, C., Graus, M., Hansel, A., Karl, M., King, S., Musabila, M., Müller, M. Schmidbauer, N., Stenstrøm, Y., Wisthaler, A. (2010) Atmospheric degradation of amines (ADA). Gas phase photo-oxidation of 2-aminoethanol (MEA). CLIMIT project no.193438. Kjeller. (NILU OR 08/2010).
- Nielsen, C.J., Hoffmann, D., Herrmann, H. (2011) Evaluation of worst case assumptions – atmospheric chemistry. Final Report, February 24, 2011. Oslo, University of Oslo, Department of Chemistry.
- Nielsen, C.J., D'Anna, B., Karl, M., Aursnes, M., Boreave, A., Bossi, R., Bunkan, A.J.C., Glasius, M., Hallquist, M., Hansen, A.M.K., Kristensen, K., Mikoviny, T., Maguta, M.M., Müller, M., Nguyen, Q., Westerlund, J., Salo, K., Skov, H., Stenstrøm, Y., Wisthaler, A. (2011) Atmospheric degradation of amines (ADA) Summary report: Photo-oxidation of methylamine, dimethylamine and trimethylamine. CLIMIT project no. 201604. Kjeller (NILU OR 2/2011).
- Rudolph, J., Koppmann, R., Plass-Dülmer, C. (1996) The budgets of ethane and tetrachloroethene: Is there evidence for an impact of reactions with chlorine atoms in the troposphere? *Atmos. Environ.*, 30, 1887-1894.
- Selin, N.E. (2011) Environmental guidelines and regulations for nitrosamines: A policy summary. Cambridge, MA, Massachusetts Institute of Technology.
- Tønnesen, D. (2008) Air quality monitoring at Mongstad, November 2006 - October 2007. Kjeller (NILU OR 47/2008). (In Norwegian).

Appendix A

Setup for TAPM model runs

Two input files are shown, The *.pse file, and the *.def file. To compress the *.def file it is shown in 3 tables, they show the data in sequence column-row table.

*.pse file:

```

1, 1
1, 0.00, 0.00, 60.00, 22.75, 1.00,
1.00, 0.50
10.00, 313.00, 40.0000, 0.0000, 0.0000,
0.0000

```

*.def file:

"TAPM.DE F"	""	"	1	25	"inline"	""	""
16	""	"t003a"	5	30000	""	""	""
"C:\tapm\Ter rain"	""	""	1	-360000	""	""	""
60.80833	"soil.aus"	""	"GRS"	"master"	""	""	1
5.033333	""	""	2	""	""	""	25
0	""	""	0	""	""	1	25
0	""	1	0	""	""	25	10000
20070101	0	6	0	""	""	25	-120000
20070131	0	35	0	""	1	30000	1
.3	30	1	0	""	25	-360000	25
.15	1	6	0	""	25	1	25
.15	1	35	0	1	30000	25	-120000
.15	3	1	0	25	-360000	25	"inline"
.15	2	0	1	25	1	30000	""
.15	0	0	1	30000	25	-360000	""
.15	2	0	1	-360000	25	"inline"	""
.15	2	0	1	1	30000	""	""
.15	10	0	1	25	-360000	""	""
.15	0	0	1	25	"inline"	""	""
.15	3	20	1	30000	""	""	""
.15	"t6a"	0	0	-360000	""	""	1
.15	"t2a"	4	0	"inline"	""	""	25
"C:\TAPM- MONGSTA D\jan"	"t010a"	0	1	""	""	""	25
"t15a"	"t003a"	0	0	""	""	1	10000
40	6000	0	0	""	""	1	-120000
40	2000	0	1	""	""	25	1
15000	1000	0	1	""	1	25	25
15000	300	0	1	""	25	10000	25
25	6000	0	"base"	""	25	-120000	10000
0	2000	4.5	"C:\tapm"	1	30000	1	-120000
19960701	1000	15	"C:\tapm"	25	-360000	25	"inline"
16	300	5000	1	25	1	25	""
"grid1"	1	1	1	30000	25	10000	""
".eur"	2	1000000	25	-360000	25	-120000	""
""	0	1	25	1	30000	"master"	""
""	"t300a"	0	30000	25	-360000	""	""

""	"t100a"	1	-36000	25	"inline"	""	""
""	"t030a"	0	1	30000	""	""	""
"vege.aus"	"t010a"	0	25	-36000	""	""	1

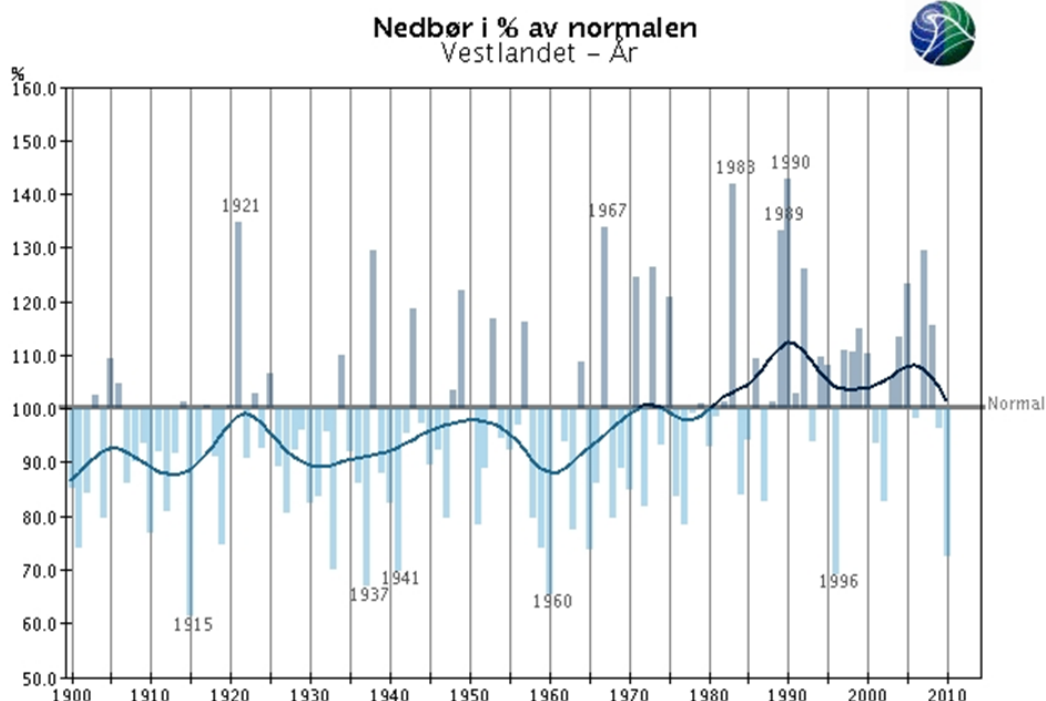
25	25	25	-36000	25	-12000	""	""
25	25	3000	1	25	"inline"	""	""
10000	10000	-36000	25	3000	""	""	""
-120000	-120000	1	25	-36000	""	""	""
1	1	25	3000	"inline"	""	""	""
25	25	25	-36000	""	""	""	1
25	25	3000	"inline"	""	""	""	1
10000	10000	-36000	""	""	""	1	25
-120000	-120000	"inline"	""	""	""	25	25
"inline"	"inline"	""	""	""	1	25	300
""	""	""	""	""	25	1000	-3600
""	""	""	""	""	25	-12000	1
""	""	""	""	1	1000	1	25
""	""	""	""	25	-12000	25	25
""	""	""	1	1000	1	25	300
""	""	""	25	-12000	25	1000	-3600
""	""	1	25	1	25	-12000	"master"
1	1	25	3000	25	1000	"inline"	""
25	1	25	-36000	25	-12000	""	""
""	25	3000	1	1000	"inline"	""	""
""	25	-36000	25	-12000	""	""	""
25	3000	1	25	"master"	""	""	""
10000	-36000	25	3000	""	""	""	""
-120000	1	25	-36000	""	""	""	""
1	25	3000	"inline"	""	""	""	1
25	25	-36000	""	""	""	1	25
25	3000	"inline"	""	""	""	25	25
10000	-36000	""	""	""	1	25	300
-120000	"master"	""	""	""	25	1000	-3600
"inline"	""	""	""	1	25	-12000	1
""	""	""	""	25	1000	1	25
""	""	""	""	25	-12000	25	25
""	""	""	1	1000	1	25	300
""	""	""	25	-12000	25	1000	-3600
""	""	1	25	1	25	-12000	"inline"
""	""	25	3000	25	1000	"inline"	""
""	1	25	-36000	25	-12000	""	""
1	25	3000	1	1000	"inline"	""	""

""	""	13	0				
""	""	1	"Site 3"				
""	1	3	0				
""	25	1	-1000				
1	25	1	#TRUE#				
25	300	3	#TRUE#				
25	-3600	5	#TRUE#				
300	1	7	#TRUE#				
-3600	25	9					
1	25	0					
25	300	0					
25	-3600	0					
300	"inline"	0					
-3600	""	0					
"inline"	""	#TRUE#					
""	""	#TRUE#					
""	""	#TRUE#					
""	""	#TRUE#					
""	""	#TRUE#					
""	""	"C:\tapm\GIS"					
""	1	11					
""	25	10					
1	25	1					
25	300	17					
25	-3600	15					
300	1	1					
-3600	25	"c:\surfer"					
1	25	"Notepad"					
25	300	4					
25	-3600	"Stack"					
300	"inline"	10					
-3600	""	0					
"inline"	""	0					
""	""	"Site 1"					
""	""	-1000					
""	""	0					
""	""	"Site 2"					
""	""	1000					

Appendix B

Data for wind and precipitation in 2007 versus average

A comparison of precipitation amount over the year is based upon data from www.yr.no, and shown in the figure below. 2007 had a precipitation amount above the average.



To compare the meteorological conditions for 2007 with the long term averages we have collected data from several stations in the vicinity of Mongstad. Data were downloaded from the met.no database eklima. Observations of wind speed for the 2001-2010 period were compared with observations from 2007 for the stations Flesland Airport, Bergen Florida and Slåtterøy Lighthouse. These are the stations in the coastal areas of Hordaland county with data for the entire 10-year period and hence most suitable for this comparison. The stations Fedje (data from August 2004) and Hellisøy Lighthouse (closed July 2005) unfortunately do not have data for the 10-year period and are therefore excluded. Also the station Takle (in Sogn county north of Mongstad somewhat inland) was included for comparison. The average wind speed for 2001-2010 and for 2007 for the 4 stations investigated is shown in table B1. These results show that the average wind speed in 2007 were slightly stronger than the 10-year period from 2001-2010.

Table B1: Average wind speed at 4 stations for a 10 year period and for 2007.

	2001-2010	2007
Flesland Airport	3,7 m/s	4,0 m/s
Bergen Florida	3,4 m/s	3,5 m/s
Slåtterøy Lighthouse	6,0 m/s	6,8 m/s
Takle	3,0 m/s	3,1 m/s

Appendix C

Detailed emission estimate from ACC

Emission estimates from ACC:

	Amine plant	
	CHP Absorber out	RFCC Absorber out
Scenario 1 - Expected (MEA likely case)		
MEA (g/s)	0.020517418	0.015583844
NH3 (g/s)	0.029746897	0.143385138
Formaldehyde (g/s)	0.026227226	0.012641972
Acetaldehyde (g/s)	0.038471838	0.018544085
Acetone (g/s)	0.005072518	0.024450408
Formamide (g/s)	0.007867294	0.037921707
Acetamide (g/s)	0.00010318	0.000497344
Methylamine (g/s)	0.000626003	0.000475476
Ethylamine (g/s)	6.05714E-05	4.60065E-05
Dimethylamine (g/s)	0.000151428	0.000115016
Diethylamine (g/s)	0.000589644	0.000447859
1-Butanamine (g/s)	0.000127756	0.000615807
Dibutylamine (g/s)	0.000225748	0.001088144
N-methylethanamine (g/s)	0.00010325	0.00049768
N-methyl 1-butanamine (g/s)	0.000152245	0.000733849
N-ethyl 1-butanamine (g/s)	0.000176752	0.000851975
1-Propanamine (g/s)	5.16248E-05	0.00024884
Dipropylamine (g/s)	1.76752E-05	8.51975E-05
Formic acid (g/s)	0.000927718	0.003875524
Acetic acid (g/s)	0.001210286	0.005055947
Butyric acid (g/s)	0.001775726	0.007418063
Propionic acid (g/s)	0.001493055	0.006237211
DEA (g/s)	0.000282541	0.000214602
HEI (g/s)	7.53313E-05	5.72173E-05
HEF (g/s)	0.001496314	0.001136513
OZD (g/s)	0.000292511	0.000222174
Nitrosamines (MW 90 given)	9.06959E-05	6.88873E-05
Scenario 3 - Worst case (MEA worst case)		
MEA (g/s)	0.123104506	0.093503062
NH3 (g/s)	0.117843475	0.571802552
Formaldehyde (g/s)	0.103900163	0.050414653
Acetaldehyde (g/s)	0.152407665	0.073951563
Acetone (g/s)	0.020094977	0.097505262
Formamide (g/s)	0.031166589	0.151227169
Acetamide (g/s)	0.00040875	0.001983346
Methylamine (g/s)	0.001252006	0.000950951
Ethylamine (g/s)	0.000121143	9.20131E-05
Dimethylamine (g/s)	0.000151428	0.000115016
Diethylamine (g/s)	0.001179288	0.000895719
1-Butanamine (g/s)	0.000506111	0.002455763
Dibutylamine (g/s)	0.000894309	0.004339387
N-methylethanamine (g/s)	0.000409027	0.001984689
N-methyl 1-butanamine (g/s)	0.000603126	0.002926501
N-ethyl 1-butanamine (g/s)	0.00070021	0.003397575
1-Propanamine (g/s)	0.000204513	0.000992344

Dipropylamine (g/s)	7.0021E-05	0.000339757
Formic acid (g/s)	0.003185164	0.015455121
Acetic acid (g/s)	0.004155315	0.020162503
Butyric acid (g/s)	0.006096659	0.029582338
Propionic acid (g/s)	0.005126157	0.024873243
DEA (g/s)	0.000282541	0.000214602
HEI (g/s)	0.000150663	0.000114435
HEF (g/s)	0.002992627	0.002273027
OZD (g/s)	0.000585022	0.000444349
Nitrosamines (MW 90 given)	0.000362783	0.000275549

**Scenario 5c - Improved solvent 2 - (S1,S4,S9)
Design - For discharge application**

Primary amine (g/s) - MW 100 given	0.05912026	0.04490433
Secondary amine (g/s) - MW 100 given	0.007725943	0.005868179
Tertiary amine (g/s) - MW 100 given	0.000335911	0.000255138
Ammonia (g/s)	0.011441114	0.008690008
Formaldehyde (g/s)	0.004034958	0.003064721
Acetaldehyde (g/s)	0.011837489	0.008991072
Acetone (g/s)	0.003901937	0.002963686
Formamide (g/s)	0.000605176	0.000459657
Acetamide (g/s)	7.93689E-06	6.02841E-06
Piperazine (g/s)	0.005787067	0.004395522
1,2 ethylenediamine (g/s)	0.004037645	0.003066762
4,4-dimethyl-2-oxazolidinone (g/s)	0.007734677	0.005874813
2-methyl-2-(methylamino)-1-propanol (g/s)	0.006930507	0.005264012
NO (g/s)	0.002016135	0.00153134
Nitrosamines (MW 90 given)	0.000181392	0.000137775

Scenario 5d - Improved solvent 2 - (S1,S4,S9) Worst case

Primary amine (g/s) - MW 100 given	0.150487936	0.114301931
Secondary amine (g/s) - MW 100 given	0.04702748	0.035719353
Tertiary amine (g/s) - MW 100 given	0.004030927	0.003061659
Ammonia (g/s)	0.011441114	0.008690008
Formaldehyde (g/s)	0.004034958	0.003064721
Acetaldehyde (g/s)	0.011837489	0.008991072
Acetone (g/s)	0.003901937	0.002963686
Formamide (g/s)	0.000605176	0.000459657
Acetamide (g/s)	7.93689E-06	6.02841E-06
Piperazine (g/s)	0.005787067	0.004395522
1,2 ethylenediamine (g/s)	0.004037645	0.003066762
4,4-dimethyl-2-oxazolidinone (g/s)	0.007734677	0.005874813
2-methyl-2-(methylamino)-1-propanol (g/s)	0.006930507	0.005264012
NO (g/s)	0.002016135	0.00153134
Nitrosamines (MW 90 given)	0.000181392	0.000137775



Norwegian Institute
for Air Research

Norwegian Institute for Air Research
P.O. Box 100, N-2027 Kjeller, Norway
*Associated with CIENS and the
Environmental Research Alliance of Norway*
ISO certified according to NS-EN ISO 9001/ISO 14001

REPORT SERIES Scientific report	REPORT NO. OR 41/2011	ISBN: 978-82-425-2422-5 (print) 978-82-425-2423-2 (electronic) ISSN: 0807-7207	
DATE 2011-08-12	SIGN. <i>De-Anders Braathen</i>	NO. OF PAGES 48	PRICE NOK 150.-
TITLE Update and Improvement of Dispersion Calculations for Emissions to Air from TCM's Amine Plant Part I-Worst case Nitrosamines and Nitramines		PROJECT LEADER Dag Tønnesen	
		NILU PROJECT NO. O-111077	
AUTHOR(S) Dag Tønnesen		CLASSIFICATION * A	
		CONTRACT REF.	
REPORT PREPARED FOR Technology Centre Mongstad			
ABSTRACT Inert dispersion of a unitary emission has been combined with time dependent air chemistry to provide maximum impact of nitrosamines and nitramines in air and water for emissions from the amine absorber at TCM. The calculations show that worst case impact of nitrosamines and nitramines in air is 5 % of the recommended guideline value. The maximum concentrations in fresh water range from 13 % to 53 % of the guideline depending on the use of absorbent and flue gas. Estimates for a likely case impact show that air concentrations will be a factor of 3 lower than the worst case, while water concentrations will be a factor from 10 to 20 lower than the worst case depending on the type of absorber.			
NORWEGIAN TITLE Oppdaterte og forbedrede spredningsberegninger for utslipp til luft fra TCMs aminanlegg.			
KEYWORDS Atmosphere and Climate	Carbon Capture and Storage	Modelling	
ABSTRACT (in Norwegian) Inert spredning av et enhetsutslipp er kombinert med tidsavhengig luftkjemi for å beregne maksimal belastning i luft og ferskvann for utslipp fra aminabsorber ved TCM. Beregningene for et worst case viser at maksimal belastning av summen av nitrosaminer og nitraminer er 5 % av anbefalt retningslinje for luftkvalitet. Maksimale konsentrasjoner i ferskvann fra utslippet er fra 13 % til 53 % av retningslinjen avhengig av hvilken absorbent som benyttes og hvilken avgass som renses. Effekten av et "likely case" er estimert. Estimert viser at luftkonsentrasjonene blir en faktor 3 lavere enn worst case. Ferskvannkonsentrasjonene blir en faktor fra 10 til 20 lavere enn worst case avhengig av hvilken absorbent som benyttes.			

* Classification
A Unclassified (can be ordered from NILU)
B Restricted distribution
C Classified (not to be distributed)

REFERENCE: O-111077
DATE: AUGUST 2011
ISBN: 978-82-425-2422-5 (print)
978-82-425-2423-2 (electronic)

NILU is an independent, nonprofit institution established in 1969. Through its research NILU increases the understanding of climate change, of the composition of the atmosphere, of air quality and of hazardous substances. Based on its research, NILU markets integrated services and products within analyzing, monitoring and consulting. NILU is concerned with increasing public awareness about climate change and environmental pollution.