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CO2 Technology Centre Mongstad – updated air dispersion calculations

Update of OR 12/2008

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Norsk institutt for luftforskning
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NILU

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Summary

The CO2 Technology Centre Mongstad has given the Norwegian Institute for Air Research (NILU) the task of calculating and assessing the dispersion of emissions to air of carbon dioxide (CO_2), nitrogen oxides (NO_X), ammonia (NH_3), amines and amine degradation products from activities at CO2 Technology Centre Mongstad (TCM). This is an update of the report "Test Centre Mongstad, Dispersion calculations for emissions to air from Test Centre Mongstad (TCM)" (Berglen et al., 2008).The calculated maximum hourly mean concentrations and yearly averages are well below norms and guidelines for NH_3, CO_2, MEA, formaldehyde, acetaldehyde, and piperazine. "Worst case calculations" for nitrosamines in air show that there may be a problem, but further research must be done to reduce the uncertainties. Based on the "worst case calculations" for water it is not possible to conclude that there will be a problem, but the uncertainties have to be reduced, especially concerning nitrosamine degradation.

Since the previous report two technology vendors have been contracted to test their capture technology at TCM; Alstom using "Chilled ammonia" and Aker Clean Carbon (ACC) using amines. Both vendors have provided new emission data and NILU has made dispersion calculations based on these emission data. The results have been compared with existing threshold values and air quality guidelines. Maximum hourly mean concentrations have been estimated using CONCX, these are valid inside the Mongstad industrial area and up to approximately 5 km from the emission points. For regional dispersion The Air Pollution Model (TAPM) have been applied. These results are important concerning long term exposure and deposition.

TCM will use flue gas from existing facilities at Mongstad, like the Residual Fluid Catalytic Cracker (RFCC) and the Combined Heat and Power plant (CHP). In this study, the additional emissions from the CO_2 capture plant is investigated. There will be emissions of NH_3 from the Alstom plant, and emissions of amines and amine degradation products from the ACC plant. ACC will test the use of monoethanolamine (MEA), as well as other proprietary blends for carbon capture. Both plants will emit the captured CO_2 to air separately. For the Alstom plant, emitting NH_3, the impacts of these emissions on air quality and eutrophication of the ecosystems were investigated. For the ACC plant the most important issues are the emissions to air of amines and amine degradation products formed in the capture process and their subsequent fate in the atmosphere. Several amine degradation products have severe health effects. In addition, the chemical degradation of amines is not well known. The content in this report is based on existing knowledge at this stage and will be upgraded when new knowledge is available. Concerning the ACC amine plant, the emission data contain some well-documented substances, but also substances where large knowledge gaps exist. The emissions of well-known substances are of the same order of magnitude as the emissions of substances where the atmospheric degradation is poorly known.

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Model calculations have been performed on a very local scale (~up to 8 km using CONCX) to investigate dispersion, and on a regional scale (~up to 30 km using TAPM) to investigate dispersion and deposition. CONCX and TAPM are well-known models used in the scientific community. Weather data for 2007 are used for regional calculations. Concerning chemistry, atmospheric degradation of amines and amine chemistry is very complex with several hundred compounds involved and reactions taking place both in gas phase, aqueous phase and on particles. At present, no full atmospheric model chemistry scheme exist for amines. To account for chemical reactions, a <u>scaling</u> method is applied using chemical degradation rates found in the literature. In addition there are large uncertainties. Some processes, like gas to aerosol (particle) conversion or chemistry on aerosols have not been included. The simplifications made in the scaling method imply that the calculated model concentrations represent an upper limit of the concentrations to be expected in the real atmosphere.

The calculated maximum hourly mean concentrations from the Alstom facility are 55 $\mu g/m^3$ for NH_3 and 72 mg/m^3 for CO_2. From the ACC plant the maximum calculated hourly concentration of MEA is about 2 $\mu g/m^3$ and the maximum calculated hourly mean NH_3 concentration is just below 10 $\mu g/m^3$. The maximum calculated hourly concentrations of formaldehyde, acetaldehyde, and alkylamines are 1,4 $\mu g/m^3$, 2,1 $\mu g/m^3$, and 0.8 $\mu g/m^3$ respectively. Maximum CO_2 concentration from the export gas stack is 71 mg/m^3 for ACC. All these calculated hourly maximum concentrations for Alstom and ACC are much lower than the Administrative norm and lower than long term exposure guidelines for CO_2, MEA, formaldehyde and acetaldehyde.

Concerning regional dispersion, the model calculations estimate a maximum 8-hours mean concentration of NH_3 of 6.1 $\mu g/m^3$, and a maximum deposition of 3.1 mg N/(m^2 year), using Alstom emission data. This deposition is a small increase of 0.3 % compared to the current background deposition, but in an area where the vegetation critical loads are already exceeded. Concerning the ACC plant, the calculated maximum annual mean concentration of MEA is 1,3 ng/m^3, while the maximum annual mean concentrations of formaldehyde and acetaldehyde are 1,6 ng/m^3 and 2,4 ng/m^3, respectively. The maximum annual mean concentration of alkyl amines (methylamine, ethylamine, dimethylamine, diethylamine) is just below 1,0 ng/m^3. The maximum concentrations for both plants and all emission scenarios are found about 10 km to the S-E of Mongstad in the area around Sundsbø and Kolås.

A "Worst case" estimate has been calculated to provide a "worst possible scenario" estimate of concentrations of nitrosamines in air and water. This method is used when there are large uncertainties to estimate the highest possible (but not necessarily plausible) concentrations of compounds (nitrosamines in this case). The calculated nitrosamines concentrations in ambient air are compared to the 0.07 ng/m^3 threshold value from EPA/IRIS. A formation range of nitrosamines between 2 and 10 % is assumed for components with nitrosamines formation potential (e.g. Pitts et al., 1978, Karl et. al 2008, Bråten et. al 2008). This wide range reflects the uncertainties in these calculations. Yearly average maximum value of nitrosamines have been calculated for all the scenarii apart from the upset scenario. Considering these results it must be remembered that the emission

conditions must be valid for the duration of the year for the concentration value to be valid. For the MEA scenarii, only one scenario exceed the limit value. For the improved solvents scenarii, all exceed the limit except scenario 5c (if 10% formation of nitrosamines occur).

The main conclusion from the worst case study of nitrosamines in air is that there may be a potential problem concerning the EPA/IRIS threshold value of 0.07 ng/m^3. Further research, including more detailed modeling, and monitoring is needed to reduce the present uncertainties associated with nitrosamines in air from CCS.

Calculations of the maximum amount of components with nitrosamine formation potential in the emissions show that the concentration of nitrosamines in air can be below the threshold value, if the sum of component emission is no larger than about 0.02 g/s. This figure is dependent on the amount of directly emitted nitrosamines.

Concerning nitrosamines in drinking water, the degradation of nitrosamines in water is a key question. Some studies indicate that nitrosamines are persistent. If this is the case, then all worst case scenarii exceed the 0.7 ng/l threshold value. Other studies, like e.g. Drewes et al. (2006) report a degradation under anoxic conditions with a lifetime of the order of days. If these results are applied, the worst case scenarii equilibrium concentrations are below the threshold value. Based on these calculations, it is not possible to conclude that there will be a problem with nitrosamines in drinking water, but the uncertainties have to be reduced. Scientific research should be conducted, especially to investigate the degradation of nitrosamines in water.

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Sammendrag på norsk

CO2 Technology Centre Mongstad har gitt Norsk institutt for luftforskning (NILU) i oppdrag å beregne og vurdere spredning og utslipp til luft av karbondioksid (CO₂), nitrogenoksider (NOₓ), ammonikk (NH₃), aminer og nedbrytningsprodukter fra aminer som skal slippes ut fra testsenteret som er under bygging ved Mongstad (CO2 Technology Centre Mongstad, TCM). Dette er en oppdatering av en tidligere NILU-rapport "Test Centre Mongstad, Spredningsberegninger for utslipp til luft fra Test Centre Mongstad (TCM)" (Berglen et al., 2008). De beregnede maksimalkonsentrasjonene (time- og årlig middel) er alle under akseptkriteriene for NH₃, CO₂, MEA, formaldehyd, acetaldehyd og piperazine. "Worst case"-beregninger har blitt gjort for nitrosaminer i luft. Disse viser at nitrosaminer kan være et problem, men mer kunnskap behøves for å redusere usikkerhetene. Basert på "Worst case" beregninger for drikkevann er det ikke mulig å konkludere om nitrosaminer vil være et problem, men usikkerhetene må reduseres, spesielt med tanke på nedbrytning av nitrosaminer i vann.

Siden forrige rapport har to teknologileverandører fått i oppdrag å teste sin fangsteknologi ved TCM; Alstom som benytter "Chilled ammonia" og Aker Clean Carbon (ACC) som benytter aminer. Begge selskaper har gitt nye oppdaterte utslippstall til NILU og NILU har utført spredningsberegninger basert på disse tallene. Resultatene har blitt sammenlignet med gjeldende grenseverdier og luftkvalitetskriterier. Maksimal timemiddelkonsentrasjon er beregnet ved hjelp av CONCX-modellen. Disse resultatene er gyldige innenfor industriområdet på Mongstad og ut til omlag 5 km. For beregninger på regional skala er The Air Pollution Model (TAPM) brukt. Disse resultatene er relevante for langtidskonsentrasjoner (årlig middel) og avsetning.

TCM vil benytte røykgass fra eksisterende anlegg på Mongstad; fra Residual Fluid Catalytic Cracker (RFCC, dvs. fra selve raffineriet) og fra Combined Heat and Power plant (CHP, dvs. fra gasskraftverket). I denne studien beregnes og vurderes de "ekstra" utslippene fra CO₂-fangstanlegget. Det vil være utslipp av NH₃ fra Alstoms anlegg, samt utslipp av aminer og aminers degraderingsprodukter fra ACCs anlegg. ACC planlegger å teste bruk av monoethanolamin (MEA) i tillegg til to proprietære blandinger. Begge anleggene vil slippe ut CO₂ i en egen pipe. Angående Alstoms teknologi er utslipp av NH₃ og effekten av disse utslippene vurdert med tanke på luftkvalitet og overgjødsling (eutrofiering). Angående ACCs teknologi er utslipp av aminer og aminers degraderingsprodukter og spredning og omdanning av disse i atmosfæren det viktigste spørsmålet. Flere av degraderingsproduktene fra aminer har alvorlige helseeffekter. I tillegg er det store kunnskapshull med tanke på den kjemiske nedbrytningen i atmosfæren. Denne rapporten bygger på eksisterende kunnskap pr dags dato og nye studier vil bli gjort når ny kunnskap foreligger. ACCs anlegg vil slippe ut komponenter som er velkjente, men også komponenter hvor kunnskapsnivået er lavt. Utslippene av velkjente komponenter er av samme størrelsesorden som utslipp av komponenter hvor nedbrytningsveiene er lite kjent.

Det er gjort modellberegninger på lokal skala for å beregne spredning (opp til 8 km ved hjelp av CONCX) og på regional skala for å studere spredning og avsetning (opp til 30 km ved hjelp av TAPM). Både CONCX og TAPM er velkjente modeller brukt av forskere over hele verden. For regionale modellkjøringer er værdata for 2007 benyttet. Kjemisk nedbrytning av aminer og aminkjemien er meget komplisert med hundrevis av forskjellige komponenter og reaksjoner. Aminer brytes ned både ved gassfasekjemi, væskefasekjemi (i dråper) og på partikler. Pr dags dato finnes det intet modellkjemiskjema for aminer

For å ta høyde for kjemiske reaksjoner er det brukt en skaleringsmetode. Denne metoden er basert på kjemiske reaksjonsrater og laboratorieeksperimenter funnet i den vitenskapelige litteraturen. Det er dog store usikkerheter. Visse typer prosesser, som gass-til-partikkelovergang, er ikke tatt med. Forenklingene som er gjort i skaleringsmetoden innebærer samtidig at de beregnede konsentrasjonene er i det øvre skikt av hva man kan forvente å finne i den virkelige atmosfæren.

Maksimalt beregnet timemiddel for Alstoms anlegg er 55 $\mu g/m^3$ for NH_3 og 72 mg/m^3 for CO_2. For ACCs anlegg er maksimalt beregnet timemiddel av MEA omlag 2 $\mu g/m^3$ og maksimalt timemiddel for NH_3 er litt under 10 $\mu g/m^3$. Maksimalt beregnet timemiddel for formaldehyd, acetaldehyd, and alkylaminer er hhv. 1,4 $\mu g/m^3$, 2,1 $\mu g/m^3$ og 0,8 $\mu g/m^3$. Maksimal CO_2-konsentrasjon fra eksportgasspipen er 71 mg/m^3 for ACCs anlegg. Alle de beregnede timemiddelverdier (Alstom og ACC) er lavere enn Administrativ norm og lavere enn gjeldende luftkvalitetskriterier for CO_2, MEA, formaldehyd og acetaldehyd.

Når det gjelder regional skala viser beregningene at Alstoms utslipp gir et 8-timers maksimum lik 6,1 $\mu g/m^3$ for NH_3 og maksimal avsetning på of 3,1 $mg\ N/(m^2\ år)$. Maksimal avsetning utgjør 0.3 % av allerede eksisterende N-avsetning. Samtidig er dette i et område hvor grenseverdiene for overgjødsling allerede er overskredet. For ACCs anlegg er maksimal årlig konsentrasjon av MEA 1,3 ng/m^3, mens maksimumskonsentrasjonene av formaldehyd og acetaldehyd er hhv. 1,6 ng/m^3 og 2,4 ng/m^3. Maksimalt årsmiddel av alkylaminer (metylamin, etylamin, dimetylamin, dietylamin) er like under 1,0 ng/m^3. Beregnet maksimumskonsentrasjon forekommer om lag 10 km sør-øst for Mongstad i områdene rundt Sundsbø and Kolås.

En "worst case"-beregning er gjort for å finne det verst tenkelige scenario når det gjelder konsentrasjoner av nitrosaminer i luft og drikkevann. Dette er en metode som er brukt når det er store usikkerheter i prosessene og målet er å finne høyest mulige (men ikke nødvendigvis sannsynlige) konsentrasjon av de undersøkte komponentene (nitrosaminer i dette tilfellet). De beregnede konsentrasjonene er sammenlignet med grenseverdien fra EPA/IRIS (0,07 ng/m^3). For de komponentene som har potensiale for nitrosamindannelse er det brukt et spenn fra 2 til 10% for nedbrytning til nitrosaminer (basert på for eksempel Pitts et al., 1978, Karl et. al, 2008, Bråten et. al 2008). Dette vide spennet reflekterer de store usikkerhetene i disse beregningene. Maksimalt årlig middelkonsentrasjon av nitrosaminer er beregnet for alle scenarioer bortsett fra "Upset". Disse resultatene må sees i lys av at utslippene må være konstante over et år for at de beregnede årsmiddelkonsentrasjonene skal være direkte sammenlignbare. For MEA-

scenarioene er det bare et som overskrider grenseverdien. For scenarioene med "Improved amines" går alle over grenseverdien bortsett fra scenario 5c (forutsatt 10% nitrosamindannelse).

Hovedkonklusjonen fra "Worst case"-beregningen er at det kan være et problem med tanke på nitrosamindannelse og grenseverdien på 0,07 ng/m^3. Ytterligere kunnskap (inkludert mer detaljert modellering) og overvåkning er nødvendig for å redusere usikkerhetene i forbindelse med nitrosaminer i luft fra CO_2-fangst.

Beregninger av størst mulige utslipp av komponenter med potensiale for å danne nitrosaminer viser utslippene kan høyst være om lag 0,02 g/s for å overholde grenseverdien. Men det er viktig at dette tallet sees i sammenheng med de direkte utslippene av nitrosaminer.

Når det gjelder nitrosaminer i drikkevann er nedbrytning av nitrosaminer i vannfase et meget viktig punkt. Noen studier indikerer at nitrosaminer er bestandige (vanskelig nedbrytbare). Hvis dette er tilfelle vil alle "worst case" scenarioer gi konsentrasjoner over grenseverdien på 0,7 ng/l. Noen studier, som eksempelvis Drewes et al. (2006) har funnet nedbrytning av nitrosaminer under oksygenfattige forhold med levetider for nitrosaminer i størrelsesorden ~dager. Om disse levetidene anvendes på forholdene rundt TCM så vil de verste av "worst case" scenarioene være under grenseverdien. Konklusjonen fra disse beregningene er at det ikke er mulig å slutte at det vil være et problem med nitrosaminer i drikkevann, men at usikkerhetene må reduseres. Mer forskning behøves, spesielt for å kvantifisere nedbrytningen av nitrosaminer i vann.

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1 Introduction

Carbon capture and storage (CCS) is an important topic and measure on the political agenda. The Norwegian government puts a great effort into research and development concerning CCS.

To facilitate the development of new technologies the CO2 Technology Center Mongstad (TCM) has been built. The establishment of TCM was part of the agreement between the Norwegian government and Statoil signed in Octobre 2006 ("Gjennomføringsavtale") in connection to the emission permit for the Combined Heat and Power plant (CHP) located at Mongstad. CO_2 Technology Centre Mongstad will test various post-combustion techniques to capture CO_2. In the short term (2011) a test plant will be constructed, capturing ~100'000 tonnes CO_2 per year. Later a full scale plant is planned at Mongstad and, when in operation, it will capture and store between 1.2 and 2.0 million tonnes of CO_2 per year (CO$_2$ Master Plan Mongstad, 2009).

There will inevitably be emissions to air from these facilities. The dispersion, degradation and deposition of these emissions have to be quantified, and the concentrations in air of the compounds emitted from TCM have to be calculated.

In 2008 Norwegian Institute for Air Research (NILU) wrote a report for the CO_2 Technology Centre Mongstad, see Berglen et al. (2008). In this report NILU made dispersion calculations based on preliminary emission data. Maximum hourly mean concentrations of CO_2, NH_3 and NO_x were presented as well as annual mean concentrations and simple deposition calculations of soluble species (e.g. MEA). NILU also recommended a minimum stack height to avoid downdraft of the emissions.

Since then the consortium behind TCM (Gassnova, Statoil, Shell, and Sasol) has chosen two different technology vendors for the Technology Centre, Aker Clean Carbon (ACC) using amines and Alstom using "chilled ammonia" to capture CO_2. These are two possible post-combustion techniques to be tested in Norway and TCM is a test facility for the two chosen technologies.

The "chilled ammonia" technology will have emissions of well known substances and the level of knowledge is sufficient to give a good estimation of impacts from emissions to air.

The emissions from capture of CO_2 by amines are not so well known and the emissions vary according to the solvents used for capture. The amines also react with other substances in the atmosphere after emission. Theoretical studies have shown that toxic and carcinogenic substances can form both inside the plant and in the atmosphere. It is therefore necessary to know the toxicity and amount of these substances that are formed. Currently there are large knowledge gaps. The

level of knowledge depends strongly on the amine or amine solvent used for capture. This lack of knowledge causes some concern. The photochemical reactions after emission are complex and partly unknown. It is common knowledge that the emissions from the amine technology consist not only of the mother amine used in the carbon capture process, but also of degradation products. This adds uncertainty to the emissions from the amine technology.

To abate this uncertainty a system for measurements of emissions should in our view be implemented for the test plant. This surveillance system will need to be optimized to look at substances yet not known to be emitted. Methodology and standardization of measurement techniques need to be developed. The measurement systems must have a low detection. This monitoring system will serve two purposes; 1) to develop new analysis methods to measure new components, and 2) to monitor the substances emitted from TCM so that human and environmental exposure levels can be assessed. These emissions measurements should be made available to the scientific community and to the public.

Level of scientific knowledge
Some work have been initiated to investigate the processes connected to emissions to air of amines. The work have concentrated on the emissions of MEA (e.g. the Atmospheric Degradation of Amines (ADA) projects in 2009 and 2010). Some of the work is referred to below. In 2008 and 2009 a screening project lead by NILU summarized the current level of knowledge concerning amine emissions and transformation, as well as the impact of amines on the environment and human health. This was a broad project with contributions from the Norwegian Institute for Water Research (NIVA), the Norwegian Institute for Nature Research (NINA), the Norwegian Institute for Public Health (FHI), the Centre for Theoretical and Computational Chemistry at the University of Oslo (CTCC, UiO), in addition to NILU. The project was funded by Gassnova, Statoil and Shell Technologies Norway. The screening project summarized the current level of understanding and a number of key issues were identified. Ten reports were written in the project, they are listed in Table 1. All of the reports can be downloaded from the co2.nilu.no project web site . For this study, the report on degradation products of amines (Bråten et al., 2008), the report on analytical methods (Dye et al., 2008), the worst case report (Karl et al., 2008), the reports on health effects of amines and the degradation products (Låg et al, 2009a, 2009b), and the report on toxicity on aquatic organisms (Brooks, 2008) have been most useful.

Table 1:   *Reports published during the Phase 1 CO$_2$ and amines screening project coordinated by NILU.*

Task #	Report Title	Author
Task3	*Final report on a theoretical study on the atmospheric degradation of selected amines.*	CTCC
Task4	*Evaluation of analytical methods for amine related emissions and degradation products in emission and ambient air*	NILU
Task 5.1/5.2	*Report on models, model needs and requirements*	NILU
Task 5.3	*Amines and rainfall. Impact of amines on rainfall from plume clouds*	NILU
Task 6	*Worst Case Studies on Amine Emissions from CO$_2$ Capture Plants*	NILU
Task 7.1	*Health effects of different amines relevant for CO2 capture*	FHI
Task 7.2	*Health effects of possible degradation products of different amines relevant for CO2 capture*	FHI
Task 8	*Effects on terrestrial vegetation, soil and fauna of amines and possible degradation products relevant for CO$_2$ capture*	NINA
Task 9	*The toxicity of selected primary amines and secondary products to aquatic organisms: A review*	NIVA
Task 10	*Summary Report: Amine Emissions to Air During Carbon Capture Phase I: CO2 and Amines Screening Study for Effects to the Environment*	NILU

Based on the theoretical study done in the Phase 1 project, UiO-CTCC and partners initiated the ADA projects (Atmospheric Degradation of Amines, see Nielsen et al., 2010). These are chamber experiments performed in the EUPHORE chamber, where gas phase oxidation of MEA is investigated.

Current study
This report is an update of our previous work (Berglen et al., 2008). New model calculations have been made based on more reliable emissions estimates and new knowledge has been taken into account.

The aim of this study is to calculate dispersion and deposition of air pollutants emitted from TCM and assess the concentrations in relation to air quality threshold values and the deposition of nitrogen in relation to the vegetation critical loads. The main components that are studied are CO$_2$, NO$_x$, NH$_3$, and MEA and some reaction- and degradation products, including, but not limited to acetaldehyde, formaldehyde, nitrosamines and alkyl amines.

Maximum hourly mean concentrations of compounds emitted are calculated on a very local scale (a few kilometres from the stack), and on a semi-regional scale (up to 30 km from Mongstad). This is done to assess the concentrations inside the

Mongstad plant (exposure on the people working at Mongstad), and to assess the concentrations for people living in the communities around the Mongstad refinery.

Section 2 presents the current air quality and water quality criteria, as well as the vegetation critical loads for nitrogen deposition. The results of the calculations in this study were compared to these quality criteria and critical loads. Section 3 presents the emission data from the Alstom and ACC plants for different emission scenarios. For the concentrations of pollutants inside the Mongstad industrial area the CONCX model has been used to calculate maximum hourly mean and the results are presented in section 4. For the calculation of the dispersion at a regional scale, the model TAPM have been applied and model results showing annual mean concentrations, maximum short-term concentrations and annual nitrogen wet deposition are presented in sections 5.1-5.3. Finally, the worst case calculations/estimates of nitrosamine formation and nitrosamine concentrations are presented, both concerning air (section 5.4) and drinking water (section 5.5).

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Table 2:   *Klif's recommended air quality standards, national targets, the*
           Pollution Control Act's action thresholds and registration thresholds,
           and the EU's new limit values for air quality relating to effects on
           human health. The limit values are in µg/m^3. The figures brackets
           show how many times it is permitted to exceed the limit value.

Substance	Mean time	1 hour	8 hours	24 hours	6 months	1 year
NO$_2$	Klif's recommended air quality standards	100		75	50	30
	National targets (and the number of violations permitted)	150[1] (8 per year)				
	The Pollution Control Act's action threshold	300[1]				
	The Pollution Control Act's registration threshold	200				
	The EU's new limit values (and number of times they may be exceeded)	200[1] (18 per year)				40 [1]

[1] must be complied with by 1 January 2010

2.2   Administrative norms

The Norwegian Labour Inspection Authority has defined maximum
concentrations that must not be exceeded in the working environment (see
*Veiledning om administrative normer for forurensning i arbeidsatmosfære in
http://www.arbeidstilsynet.no/binfil/download2.php?tid=77907,*   "Guidelines
relating to administrative norms for pollution in the workplace" - in Norwegian
only, see Norwegian Labour Inspection Authority in the reference list).

It is these limit values that apply within the industrial area at TCM and they have
been used to evaluate the results (see Table 3).

Table 3:   *Administrative norms for 8-hours mean concentrations for the*
           different components discussed in this report.

Component	Administrative norm
Ammonia (NH$_3$)	18 mg/m^3
CO$_2$	9000 mg/m^3
Nitrogen dioxide (NO$_2$)	1.1 mg/m^3
MEA (CAS 141-43-5)	2.5 mg/m^3
Piperazine (CAS 110-85-0)	0.3 mg/m^3
Formaldehyde*	0.6 / 1.2 mg/m^3
Acetaldehyde	45 mg/m^3
Methylamine	12 mg/m^3
Ethylamine	4 mg/m^3
Dimethylamine	4 mg/m^3
Diethylamine	15 mg/m^3
* 1.2 mg/m^3 is maximum concentration that cannot be exceeded under any circumstances.	

The figures show that the limit for CO$_2$ is very high, it is permitted to have almost

0.5% CO_2 in the air without breaching the norm. In evaluating ambient air concentrations other than in the work atmosphere, it is common to use a factor of 1/30 to 1/100 to estimate ambient air concentrations guidelines, compared to the administrative norms for working atmosphere . This factor will vary according to how much is known about the substance and how toxic it is.

2.3 Air quality recommendations from Norwegian Institute of Public Health (FHI)

During the phase 1 of the screening project coordinated by NILU in 2008-2009 (see Table 1), the Norwegian Institute of Public Health (FHI) did a study to investigate health effects of different amines relevant for CO_2 capture and their degradation products (Låg et al, 2009a, 2009b). The aim was also to establish exposure guidelines for the general population. The four most relevant amines were investigated (MEA, Methyl diethanolamine (MDEA), AMP and piperazine). Concerning degradation products special attention was given to nitrosamines, nitramines, aldehydes and amides. Human health effects with regard to acute toxicity (short term exposure), chronic toxicity (long term exposure), mutagenicity (affect DNA), carcinogenicity (cause cancer), teratogenicity (ability to cause birth defects), irritation (in e.g. eyes or respiratorial airways), and sensitisation (the act or process of inducing an acquired sensitivity or allergy) were investigated. The guideline values established by FHI are listed in Table 4. Concerning acetaldehyde the value from FHI is higher than the WHO value. WHO regards 0.3 mg/m^3 as a limit for tolerable lifetime cancer risk.

Table 4: Exposure guidelines for the general population over time, concentrations in air. Numbers from Låg et al. (2009a and 2009b)

Component	Exposure guidelines
MEA (CAS 141-43-5)	10 µg/m^3
MDEA (CAS 105-59-9)	120 µg/m^3
AMP (CAS 124-68-5)	6 µg/m^3
Piperazine (CAS 110-85-0)	5 µg/m^3
Nitrosamines	Reduce human exposure to an absolute minimum.
Nitramines	No values concluded
Formaldehyde (CAS 50-00-0)	1.2 µg/m^3
Acetaldehyde (CAS 75-07-0)	2 mg/m^3

Table 4 only lists the well known compounds. There will also be emissions from TCM of compounds that are not well known and for which threshold values do not exist. The possible health effects and toxicity of these unknown compounds are not established. These compounds and their possible environmental effects have to be investigated further. E.g. nitrosamines is a group of compounds where some are very toxic and carcinogenic, while others cause less concern.

2.4 Water quality thresholds and guidelines

During the screening project Norwegian Institute for Water Research (NIVA) conducted a literature survey to find ecotoxicity data of amines and their

degradation products (Brooks and Wright, 2008). A summary of the data found is listed in Table 5. Please note that these values refer to effects on aquatic organisms due to concentrations in water, and that they cannot be compared directly to concentrations in air.

Table 5: Critical values for the determination of risk for each of the main chemical groups based on the most sensitive environmental effect measured. Taken from Brooks and Wright (2008).

Compound	LOEC (mg/L)	Assessment Factor	Calculated PNEC (µg/L)	Required PEC for an RQ >1 (µg/L)
MEA	0.75	100	7.5	>7.5
AMP	20	1000	20	>20
MDEA	0.5	100	5	>5
PIPA	10	100	100	>100
Amides	1.2	50	24	>24
Nitrosamines	0.025	1000	0.025	>0.025
Nitramines	0.2	1000	0.2	>0.2
LOEC: Lowest observable effect concentration PNEC: Predicted no effect concentration PEC: Predicted environmental concentration RQ: $$\frac{\text{Predicted Environmental concentration (PEC)}}{\text{Predicted No Effect Concentration (PNEC)}} = \text{Risk Quotient (RQ)}$$				

2.5 Maximum tolerable amount of nitrosamines

One important task in this project is to calculate maximum tolerable amount of nitrosamines from TCM ("worst case"). The calculations are based on normal operational flow rates for the ACC plant and the concentrations for acceptable risk levels in drinking water and air. In the calculation of the maximum tolerable emission calculation from TCM, the value corresponding to a cancer risk of one in a million (10^{-6}) is used.

The nitrosamine concentrations for acceptable risk levels used in the calculation of the maximum tolerable emission are:

0.07 ng/m^3 in air
0.7 ng/l in drinking water

Originally the nitrosamine concentration in air for the acceptable risk level was 4 ng/m^3, and it has been used in the worst case study by Karl et al. (2008). The state of California has determined that 0.04 and 0.004 µg/m^3 of NDMA (a nitrosamine) per day were equivalent to a 10^{-5} and 10^{-6} risk of cancer, respectively [1]. But recently the Environmental Protection Agency (EPA) in the US reported that threshold value for nitrosamines for 10^{-6} risk of cancer is 0.07 ng/m^3 in ambient air (see Integrated Risk Information System [IRIS],

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[1] 0,004 µg/m^3 equals 4 ng/m^3

http://www.epa.gov/ncea/iris/subst/0045.htm, section II.C.1. Summary of Risk Estimates). This threshold value of 0.07 ng/m^3 is here used for the worst case scenario calculation presented in section 5.4. It should be noted though that the 0.07 ng/m^3 value refer to a lifetime cancer risk (60 years) whereas TCM will be in operation for a shorter period of time (5 years).

The acceptable concentration of nitrosamines in water used in the worst case study by Karl et al. (2008) is 7 ng/l, which corresponds to a cancer risk of 1 in 100 000 (10^{-5}). Reference is given to the Reach guidance on information requirements and chemical safety assessments (chapter R.8, p. 47. see Reach 2008), which states that:

"Although there is no EU legislation setting the 'tolerable' risk level for carcinogens in the society, cancer risk levels have been set and used in different contexts. Based on these experiences, cancer risk levels of 10^{-5} and 10^{-6} could be seen as indicative tolerable risks levels when setting DMELs (Derived Minimal Effect Level) for workers and the general population, respectively."

The amines worst case studies by Karl et al. (2008) also refers to a 10^{-6} cancer risk level of 1 ng/l for N-Nitrosodiethylamine (NDEA). The EPA/IRIS limit of 0.7 ng/l is chosen as the concentration to be used for nitrosamines as group for the maximum tolerable emission calculations. EPA/IRIS refer to NDMA in this case.

2.6 Critical loads for nitrogen

Nitrogen acts as a fertiliser for vegetation, but adding too much nitrogen can have undesirable effects. Vegetation and soil naturally receive nitrogen in the form of wet and dry deposition. In addition, plants can absorb and bind nitrogen from the atmosphere through so-called "biological nitrogen fixation". In Norway, nitrogen compounds will largely be absorbed by the vegetation since many of the vegetation types have sub-optimal access to nitrogen (cf. Stuanes and Abrahamsen, 1996). The capacity to utilise the increased access to nitrogen is different in different types of vegetation. An increase in nitrogen can therefore lead to plant species with higher tolerance limits suppressing species with lower tolerance limits and thus affect bio-diversity (Tamm, 1991).

Figure 1 shows total deposition of nitrogen (N) in Norway 1997-2001 and 2002-2006 (Aas et al., 2008). Around Mongstad the N deposition is of the order of 800-1000 mg N/year. Figure 2 shows the vegetation critical loads for eutrophication. The critical load is defined as "A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt, 1988). Figure 3 shows the estimated exceedence of the vegetation critical loads for eutrophication (Larsen et al., 2008). The figures shows that in the southern parts of Norway the nitrogen deposition is already near or above the critical loads. This includes the areas around Mongstad. Any additional nitrogen in areas where the critical load has been exceeded will have a negative impact on vegetation and on the environment.
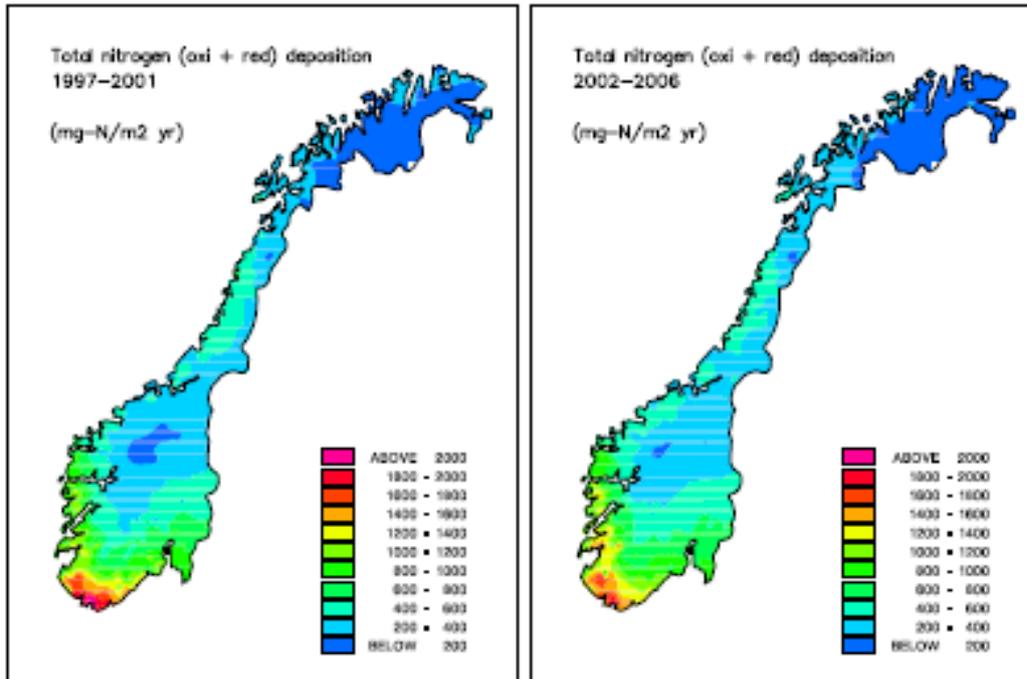
Figure 1:   Total deposition of nitrogen (oxi+red) for 1997-2001 (left panel) and 2002-2006 (right panel) taken from Aas et al. (2008). Unit: mg N/m² year.
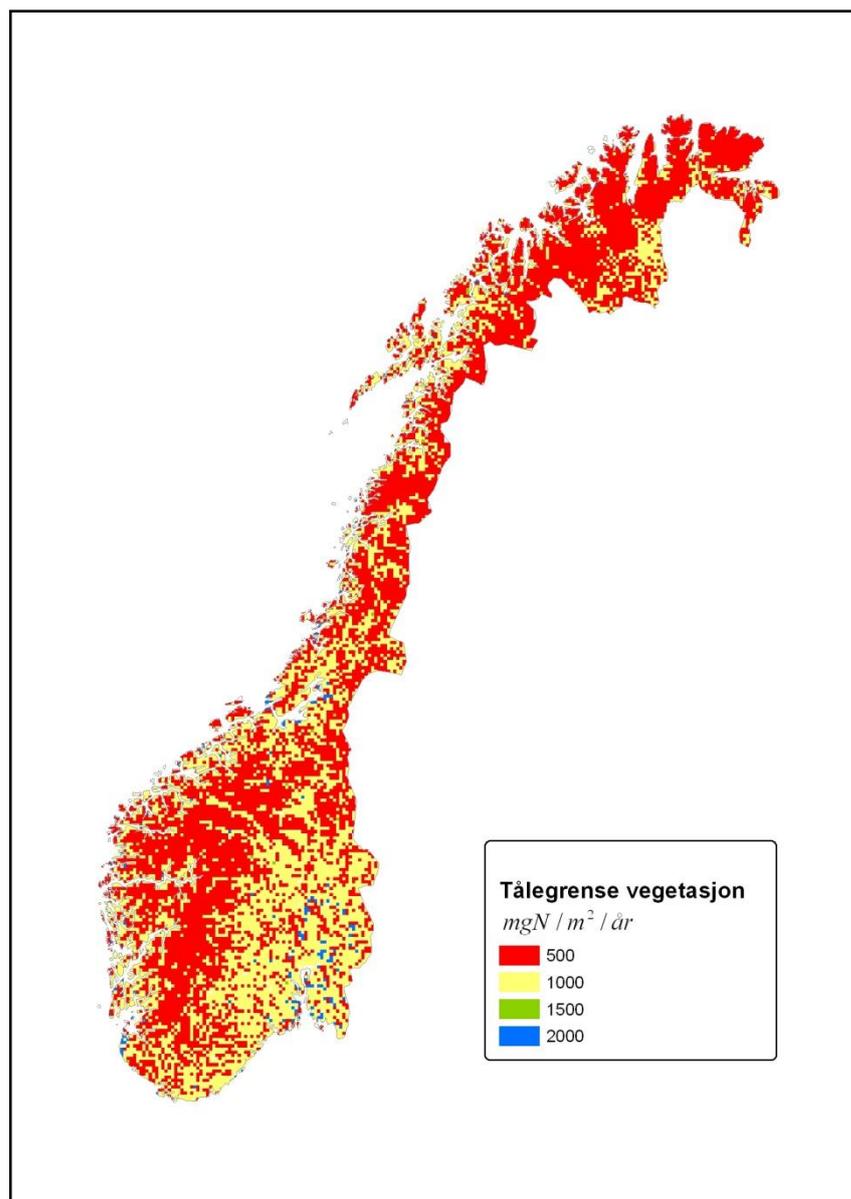
Figure 2: Map showing the vegetation critical loads for eutrophication based on the lowermost critical load for each vegetation type. Unit: mg N/m² year.
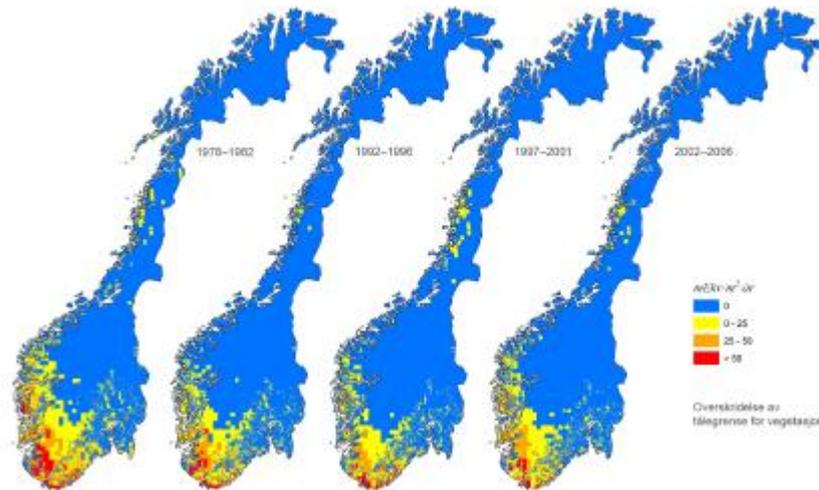
*Figure 3:   Estimated exceedence of the critical loads for eutrophication of
            vegetation (empirical values), taken from Larsen et al. (2008).*

3   Emission data

Two different companies have been contracted to test their CO_2 capture
technology at TCM; Aker Clean Carbon (ACC) and Alstom. ACC will test their
use of amines while Alstom will test their chilled ammonia technique.

There will be in all four different emissions points at TCM, two for each
technology vendor. One of these stacks will emit the "clean" flue gas, and the
other will emit CO_2 that is captured in the process. In the full scale plant the
captured CO_2 will be sent in pipelines to be stored below the seabed in the North
Sea.

The flue gas used at TCM comes from two different sources, the Residual Fluid
Catalytic Cracker (RFCC) at the Mongstad refinery and the Combined Heat-and-
Power plant (CHP), i.e. the power plant which is constructed close to the refinery
at Mongstad. One important criteria for the location of TCM at Mongstad is the
agreement between Statoil and Norwegian Government concerning the emission
permit for the CHP plant.

In addition to the components listed here there will also be emissions of e.g. NO_x,
SO_x and particles. These compounds are already part of the flue gas, while NH_3,
amines and amine degradation products come from the capture process. The
compounds from the capture process are the most important topic in this study.
However, emissions of NO_x (NO_2) will be investigated since a reduction in the
NO_x level has occured due to installation of SNCR (Selective Non-Catalytic
Reduction) in the RFCC flue gas system.

3.1   Alstom using chilled ammonia technology

The emission data provided by Alstom is listed in Table 6 and Table 7. In addition
to ammonia (NH_3) there are also emissions of CO_2 and water vapour (H_2O). N_2,
O_2 and Argon are also listed, this is just "normal" air and these components are

not part of the emission data. "Base case" is the normal emission rate expected at TCM whereas "worst case" is the maximum emissions that can occur. For some purposes the base case emission data is used, giving the average load or concentration, while for other purposes the worst case emission data is used giving the maximum values.

Table 6:   Emission data for the Alstom plant using flue gas from the RFCC. To the left the original emission data provided by Alstom, to the right the emission rates per second.

100% RFCC gas	Scenario 1	Scenario 2		Scenario 1	Scenario 2
	Base case	Worst-case		Base case	Worst-case
Stack height (m)	48	48			
Stack diameter (inch)	40	40			
Height on adjacent buildings	*	*			
Gas temperature °C	17.7	17.7			
Gas volume (m3/h)	44287	44293	Gas volume (m3/s)	12.30	12.30
Velocity out of stack (m/s)	15.7	15.7			
Amount of gas emitted (kg/h)	53144	53152	Amount of gas emitted (kg/s)	14.76	14.76
NH3 (kg/h)	0.3	8	NH3 (g/s)	0.08	2.2
CO2 (kg/h)	1799	1799	CO2 (g/s)	499.7	499.7
H2O (kg/h)	697	697	H2O (g/s)	194	194
N2 (kg/h)	47057	47057	N2 (g/s)	13071	13071
O2 (kg/h)	2840	2840	O2 (g/s)	788.9	788.9
Ar (kg/h)	751	751	Ar (g/s)	209	209
Export gas stack					
CO2 (kg/h)	10196	10196	CO2 (g/s)	2832	2832
NH3 (kg/h)	0.09	0.5	NH3 (g/s)	0.025	0.14
* Flue gas stack highest point in CAP area					

Table 7: Emission data for the Alstom plant using flue gas from the CHP. To the left the original emission data provided by Alstom, to the right the emission rates per second.

100% CHP gas	Scenario 3 Base case	Scenario 4 Worst-case		Scenario 3 Base case	Scenario 4 Worst-case
Stack height (m)	48	48			
Stack diameter (inch)	40	40			
Height on adjacent buildings	*	*			
Gas temperature °C	18.3	18.3			
Gas volume (m3/h)	48979	48987	Gas volume (m3/s)	13.61	13.61
Velocity out of stack (m/s)	17.3	17.3			
Amount of gas emitted (kg/h)	58285	58294	Amount of gas emitted (kg/s)	16.19	16.19
NH3 (kg/h)	0.3	8.7	NH3 (g/s)	0.08	2.4
CO2 (kg/h)	496	496	CO2 (g/s)	138	138
H2O (kg/h)	732	732	H2O (g/s)	203	203
N2 (kg/h)	46505	46505	N2 (g/s)	12918	12918
O2 (kg/h)	9759	9759	O2 (g/s)	2711	2711
Ar (kg/h)	793	793	Ar (g/s)	220	220
Export gas stack					
CO2 (kg/h)	2813	2813	CO2 (g/s)	781	781
NH3 (kg/h)	0.02	0.25	NH3 (g/s)	0.006	0.07
* Flue gas stack highest point in CAP area					

3.2 Aker Clean Carbon using amines

ACC has provided 6 emission scenarios. Five of these are fairly similar, the only difference is the scaling of the various components. These five emission scenarios are named "Expected" (scenario 1), "Design" (scenario 2), "Worst Case" (scenario 3), "Upset" (scenario 4), and "Minimum case" (scenario 6). The physical parameters are given in Table 8 and components emitted are listed in Table 9 for flue gas from CHP and in Table 10 for flue gas from RFCC. Scenario 1 "Expected" and scenario 2 "Design" are listed. Scenario 4 "Upset" is considered to be the maximum possible emission scenario from TCM. These large amounts of MEA (6 ppm) will not be emitted over long periods of time, but rather as events or episodes. Scenario 3 "Worst case" emitting 3 ppm of MEA (not listed here) is considered to be the largest long term emission. In the literature expected emissions from a post-combustion CO_2 plant using amines are between 1 and 4 ppm amines (Karl et al., 2010). There is continuous scientific research and efforts going on to reduce these emissions. By introducing new equipment (e.g. water wash) these emissions may be reduced considerably. It is a challenge to find the best possible technical solutions both from an engineering point of view and from an environmental point of view at the lowest possible cost. Scenario 1 (Expected) will emit 0.5 ppm MEA, this reflects the latest achievements in emission reducing technologies.

These emissions contain a mother amine (e.g. MEA) in addition to e.g. NH_3, formaldehyde, acetaldehyde, acetone and formamide. The emissions of these components are about the same order of magnitude (in g/s). These components are relatively well known and threshold values exist (Table 3 - Table 4). In addition there will be emissions of a large number of other products. These are formed chemically inside the ACC plant. Some of these compounds are not well known, and there are no threshold values. The sum of the lesser known compounds is of the same order of magnitude as the emissions of the mother amine. Hence the emissions of these less known compounds are not negligible.

Another particular aspect concerning the Technology Centre is that the CO_2 removed from the flue gas will be emitted to air separately. Also other components will be emitted along with the extracted CO_2. For example Scenario 2 (Design) estimate 0.03 g/s of acetic acid using flue gas from RFCC. In a full scale plant this CO_2 and the other products will not be emitted to air, but will be sent by pipeline to storage under the seabed in the North Sea.

Table 8:   *Physical parameters concerning emissions from Absorber stack and CO_2 stack, using flue gas from both CHP and RFCC.*

	CHP		RFCC	
	Absorber out	**CO2 out**	**Absorber out**	**CO2 out**
Vapour Fraction	1.0	1.0	1.0	1.0
Temperature [C]	45.9	27.8	48.0	27.8
Pressure [kPaa]	101.0	151.0	101.0	151.0
Molar Flow [kgmole/h]	2418.6	71.5	1837.0	226.6
Mass Flow [kg/h]	66882.7	3101.4	50148.2	9830.3
Actual Volume Flow [Am3/h]	63496.6	1175.2	48535.7	3723.8
Stack diameter [m]	1.0	0.156	1.0	0.156
Velocity out of stack [m/s]	22.5		17.2	
Mass Density [kg/m3]	1.05	2.64	1.03	2.64
Master Comp Mole Frac (CO_2)	0.0051	0.9754	0.0133	0.9757
Master Comp Mole Frac (H_2O)	0.0991	0.0242	0.1102	0.0241
Master Comp Mole Frac (Oxygen)	0.1377	0.0001	0.0435	0.0000
Master Comp Mole Frac (Nitrogen)	0.7581	0.0003	0.8329	0.0002

Table 9:   Emission data given by ACC using flue gas from the CHP. Two scenarii are given, scenario 1-Expected and scenario 2-Design, quantities given in mixing ratio and in g/s.

CHP	Scenario 1 - Expected		Scenario 2 - Design	
	Absorber out (ppmv)	Absorber out (g/s)	Absorber out (ppmv)	Absorber out (g/s)
MEA	0.5	0.020517418	1	0.041034835
NH3	2.6	0.029746897	5.1	0.058349682
Formaldehyde	1.3	0.026227226	2.55	0.051445712
Acetaldehyde	1.3	0.038471838	2.55	0.075463989
Acetone	0.13	0.005072518	0.255	0.00994994
Formamide	0.26	0.007867294	0.51	0.015432
Acetamide	0.0026	0.00010318	0.0051	0.000202391
Methylamine	0.26	0.005425359	0.51	0.01064205
Ethylamine	0.026	0.000787428	0.051	0.001544571
Dimethylamine	0.26	0.007874281	0.51	0.015445706
Diethylamine	0.0026	0.000127756	0.0051	0.000250599
1-Butanamine	0.0026	0.000127756	0.0051	0.000250599
Dibutylamine	0.0026	0.000225748	0.0051	0.000442813
N-methylethanamine	0.0026	0.00010325	0.0051	0.000202528
N-methyl 1-butanamine	0.0026	0.000152245	0.0051	0.000298635
N-ethyl 1-butanamine	0.0026	0.000176752	0.0051	0.000346706
1-Propanamine	0.0013	5.16248E-05	0.00255	0.000101264
Dipropylamine	0.00026	1.76752E-05	0.00051	3.46706E-05
Formic acid	0.026	0.000804022	0.051	0.00157712
Acetic acid	0.026	0.001048914	0.051	0.002057486
Butyric acid	0.026	0.001538963	0.051	0.003018734
Propinoic acid	0.026	0.001293981	0.051	0.002538194
DEA	0.0005	3.53176E-05	0.001	7.06353E-05
HEI	0.026	0.001958614	0.051	0.003841897
HEF	0.026	0.001556166	0.051	0.00305248
Nitrosamines	0.0015	9.06959E-05	0.003	0.000181
	Scenario 1 - Expected		Scenario 2 - Design	
	CO_2 stack (ppmv)	CO_2 stack (g/s)	CO_2 stack (ppmv)	CO_2 stack (g/s)
MEA	0.166666667	0.000202187	0.333333333	0.000404375

Table 10: Emission data given by ACC using flue gas from the RFCC. Two scenarii are given, scenario 1-Expected and scenario 2-Design, quantities given in mixing ratio and in g/s.

RFCC	Scenario 1 - Expected		Scenario 2 - Design	
	Absorber out (ppmv)	Absorber out (g/s)	Absorber out (ppmv)	Absorber out (g/s)
MEA	0.5	0.015583844	1	0.031167687
NH3	16.5	0.143385138	33	0.286770277
Formaldehyde	0.825	0.012641972	1.65	0.025283944
Acetaldehyde	0.825	0.018544085	1.65	0.03708817
Acetone	0.825	0.024450408	1.65	0.048900815
Formamide	1.65	0.037921707	3.3	0.075843413
Acetamide	0.0165	0.000497344	0.033	0.000994687
Methylamine	0.165	0.002615116	0.33	0.005230232
Ethylamine	0.165	0.003795538	0.33	0.007591077
Dimethylamine	0.0165	0.000379554	0.033	0.000759108
Diethylamine	0.0165	0.000615807	0.033	0.001231614
1-Butanamine	0.0165	0.000615807	0.033	0.001231614
Dibutylamine	0.0165	0.001088144	0.033	0.002176288
N-methylethanamine	0.0165	0.00049768	0.033	0.000995361
N-methyl 1-butanamine	0.0165	0.000733849	0.033	0.001467698
N-ethyl 1-butanamine	0.0165	0.000851975	0.033	0.001703951
1-Propanamine	0.00825	0.00024884	0.0165	0.00049768
Dipropylamine	0.00165	8.51975E-05	0.0033	0.000170395
Formic acid	0.165	0.003875524	0.33	0.007751049
Acetic acid	0.165	0.005055947	0.33	0.010111894
Butyric acid	0.165	0.007418063	0.33	0.014836127
Propinoic acid	0.165	0.006237211	0.33	0.012474423
DEA	0.0005	2.68252E-05	0.001	5.36505E-05
HEI	0.165	0.009440855	0.33	0.018881709
HEF	0.165	0.007500988	0.33	0.015001975
Nitrosamines	0.0015	6.88873E-05	0.003	0.000138
	Scenario 1 - Expected		Scenario 2 - Design	
	CO_2 stack (ppmv)	CO_2 stack (g/s)	CO_2 stack (ppmv)	CO_2 stack (g/s)
MEA	0.166666667	0.000640866	0.333333333	0.001281733
NH3	0.230325895	0.000246932	0.460651791	0.000493864
Formaldehyde	0.279895105	0.00052914	0.727727273	0.001375763
Acetaldehyde	3.816231555	0.010582793	9.922202043	0.027515263
Acetone	0.102267734	0.000373925	0.265896109	0.000972206
Formic acid	0.730414947	0.002116559	1.899078862	0.005503053
Acetic acid	3.172672773	0.011993832	8.248949209	0.031183964

In addition ACC will test two different "Improved solvents" (scenario 5). These are listed in Table 11 and Table 12, values given in ppmv only. Improved solvent 1 Design (5a) and Worst case (5b) are both based on S3. Improved solvent 2 (5c and 5d) is based on S1, S4 and S9. The emission values from the two flue gas

sources CHP and RFCC are identical in mixing ratio (ppmv), but the values are different in mass (g/s) due to different flue gas strength between the two sources (CHP has higher actual volume flow, see Table 8).

For this scenario 5 the emissions of less known degradation products are often as high or higher than the mother amine. This makes it complicated to evaluate the environmental effect of the emissions.

Table 11: Emission data given by ACC using flue gas from the CHP and RFCC. Scenario 5 – Improved solvent 1, quantities given in mixing ratio (ppmv).

Scenario 5 - Improved solvent 1	5a – Design (S3)	5b - Worst case(S3)
Tertiary amine	0.002	0.02
Ammonia	5	5
Formaldehyde	1	1
Acetaldehyde	2	2
Acetone	0.5	0.5
Formamide	0.1	0.1
Acetamide	0.001	0.001
Methylamine	0.255	0.515
Ethylamine	0.165	0.329
Dimethylamine	0.255	0.515
Diethylamine	0.0165	0.0329
1-Butanamine	0.0165	0.0329
Dibutylamine	0.0165	0.0329
N-methylethanamine	0.0165	0.0329
N-methyl 1-butanamine	0.0165	0.0329
N-ethyl 1-butanamine	0.0165	0.0329
1-Propanamine	0.0083	0.01645
Dipropylamine	0.0017	0.00329
2,2'-[[2-[(2-hydroxyethyl)methylamino]ethyl]imino]bis-Ethanol	0.1	0.1
Ethyleneglycol	0.1	0.1
N,N.dimethylethanolamine	0.002	0.02
MMEA	0.002	0.02
2-methylaminoethanol	0.1	0.1
1-hydroxyethyl-3-methyl imidazolidone	0.1	0.1
Hydroxyethyl oxazolidone	0.1	0.1
Formic acid	0.1	0.1
Acetic acid	0.1	0.1
Butyric acid	0.1	0.1
Propinoic acid	0.1	0.1
DEA	0.0002	0.002
Nitrosamines	0.003	0.003

*Table 12: Emission data given by ACC using flue gas from the CHP and RFCC.
Scenario 5 – Improved solvent 2, quantities given in mixing ratio
(ppmv).*

Scenario 5 - Improved solvent 2 (S1, S4, S9)	5c - Design	5d - Worst case
Primary amine	0,88	2.24
Secondary amine	0.115	0.7
Tertiary amine	0.005	0.06
Ammonia	1	1
Formaldehyde	0.2	0.2
Acetaldehyde	0.4	0.4
Acetone	0.1	0.1
Formamide	0.02	0.02
Acetamide	0.0002	0.0002
Piperazine	0.1	0.1
1,2 ethylenediamine	0.1	0.1
4,4-dimethyl-2-oxazolidinone	0.1	0.1
2-methyl-2-(methylamino)-1-propanol	0.1	0.1
NO	0.1	0.1
Nitrosamines	0.003	0.003

3.2.1 Mobile Test Unit

In the early phase of the project, before the construction of TCM is completed,
there will be tests run on a Mobile Test Unit (MTU). The ACC emission data
depicted in Table 9 - Table 12 will also be used. However the quantities emitted
will be very small. The actual volume flow from MTU will be maximum 1112,7
m^3/h compared to 50'000-60'000 m^3/h from the ACC plant. This means that the
emissions from the MTU in mass (g/s) are a factor 50 less than emissions from the
plant even though the emissions in ppmv are similar. Maximum emissions of
MEA will for instance be 0.0042 g/s. For this reason the emissions from MTU and
the subsequent concentrations are not investigated in detail.

3.2.2 Emissions of CO_2

The CO_2 that is captured will be emitted through a separate stack. The density of
CO_2 is about 1,5 the density of air. Some concern have been raised that pure CO_2
will sink to the ground and cause high concentrations. This situation has been
observed elsewhere during very stable and calm atmospheric conditions.
Mongstad is located at the west coast of Norway. During the NILU monitoring
project at Kollsnes (20 km from Mongstad) 2008-2009 there were wind 100% of
the time (wind speed > 0.4 m/s). This means that and there is hardly never calm
and stable conditions in the Mongstad area, and the CO_2 emitted is expected to be
well mixed.

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4 Maximum hourly mean concentrations of main pollutants

This section contains calculated maximum hourly mean concentrations in the vicinity of TCM (up to a few kilometres from Mongstad). For these calculations the CONCX model is used (Bøhler, 1987). CONCX is a simple and robust Gaussian distribution model that calculates concentrations downwind of an emission source at various wind speeds and under various atmospheric stability conditions. There is no chemical degradation included, nor loss by deposition. This means that the compounds are assumed to chemically inert. Such an assumption is valid if the components have a lifetime longer than minutes to hours.

The model requires the following input: Stack height, height of adjacent buildings (due to the turbulence zone around these buildings), emission velocity and flue gas temperature (in order to calculate thermal lift). This information is listed in section 3. Then the CONCX model calculates concentrations at ground level as a function of the distance from the source. For Gaussian models in general, there is 95 % probability that the model result is within a factor of 2 of the reality, However, due to the conservative approach in the parameter setting in CONCX a better uncertainty estimate is that it is 95 % probability for the real concentrations to be within a range of 0.25 to 1.25 of the predicted results.

The results are compared with the Norwegian Labour Inspection Authority's administrative norms and national and international air quality criteria (see section 2). The maximum short term concentrations of pollutants emitted from TCM will occur between a few hundred meters up to a few kilometres from TCM, depending on the atmospheric conditions and wind. These maxima are well within Statoil Mongstad's industrial area, where the Norwegian Labour Inspection Authority's norms apply, while other air quality criteria apply outside the area.

4.1 Unit emission

The calculations were first carried out using emissions of 1 g/s, a so-called unit emission. If the emission component is inert, i.e. not chemically degraded within the time scale of local dispersion (up to a few hours) and the emission parameters remain the same, these results can be linearly scaled in order to get concentrations for other quantities emitted. This must be regarded as a first approach to estimating concentrations. The next step in model development would be to include a chemistry scheme into the model, but for the components investigated here and their chemical lifetime (τ > minutes/hours) it is valid to assume that they remain inert at this short geographical scale (kilometres).
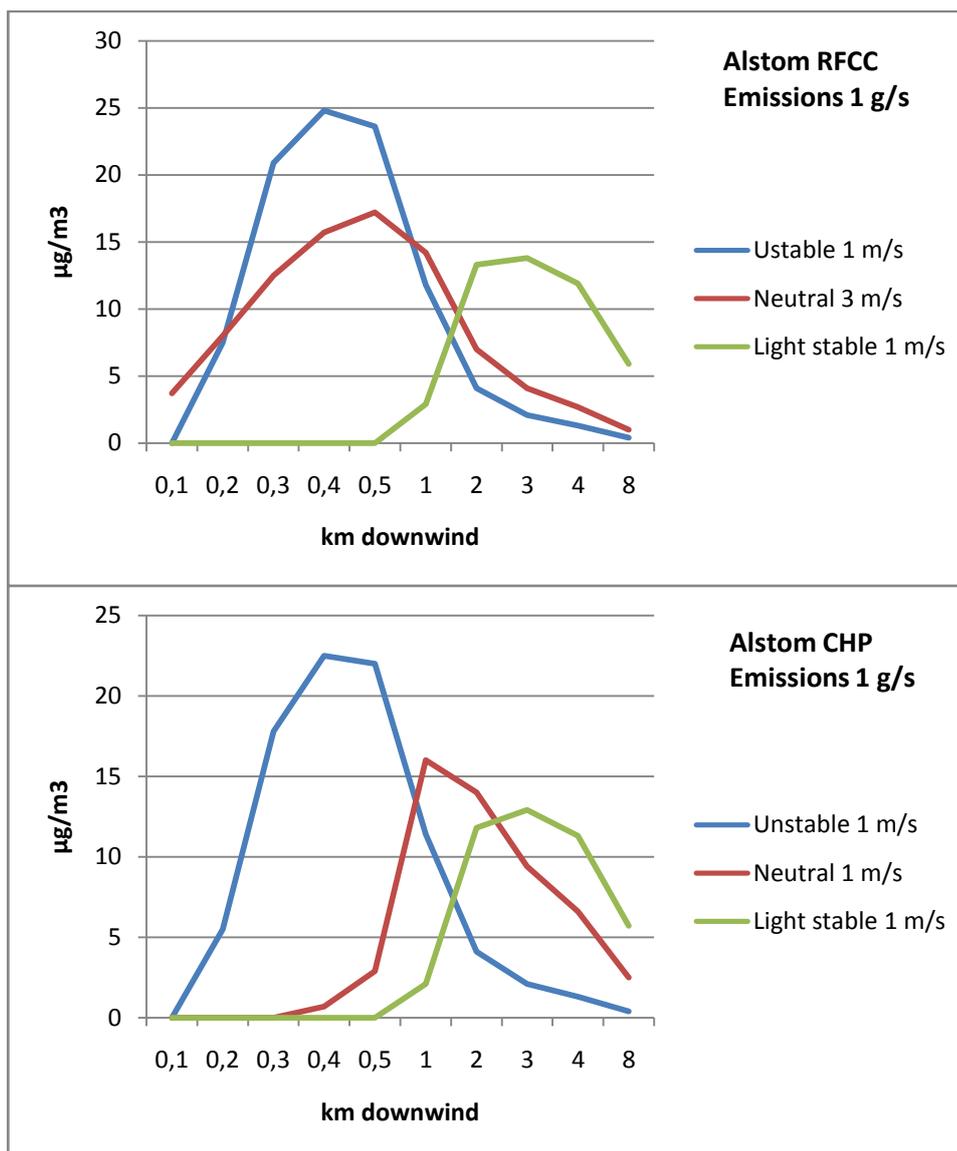
Figure 4: *Results for unit emission of 1 g/s, Alstom emission data, flue gas from RFCC (top panel) and CHP (lower panel For each source, the three meteorological conditions that provide the highest concentrations were selected. For information on the emission conditions see section 3. The horizontal axis shows the distance from the source in kilometres and the vertical axis shows concentration as an hourly mean in μg/m³.*
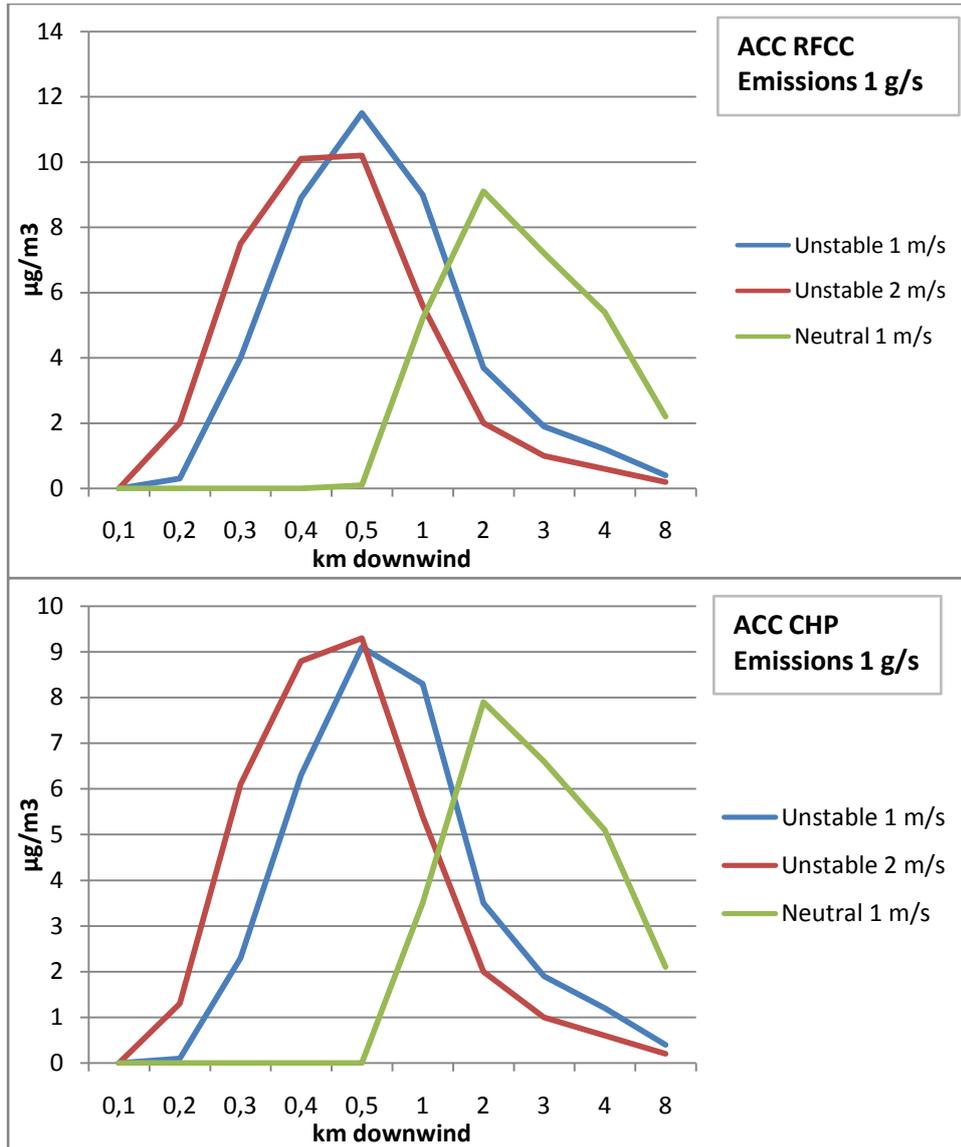
Figure 5: *Results for unit emission of 1 g/s, ACC emission data, flue gas from RFCC (top panel) and CHP (lower panel). For each source, the three meteorological conditions that provide the highest concentrations were selected. For information on the emission conditions see section 3. The horizontal axis shows the distance from the source in kilometres and the vertical axis shows concentration as an hourly mean in $\mu g/m^3$.*

Figure 4 and Figure 5 show unit emission results for the two technology vendors (Alstom and ACC). The wind speed that yield the highest concentrations for each stability class are shown for each source. The concentration profile shows zero concentration near the stack, then a maximum at a certain distance (between 400 and 3000 m), and then the concentration decreases. This concentration pattern shows that the stack height is sufficient for dispersion.

"Neutral", "unstable" and "light stable" describe the atmospheric stability, i.e. the vertical mixing. Neutral conditions, when temperature decreases with height, occur during cloudy weather, rain and during strong wind. Neutral conditions give fairly good vertical mixing. Unstable conditions, when temperature decreases

rapidly with height, occur during strong incoming solar radiation that heats the ground. Unstable conditions give very good vertical mixing of the emissions, but for emissions from high stacks this may be a disadvantage since the emissions are brought rapidly to the ground close to the stack. Light stable and stable conditions, when temperature increases with height, occur during nighttime and during wintertime when there is strong cooling at the ground by outgoing longwave radiation. Stable conditions are ideal for emissions from high stacks, since the emissons will reach the ground at a long distance from the stack.

The Alstom calculations show higher concentrations closer to the stack than the ACC calculations. E.g. for the RFCC flue gas source the calculated maximum concentrations are $25\mu g/m^3$ 400 m from the stack for Alstom while ACC have maximum $11,5\mu g/m^3$ 500 m from the stack. This is due to difference in the outlet temperature. The temperature from the ACC facility is higher (45ºC vs. 18 ºC for Alstom), hence there will be a thermal lifting. The plume is lifted higher before horizontal dispersion occurs and maximum concentration using the ACC emission data is found further downwind and is consequently lower. The results presented here are calculated using outflow temperature of 18 ºC. Lower temperatures may occur (~10 ºC). However this will not alter the results significantly regarding to compliance with the air quality guidelines.

The ACC emissions using flue gas from the CHP (Figure 5 lower panel) will give somewhat lower hourly mean. This is due to higher velocity out of the stack, 22,5 m/s for CHP vs. 17,2 m/s for RFCC. Due to this the CHP plume will rise 10 m higher than the RFCC plume before horizontal dispersion. Hence the plume will reach the ground at a longer distance from the stack, and hence show lower concentrations.

This is also valid for the Alstom emission data (Figure 4), the CHP case gives higher outlet temperature and higher velocity out of the stack. Alstom may run their process with outlet temperature down to 10ºC. In this case there will be hardly thermal lifting, vertical dispersion will depend on velocity out of the stack only.

In addition to the emissions from the absorber units discussed above there will be emissions from the export gas stack. The gas will consist mainly of CO_2, with the addition of small quantities of NH_3 for Alstom, and the components listed in the bottom part of Table 10 for ACC. Model runs have been made for CO_2, the maximum concentration value of the additional components have been calculated by scaling.

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4.2 Emissions from Alstom Chilled ammonia technology

To obtain maximum hourly concentration from TCM the results using unit emission (1 g/s) are scaled according to the emission data described in section 3.1 (Table 6). For NH_3, the results from both the RFCC and CHP emissions are shown, emitting 2,2 g/s and 2,4 g/s respectively in worst case. For CO_2, only the RFCC emission data is shown. The reason for this is that the RFCC emission data is three times larger than the CHP (499,7 g/s vs. 138 g/s). The results are shown in Figure 6 and Figure 7.
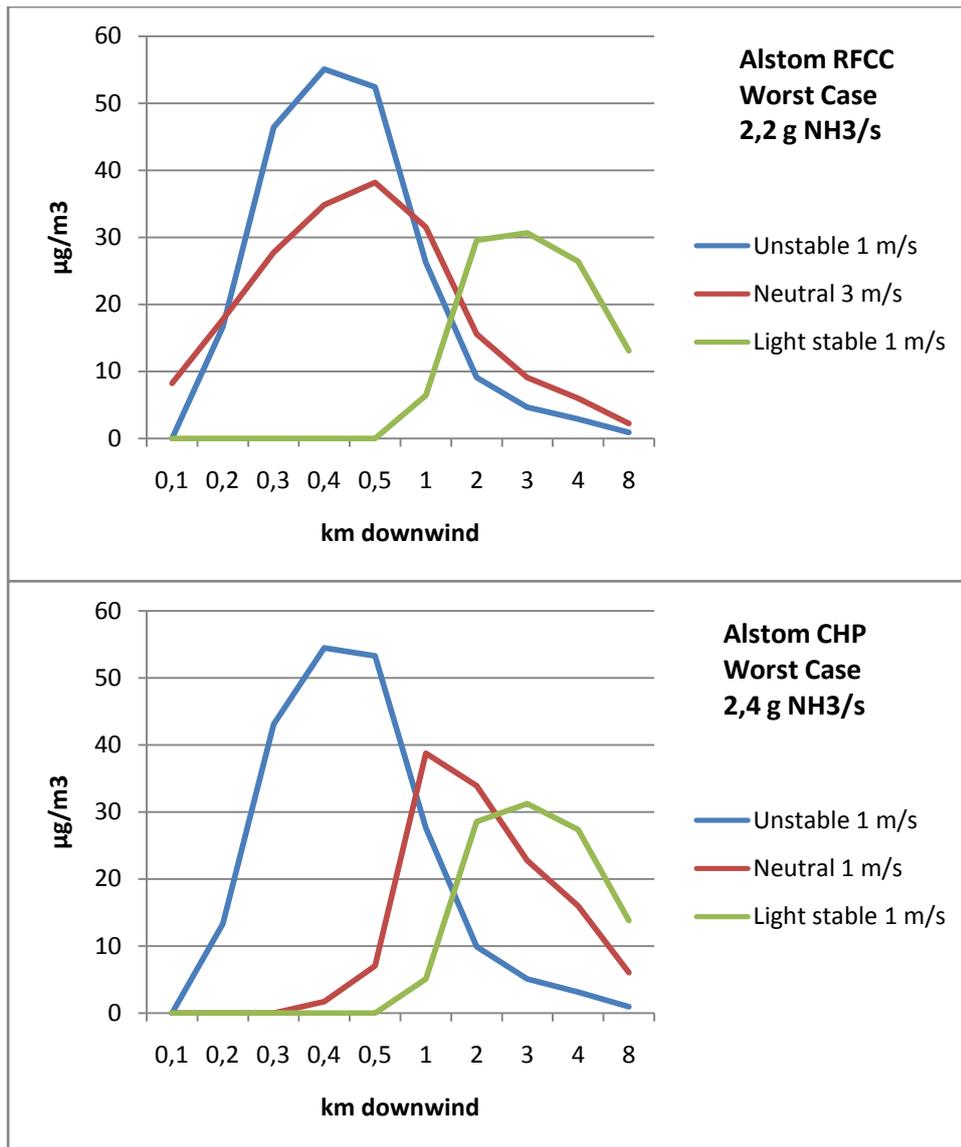

Figure 6: *Results for worst case emission scenario, Alstom emission data, RFCC emitting 2,2 g NH_3/s (top panel) and CHP emitting 2,4 g NH_3/s (lower panel). For each source, the three meteorological conditions that provide the highest concentrations were selected. For information on the emission conditions see section 3. The horizontal axis shows the distance from the source in kilometres and the vertical axis shows concentration as an hourly mean in µg/m³.*
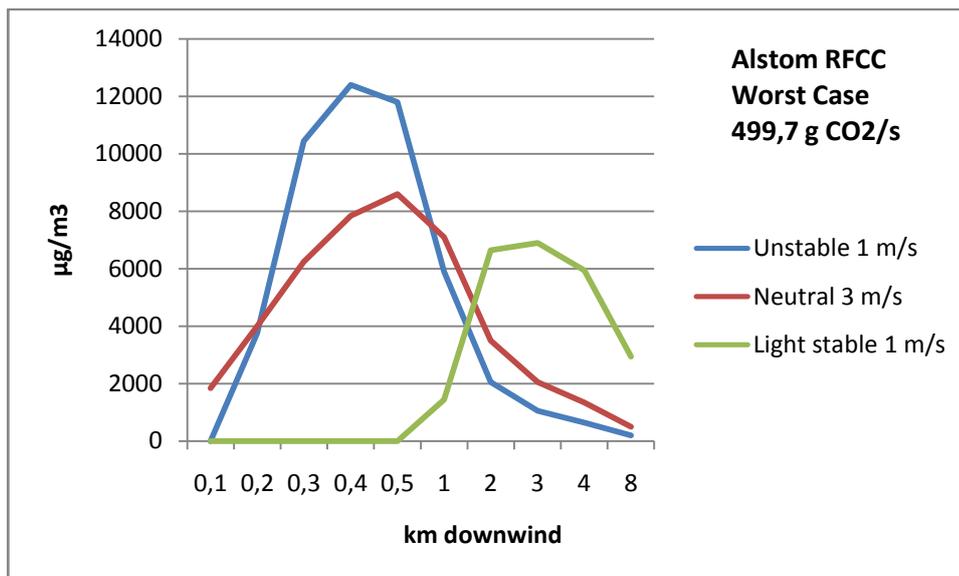
*Figure 7:   Results for worst case emission scenario, Alstom emission data,
RFCC emitting 499,7 g CO_2/s. For each source, the three
meteorological conditions that provide the highest concentrations
were selected. For information on the emission conditions see section
3. The horizontal axis shows the distance from the source in
kilometres and the vertical axis shows concentration as an hourly
mean in $\mu g/m^3$.*

For NH_3 the calculated maximum hourly concentration is 55 $\mu g/m^3$
(0.055 mg/m^3), for CO_2 the maximum is 12'400 $\mu g/m^3$ (12.4 mg/m^3).
Administrative norms for NH_3 and CO_2 that applies at the TCM plant are 18
mg/m^3 and 9'000 mg/m^3 respectively (Table 3). This means that the
concentrations are more than a factor 300 and 700 lower than the norm.

Export gas stack
The concentrations of CO_2 for emissions from the export gas stack are shown in
Figure 8. The maximum ground level CO_2 concentration is calculated to be 71
mg/m^3 using export gas from RFCC cleaning. This is less than 1 % of norm from
the Labour Authorities. For NH_3 the maximum concentration is calculated to be
3.5 $\mu g/m^3$ (worst case emissions with RFCC cleaning). This is less than 1 ‰ of
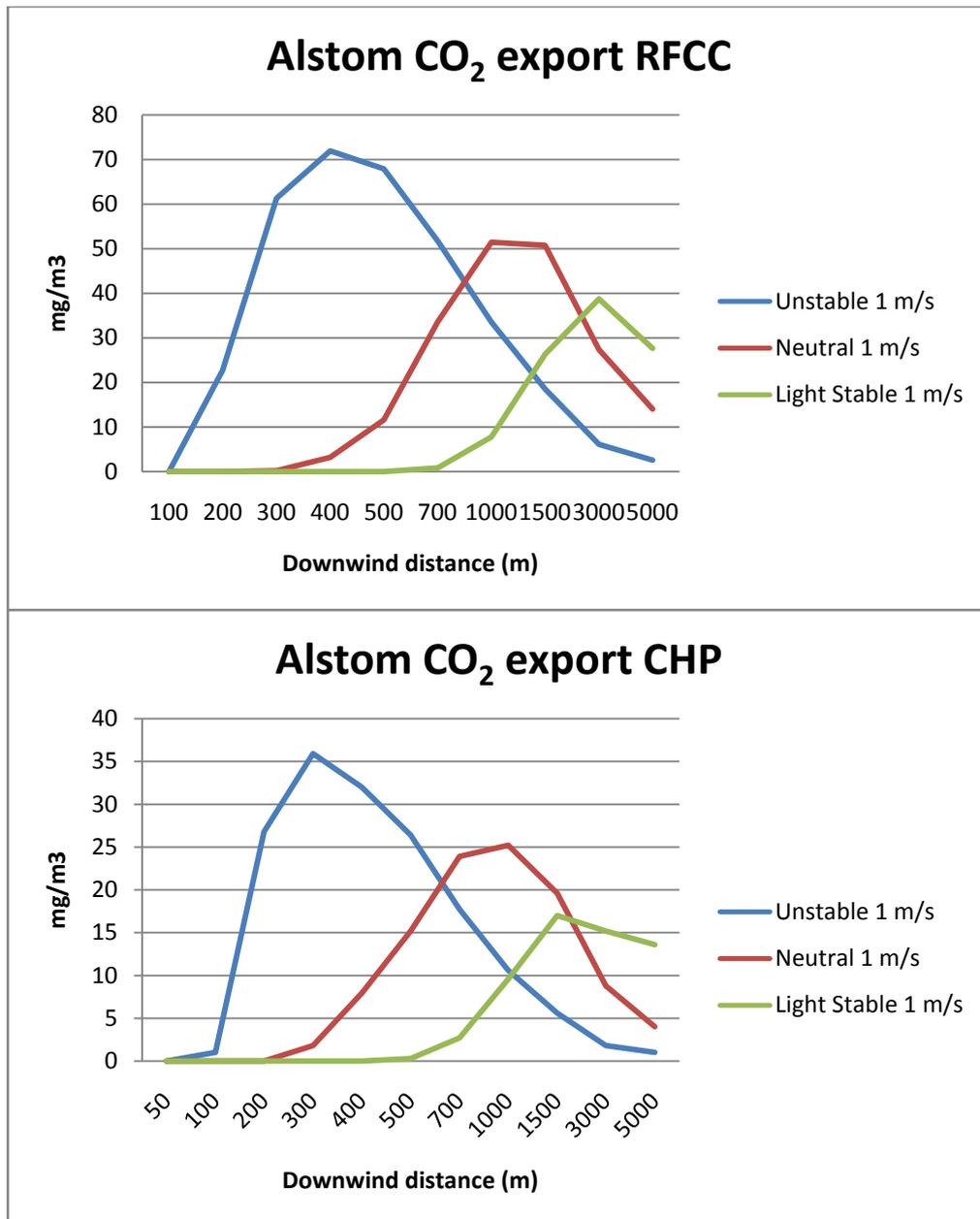the norm.

Figure 8: Concentrations of CO₂ from emissions through the export gas stack, both scenarios. Upper pane – RFCC gas, lower pane CHP – gas.

4.3 Emissions from Aker Clean Carbon amine technology

In the same manner, to obtain maximum hourly concentration from TCM the results using unit emission (1 g/s) are scaled according to the emission data described in section 3.2. In scenarii 1-4 and 6 (Table 9 and Table 10) there are 25 components emitted, for scenarii 5a-5d Improved solvents (Table 11 and Table 12) there are 30 and 14 components respectively. MEA, NH_3, formaldehyde, acetaldehyde, and alkylamines (methylamine, ethylamine, dimethylamine, diethylamine) are shown here. These are the main components emitted from the ACC facility. For the other components the quantities emitted are fairly small, i.e.

mg/s or µg/s scale. And since emissions of 1 g/s gives a maximum concentration of 25 µg/m^3 (Figure 4), then emissions of 1 mg/s will give 25 ng/m^3 maximum concentration and so on. These are much lower concentrations than any of the air quality guidelines or threshold values listed in Table 3 - Table 5.

For MEA, scenario 4 "Upset" emitting 0.187 g MEA/s (RFCC) and 0.246 g MEA/s (CHP) respectively are shown. Concerning NH_3, emitted at a rate of 0.85 g NH_3/s (equals 98,7 ppmv, see Table 10) only the RFCC emission data is displayed. Formaldehyde, acetaldehyde, and alkylamines are emitted at a rate 0.15 g/s, 0.22 g/s and 0.08 g/s respectively using flue gas from CHP.
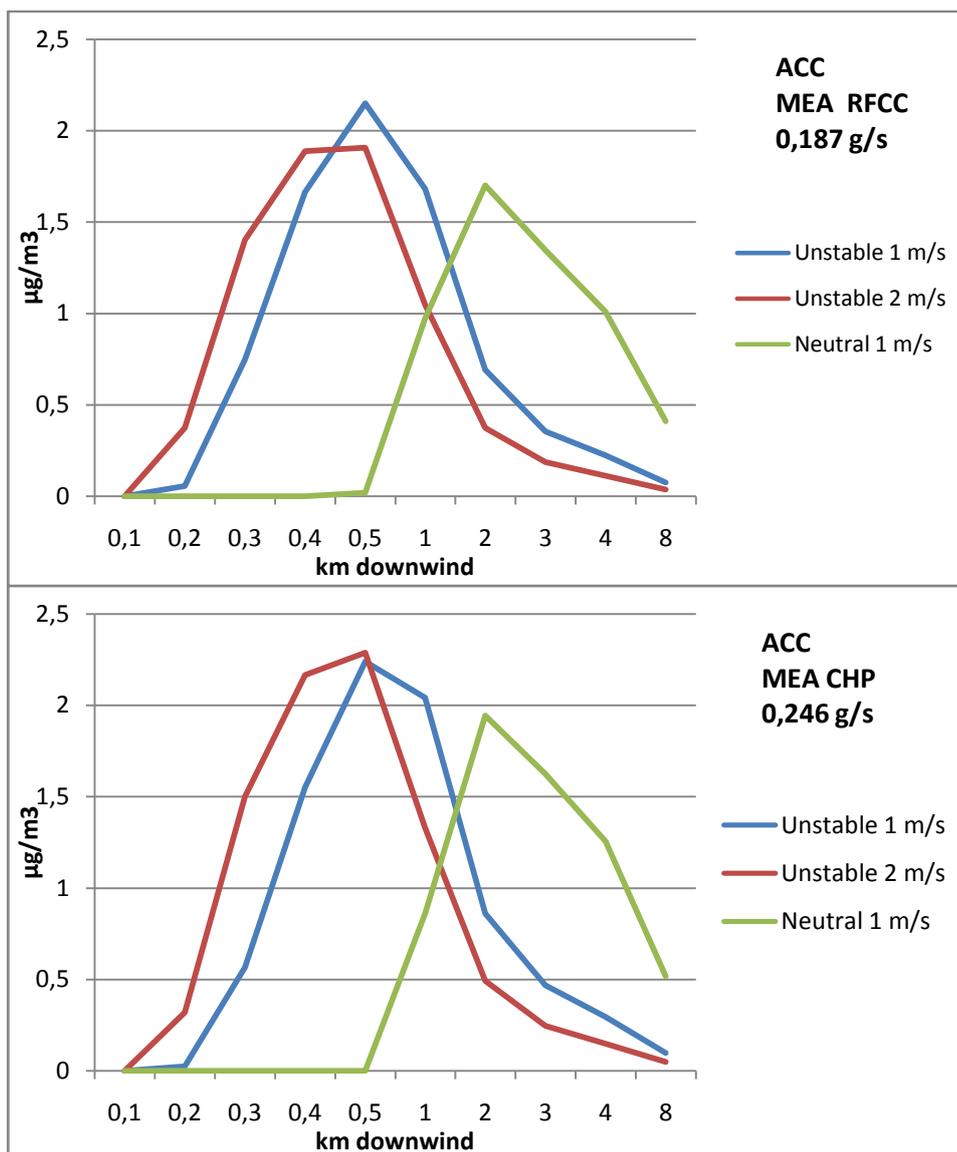

Figure 9: *Results using ACC emission data, flue gas from RFCC emitting 0.187 g MEA/s (top panel) and flue gas from CHP emitting 0.246 g MEA/s (lower panel). For each source, the three meteorological conditions that provide the highest concentrations were selected. For information on the emission conditions see section 3. The horizontal axis shows the distance from the source in kilometres and the vertical axis shows concentration as an hourly mean in µg/m^3.*
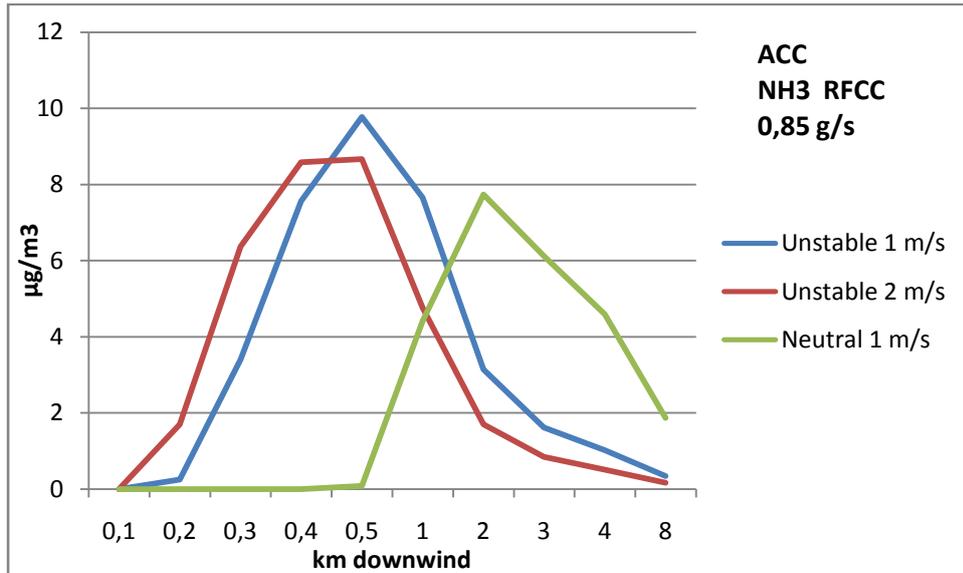
Figure 10: Results using ACC emission data, flue gas from RFCC emitting 0.85 g NH₃/s. For each source, the three meteorological conditions that provide the highest concentrations were selected. For information on the emission conditions see section 3. The horizontal axis shows the distance from the source in kilometres and the vertical axis shows concentration as an hourly mean in μg/m³.

The maximum calculated hourly concentration of MEA is about 2 μg/m³. This is much lower than the Administrative norm (Table 3) and also lower than long term exposure guidelines (Table 4). Maximum calculated NH_3 concentration is just below 10 μg/m³. This is a factor 1800 lower than administrative norm (18 mg/m³).
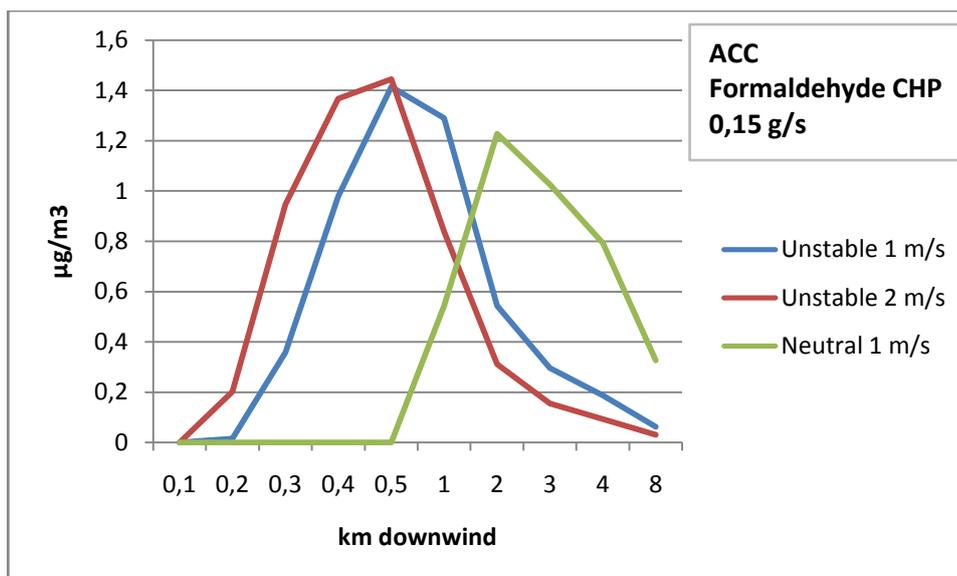
Figure 11: Results of formaldehyde, acetaldehyde, and alkylamines using ACC emission data, flue gas from CHP emitting 0.15 g/s formaldehyde (upper panel), 0.22 g/s acetaldehyde (mid panel) and 0.08 g/s alkylamines (lower panel). For each source, the three meteorological conditions that provide the highest concentrations were selected. For information on the emission conditions see section 3. The horizontal axis shows the distance from the source in kilometres and the vertical axis shows concentration as an hourly mean in µg/m³.
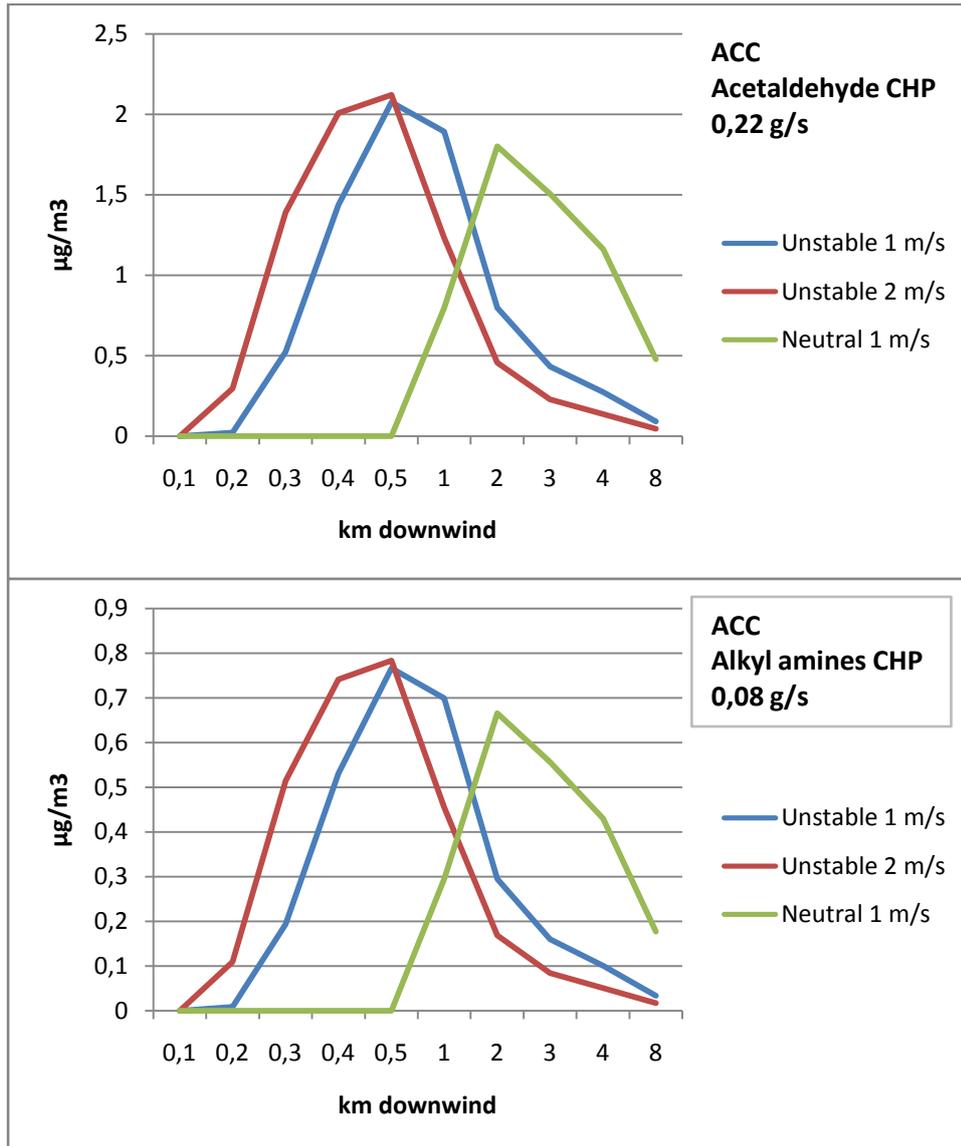
Figure 11: Contd.

The maximum calculated hourly concentrations of formaldehyde, acetaldehyde, and alkylamines are 1.4 μg/m³, 2.1 μg/m³, and 0.8 μg/m³ respectively. The administrative norms for all these components range from 0.6 mg/m³ (formaldehyde) to 45 mg/m³ (acetaldehyde, see Table 3), and all calculated maximum concentrations are well below these values.

Figure 12: *Results of methylamine using ACC emission data, flue gas from CHP emitting 0.03 g/s For each source, the three meteorological conditions that provide the highest concentrations were selected. For information on the emission conditions see section 3. The horizontal axis shows the distance from the source in kilometres and the vertical axis shows concentration as an hourly mean in µg/m³.*
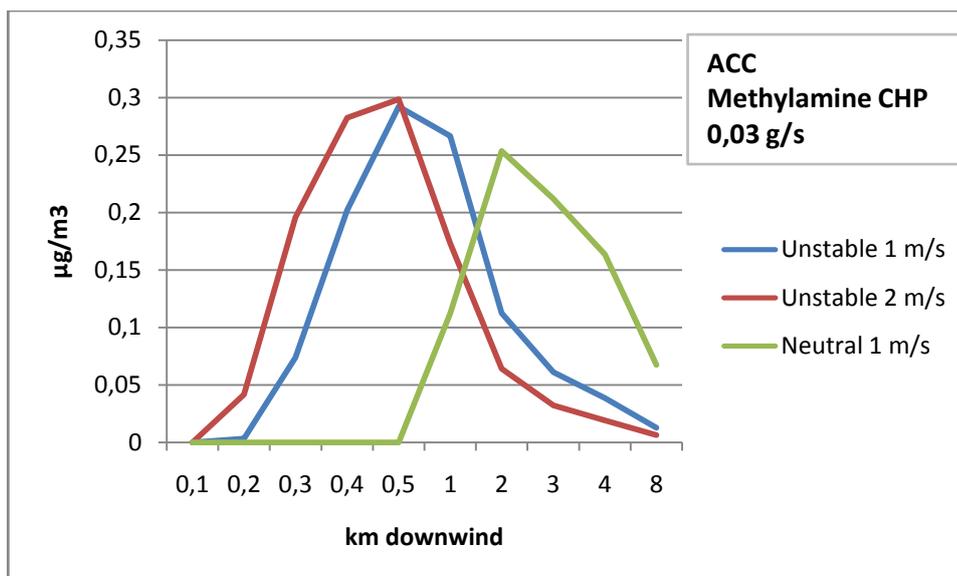
Methylamine has a strong smell (rotten fish), and therefore it is investigated separately. Maximum emissions of methylamine is 0.03 g/s (scenario 4 Upset, CHP) and the maximum hourly mean concentration is 0.3 µg/m³. This is the mean concentration for one hour. However the short term concentrations may vary considerably within one hour depending on the atmospheric conditions (turbulence etc.). For smell the short term maximum concentration is perhaps more important than the long term mean. As a general rule the maximum short term concentration within one hour is typically a factor 10 higher than the hourly mean. This means that for short periods of time methylamine concentrations of up to 3 µg/m³ may occur. The threshold value for smell ("luktterskel" in Norwegian) for methylamine is 5 ppmv. This corresponds to 6 mg/m³, i.e. that the value for smell is half the administrative norm. Then the estimated short term concentrations outlined here will be much lower than the detection limit for smell.

For Scenario 5d Improved solvent 2 Worst case (S1, S4, S9) the maximum hourly concentrations of piperazine, primary amine, secondary amine, and tertiary amine are calculated. These will be emitted at a rate of 0.1ppmv/0.005 g/s for piperazine, and 2.24 ppmv for primary amine, 0.7 ppmv for secondary amine, and 0.06 ppmv for tertiary amine. The exact composition of this solvent is not known to NILU and the molar mass is based on a given estimate. This corresponds to approximately 0.09 g/s for primary amine (assuming molar mass about 60), and 0.045 g/s for secondary and 0.004 g/s for tertiary amine (assuming molar mass of about 100).

The results are shown in Figure 13. Maximum concentrations of piperazine, primary amine, secondary amine, and tertiary amine are 0.055 µg/m³, 0.85 µg/m³, about 0,4 µg/m³, and slightly less than 0.04 µg/m³ respectively. Threshold value for working environment for piperazine is 0.3 mg/m³, so the maximum hourly concentration is well below the threshold value. Since the exact composition of these primary, secondary and tertiary amine emissions is not given, it is not possible to evaluate the environmental and health effects of these emissions.
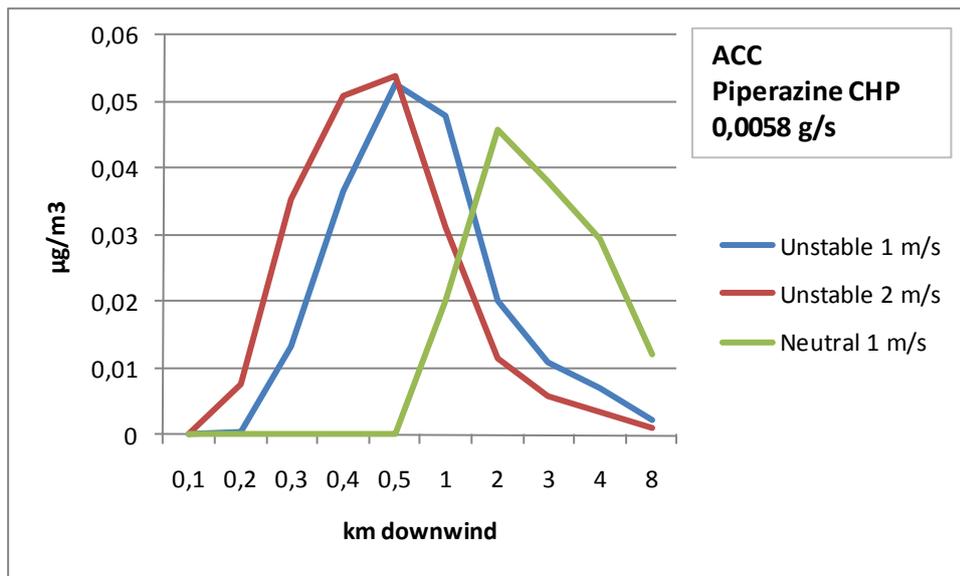
Figure 13: *Results of piperazine, primary amine, secondary amine, and tertiary amine using ACC emission data 5d Improved solvent 2 Worst case (S1, S4, S9), flue gas from CHP. For each source, the three meteorological conditions that provide the highest concentrations were selected. For information on the emission conditions see section 3. The horizontal axis shows the distance from the source in kilometres and the vertical axis shows concentration as an hourly mean in µg/m³.*

Figure 13: Contd.

The total emissions of NO_x will be between 148 and 208 ppm using gas from RFCC (TCM design basis). Flue gas from CHP will have NO_x levels below 5 ppm. Maximum emissions of NO_2 from RFCC is 6 ppm. This is equal to an emission rate of 0,14 g/s [footnote 2]. The maximum hourly concentrations of NO_2 are showed in Figure 14.

Figure 14: Results of NO_2 using ACC emission data, flue gas from RFCC emitting 6 ppm/0.14 g/s. For each source, the three met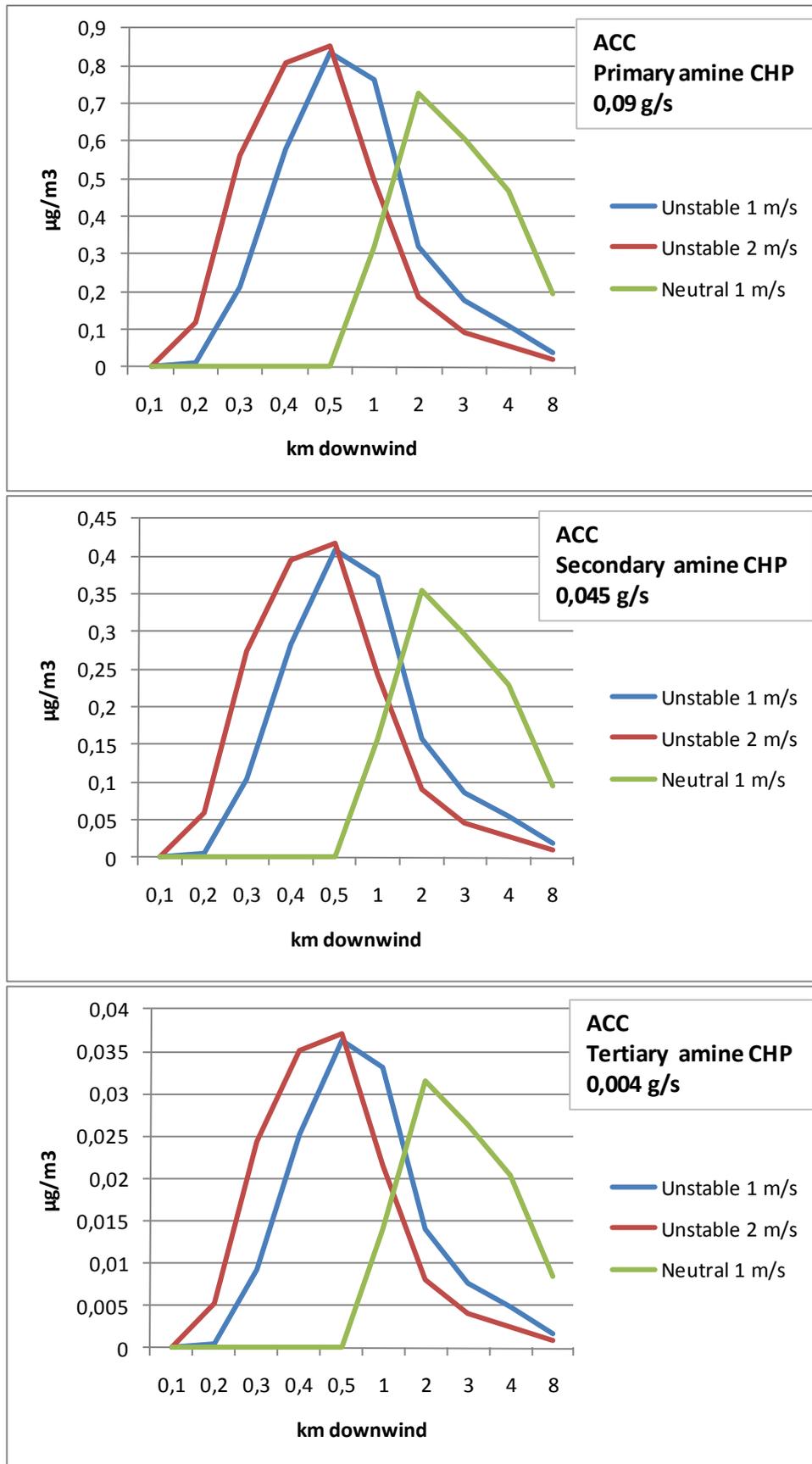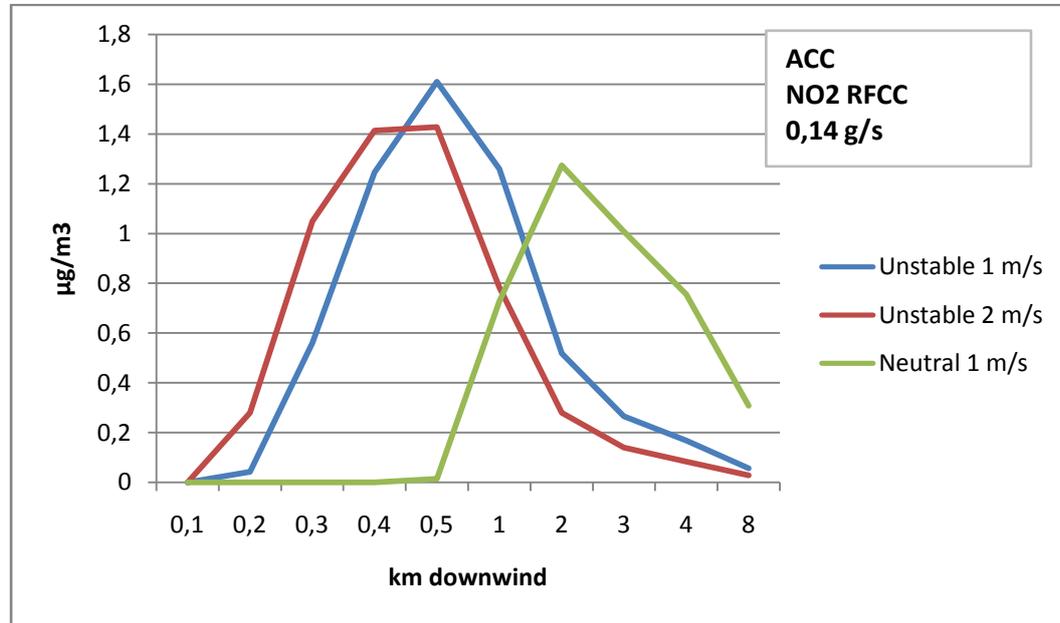eorological conditions that provide the highest concentrations were selected. For information on the emission conditions see section 3. The horizontal axis shows the distance from the source in kilometres and the vertical axis shows concentration as an hourly mean in $\mu g/m^3$.

Maximum calculated hourly concentration from TCM is then 1.6 $\mu g/m^3$. The NO_2 contribution from TCM has to be added to the background concentration. In 2008-2009 NILU performed a monitoring program at Kollsnes (report in preparation). The average background concentration of NO_2 at Kollsnes is below 4 $\mu g/m^3$. In sum the NO_2 concentration at Mongstad will be below all air quality standards outlined in Table 2. The maximum downwind NO_2 concentration from the emissions will depend upon the upwind ozone concentration rather than the small NO_2 emissions (the reaction $NO+O_3 -> NO_2+O_2$ will titrate O_3 and give enhanced NO_2 concentrations). NO_2 is photolyzed back to NO ($NO_2+h\nu -> NO+O$). This photolysis depend on the amount of sunlight and is not investigated further here.

It should be noted that recently it has been a reduction in the NO_x level due to installation of SNCR (Selective Non-Catalytic Reduction) in the RFCC flue gas system.

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[2] Assume total flow rate of 1837 kmole pr hour and molar mass 46.01 for NO2.

Emissions through the export gas stack

The primary component of the gas is obviously CO_2. The ground level concentrations will be highest for RFCC gas cleaning. The concentrations of CO_2 are shown in Figure 15. The maximum concentration is lust above 70 mg/m^3, less than 1 % of the CO_2 norm.
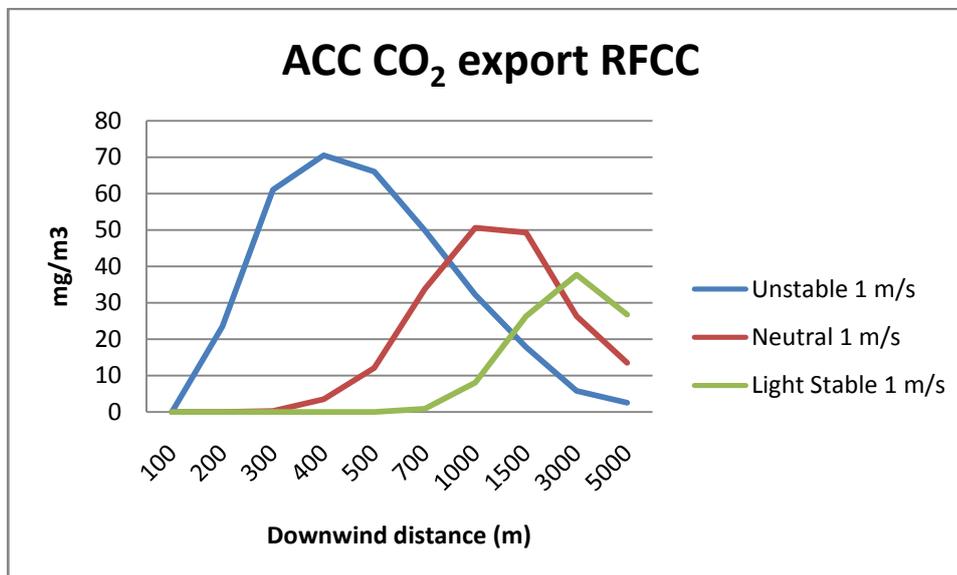
Figure 15: Ground level CO₂ concentrations from the export gas stack, cleaning of RFCC gas.

The concentrations of the additional components given in the emission scenarios will be highest for scenario 4 "upset". The calculated maximum ground level concentrations are shown in Table 13. These concentrations are small compared to the contribution from the absorber, except for acetaldehyde which is marginally smaller than the contribution from the absorber.

Table 13: Maximum ground level concentrations from additional components emitted through the export gas stack.

Component	Concentration ($\mu g/m^3$)
MEA	0.201
NH3	0.039
Formaldehyde	0.083
Acetaldehyde	1.656
Acetone	0.059
Formic acid	0.331
Acetic acid	1.877

4.4 Summary of all calculated maximum hourly mean concentrations

To give a clearer overview all results from this chapter are summarized in Table 14. These are not new results, but taken from the text. These values are lower than the Administrative norms for the components listed in Table 3 and lower than the guidelines from FHI for the components listed in Table 4.

Table 14: Maximum hourly mean concentrations of the components investigated in this section. Unit: µg/m³.

Technology vendor / component	Maximum hourly concentration
Alstom	
NH_3	55 µg/m³
CO_2 (from export gas stack)	71 900 µg/m³
ACC	
MEA	2 µg/m³
NH_3	10 µg/m³
Formaldehyde	1.4 µg/m³
Acetaldehyde	2.1 µg/m³
Alkyl amines	0.8 µg/m³
Methylamine	0.3 µg/m³
Piperazine	0.055 µg/m³
Primary amine	0.85 µg/m³
Secondary amine	~0.4 µg/m³
Tertiary amine	slightly less than 0.04 µg/m³
NO_2 (from RFCC flue gas)	1.6 µg/m³
CO_2 (from export gas stack)	70 500 µg/m³

5 Annual mean and 8-hours mean maximum concentrations and annual deposition of main pollutants

5.1 Unit emissions

To calculate annual mean and 8-hours mean concentrations, annual deposition and concentration in drinking water The Air Pollution Model (TAPM) developed by CSIRO, Australia, is applied. A detailed description of the model and its application can be found in Karl et al. (2010) or at TAPM (2009). TAPM is also used for dispersion calculations from Kårstø (Attalla and Azzi, 2010). For convenience a short description is given here.

TAPM is an integrated model consisting of a prognostic meteorological module and a set of air quality modules. For this study the meteorological module is nested three times, from an initial domain of 600×600 km^2 (grid resolution of 15 km) down to a domain of 80 x 80 km^2 (2 km resolution) centered on TCM. Meteorological data represents year 2007. Initial and boundary conditions for the outermost grid are taken from the LAPS and GASP models from the Australian Bureau of Meteorology. Physical surface data, such as topography, land use and sea surface temperature are taken from various sources (the US Geological Survey, Earth Resources Observation Systems (EROS) Data Center Distributed Active Archive Center (EDC DAAC) and the US National Center for Atmospheric Research NCAR).

The air quality modules used in the simulations are the Lagrangian Particle Model (LPM) and the Plume Rise Module (PRM). The LPM is based on the PARTPUFF model (Hurley, 1994) whereby mass is represented as a puff in the horizontal direction, and as a particle in the vertical direction. The PRM, used for point source emission, determines plume rise based on stack configuration and emission dynamics. In this study the emitted amines are assumed to be chemically inert but undergo both wet and dry deposition processes. The deposition of the amines are treated in the same way as for sulfur dioxide. The amines are assumed to be highly soluble and totally removed by wet deposition. Amines are deposited directly to the ground. Further degradation in soil/vegetation surfaces is not considered.

The first results for unity emission (1 g/s) are shown. Assuming that the emitted amines are chemically inert (see section 5.3 for discussion on this assumption), these results can be scaled according to the quantity emitted. This is the same approach used to calculate maximum hourly concentration in section 4. Both annual mean concentration, maximum 8-hours mean concentration and annual wet deposition are calculated. Results from a model run emitting 1 g/s (unity emission) are shown in Figure 16.

Annual mean concentrations are most important for the compounds where long term exposure, carcinogenic effects or *chronic* toxicity are the key parameters. Maximum 8-hours mean concentrations are important for the compounds where short term exposure or *acute* toxicity are the key parameters, whereas annual mean deposition calculation is necessary to determine possible effects on eutrophication and drinking water concentrations.
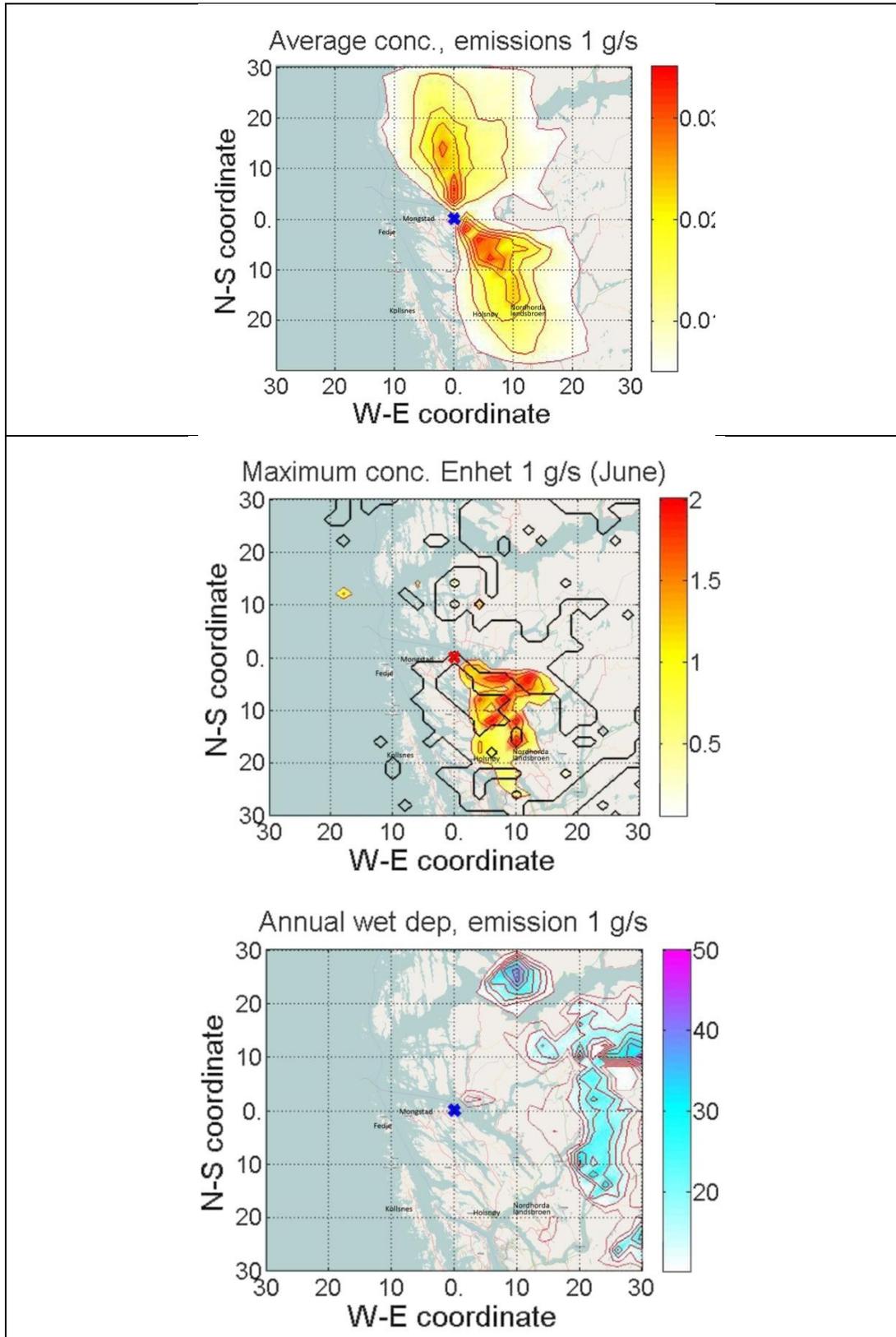
Figure 16: Annual mean concentration (upper panel), maximum short term concentration (8 hrs., mid panel) and annual wet deposition (lower panel) for a model run emitting 1 g/s. Horizontal scale is in km. Units: $\mu g/m^3$ for concentrations and $mg/(m^2\ year)$ for deposition.

For the annual mean concentration the prevailing wind directions are clearly seen, from the south and from the north-west. The maximum annual mean concentration (0.03 μg/m^3) is found about 10 km downwind of TCM in S-E direction.

Maximum monthly mean concentrations vary between 0.03 and 0.15 μg/m^3 (for the 12 months January-December, results not shown). Note that the location of the monthly maxima differ throughout the year. Hence the maximum annual mean value is **not** equal to the average of the maximum monthly values.

The highest short term concentration, 2.4 μg/m^3 for a 8-hr period is found in June, again S-E of the CO2 Technology Centre. This is considerably lower than the hourly mean concentrations showed in Figure 4 and Figure 5. This is due to differences in spatial and temporal resolution in the model results. CONCX gives a detailed description of the maximum hourly concentration close to the stack. In Figure 16 TAPM gives 8-hour average values representative for 2×2 km^2 grid squares.

The wet deposition is a combination of synoptic scale weather patterns modified by topography. Wet deposition has maximum east of TCM. This is due to orographic rainfall, a well-known phenomenon in the western part of Norway. Annual mean rainfall at Mongstad is 1890 mm/year (met.no, eKlima.no), but there are considerable local differences. Maximum annual wet deposition is calculated to be 39 mg/(m^2 year) emitting unit emission of 1 g/s.

TAPM calculates the atmospheric meteorological parameters (advection/wind, temperature, humidity, rainfall) based on the laws of physics that governs the atmosphere. There are uncertainties in these calculations. The uncertainty or error for TAPM is less than 30 % for predictions of observed mean concentrations of passive agents released from stacks.

It is also important to emphasize that the meteorological data ("weather") represents the year 2007. In the real atmosphere there are inter-annual variations in weather. Hence the dispersion from TCM will change accordingly. This means that deposition, location and magnitude of maxima etc. may vary from year to year. However the results presented here are considered representative for the situation that will occur in the vicinity of Mongstad when TCM will be in operation.

5.2 Emissions from Alstom facility

The emission data from Alstom is listed in Table 6 and Table 7. It does not contain any toxic substances, only NH_3, CO_2 and water vapour + "normal air" (N_2, O_2 and Ar). CO_2 is not toxic. It is a green house gas, but that topic is beyond the scope of this report. Concerning NH_3, the current analysis has covered concentrations in working atmosphere and ambient air and possible eutrophication effects on vegetation. The calculations of maximum hourly concentrations (section 4.2) reveal that calculated concentrations of NH_3 are much lower than the administrative norms for working environment (18 000 μg/m^3) and the estimated air quality guideline of 180 μg/m^3 (1/100 of the norms). NH_3 will, however,

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contribute to eutrophication, i.e. excess of nitrogen in soil and water. Hence, the annual mean concentration in air and annual mean deposition of nitrogen must be calculated.

The maximum emission rate from the Alstom facility is 2.4 g NH_3/s (Worst case using flue gas from CHP, see Table 7) and a total of 2.5 g/s when adding the emissions from the export stack. For short term (8 hours mean) maximum concentration, this is the correct scenario to use. Hence the results from the unity emissions are scaled by a factor 2.5. On the other hand, the average emission rate of NH_3 from Alstom is 0.08 g NH_3/s (both base case scenarii, RFCC and CHP, see Table 6 and Table 7) and a total of 0.105 g/s adding the amissions from the export stack. For calculation of annual mean deposition, the base case scenario is most correct, and 0.105 g NH_3/s equals 0.086 g N/s [3].

Both maximum short term concentration and annual mean wet deposition are shown in Figure 17. Evidently the results are very similar to the results in Figure 16 using unity emission since it is a question of scaling (for the 8-hr maximum with a factor of 2.5 and for the annual deposition with a factor of 0.086). The maximum 8-hrs mean concentration (6.1 $\mu g/m^3$) is seen S-E of Mongstad whereas wet deposition shows two maxima, one to the north of Mongstad and one to the east. Calculated maximum deposition is 3.2 mg N/(m^2 year).

Concerning wet deposition the value of 3.2 mg N/(m^2 year) is relatively low, around 0.3 %, compared to the annual nitrogen deposition of 800-1000 mg N/(m^2 year) near Mongstad (Figure 1). However if the worst case scenario applies the deposition will be nearly a factor 30 higher and wet deposition increases to over 70 mg N/(m^2 year) (results not shown). Given that nitrogen deposition at Mongstad is already over the threshold values for vegetation any extra nitrogen will contribute to eutrophication.

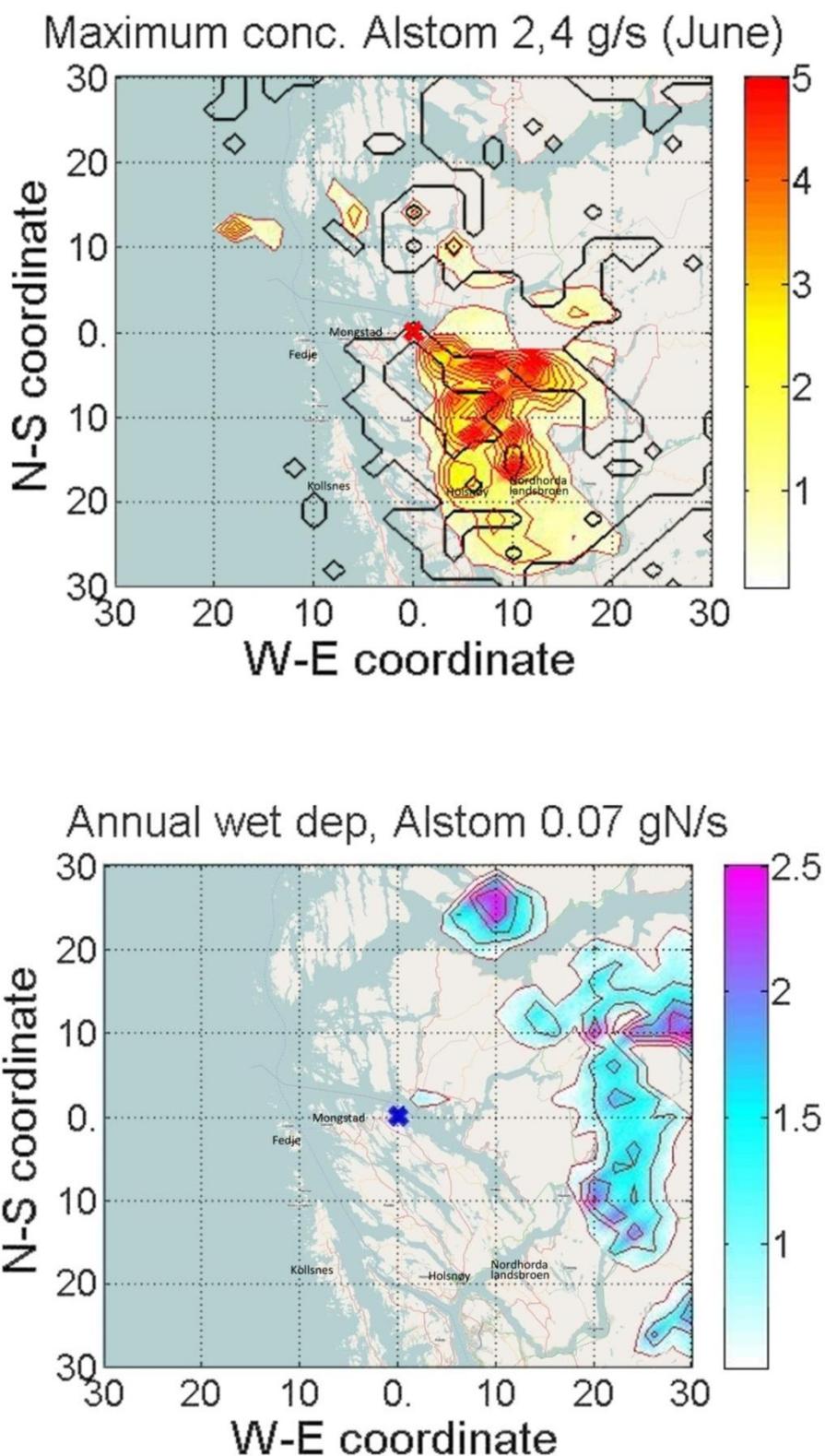[3] Molar mass 14 for N and 1 for H, thus multiply by 14/17 to get total N instead of NH_3.

*Figure 17: Maximum short term concentration of NH₃ (upper panel) and annual
mean wet deposition of N (lower panel) from the Alstom facility
assuming an emission rate of 2,4 g NH₃/s and 0.08 g NH₃/s
respectively. Horizontal scale is in km. Units: μg/m³ for
concentrations and mg/(m² year) for deposition.*

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To summarize this section, the maximum short term concentration from Alstom chilled ammonia plant is calculated to be 6.1 µg NH_3/m^3 (June) whereas the maximum wet deposition is 3.2 mg $N/(m^2$ year).

5.3 Results of amines and degradation products using emissions from ACC facility

In this section calculated concentrations of amines and degradation products are presented. The results are based on the unit emission calculations outlined in section 5.1, scaled according to the emission data given by ACC. This method is valid if the compounds are assumed to be inert or to have a lifetime longer than hours/days. For example MEA has an atmospheric lifetime of about a day, formaldehyde has a lifetime of typically 8-10 hrs, acetaldehyde about half to one day. This means that most of the mass emitted from TCM will not be degraded within the 30 km model grid. To give an example; if the wind speed is 2 m/s, or 7,2 km/hr, the flue gas emitted from TCM will be transported 30 km away in about 4 hours. So if the lifetime of a component is about half a day (12 hours) or more, most of the molecules of this component will not be degraded within 30 km from TCM, and it may be considered inert in these calculations. Of course there will be some chemical loss, even if the lifetime is long, but the loss will be small compared to the total mass/concentration of the component.

The calculated concentrations will be compared to air quality limit values (see section 2). Concentrations of MEA, acetaldehyde, formaldehyde, alkyl amines and piperazine will be shown. Concerning nitrosamines, please see section 5.4. (worst case calculations).

MEA:
Scenario 2 ("Design",) estimates 1 ppmv of MEA in the flue gas. This is equal to 0.04 g MEA/s using flue gas from CHP. Hence the results using unit emissions are scaled by a factor 0.04. The calculated annual mean concentrations are shown in Figure 18. Maximum annual concentration of MEA is below 1.3 ng/m^3 (0.0013 µg/m^3) downwind of TCM in S-E direction. This is several orders of magnitude lower than the exposure guideline for MEA (10 µg/m^3) given by FHI (Table 4).
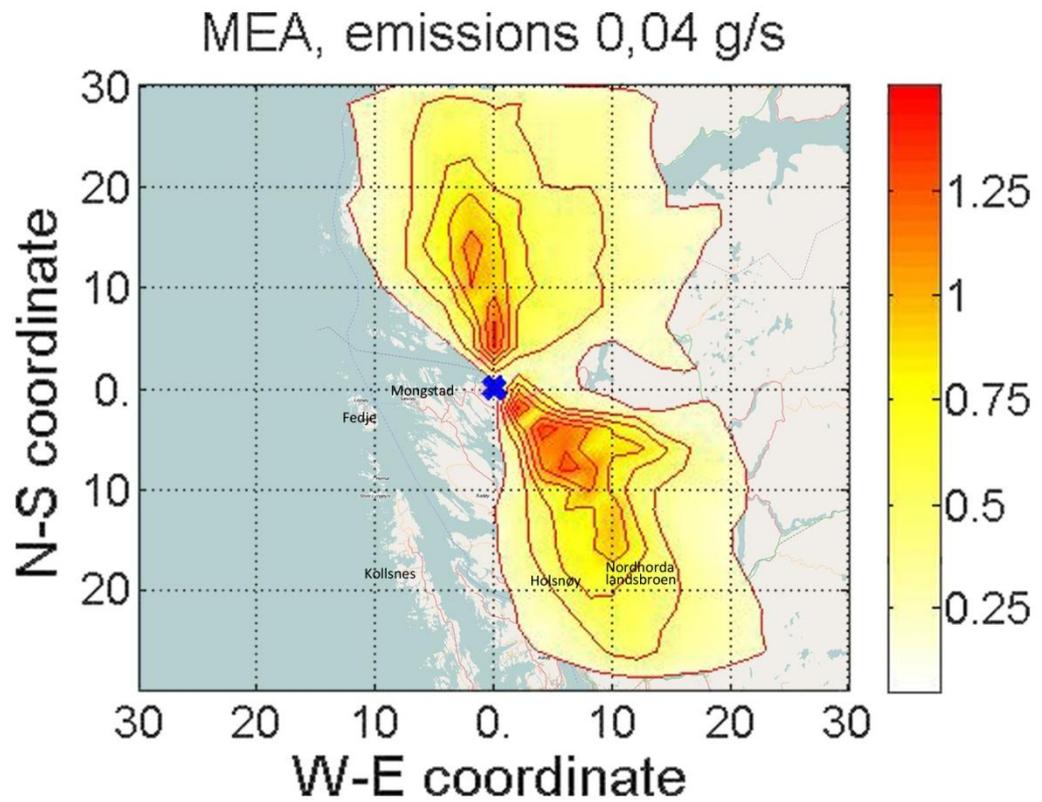
Figure 18: Annual mean concentration of MEA for a model run emitting 0.04 g/s. Horizontal scale is in km. Units: ng/m³.

Formaldehyde:

Scenario 2 ("Design") estimates 0.05 g/s of formaldehyde using flue gas from CHP. Hence the results using unit emissions are scaled by a factor 0.05. The calculated annual mean concentrations are shown in Figure 19. Maximum annual concentration of formaldehyde is just above 1.6 ng/m^3 downwind of TCM in S-E direction. This is several orders of magnitude lower than the exposure guideline (1.2 mg/m^3) given by FHI (Table 4).
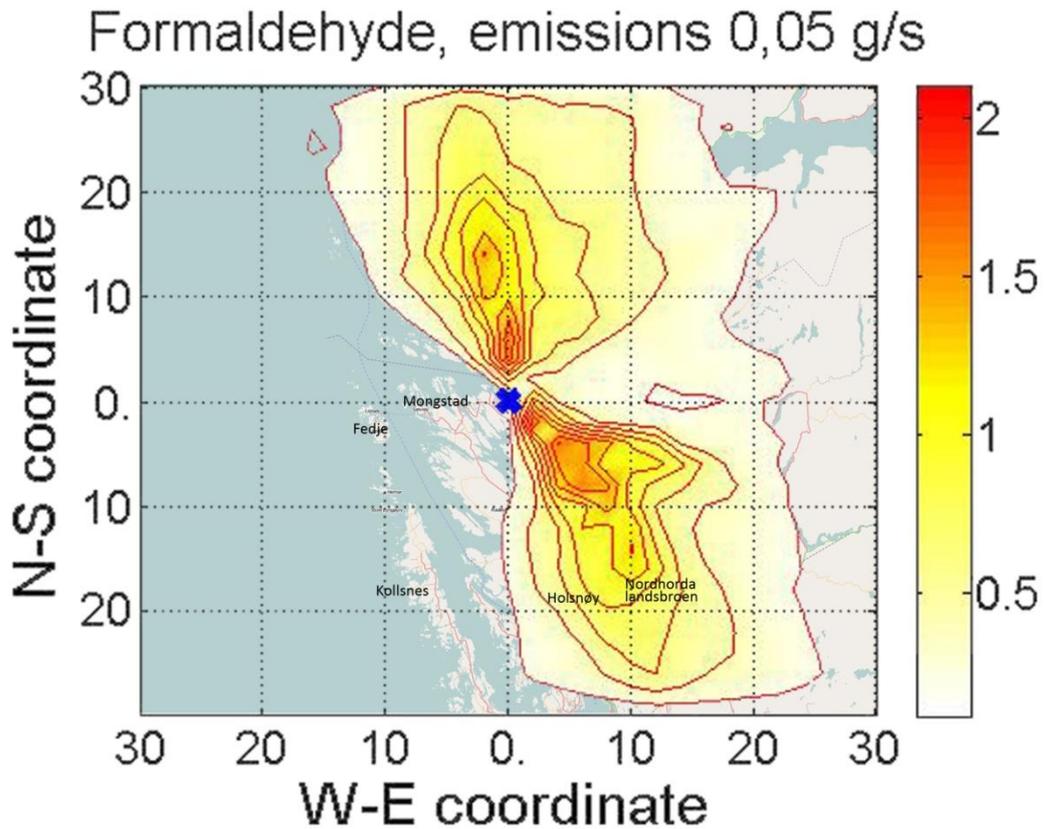
Figure 19: Annual mean concentration of formaldehyde for a model run emitting 0.05 g/s. Units: ng/m^3.

Acetaldehyde:
Scenario 2 ("Design") estimates 0.07 g/s of acetaldehyde using flue gas from CHP. Hence the results using unit emissions are scaled by a factor 0.07. The calculated annual mean concentrations are shown in Figure 20. Maximum annual concentration of acetaldehyde is 2.4 ng/m^3 (0.0024 μg/m^3) downwind of TCM in S-E direction. This is much lower than the exposure guideline (2 μg/m^3) given by FHI (Table 4).

Figure 20: Annual mean concentration of acetaldehyde for a model run emitting 0.15 g/s. Horizontal scale is in km. Units: ng/m^3.

Alkyl amines:

Scenario 2 ("Design") lists several alkyl amines, among others methylamine, ethylamine, dimethylamine, diethylamine. Methylamine (0.011 g/s) and dimethylamine (0.015) are the most important ones in terms of emission strength. In all the total emissions of alkyl amines are about 0.03 g/s using flue gas from CHP. Hence the results using unit emissions are scaled by a factor 0.03. The calculated annual mean concentrations are shown in Figure 21. Maximum annual concentration of alkyl amines is just below 1.0 ng/m^3 downwind of TCM in S-E direction. Secondary and tertiary alkyl amines have a potential to form nitrosamines, primary alkyl amines do not. However this is not investigated in further detail here.
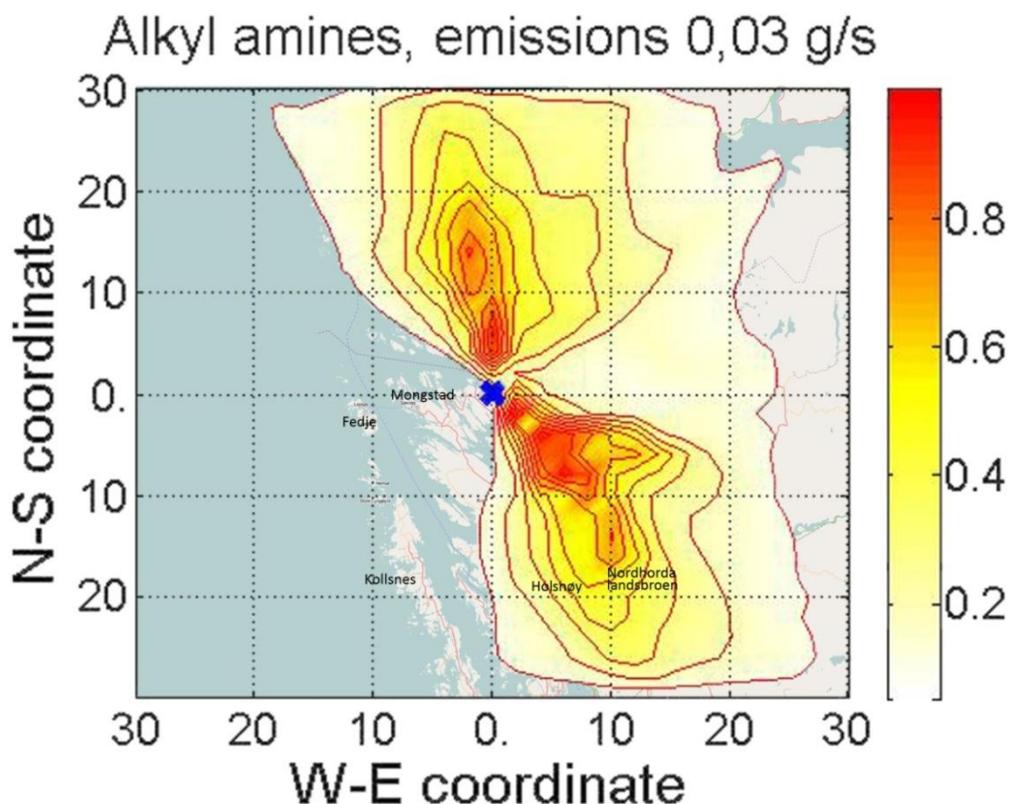
Figure 21: Annual mean concentration of alkyl amines for a model run emitting 0.03 g/s. Horizontal scale is in km. Units: ng/m^3.

Piperazine

Scenario 5c ("Improved solvent 2 Design (S1, S4, S9)") estimates 0.1 ppmv/0.0057 g/s of piperazine using flue gas from CHP. Hence the results using unit emissions are scaled by a factor 0.0057. The calculated annual mean concentrations are shown in Figure 22. Maximum annual concentration of piperazine is 0.18 ng/m^3. downwind of TCM in S-E direction. This is much lower than the exposure guideline (5 μg/m^3) given by FHI (Table 4).

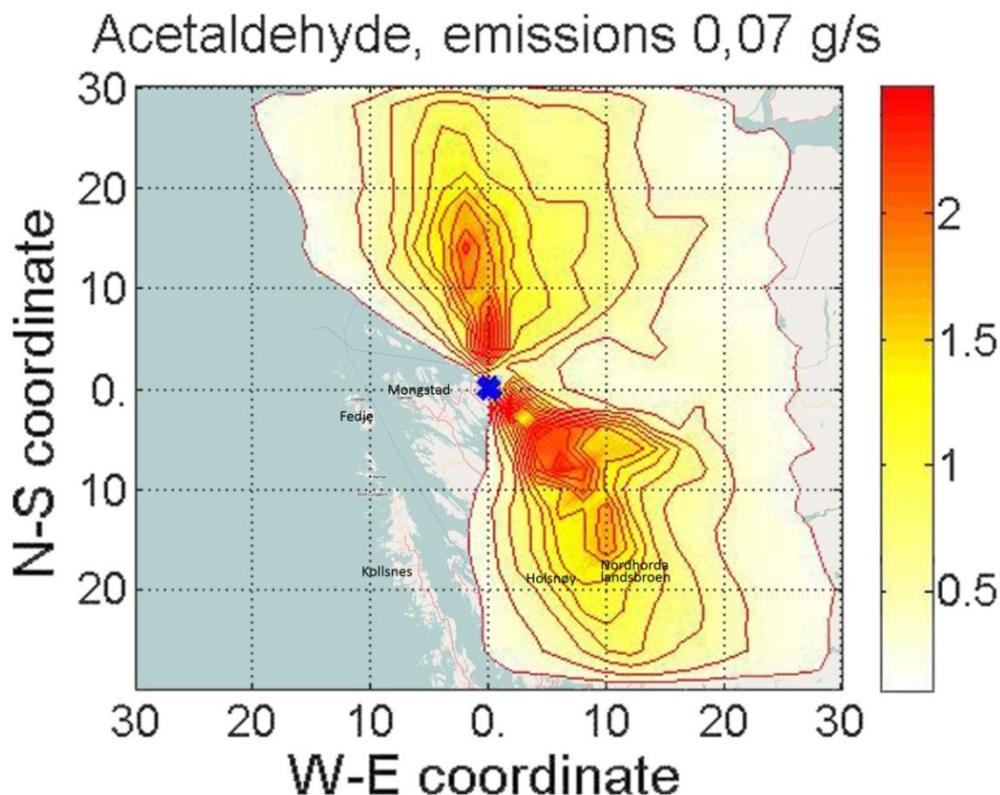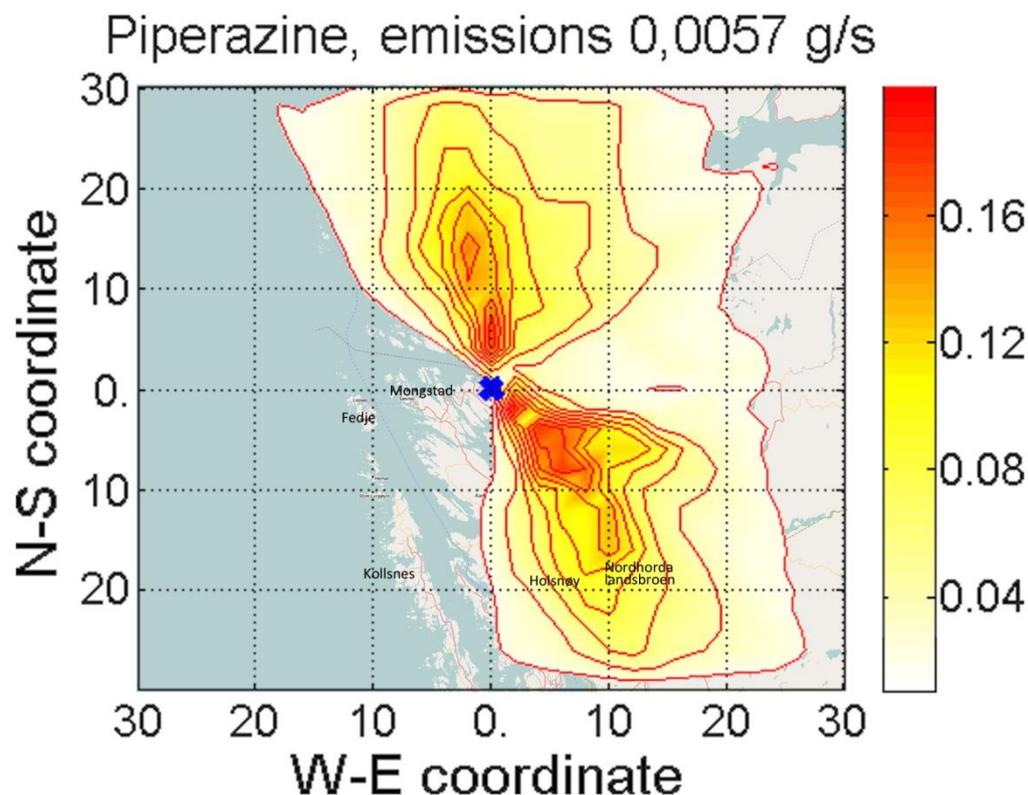*Figure 22: Annual mean concentration of piperazine for a model run emitting 0.0057 g/s (scenario 5c Improved solvent 2 Design, S1, S4, S9). Horizontal scale is in km. Units: ng/m³.*

Summary all calculated maximum annual mean concentrations
To give a clearer overview of all results from this chapter, the results from ACC facility are summarized in Table 15. These are not new results, but taken from the text above. These maximum annual mean concentrations were compared to the guidelines from FHI (Table 4) for MEA, formaldehyde and acetaldehyde and are well under the guidelines. There are no guidelines for long term exposure to alkyl amines nor for piperazines.

Table 15: Annual mean concentrations of the components investigated in section 5.3. Unit: µg/m³.

Component	Emission scenario	Emissions	Maximum annual concentration
MEA	2 ("Design")	0.04 g/s	1.3 ng/m³
Formaldehyde	2 ("Design")	0.05 g/s	1.6 ng/m³
Acetaldehyde	2 ("Design")	0.07 g/s	2.4 ng/m³
Alkyl amines	2 ("Design")	0.03 g/s	1.0 ng/m³
Piperazine	5c – Improved solvent 2 Design	0.0057 g/s	0.18 ng/m³

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5.4 Worst case scenario – nitrosamines in air

The worst case scenario is an estimate that maximizes the risk of the amine emissions to air. This is a model estimate that represents the "worst possible scenario". The model assumptions made for these calculations are a simplification of the actual processes involved in amine dispersion and degradation in air. In the model calculations there is no specific amine chemistry scheme included, i.e. the model does not have a chemistry scheme to account for degradation of the compounds emitted from TCM. The chemical degradation of amines is complicated and there are considerable knowledge gaps. For instance, gas phase degradation of MEA involves more than 100 possible degradation products, whereas degradation of piperazine involves over 500 degradation products (Bråten et al., 2008). The problem is that these degradation pathways are not well known. Simplifications have therefore to be made. Several ongoing research projects are aimed at studying amine degradation, like the ADA-2009 and ADA-2010 projects (Nielsen et al., 2010). Thus making an amine chemistry scheme is a task for future research, e.g. ExSIRA project under the KMB program (CLIMIT, Norwegian Research Council and industrial partners).

However, in order to get useful results without a chemistry scheme included, a possible approach is to apply scaling. This means multiplying the results by a factor equal to the formation rate of a certain degradation product. To explain in more detail; if for example a chemical component A is emitted at a rate of 1 g/s (unit emission, equals about 31.5 tonnes per year[4]), then the model is first run for a year emitting 1 g/s. Atmospheric processes like emissions, transport and dry and wet deposition processes are included (see chapter 5.1 for model description). The output from the model gives average concentration of component A, maximum concentration of component A, and annual deposition of component A. Now if we assume that a certain degradation product B is formed with a yield of 1%, when A is degraded/oxidized, 1% of A is degraded into B, then the results of component A may be scaled by 1% (i.e. multiplied by 0.01) to get average concentration, maximum concentration, and annual deposition of this specific degradation product B. This is a simple method to get results for degradation products without including a complex amine chemistry scheme in the model.

In section 5.3 the results were scaled according to emission strength, assuming that the components had an atmospheric lifetime of more than about a day, so that they may be considered chemically inert within the model grid. In the calculations discussed in this section, the components are assumed to have a short atmospheric lifetime (less than a few hours) so that chemical degradation occur close to TCM, and well within the model domain (30 km scale). According to the maximizing principle, contribution of directly emitted nitrosamines have been added to the potential formation.

In general, primary amines have little potential to form nitrosamines, tertiary amines have higher potential and secondary amines have the highest potential to form nitrosamines. Also cyclic amines like piperazine have large potential to form nitrosamines. The potential to form nitrosamines of the different amines is not easy to quantify. However, based on common knowledge in the literature it is

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[4] 1 g/s × 3600 s/hr × 24 hrs/day × 365 days/year = 31'536'000 g/year

most likely between 2 and 10% (see e.g. Pitts et al., 1978, Karl et. al 2008, Bråten et. al 2008). It may be lower (e.g. 1%), or it may be higher than 10% (Grosjean, 1991 refer to a 30% potential), but 2-10% is considered as a plausible range. The various amines have different chemical properties, and their atmospheric lifetimes vary. In the same manner nitrosamines are a group of compounds and their chemical properties and toxicity differ. In this "worst case" analysis we have chosen to give a range of nitrosamine formation potential. We emphasize the 10% value according to the maximizing principle as it is appropriate to carry out in a "worst case scenario" analysis.

It is important to emphasize though, that while applying the worst case method, all uncertain parameters are scaled to the worst possible value. This is according to the precautionary principle. If the calculated worst case concentrations are below the threshold values, this means that concentrations in the real atmosphere will most probably be lower than these threshold values. On the other hand, if the calculated worst case concentrations are above the threshold values, this does not necessarily mean that concentrations in the real atmosphere will be higher than these threshold values. It means that further more detailed investigations are needed to be able to establish a better estimate of the risk of amines and nitrosamines in air. This should be kept in mind when analysing the results in sections 5.4 and 5.5.

Concerning nitrosamines, there will be direct emissions of nitrosamines, but also emissions of precursors. These precursors are assumed to form nitrosamines with a 2-10% yield.

5.4.1 Formation of nitrosamines from the MEA emission scenarii

Current information for the **gas phase potential** to form nitrosamines is found in Pitts et al. (1978), and from the MEA oxidation which did not form nitrosamines by atmospheric reactions in the ADA-2009 project (Nielsen et al., 2010). There will be an update to methyl/dimethyl/trimethyl amines in ADA-2010. In the **liquid phase** all secondary and tertiary amines, but also amides, carbamates, and guanidines can form nitrosamines. Heterocyclic secondary amines (e.g. piperazine) are more easily nitrosated in the liquid phase than the secondary amines. Primary amines form no nitrosamines in the liquid phase.

There may be chemical reactions during the amine capture processes that can form nitrosamines. With high NOx concentrations (25-50 ppmv) nitrosamines may form in a plant run with MEA (Steinar Pedersen, IEAGHG seminar Oslo 16. February 2010). With low NOx, no nitrosamines will form. Therefore it is difficult to quantify the exact formation potential from MEA. It is considered to be relatively low, but some nitrosamines may occur, although in small quantities. However the potential of MEA to form nitrosamines under various NO_x conditions have to be investigated further. This will e.g. be done in MEA-Test, a project coordinated and funded by NILU.

In Table 16 the compounds with potential to form nitrosamines for the MEA emission scenarii are listed.

*Table 16:   Components with potential to form nitrosamines in the MEA emission
scenarii. In addition there are direct emissions of nitrosamines.*

Component
Dimethylamine
Diethylamine
Dibutylamine
N-methylethanamine
N-methyl 1-butanamine
N-ethyl 1-butanamine
Dipropylamine
DEA

In Table 17, the sum of the potential nitrosamine forming components (assuming 2% and 10% nitrosamine formation rate) and the direct nitrosamine emissions are given for both flue gas treatments for the five MEA scenarii.

*Table 17: Sum of the potential nitrosamine forming components + direct
nitrosamine emissions in the MEA scenarii. For the nitrosamine
forming components a 2% yield and a 10% yield is applied. Unit g/s.*

Scenario	Expected	Design	Worst case	Upset	Minimum
CHP					
2% formation yield + direct emissions	0.000265	0.000523	0.001055	0.001581	0.000108
10% formation yield + direct emissions	0.000962	0.001891	0.003822	0.005726	0.000178
RFCC					
2% formation yield + direct emissions	0.000154	0.000309	0.000618	0.000928	7.75E-05
10% formation yield + direct emissions	0.000497	0.000994	0.001987	0.002989	0.000112

The sum of direct emissions and nitrosamine precursor is higher for the CHP feed gas than for the RFCC feed gas. Now the sum of estimated sum of direct emissions and precursors may be used to scale the unitary emission results. This line of thought would build upon the inherent assumption that the emission scenario is the dominant condition over a year. For the "upset" scenario, this assumption is obviously incorrect. For the rest of the scenarii the range from lowest to highest possible emission is from 0.00011 g/s to 0.0038 g/s (for 10% yield). Two typical concentration distributions (for two emission strengths within the range above) are shown in Figure 23.

The calculated maximum annual mean concentration values associated with each of the emission strengths are shown in Table 18 , omitting the "upset" scenario.

Table 18: Maximum annual mean concentration value for the different MEA scenarii, assuming a 2% and 10% nitrosamine formation yield (+ direct emissions). Unit: ng/m³.

Scenario	Max. concentration assuming 2% nitrosamine formation yield	Max. concentration assuming 10% nitrosamine formation yield
CHP		
1-Expected	0.008	0.029
2-Design	0.015	0.057
3-Worst Case	0.032	0.11
6-Minimum	0.003	0.005
RFCC		
1-Expected	0.004	0.015
2-Design	0.009	0.030
3-Worst Case	0.019	0.060
6-minimum	0.002	0.003

Worst case emission using feed gas from CHP (over a year) may exceed the EPA/IRIS limit value. All other combinations of scenario and feed gas are calculated to be below the limit value.
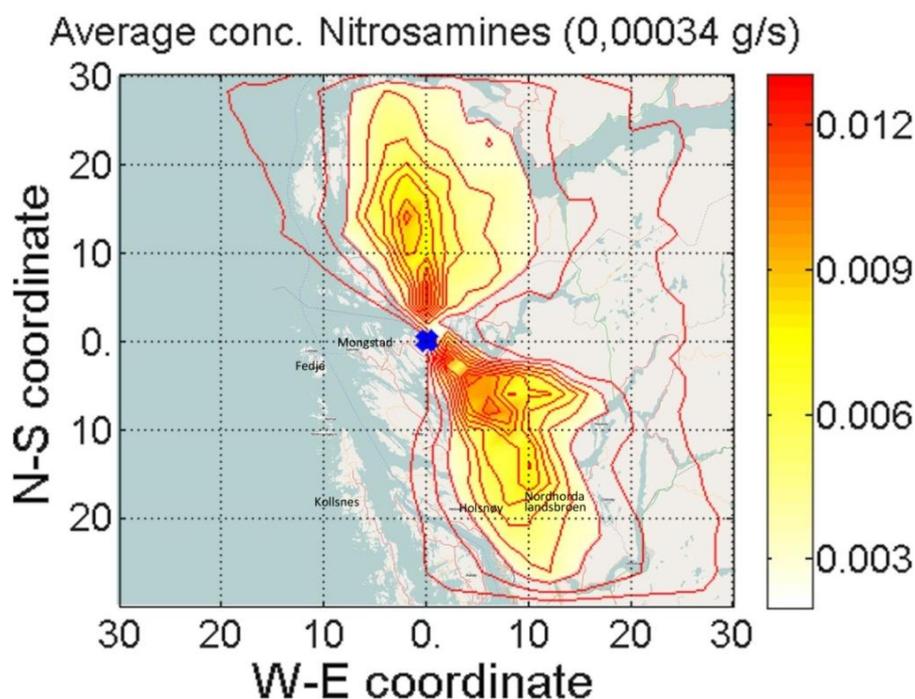
Figure 23: Annual mean concentration of nitrosamines for a model run with emissions (direct and precursors) equivalent of 0.00034 g/s (upper panel), and 0.0017g/s (lower panel). Horizontal scale is in km. Units: ng/m³
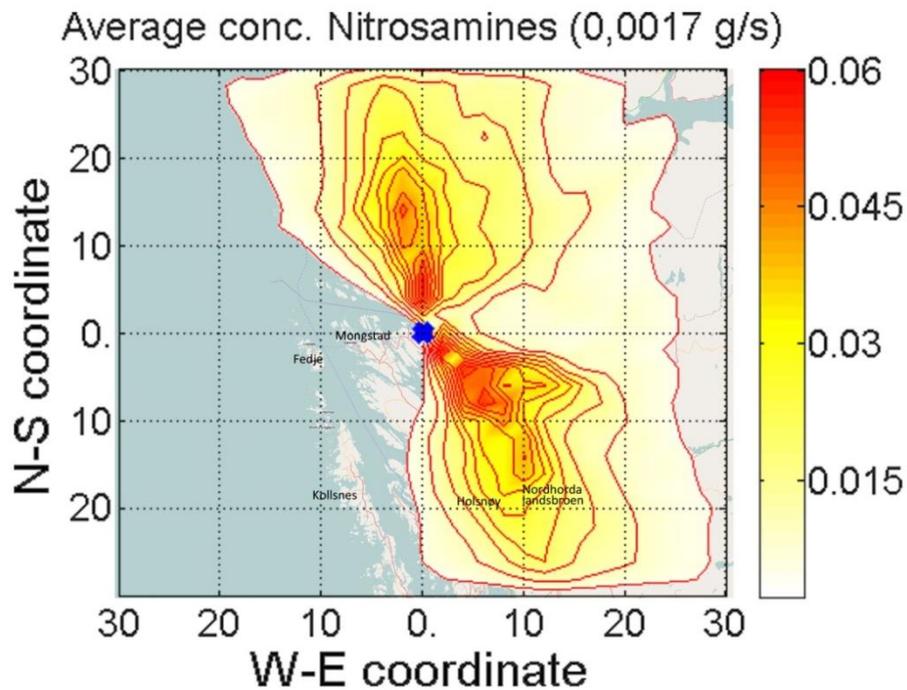
Figure 23: Contd.

5.4.2 Formation of nitrosamines from scenario 5 (improved amines)

Scenario 5 basically consist of two blends, solvent 3 (S3) forming the basis for scenario 5a (design) and 5b (worst case), and a mix of solvents 1, 4 and 9 (S1,S4,S9) forming the basis for scenario 5c (design) and 5d (worst case). The lists of emitted components are different for the two solvents, but the same for design and worst case sub scenarii. Components that have a potential to form nitrosamines are listed in Table 19.

Table 19: Components with potential to form nitrosamines in the scenario 5 emission inventory. In addition there are direct emissions of nitrosamines.

Scenario 5a and 5b	Scenario 5c and 5d
Tertiary amine	Secondary amine
Dimethylamine	Tertiary amine
Diethylamine	Piperazine
Dibutylamine	4,4-dimethyl-2-oxazolidinone
N-methylethanamine	
N-methyl 1-butanamine	
N-ethyl 1-butanamine	
Dipropylamine	
2,2'-[[2-[(2-hydroxyethyl)methylamino]ethyl]imino]bis-Ethanol	
N,N.dimethylethanolamine	
MMEA	
2-methylaminoethanol	
1-hydroxyethyl-3-methyl imidazolidone	
Hydroxyethyl oxazolidone	
DEA	

As with the MEA scenarii, the sum of the potential nitrosamine forming components (with estimated 2% and 10% nitrosamine formation rate) and the direct nitrosamine emissions are given for both flue gas treatments for the scenario 5 inventories. The results are shown in Table 20. Conversion from mixing ratio (ppm) to mass (g/s) of secondary and tertiary amines is based on a molecular weight of 100.

Table 20: Sum of the potential nitrosamine forming components + direct nitrosamine emissions in the improved amines scenarii (scenario 5a-5d). For the nitrosamine forming components a 2% yield and a 10% yield is applied. Unit g/s.

Scenario	5a (S3) Design	5b (S3) Worst case	5c (S1,S4,S9) Design	5d (S1,S4,S9) Worst case
CHP				
2% formation yield + direct emissions	0.0012	0.0015	0.00061	0.00147
10% formation yield + direct emissions	0.0063	0.0069	0.00233	0.00664
RFCC				
2% formation yield + direct emissions	0.0009	0.0012	0.00047	0.00112
10% formation yield + direct emissions	0.0047	0.0052	0.00177	0.00504

The sum of direct emissions and nitrosamine precursor is higher for the CHP feed gas than for the RFCC feed gas. Now the sum of estimated sum of direct emissions and precursors may be used to scale the unitary emission results. This line of thought would build upon the inherent assumption that the emission scenario is the dominant condition over a year. This assumption would be more valid for "design" than "worst case" scenarii. The sum of direct emissions and nitrosamine precursors (assuming 2% and 10% yield) range from 0.0005 g/s to 0.0069 g/s. Two concentration distributions are shown in Figure 24, one for emission near the lowest figure in the range and one near the highest number in the range.

The calculated maximum annual mean concentration values associated with each of the emission strengths are shown in Table 21.

Table 21: Maximum annual mean concentration value for the different improved amines scenarii (scenario 5a-5d), assuming a 2% and 10% nitrosamine formation yield (+ direct emissions). Unit: ng/m³.

Scenario	Max. concentration assuming 2% nitrosamine formation yield	Max. concentration assuming 10% nitrosamine formation yield
CHP		
5a (S3) Design	0.036	0.19
5b (S3) Worst Case	0.045	0.21
5c (S1,S4,S9) Design	0.018	0.07
5d (S1,S4,S9) Worst Case	0.044	0.20
RFCC		
5a (S3) Design	0.027	0.14
5b (S3) Worst Case	0.036	0.16
5c (S1,S4,S9) Design	0.014	0.05
5d (S1,S4,S9) Worst Case	0.034	0.15

If 2% nitrosamine formation occur, the maximum annual mean values are below the EPA/IRIS limit value of 0.07 ng/m³. For a 10% formation rate, only scenario 5 c Design has a maximum value below the limit.

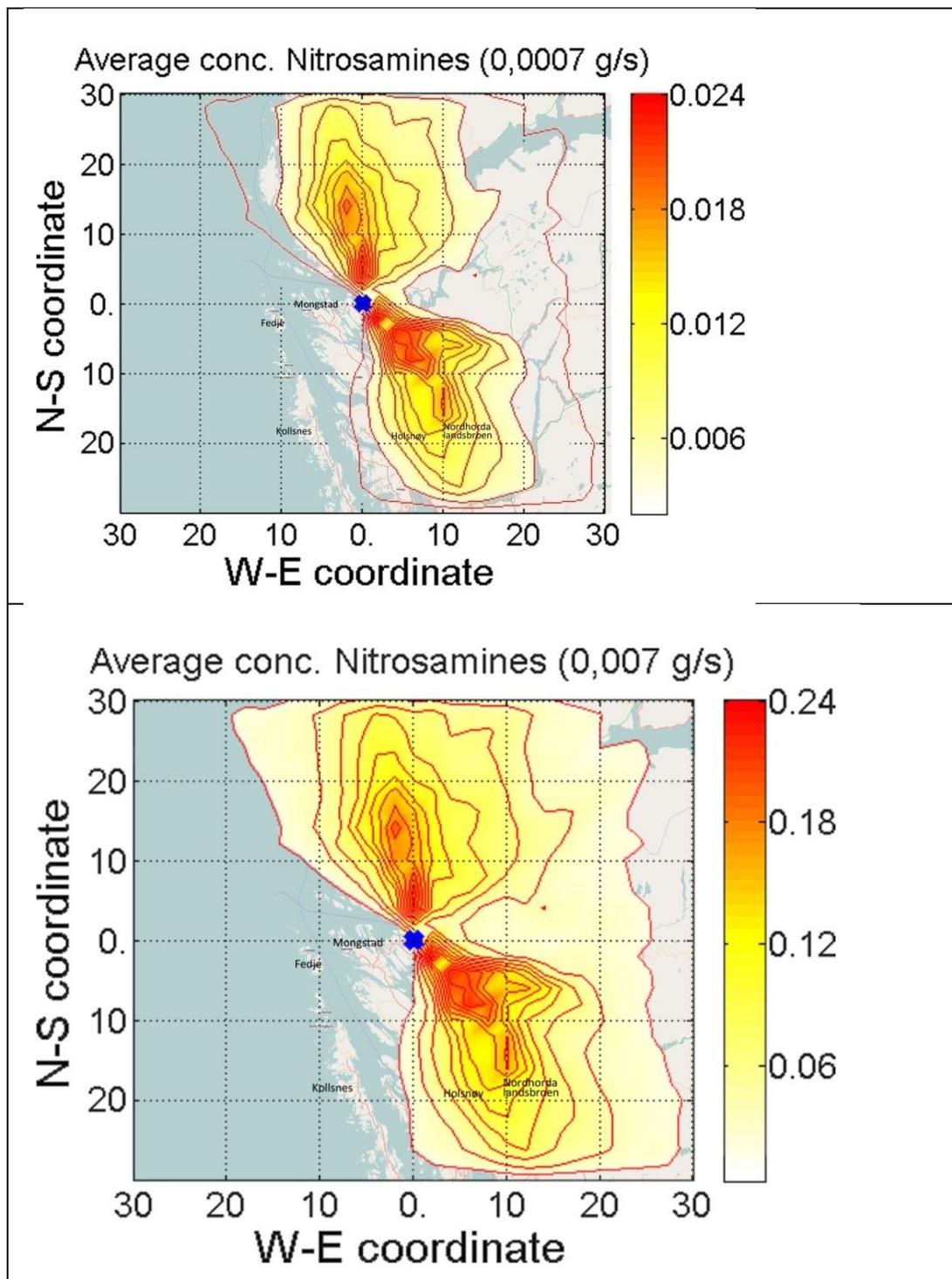*Figure 24: Annual mean concentration of nitrosamines for a model run with emissions (direct and precursors) equivalent of 0.0007 g/s (upper panel), and 0.007 g/s (lower panel). Horizontal scale is in km. Units: ng/m³.*

5.4.3 Maximum possible emissions of nitrosamines

Based on these calculations, to comply with the EPA/IRIS 0.07 ng/m³ value for nitrosamine concentration in air, the maximum possible emission is calculated to

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be 0.0023 g/s given as the sum of directly emitted nitrosamines and 10 % of the sum of components with a potential to form them through reactions after emissions. One example of maximum possible emissions can be found in scenario 5 c Improved Solvent 2 (S1,S4,S9) Design. This in turn corresponds to an emission rate of about 0.02 g/s of components with potential to form nitrosamines. This number is dependent though on the direct emissions of nitrosamines.

5.4.4 Discussion on worst case results

The calculated maximum concentrations presented in sections 5.4.1 and 5.4.2. are above the EPA/IRIS threshold value of 0.07 ng/m^3. As pointed out in the introduction to this chapter; if the calculated worst case concentrations are <u>above</u> the threshold values, this does <u>not</u> necessarily mean that concentrations in the real atmosphere will be higher than these threshold values. The worst case method reflects the uncertainties in the processes included and further investigations are needed to reduce these uncertainties to provide more accurate calculations of the concentration of amines and nitrosamines in air. The following recommendations are given:

1) Knowledge gaps to be elaborated
● Formation rate of nitrosamines. Now a 2-10% range is used. The nitrosamine formation potential vary considerably, from practically zero up to 30% (Grosjean, 1991). More scientific knowledge will reduce the uncertainties, and hence refine the formation rate (more compound specific).
● The type of nitrosamines formed (speciation). Nitrosamines is a large group of compounds where chemical properties and toxicity vary. It is hence crucial to determine which nitrosamines are formed in the atmosphere.
● The toxicity of the different nitrosamines. Knowledge exist on e.g. tobacco relevant nitrosamines, but less is known concerning the nitrosamines related to CCS. If more toxicity data on these nitrosamines exist there will be possible to identify threshold values for each specific nitrosamine, not for all nitrosamines as a group.
● Gas phase/particle phase/aqueous phase. The most recent research on amine degradation focus on gas phase chemistry (e.g. ADA-2009, ADA-2010). In the real atmosphere, and especially in the plume from TCM, there will be both gas phase, aqueous phase and particle phase taking place. More knowledge on particle phase and aqueous phase chemistry is needed to understand this chemistry both qualitatively and quantitatively.
● More information on the actual emissions and their speciation is also needed.
● In wintertime there is less sunlight in Norway and hence slower photochemistry. Nitrosamines are degraded by photolysis. More information on amine and nitrosamine chemistry in the absence of sunlight is important.

2) Elements that will modify the maximum values in the real atmosphere
● The TAPM calculations are done for one year giving annual mean concentrations. However there are seasonal variations in the weather pattern. According to the test plan, ACC will run MEA scenarii for 6 months, improved solvent 1 (S3) for 6 months, and improved solvent 2 (S1, S4, S9) for 6 months. Both Design and "Worst case" scenarii will be tested. No scenario will be run for more than 3 months. Many of these inventories give maximum annual mean values below the threshold value (even in worst case), especially those based on

MEA. Due to seasonal variations at Mongstad, the future observed annual mean concentrations to occur at Mongstad will be a combination of the various emission inventories tested.

● The TAPM model runs are performed for the year 2007. Inter-annual variations in weather exist, and hence location and magnitude of the maxima may vary.

● Gas to particle conversion. Gas molecules behave differently than particles. The calculations presented here assume that everything behaves like molecules. In the real atmosphere particles will be formed.

The main conclusion from the worst case study of nitrosamines in air is that there may be a potential problem concerning the EPA/IRIS threshold value of 0.07 ng/m^3. Further research, including more detailed modeling, and monitoring is needed to reduce the present uncertainties associated with nitrosamines in air from CCS.

5.5   Worst case scenario – nitrosamines in drinking water

There are large knowledge gaps concerning nitrosamine chemistry and the degradation of nitrosamines in water (see e.g. ATSDR, 1989 for more information). This lack of knowledge introduce uncertainties in the calculations. In this study, the worst case method used by Karl et al. (2010) is applied with some modifications. The fundamental principle using the worst case method is that when there are uncertainties, the worst possible option or the worst possible value is applied.

In these calculations, the following assumptions have been made:

- no inter-annual variation in rain pattern. This means that maximum rainfall and maximum rain water concentration will occur at the same location from year to year.
- 10% nitrosamines formation is applied. In the previous sections a 2-10% range is given. For the worst case, only the maximum value is used.
- the part of the drinking water catchment that receives the maximum deposition of nitrosamines by rain constitutes 20% of the total catchment. Model calculated maximum deposition occur over a very small area. In these model results maximum deposition would cover an area of approximately 8 km^2. It would be placed over two catchment areas, Nordgulelva and Dingja. These catchment areas have sizes of 21 km^2 and 28 km^2. The peak wet deposition would therefore be diluted by a factor of approximately 5 due to the gradients in the deposition field over these two catchment areas.

One fundamental question concerning nitrosamines in drinking water is whether there is degradation of nitrosamines in water. Some nitrosamines are very persistent (OME, 1991), while others degrade easily (Drewes et al., 2006). In this study these two cases are analyzed separately.

5.5.1 If no degradation of nitrosamines in water

This assumption is in accordance with the worst case study by Karl et al. (2008). If there is no degradation of nitrosamines in water, then at equilibrium, after some years of operation, the drinking water concentration will be 1/5 of the rain water concentration. This is valid if the rain pattern remains constant from year to year, if there is no changes in the emission pattern, and if the peak wet deposition would be diluted by a factor of approximately 5.

Then, from the results for unity emissions (section 5.1), emissions of 1 g/s give a maximum deposition of 39 mg/(m^2 year). The annual rainfall in the Mongstad region is 1890 mm/year. This is equal to 1890 litre/(m^2 year). So, if this mass of 39 mg/(m^2 year) is deposited by 1890 litre/(m^2 year) of rain, this gives an average rain water concentration of 0.02 mg/litre, or 20 μg/litre [footnote 5]. If this is in turn diluted by a factor 5 from rain water to drinking water, the drinking water concentration will in worst case be 4 μg/litre.

These results may be used to scale the different emission quantities used in this study. A summary of the results is shown in Table 22.

Table 22: Scenario related nitrosamines in drinking water assuming no degradation (persistent nitrosamines).

Scenario[a]	Emissions* g/s	Maximum deposition mg/(m^2 year)	Max. rain water concentration	Max. drinking water concentration[¶]
Unity emissions	1	39	20 μg/litre	4.0 μg/litre
1-Expected	0.00096	0.0374	19 ng/litre	3.8 ng/litre
2-Design	0.00189	0.0718	38 ng/litre	7.6 ng/litre
3-Worst case	0.00382	0.149	76 ng/litre	15 ng/litre
6-Minimum	0.00018	0.007	3.6 ng/litre	0.7 ng/litre
5a Design	0.0063	0.0246	126 ng/litre	25 ng/litre
5b Worst case	0.0069	0.269	138 ng/litre	28 ng/litre
5c Design	0.00233	0.0909	47 ng/litre	9.3 ng/litre
5d Worst case	0.00664	0.259	133 ng/litre	26 ng/litre

[a] Scenarii 1, 2, 3, and 6 are based on MEA, scenarii 5a-5d are based on improved solvents.
* Based on the highest emission from the two possible feed gas flows
[¶] Assume that the part of the drinking water catchment that receives the maximum deposition of nitrosamines by rain constitutes 20% of the total catchment

All these results show a drinking water concentration above the threshold value of 0.7 ng/litre, except for scenario 6-Minimum based on MEA.

5.5.2 If degradation of nitrosamines in water occur

Some studies report that nitrosamines do degrade in water. E.g. Drewes et al., (2006) investigated 7 different nitrosamines (NDMA, NDEA, NMEA, NDPA,

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[5] 39 mg/(m^2 year) / 1890 litre/(m^2 year) = 0.02 mg/litre

NDBA, NPIP, and NPYR). Their estimated degradation rate under anoxic conditions vary from k = 0.0976 day^{-1} to k = 0.5485 day^{-1}. This corresponds to a lifetime (e-folding time) between 1.8 and 10.2 days. This study refers to degradation in soil and soil water. In Norway typically 7-10% of the water in lakes fall directly into lakes. The rest falls onto soil/land. In some extreme cases as much as 80% of lake water may come from direct rainfall (Richard Wright, NIVA, personal communication). In that respect the results from Drewes et al. (2006) may be applicable for this study.

If the simplest formula of the mass balance equation is applied, the equilibrium concentration is defined as $C_\infty = P / k$ where C_∞ is equilibrium concentration, P is production of nitrosamines in the reservoir, and k is chemical decay. Assuming rainfall of 1890 mm/(m^2 year), rain water concentration of 138 ng/l (5b-Worst case Table 22), and a ratio of 1:5 for lake surface:lake volume, concentrations reduced by a factor 5 due to catchment size, and k=0.0976 day^{-1} (Drewes et al., 2006), then the equilibrium concentration $C_\infty = 0.3$ ng/litre. Equilibrium concentrations for the different scenarii are shown in Table 23.

These simple calculations show that even with degradation in soil water and water, there may be nitrosamine concentrations close to but below the threshold value.

Table 23: *Scenario related nitrosamines in drinking water assuming degradation with chemical lifetime equal to 10,2 days (k = 0,0976 day^{-1}).*

Scenario[a]	Emissions* g/s	Maximum deposition mg/(m^2 year)	Max. rain water concentration	Max. drinking water concentration[¶]
Unity emissions	1	39	20 µg/litre	42.4 µg/litre
1-Expected	0.00096	0.0374	19 ng/litre	0.04 ng/litre
2-Design	0.00189	0.0718	38 ng/litre	0.08 ng/litre
3-Worst case	0.00382	0.149	76 ng/litre	0.16 ng/litre
6-Minimum	0.00018	0.007	3.6 ng/litre	0.007 ng/litre
5a Design	0.0063	0.0246	126 ng/litre	0.3 ng/litre
5b Worst case	0.0069	0.269	138 ng/litre	0.3 ng/litre
5c Design	0.00233	0.0909	47 ng/litre	0.1 ng/litre
5d Worst case	0.00664	0.259	133 ng/litre	0.3 ng/litre

[a] Scenarii 1, 2, 3, and 6 are based on MEA, scenarii 5a-5d are based on improved solvents.
* Based on the highest emission from the two possible feed gas flows
¶ Assume that the part of the drinking water catchment that receives the maximum deposition of nitrosamines by rain constitutes 20% of the total catchment

5.5.3 Discussion on worst case results

As already pointed out the fundamental question concerning nitrosamines in water is whether degradation occur or not. Tate and Alexander (1975) report that

oxidation, hydrolysis, biotransformation, and biodegradation are not significant factors affecting the fate of NDMA in lake water. Hence photo-degradation is the main process for removing NDMA from the aquatic environment. In Norway, there is a long winter with less sunlight, and hence slower degradation. The lakes and reservoirs are also covered by ice, this prevents the already reduced amount of sunlight to penetrate into water. In addition there is very little sunlight at the bottom of lakes where the water intake is located. This line of thought is also supported by the studies of groundwater compartment, where, in the absence of light, NDMA has the potential to persist (OME, 1991).

Nitrosamines (NDMA) is also formed as a byproduct of chlorination , and is frequently found in municipal waste water effluents and surface waters receiving waste water discharges (Drewes et al., 2006). Chlorination is also used for treatment of drinking water. If nitrosamines are formed during chlorination, this means that there will be an existing "background" concentration of nitrosamines in the drinking water. If so, the possible nitrosamines from CCS will add to this background level and enhance the concentrations even more. This possible background level is not taken into account in this study, but should be kept in mind when investigating and monitoring nitrosamines in water.

These calculations show that if there is little degradation of nitrosamines in water, i.e. if nitrosamines are practically persistent, nitrosamines in drinking water may be a problem. However it is not possible to conclude that there will be a problem with nitrosamines in drinking water. The uncertainties in the present estimates have to be reduced, and scientific research should be conducted, especially to investigate degradation of nitrosamines in water. In addition the concentrations of nitrosamines should be monitored and analyzed when TCM will be in operation.

6 Conclusions

In this study, the Norwegian Institute for Air Research has calculated and assessed the dispersion of emissions to air of carbon dioxide (CO_2), nitrogen oxides (NO_X), ammonia (NH_3), amines and amine degradation products from activities at European CO2 Technology Centre Mongstad (TCM). This is an update of the report "Test Centre Mongstad, Dispersion calculations for emissions to air from Test Centre Mongstad (TCM)" (Berglen et al., 2008).

Two technology vendors have been contracted to test their capture technology at TCM; Alstom using "Chilled ammonia" and Aker Clean Carbon (ACC) using amines. Flue gas from the Residual catalytic cracker (RFCC) and the Combined Heat and Power plant (CHP) will be used to test CO_2 capture techniques. Alstom provided two emission scenarios for the calculations (Base case and Worst case). ACC provided five emission scenarios based on MEA (Expected, Design, Worst case, Upset, and Minimum), as well as 4 emission scenarios based on two proprietary solvents (Design and Worst case for Improved solvent 1 and Improved solvent 2 respectively).

The calculated maximum hourly mean concentrations from the Alstom facility are 55 $\mu g/m^3$ for NH_3 and 71.9 mg/m^3 for CO_2. From the ACC plant the maximum calculated hourly concentration of MEA is about 2 $\mu g/m^3$ and the maximum calculated hourly mean NH_3 concentration is just below 10 $\mu g/m^3$ and the maximum hourly concentration of CO_2 is 70.5 mg/m^3. The maximum calculated hourly concentrations of formaldehyde, acetaldehyde, and alkylamines are 1,4 $\mu g/m^3$, 2,1 $\mu g/m^3$, and 0.8 $\mu g/m^3$ respectively. All these calculated hourly maximum concentrations for Alstom and ACC are much lower than the Administrative norm and lower than long term exposure guidelines for NH_3, CO_2, MEA, formaldehyde and acetaldehyde.

Concerning regional dispersion, the model calculations estimate a maximum 8-hours mean concentration of NH_3 of 6.1 $\mu g/m^3$, and a maximum deposition of 3.1 mg N/(m^2 year), using Alstom emission data. This deposition is a small increase compared to the current background deposition, but in an area where the vegetation critical loads are already exceeded. Concerning the ACC plant, the calculated maximum annual mean concentration of MEA is 1.3 ng/m^3, while the maximum annual mean concentrations of formaldehyde and acetaldehyde are 1.6 ng/m^3 and 2.4 ng/m^3, respectively. The maximum annual mean concentration of alkyl amines (methylamine, ethylamine, dimethylamine, diethylamine) is just below 1.0 ng/m^3. The maximum concentrations for both plants and for all emission scenarios are found about 10 km to the S-E of Mongstad in the area around Sundsbø and Kolås. All calculated annual mean values are lower than the air quality guidelines for the components where guidelines exist.

The maximum tolerable amount of nitrosamines ("Worst case") have also been investigated. The calculated nitrosamines concentrations in ambient air are compared to the 0.07 ng/m^3 threshold value from EPA/IRIS. A formation range of nitrosamines between 2 and 10 % is assumed for components with nitrosamines formation potential (e.g. Pitts et al., 1978, Karl et. al 2008, Bråten et. al 2008).

Yearly average maximum value of nitrosamines have been calculated for all the scenarii apart from the upset scenario. Considering these results it must be remembered that the emission conditions must be valid for the duration of the year for the concentration value to be valid. For the MEA scenarii, only the "worst case" emissions exceed the limit value. For the improved solvents scenarii, all exceed the limit except scenario 5c.

Calculations of the maximum amount of components with nitrosamine formation potential in the emissions show that the concentration of nitrosamines in air can be below the threshold value, if the sum of component emission is no larger than about 0.02 g/s. This figure is dependent on the amount of directly emitted nitrosamines.

Concerning nitrosamines in drinking water, the degradation of nitrosamines in water is a key question. Some studies indicate that nitrosamines are persistent. If this is the case, then all worst case scenarii exceed the 0.7 ng/l threshold value. But even if degradation of nitrosamines in soil water and water occur (as pointed out by Drewes et al., 2006) then the highest worst case scenarii equilibrium concentrations are close to but below the threshold value. Based on these calculations, it is not possible to conclude that there will be a problem with nitrosamines in drinking water, but the uncertainties have to be reduced. Scientific research should be conducted, especially to investigate the degradation of nitrosamines in water.

7 References

ATSDR (1989) Toxicological profile for N-nitrosodimethylamine. Atlanta, GA, Agency for Toxic Substances and Disease Registry (ATSDR), U.S. Public Health Service in collaboration with U.S. Environmental Protection Agency (EPA). Available at: http://www.atsdr.cdc.gov/toxprofiles/tp141.pdf

Aas, W., Hjellbrekke, A., Hole, L.R. and Tørseth, K. (2008) Deposition of major inorganic compounds in Norway 2002-2006. Kjeller (NILU OR 72/2008).

Achermann, B. and Bobbink, R. (ed.) (2003) Empirical critical loads for nitrogen. Expert workshop, Berne, 11-13 November 2002. Proceedings. Bern, Swiss Agency for the Environment, Forests and Landscape, SAEFL (Environmental documentation 164).

Attalla, M. and Azzi, M. (2010) Environmental impacts of emissions from CO_2 capture Oral presentation at IEAGHG conference, Oslo 16th February 2010.

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

Brooks, S. (2008) The toxicity of selected primary amines and secondary products to aquatic organisms: A review. Oslo, Norwegian Institute for Water Research (NIVA report, 5698-2008).

Bråten, H.B., Bunkan, A.J., Bache-Andreassen, L., Solimannejad, M. and Nielsen, C.J. (2008) Final report on a theoretical study on the atmospheric degradation of selected amines. Kjeller (NILU OR 77/2008).

Drewes, J.E., Hoppe C. and Jennings, T. (2006) Fate and transport of N-nitrosamines under conditions simulating full-scale groundwater recharge operations. *Water Environ. Res., 78,* 2466-2473.

Grosjean, D. (1991) Atmospheric chemistry of toxic contaminants. 6. Nitrosamines: Dialkyl nitrosamines and nitrosomorpholine. *J. Air Waste Manage. Assoc., 41,* 306-311.

Karl, M., Brooks, S., Wright, R. and Knudsen, S. (2008) Amines worst case studies. Worst case studies on amine emissions from CO_2 capture plants (Task 6). Kjeller (NILU OR 78/2008).

Karl, M., Denby, B., Wright, R., Knudsen, S. and Berglen, T.F. (2010) Worst case study method to assess the environmental impact of amine emissions from a CO_2 capture plant. *Manuscript in preparation*.

Larsen, T., Lund, E. and Høgåsen, T. (2008) Overskridelser av tålegrenser for forsuring og nitrogen for Norge. Oppdatering med perioden 2002-2006. Oslo, Norsk institutt for vannforskning (NIVA Rapport, 5697-2008).

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. and Wisthaler, A. (2010) Atmospheric Degradation of Amines (ADA) Summary Report: Gas phase photo-oxidation of 2-aminoethanol (MEA) CLIMIT Project no. 193438**.** Kjeller (NILU OR 8/2010).

Nilsson, J. and Grennfelt, P. (Eds.) (1988) Critical loads for sulphur and nitrogen. UNECE/Nordic Council workshop report, Skokloster, Sweden, March 1988. Copenhagen, Nordic Council of Ministers (NORD 1988:15).

Låg, M., Andreassen, Å., Instanes, C. and Lindemann, B. (2009a) Health effects of different amines relevant for CO_2 capture. Report prepared by Norwegian Institute of Public Health. Oslo/Kjeller (NILU OR 5/2009).

Låg, M., Instanes, C., Lindemann, B. and Andreassen, Å. (2009b) Health effects of possible degradation products of different amines relevant for CO_2 capture. Final report. Report prepared by Norwegian Institute of Public Health. Oslo/Kjeller (NILU OR 7/2009).

Norwegian Labour Inspection Authority (2010) Veiledning om administrative normer for forurensning i arbeidsatmosfære. URL: http://www.arbeidstilsynet.no/veiledning.html?tid=78034

OME (1991) N-Nitrosodimethylamine. Toronto, Ontario, Ontario Ministry of the Environment, Hazardous Contaminants Coordination Branch (Scientific Criteria Document for Multimedia Standard Development No. 01-90).

REACH (2008) Guidance on information requirements and chemical safety assessments, dated May 2008. URL: http://guidance.echa.europa.eu/docs/guidance_document/information_requirements_en.htm

Stuanes, A.O. and Abrahamsen, G. (1996) Tålegrenser for nitrogen i skog. En vurdering av kunnskapsgrunnlaget. Ås, Skogforsk (Aktuelt fra Skogforsk, 7/96).

Tamm, C.O. (1991) Nitrogen in terrestrial ecosystems. Questions of productivity, vegetational changes and ecosystem stability. Berlin, Springer Verlag (Ecological Studies, 81).

TAPM (2009) The Air Pollution Model (TAPM). Hobart, CSIRO. URL: http://www.cmar.csiro.au/research/tapm

Tate, R.L. III and Alexander, M. (1975) Stability of nitrosamines in samples of lake water, soil, and sewage. *J. Natl. Cancer Inst., 54,* 327-330.

U.S. EPA (2010) N-Nitrosodimethylamine (CASRN 62-75-9), II.C.1. Summary of risk estimates. Washington, U.S. Environmental Protection Agency. Available from: Integrated Risk Information System (IRIS), URL: http://www.epa.gov/ncea/iris/subst/0045.htm [2010-08-17].

WHO (2006) N-Nitrosodimethylamine in drinking-water. Background document for development of WHO guidelines for drinking-water quality. Geneva, World Health Organization, Geneva. URL: http://www.who.int/water_sanitation_health/dwq/chemicals/ndma2ndadd.pdf [2010-08-17].

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ABSTRACT
Norwegian Institute for Air Research has performed new air dispersion calculations for European CO2 Technology Centre Mongstad (TCM) based on emission data from the two technology vendors Alstom (using Chilled ammonia) and Aker Clean Carbon, ACC (using amines). Flue gas from the Residual Fluid Catalytic Cracker (RFCC) and Combined Heat and Power plant (CHP) will be used. Maximum hourly mean concentrations using Alstom emission data are 55 $\mu g/m^3$ for NH_3 and 12,4 mg/m^3 for CO_2. For ACC the maximum hourly mean concentrations are 2 $\mu g/m^3$ for MEA, just below 10 $\mu g/m^3$ for NH_3, and 1,4 $\mu g/m^3$, 2,1 $\mu g/m^3$, and 0.8 $\mu g/m^3$ for formaldehyde, acetaldehyde, and alkylamines respectively. Worst case calculations for nitrosamines have also been performed. These calculations show that emission from solvents based on MEA is below the EPA/IRIS threshold value of 0.07 ng/m^3, except scenario 3. For improved solvents, most scenarii give maximum concentrations above the threshold values. For nitrosamines in drinking water, the degradation of nitrosamines in water is a crucial question. If nitrosamines are persistent, then all scenarii give worst case concentrations above the threshold value. With degradation, concentrations are below the threshold values. However, it is not possible to conclude that there will be a problem, the uncertainties have to be reduced

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ABSTRACT (in Norwegian)
Norsk institutt for luftforskning har foretatt nye spredningsberegniger for utslipp til luft fra CO2 Technology Centre Mongstad. Utslippstall fra teknologileverandørene Alstom ("Chilled ammonia") og Aker Clean Carbon (aminer) er brukt. Timemiddelverdier av NH_3, MEA, formaldehyd, acetaldehyd, alkylaminer og CO_2 er alle under gjeldende luftkvalitetskriterier. Det samme gjelder for årsmiddel på regional skala. En "worst case" studie er gjort for nitrosaminer i luft og drikkevann. Resultatene viser at nitrosaminer kan være et problem både når det gjelder luft og drikkevann, men det er store usikkerheter. Mer kunnskap behøves, spesielt ang. dannelse av nitrosaminer i luft og ang. nedbrytning av nitrosaminer i drikkevann.

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