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

Part II-Likely case Nitrosamines, Nitramines and  
Formaldehyde

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**Scientific report**



## Preface

Two different capture technologies will be tested at the CO<sub>2</sub> Technology Centre Mongstad (TCM) - the ammonia based technology developed by Alstom and the amine based technology developed by Aker Clean Carbon (ACC). The facility will capture CO<sub>2</sub> 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 CO<sub>2</sub> 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 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 was documented previously (NILU OR 41/2011), established current knowledge on a worst case study for emissions of nitrosamines and nitramines for amine capture technology. In this part, a current knowledge likely case study is described in detail.



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## Summary

*NILU has carried out updated dispersion calculations for emissions from amine based CO<sub>2</sub> capture technology at the CO<sub>2</sub> Technology Centre Mongstad (TCM). The update includes 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. With current best available knowledge, a likely case study shows a ratio 3 to 5 lower sum of concentrations for air and a ratio 16 to 22 lower values for water than in the worst case study. The likely case study shows a maximum impact of 1.5 % of the guideline for air and 3.2 % of the guideline for water.*

This report reports the results of a second phase of a study which includes a detailed modelling of a likely case study of the dispersion of nitrosamines, nitramines and formaldehyde. The first phase was on a worst case study reported in NILU report OR 41/2011. 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 does 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 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 and nitramines, atmospheric chemistry of 2-aminoethanol and health effects of amines and their derivatives associated with CO<sub>2</sub> 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 likely 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. Also shown are the results from the worst case study, and the ratio between the likely case and worst case impacts.

	NIPH guideline value <sup>1</sup>	MEA CHP	Solvent 2 CHP	MEA RFCC	Solvent 2 RFCC
Air, Likely (ng/m <sup>3</sup> )	0.3	0.0022	0.0046	0.0017	0.0035
Water, Likely (ng/l)	4	0.023	0.128	0.027	0.097
Air, Worst (ng/m <sup>3</sup> )	0.3	0.009	0.013	0.008	0.010
Water, Worst (ng/l)	4	0.52	2.1	0.63	1.59
Ratio Air	-	0.24	0.35	0.21	0.35
Ratio Water	-	0.044	0.061	0.043	0.061

<sup>1</sup> Guideline value is covers the combined concentrations of nitrosamines and nitramines

For air concentrations the contribution to the sum is about twice from nitrosamines compared to nitramines, whereas for water, the contribution from the nitramines to the sum is 2 to 8 times higher than nitrosamines.

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. Biodegradation for nitramines in water has been included only in the likely cases for nitramines formed by MEA and other primary amines, but not for other nitramines.

Comparing the impact for the current knowledge likely case with the worst case show that air concentrations are from 1/3 to 1/5 lower than in the likely case than in the worst case. The likely case maximum water concentrations are 16 times lower than the worst case for solvent 2 and 22 times lower for MEA. The maximum impact from the TCM emissions is 1.5 % of the guideline for air and 3.2 % of the guideline for water.

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 CO<sub>2</sub>-fangst for CO<sub>2</sub> 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 til 5 ganger lavere enn "worst case" og at belastningen i vann blir fra 16 til 22 ganger lavere enn "worst case". Samlet maksimal belastning for utslipp fra TCM utgjør 1,5 % av anbefalt retningslinje for luft og 3,2 % av anbefalt retningslinje for vann.*

Denne rapporten inneholder en detaljert beregning av et "likely case" studie for nåværende kunnskap. Hensikten med "worst case" studien, rapportert i NILU OR 41/2011, var å beregne effekt av forholdene for maksimal dannelse og minimal omdannelse av nitrosaminer og nitraminer under gitte utslippsforhold. Beregningene viste at retningslinjene for luft- og vannkvalitet ble overholdt, og utslippene vil 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 "likely 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 utslipps situasjonene. Resultatene fra "worst case" beregningene er også vist, samt forholdet mellom "likely case" og "worst case".

	FHIs anbefalte retningslinje 1)	MEA CHP	Solvent 2 CHP	MEA RFCC	Solvent 2 RFCC
Luft "Likely" (ng/m <sup>3</sup> )	0.3	0.0022	0.0046	0.0017	0.0035
Vann "Likely" (ng/l)	4	0.023	0.128	0.027	0.097
Luft "Worst" (ng/m <sup>3</sup> )	0.3	0.009	0.013	0.008	0.010
Vann "Worst" (ng/l)	4	0.52	2.1	0.63	1.59
Forhold Luft	-	0.24	0.35	0.21	0.35
Forhold Vann	-	0.044	0.061	0.043	0.061

1): Retningslinjen gjelder for sum av nitrosaminer og nitraminer

Bidraget til konsentrasjoner i luft er omtrent dobbelt så stort fra nitrosaminer som fra nitraminer, mens bidraget til konsentrasjoner i vann er fra 2 til 8 ganger større fra nitraminer enn fra nitrosaminer. 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 å være mindre viktig. Biologisk nedbryting av nitraminer i vann er inkludert i "likely case" for de som er dannet fra MEA og metylamin.

En sammenligning av 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 fra 1/3 til 1/5 av "worst case". For konsentrasjoner i vann blir "likely case" 16 ganger lavere enn "worst case" for solvent 2 og 22 ganger lavere for MEA. Samlet maksimal belastning for utslipp fra TCM utgjør 1,5 % av anbefalt retningslinje for luft og 3,2 % av anbefalt retningslinje for vann.

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 II-Likely case Nitrosamines, Nitramines and Formaldehyde

### 1 Introduction

Two different capture technologies will be tested at the CO<sub>2</sub> Technology Centre Mongstad (TCM) - the ammonia based technology developed by Alstom and the amine based technology developed by Aker Clean Carbon (ACC). The facility will capture CO<sub>2</sub> 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 CO<sub>2</sub> per year.

NILU-Norwegian Institute for Air Research 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 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 reports the results of a second phase of a study which includes a detailed modelling of a likely case study of the dispersion of nitrosamines, nitramines and formaldehyde. The first phase was on a worst case study reported in NILU report OR 41/2011. 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 literature 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 Zahlén, 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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)
- Christian Dye, Lise M. B. Fjellsbø, Maria Dusinska: Nitramine analysis procedures development and screening toxicity study . Report for CCM May 2011, restricted distribution.

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<sub>x</sub> 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. The differences in the 3 modelling attempts are further described in table format in Appendix D.

## 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, from "Scope of Work" by TCM with augmentations during the work process.*

Aspect	Worst case	Likely case	Common
<b>Emission estimate from absorber by ACC</b>	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
<b>Components</b>	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 <sub>3</sub> , imines, particulates, aerosols, amides and isocyanates Nitrosamines as a group
<b>Dispersion models</b>	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)
<b>Atmospheric chemistry</b>	Reaction constant k <sub>OH</sub> : 6.5 10 <sup>-11</sup> cm <sup>3</sup> /molecules.s OH concentration: 10.0 10 <sup>5</sup> molecules/cm <sup>3</sup> Max nitrosamine steady state concentration: 1% Negative corrections for liquid and dark chemistry with NO <sub>3</sub> radicals	Reaction constant k <sub>OH</sub> : 4.0 10 <sup>-11</sup> cm <sup>3</sup> /molecules.s OH concentration: 5 10 <sup>5</sup> molecules/cm <sup>3</sup> 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"> <li>• Influence of NO<sub>x</sub> concentration</li> <li>• Influence of Cl atoms</li> <li>• difference 1<sup>ary</sup>, 2<sup>ary</sup>, 3<sup>ary</sup> amines</li> <li>• degradation of nitramines in air from MEA</li> <li>• formation and degradation of nitramines in air from solvent 2</li> <li>• competition for NO<sub>x</sub> with other components than amines</li> </ul>
<b>Deposition</b>	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
<b>Degradation in water</b>	Nitrosamines: <ul style="list-style-type: none"> <li>• Photolysis lifetime: 3 weeks</li> </ul>	Nitrosamines: <ul style="list-style-type: none"> <li>• Photolysis lifetime: 1 week</li> <li>• Biodegradation of nitramines formed from MEA and other primary amines(6)</li> </ul>	Include findings from SINTEF (3) To be discussed explicitly: <ul style="list-style-type: none"> <li>• effects of different soils formation and degradation of nitramines in air from solvent 2</li> </ul>
<b>Guideline values air and water</b>	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 Zahlisen, February 2011,(4):Folkehelseinstituttet (NIPH), March 2011

(5):Selin, March 2011,(6):Dye et al, May 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 %.

## 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
<b>Likely case MEA</b>		
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
<b>Worst case MEA</b>		
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
<b>Likely case solvent 2</b>		
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
<b>Worst case solvent 2</b>		
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 CO<sub>2</sub> 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 cuts 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.

The most important overall assumptions on atmospheric chemistry are:

- Secondary and tertiary amines form nitrosamines in the atmosphere with  $\text{NO}_x$  through OH-radicals and  $\text{NO}_3$  radicals.
- Primary amines do not form nitrosamines in the atmosphere with  $\text{NO}_x$
- All amines form nitramines in the atmosphere with  $\text{NO}_x$

### 2.3 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  $\text{ng/m}^3$  in air
- 4  $\text{ng/l}$  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 the dispersion modelling tool 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).

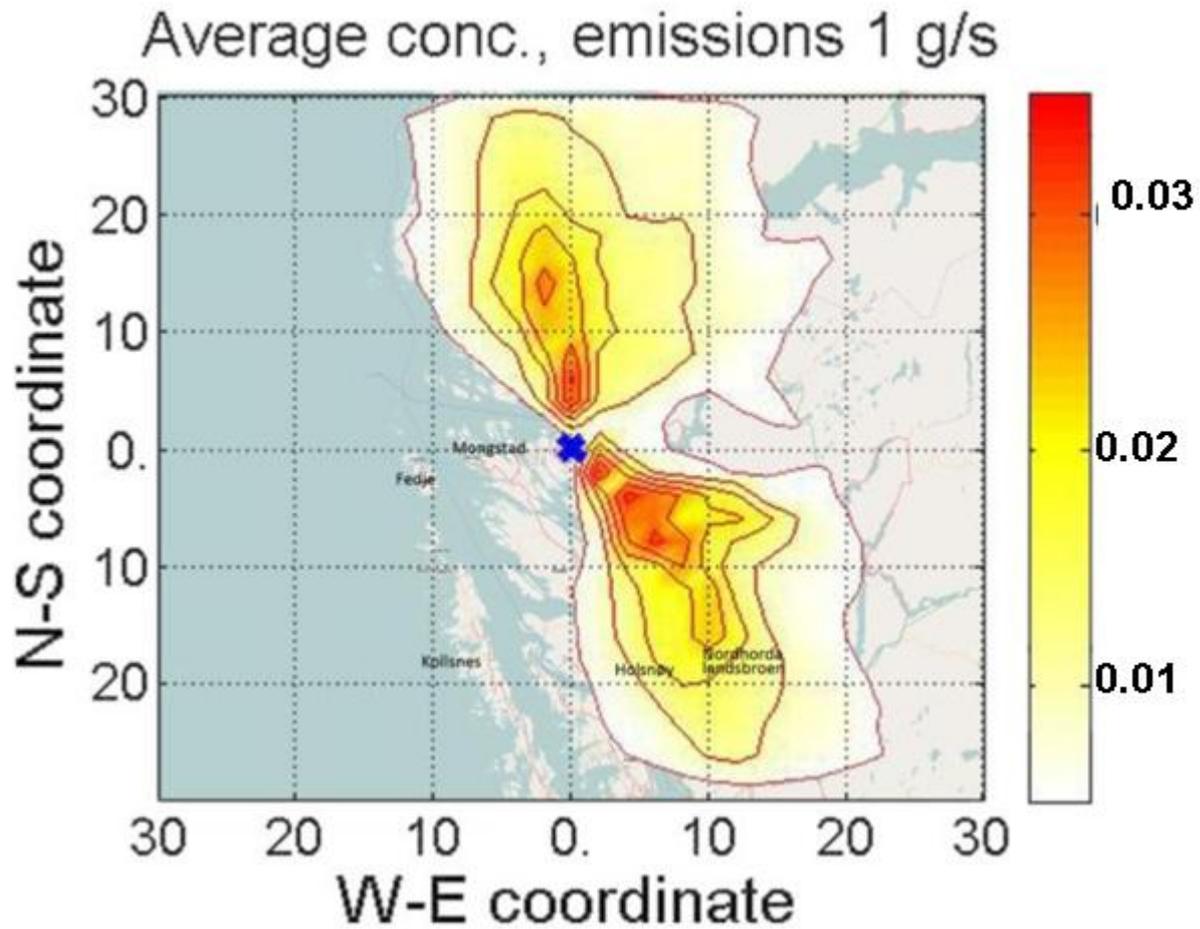


Figure 1: Yearly average concentrations ( $\mu\text{g}/\text{m}^3$ ) from a unitary inert emission of 1 g/s from the TCM absorber (CHP case). Maximum ground level impact is  $0.03 \mu\text{g}/\text{m}^3$ .

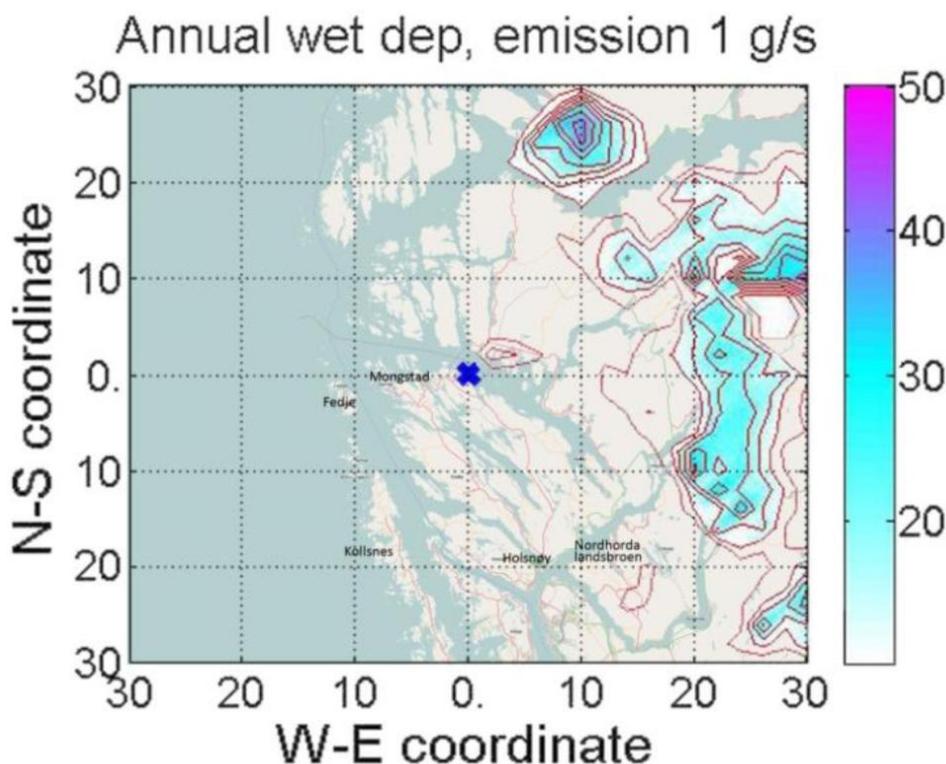


Figure 2: Yearly wet deposition ( $\text{mg}/\text{m}^2/\text{yr}$ ) from a unitary emission of 1 g/s through the TCM absorber (CHP-case), applying sulphur chemistry. Maximum deposition  $39 \text{ mg}/\text{m}^2/\text{yr}$ .

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.

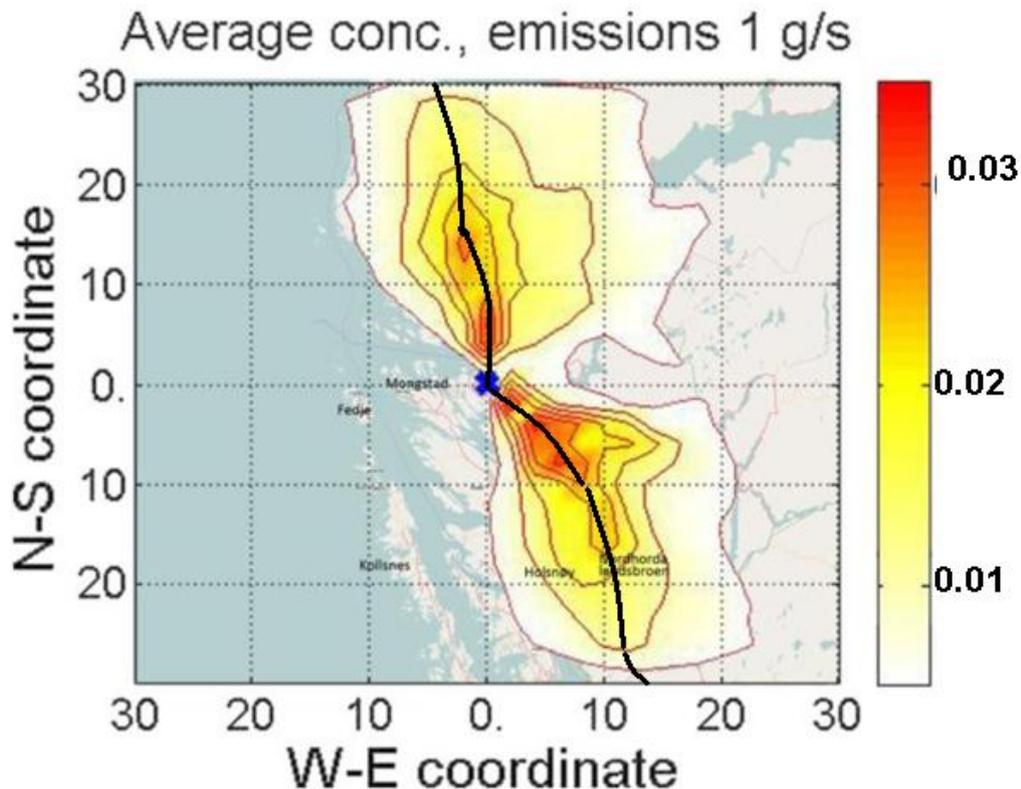


Figure 3: Pathways of minimum dispersion towards north and southeast.

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  $10 \text{ ng/m}^3$  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 <sup>3</sup>	(from max) 5.4	6	5.7	80.6
Southeast 10 ng/m <sup>3</sup>	(from max) 4.4	3.9	4.15	111
Wet Deposition Max	(from centre) 4.6	4.6	4.6	115

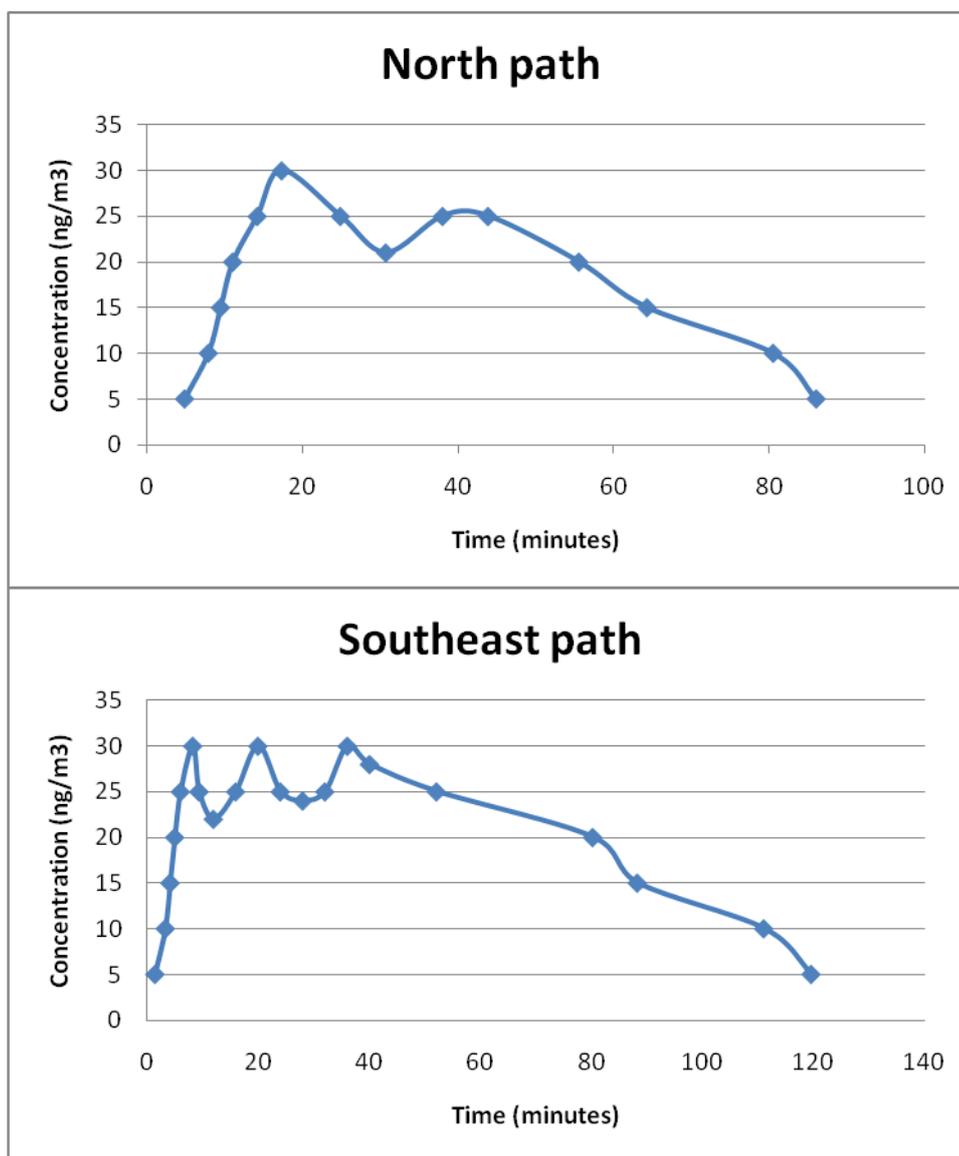


Figure 4: Concentration in north and south east paths of a unitary inert emission of 1 g/s as function of time spent after emission. The paths are along the minimum dispersion.

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. Figure 5 show the effect of the different assumptions for reactions in the atmosphere for the worst case and the likely case.

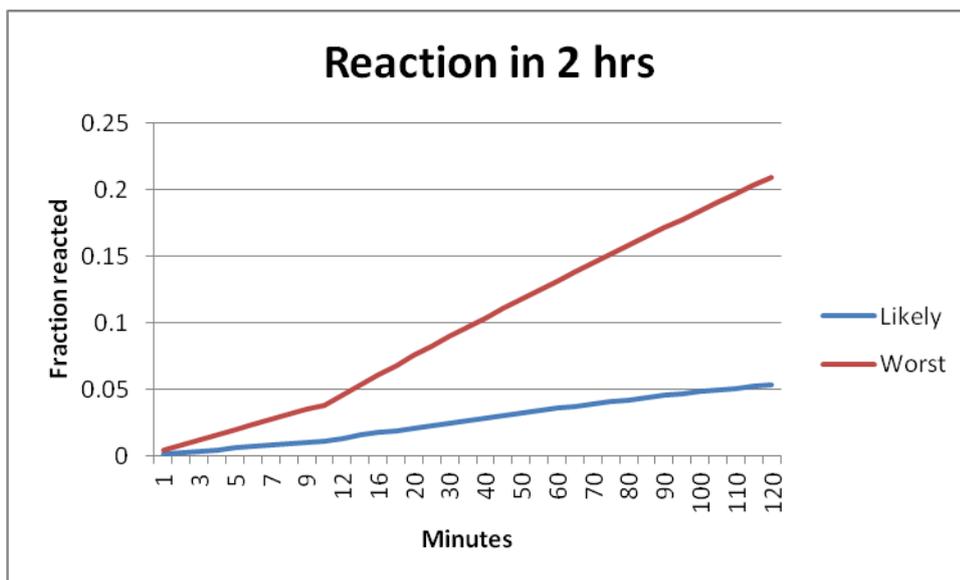


Figure 5: The fraction of reacting emissions that have been able to react with OH within the first 2 hours of atmospheric transport, given worst case and likely case assumptions of reaction constant and OH-concentration.

##### 4.1 Likely case for nitrosamines

The ADA 2010 report clearly recommends the use of steady state calculations for nitrosamines in air, worst case concentration of 1 % and likely case 0.2 % 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 NO<sub>3</sub> 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 NO<sub>3</sub> concentrations. For clean marine air, the level before sunrise is given as 10 ppt.

In Ge et al. (2010), reaction constants for NO<sub>3</sub> towards trimethylamine and two amides are given, the constants range from  $5 \times 10^{-16}$  to  $5 \times 10^{-14}$ . Comparing the reaction constants and the concentration levels of OH and NO<sub>3</sub> indicate that the NO<sub>3</sub> reaction would be at least 10 times less efficient in forming nitrosamines than the OH reaction. In the likely case calculations, a formation of nitrosamines by NO<sub>3</sub> during night has been set at 1/10 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, photolysis reduction of recently formed nitrosamines	Formation by NO <sub>3</sub> reaction at 1/10 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.

One known effect have been omitted from these calculations, in order to simplify the calculation and because the concentration level at the initial plume height is

unknown. 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 NO<sub>2</sub> and no OH would be present in the plume until that has happened, because the oxidizing of NO would consume all the present O<sub>3</sub>.

Due to the extra dilution before the reactions will start, and due to the fact that photolysis will start immediately, the omission of this effect will contribute to an overestimation of the impact of nitrosamines.

The results of the calculations of transformation and reduction are shown in Table 5 in the unit mg/s, and Figure 6 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. A comparison of worst case and likely case nitrosamines after 100 minutes of transport in air is shown in Figure 7.

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 in the likely case 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 <sup>1</sup>	0	0.00000 3	0.00000 4	0.00000 5	0.00000 6	0.00000 8
	Nitrosamines	0.091	0.091	0.091	0.091	0.091	0.091
	Sum	0.091	0.091	0.091	0.091	0.091	0.091
	Amines <sup>1</sup>	0	0.00003	0.00004	0.00005	0.00007	0.00008
	Nitrosamines	0.091	0.027	0.0083	0.0025	0.0002	0.0009
	Sum	0.091	0.027	0.0083	0.0025	0.0003	0.00017
	Average sum	0.091	0.059	0.050	0.047	0.046	0.046
Solvent 2 CHP	Amines <sup>1</sup>	0	0.00002	0.00003	0.00004	0.00005	0.00006
	Nitrosamines	0.181	0.181	0.181	0.181	0.181	0.181
	Sum	0.181	0.181	0.181	0.181	0.1811	0.1811
	Amines <sup>1</sup>	0	0.00024	0.00033	0.00041	0.00045	0.0006
	Nitrosamines	0.181	0.0545	0.0164	0.0049	0.0004	0.0002
	Sum	0.181	0.0548	0.0167	0.0054	0.001	0.0008
	Average sum	0.181	0.118	0.099	0.093	0.091	0.091
MEA RFCC	Amines <sup>1</sup>	0	0.00000 5	0.00000 6	0.00000 8	0.00001	0.00001
	Nitrosamines	0.069	0.069	0.069	0.069	0.069	0.069
	Sum	0.069	0.069	0.069	0.069	0.069	0.069
	Amines <sup>1</sup>	0	0.00005	0.00006	0.00008	0.00011	0.00012
	Nitrosamines	0.069	0.021	0.00063	0.0002	0.00017	0.00007
	Sum	0.069	0.021	0.00063	0.0002	0.00028	0.00018
	Average sum	0.069	0.045	0.038	0.035	0.035	0.035
Solvent 2 RFCC	Amines <sup>1</sup>	0	0.00001 8	0.00002 5	0.00003 1	0.00004 1	0.00004 5
	Nitrosamines	0.138	0.138	0.138	0.138	0.138	0.138
	Sum	0.138	0.138	0.138	0.138	0.138	0.138
	Amines <sup>1</sup>	0	0.00018	0.00025	0.00031	0.00041	0.00045
	Nitrosamines	0.138	0.0416	0.0125	0.0038	0.0003	0.0001
	Sum	0.138	0.0417	0.0128	0.004	0.00075	0.00059
	Average sum	0.138	0.0899	0.0754	0.071	0.069	0.069

1: sum of secondary and tertiary amines

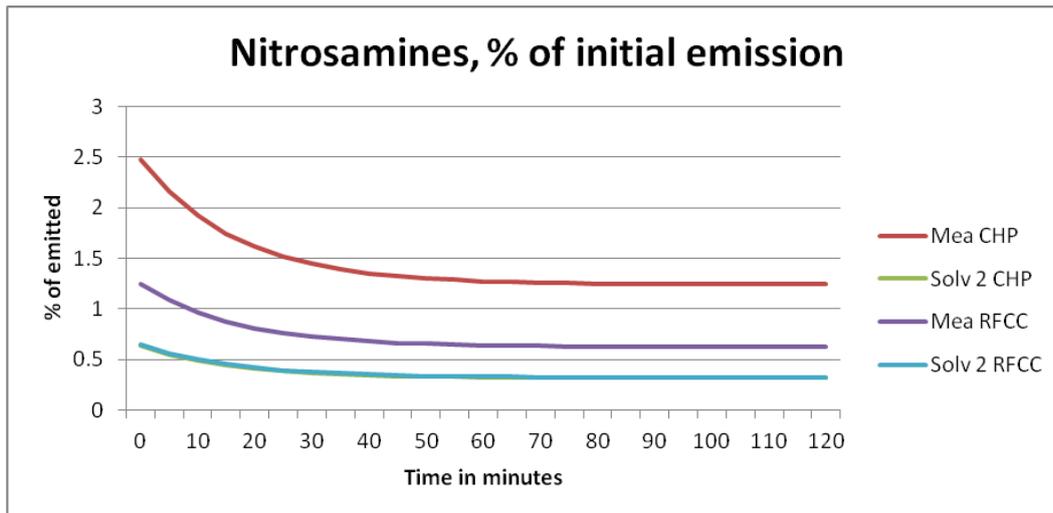


Figure 6: Time dependent part of the emissions that remain as or have reacted to nitrosamines for night and day conditions. Unit % of amines (secondary and tertiary) and nitrosamines emitted. The curve for solvent 2 CHP is covered by the curve for solvent 2 RFCC.

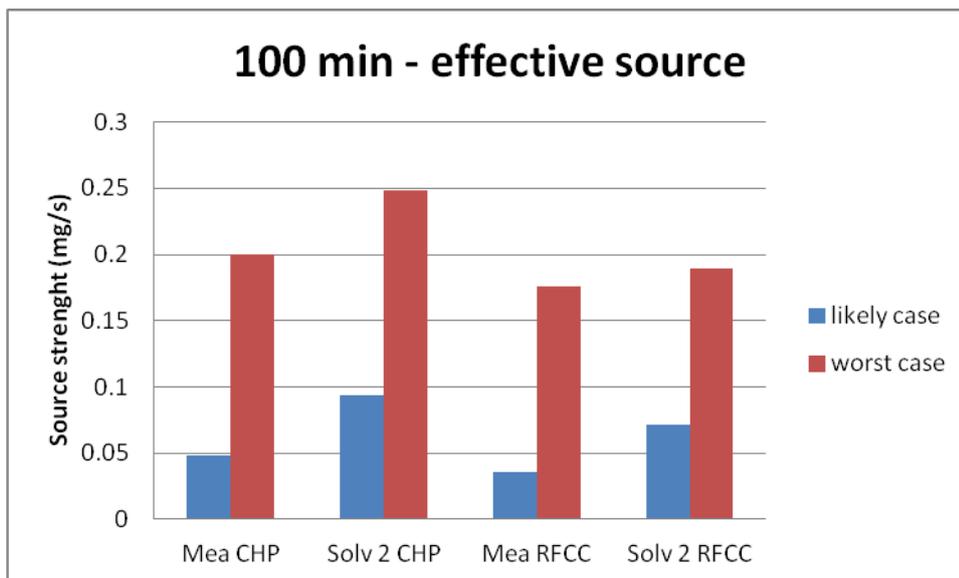


Figure 7: Source strength (mg/s) of the initial emissions of nitrosamines or nitrosamine forming components that would be present as nitrosamines after 100 minutes advection and reactions in the atmosphere. Comparison of worst case and likely case.

The combined effect of atmospheric dispersion and chemical reactions for the two paths of minimum dispersion is shown in Figure 8. The maximum impact as a yearly average value (the highest concentration from Figure 8) is  $0.0044 \text{ ng/m}^3$ , occurring along the southeast path with Solvent 2 used together with CHP flue gas. Figure 8 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.

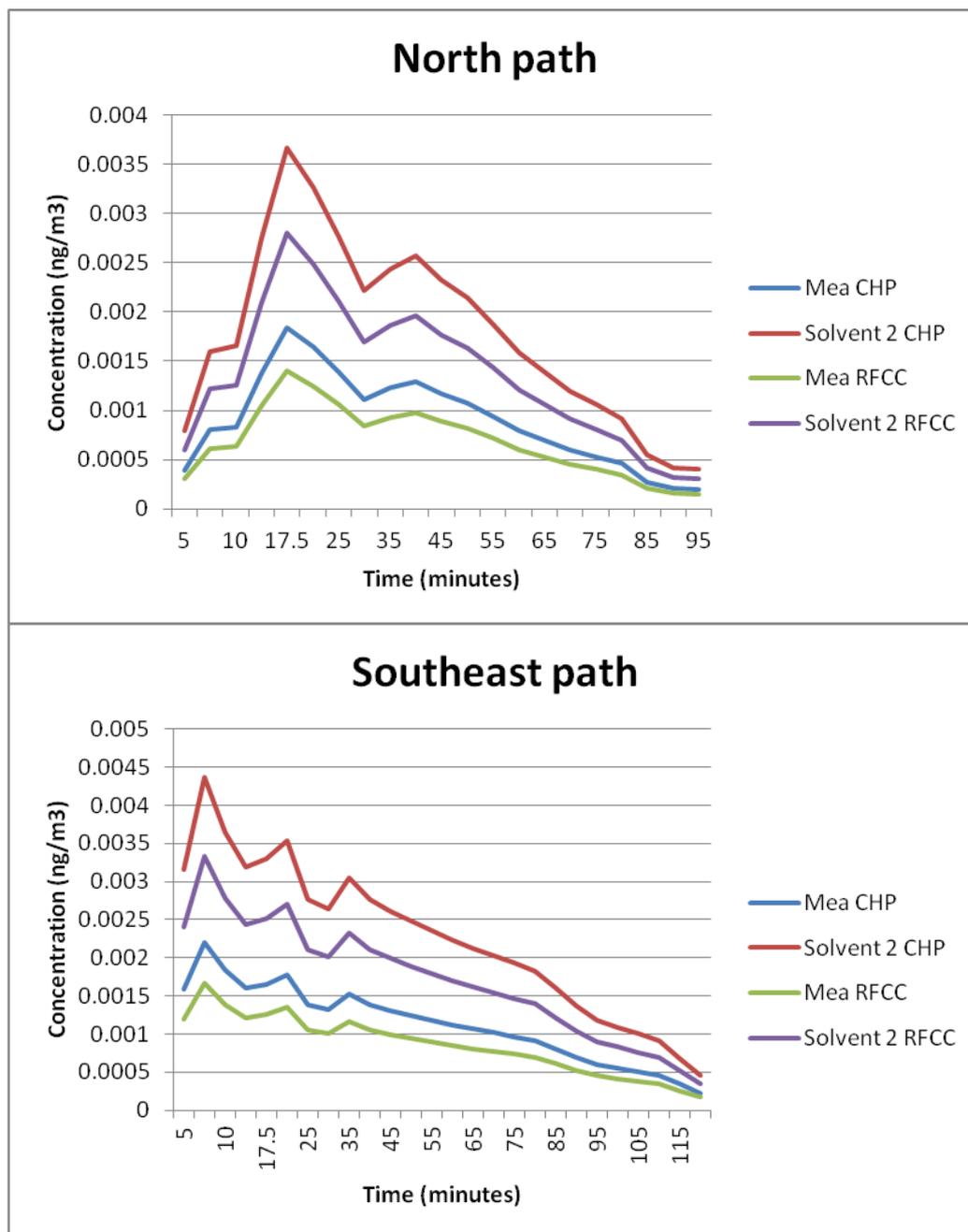


Figure 8: Nitrosamine concentration along the two paths of minimum dispersion as function of time spent after emission for the 4 emission scenarios in the likely case.

#### 4.2 Likely 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 (NO<sub>3</sub>) 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. The yields presented in the table are mass conversion yields, and are the same as in the worst case calculations, but the actual formation is less due to less conservatism in the estimates for reaction constants and OH-concentration.

*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 the nitrosamine fraction is larger than the nitramine fraction in all the emission scenarios. A comparison between worst case and likely case nitramine formation is shown in both Table 7 Figure 9. Comparing the formations after 100 minutes for nitrosamines and nitramines show that the reduction from worst case to likely case is larger for the nitramines than the nitrosamines.

Table 7: Nitramine formation from the original emissions, given as mg/s, for different travel times from the emission. The worst case study results are shown for comparison (shaded background).

Scenario	Emission	20 min	40 min	60 min	100 min	115 min
MEA CHP	24.9 <sup>1</sup>	0.0033	0.0045	0.0057	0.0076	0.0083
worst case	133.2	0.0438	0.0604	0.0756	0.1071	0.1181
Solvent 2 CHP	91.6	0.021	0.028	0.035	0.048	0.052
worst case	226.0	0.1886	0.2601	0.3294	0.4616	0.5091
MEA RFCC	22.4 <sup>1</sup>	0.0041	0.0055	0.0069	0.0093	0.010
worst case	115.0	0.0547	0.0755	0.0956	0.1340	0.1477
Solvent 2 RFCC	69.6	0.016	0.022	0.027	0.036	0.039
worst case	171.6	0.1433	0.1976	0.2502	0.3506	0.3867

1: Sum of amines including MEA

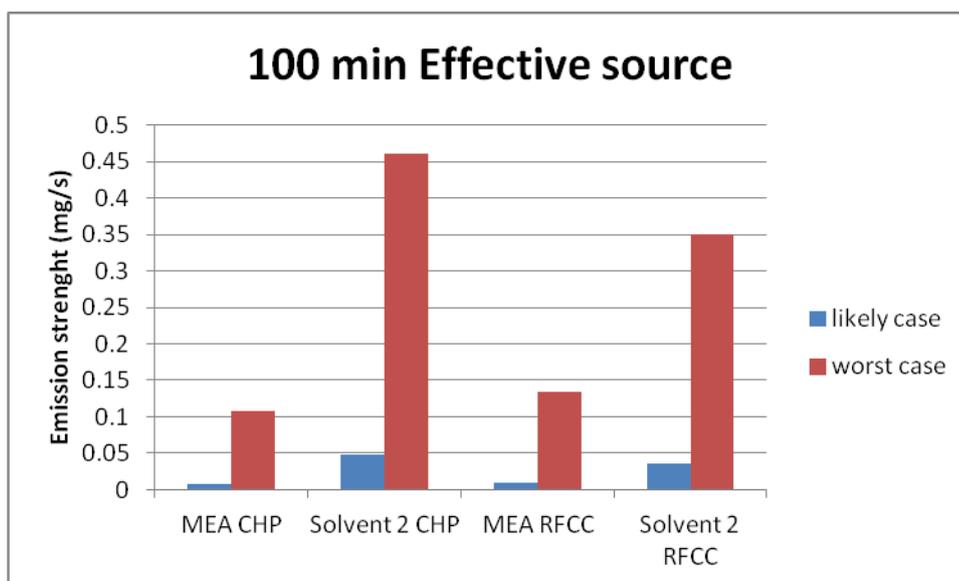


Figure 9 : Source strength (mg/s) of the initial emissions of nitramine forming components that would be present as nitramines after 100 minutes advection and reactions in the atmosphere. Comparison of worst case and likely case.

The combination of dispersion and chemistry for the paths of minimum dispersion, corresponding to those previously shown for nitrosamines, are shown in Figure 10 . 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.

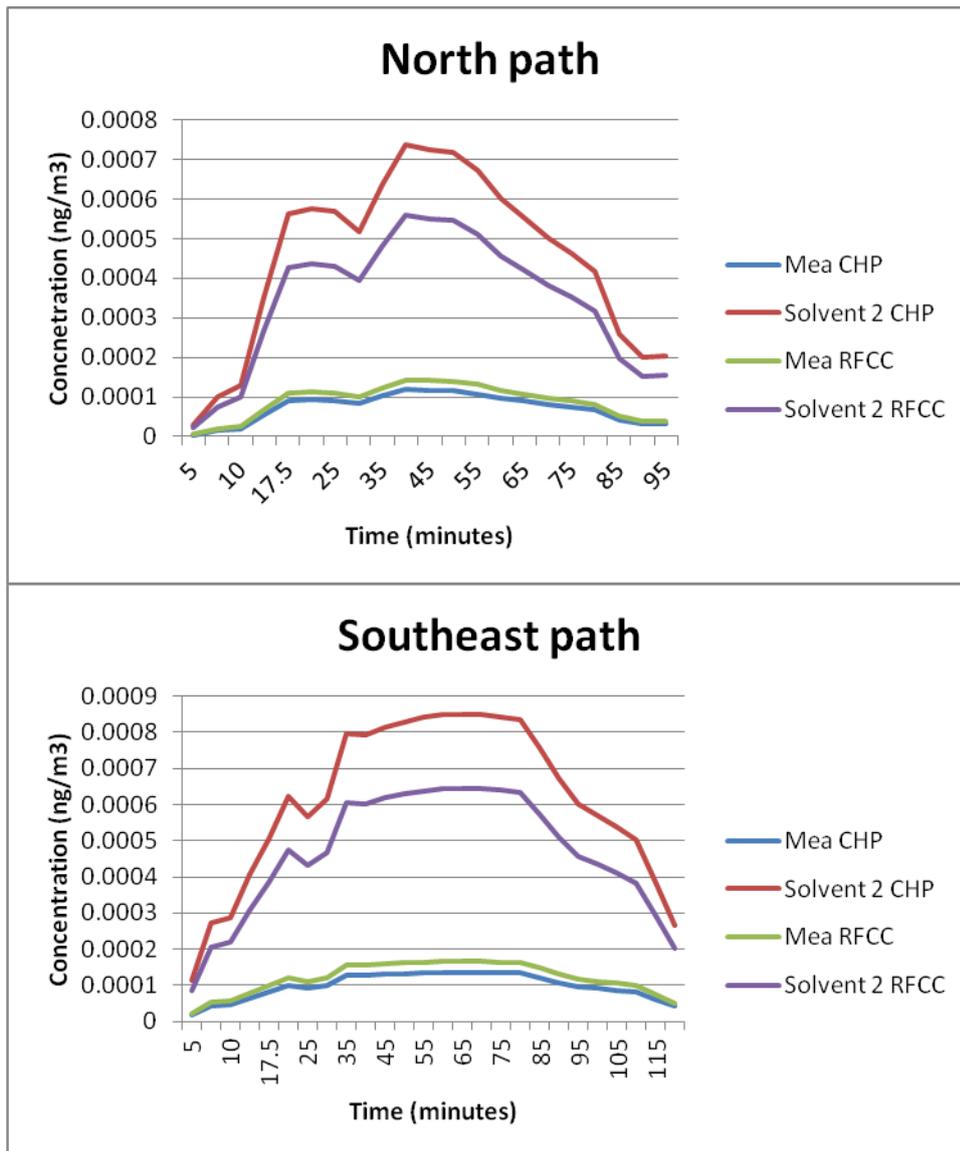


Figure 10: Nitramine concentrations along the paths of minimum dispersion as function of time spent after emission

#### 4.3 Total likely case air concentrations of nitramines and nitrosamines

In order to compare the maximum impact from the emissions with the air quality guideline value ( $0.3 \text{ ng/m}^3$  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 11. The likely case maximum concentration in air is  $0.0046 \text{ ng/m}^3$  for the sum of the two components. This is less than 2 % 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. The corresponding results from the worst case study are shown for comparison.

Table 8: Maximum air concentration ( $\text{ng}/\text{m}^3$ ) of nitrosamines and nitramines for the four emission scenarios. Worst case results are shown on shaded background.

Scenario	MEA CHP	Solvent 2 CHP	MEA RFCC	Solvent 2 RFCC
Nitrosamines L	0.0022	0.0045	0.0016	0.0033
Nitrosamines W	0.0089	0.055	0.0069	0.0042
Nitramines L	0.00014	0.00085	0.00017	0.00065
Nitramines W	0.0019	0.0080	0.0023	0.0062
Both components L	0.0022	0.0046	0.0017	0.0035
Both components W	0.009	0.013	0.008	0.010

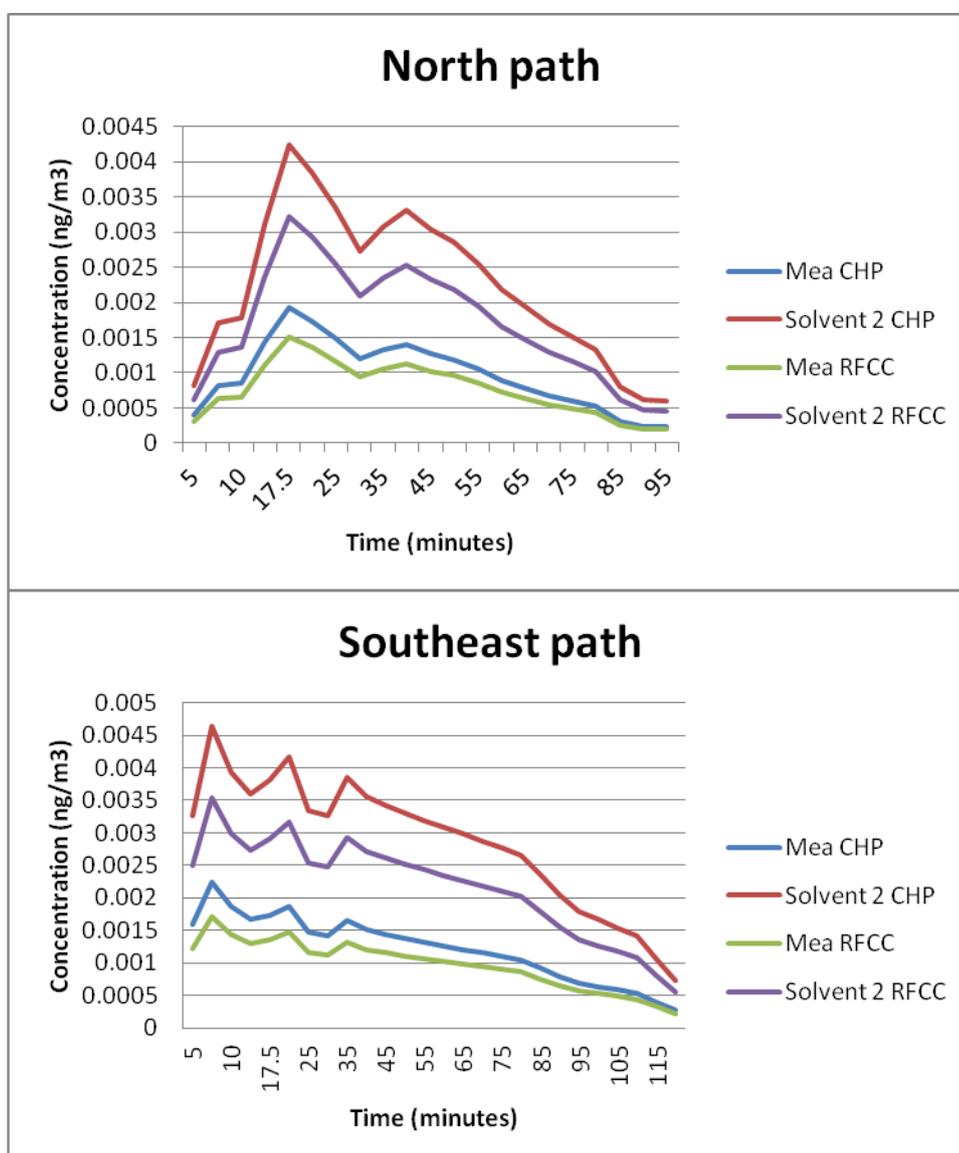


Figure 11: Sum of nitrosamine and nitramine concentrations for the paths of minimum dispersion as function of time spent after emission.

To illustrate the effect of air chemistry versus inert dispersion, the solvent 2 CHP emission with chemistry is shown in Figure 12 together with a dispersion curve for inert dispersion of primary and secondary amines in the same emission scenario.

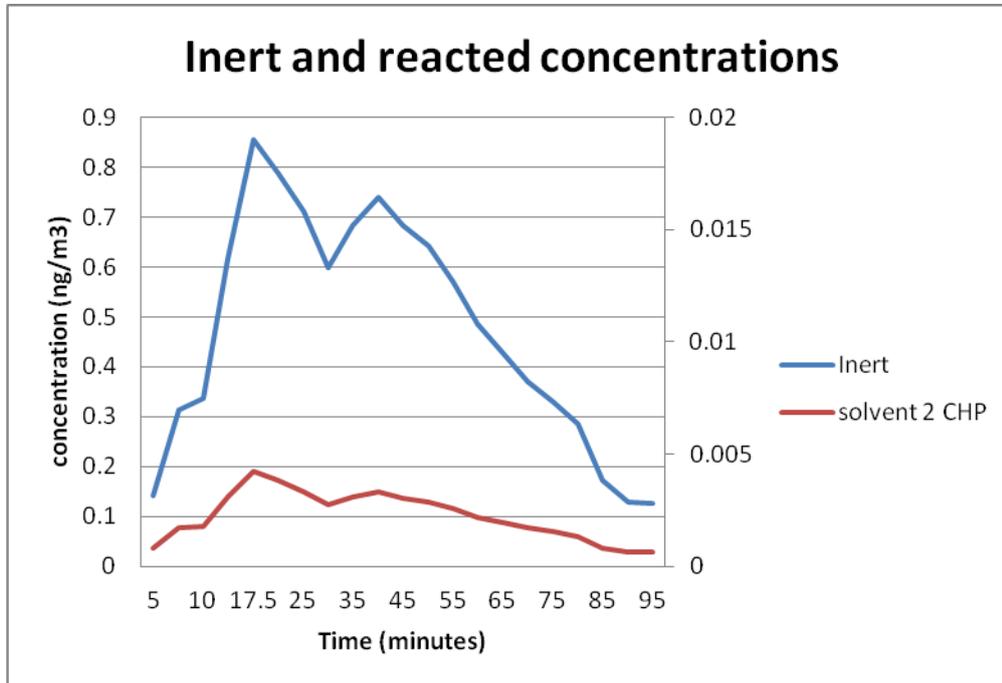


Figure 12: Inert dispersion (left axis) and concentrations of nitramines and nitrosamines after air chemistry is applied (right axis) along the North path for minimum dispersion

## 5 Nitrosamines and nitramines in fresh water

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 km<sup>2</sup> and 28 km<sup>2</sup>) and runoff (83.1 Mm<sup>3</sup>/yr and 79.9 Mm<sup>3</sup>/yr) for these catchment areas can be found at [www.nve.no](http://www.nve.no). The model wet deposition maximum from a unitary emission is 39 mg/m<sup>2</sup>/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. Comparison of the model precipitation with measured precipitation regarding amount and frequency indicate that the model overestimate deposition by 30 % (M. Karl et al., 2011). For these likely case calculations, the deposition has been scaled down by a factor of 0.7 to correct this overestimate.

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 2.8 µg/l (as compares to 4.0 µg/l in the worst case study) 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. The results from the worst case study are shown in the 2<sup>nd</sup> half of the table for comparison.

*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	0.0456	0.0083	0.128	0.023
Solvent 2 CHP	0.0909	0.0517	0.255	0.145
MEA RFCC	0.0346	0.0101	0.097	0.028
Solvent 2 RFCC	0.0693	0.03925	0.194	0.110
Worst case				
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 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. As the biodegradation varies with different species of nitrosamines, and as its effect is minor, it is not considered in these calculations.

For nitramines, there is recent documentation of biodegradation in fresh water for the components formed from MEA and methylamine (C. Dye et al., 2011). Results from studies of biodegradation of nitramines show that none are readily biodegradable, but nitramines formed from MEA and methylamine show 33 % reduction over a period of 28 days. This can be transformed into a reduction of the yearly average concentration in water to 15 % of the input concentration value for the nitrosamines formed from MEA and other primary amines. The distribution between MEA and primary, secondary and tertiary amines in the emission scenarios will have different yields for forming nitramines, and the formation

products of secondary and tertiary amines are assumed for the time being not to be reduced by biodegradation. In Table 10, the effect of this partial biodegradation is summarized.

The first row shows the different emission of nitramine forming components for the different emission scenarios.

The second row show how much of the initial emission that will react to nitramines as time approaches eternity.

The third row show how much of the amount in the second row that originated from secondary and tertiary amines (and will not be subject to biodegradation).

The fourth row show how much of the amount in the second row that originated from MEA and other primary amines. This part of the nitramines will be subject to biodegradation.

The fifth row show the sum of the third row (non-degradation) and the remaining part of the fourth row after reduction to 15 % of the original value due to biodegradation.

The last row, which is the reduction factor due to partial biodegradation of nitrosamines, is the ratio between the fifth and the second row in the table.

*Table 10: Biodegradation of nitramines in fresh water for the 4 emission scenarios. Unit mg/s except for reduction factor.*

	MEA CHP	Solvent 2 CHP	MEA RFCC	Solvent 2 RFCC
Capacity emission	24.9	91.7	22.4	69.6
Corrected for yield	0.156	0.974	0.190	0.740
Persistent	0.091	0.721	0.138	0.548
Degradable	0.065	0.253	0.052	0.192
Remain	0.101	0.760	0.146	0.577
Reduction factor	0.646	0.780	0.766	0.780

The likely case concentrations in fresh water for total nitrosamines and nitramines have higher contribution from the nitramines, 2 times higher for MEA scenarios and 8 times higher for Solvent 2 scenarios. All the scenarios are well below the guideline value of 4 ng/l proposed by NIPH. The results are shown in Table 11.

Table 11: Likely case (**L**) concentrations of nitrosamines and nitramines in the most exposed fresh water reservoir around Mongstad (ng/l). Worst case (**W**) calculations are also shown for reference.

Scenario	MEA CHP	Solv 2 CHP	MEA RFCC	Solv 2 RFCC
Nitrosamines L	0.008	0.015	0.006	0.011
Nitramines L	0.015	0.113	0.021	0.086
Total load <b>L</b> (ng/l)	<b>0.023</b>	<b>0.128</b>	<b>0.027</b>	<b>0.097</b>
Nitrosamines W	0.048	0.042	0.042	0.047
Nitramines W	0.472	2.036	0.591	1.547
Total load <b>W</b> (ng/l)	<b>0.52</b>	<b>2.1</b>	<b>0.63</b>	<b>1.59</b>

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

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

A calculation of how much the emissions in the different likely case scenarios in Table 2 can increase before the concentration of nitrosamines and nitramines in air reach  $0.3 \text{ ng/m}^3$  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 12.

Table 12: 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 $0.3 \text{ ng/m}^3$	136	65	176	85
Factor to reach 4 ng/l	173	31	148	41

The factors given in Table 12 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, and the degradability in water is different for different nitramines. 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 Formaldehyde

Formaldehyde is emitted directly from the scrubber, and will be formed as a reaction product (primarily from MEA). 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 only Norwegian limit value for formaldehyde in air is the administrative norm for working conditions, which is  $600 \mu\text{g}/\text{m}^3$  for an 8 hour averaging time.

The maximum one hour average concentrations from direct emissions of formaldehyde will be  $1.2 \mu\text{g}/\text{m}^3$ , and occur at approximately 500 m distance from the stack. Assuming that there would be no dilution beyond this point until all the components in the emission would have time to react into formaldehyde, or that all components that can form formaldehydes have reacted within 10 minutes after the release, the concentration would reach only  $2.9 \mu\text{g}/\text{m}^3$  for the most potent emission (Worst case MEA CHP) for formaldehyde formation. Even for these totally unrealistic assumptions, the impact is only 0.5 % of the limit value, and less than 6 times the background value ( $0.5$  to  $1.5 \mu\text{g}/\text{m}^3$ ). Thus, emissions of and formation of formaldehyde from TCM is of low importance regarding environmental impact.

## 8 Discussion

### 8.1 Processes not included in calculations

#### 8.1.1 Influence of $\text{NO}_x$ concentration

According to the conclusions in ADA 2010 (Nielsen et. al. 2011) the level of  $\text{NO}_x$  and the balance between NO and  $\text{NO}_2$  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  $\text{NO}_x$ ) would give from 3 to 5 times more nitrosamines and nitramines than a rural scenario (0.2 – 10 ppb  $\text{NO}_x$ ). The formations for rural conditions have been applied here because they are the predominant conditions around TCM.

#### 8.1.2 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  $1 \times 10^3$  and  $2 \times 10^3$  atom  $\text{cm}^{-3}$  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.

### **8.1.3 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 isocyanic 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.

## **8.2 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 8.1.1. 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.

## **8.3 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.

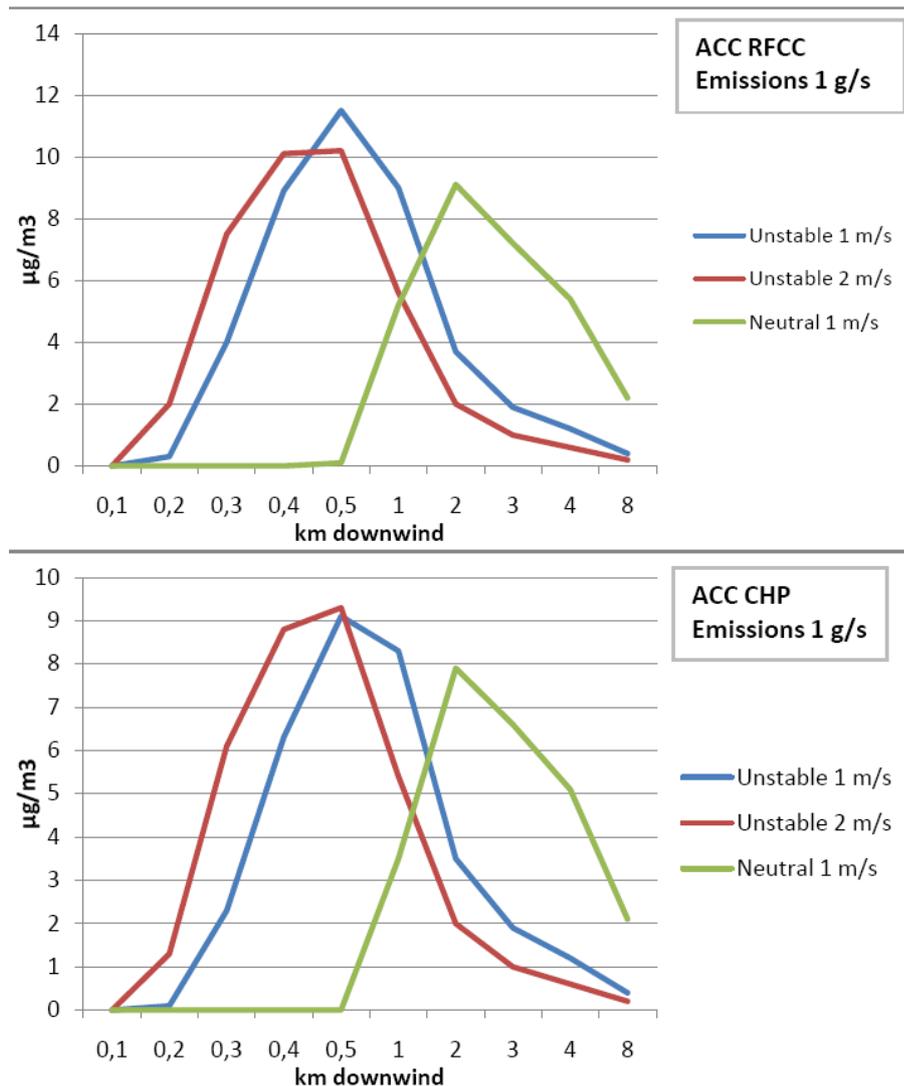


Figure 13: Maximum one hour ground level concentrations from a unitary emission through the TCM absorber from CONCX. Maximum ground level impact,  $\mu\text{g}/\text{m}^3$ .

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.

#### 8.4 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 13. It shows the gradual improvement in the underlying information and the calculations and models and results over the years.

Table 13: Comparison of different aspects in dispersion calculations made by NILU for TCM.

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

More information regarding the modelling of emissions from the amine plant is given in Appendix D.

## 9 Conclusions

The second phase of the update of dispersion modelling for the emissions from TCM's amine plant is reported. This second phase discusses a likely case while the first phase discussed a worst case. 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 likely case assumptions regarding emissions, chemistry and deposition and compared with a previous worst case study.

The likely 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 14 below show that the guideline for air concentrations of 0.3 ng/m<sup>3</sup> and the guideline for drinking water of 4 ng/l is upheld with good margins.

Table 14: 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 <sup>3</sup> )	0.3	0.0022	0.0046	0.0017	0.0035	
Water (ng/l)	4	0.023	0.128	0.027	0.097	

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

## 10 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<sub>x</sub>: Nitrogen oxides

OH: Hydroxyl radical

RFCC: Residue Fluid Catalytic Cracker

TAPM: The Air Pollution Model

TCM: Technology Centre Mongstad

TOR: Tropospheric Ozone Research

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# **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"
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".eur"	2	1000000	25	-360000	25	-120000	""
""	0	1	25	1	30000	"master"	""
""	"t300a"	0	30000	25	-360000	""	""

""	"t100a"	1	-360000	25	"inline"	""	""
""	"t030a"	0	1	30000	""	""	""
"vege.aus"	"t010a"	0	25	-360000	""	""	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
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""	""	""	1	1000	1	25	300
""	""	""	25	-12000	25	1000	-3600
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25	3000	1	25	"master"	""	""	""
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-120000	1	25	-36000	""	""	""	""
1	25	3000	"inline"	""	""	""	1
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25	3000	"inline"	""	""	""	25	25
10000	-36000	""	""	""	1	25	300
-120000	"master"	""	""	""	25	1000	-3600
"inline"	""	""	""	1	25	-12000	1
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1	25	3000	1	1000	"inline"	""	""

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25	300	3	#TRUE#				
25	-3600	5	#TRUE#				
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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					
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""	""	-1000					
""	""	0					
""	""	"Site 2"					
""	""	1000					

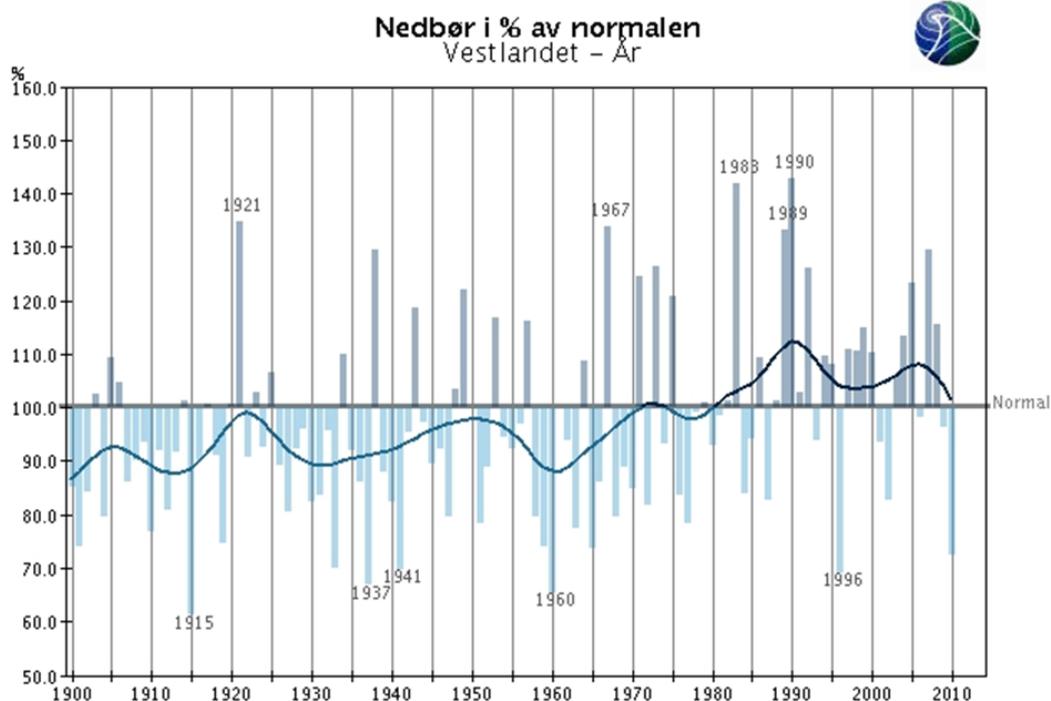


## **Appendix B**

### **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](http://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.*

	<b>2001-2010</b>	<b>2007</b>
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
<b>Scenario 1 - Expected (MEA likely case)</b>		
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
<b>Scenario 3 - Worst case (MEA worst case)</b>		
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

## **Appendix D**

### **Differences in modeling 2008-2010-2011**



Amine plant		2008	2010	2011									
UNIT		Worst case scenario for MEA, no reaction products considered, nor any other amines in the emission	Worst case dispersion and chemistry, 5 different emission scenarios for two fluegases, nitrosamine formation considered, many different components in the emission	Worst case dispersion and chemistry, 2 different emission scenarios for two fluegases, nitrosamine and nitramine formation considered for grouped components in the emission									
<b>CASE MEA</b>													
<b>INPUT</b>													
Volume flow flue gas	m <sup>3</sup> /s	12.4	17.7	17.7									
Stack height	m	51	65	65									
Operation hours	h/year	8760	8760	8760									
Emission profile: Type of amine concentrations (ppmv and g/s) and sum of directly emitted nitrosamines (ppmv and g/s) giving the highest calculated max impact concentration		MEA-worst case, feed gas not defined											
		MEA-worst case, CHP											
		MEA	other prim. amines	sec. and tert. amines	Nitrosamines	Other?	MEA	other prim. amines	sec. and tert. amines	Nitrosamines	Formaldehyd		
	ppmv	ND	ND	ND	ND	ND	3	NC	3	*	*	0.006	
	g/s	0.1	0	0	0.07	0.123	NC	0.0346	4E-04	0.12	0.0021	0.008	0.0004
Amine Chemistry (short description related to formation and degradation, time dependent formation etc.)		No degradation of initial emission of nitrosamines, instant yields of 2 % and 10 % form potentially forming components											
Nitrosamine yield	%	10 % instantaneous											
Nitramine yield	%	Not considered											
Weather data	year	1991-1992											
<b>DISPERSION MODEL</b>		CONCX, CONDEP and INPUFF											
Type of model		CONCX and TAPM											
Any change of model parameters?		No											
<b>RESULTS - AIR</b>		Input for hourly max changed											
Unit emission (1 g/s) - basis for scaling:													
Max annual average ground level													
- Concentration	ng/m3	2.40											
- Distance from stack	km	0.6											
- Direction relative to stack		North											
Dilution factor		0.37											
Calculated max annual average nitrosamine concentration	ng/m3	1.88											
Calculated max annual average nitrosamine + nitramine concentration	ng/m3	Not considered											
H&E guideline value in air	ng/m3	Not considered											
		0.07 for nitrosamines and nitramines											
		0.3 for sum of nitrosamines and nitramines											
		2 % of the reacted components											
		Dependent on amine, from 0.3 % to 5 %											
		2007 model data											
		CONCX and TAPM											
		No											
		Photolytic reduction of initial emission of nitrosamines, yield of 2 % based on time dependent reaction with OH for day conditions. During night no degradation of nitrosamines, and night radical yield 1/5 of daytime											

RESULTS - WATER							
Unit emission (1 g/s) - basis for scaling: Max annual average wet deposition							
- Deposition	mg/(m <sup>2</sup> year)	2.1			39		
- Distance from stack	km	20			27		
- Direction relative to stack		North west			Noth-northwest		
Assumptions		Rain frequency as observed in the meteorological input measurements, amines 100% removed by wet deposition, no degradation through soil/vegetation surfaces		Rain frequency as determined by the meteorological model data, amines 100% removed by wet deposition, no degradation through soil/vegetation surfaces		Rain frequency as determined by the meteorological model data, amines 100% removed by wet deposition, no degradation through soil/vegetation surfaces	
Annual rainfall in Mongstad area	V(m <sup>2</sup> year)	1402			1860		1860
Catchment area		Not considered			49 km <sup>2</sup> total		49 km <sup>2</sup> total
Dilution factor from rain water to drinking water		Not considered			5		5
Drinking water concentration corresponding to unit emission rate 1 g/s (basis for scaling)	µg/l	Not considered			4 µg/l		4 µg/l
Degradation in drinking water:		Not considered		Calculations for no degradation of nitrosamines and degradation of nitrosamines in water made, nitramines not considered		Nitrosamine degradation through photolysis. No degradation of nitramines	
- Biodegradation (nitrosamines)	days	Not considered			Combined lifetime (e-folding) 10.2		initially considered, but omitted
- Photolysis (nitrosamins)	weeks	Not considered			Included in factor above		e-folding time 3 weeks
Calculated max annual average concentration of nitrosamines in drinking water	ng/l	Not considered			0.16 for degradation, 15 without		0.047
Calculated max annual average concentration of nitrosamines and nitramines in drinking water	ng/l	Not considered					0.63 (from RFCC flue gas)
H&E guideline value in water	ng/l	Not considered			0.7		4



REFERENCE: O-111077  
DATE: NOVEMBER 2011  
ISBN: 978-82-425-2444-7 (print)  
978-82-425-2445-4 (electronic)

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