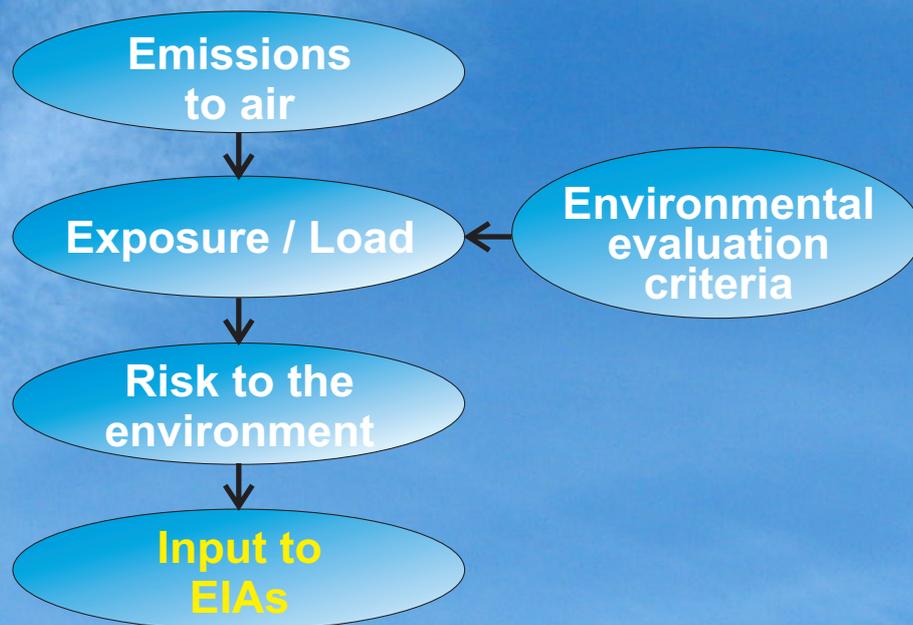# Task 6 Report:
Amines Worst Case Studies: Worst Case Studies on Amine Emissions from CO_2 Capture Plants

Phase I: CO_2 and Amines Screening Study for Environmental Risks

Emissions to air

↓

Exposure / Load ← **Environmental evaluation criteria**

↓

Risk to the environment

↓

Input to EIAs

NILU: OR 78/2008

Amines Worst Case Studies

Worst Case Studies on Amine Emissions from CO$_2$ Capture Plants (Task 6)

Matthias Karl, Steve Brooks, Richard Wright, and Svein Knudsen

Project report
Project title: CO$_2$ and amines

Amines Worst Case Studies

Worst Case Studies on Amine Emissions from CO$_2$ Capture Plants (Task 6)

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Preface

CO_2 capture and storage (CCS) has been proposed for two Norwegian gas-fired power plants as a measure to reduce CO_2 emissions to the atmosphere, thus reducing the main contributor to global warming. A leading technology for CO_2 capture is through the use of amines. The *CO_2 and Amines Screening Project* began with *Phase I* in May 2008. The project was initiated by NILU based on the results of an expert meeting in October 2007, and discussions with SFT. The expert meeting and the following Phase I project is based upon the concern that the emissions from CO_2 capture using amines could be potentially harmful to the environment and human health, and that the existing information regarding these subjects were quite limited, thus demanding further examination and analysis.

The project was graciously sponsored by the following:

- Gassnova SF (CLIMIT)
- Statoil Hydro ASA
- Shell Technology Norway AS

The following institutes participated in the project:

- Centre for Theoretical and Computational Chemistry (CTCC) Department of Chemistry at the University of Oslo, responsible for the theoretical study on the atmospheric degradation of selected amines (Task 3).
- The Norwegian Institute of Public Health (FHI), responsible for the effects to human health (Task 7).
- Norwegian Institute for Nature Research (NINA), responsible for the effects to terrestrial ecosystems (Task 8).
- Norwegian Institute for Water Research (NIVA), responsible for the effects on freshwater ecosystems (Task 9).
- Norwegian Institute for Air Research (NILU), responsible for project management/coordination, including the chemical screening report, models report, worst case study report, and the summary report (Task 4, 5, 6, and 10).

The project sponsors comprised the Steering Committee, which gave useful guidance to the project and its administration. The project sponsors function within the Steering Committee also gave them an active role in reviewing all project reports and documentation.

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Executive Summary

Multiple effects of amine emissions from the CO$_2$ capture plant on ecosystems and human health have been identified and studied in this report. Emissions of amines contribute to the nitrogen load in the atmosphere. Nitrogen loads to ecosystems above the critical load lead to eutrophication. The exceedance of a critical load of 5 kg N/ha/yr may result in a decline in lichens, mosses, and evergreen shrubs. A worst case scenario revealed that the yearly amine emissions have to be 60 times higher than expected to impose a threat to sensitive Norwegian ecosystems, as mires and arctic heath land. However, amine emissions add to already existing emission of reactive nitrogen and increase the total load of airborne nitrogen locally. The worst case studies revealed that toxic compounds produced in the atmospheric oxidation of emitted amines, like nitrosamines, nitramines and amides are a much more profound problem than that of airborne nitrogen.

In the Worst Case studies a series of assumptions are made; the most important are 1) no photochemical degradation during transport, 2) no biodegradation in soil and water, 3) no peak emissions. Currently, in Norway no regulations on permissible levels of exposure via air and drinking water exist for of amines, nitrosamines, and other problematic compounds that could be formed in the atmospheric oxidation. In order to prioritize the problematic compounds and to rank them accordingly, recommendations on threshold values and predictions of critical loads are made in this report. The results in this report strictly apply for the studied meteorological and geographic situation only, and loads to the environment would be different (lower or higher) for other situations.

No quantitative experimental data for the formation of nitrosamines or nitramines by atmospheric degradation of MEA exist today. The report on atmospheric degradation routes of amines used in CO2 capture ("Progress report on a theoretical study on the atmospheric degradation of selected amines" by Bråten et al., 2008) identified aldehydes, amides, nitrosamines, and nitramines as main products based on quantum chemical calculations and theoretical considerations.

Exposure by inhalation
Predicted worst case MEA levels in air for long term exposure are two orders of magnitude below the threshold of 10 μg/m^3 (for MEA) recommended in Låg et al., 2008. Based on this, long term exposure levels of MEA in air that can cause adverse health effects are predicted not to be exceeded. On the short time scale amine concentrations in air in vicinity of the plant can be close to the recommended MEA limit under worst case conditions. For aldehydes tolerable inhalation threshold have been suggested (formaldehyde: 2 mg/m^3; acetaldehyde: 0.3 mg/m^3) for long-term exposure. However, expected levels of aldehydes in air caused by the CO$_2$ capture plant are several orders of magnitude lower than the given thresholds. The inhalation exposure risk to formamide, acetamide, nitrosamines, and nitramines could only partly be assessed in this worst case report due to missing reliable threshold information. The long term risk threshold for exposure of the general population by nitrosamines through inhalation is

4 ng/m^3 nitrosamines in air, corresponding to a 10^{-6} lifetime cancer risk. Calculated maximum nitrosamine concentration in air for expected maximum emission from the CO_2 capture plant is only a factor of two below this critical level.

Exposure by drinking water

The exceedance of a recommended critical load of 7 ng/l nitrosamines or 1 μg/l nitramines in the precipitation to lakes may threaten drinking water quality. Of the total amount of amine emissions from a CO_2 capture plant, 2% are here assumed to be nitrosamines and 7% nitramines. Based on this assumption, in order not to exceed the critical load for nitrosamines in the precipitation to lakes, the maximum tolerable amine (e.g. MEA) emissions from the plant is calculated to be 24 tonnes per year. This is 1/7 of the expected maximum emissions of amines from a CO_2 capture plant given in NEV (2006). This worst case calculation assumes no degradation of the emitted nitrosamines in air, soil or water. Nitramines, in contrary to the nitrosamines, do not photolyse and thus can be expected to accumulate in the atmosphere. Based on the assumption that 7% of the emitted amine (e.g. MEA) generates nitramines, drinking water exposure levels of nitramines that can cause adverse health effects are predicted not to be exceeded.

Aquatic organisms

In order to avoid risk of chronic effects in algae the maximum concentration of nitrosamines in precipitation is recommended to be 25 ng/l. Based on the assumption that 2% of the emitted amine (e.g. MEA) generates nitrosamines, the predicted maximum emissions of amines thus a factor of 2 above the recommended threshold for aquatic organisms. Based on the assumption that 7% of emitted amine (e.g. MEA) generates nitramines, the predicted worst case nitramine levels in precipitation would not be problematic for aquatic organisms, unless emission peaks occur for four weeks or longer.

Recommendations

Quantiative studies on the production of nitrosamines and nitramines from the atmospheric degradation of amines, their atmospheric fate and their biodegradation in soil and water should be given the highest priority. It cannot be excluded that other toxic compounds may form in the atmospheric degradation of amines. In addition, quantiative studies on the possible production of nitrosamines or other substances of concern from reactions in the absorber unit of the plant should also be considered. Further studies on the toxicity of nitrosamines, nitramines, and amides to 1) different *in vitro* (cellular) and *in vivo* (animals/organisms) model systems to evaluate the human health impact, and 2) to aquatic organisms are recommended.

Amines Worst Case Studies

Worst Case Studies on Amine Emissions from CO2 Capture Plants (Task 6)

1 Introduction

In this report effects of amine emissions from the CO_2 capture plant are studied in terms of worst case scenarios and possible range of emission rates. The concept of critical levels and critical loads is applied to quantify the impact of amines and degradation products on ecosystems and human health.

The term "Critical Load" means 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.

An exceedance of the critical level or load may thus have an adverse effect on a specified organism, for example a species of fish in lakes, a species of moss in forests, or on human health.

Air pollution abatement policies in Europe are intended to decrease human and ecosystem exposure to sulphur and nitrogen pollutants, particles and ground level-ozone. Countries have agreed on reductions of air pollutants as specified by several protocols under the United Nations Convention on Long-Range Transboundary Air Pollution (CLRTAP). The most recent protocol, the Gothenburg Protocol, called for reduction of 4 pollutants (SO_2, NO_x, VOCs and NH_3) to abate 3 effects: 1) acidification; 2) eutrophication; and 3) the effects of tropospheric ozone on human health and vegetation. These four pollutants will also be emitted from the CO_2 capture plant in addition to amines. However, reduction technologies will be implemented in the CO_2 capture plant to reduce the levels of these pollutants in the emissions. The emissions and environmental impact of these four pollutants per se are therefore not studied in the frame of this report. Instead, this report focuses on expected concentration levels and ecosystem loads of amines and the toxic atmospheric degradation products from emitted amines.

A power plant with CO_2 capture will have an estimated amine release of 1-4 ppm. This number is taken from the NVE-report "CO2-håndtering på Kårstø" (NEV, 2006), where it is stated (in chapter "7.4 Typiske utslippsmengder"): 1-4 ppm amines, (40-160 tonnes/year, for the Kårstø plant). Emissions of nitrogen from a plant will originate from NO_x emissions, NH_3 emissions and emissions of amines. A typical emission rate will be **2-10 ppm NO_x, 1-5 ppm NH_3, and 1-4 ppm amines**. This means in total 4-20 ppm of molecules containing nitrogen. It is however not fully understood how these different processes interact, but it is assumed that the emissions from NO_x and NH_3 will be reduced in the CO_2 capture process. Nitrogen emissions have the potential of causing acidification of surface water and contribute to the eutrophication of terrestrial ecosystems.

In this report several aspects of the pollution from the CO_2 storage plant are studied. This report provides an estimate of the deposition of amines, secondary products, and also of airborne nitrogen to ecosystems. Expected concentrations and deposition fluxes are calculated with dispersion models for:

1. unity emissions;
2. maximum emissions;
3. maximum tolerable emissions

of the CO_2 capture technology.

The toxicity of emitted substances are normally characterised by concentration in air and by deposition. Acute effects are related to short time exposure, which is estimated using short time averages (minute to 24 hour period) , while cronic effects relate to averages from months to years, depending on the receptor organism (several days for algae, several years for humans).

In this report we will describe the following average times:

1. hourly averaged concentrations;
2. yearly average concentrations;
3. yearly deposition on different exposure areas.

2   Amines and degradation products

2.1   Amines

The toxicity of the amines used for the CO_2 absorption towards aquatic organisms in freshwater ecosystems is being investigated as in Task 9 of the project (Brooks and Wright, 2008; "Effects of amines on surface water and aquatic organisms"); effects of amines on terrestrial fauna and vegetation is being investigated in Task 8 of the project (Aarrestad and Gjershaug, 2008, "Effects of amines on vegetation and terrestrial fauna"). The health effects of amines are investigated in Task 7 report of Låg et al. (2008a) and the toxicity of degradation products in the Task 7 report of Låg et al. (2008b).

The indications on toxicity of the amines studied in this project (Monoethanolamine (MEA), 2-Amino-2methylpropanol (AMP), Methyl-diethanolamine (MDEA) and Piperazin (PIPA) differ substantially. Depending on the receptor organism, the effects range from low acute toxicity to mutagenic and teratogenic (Låg et al., 2008a). For MEA and PIPA there are indications of reproductive and developmental toxicity (Låg et al., 2008a). None of these amines have been reported to be carcinogenic (Låg et al., 2008a).

Limit values for amine exposure in air are given in the report of **Task 7** (Låg et al., 2008) and are used in this Worst Case study. For MEA, a lowest observed effect level (LOAEL) of 12 mg/m^3 for behavioural effects in rats seems to be the best available basis for proposing an exposure limit for the population. Låg et al. suggest that *the general population, over time, should not be exposed to higher ambient air levels of MEA than 10 μg/m^3*. For piperazine a LOAEL for inducing

occupational asthma has been estimated to be 8.6 mg/m^3 during normal work for an 8-hour day. Låg et al. suggest that the population should not be exposed to higher levels than 5 µg/m^3 piperazine base. To propose an exposure guideline for AMP a 90-days inhalation study with monkeys was used. Based on this, Låg et al. suggest, that the population should not be exposed to levels higher than 6 µg/m^3 AMP. For MDEA the lowest systemic no observed effect level (NOAEL) (dermal exposure) identified was 250 mg/kg bw, resulting in mild anaemia in dams in a rat developmental study. Låg et al. suggest, that the general population, over time, should not be exposed to higher ambient air levels of MDEA than 120 µg/m^3.

Information from **Task 8** indicates that amines (at relative high concentrations) act as a growth stimulating medium and will probably contribute to eutrophication of terrestrial ecosystems. Task 8 found that MEA and MDEA can cause moderately skin irritation, eye irritancy and allergic reaction to animals (mice, rats, rabbits, dogs, cats, guinea pigs) depending on doses used (Aarrestad and Gjershaug, 2008). For MEA, MDEA, and AMP no data on carcinogenic effect on terrestrial fauna was found. There are indications that piperazine could interact with nitrosating agents in vivo to form nitrosamines with possible carcinogenic risk in rats (Aarrestad and Gjershaug, 2008).

In **Task 9**, NIVA carried out a review of the current literature on the acute and chronic toxicity of the selected amines and degradation products to aquatic organisms. A literature search of the known ecotoxicological effects (acute and chronic toxicity) of these compounds to freshwater organisms (i.e. algae/bacteria, invertebrates and fish) is presented in the report of Task 9 (Brooks and Wright, 2008).

Emissions of amines contribute to the nitrogen load in the atmosphere. Airborne nitrogen is a threat to European biodiversity, as nitrogen is the limiting nutrient for the growth of vegetation in oligotrophic ecosystems. Increased nitrogen deposition leads to eutrophication, increased biomass production and reduced plant biodiversity.

2.2   Theoretical mechanism of the atmospheric degradation of amines

The atmospheric degradation of the amines of interest following their use in the CO_2 capturing process within a gas fuelled power station was calculated by the University of Oslo in **Task 3** of this project. Based on the theoretical evaluation of the atmospheric degradation of amines (Bråten et al., 2008), major products from the atmospheric reaction of MEA and AMP with the hydroxyl radical (OH) have been identified based on a literature survey of similar amines and theoretical chemistry. Main products from the atmospheric degradation of these amines identified in the report of Task 3 "Progress report on a theoretical study on the atmsopheric degradation of selected amines" (Bråten et al., 2008) include aldehydes, amides, nitrosamines, and nitramines. From the atmospheric degradation of MEA and AMP, formamide is probably the amide with the largest formation yield. Other products, like organic nitrates, and PAN-like compounds (compounds that have similar structure to peroxyacetylnitrate, known to be thermally instable storage compounds of NO_2) can become important under high NO_x conditions. Experimental evaluation of the theoretical findings on the

atmospheric degradation pathways for the OH-initiated oxidation of amines is pending.

2.3 Atmospheric degradation products from amines

The evaluation of health effects (**Task 7** of this project) assessed the potential hazard of the three identified compound classes, amides, nitrosamines, and nitramines, and found that they can have strong effects on human health and thus should receive special attention (Draft status reports, *Amines, emissions to air – A screening project for environmental effects*, 16 June 2008) However, data on health effects of the specific degradation products are sparse (Låg et al., 2008b).

Aldehydes
Formaldehyde is genotoxic, but only in the presence of cytotoxicity it may lead to cancer (COMEAP, 2000). In rodents and monkeys, a no-observable-effect level (NOEL) of 2.5 mg/m^3 for inhaled formaldehyde has been suggested. On the basis of data on irritancy in humans, a tolerable concentration of 2 mg/m^3 has been derived for acetaldehyde. The mechanism of carcinogenicity observed with acetaldehyde has been suggested to be very similar to the mechanism of carcinogenicity of formaldehyde (Låg et al., 2008b). WHO has suggested a tolerable concentration of 0.3 mg/m^3 for lifetime cancer risk (EHC 167, 1995). The inhalation exposure risk to aldehydes from CO_2 capture plants is not included in this worst case report because expected levels of aldehydes in air caused by the CO_2 capture plant are 3-4 orders of magnitude lower than the given thresholds.

Amides
Formamide is hazardous to health, can cause cancer and is a reproductive effector (TOXNET, 2008). However, there are no appropriate, sub chronic (90 days) studies to assess effects by inhalation (Låg et al., 2008b). The inhalation exposure risk to formamide from CO_2 capture plants to humans is thus not assessed in this worst case report.

Nitrosamines
Based on experimental data, there seems little doubt that some nitrosamines are extremely potent carcinogens, that can pose a serious hazard to humans if present in the environment (Låg et al., 2008b). Most nitrosamines are suspected to be human carcinogens, but direct causal associations have not yet been found (Låg et al., 2008b). The degradation products formamide and acetamide has been reported to induce development toxicity and carcinogenicity, respectively, in experimental animals (Låg et al., 2008b).

Nitramines
From the oxidation of MEA, different nitramines have been identified theoretically (2-N-nitro amino-ethanol, N-nitro amino-glycol). Nitramines are structurally related to nitrosamines, with the nitroso group being replaced by a nitro group. Compared to the nitrosamines, there are few studies on the health effect of nitramines (Låg et al., 2008b). The metabolism of aliphatic nitramines in the human body resemble that of the corresponding nitrosamine. The mutagenic and carcinogenic activity of aliphatic nitramines seem in general to be much lower than those of the corresponding nitrosamines (Låg et al., 2008b). Several of the

nitramines are mutagenic and carcinogenic in rodents, although they seem considerably less potent than the corresponding nitrosamines (Låg et al., 2008b).

The compound groups that are investigated in this report are:

1. **Amines**
2. **Nitrogen (from amines)**
3. **Nitrosamines**
4. **Nitramines**
5. **Amides (mainly formamide)**

Table 1 provides an overview of the selected compounds (compound classes).

Table 1: *Toxic compound groups/classes emitted from CO_2 capture, expected emission range, possible effects on exosystems. The current status of the worst case studies is also indicated. Emission amount for amines from NVE-report "CO2-håndtering på Kårstø".*

Compound	Minimum and max. emission (t/yr)	Toxicity	Possible effects (worst case)	Status worst case study
Amines	40 – 160	None to high	Human health, air Terrestrial fauna, Aquatic organisms	Done
Nitrogen [1]	9 – 37	Low	Terrestrial fauna, Aquatic organisms	Done
Nitrosamines [2]	0.8 – 3	High	Human health, air Human health, drinking water, Aquatic organisms	Done [5]
Nitramines [3]	3 – 11	High	Human health, air Human health, drinking water, Aquatic organisms	Done [5]
Formamide [4]	4 – 14	High	Human health, air Aquatic organisms	Done [5]

[1] Airborne nitrogen from amine emissions only.
[2] Assuming an instantaneous formation yield of 2% fraction of the total amine emissions (see section 7.2).
[3] Assuming an instantaneous formation yield of 7% fraction of the total amine emissions (see section 7.2).
[4] Assuming an instantaneous formation yield of 9% fraction of the total amine emissions (see section 7.2).
[5] The risk of the uptake of nitrosamines, nitramines, and formamide via inhalation is not studied in this report due to paucity of studies on acute and chronic effects of inhalation and/or lack of corresponding limit values (NOAEL values) for human health with respect to inhalation exposure.

Table 1 includes expected minimum and maximum emission from the CO_2 capture plant, together with possible effects on ecosystems and human health. The current status of the worst case evaluation is indicated for each compound.

3 Deposition

Deposition can be divided into two main mechanisms: 1) dry deposition, which depends on the concentration at ground level and is caused by uptake on surfaces and vegetation; and 2) wet scavenging by rainfall. To be available for scavenging it is necessary that the substance is soluble in water or that a sublimation/ condensation onto a particle causes the substance to be contained in the water droplet.

3.1 Deposition of amines and nitrogen

Amines that are used for CO_2 capture are easily soluble in water. This is a good approximation because the primary amines used in the capture process all need to have this property. This means that amines are available for deposition through rainfall.

Wet deposition (rain) will dominate the deposition of amines from a gas power plant because of the high solubility of the applied amines and the high precipitation amounts and frequencies in Norway. The amount deposited is strongly dependent on simultaneous occurence of rain and transport of the pollutants. This means, that a plant on the east coast and the west coast of Norway will have a different impact on the environment. This is because the rain patterns will be different. This means that the total deposition in this report have to be estimated for a low impact zone and a high impact zone, with low and high estimates. We note, that the critical loads may also change with the geography of the terrain.

3.2 Deposition of other substances

The input to the CO_2 capture system is the primary amine. This amine will be continously recycled, but a certain portion will degrade in the absorbtion process. Further, some portion of the amine will evaporate and the minor portion not recovered through the wash water process will escape to air through the stack. The main emission will be of the primary amine, but it is likely that there will be emissions of secondary products (reaction and degradation substances not removed in the purification process). The identities, properties, and quantities of these substances are not known in detail. In addition to this, the emitted substances may react chemically and produce still other chemical compounds in the atmosphere. The identities, properties, and quantities of these, as well as their fate (stability and lifetime in atmosphere) are not known in detail.

The load of these compounds can be characterised as either short or long term concentrations and deposition. The plumes will be emitted from a stack and the stacks can be designed to satisfy the short term and the long term concentration limits in the local environment.

With respect to deposition, the substances that are evaluated in this report, can be divided into two groups:

1. Soluble in water
2. Insoluble in water

Depending on the solubility of the compounds of interest (amines and degradation products), these substances will be transported and mixed on different spatial scales. Soluble substances which undergo primarily wet deposition will have maximum concentrations closer to the source (3-10 km) – depending on the plant layout – than insoluble substances which mainly undergo dry deposition. Insoluble substances (if chemically stable) are more likely to have a longer residence time and therefore a better mixing and lower load in a larger area. The chemical stability is dependent on the gas phase chemistry, which is different from the water phase chemistry.

The substances that are soluble in water will deposit more rapidly and the pattern will follow the description on deposition of nitrogen. However the chemistry of the substances soluble in water is more complex. Chemical reactions occur in the gas phase, particulate phase and the water phase. The plume will probably be at saturation close to the source and some of the emissions that are soluble in water will be contained in the water droplets available (see separate report on "Amines and Rainfall"; Karl, 2008). Such will be the case as long as the plume is visible. After the plume becomes invisible, the emitted substances will either be in the form of gas or attached to the particles that formed the droplet. Then chemical reactions can either be in the gas phase or on the surface of the particle. Once the plume has entered into a raining cloud, the emissions that are soluble in water will again be in the water phase and available for scavenging. The possibilities for chemical transformation of the different substances are therefore complex and need to be studied in more detail.

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4 Model Description

Model calculations are performed with the NILU in-house steady state Gaussian dispersion models CONCX and CONDEP. Table 2 lists the parameters of the emission source (stack parameres) applied in the model runs. The displayed data is assumed to be representative for a CO_2 capture plant stack.

Table 2: CONDEP and CONCX input parameters for the worst studies.

Stack height (m)	Stack diameter (m)	Building height/ width (m)	Plume velocity (m/s)	Plume gas temperature (K)	Ambient temperature (K)
60	7.14	25/50	15	328	280

Model calculation consider transport and deposition of the released compounds but do not take into account chemical degradation. Amines and the degradation compounds are treated as **inert tracers** in the model calculations. From the model runs, distributions of concentrations in air (at surface) and in the deposition are obtained.

CONDEP calculates annual concentrations based on average meteorological conditions (wind, so-called "typical weather") at a certain geographic location and CONCX calculates concentrations and wet deposition fluxes with distance from the plant (up to 10 kilometres) for different meteorological stability conditions.

The domain for the CONDEP model has an extent of 38×38 km^2, with a horizontal grid resolution of 1000 m. The source is located in the center of the grid. The wind rose with four stability classes and four wind speed classes from Mongstad (Norway) is applied in the calculations. CONDEP calculates long term sector averaged concentrations for twelve 30° wind sectors in a given grid. The input consists of a meteorological joint frequency matrix of four wind speed classes, four stability classes and twelve wind sectors. The mixing height of the boundary layer was set to 1000 m. The output contains average concentrations in air and in deposition in the specified grid.

For calculations with the dispersion model CONCX only results for meteorological conditions that prevail in Norway are used:

- Unstable: wind speed 1, 2 and 3 m/s
- Neutral: all wind classes
- Light stable and stable: 2 m/s

CONCX calculates short term downwind concentrations at ground level. The output contains concentration and wet removal flux for each downwind distance and meteorological stability class. CONCX treats wet removal of substances from the plume, by applying a scavenging coefficient for the process of scavenging of gases by falling rain through a Gaussian plume. The half-life of the substances towards wet removal usually ranges from about two hours to one day.

4.1 Sensitivity test on stack parameters

Two sensitivity tests were performed with respect to the parameterization emission source in Table 2. The value of the plume velocity may overestimate the actual plume velocity at the CO_2 capture plant in Kårstø. The carbon capture plant at Kårstø will be ten times larger than the largest existing plant of the same type in the USA. The actual plume velocity is considered to more close to 10 m/s. The CO_2 absorption towers will be operated at 50-55°C (Report of the Expert Meeting on October 18th, 2007, Knudsen et al., 2008). The exhaust temperature was assumed to be the same. The actual exhaust temperature at Kårstø is considered to be more close to 40°C. The impact of both the changed values for plume velocity and for exhaust temperature on maximum short term concentrations in air will be studied in a sensitivity test (see section 7.3).

4.2 Description of deposition

The physical treatment of emitted compounds in the applied dispersion models is the same as for NO_x. Wet and dry deposition cannot be seperated in the chosen dispersion models. The deposition route of compounds largely depends on their solubility in water, as outlined in Chapter 0. The partitioning equilibrium of a compound between the gas phase and the aqueous phase is described with Henry's Law. Henry's Law shows that the concentration of a solute gas in an aqueous solution is directly proportional to the partial pressure of that gas above the solution; the Henry's Law constant is related to the solubility of the gaseous compound in water. The Henry's Law constant of a gas defines how efficient it will be scavenged by precipitation; at values $>10^3$ M/atm wet deposition will be the dominant process of removal from the atmosphere. Henry's Law constants for alkylamines vary from about 10 to several 10^2 M/atm, but the Henry's Law constant for MEA is several orders of magnitude higher: 6.2×10^6 M/atm at room temperature (Sander, 1999). Amides and nitrosamines are very polar compounds and in general more soluble than the parent amines. Henry's Law constants for these compounds could not be found in the compilation of Sander (1999). However, it is known that formamide and N-nitrosodimethylamine (NDMA) are infinitely soluble in water (solubility: 10^6 mg/l) (TOXNET, 2008). For nitramines less is known, their solubility seems to be lower than that of amides and nitrosamines. The solubility of Cyclotetramethylenetetranitramine (CAS: 2691-41-0), an explosive, is 1.4×10^2 mg/l at room temperature. For simplicity, deposition of nitramines is treated in the same way as the deposition of the other degradation products. Both parent amines and the expected degradation products are polar and very soluble in water. It can be concluded, that wet deposition is the main removal pathway for all studied compounds. The different parameterisations of the deposition mechanism in the two dispersion models CONCX and CONDEP are described in the following.

CONDEP calculates deposition of an emitted compound as long-term average. The deposition method used in CONDEP is the "partial reflection" model summarized by Overcamp (1976). The deposition of the emitted compound is parameterized using a **deposition velocity**, v_D, which is prescribed in the input to the model run. The deposition velocity of SO_2 can vary from 0.005 to 0.008 m/s depending on the surface characteristics of the terrain (grass, crops, bare soil, forest, etc.), according to McMahon and Denison (1979). It was decided to use

one (lower) deposition velocity value for amines and one (higher) deposition velocity value for all degradation products in order to reflect their differing solubility in water and biological/chemical activity. Thus , a deposition velocity of 0.01 m/s is used for amines and nitrogen. The value of 0.01 m/s corresponds to a moderately soluble gas. A deposition velocity of 0.03 m/s is used for nitrosamines, nitramines and formamide. The value of 0.03 m/s corresponds to a very soluble gas.

CONCX calculates wet deposition of an emitted compound on a short term basis. Dry deposition is not included in CONCX. The concentration of a released compound is assumed to decrease exponentially with time:

$$C(t) = C_0 \cdot \exp^{-\lambda t} \tag{1}$$

Where λ is the scavenging coefficient (s^{-1}) and t is the time since precipitation started. The **scavenging coefficient** is theoretically a function of the droplet size spectrum, physical and chemical characteristics of the gas, and precipitation rate. The median scavenging coefficient value for SO_2 is about 2×10^{-5} s^{-1}. A lifetime of 2.8 hours for wet removal is assumed for all studied compounds in this report. A scavenging coefficient of 1×10^{-4} s^{-1} is used in the model calculations.

4.3 Unity emissions

The model simulations are performed with unity emission (1 g/s) of the compounds of interest (parent amines or degradation product from amine oxidation).

In order to get the resulting concentration and deposition for the **maximum emission** of the compound k, $E_{max,k}$ (in g/s) from the plant, the model results obtained for unity emissions, E_{unit}, are scaled with the respective emission ratio $E_{max,k}/E_{unit}$. For instance, the maximum concentration of a compound k in air, $C_{max,k}$, is calculated from the output maximum concentration $C_{max,k,out}$ as:

$$C_{max,k} = C_{max,k,out} \cdot \frac{E_{max,k}}{E_{unit}} \tag{2}$$

In order to obtain the **worst case estimate**, model results using unity emissions are scaled until the critical concentration levels in either air, $C_{crit,k}$, or deposition are reached. From this the maxmimum tolerable emission, E_{tol}, from the plant is obtained (back calculation of emissions). For instance, the output maximum concentration $C_{max,k,out}$ in air (at unity emission) is scaled until the critical level for the air concentration $C_{crit,k}$ is reached. By this procedure, the scaling factor f of the emission source strength is obtained:

$$f = \frac{C_{max,k,out}}{C_{crit,k}} \tag{3}$$

A similar procedure is applied to obtain the scaling factor for the modeled maximum deposition flux. The unity emission (1 g/s) is then multiplied by the scaling factor f to give the maximum tolerable emission, $E_{tol,k}$, for a compound k from the CO_2 capture plant with respect to the critical concentration in air:

$$E_{tol,k} = E_{unit} \cdot f \tag{4}$$

The maximum tolerable emission of nitrogen, nitrosamines and other toxic degradation products is finally translated into maximum tolerable amine emissions (as will be described in section 7.2).

5 Limits

5.1 Amines

Amines released from the CO_2 capture plant are transported in the atmosphere and removed by chemical reaction with the hydroxyl radicals, wet and dry deposition. In the present of NO_x, nitrosamines and nitramines may form in the atmospheric oxidation of amines in the first minutes of the moving plume. NO_x is emitted from the power plant and will be affected by dry and wet deposition as well. Dry deposition of amines and other gases involves the adsorption to surfaces and vegetation, whereas wet deposition of dissolved amines and other gases involves precipitation (including fog). With the deposition fluxes, amines are transferred to the ground, i.e. lakes, soils and grassland.

Task 8 found that concentrations of 1.5 kg/ha MEA changes growth and grain yield of cereals (**report of Task 8**). However a critical load to agriculture is not provided by Task 8. Assuming a MEA lifetime in soil and water of 200 days, the critical load to the soil is 27 kg/ha/yr, which is **2.7 g/m^2/yr** in a steady state equilibrium between air and vegetation.

The report of **Task 7** on health effects of different amines from the CO_2 capture (Låg et al., 2008) suggest limit values for the exposure to amines in order to avoid adverse health effects as allergic reactions. For MEA, using an uncertainty factor of 1200, Task 7 suggests the population should, over time, not be exposed to atmospheric concentrations higher than **10 μg/m^3**. This threshold for human health effects is used in addition in this study.

5.2 Airborne nitrogen

Soil microorganisms can transform amines to ammonia, acetate, and N_2, and in turn the soil content of plant available nitrogen (N) can increase. Increased N deposition leads to eutrophication, increased biomass production and reduced plant biodiversity since nitrogen is the limiting nutrient for plant growth in oligotrophic ecosystems. A critical load of 5-10 kg N/ha/yr to arctic heath lands and bogs (mires) may result in a decline in lichens, mosses, and evergreen shrubs, whereas there might be an increase of grasses. For this study a critical nitrogen load is set to **500 mg N/m^2/yr** which corresponds to the lower limit of the given range.

However, the effect of nitrogen is strongly dependent on the background load and thus the effect of amine emissions from the CO_2 capture plant on the eutrophication of ecosystems cannot be fully assessed. Other tasks of this project, **Task 8** and **Task 9** will provide a more comprehensive evaluation of the airborne nitrogen from emissions of the CO_2 capture plant in their project reports.

5.3   Nitrosamines

For Norwegian lakes with small catchments, surrounded by bare soils or sparsely vegetated soils, the critical load is 7 ng/l nitrosamines in precipitation (rain water), given the assumptions that there is no degradation in soil and no degradation in water. This value should not be exceeded in order to avoid harmful concentrations of nitroamines for drinking water (human consumption). Toxic effects on aquatic organisms like fishs and invertebrates occur at much higher concentrations (several mg/l), however for algae chronic toxic effects occur already at 0.025 mg/l (see report from Task 9 for details). Dimethyl and diethyl derivatives of nitrosamines are soluble in water. In particular NDMA is very soluble in water. NDMA has a solubility of $1x10^6$ mg/l at 25 °C. Table 3 shows critical levels of different nitrosamines in drinking water, as defined by Californian regulations from 1 May 2007. The drinking water standard for NDMA is 10 ng/l (notification level, see Table 3).

Table 3:   Critical levels of different nitrosamines according to California (USA) regulations from 1 May 2007.

Nitrosamine	10^{-6} Risk Level (ng/l) [1]	Notification Level (ng/l) [2]	Response Level (ng/l) [3]
N-Nitrosodiethylamine (NDEA)	1	10	100
N-Nitrosodimethylamine (NDMA)	3	10	200
N-Nitrosodi-n-propylamine (NDPA)	5	10	500
N-Nitrosodi-n-butylamine (NDBA)	3	—	—
N-Nitrosomethylethylamine (NMEA)	1.5	—	—
N-Nitrosopiperidine (NPIP)	3.5	—	—
N-Nitrosopyrrolidine (NYPR)	15	—	—

[1] Level of nitrosamines in drinking water that induce no more than one excess cancer per 1 million individuals exposed over lifetime.
[2] 10 ng/l is the notification level of this nitrosamine in drinking water to US EPA.
[3] Level where the Californian Department of Public Health recommends to remove the drink water source out of service.

For Ontario the threshold for drinking water is 9 ng/l (notification level). In order to comply with a lifetime risk of no more than one excess cancer per 100,000 inhabitants (i.e. 10^{-5} lifetime cancer risk) the value must be reduced to 7 ng/l (Richardson et al., 2007).

To conform to this drinking water threshold, the critical load of 7 ng/l nitrosamines in wet deposition must not be exceeded and this limit value is applied in the worst case study.

A similar regulation for nitrosamines in drinking water does not exist in Norway.

5.4   Nitramines

Nitramines have been detected and identified in soil and water at military sites, since they have been used as explosives by the U.S. Military. The mutagenic and carcinogenic activity of aliphatic nitramines seem to be much lower than those of the corresponding nitrosamines, however it can be concluded that several of the nitramines are mutagenic and carcinogenic in rodents (Låg et al., 2008b). No drinking water threshold for aliphatic nitramines exists. For aromatic nitramines a drinking water threshold exists, but it is unclear how their carcinogenic potential is compared to aliphatic nitramines formed in the atmospheric degradation of amines. The report by Wollin and Dieter (2005) provides toxicologically based drinking water guide value for aromatic nitramines (RDX and HMX) ranging from 1 to 175 µg/l. The lowest of these recommended limit values was chosen.

Due to lack of more appropriate limit values, the critical load of nitramines in precipitation is set to 1 µg/l in the worst case study.

5.5   Amides

For Formamide no recommendations on critical loads and levels are available at the current time. When released into the soil, formamide is expected to leach into groundwater (TOXNET, 2008). Formamide is not expected to significantly bioaccumulate (TOXNET, 2008). When released into the air, formamide is expected to be readily degraded by reaction with photochemically produced hydroxyl radicals within hours (Bråten, 2008). For formamide exposure at working places a limit value of 10 ppmv is given (NIOSH, USA). However, there are no appropriate, sub chronic (90 days) studies to assess effects by inhalation (Låg et al., 2008b).

5.6   Aquatic organisms

Amines, amides, nitrosamines, and nitramines are toxic for freshwater aquatic organisms. Ecotoxicological studies show that acute toxic effects of MEA may occur at levels of 6 mg/l for algae and at 20 mg/l for fishes. The highest chronic effect is found for certain nitrosamines in algae (at 0.025 mg/l nitrosamine) and the highest acute effect for nitramines in invertebrates (at levels above 1.9 mg/l). Table 4 provides an overview of the acute and chronic toxicity threshold values for certain freshwater aquatic organisms.

For the risk assessment of the compounds with respect to aquatic organism toxicity a safety factor is introduced. A safety factor ranging from 50-1000 is

introduced for the different compounds based on the European Union Technical guidance document on risk assessment (Brooks and Wright, 2008). The ecotoxicological limit values given in Table 4 have to be multiplied by the safety factor (assessment factor) to obtain a safety threshold, the so-called "Predicted No Effect Concentration" (PNEC), for the worst case calculations. A safety or assessment factor, often referred to as an uncertainty factor is typically applied to ecotoxicity data to account for the level of uncertainty, and provide a safety margin for environmental protection. Such safety factors are needed particularly in cases where ecotoxicity data for the selected chemical(s) is limited. From the review of ecotoxicological effects of amine and degradation products carried out by NIVA in **Task 9**, many missing knowledge gaps were identified. The incomplete data for some of the amines and secondary products suggests a high level of uncertainty. Under such circumstances a high safety factor should be applied in order to provide an adequate level of environmental protection. The assessment factor is 100 for MEA and MDEA, 1000 for AMP, and 100 for PIPA. For amides an assessment factor of 50 is introduced, while a factor of 1000 has been applied for nitramines and nitrosamines.

Table 4: Summary of the worst case toxicity values for the four main groups of compounds. Data included for both acute and chronic exposures to fish, invertebrates and algae/bacteria. All data obtained from the toxicity review carried out by NIVA in Task 9 (Brooks, 2008). (data expressed as mg/L; — data not available)

Group	Test	MEA	Formamide	Nitrosamine	Nitramine
Fish	Acute	20	5000	5.85 [1]	3.6 [3]
	Chronic	—	—	200 [2]	0.2 [4]
Invertebrate	Acute	83.6	13	7.76 [1]	1.9 [3]
	Chronic	—	1.2	100 [2]	0.4 [4]
Algae/bacteria	Acute	6-39	8000	—	3.2 [3]
	Chronic	0.75	—	0.025 [2]	—

[1] N-Nitrosodiphenylamine
[2] N-Nitrosodimethylamine, NDMA
[3] RDX
[4] CL-20

6 Worst Case

6.1 Worst Case calculation

Maximum tolerable levels in the environment for a certain compound are defined according to current air quality regulations and standards. In these regulation different averaging intervals, short term and long term averages, are defined. For the given compounds, such regulations are only in place for nitrosamines in drinking water. For all other compounds and their effects on receptor organisms, thresholds were derived from the information obtained in the related tasks of this project (Chapter 5, "Limits"). With the use of atmospheric dispersion models, maximum acceptable emissions can be calculated on the basis of the predefined target levels for the respective compounds. The unity emissions are then scaled until the critical concentration levels (limits, Chapter 5) in either air or deposition are reached. By this back calculation procedure, the maximum tolerable emission rates are obtained. A further increase of the emission would then imply directly an exceedance of the critical levels and loads of certain compounds that impact ecosystems and human health. Table 5 gives a summary of the accomplished worst case studies and lists the effects, deposition velocity, time averaging interval and critical loads for the problematic compounds.

The modeled maximum deposition flux level is taken as the reference level for estimating the maximum tolerable emission. This value is the reference level at unity emissions. The reference value is scaled until the critical level for the deposition flux is reached. By this procedure, the scaling factor of the emission source strength is obtained. The unity emission (1 g/s) is then multiplied by the scaling factor to give the maximum tolerable emission from the CO_2 capture plant. The maximum emission of nitrogen, nitrosamines and other toxic degradation products is finally translated into maximum amine emissions.

Table 5: Worst case studies: critical loads in deposition (no chemical reactions considered).

Worst case compounds	Effects	Depos. velocity (m/s)	Average time	Critical deposition flux [1,2]
Amines	Terrestrial vegetation damage	0.01	1 year	2700 mg/m^2/yr
	Aquatic algae chronic	0.01	1 year	300 mg/m^2/yr
Nitrogen	Terrestrial eutrophication	0.01	1 year	500 mgN/m^2/yr
Nitrosamines	Human health	0.03	1 year	0.3 mg/m^2/yr
	Aquatic algae chronic	0.03	1 year	1.0 mg/m^2/yr
Nitramines	Human health	0.03	1 year	40 mg/m^2/yr
	Aquatic fish/Invertebrates chronic	0.03	1 year	8.0 mg/m^2/yr
Formamide	Aquatic invertebrates chronic	0.03	1 year	960 mg/m^2/yr

[1] Critical deposition flux for aquatic organisms based on safety factor given in section 5.6.
[2] Critical deposition flux F_{crit} is calculated from given critical levels L_{crit} in rainfall (given in Chapter 5) as follows:

$$F_{crit}(mg/m^2/yr) = L_{crit}(ng/l) \cdot 10^{-6}(mg/ng) \cdot 2000(l/m^2/yr) \cdot \frac{1}{v}$$

Assuming a precipitation rate of 2000 mm and a rainfall and plume frequency v at the target site of 0.05.

[3] Critical deposition flux F_{crit} of amines to terrestrial vegetation is calculated using the critical soil or water area concentration of 1.5 kg/ha (150 mg/m^2) assuming steady state between soil and air (dC/dt=0) and a homogeneous distribution over a length of 10m (depth of soil) in soil, and an amine lifetime of 200 days in soil:

$$F_{crit}(mg/m^2/yr) = \frac{L_{crit}(mg/m^2)}{200 days} \cdot 360 \frac{days}{yr} \cdot 10 \frac{m}{m}$$

6.2 Worst Case scenario concept

Several simplifications have been made for the design of worst case scenarios in this report. The following list is intended to give a brief overview of the conceptional simplifications:

1) Degradation products are formed instantaneously, when they leave the stack of the CO_2 capture plant, with a fixed formation yield from the parent amine. The instantaneous formation yield translates into a direct emission of the degradation product from the plant. The emissions of the degradation product corresponds to a certain fraction of the total amine emissions.
2) Formation of the degradation products takes place in the gas phase under atmospheric conditions.
3) Photochemical depletion of the degradation products and of the parent amine is not taken into account.

4) Liquid phase formation/depletion of degradation products is not included.

The results from the calculations (sections 7.1 and 7.2) are valid for all kinds of amines used in CO_2 capture. However, the worst case study of the parent amine focuses on MEA, since the most reliable information about effects on ecosystems and human health is available for MEA.

6.3 Worst Case assumptions

The Worst Case study calculations rely on two basic assumptions:1) estimated stack parameters correspond to a real CO_2 capture facility, 2) dominating wind direction/speed and terrain of the location is similar to Mongstad, and the simplifications mentioned in section 6.2. These worst case calculations addressing the impact on aquatic organisms further involve a series of assumptions:

1. We assume that emissions based on yearly averages also hold for shorter periods (i.e. no peak emissions);
2. Chemical compounds are stabile in air, water and soil, with no degradation or loss during transport through each medium;
3. Uniform dispersal and mixing within each medium (air, water, soil);
4. We assume that the lower limit for toxicity for each compound is as found in the literature. This implies that there are no other organisms for which toxicity is higher;
5. No adverse ecosystem effects occur at lower levels;
6. We assume that the toxicity is not higher for other life stages of each organism. For example, we assume that the limit for fish also holds for reproductive life stages;
7. No seasonal differences in acute or chronic effects.

7 Results

7.1 Concentration and deposition distributions at unity emission

Yearly averaged air concentration distributions and deposition distributions are obtained from the model CONDEP for unity emissions (i.e. 1 g/s). A deposition velocity of 0.01 m/s is used for amines and nitrogen; a deposition velocity of 0.03 m/s is used for nitrosamines, nitramines and formamide (see section 4.2).

From the CONDEP model run, the distribution of amine and nitrogen concentrations (Figure 1) from the amine plume at unity emissions are obtained.

Maximum amine and nitrogen concentrations in air at the surface can be found in a distance of 4 to 8 kilometers north of the plant. The maximum air concentration is 16.4 ng/m^3.

Yearly averaged amine and nitrogen deposition fluxes for unity emissions are shown in Figure 2. Maximum amine and nitrogen deposition fluxes can be found north of the plant, in a distance of 4 to 8 kilometers from the plant. The maximum deposition flux is 5.18 mg/m^2 with unity emission on a yearly average.
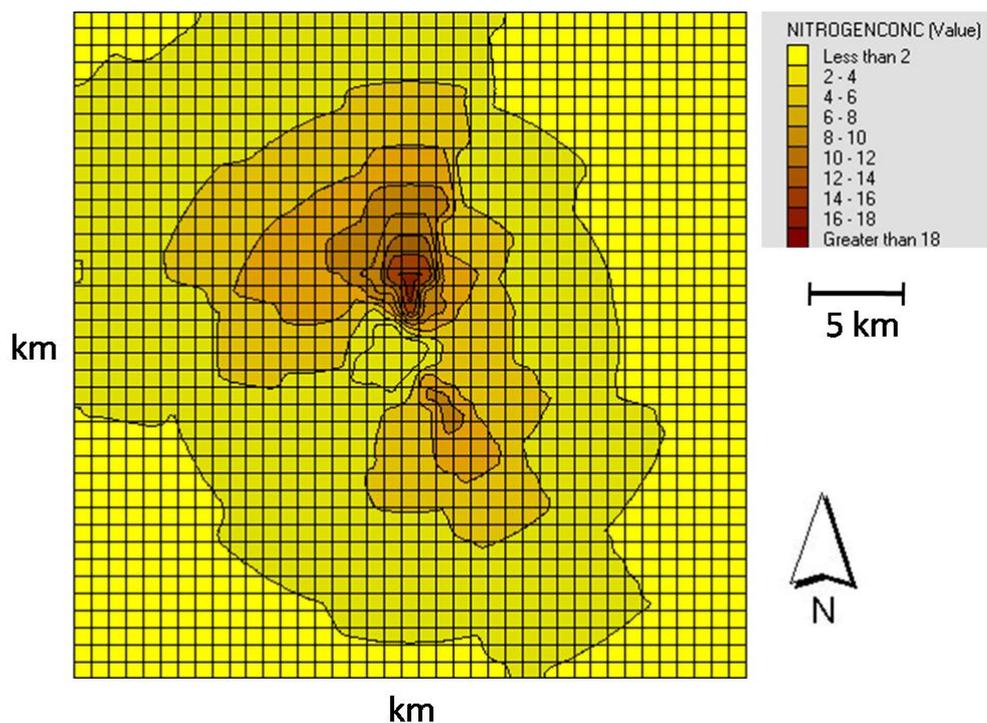

Figure 1:   Yearly averaged amine air concentration (ng/m^3) and nitrogen concentration (ng N/m^3) distribution for unity emission. Deposition for amine and nitrogen is treated identical, thus concentration values given in the legend apply for both amine and nitrogen.
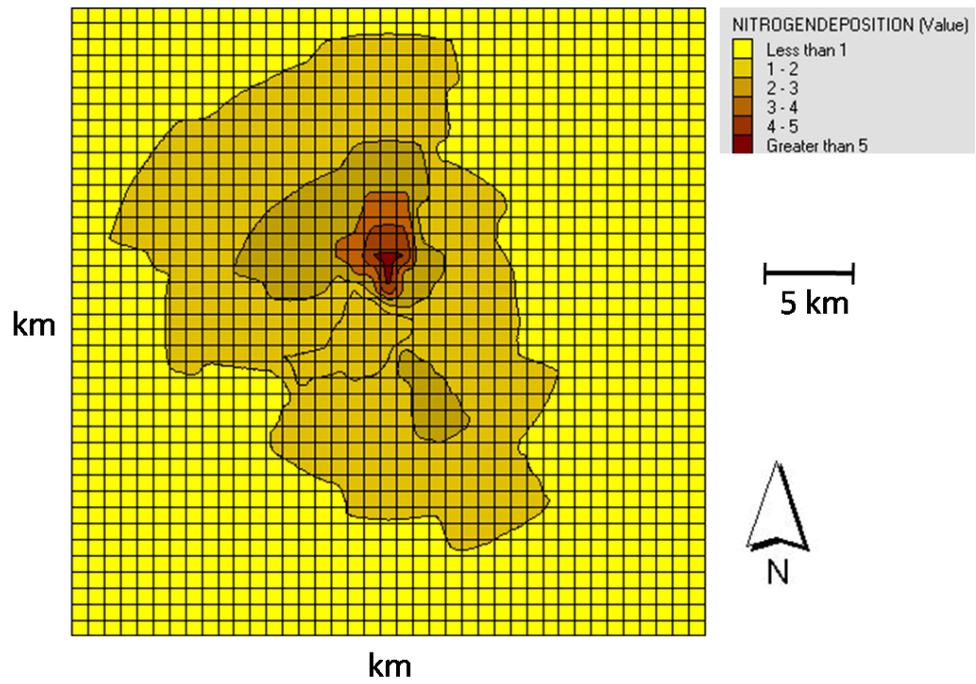
Figure 2: *Yearly averaged amine deposition flux (mg/m^2) and nitrogen deposition flux (mg N/m^2) distribution for unity emission. Deposition for amine and nitrogen is treated identical, thus deposition flux values given in the legend apply for both amine and nitrogen.*
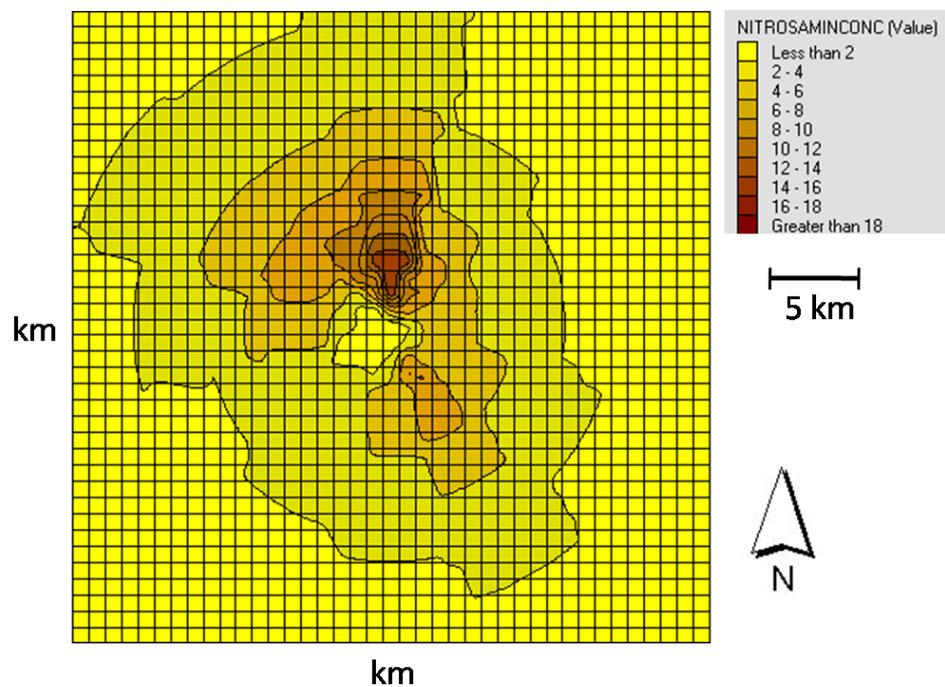

Figure 3: *Nitrosamine, nitramine and formamide concentration (ng/m^3) distribution for unity emission.*
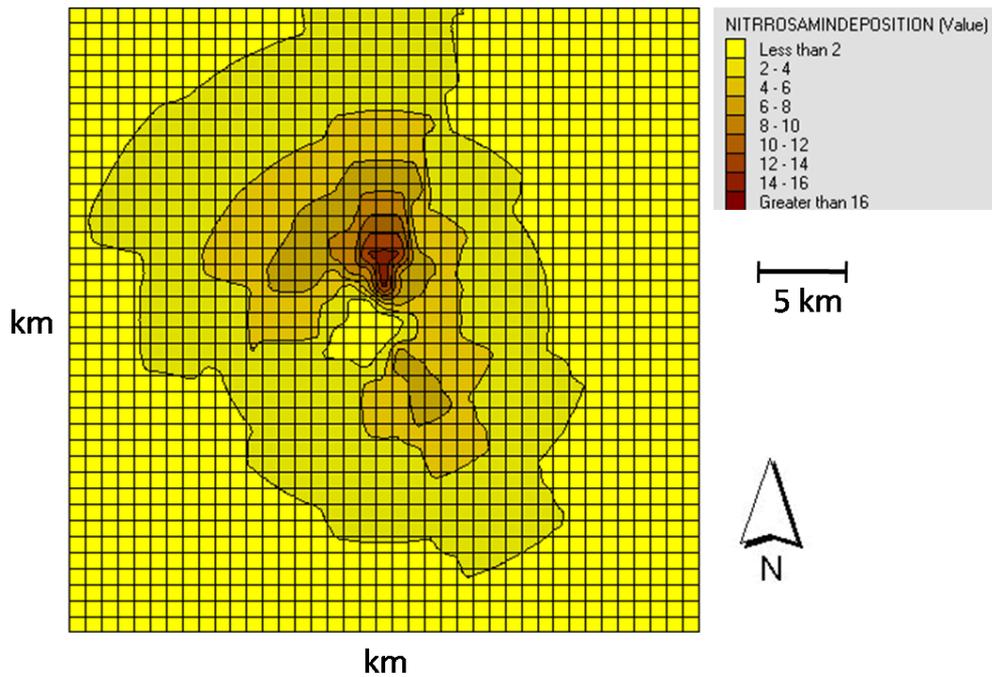
Figure 4:   Nitrosamine, nitramine and formamide deposition flux (mg/m²)
distribution for unity emission.

From the CONDEP model run, the distribution of nitrosamine, nitramines and
formamide concentrations (Figure 3) and nitrosamine deposition fluxes (Figure 4)
from the amine plume at unity emissions are obtained (deposition velociy is
0.03 m/s).

Maximum concentrations and deposition fluxes of nitrosamines, nitramines and
formamide can be found north of the plant, in a distance of 4 to 8 kilometers from
the plant. For each of these compounds, the maximum deposition flux is
16.1 mg/m² and the maximum concentration is 17.0 ng/m³ at unity emission on a
yearly average.

To obtain hourly averaged (short-term average) concentrations and deposition,
additional simulations were performed with the model CONCX using the
parameters given in Table 2. With CONCX the wet deposition flux of the
compounds can be calculated. A lifetime of 2.8 hours for wet removal is assumed
for all compounds. A scavenging coefficient of $1 \times 10^{-4} \text{ s}^{-1}$ is used in the model
calculation. Maximum hourly averaged concentrations in air and wet deposition
fluxes in a distance of up to 10 km from the plant are shown in Figure 5 and
Figure 6. Hourly averaged air concentration are highest in 1 km distance from the
plant. A maximum concentration of 1.9 μg/m³ is found at unity emission. The
maximum hourly averaged wet deposition flux decreases almost exponentially
with increasing distance to the plant. In a distance of ≥1 km the maximum hourly
averaged wet deposition flux is 0.8 mg/m²/hr at most. The shown maximum
hourly averaged air concentrations and wet deposition fluxes with distance from a
plant apply to each of the compounds (unity emission), assuming they are all
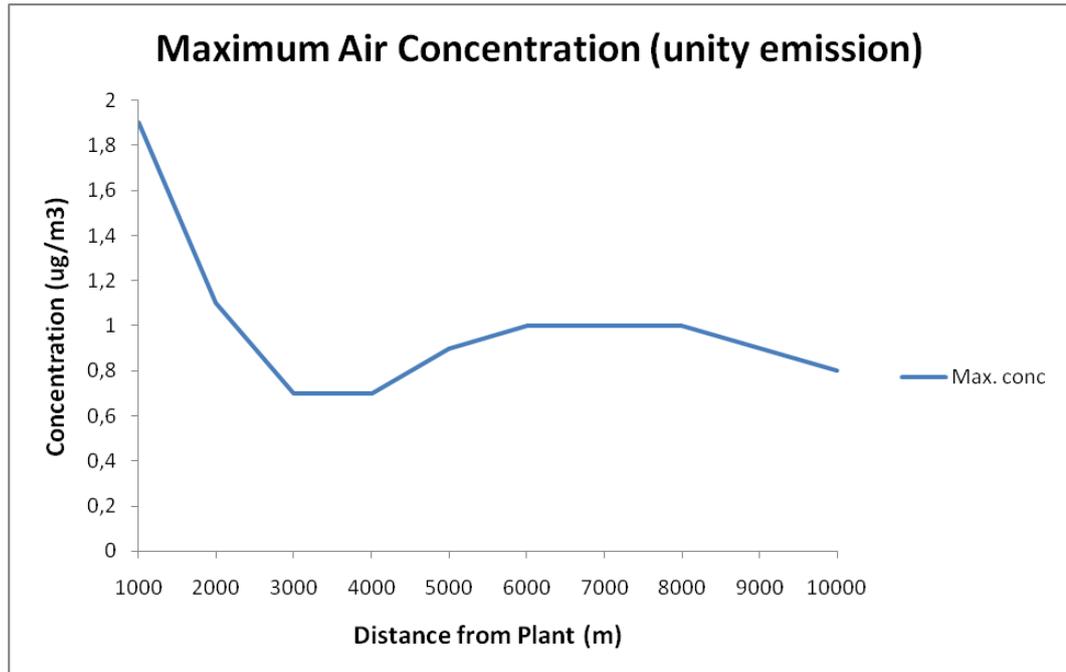scavenged with the same rate.

Figure 5: *Maximum hourly average concentrations (μg/m³) with distance from the plant at unity emission. A total scavenging coefficient of $1x10^{-4}$ s^{-1} is used for all compounds in the model calculation.*

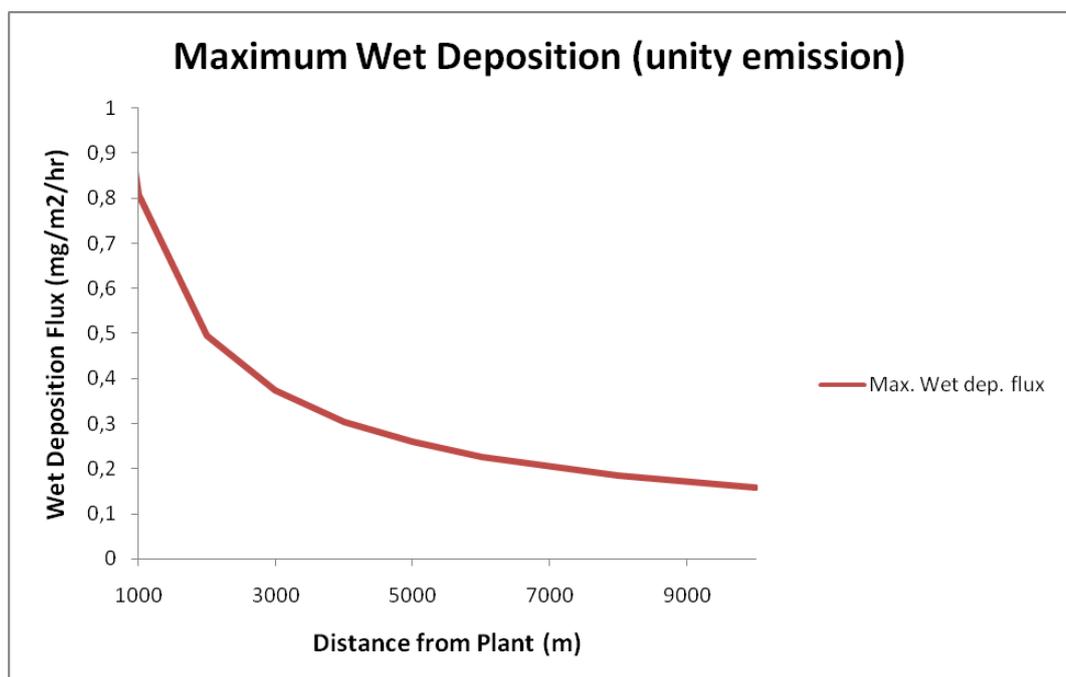*Figure 6:* *Maximum hourly average wet deposition flux (mg/m²/hr) with distance from the plant at unity emission. The distribution is for the local field around the plant and it is assumed that the emitted compounds are highly soluble in water. A total scavenging coefficient of $1x10^{-4}$ s^{-1} is used for all compounds in the model calculation.*

Increasing the wet scavenging coefficient in the CONCX calculation by a factor of 10, i.e. using a scavenging coefficient of 1×10^{-3} s^{-1} instead of 1×10^{-4} s^{-1}, increases the maximum hourly averaged deposition flux by roughly 50%. In a distance of ≥ 1 km the maximum hourly averaged wet deposition flux is 1.2 mg/m^2/hr at most when using a scavenging coefficient of 1×10^{-3} s^{-1}.

Both the deposition velocities applied in CONDEP (see Table 5) and the applied wet scavenging coefficient in CONCX are rough estimates for the wet removal of a very soluble compound. Results from both models are not comparable since CONDEP calculates a **long term** averaged deposition concentration while CONCX calculates a **short term** deposition concentration.

7.2 Concentration distributions at maximum emissions

The estimated emission of amines from the CO_2 capture facility is 40 to 160 tonnes per year, about 75 tonnes per year on average. The maximum emission is 160 t/yr of amines. This corresponds to a maximum nitrogen emission of 37,000 kg N/yr (using MEA). In the gas phase reaction of amines with hydroxyl radical (OH) nitrosamines can be formed. In the reaction of MEA with OH, various nitrosamines and nitramines can be formed by hydrogen abstraction from the amino group; and formamide is a major product from the hydrogen abstraction of the C atoms (Bråten et al., 2008). **Task 3** provides no product yields for these compounds yet, as they have to be evaluated in smog chamber studies. A smog chamber is a stirred chemical reactor for the investigation of atmospheric reactions under close-to-ambient conditions. Pitts et al. (1978) published product yields from a smog chamber study with triethylamine (TEA, $(CH_3CH_2)_3N$). Based on their results the following yields are applied in this worst case study:

1. Nitrosamines: 2%
2. Nitramines: 7%
3. Formamide: 9%

TEA is a tertiary amine. In the present project, two primary amines (MEA and AMP), one secondary amine (PIPA) and one tertiary amine (MDEA) are studied. Pitts et al. (1978) found formation of nitrosamines also for two secondary amines: dimethylamine, DMA, and diethylamine, DEA. For primary amines no product studies can be found in literature. The current project has suggested that all listed products also form in the photochemical degradation of MEA. This is based on quantum chemical calculations as carried out in Task 3 (Bråten et al., 2008). Product yields from MEA could be either lower or higher than the ones given above. These compounds form in the atmospheric oxidation of amines, but for the sake of simplicity, it is assumed in the model calculations, that these compounds are formed instantaneously in the stack of the CO_2 capture plant. The given yields should therefore be seen as upper limits since photochemical oxidation of these products can occur in the atmosphere, but is not taken into account by the dispersion model. A maximum emission of 3,200 kg/yr, 11,000 kg/yr, and 1,400 kg/yr of nitrosamines, nitramines and formamide is obtained, respectively. Furthermore, it is assumed that both amines and their atmospheric degradation products are stable compounds in the air and behave as inert tracers. The

maximum yearly emissions from the CO_2 capture facility are summarized in Table 6.

Table 6: Estimated maximum emissions from the CO_2 capture plant.

Unit	Amines	Nitrogen (N)	Nitrosamines	Nitramines	Formamide
kg/y	160,000	37,000	3,200	11,000	14,000
g/s	5.9	1.35	0.12	0.42	0.53

For the estimated maximum emissions, the maximum hourly averaged air concentrations in a distance of up to 10 km from the plant are calculated with the dispersion model CONCX. These model results can be seen as a guideline for possible distribution of pollutant concentrations in the proximity of the plant and expected levels. However, it should be noted again, that chemical degradation of the compounds is not taken into account, thus actual measured concentrations would be lower. In addition the results refer to yearly averaged emissions and on a shorter term, emissions can be either higher or lower.

Highest concentration of amines emitted from the CO_2 capture plant are found at 1 km distance. Peak maximum hourly averaged concentration is 11 $\mu g/m^3$ at the maximum amine emission of 160 t/yr. At a distance of >3 km maximum amine concentrations are almost constant, and remain on the same level of about 4 $\mu g/m^3$ up to 10 km (Figure 7). Concentrations will further decline with increasing distance from the plant.

Figure 7: Maximum hourly averaged amine concentrations ($\mu g/m^3$) with distance from the plant, at maximum amine emissions.

Highest concentration of airborne nitrogen from amines emitted from the CO_2 capture plant are found at 1 km distance. Peak maximum hourly averaged concentration is 2.5 µg N/m^3 at the maximum amine emission of 160 t/yr. At a distance of >3 km maximum amine concentrations are almost constant, and remain on the same level of about 1 µg N/m^3 up to 10 km (Figure 8). Concentrations will further decline w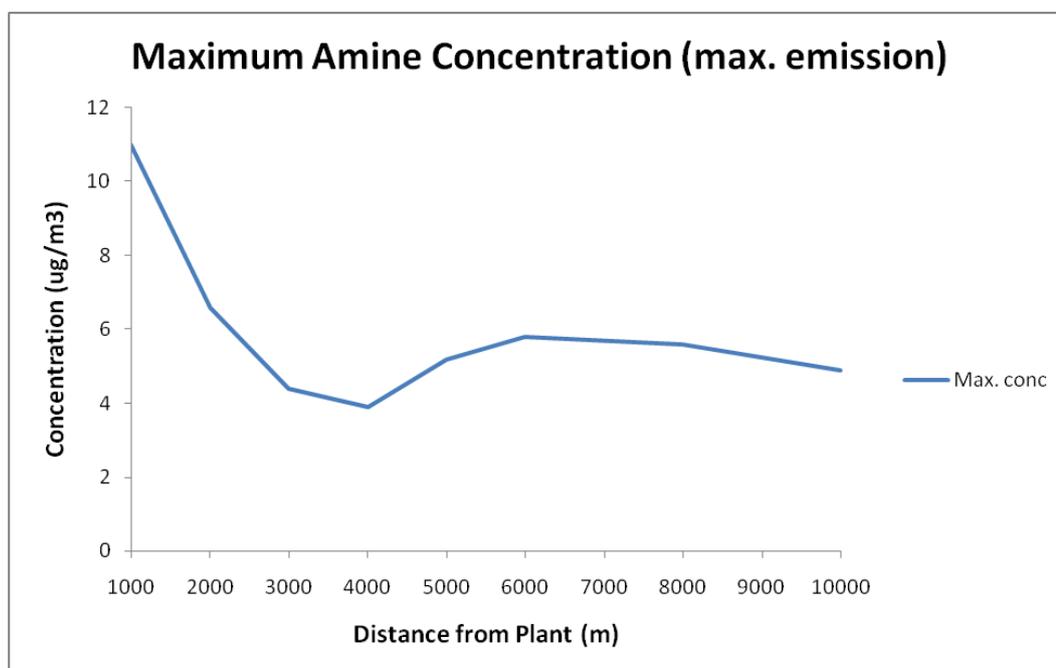ith increasing distance from the plant. Highest concentration of nitrosamines formed photochemically from amines emitted from the CO_2 capture plant are found in close distance to the plant.
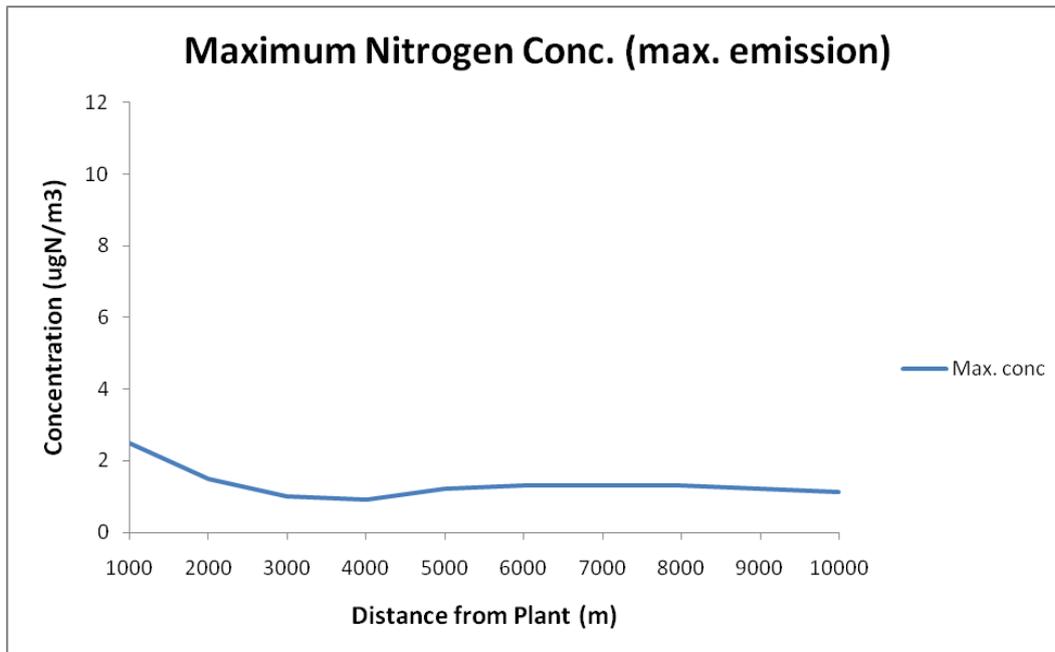

Figure 8: Maximum hourly averaged nitrogen concentrations (µg N/m^3) with distance from the plant, at maximum amine emissions.

Peak maximum hourly averaged concentration is 0.2 µg/m^3 at the maximum amine emission of 160 t/yr and the assumed 2% formation yield of nitrosamines. At a distance of >2 km maximum amine concentrations are almost constant, and remain on the level of about 0.1 µg/m^3 up to 10 km (Figure 9) and are expected to gradually decline at distances >10 km. Concentrations below 0.1 µg/m^3 are not resolved by the program. Concentrations are about a factor of 60 lower than the amine concentrations. Concentrations of nitramine are shown in Figure 10. Highest maximum nitramine concentrations of 0.8 µg/m^3 are found within 1000 m distance from the plant.

Figure 9:   Maximum hourly averaged nitrosamine concentrations ($\mu g/m^3$) with distance from the plant, at maximum amine emissions (see Table 7).

They are constant at about 0.3 $\mu g/m^3$ for a distance >3 km. Nitramines are photochemically stable (chemical lifetime > 15 hours). Maximum hourly formamide concentrations of 1.0 $\mu g/m^3$ are found within 1000 m distance from the plant. They are constant at about 0.4-0.5 $\mu g/m^3$ for a distance of 3-10 km (Figure 11) and are expected to deline gradually with further distance from the local domain.
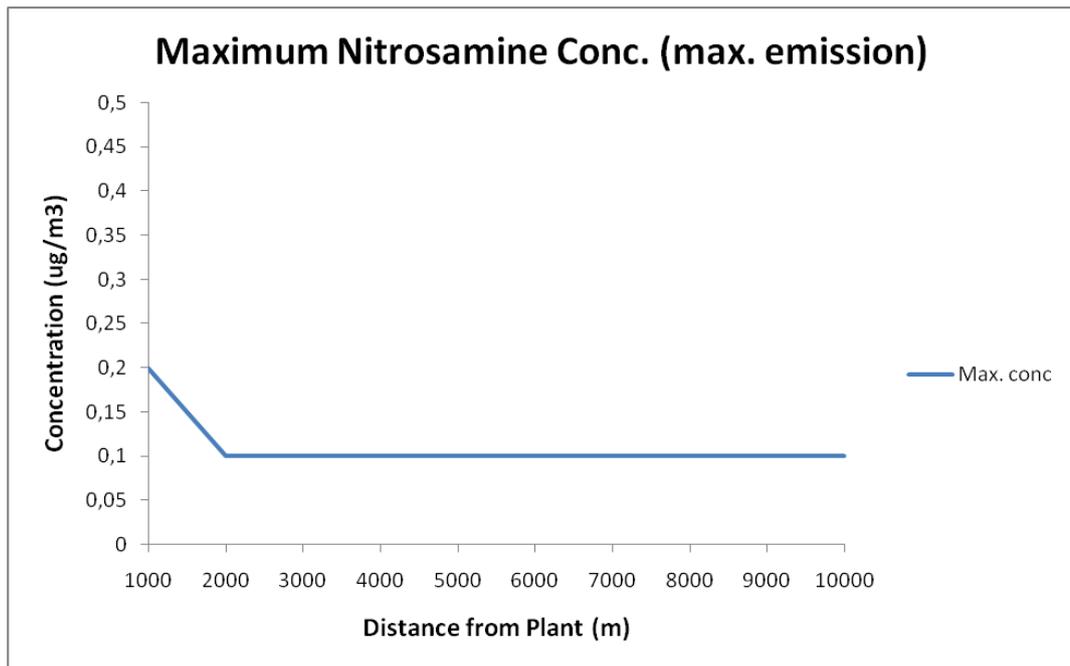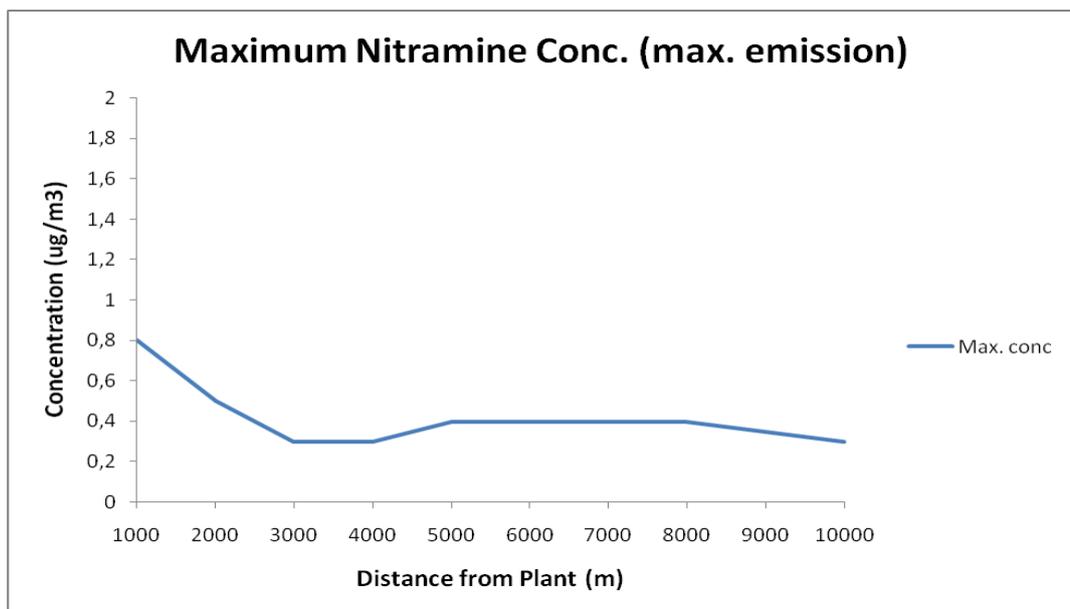

Figure 10: Maximum hourly averaged nitramine concentrations ($\mu g/m^3$) with distance from the plant, at maximum amine emissions (see Table 7).
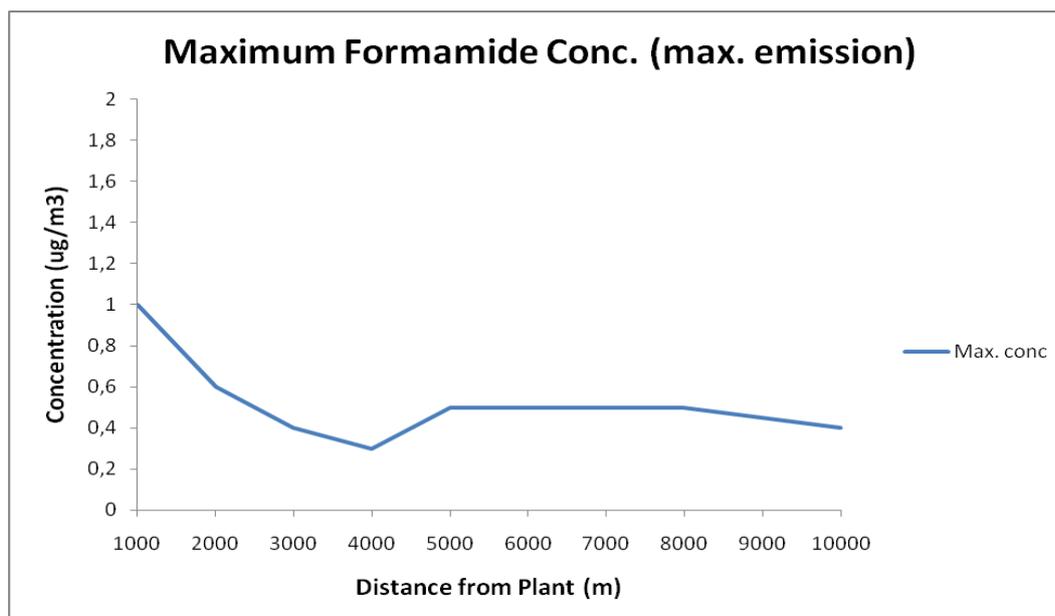
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Figure 11: Maximum hourly averaged formamide concentrations (µg/m³) with distance from the plant, at maximum amine emissions (see Table 7).

Table 7 lists maximum hourly averaged concentrations for maximum amine emissions with distance from the plant for amines, nitrogen, nitrosamines, nitramine and formamide.

Table 7: Maximum hourly concentrations of the problematic compounds in air (in µg/m³) with distance from the plant (in km), calculated with CONCX for maximum amine emissions. Emission source parameters as given in Table 2.

Problematic Compound	Distance from plant (km)							
	1	2	3	4	5	6	8	10
Amines	11	6.6	4.4	3.9	5.2	5.8	5.6	4.9
Nitrogen	2.5	1.5	1.0	0.9	1.2	1.3	1.3	1.1
Nitrosamines	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Nitramines	0.8	0.5	0.3	0.3	0.4	0.4	0.4	0.3
Formamide	1.0	0.6	0.4	0.3	0.5	0.5	0.5	0.4

7.3 Sensitivity towards parameterisation of the emission source

The sensitivity of the maximum hourly averaged air concentrations of the emitted compounds towards the parameterization of the emission source was studied. The parameters of the emission source (stack) are given in Table 2. The influence of changed plume velocity and exhaust temperature (emission temperature) on the modelled maximum short term air concentrations in the vicinity of the plant was tested. In a first test the temperature of the emissions was changed to 40°C

(313 K). The resulting maximum hourly air concentrations of released compounds are shown in Table 8. Concentrations within 10 kilometre distance from the plant increased by roughly 30% compared to the standard parameterisation.

Table 8 Maximum hourly concentrations of the problematic compounds in air (in μg/m³) with distance from the plant (in km), calculated with CONCX for maximum amine emissions for a exhaust temperature of 40°C.

Problematic Compound	Distance from plant (km)							
	1	2	3	4	5	6	8	10
Amines	14.5	7.8	5.1	6	7.2	7.5	6.7	5.5
Nitrogen	3.3	1.8	1.2	1.4	1.7	1.7	1.5	1.3
Nitrosamines	0.3	0.2	0.1	0.1	0.1	0.2	0.1	0.1
Nitramines	1.3	1.2	1.0	0.6	0.4	0.4	0.5	0.5
Formamide	1.3	0.7	0.5	0.5	0.7	0.7	0.6	0.5

In a second test the plume velocity was changed to 10 m/s. The resulting maximum hourly air concentrations of released compounds are shown in Table 9. Concentrations in 1 kilometre distance from the plant increased by roughly 50%, while for larger distances the increase was lower.

Table 9 Maximum hourly concentrations of the problematic compounds in air (in μg/m³) with distance from the plant (in km), calculated with CONCX for maximum amine emissions for a plume velocity of 10 m/s.

Problematic Compound	Distance from plant (km)							
	1	2	3	4	5	6	8	10
Amines	17	8.7	5.8	6.3	7.5	7.7	6.8	5.6
Nitrogen	3.9	2.0	1.3	1.4	1.7	1.8	1.6	1.3
Nitrosamines	0.3	0.2	0.1	0.1	0.2	0.2	0.1	0.1
Nitramines	1.2	0.6	0.4	0.5	0.5	0.5	0.5	0.4
Formamide	1.5	0.8	0.5	0.6	0.7	0.7	0.6	0.5

Both changes lead to higher short term concentrations close to the CO_2 capture plant. A careful choice of the emission source parameters will be important for a more detailed and precise evaluation of the population exposure to the released compounds.

7.4 Inhalation exposure

Long term inhalation exposure towards amines and their toxic degradation products can be derived from yearly averaged air concentrations obtained from the CONDEP simulations. To obtain long term maximum exposure levels of amine in air, the results from the dispersion model CONDEP (section 7.1) for unity emission (i.e. 1 g/s) are scaled to maximum amine emission (i.e. 5.9 g/s, Table 6). For unity emission, the maximum yearly averaged air concentration is 16.4 ng/m^3. By scaling to maximum amine emissions (i.e. multiplication by 5.9), a value of 0.1 µg/m^3 is obtained. Based on this maximum estimate, exposure levels of amine that can cause adverse health effects are not exceeded.

On the basis of intake, the state of California has determined that 0.04 and 0.004 µg/m^3 of the nitrosamine NDMA per day were equivalent to a 10^{-5} and 10^{-6} risk of cancer, respectively (Låg et al., 2008b). In this worst case study, the value of 4 ng/m^3 nitrosamines in air (corresponding to a 10^{-6} lifetime cancer risk) is used as critical level for the long term exposure through inhalation. Scaling the maximum nitrosamine air concentration from the CONDEP simulation to maximum emission, a maximum air concentration in vicinity of the CO_2 capture plant of 2 ng/m^3 nitrosamines is obtained. This is only a factor of two below the critical inhalation exposure limit.

The California Environmental Protection Agency (1999) has established an inhalation unit risk estimate of 2.0×10^{-5} (µg/m^3)$^{-1}$ on cancer caused by the intake of acetamide (Låg et al., 2008b). This corresponds to a critical level of 50 ng/m^3 acetamide in air for long term inhalation exposure (corresponding to a 10^{-6} lifetime cancer risk). In the worst case study, yearly averaged air concentrations for formamide at maximum emission are found to be 9 ng/m^3, i.e. about a factor of 10 below the critical limit derived for acetamide. If the same formation yield for acetamide as for formamide is assumed, this result would be the expected inhalation exposure towards acetamide.

7.5 Deposition of amines and nitrogen

Experience from deposition of nitrogen from NO_x emissions with regional scale models show that approximately 30-40% of the emitted nitrogen is deposited in a 1000×1000 km^2 grid around a plant in one year. A CO_2 capture plant may emit in the range of 50-200 tonnes of amines a year. The amount refers to a power plant of 400-500 MW. The emissions obviously depend on the size of the plant and operating conditions. This means that 15-80 tonnes of amines can be deposited within a distance of 1000 km from the plant, and implies that the average impact can be 0.02-0.2 mg amines per square meter per year. The maximum deposition would cover a smaller area and is roughly estimated to be in the range of 1.5-7 mg/m^2 depending on the frequency of wind direction and rainfall. The maximum deposition will be inside an area of 100 km^2 to 600 km^2 depending on the geographical position and meteorological climate on site. The maximum deposition will occur in a distance between 30 and 50 km from the plant. The assumption here is that all the parent amines still have the same characteristics as NO_x in respect to solubility. The real deposition also depends on the chemical transformation of the emitted compound after emission and the ambient concentrations in the air that the compounds are released to.

7.6 Worst Case amines

To estimate the worst case effect of amine emissions on ecosystems, the deposition results from the unity emission calculation with CONDEP (section 7.1) are scaled until the critical load of amines to vegetation (2.7 g/m^2/yr) is reached. In this study the critical load is defined for MEA. For other amines the result may be different, depending on their expected effects on vegetation or aquatic organisms.

The maximum yearly averaged concentration of amines in deposition in a distance between 4 and 10 km from the plant is applied to assess the critical load of amines to vegetation. From this backward calculation the maximum tolerable emission of amines from the plant is 14,400 tonnes per year. That is 90 times higher than the expected maximum emission from the CO$_2$ capture plant. Thus harmful effects of amines to the vegetation is not expected to occur. However, the critical load applied here is a rough estimate. There are other effects of amines, like corrosion and smell, and amines are irritative to human skin and are known to be toxic to aquatic organisms.

For the worst case estimate for amines, the threshold for human health effects is applied in addition. Task 7 suggests the population should, **over time**, not be exposed to atmospheric concentrations higher than **10 μg/m^3 MEA**. This limit value refers thus to a long term exposure with amines. Peak maximum hourly averaged amine concentration is 11 μg/m^3 at the maximum amine emission of 160 t/yr. At a distance of >3 km maximum amine concentrations are almost constant, and remain on the same level of about 4 μg/m^3 up to 10 km (Figure 7, section 7.2). Table 7 shows that the maximum concentration decreases with distance from plant, and in a distance of 2 km from the plant, the maximum hourly averaged concentration is below 10 μg/m^3. On the short time scale, the amine threshold for human health is exceeded in close vicinity of the plant. But the recommended limit value for amine exposure from Task 7 refers to a long term exposure. *As described in section 7.4, the worst case amine levels for long term inhalation exposure are two orders of magnitude below the threshold of 10 μg/m^3 MEA.*

Chronic and acute toxicity of amines (represented by MEA) in freshwater aquatic organisms has been evaluated by Task 9. Algae have lowest threshold levels and seem to be most sensitive to amine exposure. **Chronic effects** in algae have been found for levels above 0.75 mg/l, corresponding to a risk threshold of **7.5 μg/l** when a risk factor of 100 is applied (see section 5.6). **Acute effects** in algae occur below a limit of **60 μg/l**. Assuming an average precipitation rate of 2000 mm per year ocurring at the target location with a frequency of 50% and that the location is within the amine plume during 10% of the rain events, the yearly amine emissions from the plant should not exceed **1570 t** in order to avoid chronic toxic effects in algae. Thus the risk threshold for aquatic organisms to amine exposure is not exceeded.

For fish and invertebrates no chronic toxicity thresholds could be found in literature. Acute effects in algae would occur for MEA emissions above 1270 t per year, which is about 8 times higher than the maximum expected emissions. For

fishs and invertebrates acute toxic effects would only occur at 80 times higher emissions. Thus aquatic freshwater organisms are not threatened by amine emissions from the plant directly, unless emission peaks occur for one week or longer (assuming one week of exposure leads to chronic damages).

7.7   Worst Case nitrogen

For a critical nitrogen load of 5 kg N/ha/yr, the maximum tolerable amine emissions from the plant are 11,400 tonnes per year, that is 57 times more than the expected maximum emission from the CO_2 capture plant.

Ammonia emissions from the CO_2 capture plant are estimated to be 100 tonnes per year at maximum. Ammonia is reactive nitrogen compound in the atmosphere and the emissions of ammonia add to the existing airborne nitrogen. If maximum ammonia emissions are included in the worst case study on nitrogen, the maximum tolerable emissions of amine are reduced to 11,000 tonnes per year. The maximum total emissions of amines and ammonia from the plant can be 20 times higher than the expected total emissions from both.

However, the airborne nitrogen deposition in many parts of Norway is dominated by the background nitrogen from other sources. The problem is that the background levels are already high and in areas where the critical nitrogen load is exceeded today any additional load is unwanted.

Environmental Factor for Air (EIF Air) is a model instrument to assess the impact of nitrogen and other emissions from industrial installations on eutrophication and acidification of ecosystems. More information on EIF Air can be found on the following website: http://eifbusiness.nilu.no. Using EIF-Air, the critical load from nitrogen emissions from a single CO2 capture plant could be evaluated with respect to already present background nitrogen concentrations.

7.8   Worst Case nitrosamines

To assess the concentration of nitrosamines in precipitation, a yearly precipitation (rainfall) amount of 2000 mm is assumed. Futhermore, it is assumed that rainfall at a specific location of interest occurs with a frequency of 50% and that the location is downwind of the plant during 10% of the rain events. These assumptions are representative for typical precipitation and wind conditions on the west coast of Norway.

For a critical nitrosamine load of 7 ng/l in precipitation, the maximum tolerable total amine emissions from the plant is calculated to be 24 tonnes per year. This result is based on the assumption of a 2% nitrosamine formation yield in the flue gas and no degradation of nitrosamines in the atmosphere. The expected maximum emissions of amines from the CO_2 capture plant (see Table 6) are a factor of 7 above the tolerable maximum emissions.

A possible worst case range of nitrosamine concentrations in precipitation is studied for differing rainfall conditions (at maximum amine emissions in 1000 m distance from the plant). A range of nitrosamine concentrations in precipitation

was calculated for a typical annual precipitation (rainfall) amount between 1000 to 3000 mm. Futhermore, it was assumed that rainfall at a specific location of interest occurs with a frequency ranging from 10% to 50%. During these events, the location is affected by the nitrosamine plume from the CO_2 capture facility, i.e. it is downwind from the plant, with an assumed frequency of 1-10%. The parameters for the lower and upper range are given in Table 10.

Table 10: Parameters used for calculating the lower and upper limit of estimated nitrosamine concentrations in rainfall at maximum amine emissions.

Max. nitrosamine deposition flux ($\mu g/m^2/s$) [1]	Annual rainfall amount (mm)	Rainfall frequency	Downwind frequency	Nitrosamine concentration in rain (ng/l)
0.027	1000	0.1	0.01	6.1
0.027	3000	0.5	0.1	911

[1] Maximum deposition flux in 1000 m distance from the plant calculated by CONX for maximum emission. Scavenging coefficient for the calculation was 1×10^{-4} s^{-1}.

For this maximum estimate the range of nitrosamine levels in precipitation is between 6 ng/l and 900 ng/l. Only the lower bound of this range fulfils the critical limit for nitrosamines loads to Norwegian lakes and for the use of this water as drinking water. For almost all rainfall conditions the critical limit will be exceeded. The estimated maximum deposition of nitrosamines clearly exceeds the critical loads that can be tolerated for drinking water under typical meteorological conditions, average rainfall amounts and deposition fluxes of Western Norway.

Chronic and acute toxicity of different nitrosamines in freshwater aquatic organisms has been evaluated by Task 9. Algae have lower threshold levels than fish and invertebrates and seem to be the most sensitive aquatic organisms towards nitrosamine exposure. Chronic effects in algae have been found for levels above 0.025 mg/l, corresponding to a risk threshold of 25 ng/l when a risk factor of 1000 is applied (see section 5.6). This risk threshold is very close to the human health threshold of drinking water. ***For a nitrosamine load of 25 ng/l in precipitation which is critical for aquatic organisms, the maximum tolerable amine emissions from the plant is calculated to be 84 tonnes per year.*** The expected maximum emissions of amines from the CO_2 capture plant are by a factor of 2 above the tolerable threshold for aquatic organisms and could cause chronic damage to algae. Chronic effects for fish and invertebrates have been observed for levels of 100-200 mg/l, four orders of magnitude higher than for algae. Acute effects for fish and invertebrates have been observed for levels of 6-8 mg/l and maximum amine emissions would have to be more than 100 times higher to critically affect fish or invertebrates.

In this worst case study, the value of 4 ng/m^3 nitrosamines in air (corresponding to a 10^{-6} lifetime cancer risk) is used as critical level for the long term exposure of the population through inhalation. ***For estimated maximum emission from the CO_2 capture plant, a long term air concentration of 2 ng/m^3 nitrosamines is***

obtained. This is only a factor of two below the critical inhalation exposure limit.

7.9   Worst Case nitramines

Nitramines have been included in the worst case study because their carcinogenic potential is evident, though nitramines may be less hazardous than equivalent nitrosamines. A drinking water threshold for nitramines of 1 μg/l was applied in the worst case study. The yearly averaged deposition flux from CONDEP (section 7.1) for emission of unity can be scaled to obtain the maximum permissible amine permissions with respect to the exposure of nitramines in drinking water.

For a critical nitramine load of 1 μg/l in precipitation with respect to drinking water quality, the maximum tolerable amine emissions from the plant is calculated to be 960 tonnes per year. This result is based on the assumption of a 7% nitramine formation yield in the flue gas and no degradation of nitramines in the atmosphere. The current maximum amine emissions from the plant are thus 6 times below the proposed tolerable amount.

Table 11 shows the range of concentrations of nitramine in rainfall for different rainfall conditions as described in section 7.8.

Table 11: Parameters used for calculating the lower and upper limit of estimated nitramine concentrations in rainfall at maximum amine emissions.

Max. nitramine deposition flux ($\mu g/m^2/s$) [1]	Annual rainfall amount (mm)	Rainfall frequency	Downwind frequency	Nitramine concentration in rain (ng/l)
0.095	1000	0.1	0.01	21
0.095	3000	0.5	0.1	3190

[1] Maximum deposition flux in 1000 m distance from the plant calculated by CONX for maximum emission. Scavenging coefficient for this calculation was 1×10^{-4} s^{-1}.

For the maximum amine emissions and an assumed production yield of 7% nitramines from the emitted amines, the nitramine levels in rain range between 21 ng/l and 3200 ng/l. This result implies that, under extreme weather conditions, the nitramine concentration in rain may exceed the critical load for nitramine of 1000 ng/l.

Chronic and acute toxicity of different nitramines in freshwater aquatic organisms has been evaluated by Task 9 (Brooks and Wright, 2008). Chronic ecotoxicological effects in freshwater fish and invertebrates have been observed for levels between 0.2-2.0 mg/l, corresponding to a risk threshold range of 0.2-2.0 μg/l when a risk factor of 1000 is applied (see section 5.6). *For a critical nitramine load of 0.2 μg/l to aquatic organisms, the maximum tolerable amine emissions from the plant is calculated to be 190 tonnes per year.* Thus the expected maximum nitramine emissions are not harming aquatic organisms, unless emission peaks occur for four weeks or longer (assuming one month of exposure leads to chronic damages in fish and invertebrates).

7.10 Worst Case formamide

For formamide, no regulations and recommendations for critical levels or critical loads to ecosystems exist. The NIOSH standard (USA) provides a limit value of 10 ppmv for exposure by formamide at working places. Further evaluation of the toxicity of formamide should be done, before a threshold value can be recommended for human health. The formation yield from the amine reaction with OH is not determined yet. Formamide is very soluble in water and thus the CONDEP result from section 7.1 for emission of unity can be scaled to obtain the maximum permissible amine emissions. Table 12 shows the range of formamide concentrations in rain for different rainfall conditions as described in section 7.8.

Table 12: Parameters used for calculating the lower and upper limit of estimated nitramine concentrations in rainfall at maximum amine emissions.

Max. Formamide deposition flux ($\mu g/m^2/s$) [1]	Annual rainfall amount (mm)	Rainfall frequency	Downwind frequency	Formamide concentration in rain (ng/l)
0.119	1000	0.1	0.01	27
0.119	3000	0.5	0.1	4016

[1] Maximum deposition flux in 1000 m distance from the plant calculated by CONX for maximum emission. Scavenging coefficient for this calculation was 1×10^{-4} s^{-1}.

For the maximum amine emissions and an assumed 9% production yield of formamide from the emitted amines, the levels of formamide in rain range between 27 ng/l and 4000 ng/l on the local scale of 10×10 km^2.

On the regional scale, the average amine deposition flux of 0.02-0.2 mg/m^2/yr gives raise to average levels of 0.06-9.0 ng/l formamide in rain (annual rainfall amount: 1000-3000 mm), with the assumption of a 9% production yield of formamide from emitted amines.

Chronic and acute ecotoxicity of formamide in freshwater aquatic organisms has been evaluated by Task 9. Chronic ecotoxicological effects in invertebrates have been observed for 1.2 mg/l, corresponding to a risk threshold of 24 µg/l when a risk factor of 50 is applied (see section 5.6). For a critical formamide load of 24 µg/l, the maximum tolerable amine emissions from the plant is calculated to be 17,800 tonnes per year. Thus the expected maximum formamide emissions (assuming instantaneous formation in the stack) are not harming aquatic organisms.

8   Summary and Conclusions

The task of quantifying the emissions of amines from a CO_2 capture plant and their atmospheric degradation products is underway, but not yet completed. Maps of concentration and deposition distributions for unity emissions have been produced with a Gaussian dispersion model. The results from the dispersion and deposition calculations can be scaled if the emitted compounds are not chemically transformed and if emission parameters, such as stack hight, flue gas temperature, exit velocity and other relevant plant characteristics, are not very different from the assumptions made in this study. The emission parameters of a typical layout of a gas power plant with CO_2 capture were applied for this task.

Two major effects of amine emissions from the CO_2 capture plant, namely on ecosystems and on human health, have been identified and studied in this report. Emissions of amines have a direct impact on ecosystems, if deposited to plants and lakes, and contribute to the nitrogen load in the atmosphere. Nitrogen loads to ecosystems above the critical load level lead to eutrophication, increased biomass production and reduced plant biodiversity.

8.1   Amines

The report of Task 7 on health effects of different amines from the CO_2 capture process (Låg et al., 2008) states that all the amines of interest are irritative to human skin and eyes, but only piperazine is reported to be sensitizing. For piperazine and MEA there are indications of reproductive and developmental toxicity. Task 7 suggests the population should, over time, not be exposed to atmospheric concentrations higher than 10 µg/m^3 MEA (Låg et al., 2008). Predicted worst case amine levels for long term exposure are two orders of magnitude below the threshold of 10 µg/m^3 MEA. Based on this, long term exposure levels of amine that can cause adverse health effects are not exceeded. On the short time scale amine concentrations in air in vicinity of the plant can be close to the recommended MEA limit under worst case conditions.

Task 8 found that MEA changes growth and grain yield of cereals (**report Task 8**). A critical load of amines to vegetation (2,700 mg/m^2/yr) should, over time, not be exceed in order to avoid damage to plants. From the worst case calculation, the maximum tolerable emission of amines from the plant could be as high as 14,400 tonnes per year in order to not exceed the critical load. That is 90 times higher than the expected maximum emission from the CO_2 capture plant. Based on the worst case study, harmful effects of amines to the vegetation are not expected.

Task 9 found that MEA exposure can cause chronic effects in algae for levels above 0.75 mg/l, corresponding to a risk threshold of 7.5 µg/l. The expected maximum amine emissions would not be harmful to aquatic organisms. For fish and invertebrates no chronic toxicity thresholds could be found in literature.

8.2   Airborne Nitrogen

Nitrogen concentrations in wet and dry deposition are currently high over Western Norway and critical loads for many surface waters are already exceeded in many

places. Thus additional sources of nitrogen, as from the emissions of the envisaged CO_2 capture may exacerbate the problem.

Wet scavenging dominates the deposition of amines from a gas power plant. The amount deposited is strongly dependent on simultaneous occurence of rain and transport of the pollutants. A CO_2 capture plant build in eastern Norway and one in the west coast of Norway will have a different impact on the environment due to different rain patterns and amounts.

Among the ecosystems that can be found in Norway, arctic heath land and bogs are probably the most sensitive ones towards eutrophication and thus are associated with the lowest critical load (Table 1 in the report by Aarrestad and Gjershaug, 2008). A critical load of 500 mg N/m^2/yr may result in a decline in lichens, mosses, and evergreen shrubs in this ecosystem. With a maximum amine emission of 200 tonnes per year from the CO_2 capture plant, model calculations predict nitrogen loads to ecosystems which are well below the critical limit. A worst case scenario revealed that the yearly amine emissions of a single CO_2 capture plant have to be 60 times higher than expected in order to impose a threat to the heath land and bogs within a 38×38 km^2 local domain. It should be noted, that amine emissions from the plant add to already existing emission of reactive nitrogen (background nitrogen) and increase the load of airborne nitrogen locally. In consequence nitrogen released from the plant aggravates the problem of eutrophication in regions with already high nitrogen loads like Western Norway. Emissions of other reactive nitrogen compounds from the facility like NO_x and ammonia, which also contribute to the nitrogen burden from the CO_2 capture plant are not included in the present estimate.

The evaluation of the relative cost-effectiveness of reducing N emisssions from various sources can be made by the use of Environmental Factor for Air (EIF Air, http://eifbusiness.nilu.no). The effects that are evaluated in this factor are eutrophication, acidification and effects of increased or decreased ozone on ecosystems.

The effect of nitrogen on ecosystems is strongly dependent on the background load. In Norway this is dependent on the geographical location. In general there is a gradient from south to north and west to east, where the south and south west coast of Norway has a load and above the critical levels.

8.3 Nitrosamines, nitramines and formamide

It should be noted that this is a maximum estimate and that released nitrosamines are probably rapidly destroyed by photolysis (Bråten et al., 2008). The lifetime of nitrosamines against photolysis is in the range of 10 to 30 minutes, depending on the available sunlight (Lindley et al., 1978). However during night time and during the polar winter they can be expected to be stable. Nitrosamines are formed in the night through the reaction with nitrous acid (HONO) (Grosjean, 1991). There are several sources of HONO at night time and during day time. Ambient atmospheric concentrations of HONO range from about 10 ppt to more than 10 ppb, and it can be found in remote, rural and urban areas (Lammel and Cape,1996).

The atmospheric fate of amides is practically unknown. Nitramines, in contrary to the nitrosamines, do not photolyse and thus can be expected to accumulate in the atmosphere (Grosjean, 1991). The reactions of nitramines with OH and with ozone are known to be slow.

For formamide, no regulations and recommendations for critical levels or critical loads to ecosystems exist to date. For nitrosamines a drinking water threshold was derived from regulations in the U.S., while for nitramines a recommendation from Wollin and Dieter (2005) was adopted in this worst case study.

For all these compounds, the worst case assumption is that the compounds are not degraded in the atmosphere or in soil and water. If nitramines and amides are positively confirmed to be formed in the atmospheric degradation of amines, these toxic compounds will lead to a further reduction of the tolerable emissions of amines from the CO_2 capture plant proposed in this study.

In Germany, numerical regulations for occupational exposure to nitrosamines have been established. The guidelines are intended to apply to nitrosamines as a class, and in general industry, the total exposure to nitrosamines cannot exceed a technical orientation value of 1 $\mu g/m^3$, measured as an 8 hour time-weighted average (Låg et al., 2008b).

For amides and nitramines the data coverage is too low to derive reliable threshold for the general inhalation exposure to humans. For this reason, the inhalation exposure risk to nitramines could not be assessed in this worst case report. For formamide the exposure risk could only be assessed by assuming the same carcinogenic potential as for acetamide. Further clarification of the toxicity of formamide is thus necessary. For maximum emissions of amine from the plant, short term averaged concentrations of these compounds within 10 kilometres distance from the CO_2 capture plant are calculated to range from 0.4 to 1 $\mu g/m^3$, from 0.1 to 0.2 $\mu g/m^3$, and from 0.3 to 0.8 $\mu g/m^3$ for amides, nitrosamines, and nitramines, respectively (see Table 7) – assuming no chemical degradation. The long term maximum concentrations are 2, 7 and 9 ng/m^3 for nitrosamines, nitramines and formamide, respectively.

8.4   Summary of the worst case studies

The worst case studies reveal that possible emissions of nitrosamines and nitramines could be a serious problem to human health and/or aquatic organisms. The effect of nitrosamines and nitramines should thus be ranked as an aspect of higher risk than that of airborne nitrogen. Table 13 lists the results from the worst case studies.

Table 13: Summary of results from the worst case studies.

Worst case run	Critical depostion flux	Maximum dep. flux (mg/m^2) [1]	Max. tolerable emission (t/yr)	Max. tolerable amine emiss. (t/yr)	Effect
Amines	2700 mg/m^2/yr	5.18	14400	14400	Vegetation
	300 mg/m^2/yr	5.18	1570	1570	Aquatic algae
Nitrogen [2]	500 mg/m^2/yr	5.18	2610	11400	Terrestrial Eutrophication
Nitros-amines	0.3 mg/m^2/yr	16.1	0.5	24	Human Health[3]
	1.0 mg/m^2/yr	16.1	1.7	84	Aquatic algae
Nitramine	40 mg/m^2/yr	16.1	67	960	Human Health[3]
	8.0 mg/m^2/yr	16.1	13.4	192	Aquatic Fish / Invertebrates
Formamide	960 mg/m^2/yr	16.1	1620	17800	Aquatic Invertebrates

[1] Maximum deposition flux at unity emission.
[2] Only airborne nitrogen derived from N contained in amine.
[3] Only drinking water threshold; inhalation risk not considered.

Nitrosamines
A critical nitrosamine load of 7 ng/l in the precipitation to lakes with respect to drinking water quality corresponds to a critical deposition flux of 0.3 mg/m^2/yr under worst case conditions. In the worst case study for nitrosamines, the maximum tolerable amine emissions from the plant is calculated to be 24 tonnes per year. The expected maximum emissions of amines from the CO_2 capture plant exceed the tolerable threshold by a factor of 7. Depending on the nitrosamine formation yield from the applied amines and the degradation of nitrosamines in the atmosphere, the actual nitrosamine production may be lower than predicted.

Short term averaged concentrations of nitrosamines in air calculated for maximum amine emissions range between 0.1 to 0.2 μg/m^3 within 10 kilometres distance from the CO_2 capture plant. Since nitrosamines are rapidly decomposed by photolysis, it seems unlikely that concentrations in ambient air exceed a few μg/m^3, except very close to the emission source (Fine et al., 1977 a). However, nitrosamines can be formed from secondary amines in the night through the reaction with nitrous acid, HONO, and thus potentially accumulate at night (Rolle and Gnauck, 1982; Grosjean, 1991).

In order to avoid chronic toxicity in algae, a risk threshold of 25 ng/l nitrosamine applies. This risk threshold is very close to the human health threshold of drinking water. For a nitrosamine load of 25 ng/l in precipitation which is critical for aquatic organisms, the maximum tolerable amine emissions from the plant is calculated to be 84 tonnes per year. The expected maximum emissions of amines from the CO_2 capture plant are by a factor of 2 above the tolerable threshold for aquatic organisms and could cause chronic damage to algae.

The long term risk threshold for exposure of the general population by nitrosamines through inhalation is 4 ng/m^3 nitrosamines in air, corresponding to a 10^{-6} lifetime cancer risk. Calculated maximum nitrosamine concentration in air for expected maximum emission from the CO_2 capture plant is only a factor of two below this critical level.

Nitramines

Nitramines may have carcinogenic effects and, in contrary to nitrosamines, are photochemically stable (Grosjean, 1991). Thus it can be expected that nitramines are transported over a longer distance and deposited in a larger distance from the plant. Assuming an instantaneous production yield of 7% from the emitted amines, the maximum tolerable amine emissions from the plant is calculated to be 960 tonnes per year to comply with the recommended drinking water threshold of 1 µg/l. The current maximum amine emissions from the plant are thus 6 times below the proposed tolerable amount. However, under extreme weather conditions, the nitramine concentration in rain may exceed the critical load for nitramine of 1000 ng/l.

Short term averaged concentrations of nitramines in air calculated for maximum amine emissions range between 0.3 to 0.8 µg/m^3 within 10 kilometres distance from the CO_2 capture plant. Since nitramines are photochemically stable and have a chemical lifetime of several days, they may accumulate in the atmosphere and transported over long distances. For nitramines the few available toxicity data does not allow for a reliable threshold for inhalation exposure to humans.

A risk threshold range of 0.2-2.0 µg/l nitramine for chronic ecotoxicological effects in freshwater fish and invertebrates is used based on the recommendation from Brooks and Wright (2008). For a critical nitramine load of 8.0 µg/l nitramine, the maximum tolerable amine emissions from the plant is calculated to be 190 tonnes per year. Thus the predicted nitramine levels are not problematic for aquatic organisms, unless emission peaks occur for four weeks or longer (assuming one month of exposure leads to chonic damages in fish and invertebrates).

Limitations of the Worst Case studies

The Worst Case calculations make use of the wind rose of Mongstad as basic input for the meteorological and geographic situation. Thus results from the worst case analysis can, in a strict sense, only be applied to locations in Norway with similar dominating wind direction and speed and a geographic landscape that resembles the Mongstad area. If the CO_2 capture plant would be placed in the outflow of a big fjord (like in Årdal, for example) with a preferred wind direction different from the large scale winds, or in a very windy and well ventilated place such as the island Smøla, the results obtained here may not hold . There may be either higher concentrations in the vicinity of the plant (fjord) or the plume may spread far more out, diluting all compounds to a level which does not affect the environment.

We assume that chemical compounds are stabile in air, water and soil, with no degradation or loss during transport through each medium. Apart from this, the presented worst case calculations involve a series of assumptions:

1. Formation yields for atmospheric degradation products inferred from other alkyl amines (here: TEA), are applicable to the amines used in CO_2 capture. Actual product formation yields could be either higher or lower;
2. It is assumed that atmospheric degradation products are formed instantaneously in the stack of the CO_2 capture plant;
3. It is assumed that emissions based on yearly averages also hold for shorter periods (i.e. no peak emissions);
4. Uniform dispersal and mixing within water and soil;
5. It is assumed that the lower limit for toxicity for each compound is as found in the literature. This implies that there are no other organisms for which toxicity is higher;
6. It is assumed that there are no adverse ecosystem effects that occur at lower levels;
7. It is assumed that the toxicity is not higher for other life stages or each organism. For example, we assume that the limit for fish also holds for reproductive life stages;
8. And that there are no seasonal differences in acute or chronic effects.

For many of the primary and secondary chemical compounds there are little or no data available on critical concentrations for toxic effects on terrestrial and aquatic organisms. Thus it is simply not possible here to make worst case calculations for these compounds and these organisms. Toxicity studies and field experiments are required before final conclusions can be drawn with respect to the maximum allowable emissions of amines and their secondary products from CO_2 capture plants.

A further conclusion from the worst case study is that there is urgent need for:

1. Studies on nitrosamine, nitramine, and amide production from the atmospheric degradation of amines;
2. Studies on the atmospheric lifetime and fate of nitrosamines, nitramines and amides;
3. Studies on the biodegradation of these compounds in soil and water;
4. Studies on the toxicity of nitrosamines, nitramines, and amides to different *in vitro* (cellular) and *in vivo* (animals/organisms) model systems;
5. Studies on the toxicity of nitrosamines, nitramines and amides to aquatic organisms;

These studies deserve high priority and are very important to assess the impact of the CO_2 capture plant on the environment and human health. The hazard of amines and the three identified hazardous compound classes for different components of the ecosystems and for human health has to be further quantified, in order to derive recommendations on applicable critical levels and loads.

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TITLE	PROJECT LEADER
Amines Worst Case Studies	Svein Knudsen
Worst Case Studies on Amine Emissions from CO2 Capture Plants (Task 6)	NILU PROJECT NO. N-108068

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ABSTRACT

Norway does not currently have any established exposure limits for amines or other hazardous compounds that could be formed in the atmospheric photo-oxidation of amines released from CO_2 capture plants. Consequently, in the worst case studies, a number of safety limits for both acute (short-term) and chronic (long-term) toxic/hazardous effects for each of the compound groups (four selected amines and corresponding photo-oxidation products) were introduced. These criteria are based on available lowest/no effect levels in literature recommendations or various international regulations. Following the precautionary principle, the worst case approach sets the strongest toxicological effect (lowest effect level) in relation to the maximum assumed emission. A series of assumptions are made; the most important are 1) no photochemical degradation during transport, 2) no biodegradation in soil and water, 3) no short-term peak emissions. In the model study, degradation products are formed instantaneously after leaving the stack of the CO_2 capture plant with a fixed formation yield adopted from experimental studies of related alkyl amines. Consequently, the worst case studies rather provide recommendations to prioritize the problematic compounds and to rank them accordingly with respect to proposed safety limits than accurate predictions of concentration levels or deposition loads. Emissions of amines contribute to the nitrogen load in the atmosphere and could potentially cause eutrophication of sensitive terrestrial ecosystems. The exceedance of a critical load of 5 kg N/ha/yr is known to result in a decline in lichens, mosses, and evergreen shrubs. A worst case scenario revealed that the yearly amine emissions have to be 60 times higher than expected to impose a threat to Norwegian ecosystems. Predicted worst case amine levels for long term exposure are two orders of magnitude below the threshold of 10 $\mu g/m^3$ (for MEA). Based on this, long term exposure levels of amine in air that can cause adverse health effects are not exceeded. Toxic compounds produced in the atmospheric oxidation of emitted amines, like nitrosamines, nitramines and amides could be a hazard for ecosystems and human health. Based on a specific US state drinking water standard, the exceedance of the critical load of 7 ng/l nitrosamines in the precipitation to Norwegian lakes would threaten the drinking water quality. Assuming the conversion of 2% of the emitted amine into nitrosamines, the maximum tolerable amine emissions from the plant would be 24 tonnes per year. The inhalation exposure risk of the population to formamide, acetamide, and nitramines could not be assessed in this worst case report due to missing reliable toxicological threshold information.

NORWEGIAN TITLE

Maksimalbelastninger av Aminer

Studier av maksimal miljøbelastning ved utslipp av amin fra et CO_2 fangst anlegg (Aktivitet 6)

KEYWORDS		
CO_2 capture	Amines	Worst Case

ABSTRACT (in Norwegian)

Norge har ingen lovbestemte grenseverdier for eksponering av aminer eller av degraderingsprodukter av aminer. En del av disse degraderingsproduktene er giftige og de dannes ved fotooksidasjon av aminer som slippes ut fra CO2-fangstanlegg. I denne studien om "verst tenkelige scenario" er det derfor brukt flere sikkerhetsgrenseverdier for både akutte (kortsiktige) og kroniske (langsiktige) effekter for hver av de angjeldende komponentene og komponentgruppene (fire aminer og fotokjemiske degraderingsprodukter). Disse sikkerhetsgrenseverdiene bygger på kjente nivåer fra den vitenskapelige litteraturen hvor det observeres liten eller ingen effekt eller på anbefalinger fra andre land. "Føre var"-prinsippet er fulgt, dette betyr at den verst tenkelige effekt angående giftighet settes i sammenheng med det høyest forventede utslipp. I beregningene er det gjort visse antagelser; 1) ingen fotokjemisk nedbrytning under transport, 2) ingen biologisk nedbrytning i vann eller jord, 3) ingen kortvarige, høye utslipp, såkalte episoder. I beregningene antas det at nedbrytningsproduktene dannes øyeblikkelig etter at utslippet forlater pipemunningen, innbyrdes fordeling mellom de ulike nedbrytningsproduktene er hentet fra studier av alkyl-aminer. Formålet med denne studien om det "verst tenkelige scenario" er derfor fortrinnsvis å fremheve de problematiske komponentene og rangere dem etter de foreslåtte sikkerhetsgrenseverdier, formålet er ikke å forutsi nøyaktige konsentrasjoner og avsetninger. Utslipp av aminer bidrar til økt nitrogen i atmosfæren og kan potensielt bidra til eutrofiering av følsomme terrestriske økosystemer. Overskridelse av kritisk grense på 5 kg N/ha/år vil eksempelvis gi tilbakegang for lav, mose og eviggrønne kratt. Denne "verst tenkelig scenario"-studien avdekket at årlig nitrogenavsetning fra aminutslipp ikke overskrider tålegrensene for nitrogen for følsomme økosystemer i Norge. Beregnet maksimumskonsentrasjon av aminer er 1/100 av grenseverdien for innånding på 10 µg/m^3 (for MEA). Dette vil si at de forventede konsentrasjonene ikke forventes å gi skadelige helseeffekter ved langvarig eksponering. Aminer kan brytes ned til giftige forbindelser ved fotooksidasjon i atmosfæren, eksempelvis nitrosaminer, nitraminer og amider som er skadelige for økosystemer og human helse. De foreslåtte sikkerhetsgrenseverdier for nitrosaminer i drikkevann overskrides i denne studien, dette kan potensielt skade drikkevannskvaliteten i norske vannkilder. For nitrosaminer vil grenseverdien for innånding som gir 1:1'000'000 krefttilfeller i befolkningen overskrides. For formamid, acetamid og nitraminer er det ikke mulig å konkludere i og med at det ikke finnes tilstrekkelig grunnlagsmateriale for å fastsette grenseverdier for toksisitet ved innånding.