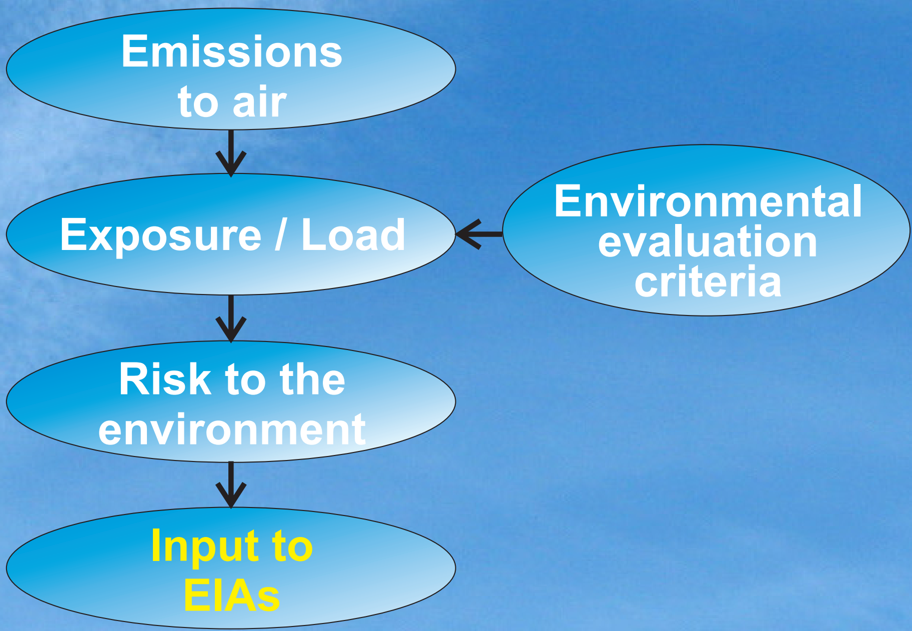
# Summary Report:
# Amine Emissions to Air during Carbon Capture

Phase I: $CO_2$ and Amines Screening Study for Environmental Risks

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# Summary Report: Amine Emissions to Air During Carbon Capture

## Phase I: $CO_2$ and Amines Screening Study for Effects to the Environment

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NILU

# 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. A leading technology for $CO_2$ capture is through the use of amines. The *$CO_2$ and Amines Screening Study Project* began with *Phase I* in May 2008. The project was initiated by the Norwegian Institute for Air Research (NILU) based on the results of an expert meeting in October 2007, and discussions with the Norwegian Pollution Control Authority (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 photo-oxidation 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.

# Terms and Abbreviations

| **Term** | **Abbreviation** |
|---|---|
| 2-aminoethanol | MEA |
| 2,2'-(methylimino)di-Ethanol | MDEA |
| 2-amino-2-methyl-1-Propanol | AMP |
| Piperazine | PIPA |
| N-Nitrosodimethylamine | NDMA |
| Carbon Capture and Storage | CCS |
| Environmental Impact Assessment | EIA |
| Limit of Detection | LoD |
| Chemical Abstract Service registry number | CAS# |
| Gas Chromatography and Mass Spectrometry | GC/MS |
| Liquid Chromatography and Mass Spectrometry | LC/MS |
| Lethal Dose 50% | LD50 |
| Predicted No Effect Concentration | PNEC |
| Lowest Observable Effect Concentration | LOEC |
| Norwegian Institute for Air Research | NILU |
| Norwegian Institute for Water Research | NIVA |
| Norwegian Institute for Nature Research | NINA |
| Centre for Theoretical and Computational Chemistry | CTCC |
| Norwegian Institute of Public Health | FHI |
| Norwegian State Pollution Control Authority | SFT |

# Contents

# Executive Summary

***Carbon Capture and Storage (CCS) has arisen to a national priority on the Norwegian agenda. One of the more promising technologies for efficient post combustion $CO_2$ capture is through the use of amines. A $CO_2$ capture plant using amines will produce amine emissions to the air, while possibly also forming other compounds in the atmosphere after emission. The particular amines studied were MEA, AMP, MDEA, and Piperazine, where of immediate concern are toxic compounds such as nitrosamines, nitramines, and amides - all of which may be formed by the reaction of amines with oxidized nitrogen compounds. This screening study has been conducted to understand more about atmospheric amine chemistry and to evaluate if the emissions caused by $CO_2$ capture using amines may pose a risk to human health and the natural environment.***

***Main Results***

- Amines themselves most likely pose little risk to human health and the environment. The amine emissions will, however, contribute to the nitrogen load and potentially to eutrophication of sensitive terrestrial ecosystems.
- Various compounds that may be formed from the amines and by photo-oxidation in the atmosphere pose a potential risk to human health and the environment. Theoretical chemistry calculations suggest the formation of the following main amine photo-oxidation products: nitrosamines, nitramines, aldehydes, and amides.
- Of particular concern are nitrosamines, which can be toxic and carcinogenic at extremely low levels.
- Nitramines are also of concern as they are suspected to be carcinogenic, though considerably less potent than the nitrosamines. The suggested longer life-time in the atmosphere may lead to higher exposure values.
- Atmospheric dispersion models show that amine emissions can have impacts at both local *and* regional scales; modeling also indicates that amines lower the surface tension of water droplets which under appropriate climatic conditions can be a trigger for rain with the potential of causing negative impacts to the local environment.
- Results from a worst case study of emissions from a generic full-scale amine plant with environmental conditions representing the west coast of Norway, show that the predicted concentrations of suggested photo-oxidation compounds are at the same level of magnitude as the proposed “safety limits”, implying that risks to human health and the natural environment can not be ruled out

***Primary Recommendations***

- More qualitative and quantitative information is needed for the compounds that may be created in the atmosphere from amine emissions (nitrosamines, nitramines, aldehyds, and amides), especially in regards to the chemical pathways, chemical mass fluxes, dispersion, concentration, deposition, and the relative quantification of toxicity and other potential effects.
- Development of models is necessary to quantify the mass fluxes and to integrate this in a dispersion model to quantify the load. These models need

to be specifically designed to handle emissions of amines. This development should begin after chemical pathways/reactivity has been well established.

- Laboratory and field experiments are necessary to obtain more precision in the estimates of toxicity, as little information exists in open literature.
- It is necessary to identify and quantify the specific compounds that will be emitted or formed post-emission, where particular focus should be put on nitrosamines and nitramines.
- Further compile data and information to create a relative ranking of the four amines with respect to potential environmental and health effects and toxicity.

**It is important that the above recommendations be strongly considered so information on the possible human health and environmental effects can be thoroughly researched and well established before full-scale $CO_2$ sequestration with amines is put into operation.**

# Summary Report:
# Amine Emissions to Air During Carbon Capture
## Phase I: $CO_2$ and Amines Screening Study for Effects to the Environment

## 1 Background

Carbon Capture and Storage (CCS) has been internationally established as a promising method for reducing $CO_2$ emissions and limiting the stressors to global climate change. Use of amines to capture $CO_2$ is the closest technology to being operational in post-combustion $CO_2$ capture. There are currently no regulations in Norway regarding permissible levels of exposure via air and drinking water for amines and other potential problematic compounds that could be formed in the atmospheric oxidation of amines released from $CO_2$ capture plants. Preliminary research has been conducted prior to this study to gather the most basic information about amines, where concern arose early regarding potential toxicological impacts to humans and the environment – giving credence to initiating this study.

The Norwegian Pollution Control Authority (SFT) began discussions with the Norwegian Institute for Air Research (NILU) in the Fall 2007 in which an expert meeting was held with invited stakeholders to assess available knowledge of environmental processes related to amine emissions. The report from this workshop (Knudsen et al., 2008) preliminarily concluded that there were potential risks to human health and the environment from amine emission. Information concerning these processes were relatively unknown, thus the necessity for a screening project to gather further information was deemed urgent. It was assessed that the screening project needed to research the following main points:

- amine photochemistry
- critical loads and toxicity of amines and photo-oxidation products
- risk of amine emissions to the environment

Gassnova SF, Shell Technology Norway AS, and StatoilHydro ASA agreed to sponsor such a screening study project (in collaboration with the *CLIMIT* program). Led by NILU, the following additional research institutes participated in the study: Norwegian Institute of Public Health (FHI), Norwegian Institute for Nature Research (NINA), Norwegian Institute for Water Research (NIVA), and the University of Oslo Center for Theoretical and Computational Chemistry (CTCC). A six month work program was established, and this report is a summary report from all of the finalized project tasks, reports, and activities.

# 2 Scope of Work

## 2.1 Project Purpose

The greater purpose of the project was to perform a screening study to gain additional knowledge on amine chemistry in the environment and the effects of amines to the environment and human health. In order to best evaluate the effects of amines on the environment, and the compounds produced after emission, the building blocks shown in Figure 1 were a framework for accomplishing the greater project purpose.

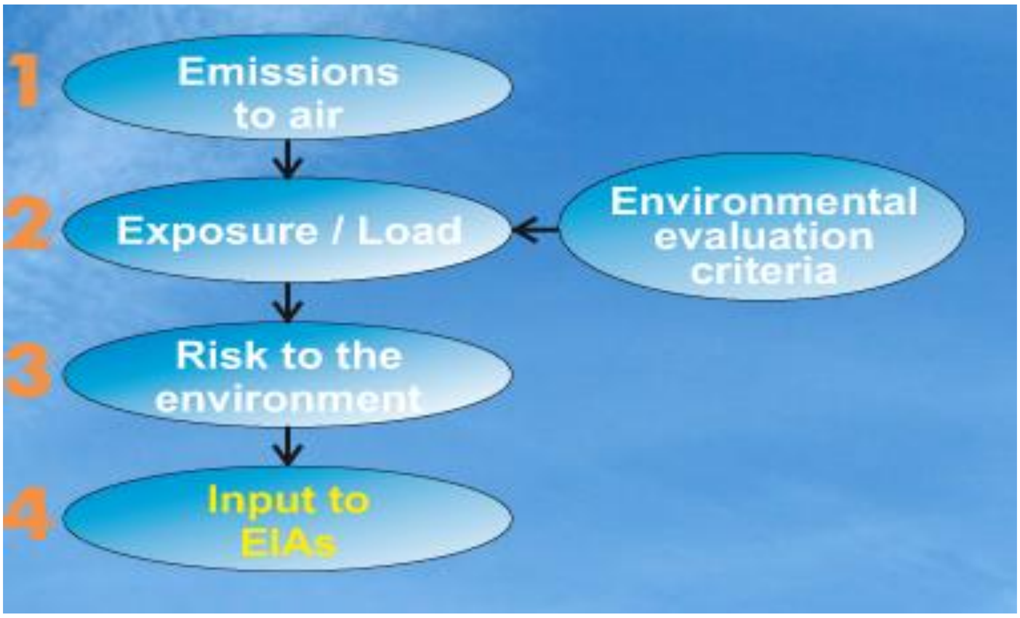



*Figure 1: Building blocks for evaluation of environmental and health effects (screening project only addresses levels 2 and 3).*

The *Emissions to Air* stage refers to the airborne substances emitted during the $CO_2$ capture process using amines, which was not a part of this study. The *Exposure/Load* stage examines the load on the environment from direct emissions of the amine, including mass fluxes from chemical reactions after emission, concentration, and deposition. To evaluate the precise risks of these loads, it is first necessary to establish the certain degrees of effect causation (*Environmental Evaluation Criteria* stage) focusing on: 1) emission of amines, 2) the substances produced by photochemical oxidation of the initially emitted amines in the atmosphere (photo-oxidation products).

The project proposed a number of safety limits for both acute (short-term) and chronic (long-term) toxic/hazardous effects for each of the compound groups (four amines, photo-oxidation products). These evaluation criteria were chosen based on available lowest/no effect levels in literature recommendations or state authority regulations. Following the precautionary principle, the most sensitive adverse effect caused by the respective compound group in each target group (vegetation, terrestrial fauna, aquatic organisms, ecosystem types, humans) was considered when establishing the proposed safety limits. After both the evaluation criteria and the environmental load had been determined, the various effects to human health and environmental (*Risks to the Environment*) was assessed. The information from this process could be used in preparing any necessary Environmental Impact Assessments (*Input to EIA's*).

Since CCS technology with amines is under development, the precise knowledge of the environmental effects determined from the above evaluation can give valuable guidance to the particular cautionary amines which should be focused on during the CCS process.

### 2.2 Goals and Deliverables

While the greater project purpose is to increase the knowledge of amines and their potential environmental and health risks, the specific goals set forth to accomplish the purpose were as follows:

- Theoretical chemical analysis and laboratory chemical analysis for better understanding of amine structure and reactions.
- Literature review for toxicology (human and environmental) to establish mechanisms and thresholds of effects.
- Determine the dispersion of potential amine emissions, as well as localized climatic effects.
- Make considerations regarding worst case scenarios that could be encountered with amine emissions.
- Project task reports based on analysis and reviews to summarize findings and improve the knowledge base.
- Develop an open information flow and dissemination of project results.
- Make recommendations to prepare for additional studies to narrow the knowledge gaps discovered.

To accomplish these goals, specific tasks were derived with corresponding deliverables, and responsible institutes, see Table 1.

*Table 1: Project Tasks, Deliverables, and Responsibilities.*

| Task # | Task Description | Deliverable | Responsibility |
|---|---|---|---|
| Task 1 | Project Administration | Kick-Off Workshop,<br>Status Meetings,<br>Steering Committee Meetings,<br>Final Workshop | NILU |
| Task 2 | Information Flow | Web portal operation and maintenance | NILU |
| Task3 | Review of Theoretical and Experimental data | Theoretical chemistry evaluation report | CTCC |
| Task 4 | Development of Material Chemical Screening | Analytical screening report | NILU |
| Task 5 | Model Calculations | Dispersion model report,<br>Rainfall probability report | NILU |
| Task 6 | Worst Case Studies | Worst case studies report | NILU |
| Task 7 | Evaluation of Health Effects | Human health effects report | FHI |
| Task 8 | Evaluation of Terrestrial Environment Effects | Effects on soil, fauna and vegetation report | NINA |
| Task 9 | Evaluation of Surface Water Effects | Effects on aquatic organisms report | NIVA |
| Task 10 | Project summarization and recommendations | Summary report | NILU |

## 2.3 Emissions and Emission Assumptions

Based on the building blocks necessary for effects evaluation presented in Figure 1, the specific emissions pathways are critical components during research and analysis (see Figure 2).

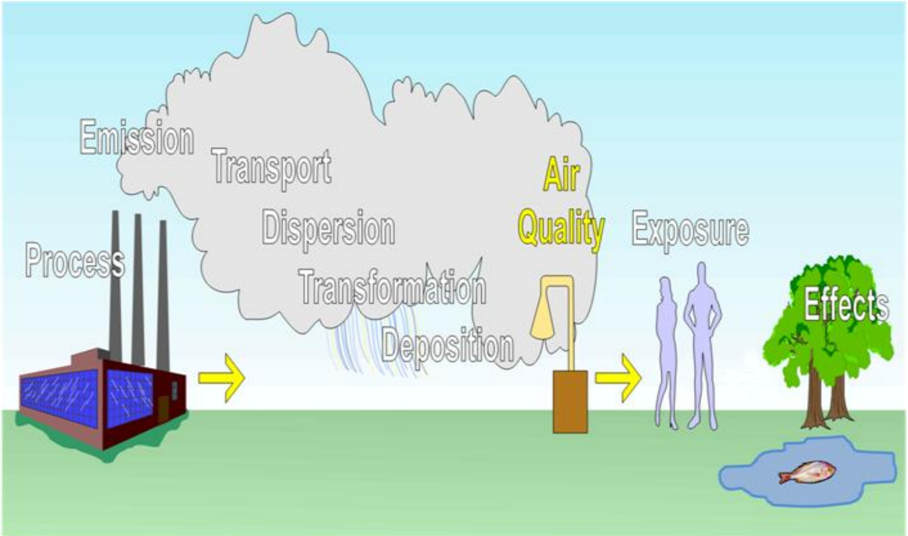



*Figure 2: Pathway of amines through the atmosphere, from emission to exposure/load and effects/risks.*

Since specific data for amines/amine mixture and the actual emissions from the CCS plants are not available in open literature, the project had to make some assumptions. The main assumption was the selection of the following four candidate amines for representativeness of the relevant amine family:

- MEA (2-aminoethanol): $H_2NCH_2CH_2OH$
- AMP (2-amino-2-methyl-1-Propanol): $(CH_3)_2C(NH_2)CH_2OH$
- MDEA (2,2'-(methylimino)bis-Ethanol): $CH_3N(CH_2CH_2OH)_2$
- PIPA (Piperazine): $HN(CH_2CH_2)_2NH$ – an approximate scheme

Section 3 (Task 3) of this report also suggests that the main chemically produced substances from photo-oxidation of amines were as follows: Aldehydes, Amides, Nitrosamines, and Nitramines. Experimental studies of related alkyl amines in atmospheric chambers (Pitts et al., 1978) have found similar photo-oxidation products as proposed by Task 3 (i.e. amides, nitramines, and nitrosamines). Formation yields of photo-oxidation products from this study have been applied in the worst case model study (Task 6) within this project. Other assumptions made in the various tasks were based on the knowledge of similar methods and/or processes most related to $CO_2$ capture.

It should be noted that although this project did <u>not</u> include an analysis of amine degradation which occurs inside the amine plant, this specific process will usually release between 1-4 ppmv of the substance to air. For a full-scale gas-fired power plant (collecting 1 million tonnes $CO_2$), this specific process results in amine emissions in the range of 40-160 tonnes/year. The values of 4 ppm and 160 tonnes were used as input values for the investigations in this project which have reference to the “CO2-håndtering på Kårstø” report (NVE, 2006).

# 3 Methods and Results

The following results, and basic methods used to obtain the results, are assembled and summarized from each task report in a chronological order, where references are given to each specific report in each task sub-heading. Specific recommendations for each task are also listed at the end of each section; these detailed recommendations are in turn compiled and summarized in the Conclusion section at the end of this report.

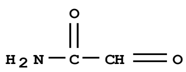
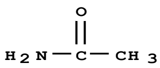
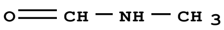
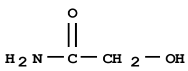
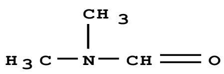
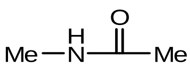
## 3.1 Chemistry

### *3.1.1 Theoretical and Experimental Chemistry (Task 3, CTCC)*

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

The amine chemistry task was performed based on quantum chemical calculations, theoretical considerations, and a literature survey. Chemical reactions in the gas phase are considered the main removal pathway of most volatile organic chemicals in the atmosphere. Other removal pathways are wet and dry deposition, and photolysis. This task investigated the theoretical reaction pathways (photo-oxidation schemes) of amines in the gas phase and rate constants of chemical reactions for the four specific selected amines. Amides, nitramines, and nitrosamines predicted to be formed from atmospheric degradation of these amines are shown in Table 2 and Table 3 (only CAS registered compounds are listed).

*Table 2: Amide compounds predicted in the theoretical study for the photo-oxidation of MEA, AMP, and MDEA. Only CAS registered compounds are included.*

| Registry # | Formula | Structure | Name |
|---|---|---|---|
| 75-12-7 | C H3 N O |  | Formamide |
| 60939-21-1 | C2 H3 N O2 |  | Acetamide, 2-oxo- |
| 60-35-5 | C2 H5 N O |  | Acetamide |
| 123-39-7 | C2 H5 N O |  | Formamide, N-Metyl- |
| 598-42-5 | C2 H5 N O2 |  | Acetamide, 2-Hydroxy- |
| 68-12-2 | C3 H7 N O |  | Formamide, N,N-Dimetyl- |
| 79-16-3 | C3 H7 N O |  | Acetamide, N-Metyl- |
| 20546-32-1 | C3 H7 N O2 |  | Formamide, N-(hydroxymethyl)-N-methyl- |

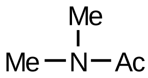
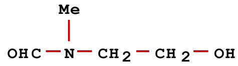
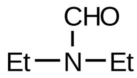
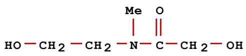
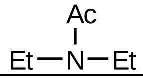
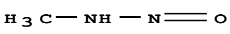
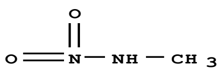
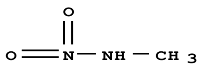
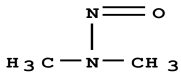
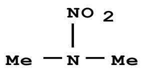
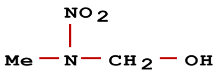
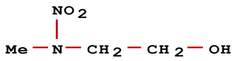
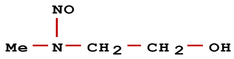
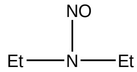
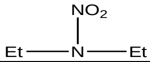
| Registry # | Formula | Structure | Name |
|---|---|---|---|
| 127-19-5 | C4 H9 N O |  | Acetamide, N,N-Dimetyl- |
| 1590-50-7 | C4 H9 N O2 |  | Formamide, N-(2-hydroxyethyl)-N-methyl- |
| 617-84-5 | C5 H11 N O |  | Formamide, N,N-Dietyl- |
| 17236-38-3 | C5 H11 N O3 |  | Glycolamide, N-(2-hydroxyethyl)-N-methyl- |
| 685-91-6 | C6 H13 N O |  | Acetamide, N,N-Dietyl- |

*Table 3: Nitramine and Nitrosamine compounds predicted in the theoretical study for the photo-oxidation of MEA, AMP, and MDEA. Only CAS registered compounds are included.*

| Registry # | Formula | Structure | Name |
|---|---|---|---|
| 675141-02-3 | C H2 N2 O2 |  | Formamide, N-nitroso- |
| 51883-27-3 | C H2 N2 O3 |  | Formamide, N-nitro- |
| 64768-29-2 | C H4 N2 O |  | Methanamine, N-Nitroso- |
| 598-57-2 | C H4 N2 O2 |  | Methanamine, N-nitro- |
| 598-57-2 | C H4 N2 O2 |  | Methanamine, N-Nitro- |
| 62-75-9 | C2 H6 N2 O |  | Methanamine, N-Methyl-N-nitroso- |
| 98033-27-3 | C2 H6 N2 O2 |  | Ethanol, 2-(nitrosoamino)- |
| 4164-28-7 | C2 H6 N2 O2 |  | Methanamine, N-Methyl-N-nitro- |
| 74386-82-6 | C2 H6 N2 O3 |  | Ethanol, 2-(nitroamino)- |
| 32818-80-7 | C2 H6 N2 O3 |  | Methanol, (methylnitroamino)- |
| 42499-46-7 | C3 H8 N 2O3 |  | Ethanol, 2-(methylnitroamino)- |
| 26921-68-6 | C3 H8 N2 O2 |  | Ethanol, 2-(methylnitrosoamino)- |
| 55-18-5 | C4 H10 N2 O |  | Etanamine, N-Etyl-N-Nitroso- |
| 7119-92-8 | C4 H10 N2 O2 |  | Etanamine, N-Etyl-N-Nitro- |

While the atmospheric degradation of amines is initiated by reaction with the OH radical during daylight, reaction with $O_3$ and $NO_3$ could play a role in the amine oxidation during night time. The main products of the atmospheric degradation of amines are different amides and aldehydes, but a number of nitrosamines and nitramines may also result. Some of these photo-oxidation products are subject to subsequent breakdown by sunlight, in particular the nitrosamines.

There is no theoretical way to predict the relative amounts of nitrosamines and nitramines formed in the atmospheric degradation of amines – there is a serious lack of experimental data.

- **It is recommended that the atmospheric degradation of every amine should be studied experimentally in precise detail before use at an industrial scale.**

It is evident that the chemical photo-oxidation of amine routes are not only dependent on the gas phase chemistry, but also the chemical processes on primary and secondary particles, water droplets (both as clouds and raindrops), and processes related to snow.

- **It is recommended that these processes be further assessed, as well as the effects of polar night, or in areas with large variations of daylight.**

### *3.1.2 Chemical Screening Methods (Task 4, NILU)*

Dye, C., Schmidbauer, N., and Schlabach, M. (2008) *Evaluation of analytical methods for amine related emissions and degradation products in emission and ambient air*. Kjeller (NILU OR 80/2008)

During this initial chemical screening phase, two complementary analytical methods have been evaluated for this task: the exposure of adsorbent tubes followed by thermo desorption and analysis by gas chromatography and mass spectrometry (TD-GC/MS), and the exposure of impregnated filters followed by extraction and analysis by liquid chromatography and mass spectrometry on a time-of-flight instrument (IF + LC/MS), (see Figure 3).

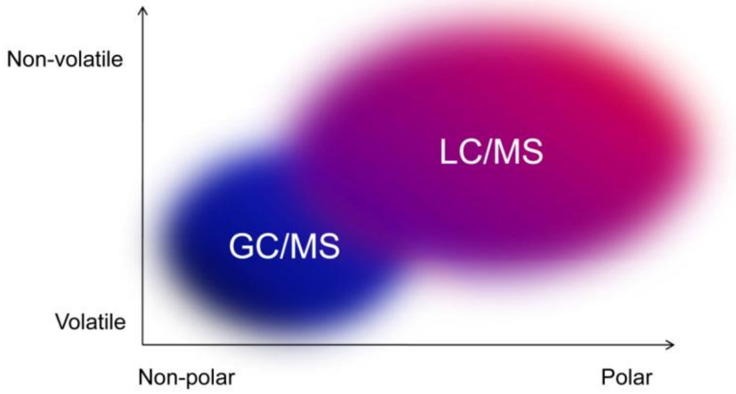



*Figure 3: Areas of applicability of GC/MS and LC/MS (source: Waters Corp.).*

Due to a lack of relevant stack samples for CCS and amines, the evaluation was based on laboratory experiments and former experience from real samples collected from the vulcanization industry (the closest available paradigm incorporating amines), as well as from ambient air samples. Performing both methods in conjunction produces valuable insight to the existence and concentration of potential compounds directly emitted, or secondarily formed by photo-oxidation, from the $CO_2$ capture process.

Based on the instrumental sensitivity obtained in the experiments performed for this task (for MEA, AMP, MDEA, and PIPA), combined with the experience from previous work (Dye, et. al., 2006; Wiklund et. al., 2008), a typical limit of detection (LoD) for ambient air samples can be estimated in the range of 1 – 100 ng/m$^3$. In stack samples with a smaller sample volume, the LoD is expected to be approximately 0.1 – 10 µg/m$^3$. Due to sample matrix dependency, the use of real stack samples and plant vicinity samples are necessary to provide more specific LoDs for the LC/MS analysis.

Two complimentary analytical methods (TD-GC/MS and IF LC/MS) have been evaluated, which indicates that both methods can give important information on the existence and concentration of compounds directly emitted or secondarily formed by the $CO_2$ capture process.

- **It is recommended that this evaluation is actually tested, in which real stack samples and samples close to emission sources are utilized.**

## 3.2 Modeling

### *3.2.1 Modeling Requirements (Task 5.1 and 5.2, NILU)*

Flatlandsmo Berglen, T., Cassiani, M., Karl, M., and Knudsen S. (2008) *Report on models, model needs and requirements*. Kjeller (NILU OR 50/2008).

Preliminary results from atmospheric dispersion models show that amine emissions can have impacts at both local and regional scales. Dispersion models that are suitable to cope with the complex task of resolving different temporal and spatial scales, as well as including an appropriate chemistry scheme, thus have to be established (see Figure 4).

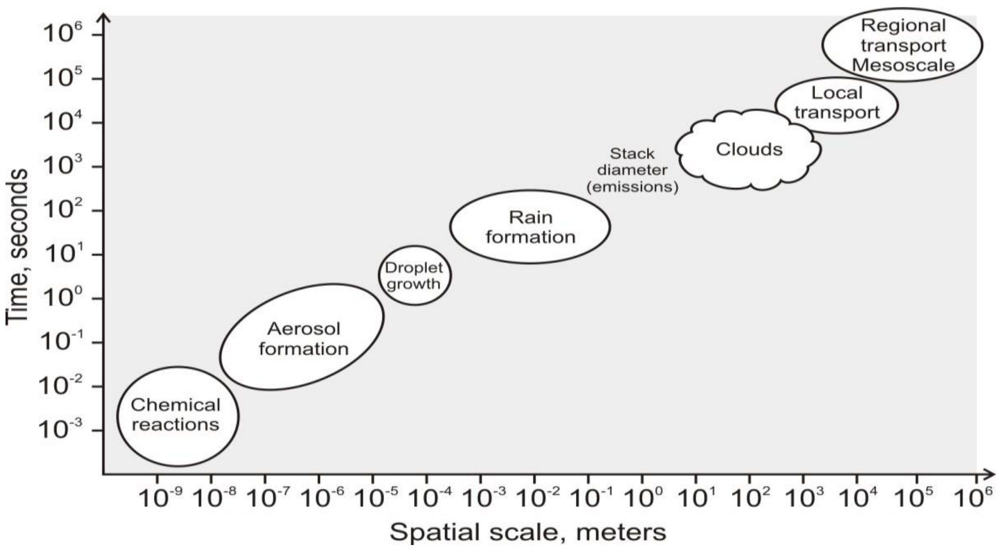



*Figure 4: Range of scales important for the amine modelling processes.*

To best address these scales, it is concluded that *box models* are best applied to chemical reactions, *local small-scale models* for dispersion of the plume and short time scale chemical reactions within the plume, and *regional models* for transport including the more long-lived compounds.

To cover the spatial and temporal scales that are needed to describe the involved processes for amines in the atmosphere properly, a combination of models is needed.

- **It is recommended that a combination of three model concepts: box models, local small scale, and regional transport models be applied.**

Existing models which include amine chemistry do not currently exist.

- **It is recommended that amines and amine chemistry be included within model development.**

### *3.2.2 Effects of Amines on Clouds and Rainfall (Task 5.3, NILU)*

Karl, M. (2008) *Amines and rainfall. Impact of amines on rainfall from plume clouds (Task 5.3)*. Kjeller (NILU OR 74/2008).

An equilibrium model approach was used to study the possibility of rainfall directly from the plume cloud of a $CO_2$ capture facility. The growth of water droplets in the atmosphere strongly depends on their surface tension, and an important effect of amines is to precisely lower the surface tension (see Figure 5). Thus, amines enhance the probability that very small water droplets can grow to cloud droplet size (10-20 µm) and cause cloud formation in the plume of the $CO_2$ capture plant at a lower ambient humidity. Added amines promote the formation of supercritical droplets that can cause rainfall from the plume - making amines act as a trigger for rain. It could also be shown that the initial growth of fine droplets is very sensitive to gas phase concentrations of MEA in the plume.

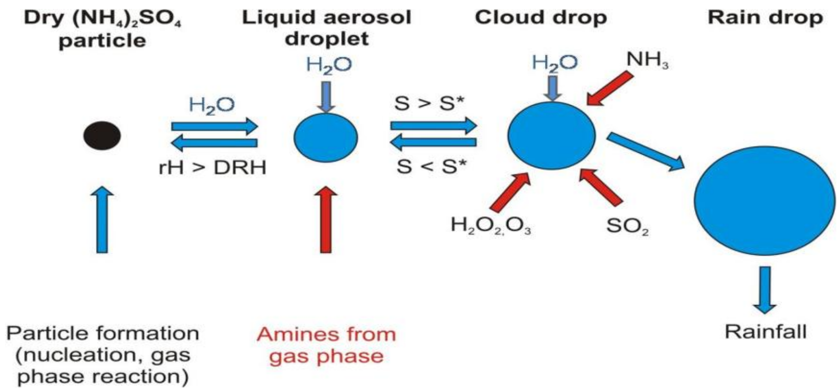



*Figure 5: Processes involved in the growth from a nanometre sized dry particle to a rain drop. (S = saturation ratio and S* = critical saturation ratio).*

The effect of amines on droplet growth is relatively unknown, and can produce unwanted outcomes.

- **It is recommended that further work on this issue be developed to evaluate existing experimental data on surface tension of amine solutions – which includes different concentrations of amines, and at different temperatures.**

## 3.3 Toxicology

### *3.3.1 Human Toxicology (Task 7.1 and 7.2, FHI)*

Låg, M., Andreassen, Å., Instanes, C. and Lindemann, B. (2008a) *Health effects of different amines relevant for CO2 capture*. Oslo (NILU OR 05/2009)

Låg, M., Instanes, C., Lindemann, B., and Andreassen, Å. (2008b) *Health effects of possible degradation products of different amines relevant for CO2 capture*. (NILU OR 06/2009)

The effects of the four selected amines to human health were investigated in literature, specifically researching existing data available on toxicokinetics/metabolism, experimental toxicology, human data, and occupational exposure limits. It was found that all amines seem to be epidermal irritating, where PIPA is also found to have a sensitizing effect. For PIPA and MEA, there are indications of reproductive and developmental toxicity. None of the amines have been reported to be carcinogenic, but it should be noted that the available information to this regard is limited.

From this investigation, preliminary guidelines can be established for human exposure. Based on inhalation exposure risk, the general population, over time, should not be exposed to levels in the air higher than:

- MEA: 10 $\mu g/m^3$
- AMP: 6 $\mu g/m^3$
- MDEA: 120 $\mu g/m^3$
- PIPA: 5 $\mu g/m^3$

The guidelines presented above for this task are preliminary. They can be used as general indications, and not as specific limit values for safety.

- **It is recommended that further research generate more complete data that can be used for safety standard determinations.**

Furthermore, as a group, amines seem to have similar adverse effects and might therefore also show additive or synergistic effects.

- **It is recommended that the exposure guidelines should be re-evaluated if two or more amines are proposed to be used simultaneously.**

Potential health hazards of different possible photo-oxidation products of the four amines were also assessed; the selected products to be analyzed were chosen based on the findings from Task 3, which were different nitrosamines, nitramines, aldehydes and amides. The toxicological data is lacking for many of the specific compounds; therefore available data for similar compounds belonging to the same chemical group were evaluated. But, nonetheless, data on health effects of the specific photo-oxidation products is sparse, so only broad generalizations could be formulated.

Based on experimental data, there seems little doubt that some nitrosamines are extremely potent carcinogens which can pose a serious hazard to humans if present in the environment. Several of the nitramines are mutagenic and carcinogenic in rodents, although they seem considerably less potent than the corresponding nitrosamines. With regard to the aldehydes, it has been concluded that at airborne levels for which the prevalence of sensory irritation is minimal, both in incidence and degree (<1.2 $mg/m^3$), risks of respiratory tract cancer are considered to be negligibly low. The amine photo-oxidation products formamide and acetamide has been reported to induce development toxicity and carcinogenicity, respectively, in experimental animals. Acetamide may also induce skin irritation.

Of the photo-oxidation products, nitrosamines are the most hazardous, with less potent harmful effects also present for nitramines.

- **It is recommended that preliminary caution be assigned to human exposure to nitrosamines, where nitramines may need similar warnings.**

Both aldehydes and main amines have the potential to cause epidermal irritation.

- **It is recommended that the synergetic effects of amines and the amine photo-oxidation product compounds be analyzed to this effect.**

### *3.3.2 Ecotoxicology - Terrestrial Organisms (Task 8, NINA)*

Aarrestad, P. A. and Gjershaug, J. O. (2008) *Effects on terrestrial vegetation, soil and fauna of amines and possible degradation products relevant for $CO_2$ capture*. Trondheim (NILU OR 03/2009)

Research was conducted to analyze the effects of amines and some of the photo-oxidation products on terrestrial vegetation, soil, and fauna. This task was performed through a search of available biological/ecological databases, as well as literature reviews. No information was found on the direct toxicity of the amines MEA, MDEA, AMP and PIPA to terrestrial plants and vegetation. It is known that amines sprayed directly onto plants act as a plant bio-regulator, increasing plant growth and seed yield, while also reducing plant stress. Amines biodegrade in soil (and soil water) into nitrogen components which are then available for plant growth. Thus, the main effect of amines is probably related to eutrophication of plant communities leading to increased growth of grasses and reduced plant diversity in areas with high nitrogen background deposition. A critical load of 5-10 (15) kg N/ha per year is known to produce effects to the sensitive Norwegian habitats of mire, alpine/arctic vegetation, and inland surface waters (Achermann & Bobbink, 2003). Very little is known on effects on terrestrial vegetation of the amine photo-oxidation products - amides, nitrosamines, and nitramines. However, amides are known to be growth restrictive and are widely used in herbicides.

There is also very little information on effects of the selected four amines on terrestrial free-living fauna. Laboratory experiments on animals, related to human health risks, show that all relevant amines are irritating to skin and also toxic at high concentrations with almost the same oral LD50. None of the amines have been reported to be carcinogenic or gentoxic. While these experimental test where geared for humans, the results may also apply for free-living terrestrial animals. Based on the data available it is difficult to range the amine’s toxicity effect on free-living fauna. However, PIPA has been found highly toxic to dung beetle. It can also interact with nitrosating agents *in vivo* to form nitrosamines with possible carcinogenic risks. Thus, PIPA may be the most unfavorable amine of the four studied to fauna. The amine photo-oxidation products - amides, nitrosamines and nitramines - are known to be toxic to mammals and soil invertebrates, and they might also affect soil microorganisms - especially where nitrosamines and nitramines, as also found in Task 7.2, are carcinogenic to mammals.

Due to a lack of available data, an experimental and simultaneous laboratory approach should be considered.

- **It is recommended that an amine spraying experiment be performed in a selected habitat known to be sensitive to nitrogen enrichment, examining the effects of amines on vegetation, soil processes, and soil fauna – with a primary focus on nitrogen eutrophication.**
- **It is recommended to carry out eco-toxicological tests on selected terrestrial fauna in controlled laboratorial environments, using relevant doses of amines and their photo-oxidation products.**

### *3.3.3 Ecotoxicology - Freshwater Organisms (Task 9, NIVA)*

Brooks, S., and Wright, R. (2008) *The toxicity of selected primary amines and secondary products to aquatic organisms: A review*. Oslo (NIVA Report 5698-2008).

The main aim of this task was to review the effects of the four selected amines and their photo-oxidation products on freshwater species. Data was also presented on marine species in cases where freshwater data was unavailable. The ecotoxicity data were separated into three main trophic groups: fish, invertebrates, and algae/bacteria. In many cases no ecotoxicological data was found in the literature.

The most sensitive response to amine exposure was found in chronic studies with fish and algae with a Lowest Observable Effect Concentration (LOEC) of 0.5 mg/l MDEA and 0.75 mg/l MEA respectively. For nitrosamines, the most toxic effect was found in algae with a LOEC of 0.025 mg/l NDMA, which was the lowest effect concentration found for all compounds and test species. The highest toxicity of nitramines was found in chronic studies with fish and invertebrates at 0.2 mg/l and 0.4 mg/l CL-20 respectively. The potential risk of these compounds in the environment was assessed using the simple risk assessment equation (PEC/PNEC = RF). Individual PNECs were calculated by dividing the LOEC for each chemical group by the appropriate assessment factor (AF). The AF used depended on the toxicity data available and was based on the European Union technical guidance document on risk assessment (ECB, 2003). From these calculations it was estimated that environmental concentrations that exceed the following threshold concentrations could potentially cause environmental harm (i.e. 5,000 ng/l amines; 24,000 ng/l amides, 25 ng/l nitrosamines, and 200 ng/l nitramines – see Table 4). It was concluded that nitramines and nitrosamines were the most toxic with the highest risk for causing harm to the freshwater environment.

*Table 4: Summary of critical values for risk assessment. Calculated predicted no effect concentration (PNEC) for the four main groups of compounds (data expressed as µg/l; "-" denotes data not available). Values in bold have been selected for the proposed safety limits in the Worst Case Studies.*

| Group | Test | Amines | Amides (Formamide/ Acetamide) | Nitrosamine | Nitramine |
|---|---|---|---|---|---|
| Fish | Acute | 100 (AMP) | 100,000 (Formamide) | 5.85 (NDPA) | 3.6 (RDX) |
| | Chronic | 5 (MDEA) | – | 200 (NDMA) | **0.2 (CL-20)** |
| Invertebrate | Acute | 100 (PIPA) | 260 (Formamide) | 7.76 (NDPA) | 6.01 (RDX) |
| | Chronic | – | **24 (Formamide)** | 100 (NDMA) | 0.4 (CL-20) |
| Algae/Bacteria | Acute | 20 (AMP) | 980 (Acetamide) | – | 3.2 (RDX) |
| | Chronic | **7.5 (MEA)** | 132,000 (Acetamide) | **0.025 (NDMA)** | – |

For both nitrosamines and nitramines, the toxicity data available were not specific to the actual compounds that have been calculated to occur from the $CO_2$ capture process as presented in Task 3. Therefore, there is a great deal of uncertainty about the aquatic toxicity of these specific nitramine and nitrosamine compounds.

- **It is recommended that future ecotoxicity work focuses on the acute and chronic toxicity of nitrosamine and nitramine compounds for a better evaluation of the potential impact.**

## 3.4 Worst Case Studies

### *3.4.1 Worst Case Studies Examination (Task 6, NILU)*

Karl, M., Brooks, S., Wright, R., Knudsen, S. (2008) *Worst Case Studies on Amine Emissions from $CO_2$ Capture Plants (Task 6).* Kjeller/Oslo (NILU OR 78/2008).

Norway does not currently have any established exposure limits for amines or other toxic compounds that could be formed in the atmospheric oxidation of amines released from $CO_2$ capture plants. 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 short-term peak emissions. In the model study, degradation products are formed instantaneously, when they leave the stack of the $CO_2$ capture plant, with a fixed formation yield from the amine adopted from the work of Pitts et al. (1978). Thus, emissions of these compounds could be either higher or lower than the predicted concentrations. 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.
The worst case studies reveal that possible atmospheric formations after amine emission of nitrosamines and nitramines could be a serious problem to aquatic organisms and/or human health. The effect of nitrosamines and nitramines should thus be ranked as an aspect of higher risk than that of other concerns such as airborne nitrogen. The atmospheric fate of amides is practically unknown. For formamide, no information regarding critical levels/loads to ecosystems exists to date. Table 5 lists the critically selected results from the worst case studies.

*Table 5: Summary of select critical results from the worst case studies.*

| Compound | Critical depostion flux | Max. dep. flux ($mg/m^2$) [1] | Max. tolerable emission (t/yr) | Max. tolerable amine emiss. (t/yr) | Effect |
|---|---|---|---|---|---|
| Nitrosamine | 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 |

[3] *Only drinking water threshold; inhalation risk not considered here.*

Additionally, it was discovered that 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. The calculated maximum nitrosamine concentration in air for the expected maximum emission from the $CO_2$ capture plant is only a factor of 2 below this critical level.

There is considerable uncertainty connected to the production and persistence of nitrosamines and nitramines in the atmosphere.

- **It is recommended that this uncertainty should be reduced through atmospheric experiments.**

For small scale dispersion models the atmospheric lifetime of chemical compounds is crucial. If the lifetime of the compound is assumed to be in the range of one day, then a Gaussian type dispersion model as the one used in the Worst Case Studies is suitable. If the lifetime is shorter, a dispersion model that includes treatment of chemistry should be applied. Moreover, if the lifetime is in the atmospheric turbulence time scales range, turbulence-chemistry interactions need to be included. The chemical lifetime of amines ranges from 6 hours to one day, while the lifetime of their possible photo-oxidation products may range from a few minutes up to a few days in the atmosphere. Moreover, long-lived products can be transported several hundred kilometers away from the emission source before they are lost by deposition.

- **A model needs to be established to handle chemistry and dispersion simultaneously in order to provide a realistic estimate of concentration and deposition flux distributions in the surroundings of the $CO_2$ capture plant and on the regional scale.**

For nitrosamines and nitramines, the results show that the exposure levels may be of the same order of magnitude as the critical levels.

- **It is recommended that there should be greater precision in the exposure estimations in order to obtain better precision on the evaluation of risks.**

# 4 Conclusions and Final Recommendations

The risk related to the studied amines themselves seems to be sufficiently low. However, photo-oxidation of amines in the atmosphere may produce compounds of high concern. The results from the worst case study show that the predicted concentrations of suggested photo-oxidation compounds are at the same level of magnitude as the proposed “safety limits”, implying that risks to human health and the environment cannot be ruled out. It has been shown that it is highly relevant which precise amine is used in CCS, because each individual amine has varying effects and potential risks. These statements should raise concern, and underscore the necessity for further testing and analysis of amine effects in order to limit the risks or to find alternatives for their use in CCS planning.

This screening study greatly improved the current knowledge available on amines and their effects to human health and the environment. With respect to these effects, little information was available for some of the compounds and target organisms, and the findings are partly based on old and/or related data. Thus, the study disclosed that <u>numerous knowledge-gaps exist</u>, and that these gaps need to be addressed before amines can be used wide-spread in full-scale CCS production. It is therefore recommended that a second phase is implemented to target the knowledge gaps identified in this study. Overall recommendations from this screening phase to <u>incorporate into continued research</u> are as follows:

- **Greater precision regarding the photochemical lifetime of each amine is needed.**
- **Atmospheric experiments should be performed to reduce uncertainty regarding the production and persistence of nitrosamines and nitramines in the atmosphere.**
- **A dispersion model needs to be developed to handle amine chemistry and dispersion simultaneously – to overall improve exposure assessments.**
- **Human toxicity exposure limits values need to be further developed to derive proposed safety limits.**
- **An experimental and simultaneous laboratory approach should be considered for studying the effects of amines on terrestrial ecology.**
- **The acute and chronic ecotoxicity of the amine related photo-oxidation compounds should be analyzed for a better evaluation of the potential impacts to aquatic ecology.**
- **The synergetic effects of the amines used in CCS and their photo-oxidation products should be analyzed with respect to human and ecological toxicity, where exposure limit values should also be corrected to this effect.**
- **Real samples from the capture plants emission plume should be collected and chemically analyzed using determined analytical methods**.

- **Existing experimental data on surface tension of amine solutions needs to be further examined to evaluate the effect of rainout from the capture plant's plume.**

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ABSTRACT
Carbon Capture and Storage (CCS) has arisen to a national priority on the Norwegian agenda. One of the more promising technologies for efficient post combustion $CO_2$ capture is through the use of amines. A $CO_2$ capture plant using amines will produce amine emissions to the air, while possibly also forming other compounds in the atmosphere after emission. Of immediate concern are toxic compounds such as nitrosamines, nitramines, and amides - all which can be formed by the reaction of amines with oxidized nitrogen compounds. This screening study has been conducted to understand more about atmospheric amine chemistry and to evaluate if the emissions caused by $CO_2$ capture using amines may pose a risk to human health and the natural environment. Project results discovered that amines appear not to be severely harmful, but photo-oxidation of amines in the atmosphere produces compounds of relatively unknown effects; thus there exists potential risks which preliminarily appear to be harmful to both humans and the local ecosystem.

NORWEGIAN TITLE
Oppsummeringsrapport: Aminutslipp til luft ved Karbonfangst
Fase I: $CO_2$ og aminer. Screeningstudie for effekter på miljøet.



| KEYWORDS | | |
|---|---|---|
| Carbon capture and storage (CCS) | amines | toxicology |



ABSTRACT (in Norwegian)
Karbonfangst og lagring (CCS) har oppstått som en nasjonalprioritet på norsk agenda. Bruk av aminer er en av de meste lovende teknologier for effektiv post-forbrenning av $CO_2$ fangst. Et $CO_2$ fangstanlegg som bruker aminer kan produsere aminutslipp til luften, med mulig dannelse av andre komponenter i atmosfæren etter utslipp. Mest bekymringsfullt er giftige komponenter som nitrosamines, nitramines, og amides – alle kan bli dannet gjennom reaksjonen av aminer med oksiderte nitrogenkomponenter. Denne screeningstudie har vært gjennomført for å øke kunnskapen av atmosfærisk aminkjemi og for å evaluere om aminutslipp fra $CO_2$ fangst kan være en risiko for helse og miljø. Prosjektresultatene viser at aminer ikke er særlig skadelig, men foto-oksidasjon av aminer i atmosfæren kan produsere komponenter med ukjente effekter; dette påviser at risiko eksisterer, og de kan være skadelige for mennesker og lokalt økosystem.

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