

Worst Case study method to assess the environmental impact of amine emissions from a CO₂ capture plant

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Abstract

Use of amines is one of the leading technologies for post-combustion carbon capture from gas and coal-fired power plants. A CO₂ capture plant using amine technology will release amines (as gas and dissolved in droplets) to the air. These will undergo photo-oxidation and other reactions to form hundreds of different chemical compounds in the atmosphere after their release. The main aim of the current study is to estimate the potential adverse human health and environmental impacts given “worst case” assumptions on emission, dispersion and deposition of amines and their photo-oxidation products. We used a 40 x 40 km² study area in the vicinity of a planned 1 Mg/yr CO₂ capture facility at the gas-fired power plant at Mongstad, western Norway. We assumed that the plant would release 40 t/yr monoethanol amine (MEA) and 5 t/yr diethyl amine. With respect to inhalation exposure, the recommended risk threshold for N-nitrosodiethylamine (0.02 ng/m³ in air; US EPA) was exceeded in the 40 x 40 km² study region. Drinking water standards for nitrosamines would be exceeded by about a factor of 3. MEA concentrations would exceed toxicity limits for aquatic organisms also by about a factor of 3. The “worst case” conditions may be different at other sites because the geographic location and the local meteorology have a large influence on both the atmospheric dispersion of pollutants and the local exposure of the population and the environment. Additional toxicity studies and field experiments are necessary to investigate biodegradation and retention of the compounds in soil and water before final conclusions can be drawn with respect to the maximum allowable emissions of amines and their oxidation products from CO₂ capture plants. The “worst case” approach can be applied to other emitted air pollutants.

1. Introduction

Post-combustion CO₂ capture has been proposed for two Norwegian gas-fired power plants (Kårstø, Mongstad) as a measure to reduce CO₂ emissions to the atmosphere. The most commonly used capture method is amine scrubbing. A CO₂ capture plant using amine technology will release amines (as gas and liquid) to air. In sunlight, amines undergo reactions with atmospheric oxidants involving oxidized nitrogen compounds (photo-oxidation) to form compounds such as nitrosamines, nitramines, and amides (Pitts et al., 1978). Nitrosamines are of particular concern, as they are toxic and carcinogenic to humans at extremely low levels (e.g. Reh et al., 2000). A recent screening project concluded that photo-oxidation of amines in the atmosphere produces compounds which based on reviewed toxicity data appear to be harmful to both humans and the local ecosystem (Knudsen et al., 2009).

Monoethanol amine (MEA, 2-aminoethanol) is the most widely studied solvent for the removal of CO₂ from flue gases. This study thus focuses on MEA, but in principle the methodology is applicable to other amines. A CO₂-capture plant that removes 1 Mt CO₂ per year from flue gas may emit 1-4 ppmv amines (NEV, 2006), which corresponds to the amount of 40-160 t/yr. In this study we assume that a blend of two amines, MEA and diethyl amine (DEYA), a secondary amine, is used for CO₂ capture and that maximum emission of 40 t/yr MEA and of 5 t/yr DEYA occurs due to volatilisation of the two amines from the scrubbing solvent.

Atmospheric dispersion modelling can be used to quantify the link between load (emission to air) and the resulting concentrations in air and flux in wet and dry deposition. The “worst case” approach here follows the precautionary principle and sets the most severe toxicological effect (lowest concentration at which an undesirable effect occurs) in relation to the expected maximum emission. By this approach it is possible to rank the hazard risk of the different chemical compounds and to prioritize the problematic compounds accordingly.

2. Methodology

The toxicology of generic amines and their possible photo-oxidation products was recently reviewed based on existing literature (Knudsen et al., 2008). Safety limits for the various compounds in air and in deposition were derived (Fig. 1, box 2) (Knudsen et al., 2008). Safety limits refer to the upper limit of the respective compounds in air and in deposition in order to avoid harmful effects to human health or to ecosystems. We used one year (2007) of synoptic meteorological data for Norway as input for the dispersion calculations with the dispersion model The Air Pollution Model (TAPM) developed by CSIRO, Australia (Hurley et al., 2005; TAPM 2009) (Fig. 1, box 3). Monthly average and 8-hourly maximum air concentration fields together with dry and wet deposition fields were obtained (Fig. 1, box 4). The maximum concentration and deposition flux in the study grid were compared to the pre-defined safety limits of the respective toxic compounds. Maximum tolerable emission rates were obtained by a back calculation procedure in which emissions from the plant were scaled until the safety limits in either air or deposition were reached (Fig. 1, box 5). An increase of the emission leading to concentrations and/or deposition fluxes beyond the critical level would then imply exceedence of the safety limit for a compound with negative impact on ecosystems and human health.

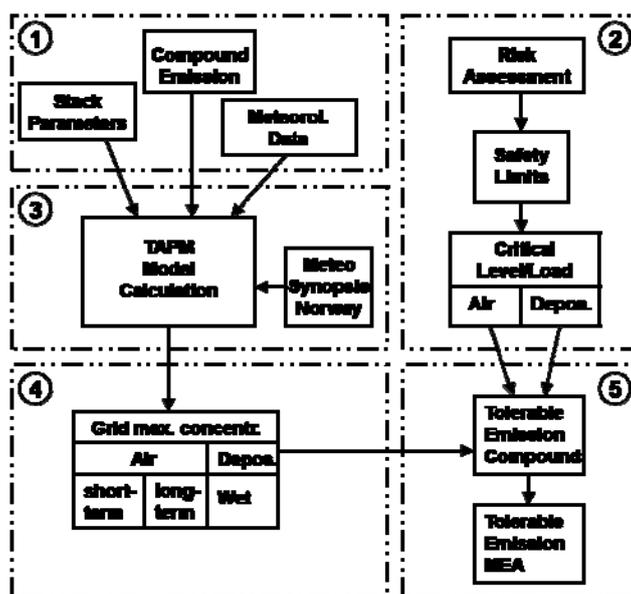


Figure 1: Flow scheme of the “worst case” method: 1) Emission input and local meteorological input; 2) determination of critical loads and levels for inhalation exposure, drinking water and aquatic environment; 3) dispersion calculations; 4) maximum air concentration and wet deposition fluxes in the grid obtained from the model run; 5) determination of tolerable emission amounts for the respective compounds and MEA.

For practical reasons, instantaneous conversion of the parent amines (MEA and DEYA) into photo-oxidation products was assumed to occur directly at the stack. Photo-oxidation products were grouped in chemical classes and the emissions were calculated as fraction of the parent amine emission using fixed chemistry formation yields. Atmospheric formation yields of MEA oxidation products were based on results from recent chamber experiments (Nielsen et al., 2010): 1% nitramines, 50% formamide, and 3% acetamide. Nitrosamines were not detected in the experiments.

Formation yields of DEYA oxidation were adopted from an experimental study by Pitts et al. (1978), and are as follows: 3% nitrosamines, 32% nitramines, and 3% acetamide.

The dispersion model TAPM is an integrated model consisting of a prognostic meteorological module and a set of air quality modules (Hurley et al., 2005; TAPM 2009). In this application the meteorological module was nested three times, from an initial domain of 600 x 600 km (grid resolution of 15 km) down to a domain of 80 x 80 km (2 km resolution) centred on the Mongstad plant. Initial and boundary conditions for the outermost grid were taken from the six-hourly synoptic scale analyses derived by the LAPS or GASP models from the Australian Bureau of Meteorology. Surface boundary data, such as topography, land use and sea surface temperature were taken from the US Geological Survey, Earth Resources Observation Systems (EROS) Data Center Distributed Active Archive Center (EDC DAAC) and the US National Center for Atmospheric Research (NCAR). Emitted amines and their photo-oxidation products were assumed to be chemically inert in the atmosphere but undergo both wet and dry deposition processes. Deposition was treated in the same way as for sulphur dioxide.

3. Study Site

Mongstad (60°48'17'' N, 5°01'50'' E), Norway is located approximately 60 kilometres north of Bergen. Mongstad is situated at the coast and located only a few meters above sea level. The region is influenced by strong westerly winds from the Northern Atlantic for most of the year. To the east, the region is surrounded by a chain of hills and mountains up to 600m in elevation.

4. Results

Meteorological data of wind and precipitation for the year 2007 were retrieved for the few local meteorological stations within the study grid. Wind data were obtained with a six-hour resolution and rainfall data on a daily basis for the year 2007 from the Norwegian Meteorological Institute (met.no) (eKlima, <http://sharki.oslo.dnmi.no>). These data were used to evaluate prognostic wind and rain fields computed with TAPM. Monthly averaged wind speed as well as the seasonality of wind direction and speed at the met.no stations Takle, 30 kilometres northeast and Fedje, 18 kilometres were well reproduced by the dispersion model. Monthly averaged wind speed was underestimated by 10-50%. TAPM systematically overestimated the monthly rainfall amounts during the year 2007. The yearly rainfall pattern, however, was well captured by the model. The frequency of days with rain (rainfall amount >0.1 mm) in TAPM was about 20% higher than observed.

Based on TAPM calculations for the year 2007, yearly mean concentrations of MEA in air were below 0.05 $\mu\text{g}/\text{m}^3$ inside the 40x40 km² study domain (Figure 2). Monthly mean concentrations of MEA in air reached maximum values of 0.05-0.25 $\mu\text{g}/\text{m}^3$. Highest levels were 5-15 km to the north of Mongstad. In most months, the simulated plume also impacted the region south-east of Mongstad at a distance of 2-20 km, but monthly average concentrations were below 0.08 $\mu\text{g}/\text{m}^3$.

Inhalation Exposure. The inhalation exposure for MEA, nitrosamines (as group) and acetamide using the yearly average (MEA and acetamide) or 8-hourly average (nitrosamines) of air concentration assuming emission of 40 tonnes/yr MEA and 5 tonnes/yr DEYA was evaluated. The maximum yearly mean concentrations in air simulated in the study grid were 0.22 $\mu\text{g}/\text{m}^3$ MEA (safety limit: 10 $\mu\text{g}/\text{m}^3$) and 0.007 $\mu\text{g}/\text{m}^3$ acetamide (safety limit: 0.05 $\mu\text{g}/\text{m}^3$), respectively. The maximum 8-hourly average nitrosamine concentration was 0.011 $\mu\text{g}/\text{m}^3$ (safety limit: 1.0 $\mu\text{g}/\text{m}^3$). In the photo-oxidation of DEYA, N-nitrosodiethylamine (DEN) is formed. For DEN, the US Environmental Protection Agency (EPA) recommends a long-term risk threshold of 0.02 ng/m³ in air, corresponding to a 10⁻⁶ lifetime cancer risk (US EPA, IRIS database: <http://www.epa.gov/IRIS/subst/0042.htm>). This criterion was exceeded by a factor of 32 in this study. These calculations assumed no chemical degradation of the compounds in air.

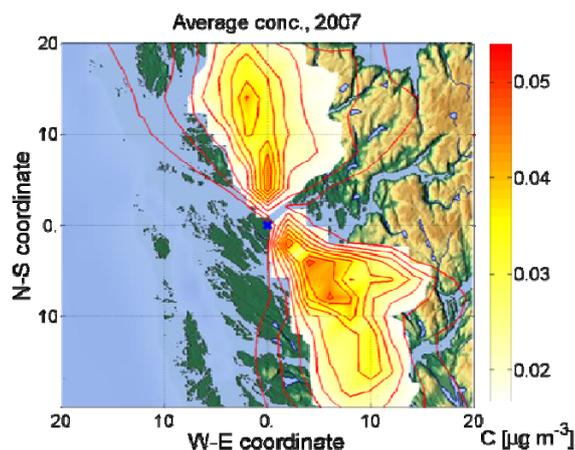


Figure 2: Simulated yearly mean MEA concentration in air ($\mu\text{g}/\text{m}^3$) given meteorological conditions of 2007 in the $40 \times 40 \text{ km}^2$ domain around Mongstad (blue cross).

Drinking Water Quality. The critical nitrosamine load in the precipitation to Norwegian lakes with respect to drinking water quality is 7 ng/l. This corresponds to a critical annual deposition flux of $0.013 \text{ mg}/\text{m}^2$ under worst case conditions. This flux is reached with emissions of DEYA of 1.9 tonnes per year (Table 1), assuming a conversion of 3% of the emitted diethyl amine into nitrosamines. The assumed emissions of DEYA of 5 tonnes/yr exceed this value by about a factor of 3. The value was based on the predicted maximum annual wet deposition flux inside the study grid. The high wet deposition flux was only reached within a limited area of the study grid. With an instantaneous production yield of 1% nitramines from MEA and 32% from diethyl amine, maximum tolerable amine emissions of MEA and DEYA from the CO_2 capture facility are calculated to be 164 and 26 tonnes per year, respectively, to comply with the recommended drinking water threshold of $1 \mu\text{g}/\text{l}$. Thus the drinking water criterion for nitramines was not exceeded (Table 1).

Compound	Safety Limit (ng/l)	Critical deposition flux (mg/m^2)	Deposition flux (mg/m^2)		Max. tolerable emission (t/yr)		Target
			Grid average	Grid max.	MEA	DEYA	
MEA	7,500	14.2	3.1	46	12		Aquatic algae/bacteria
	7	0.013	0.01	0.03		1.9	Drinking water
Nitrosamines	25	0.047	0.01	0.03		6.9	Aquatic algae/bacteria
	1,000	1.9	0.22	0.83	164	26	Drinking water
Nitramine	200	0.38	0.22	0.83	33	5.1	Aquatic Fish
	24,000	45.4	1.6	23	79		Aquatic Invertebrates

Table 1: Summary of maximum tolerable emission results for MEA and DEYA from the worst case studies. For the different compound classes, tolerable emissions of the parent amines MEA and DEYA were derived by converting the respective compound emission with the fractional yield.

Aquatic Environment. The safety limit of MEA with respect to aquatic organisms is $7.5 \mu\text{g}/\text{l}$ and corresponds to a critical annual deposition flux of $14.2 \text{ mg}/\text{m}^2$. Based on the maximum deposition

flux found in the study grid, the maximum tolerable MEA emissions from a CO₂ capture plant would be 12 tonnes per year, about 3 times less than the assumed MEA emissions of 40 tonnes/yr (Table 1). Concentrations of formamide did not exceed the critical limit to aquatic organisms. Concentrations of nitramines were calculated to reach about 22% above the tolerable threshold for aquatic organisms and could cause chronic damage to fish.

5. Conclusions

The “worst case” approach evaluates the exposure to expected toxic compounds released from a CO₂ capture facility. Three exposure pathways were considered: 1) inhalation of air, 2) drinking water consumption, and 3) deposition to aquatic ecosystems. Among the expected substances, two compound groups are of particular concern due to their carcinogenic potential: nitrosamines and nitramines. Maximum wet deposition flux of nitrosamines (from diethyl amine) exceeded the safety limit for drinking water and maximum deposition flux of nitramines (from MEA) exceeded the safety limit for aquatic organisms. Toxicity to aquatic organisms is a major concern for the use of MEA since maximum tolerable MEA emissions are found to be only 12 t/yr. In this worst case study, we assumed that chemical compounds are stable in air, water and soil, with no degradation or loss during transport through each medium. Biodegradation of the compounds in soil and water is probably the highest uncertainty in the calculation of tolerable emissions. Though nitrosamines in water decay rapidly with light, they are more stable in drinking water systems and when mixed into deeper parts of lakes. Another uncertainty is the retention of amines in soils or sediments which might also reduce the concentrations in the lake, but was assumed to be negligible. Toxicity studies and field experiments are required before final conclusions can be drawn with respect to the maximum allowable emissions of amines and their oxidation products from CO₂ capture plants.

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