Amine Emissions to Air During CO_2-Capture:
CO_2 and Amines Screening Study for Effects to the Environment

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Introduction

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 the toxic compounds 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.

Methods

The project was a theoretical screening study basing all outcomes on calculations, previous documented work, and thorough literature reviews. No laboratory or field experiments were conducted in this Phase I study, this future work is reserved for Phase II. The following candidate amines were used to represent the relevant amine groups:

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

The main chemically produced substances from photo-oxidation of the selected amines were estimated to be: **Aldehydes, Amides, Nitrosamines, and Nitramines**.

Main Results

1. 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, and processes related to snow.
2. The effect of amines on droplet growth is relatively unknown, and can produce unwanted outcomes.
3. Based on inhalation exposure risk, the general population, over time, should not be exposed to levels in the air higher than: MEA: 10 µg/m^3, AMP: 6 µg/m^3, MDEA: 120 µg/m^3, and PIPA: 5 µg/m^3. – preliminary.
4. Of the photo-oxidation products, nitrosamines are the most hazardous to humans, with less potent harmful effects also present for nitramines. Both aldehydes and main amines have the potential to cause epidermal irritation.
5. 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, while little is known on effects on terrestrial vegetation of the amine photo-oxidation products.
6. It was concluded that nitramines and nitrosamines were the most toxic with the highest risk for causing harm to the freshwater environment.

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)**	–

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Project Sponsors:
- **Gassnova (CLIMIT)**
- **Shell Technology Norway**
- **StatoilHydro**

Goals

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.

Task #	Task Description	Deliverable	Responsibility
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, 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

Conclusions & Recommendations

The study disclosed that numerous knowledge-gaps exist, and that these gaps need to be addressed before amines can be used extensively 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 incorporate into continued research 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 limit values need to be further developed to derive proposed safety limits or acceptable exposure risk.
- An field experiment 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, particularly nitrosamines and nitramines, 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.