

Amine dispersion modelling Carbon Capture
Filborna EfW plant

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Abstract:

Öresundskraft plans to install carbon capture at Filborna EfW Plant. As part of the work with the environmental assessment process, amine dispersion modelling has been performed.

Norsk Energi has performed dispersion modelling of nitrosamines, nitramines and NO₂ from emission at the planned carbon capture plant. The modelling was done for combustion capacity of 250 000 tonnes of waste per year.

Input data and assumptions, model results and this report has been reviewed by Cambridge Environmental Research Consultants (CERC).

Nitrosamines and nitramines dispersion modelling was carried out with the CERC model ADMS 5 with amine chemistry module. ADMS is among the models recommended by Gassnova (Norwegian state enterprise for carbon capture and storage). Gassnova also recommends lake catchment modelling to estimate the contribution to drinking water sources. The English Environment Agency describe dispersion and deposition modelling with ADMS in their recommendation document for the assessment and regulation of impacts to air quality from amine-based post-combustion carbon capture plants, but do not require applicants to consider the effects on drinking water.

Öresundskraft has no pilot plant amine emission data. Emission data from the pilot plant at Klemetsrud waste to Energy plant have been used in the model.

Supplier of CC plant and solvent have not been decided yet. Modelling was therefore done with a worst-case type of solvent, i.e. solvent with the highest potential for reacting to nitrosamines and nitramines in the atmosphere (piperazine with adjusted branching ratio for amine/OH reaction).

Norwegian Institute of Public Health (NIPH) has published guidelines which is based on N-nitroso dimethylamine (NDMA) risk estimates. NDMA is one of the most potent and best investigated nitrosamines. NIPH consider this to be a conservative approach for total air concentration. If an amine with greater toxicity constitutes a significant proportion of the total emissions of these substances, NIPH recommends that a new risk assessment be made.

There is a lack of knowledge about nitramines, but the substances in this group are generally believed to be less carcinogenic than the nitrosamines according to NIPH. NIPH writes that the NDMA risk estimate should be used for the total concentration of both nitrosamines and nitramines in air and water. Based on the NIPH assessment, the guidelines values for sum nitrosamines+nitramines are 0,3 ng/m³ for air quality and 4 ng/l for drinking water

concentration. The English Environment Agency/AQMAU has given a long-term EAL (Environmental Assessment Level) of 0,2 ng/m³ NDMA.

Dispersion modelling with emission concentrations 0,4 ppmvol amine and 0,58 weight-% nitrosamine gave nitrosamine+nitramine concentration 0,21 ng/m³ (about 2/3 of the NIPH air quality guideline value and slightly above the English EAL value).

Note that this report assesses impacts on concentrations in air only. An assessment of deposition and drinking water impacts is recommended.

Contents

| | | |
|-----------|---|-----------|
| 1 | INTRODUCTION | 4 |
| 2 | FILBORNA EFW PLANT | 4 |
| 3 | NITROSAMINE AND NITRAMINE FORMATION | 5 |
| 4 | GUIDELINES FOR NITROSAMINES AND NITRAMINES IN AIR AND DRINKING WATER..... | 6 |
| 4.1 | Norwegian Institute of Public Health (NIPH) risk assessment and guideline..... | 6 |
| 4.1.1 | The English Environment Agency/AQMAU recommendations | 7 |
| 5 | AMINE AND NITROSAMINE EMISSION LEVELS – KLEMETSRUD | 8 |
| 6 | SOLVENT DATA..... | 10 |
| 6.1 | Solvents for post-combustion carbon dioxide capture | 10 |
| 6.2 | Solvent for worst-case modelling at Filborna | 12 |
| 7 | DISPERSION MODELLING | 14 |
| 7.1 | Methods..... | 14 |
| 7.1.1 | NO ₂ dispersion modelling..... | 14 |
| 7.1.2 | Nitrosamines and nitramines dispersion modelling | 14 |
| 7.2 | Modelling and calculation inputs and assumptions..... | 15 |
| 7.2.1 | Reaction rates and constant that determines hourly varying OH concentration | 15 |
| 7.2.2 | Building data | 17 |
| 7.2.3 | Emission data | 18 |
| 7.2.4 | Background concentrations | 18 |
| 7.2.5 | Terrain and surface roughness | 19 |
| 7.2.6 | Grid and receptors | 19 |
| 7.2.7 | Meteorology and dispersion..... | 20 |
| 8 | DISPERSION MODELLING RESULTS | 21 |
| 8.1 | Annual NO ₂ concentrations..... | 21 |
| 8.2 | Annual nitrosamine and nitramine concentrations..... | 23 |
| 9 | SUGGESTIONS FOR FURTHER WORK | 24 |
| 10 | UNCERTAINTY | 25 |

1 Introduction

Öresundskraft plans to install carbon capture at Filborna EfW Plant. As part of the work with the environmental assessment process, amine dispersion modelling must be performed. If the modelled nitrosamine+nitramine air concentration at drinking water source locations is above a certain level, it may be necessary to carry out deposition modelling followed by catchment modelling of drinking water concentration. Note that this report assesses impacts on concentrations in air only.

Norsk Energi has performed dispersion modelling of nitrosamines, nitramines and NO₂ from emission at the planned carbon capture plant. The modelling was done for combustion capacity of 250 000 tonnes of waste per year.

The modelling input data and assumptions, the model results and this report has been reviewed by Cambridge Environmental Research Consultants (CERC).

Öresundskraft has no pilot plant amine emission data. Therefore, pilot plant emission data from other waste incineration plants have been used in the dispersion modelling.

Supplier of carbon capture (CC) plant and solvent have not been decided yet. Modelling was therefore done with a worst-case type of solvent, i.e. solvent that have the highest potential for reacting to nitrosamines and nitramines in the atmosphere.

2 Filborna EfW plant

Filborna EfW plant is located east of Helsingborg, see the figure below. The boiler's thermal input is currently approximately 85 MW, but there is a permit for 90 MW thermal input and incineration of a total of 250,000 tonnes of waste per year.

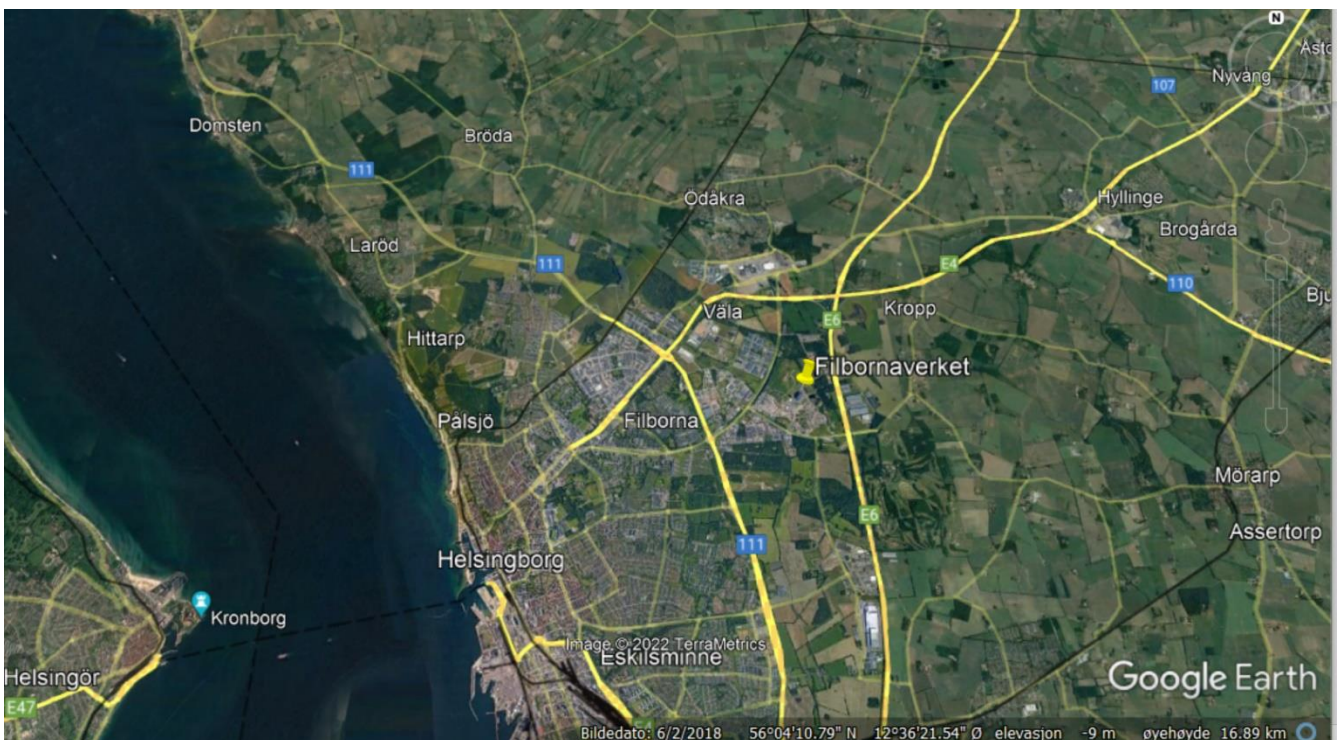


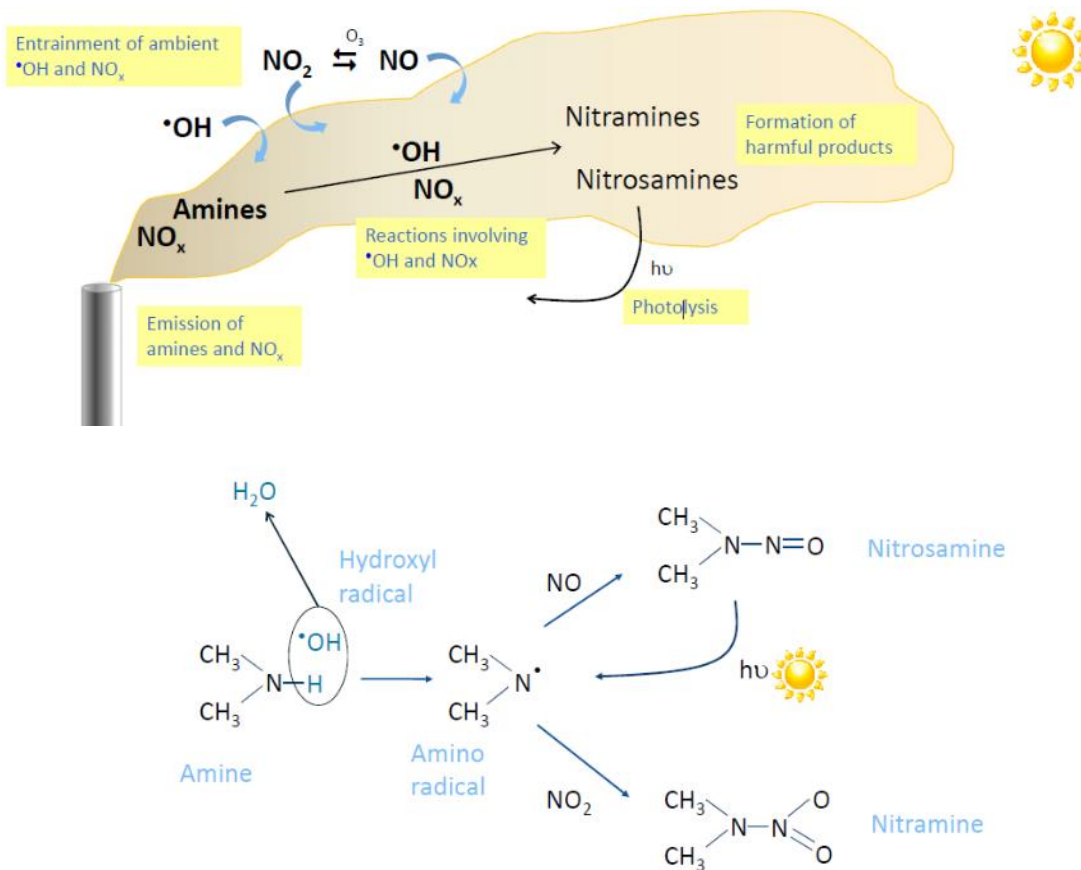
Figure 1 Location of Filborna EfW plant

3 Nitrosamine and nitramine formation

A small amount of the amines used in the carbon capture process are lost and may react to nitrosamines and nitramine in the stack or in the atmosphere.

Hydroxyl radicals in the atmosphere act to abstract (remove) a hydrogen atom from the amine. The site of initial attack determines the type of species formed, through two separate branches of reactions.

Once the H atom has been removed from the nitrogen atom of the amine, the next step is the reaction with nitric oxide (NO) to nitrosamine and nitrogen dioxide (NO₂) to nitramine. The amount of nitrosamine and nitramine formed depends on the amount of NO_x and the ratio of NO to NO₂. Nitrosamines are reduced by photolysis. The figure below shows overview of amine chemistry and reaction pathways.



CERC

ADMS User Group Meeting 2021

Figure 2 Overview of amine chemistry, reaction pathways (from presentation by Catheryn Price, CERC. ADMS User Group meeting 2021)

4 Guidelines for nitrosamines and nitramines in air and drinking water

4.1 Norwegian Institute of Public Health (NIPH) risk assessment and guideline

The Norwegian Institute of Public Health (NIPH) gave a risk assessment and guideline value for the protection of human health for nitrosamines and nitramines in 2011¹. NIPH states that «*We have not worked on risk assessment of nitrosamines/nitramines after this, and what is on the website is therefore our latest updates.*»² On the website we find the following summary (Norwegian summary translated to English)³:

«In a mandate from the Climate and Pollution Directorate (Klif), the Norwegian Institute of Public Health (NIPH) has been commissioned to assess the risk of potential health damage in connection with emissions of amines, nitrosamines and nitramines from CO₂ capture plants. As part of this, Klif requested a thorough review of the risk estimate for nitrosodimethylamine (NDMA) in air and water, prepared by foreign institutions. In addition, Klif wanted NIPH to assess whether there is a basis for developing air quality criteria for NDMA. NIPH has now completed its assessment of risks related to exposure to nitrosamines and nitramines.

Several international institutions have set tolerable risk levels for carcinogens in case of lifelong exposure of the general population. These levels are in the range of 10⁻⁶ and 10⁻⁵. This means that for life-long exposure, one can expect an increase in cancer incidence, which is between one and ten extra cases per million inhabitants.

Nitrosamines and nitramines are groups of substances, which are formed by the breakdown of amines. Although there is relatively little data available on the health effects of many of these substances, it is known that substances in both groups can be highly carcinogenic.

Among the nitrosamines, NDMA is one of the most potent and best investigated substances. NDMA is therefore used as a basis for calculating the concentrations of nitrosamines and nitramines that can lead to an increase in the risk of cancer in the population. Concentrations of NDMA in drinking water presenting negligible or minimal risk have been prepared by several institutions (WHO, Health Canada, US EPA and California EPA), primarily on the basis of a comprehensive study by Peto and co-workers (1991a; 1991b).

This study is very solid and well suited to calculate the risk of tumor development in the liver. Overall, the risk estimates from the various authorities varied within a factor of 10. Based on available information, NIPH has assessed that the Health Canada risk estimate is a well-founded and conservative proposition. A lifelong use of drinking water with 40 ng/l or 4 ng/l NDMA will lead to an increased risk of cancer of 10⁻⁵ and 10⁻⁶ respectively.

Risk estimates for exposure through air are set only by the US EPA. These are also based on the drinking water study by Peto and co-workers. Therefore, the NIPH has calculated the risk estimates drawn up by the other drinking water authorities to apply to air concentrations. The conversion was carried out in accordance with recommendations from REACH (EU chemicals regulations). In addition, NIPH has used an inhalation study by Klein and co-workers (1991) to calculate cancer risk in exposure to NDMA via air. This study suggests that NDMA may be more potent when ingested via inhalation than through drinking water. Compared to the drinking water study, the inhalation study used few doses, with fewer animals in each exposed group. In addition, the reporting of the study is somewhat incomplete. Therefore, there are some uncertainties associated with the results of the inhalation study for Klein and co-workers.

Based on the data from the drinking water study, a lifelong exposure to an air concentration of 0.3 ng/m³ will cause a cancer risk of 10⁻⁶. That is, in a population of 1 million that is exposed throughout life, one additional case of cancer may result from this exposure. The study of Klein and co-workers presents a somewhat higher risk than this. Overall, NIPH considers that the concentration of NDMA in air should not exceed 0.3 ng/m³.

NIPH has also assessed the carcinogenic potential of other nitrosamines that may be relevant for CO₂ purification. NDMA was found to be one of the most potent, and we therefore consider it conservative if the value of this

¹ <https://www.fhi.no/globalassets/dokumenterfiler/rapporter/2011/health-effects-of-amines-and-derivatives-associated-with-co2-capture.pdf>

² E-mail from Marit Låg, NIPH, dated 30 August 2019

³ <https://www.fhi.no/en/publ/2011/co2-capture-health-effects-of-amine/>

substance is used to calculate the risk from the total amount of nitrosamines in the air, which together should therefore not exceed 0.3 ng/m³. However, there is one nitrosamine that is probably more potent than NDMA, N-nitrosodiethylamine (NDEA). If NDEA constitutes a significant proportion of the total emissions of these substances, NIPH recommends that a new risk assessment be made.

When it comes to nitramines, there is a great lack of knowledge, but the substances in this group are generally believed to be less carcinogenic than the nitrosamines. However, studies show that the most known nitramine (N-nitrodimethylamine) is highly carcinogenic, though not as potent as NDMA. The NIPH therefore recommends that the NDMA risk estimate be used for the nitramines as well. This must be regarded as a conservative risk estimate that will provide good protection for the population. If nitramines are detected in significant quantities in discharges, there will be a need for more knowledge in order for NIPH to carry out a complete risk assessment. Therefore, when discharging from CO₂ capture facilities, NIPH recommends that the NDMA risk estimate should be used for the total concentration of both nitrosamines and nitramines in air and water.»

Based on the NIPH recommendations, we used 0,3 ng/m³ (sum nitrosamines+nitramines) as air quality guideline value, and 4 ng/l as drinking water guideline value (sum nitrosamines+nitramines) in the Klemetsrud project.

4.1.1 The English Environment Agency/AQMAU recommendations

The Air Quality Modelling & Assessment Unit (AQMAU) at the English Environment Agency has given recommendations for the assessment and regulation of impacts to air quality from amine-based post-combustion carbon capture plants⁴. In chapter 4, Advice for regulators there are EALs⁵ (Environmental Assessment Levels) for MEA and NDMA, see the table below.

Table 1 EALs (Environmental Assessment Levels) for MEA and NDMA

| Compound | MEA | NDMA |
|----------------|---------------------------------------|-----------------------|
| Short-term EAL | 400 µg/m ³ | none |
| Long-term EAL | 100 µg/m ³ (24-hour means) | 0.2 ng/m ³ |

There are no nitramine EALs in the AQMAU recommendations. The AQMAU document states: “According to the air emissions risk assessment guidance, where an environmental standard or EAL is not listed for the substance assessed, the applicant can propose an EAL using the hierarchy included within the consultation document. For amine-based post-combustion carbon capture facilities, the applicant is required to be transparent in the chemical composition of the solvent and degradation products, proposing EALs for each substance if not defined, justifying that values are appropriate. In addition to these already established regulatory processes to devise risk assessment criteria, when deemed appropriate, we recommend steer on the following to streamline risk assessments as experience increases: ...Derivation of precautionary risk-based assessment criteria (e.g. one EAL for total nitrosamines, another for total nitramines) or grouped substances approaches, where these may be appropriate and based on sound criteria.”

The English Environment Agency/AQMAU do not require applicants to consider the effects on drinking water. The AQMAU guidance describes dispersion and deposition modelling using ADMS with amine module. ADMS with amine chemistry module is also among the dispersion and deposition

⁴ “AQMAU recommendations for the assessment and regulation of impacts to air quality from amine-based post-combustion carbon capture plants”
AQMAU reference: AQMAU-C2025-RP01 AQMAU report date: November 2021

⁵ If you exceed these assessment levels, you might need to take further action to reduce your impact on the environment

models recommended by Gassnova⁶. Gassnova also recommends lake catchment modelling to estimate the contribution to drinking water sources.

5 Amine and nitrosamine emission levels – Klemetsrud

This chapter summarizes typical amine and nitrosamine emission levels from carbon capture pilot at Klemetsrud Waste to Energy plant.

Klemetsrud Waste to Energy plant has three combustion lines. Line K1 and K2 has SNCR (selective non catalytic reduction) for NO_x-reduction, Ca(OH)₂ and active coal injection and bag filters. Line K3 has ESP (electrostatic precipitator) scrubber and SCR (selective catalytic reduction) for NO_x-reduction.

The pilot plant test is described in the paper “Performance of an amine-based carbon capture pilot plant at the Fortum Oslo Varme Waste to Energy plant in Oslo”⁷. The flue gas tested in the pilot plant consisted of ca. 23 % flue gas from K1, 23 % from K2 and 54 % from K3. Annual average NO_x concentration for this flue gas mix was 43,9 mg/Nm³ NO and 1,2 mg/Nm³ NO₂.

The amine used in the pilot plant was Shells DC103. The average amine emissions to air remained well below the emission target concentration (0,4 ppm) during the test period. However, excursions were observed during upsets. The pilot plant tests were done both without and with aerosol mitigation device (AMD). The AMD had neglectable effect during normal flue gas conditions. At upset gas conditions the AMD helped to reduce the amine emission. The first 2000 hours normal conditions were tested. One of the reasons for as much as 2000 hours is that estimated time for degradation of the solvent is 1000-1500 hours. Amine emission results for the last 500 hours of the test is shown in the table below.

Table 2 Amine emissions during the final 500 h of the first pilot plant test campaign

| | Units | Value |
|--|-------------|----------------|
| Target | ppmv | <0.4 |
| 500 h test period | ppmv | 0.16 |
| 500 h test period excluding ESP malfunction | ppmv | 0.04 |

From the table we see that the 500 hours test period excluding ESP malfunction period had emission at 1/10 of the target. During the malfunction period, K3 dust emissions were up to 30 mg/Nm³. During this period, amine emissions were significantly increased. In normal periods, the K3 dust emission was well below 5 mg/Nm³. Filborna EfW plant has wet flue gas cleaning, which gives a lower risk of high dust emission episodes. Only the main and most volatile amine had significant emission during the emission measurement campaign. (Ref. chapter 3.2.1 in the paper about the test). The paper about the test does not mention nitrosamine emission results.

⁶ Helgesen, L.I. og E. Gjernes: «A way of qualifying Amine Based Capture Technologies with respect to Health and Environmental Properties», Energy Procedia, Volum 86, Januar 2016, side 239-251.

⁷ Performance of an amine-based CO₂ capture pilot plant at the Fortum Oslo Varme Waste to Energy plant in Oslo, Norway Johan Fagerlund. International Journal of Greenhouse Gas Control Volume 106, March 2021, 103242 <https://doi.org/10.1016/j.ijggc.2020.103242>

Emission and flue gas data used in the dispersion and deposition modelling at Klemetsrud

The table below shows emission data used in the dispersion and deposition modelling at Klemetsrud⁸.

Table 3 Data used in the dispersion modelling for the Klemetsrud site

| | Unit | 95 % CO ₂ capture, Reheat |
|--|--|--|
| Waste incinerated | tonnes/year | 410000 |
| Volume flow rate | Nm ³ /h, dry, 11 % O ₂ | 298 838 |
| Flue gas temperature* | °C | 65 |
| Volume flow rate | m ³ /h, wet | 297 134 |
| Emission velocity | m/s | 13.6 |
| Stack height | m | 80 |
| NO _x emission (as NO ₂) | Nm ³ /h, dry, 11 % O ₂ | 56 (upstream CC Plant) |
| NO _x emission (as NO ₂) | g/s | 5.6 |
| NO ₂ share | vol-% | 0 |
| Amine emission Sum of all amine species | ppmv, wet | max 0.2** |
| Share of amines/ nitrosamines (stack) | weight-% | 99.42 weight-% DC103, 0.58 weight-% nitrosamine*** |
| Nitramine emission (stack) | ppmv, wet | 0**** |

*Reheat winter temperature is 65 C. In summer the temperature is 80 C

**Currently (with the pilot plant) no unknown amine species of significance (above 5 ppbv) have been detected. The sum of all amines is based on proprietary information

***from NILU report 11/2018. Email from Johan Fagerlund October 09, 2019: "Previously (pre Klemetsrud pilot plant that is), Shell provided UiO and NILU with the composition of the emitted amine emissions as: 99.42% Am1 and 0.58% nitrosamine. This should still be used for the comparison case with NILU, but the question is what should we use for the other cases as the pilot plant has only seen 100% Am1."

****0/Negligible. Confirmed with Shell 8 October according to email from Johan Fagerlund, CCS Advisor, Partners Fortum

Reheat case with 0.2 ppmvol amine and 0.58 weight-% nitrosamine gave nitrosamine+nitramine concentration below the air quality guideline value of 0.3 ng/m³. Our rough estimate and NIVAs (Norwegian Institute for Water Research) catchment modelling gave drinking water concentrations close to the drinking water guideline value. The share from directly emitted nitrosamines was 50-70% of total nitrosamines for all cases.

⁸ <https://www.miljodirektoratet.no/hoeringer/2021/august-2021/fortum-oslo-varme-as-soker-om-etablering-av-karbonfangstanlegg-/>

6 Solvent data

6.1 Solvents for post-combustion carbon dioxide capture

The English Environmental Agency has published the guidance “Post-combustion carbon dioxide capture: best available techniques (BAT)”. The guidance was based on a BAT Review for New-Build and Retrofit Post-Combustion Carbon Dioxide Capture⁹. The following text is from chapter 2.3.4 Solvents in the BAT review:

“Solvent issues are covered in more detail in a report by the Scottish Environment Protection Agency (SEPA), last updated in 2015 (SEPA, 2015), from which the text below is taken:

‘Most reported work has concentrated on the use of 2-aminoethanol (often referred to as monoethanolamine, MEA). This solvent is normally used as a baseline when comparing the performance of other types of amine solvents or mixtures of solvents.

Other alkanolamine compounds (either alone or in blended mixtures) have been proposed as carbon capture solvents include 2-(2-hydroxyethylamino)ethanol (often referred to as diethanolamine or DEA), 2-(2-hydroxyethyl(methyl)amino)ethanol (referred to as methyldiethanolamine or MDEA), 1-(2-hydroxypropylamino)propan-2-ol (referred to as di-isopropanolamine or DIPA) and 2-(methylamino)ethanol (referred to as monomethylethanolamine or MMEA). Other amine compounds have also been investigated as potential carbon capture solvents including cyclic and glycol amines such as 2-amino-2-methyl-propanol (referred to as aminomethylpropanol or AMP), the cyclic compound 1,4-diethylenediamine (universally referred to as piperazine or PIPA [or PZ]) and 2-(2-aminoethoxy)ethanol (referred to as di-glycolamine or DGA). A wide range of other, more highly substituted alkanolamines and polyamines are also being investigated at the laboratory scale (Lepaumier et al 2009). Proprietary solvents and solvent mixes are also being developed however information on the composition of these solvents is in some cases confidential.’”

Table 2.1 in the BAT review shows solvent characteristic for amines typically used in PCC (Post Combustion Capture) applications and pilot tests, see below.

⁹ Gibbins, J., Lucquiaud, M. (2021) BAT Review for New-Build and Retrofit Post-Combustion Carbon Dioxide Capture Using Amine-Based Technologies for Power and CHP Plants Fuelled by Gas and Biomass as an Emerging Technology under the IED for the UK, UKCCSRC Report, Ver.1.0, July 2021. <https://ukccsrc.ac.uk/best-available-techniques-bat-information-for-ccs/>

Table 4 Classes of amines and relevant characteristics for PCC (table 2.1 in the BAT review)

(Summary for amines in aqueous solution, as typically used in PCC applications and pilot tests, based on amine-related references cited in this review)

| Type of amine | Examples in use | Relevant characteristics for PCC |
|---|---------------------|--|
| Primary | MEA | Widely used for other purposes, rapid kinetics, low CO ₂ capacity, moderate volatility and can form mists with aerosols, moderate to low stability and resistance to thermal degradation, pure material will not form stable nitrosamines, liquid at all relevant temperatures, easy to reclaim thermally. Proposed for use at increasing concentrations in water (now 35-40% w/w, was 30% w/w) to partially overcome lower CO ₂ loading capacity and hence higher regeneration energy requirements than secondary and tertiary amines/blends. |
| Secondary/ secondary blends | PZ Piperazine | Rapid kinetics, moderate CO ₂ capacity, lower volatility compared to MEA but can still form mist with aerosols, good thermal and oxidative stability, as secondary amine the pure material forms nitrosamines, can 'freeze' at lower temperatures so often used as an accelerator in blends with 'slower' amines, reported to be reclaimable thermally (Sexton, 2014) but limited practical evidence available at the time of writing. |
| | PZ + AMP blends | AMP is a sterically-hindered amine with higher capacity and PZ an accelerator in this blend. Non-proprietary version known as CESAR1, with public domain information available (e.g. Brüder, 2011). More toxic, rapid kinetics, high CO ₂ capacity, low volatility but can still form mist with aerosols, good thermal and oxidative stability, readily forms nitrosamines, limited published evidence on reclaimability to date, precipitation reported for CESAR1 blend at low flue gas temperatures (30°C vs 40°C) (Languille, 2021). |
| Tertiary/tertiary blends Good capacity but slow kinetics so used in blends | PZ + MDEA blends | PZ is an accelerator for the slower, tertiary amine MDEA in this blend. Rapid kinetics, high CO ₂ capacity, lower volatility than MEA but can still form mist with aerosols, good thermal and oxidative stability, forms nitrosamines, liquid at all relevant temperatures, may not be easily reclaimable thermally due to the difference between the boiling points of MDEA of 246.1°C and that of PZ of 146°C. |

The amine used in the pilot plant at Klemetsrud (Shells DC103) consists of three cyclic amines, ethanediol and water, see the table below¹⁰.

Table 5 Composition/information on ingredients, Shell Cansolv DC103

3. COMPOSITION/INFORMATION ON INGREDIENTS

Substance / Mixture : Mixture

Hazardous components

| Chemical name | CAS-No. | Classification | Concentration [%] |
|------------------|--------------|---|-------------------|
| Cyclic Amine (1) | Not Assigned | Eye Dam.1; H318 | 0.25 - <= 0.75 |
| Cyclic Amine (2) | Not Assigned | Flam. Sol.1; H228 Skin Corr.1B; H314 Eye Dam.1; H318 Resp. Sens.1B; H334 Skin Sens.1B; H317 Repr.2; H361 Aquatic Acute3; H402 | >= 1.75 - <= 2.25 |
| Cyclic Amine (3) | Not Assigned | Acute Tox.4; H302 Skin Irrit.3; H316 Eye Dam.1; H318 | >= 46 - <= 49 |
| Ethanediol | 107-21-1 | Acute Tox.4; H302 STOT RE2; H373 | <= 0.5 |
| Water | 7732-18-5 | | >= 48 - <= 52 |

For explanation of abbreviations see section 16.

A recently proposed new benchmark solvent - a blend of AMP (amino-methyl-propanol) and PZ (piperazine) (33 wt% AMP and 12 wt% PZ) has been used at PREEM¹¹. A blend of piperazine and AMP is also mentioned in the BAT for PCC.

6.2 Solvent for worst-case modelling at Filborna

Öresundskraft has not decided on contractor for the planned carbon capture plant at Filborna EfW. All solvents suitable for a PCC plant may be applicable, such as any of the solvents protected by IP as Cansolv DC103, MHI KS-1 or Aker S26. Data for IP solvents are not publicly available due to the risk that a competing company may use the solvent recipe, which means that the necessary solvent data for dispersion modelling is not available.

We are therefore looking for a worst-case type of solvent, i.e. solvent that have the highest potential for reacting to nitrosamines and nitramines in the atmosphere.

Primary amines as MEA does not form stable nitrosamines. The most important other solvent characteristic is probably the amine/OH reaction rate as this step determines the overall reaction rate. The branching ration for the amine/OH reaction is also important. Higher value for these parameters results in higher formation of nitrosamine and nitramines.

The table below shows amine OH reaction rates and branching ratios for piperazine, Klemetsrud solvent, AMP and MEA (ranked after decreasing amine/OH reaction rate).

¹⁰ <https://www.miljodirektoratet.no/hoeringer/2021/august-2021/fortum-oslo-varme-as-soker-om-etablering-av-karbonfangstanlegg-/>

Vedlegg 11

¹¹ Preem CCS - Synthesis of main project findings and insights. Chalmers University of Technology, February 2022

Table 6 Amine OH reaction rates and branching ratios for piperazine, Klemetsrud solvent, AMP and MEA (ranked after decreasing amine/OH reaction rate)

| Parameter | Parameter | Piperazine | Klemetsrud solvent | AMP | MEA |
|--|---------------|------------------|--------------------|-------------------|----------------|
| Amine/OH reaction rate constant | k1 | 2.8E-10** | 2.50E-10* | 2.8E-11*** | 1.6E-13 |
| Branching ratio for amine/OH reaction | k1a/k1 | 0.18** | 0.37* | | 0.08 |

*From Claus J. Nielsen: «Klemetsrud-Solvent for modellers», attachment to email from Claus J. Nielsen 6 September 2019

** Experimental and Theoretical Study of the OH-Initiated Degradation of Piperazine under Simulated Atmospheric Conditions (Tan et al. 2021, <https://pubs.acs.org/doi/10.1021/acs.jpca.0c10223>)

*** Theoretical evaluation of the fate of harmful compounds post emission. Claus J. Nielsen Dirk Hoffmann and Hartmut Herrmann

From the table above, we can see that piperazine has the highest amine/OH reaction rate, slightly higher than the Klemetsrud Solvent, higher than AMP and much higher than MEA. The amine/OH branching ratio for piperazine is lower than for the Klemetsrud solvent.

For the modelling we therefore use piperazine with adjusted branching ratio for amine/OH reaction (adjustment from 0.18 to 0.4).

7 Dispersion modelling

7.1 Methods

Initial NO₂ dispersion modelling was carried out to find worst-case meteorology year and worst-case locations for the carbon capture plant.

Then dispersion modelling of nitrosamines and nitramines with meteorological data for worst-case year and worst-case carbon capture plant location was carried out.

7.1.1 NO₂ dispersion modelling

NO₂ dispersion modelling has been carried out with the US EPA model AERMOD. AERMOD is an advanced Gaussian plume model. Building and terrain impacts, and impact of different surface roughness can be considered.

Meteorological hourly data (wind speed, direction, ambient temperature and observed cloud cover) from a meteorological station is used in the model. Meteorological data sets based on prognostic meteorological data (WRF) can also be used. AERMOD is used in the US and several other countries as authority approved model.

Atmospheric chemistry is generally not included. However, the model has included simplified NO_x chemistry (Plume Volume Molar Ratio Method (PVMRM), Ambient Ratio Method (ARM) and Ozone Limiting Method (OLM)).

7.1.2 Nitrosamines and nitramines dispersion modelling

Nitrosamines and nitramines dispersion modelling has been carried out with the CERC model ADMS 5. ADMS 5 is an advanced Gaussian plume model. Impacts of buildings, terrain, variations in surface roughness and dry and wet deposition can be modelled.

ADMS 5 has an in-built meteorological pre-processor that allows processing of both hourly sequential and statistical data. ADMS is used for a large proportion of the regulatory modelling in the UK, as well as by the main regulators themselves. It is also used extensively for regulatory modelling in many countries.

The model includes atmospheric chemistry; reaction of NO with O₃, photolysis of NO₂ and amine chemistry. The rate expressions for amine chemistry used in the model are as follows:

1. Loss of the AMINE

$$\frac{d[AMINE]}{dt} = -k_1[AMINE][OH]$$

2. Production of the amino RADICAL

$$\begin{aligned} \frac{d[RADICAL]}{dt} = & k_{1a}[AMINE][OH] + j_5[NITROSAMINE] - k_2[RADICAL][O_2] \\ & - k_3[RADICAL][NO] - k_4[RADICAL][NO_2] \end{aligned}$$

3. Production of NITRAMINE

$$\frac{d[\text{NITRAMINE}]}{dt} = k_{4a}[\text{NO}_2][\text{RADICAL}]$$

4. Production of NITROSAMINE

$$\frac{d[\text{NITROSAMINE}]}{dt} = k_3[\text{RADICAL}][\text{NO}] - j_5[\text{NITROSAMINE}]$$

The methodology is further described in users guides for ADMS 5 and amine chemistry¹².

7.2 Modelling and calculation inputs and assumptions

7.2.1 Reaction rates and constant that determines hourly varying OH concentration

Values for the reaction rate constants are needed for the amine chemistry modelling. The figure below shows amine reaction pathways with the rate constants in grey boxes. The reaction numbering system is based on that of the DMA reaction scheme¹³.

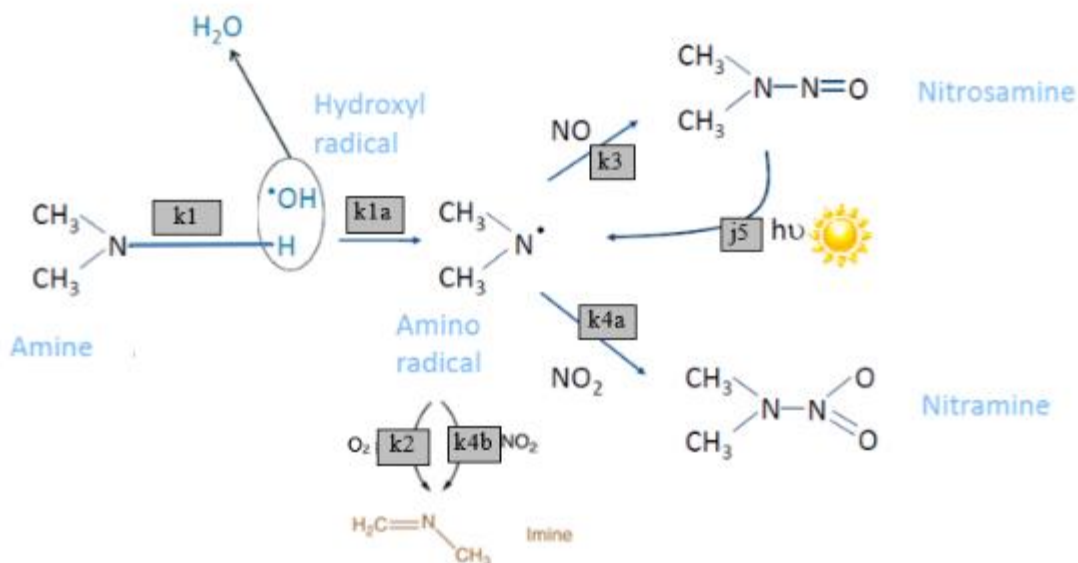


Figure 3 Amine reaction pathways with the rate constants in grey boxes

¹² ADMS 5 User guide, Cambridge Environment Research Consultants, 2016
ADMS 5 Amine Chemistry Supplement, Cambridge Environment Research Consultants, 2016

¹³ NILU OR 2 2011: Atmospheric degradation of amines (ADA). CLIMIT project no. 201604

The table below lists reaction rate constants and other constants needed for the amine modelling. The reaction rate data are based on piperazine with adjusted branching ratio for amine/OH reaction.

Table 7 Reaction constants and other constants needed for the amine modelling. The reaction rate data are based on piperazine with adjusted branching ratio for amine/OH reaction

| Parameter | Parameter | | Unit | Data for ADMS | Unit |
|--|---------------------|------------|--|-----------------|-----------------------------------|
| Amine/OH reaction rate constant | k1 | 2.80E-10* | cm ³ molecule ⁻¹ s ⁻¹ | 7 | ppb ⁻¹ s ⁻¹ |
| Amino radical/O ₂ reaction rate constant | k2 | 3.18E-20** | cm ³ molecule ⁻¹ s ⁻¹ | 7.95E-10 | ppb ⁻¹ s ⁻¹ |
| Rate constant for formation of nitrosamine | k3 | 9.54E-14** | cm ³ molecule ⁻¹ s ⁻¹ | 2.39E-03 | ppb ⁻¹ s ⁻¹ |
| Rate constant for formation of nitramine | k4a | 3.18E-13** | cm ³ molecule ⁻¹ s ⁻¹ | 7.95E-03 | ppb ⁻¹ s ⁻¹ |
| Amino radical/NO ₂ reaction rate constant | k4 | 4.13E-13** | cm ³ molecule ⁻¹ s ⁻¹ | 1.03E-02 | ppb ⁻¹ s ⁻¹ |
| Branching ratio for amine/OH reaction | k1a/k1 | | | 0.4*** | |
| Ratio of j (nitrosamine) to j(NO ₂) | j5/jNO ₂ | | | 0.34** | |
| Constant for OH concentration calculations | c | | | 2018: 7.830E-04 | s |
| Atmospheric oxygen concentration | | | | 209406000 | ppb |

*Experimental and Theoretical Study of the OH-Initiated Degradation of Piperazine under Simulated Atmospheric Conditions (<https://pubs.acs.org/doi/10.1021/acs.jpca.0c10223>)

Based on data from Claus J. Nielsen et.al.: "Atmospheric chemistry and environmental impact of the use of amines in carbon capture and storage (CCS)", Chem. Soc. Rev., 2012, **41, 6684–6704

***Adjusted from 0.18 to 0.4 for worst case modelling

The hydroxyl radical concentration [OH] is modelled by the equation

$$[OH] = c[O_3]j_{NO_2}$$

The constant c that determines hourly-varying OH concentration has been calculated based on annual average of OH- and ozone concentrations and jNO₂. Average value for O₃ was based on measured concentrations. Average jNO₂ (photodissociation rate of NO₂ by sunlight) was derived from the meteorological data (incoming solar radiation).

The average value for the OH concentration at the Filborna plant latitude is approximately 7 x 10⁵ molecules/cm³ (see figure 1 in "Global tropospheric hydroxyl distribution, budget and reactivity"¹⁴ and figure 3 (first column) in "Trends in global tropospheric hydroxyl radical and methane lifetime since 1850"¹⁵).

¹⁴ <https://acp.copernicus.org/articles/16/12477/2016/acp-16-12477-2016.pdf>

¹⁵ <https://acp.copernicus.org/articles/20/12905/2020/acp-20-12905-2020.pdf>

7.2.2 Building data

The figure below shows Filborna EfW plant.



Figure 4 Filborna EfW plant

The figure below shows Filborna EfW plant with planned carbon capture (two alternative locations). Stack and building heights used in the model are also shown in the figure.

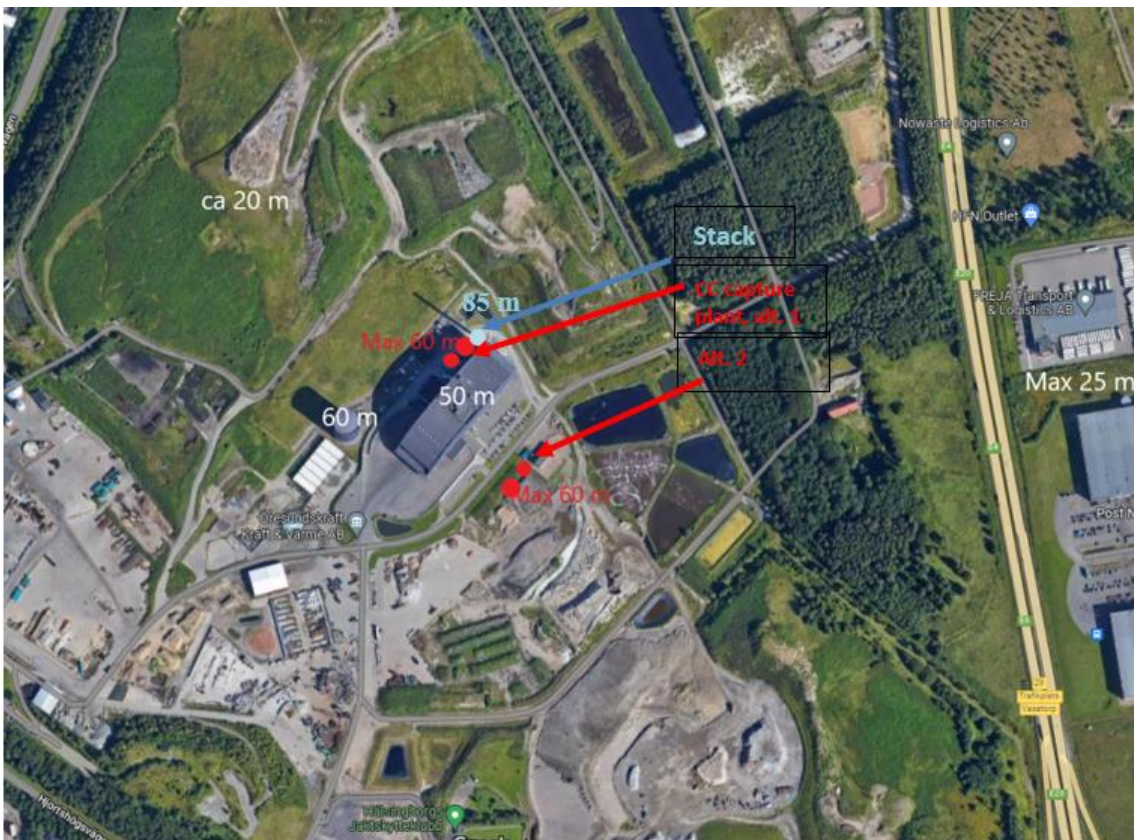


Figure 5 Filborna EfW plant with planned carbon capture (two alternative locations). Stack and building heights used in the model

7.2.3 Emission data

Filborna EfW Plant is permitted to incinerate a total of 250,000 tonnes waste per year.

Permitted NO_x-emission (annual average) is 105 mg/Nm³ at 11 % O₂. The NO₂ share is approx. 2%. The stack height is 85 meter and flue gas outlet temperature is 65 C (without flue gas condensation) and 54 (with flue gas condensation) (temperatures without Carbon capture (CC)). The table below shows flue gas data for the dispersion modelling based on data from Öresundskraft and our suggestions for amine emission based on Klemetsrud pilot plant data.

Table 8 Data for amine dispersion modelling at Filborna EfW Plant

| | Unit | Without CC | With CC |
|--|--|------------|--|
| Installed effect | MW | 90 | 90 |
| Waste total | ton/year | 250 000 | 250 000 |
| Stack height | m | 85 | 85 |
| Stack diameter | m | 1.8 | 1.8 |
| Operation time | h/year | 8 760 | 8 760 |
| Flue gas flow | Nm ³ /h, dry | 142 015 | 143 711 |
| | Nm ³ /h, wet | 163 800 | 154 031 |
| | m ³ /h, wet | 196 200 | 176 600 |
| O ₂ | Vol-%, wet | 6.3 | 8.9 |
| | Vol-%, dry | 7.3 | 9.5 |
| Flue gas temperature, condenser in operation | °C | 54 | 40 |
| H ₂ O, condenser in operation | Vol-% | 13.3 | 6.7 |
| Flue gas velocity | m/s | 21.4 | 19.3 |
| NO _x (as NO ₂) | mg/Nm ³ , 11 % O ₂ | 105 | 105 |
| | g/s | 5.7 | 4.8 |
| NO ₂ share | vol-% | 2 | 0* |
| Amine emission Sum of all amine species | ppmv, wet | | max 0.4 |
| | g/s | | 0.0654 |
| Share of amines/ nitrosamines (stack) | weight-% | | 99.42 weight-% piperazine, 0.58 weight-% nitrosamine* |
| Nitrosamine emission | g/s | | 0.00038 |
| Nitramine emission (stack) | ppmv, wet | | 0* |

*Same as the Klemetsrud dispersion modelling

The carbon capture plant will result in reduced outlet temperature and reduced flue gas volume and higher concentration of NO_x. The NO_x-concentration is assumed to still be within the permitted annual average of 105 mg/Nm³. NO₂ is assumed to be absorbed in the carbon capture plant (same assumption as in the Klemetsrud dispersion modelling).

7.2.4 Background concentrations

NO_x, NO₂ and O₃

For the amine dispersion modelling we need hourly background values of NO_x, NO₂ and O₃, all from the same measurement station. At the measurement station Helsingborg Norr, there are hourly urban background data of NO₂ and O₃, not NO_x. The Helsingborg Norr station uses stretch measurements 25 m above the street.

Background values for NO_x, NO₂ and O₃ for 2018, 2019 and 2020 were available from the measurement station at Malmö Rådhuset (urban background measured at a roof 20 m above ground). Malmö is approx. 50 km south/southeast of Helsingborg. The values for 2020 were influenced by Covid-19 restrictions, therefore we obtained 2018 and 2019 data.

The table below shows NO_x, NO₂ and O₃ at Malmö Rådhuset and NO₂ and O₃ at Helsingborg Norr for comparison.

Table 9 NO_x, NO₂ and O₃ at Malmö Rådhuset. NO₂ and O₃ at Helsingborg Norr

| | | NO _x as NO ₂ (µg/m ³) | NO ₂ (µg/m ³) | | O ₃ (µg/m ³) | |
|-------------|-------------|--|---|------------------|--|------------------|
| | | Malmö Rådhuset | Malmö Rådhuset | Helsingborg Norr | Malmö Rådhuset | Helsingborg Norr |
| 2018 | Mean | 15 | 12 | 16 | 60 | 59 |
| | Max | 242 | 86 | 108 | 165 | 134 |
| 2019 | Mean | 12 | 10 | 16 | 60 | 60 |
| | Max | 194 | 87 | 105 | 177 | 141 |

For the amine modelling, we must use data from Malmö Rådhuset because of the need for NO_x, NO₂ and O₃ data. As can be seen from the table above, the NO₂ mean and max values are significantly higher at the measurement station Helsingborg Norr than at Malmö Rådhuset. Higher NO₂ concentration may cause higher nitramine formation in the atmosphere. The main formation will occur near stack outlet more than 85 m above ground, and therefore high above and far from road sources. This means that both the Malmö Rådhuset and Helsingborg Norr background data probably represent conservative NO₂ data.

Nitrosamines and nitramines

Background concentrations are not available.

7.2.5 Terrain and surface roughness

AERMOD modelling have been performed with no (flat) terrain. The meteorology data for the NO₂ modelling (AERMOD) was based on surface roughness values for 12 sectors. Nitrosamine and nitramine (ADMS) modelling have been performed with no (flat) terrain. Surface roughness was chosen to 0.1 for the meteorology data site and 0.5 for the source site.

7.2.6 Grid and receptors

Grid resolution for the NO₂ modelling (AERMOD) is 50 m. Grid resolution for the nitrosamine and nitramine (ADMS) modelling is 100 m and grid extent 20x20 km.

7.2.7 Meteorology and dispersion

There are no relevant measured meteorology data at the site. Trinity (supplier of AERMOD and meteorology data) proposes to use meteorology data from Ängelholm airport approx. 25 km north/northeast of Filborna EfW plant. Data for both 2018 and 2019 have been used for the NO₂ dispersion modelling.

The figure below shows wind roses.

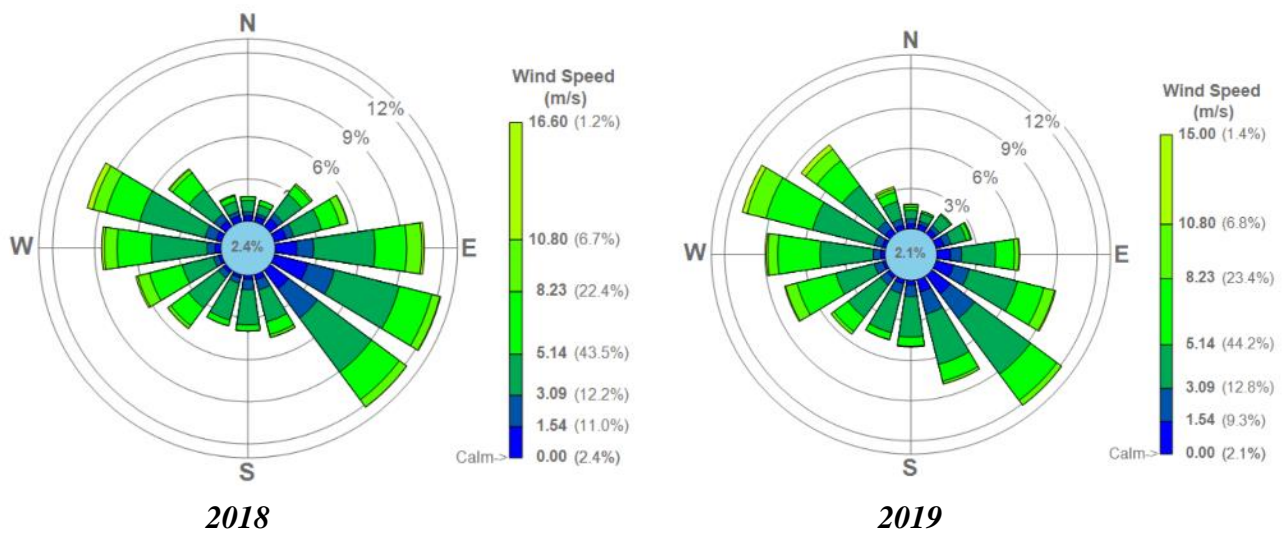


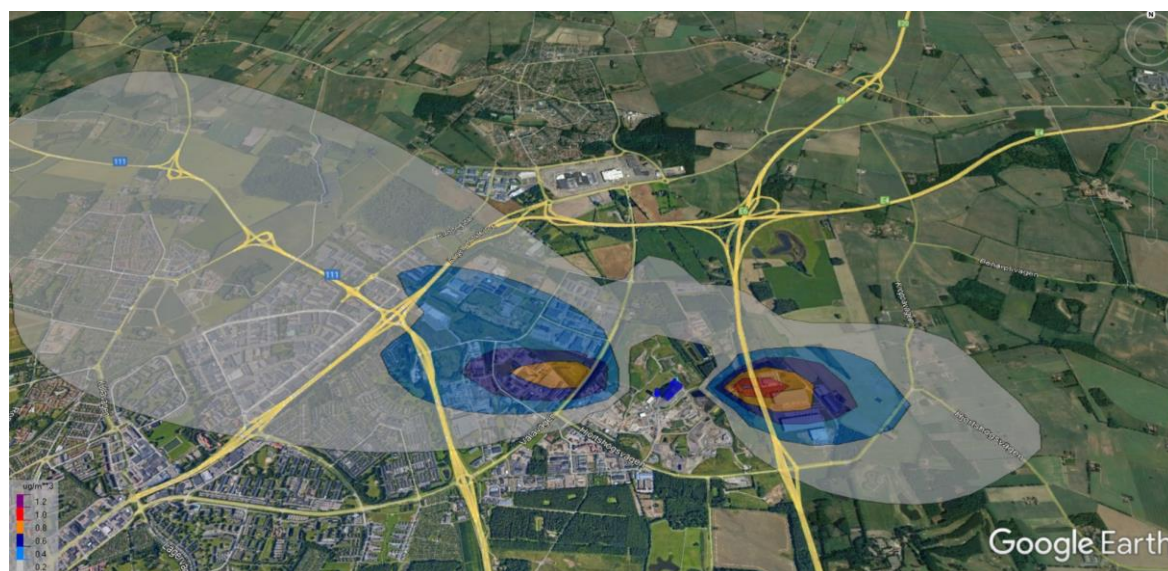
Figure 6 Wind roses for Ängelholm airport, 2018 and 2019

8 Dispersion modelling results

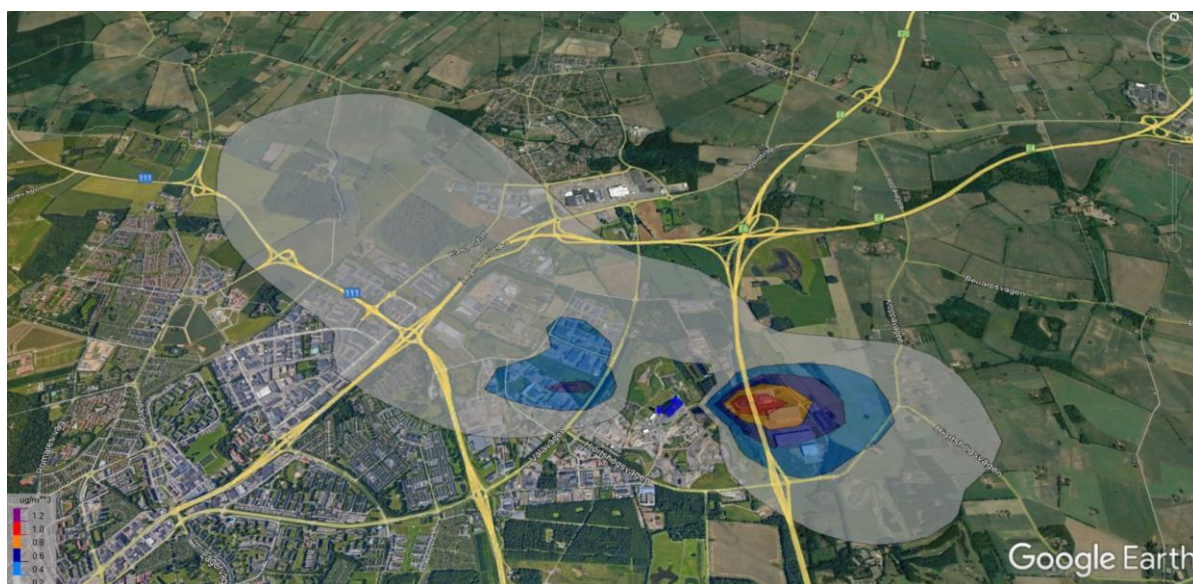
8.1 Annual NO₂ concentrations

Modelling of annual NO₂-concentrations was used to find worst-case meteorology year (2018 or 2019) and worst-case locations (alternative 1 or alternative 2) for the carbon capture plant.

The figure below shows results for location alternative 1.



2018



2019

Figure 7 Annual NO₂ contributions (all NO in the emission assumed to be oxidized NO₂). Carbon capture plant location alternative 1 (close to the northeast corner of the EfW plant)

The figure below shows results for location alternative 2.



2018



2019

Figure 8 Annual NO₂ contributions (ug/m³) (all NO in the emission assumed to be oxidized NO₂). Carbon capture plant location alternative 2 (southeast of the EfW plant)

The model results showed that worst-case location for the carbon capture plant is alternative 1 (close to the northeast corner of the EfW plant). At this location, the max annual NO₂-contribution was 1.2 ug/m³ both in 2018 and 2019. Alternative 2 gave max annual NO₂-contribution below 0.6 ug/m³ for 2018 and 2019.

8.2 Annual nitrosamine and nitramine concentrations

The table below shows maximum annual nitrosamine and nitramine concentration contributions modelled with 2018 meteorology and background concentrations.

Table 10 Maximum annual nitrosamine and nitramine concentration contributions

| | Maximum annual concentration (ng/m ³) |
|------------------------|---|
| Nitrosamine | 0.120 |
| Nitramine | 0.104 |
| Nitrosamine+ Nitramine | 0.211* |

*Maximum sum nitrosamine+nitramine occurs at other location than maximum nitrosamine and nitramine

Modelled nitrosamine+nitramine concentration contribution was 0.21 ng/m³ (see the table above). This is about 2/3 of the NIPH air quality guideline value and slightly above the English EAL value.

The figure below shows contour plots of the total nitrosamine+nitramine concentration contribution.

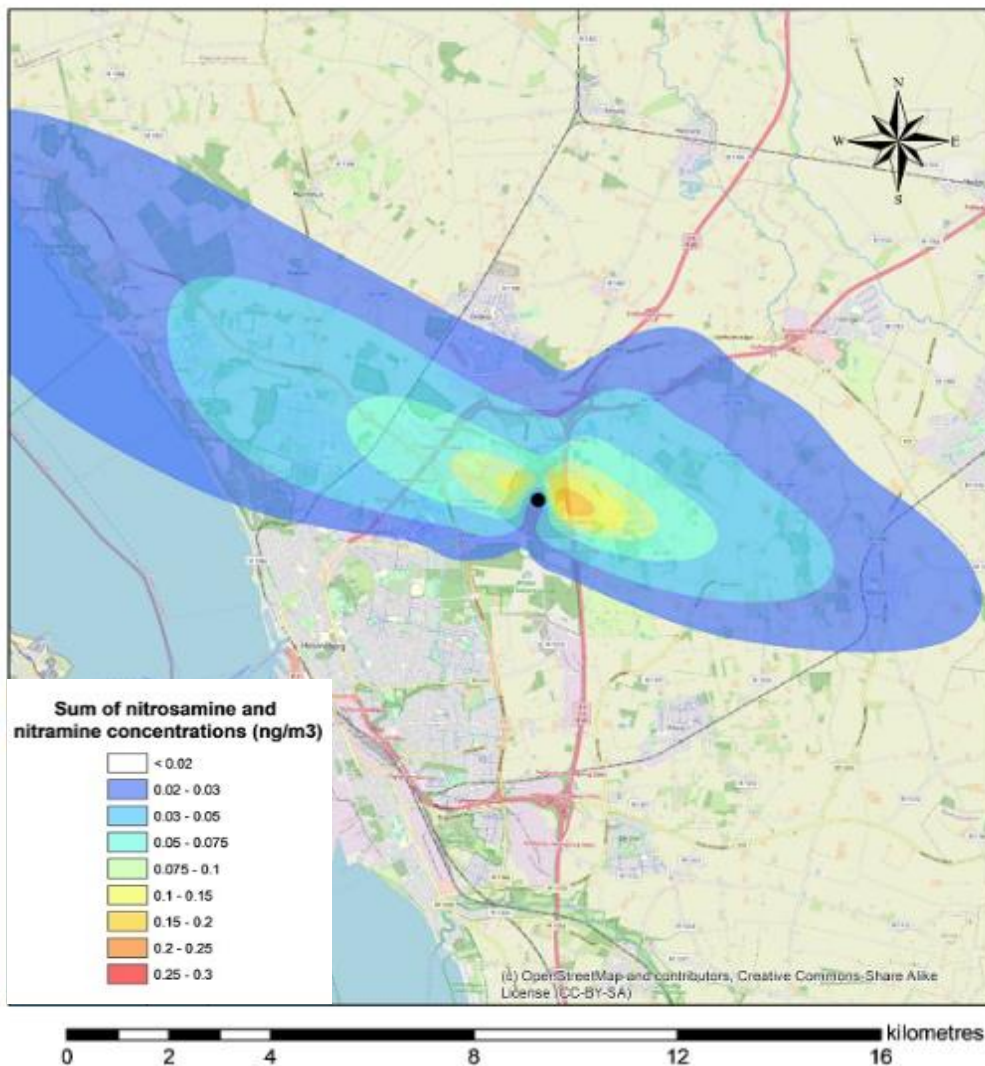


Figure 9 Annual nitrosamine and nitramine concentration contributions (ng/m³). Carbon capture plant location alternative 1 (close to the northeast corner of the EfW plant)

Annual nitrosamine and nitramine concentration contributions are above 0,2 ng/m³ until 1-1,5 km east of the plant.

9 Suggestions for further work

Assessment of deposition and drinking water impacts is recommended.

Further work could also include the following:

- further amine dispersion modelling using additional meteorology year
- further dispersion modelling using other stack parameters and NO_x and amine emission

10 Uncertainty

Concentration

The uncertainty using dispersion models is related to the following conditions:

- Quality of input data: Emission data, meteorology data, receptor data and terrain data
- Scope: Highest short-term average value, short-term average value at a specific location or annual average value at a specific location.
- Mathematical formulas in the model: How well the formulas in the model describe reality
- Inherent uncertainty: uncertainty due to the fact that the dispersion varies under the same meteorological conditions

The US EPA Guideline on Air Quality Models (2005) lists the following about uncertainty in the dispersion models including AERMOD (this will also apply to ADMS):

- the models are better suited for estimating average concentrations for longer periods than for estimating short-term concentrations at specific locations;
- the models are reasonably reliable in estimating the magnitude of the highest concentrations that occur once, somewhere within a range (errors of the highest estimated concentrations of ± 10 to 40 percent are found to be typical);
- calculated concentrations at a particular hour are poorly correlated with actual observed concentrations and have high uncertainty;
- uncertainty of five to ten degrees in the measured wind direction transporting the plume can result in concentration errors of 20 to 70 percent for a specific time and place, depending on stability and the location of the station. Such uncertainties do not mean that estimated concentration does not occur, but that time and place for it are uncertain;
- The US EPA has estimated that even for a perfect model, inherent uncertainty alone can result in typical deviations from true concentration of up to $\pm 50\%$

Model validation for AERMOD: <https://www.epa.gov/scram/air-quality-dispersion-modeling-preferred-and-recommended-models#aermod>

Model validation for ADMS: <http://www.cerc.co.uk/environmental-software/model-validation.html>