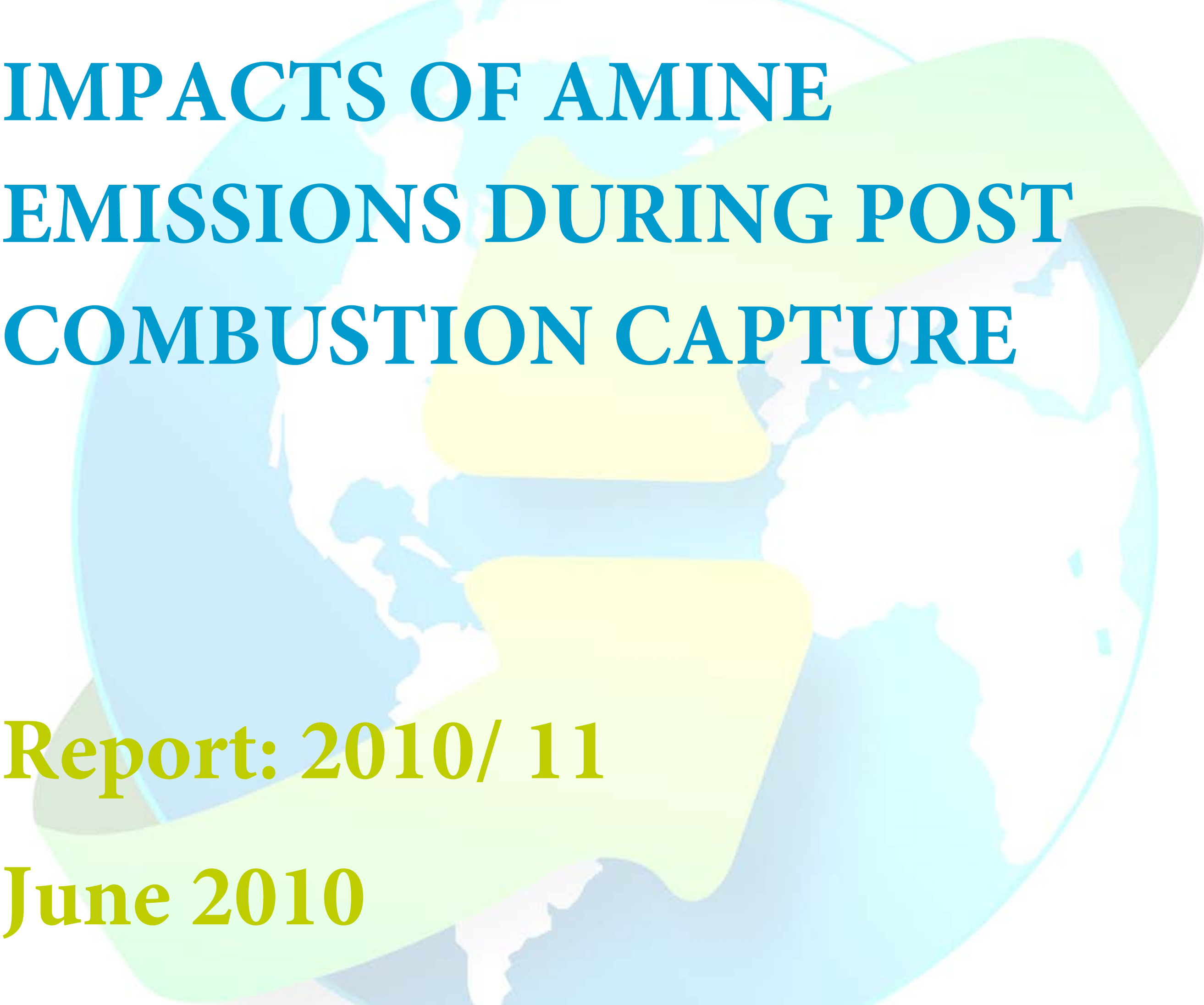


ENVIRONMENTAL IMPACTS OF AMINE EMISSIONS DURING POST COMBUSTION CAPTURE

Report: 2010/ 11

June 2010

INTERNATIONAL ENERGY AGENCY

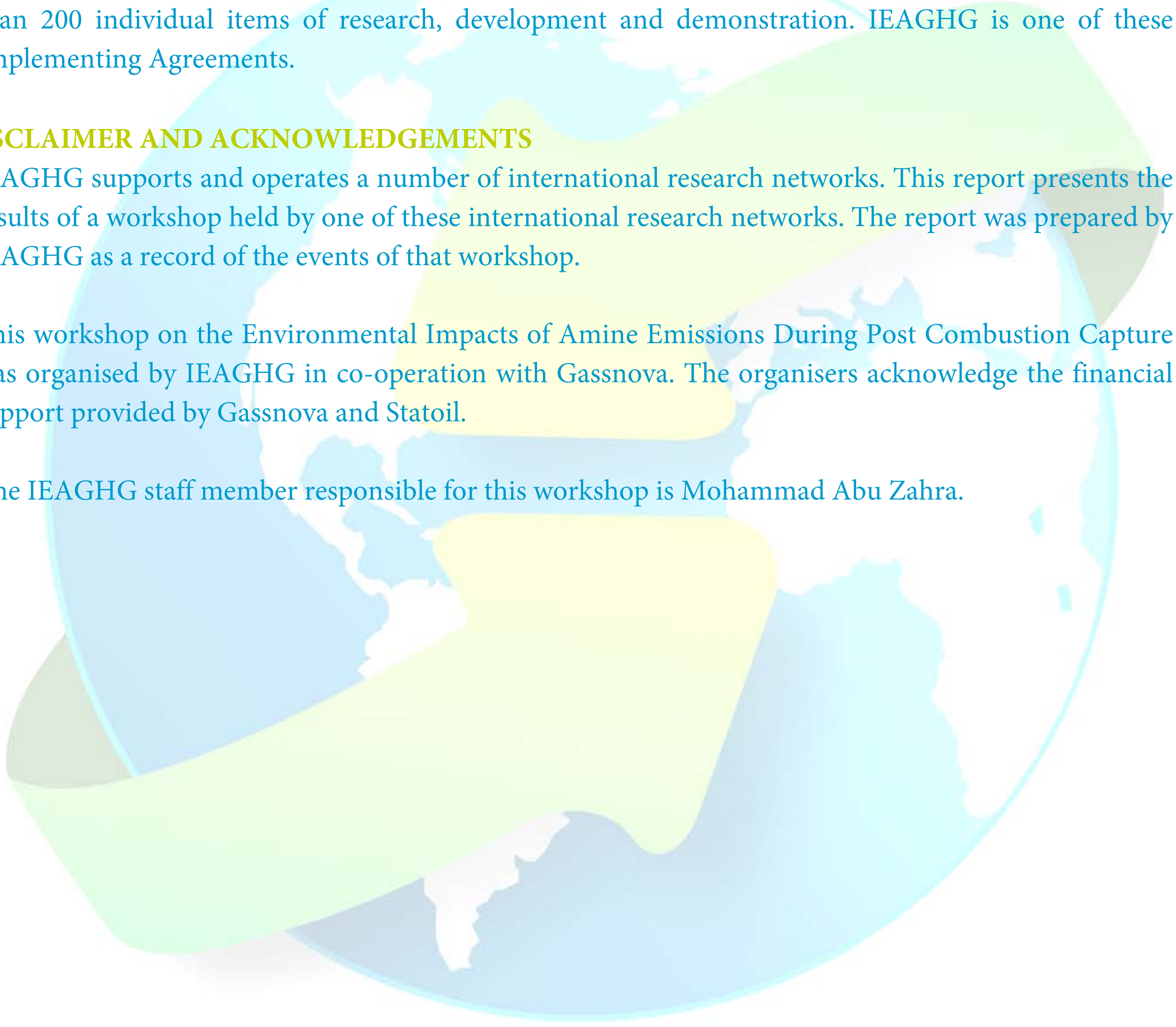
The International Energy Agency (IEA) was established in 1974 within the framework of the Organisation for Economic Co-operation and Development (OECD) to implement an international energy programme. The IEA fosters co-operation amongst its 28 member countries and the European Commission, and with the other countries, in order to increase energy security by improved efficiency of energy use, development of alternative energy sources and research, development and demonstration on matters of energy supply and use. This is achieved through a series of collaborative activities, organised under more than 40 Implementing Agreements. These agreements cover more than 200 individual items of research, development and demonstration. IEAGHG is one of these Implementing Agreements.

DISCLAIMER AND ACKNOWLEDGEMENTS

IEAGHG supports and operates a number of international research networks. This report presents the results of a workshop held by one of these international research networks. The report was prepared by IEAGHG as a record of the events of that workshop.

This workshop on the Environmental Impacts of Amine Emissions During Post Combustion Capture was organised by IEAGHG in co-operation with Gassnova. The organisers acknowledge the financial support provided by Gassnova and Statoil.

The IEAGHG staff member responsible for this workshop is Mohammad Abu Zahra.



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'IEAGHG, "Environmental Impacts of Amine Emissions During Post Combustion Capture Workshop, 2010/11, June, 2010.'

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Workshop on Environmental Impact of Amine Emission during Post-Combustion Capture:

Report on Meeting

16th February 2010, Hotel Folketeateret, Oslo, Norway

Executive Summary

The amine post combustion capture technology is based on washing the flue gas with a solvent that captures CO_2. Thus, a small fraction of this solvent will be released through the stack together with the cleaned flue gas. This release may cause environmental concerns both directly and indirectly through subsequent solvent degradation into other substances in the atmosphere. There is a clear lack of understanding of the characteristics of the used solvent and their degradation products, which are an additional concern. From the global prospective, it is clear that the activities in relation to this topic are limited and there is a clear need for cooperation and knowledge exchange between the different institutes. Therefore, the "Environmental Impact of Post Combustion Capture" workshop was held, primarily to share information on the environmental effect of using chemical solvents for capturing CO_2, associated with conventional combustion based fossil fuel fired power stations.

Considering the above mentioned motivation, a workshop with the following objectives was organised:

- To give an overview of the current ongoing environmental impact activities,
- A starting point to define gaps of knowledge and R&D areas of interest,
- An opportunity for the different active groups to meet and to discuss the related environmental issues,
- To build the basis for a future detailed IEAGHG study on the environmental impact of post combustion capture, the first activity for follow up workshops or symposiums

The workshop was organised by the IEAGHG in partnership with Gassnova SF, Norway. The objective was to bring together researchers and industry involved in post combustion capture of carbon dioxide to discuss the expected environmental impact of large scale deployment of this technology, the current ongoing activities in relation to this topic and to share knowledge, experience and future plans. The programme of the meeting consisted of four oral presentation sessions, which covered the following topics:

- Post combustion capture plant: chemistry inside the plant, amine emission control, main sources of amine emissions and by products.
- Post combustion capture life cycle analysis and general environmental impacts.
- Experimental results of capture pilot plants with real flue gas.
- The expected emissions of the currents technologies and the progress on the technologies development.
- Atmospheric chemistry and dispersion.
- Effects and impact on the environment.

There was clear interest in joining the workshop and the number of participants (68 delegates) was limited to the capacity of the venue. This increasing interest in the environmental impact of post combustion capture makes it one of the important topics to focus on in the future activities for IEAGHG.

There was a general consensus at the workshop to continue working on this topic and to monitor the regulations and technologies development lines. However, it was agreed to include the environmental impact workshop activities within the international capture network, which will be extended to a full post combustion capture conference and will be held in the spring of 2011.

Contents

WORKSHOP ON ENVIRONMENTAL IMPACT OF AMINE EMISSION DURING POST COMBUSTION CAPTURE:

REPORT ON 1st Meeting

(16th February 2010, Hotel Folketeateret, Oslo, Norway)

1 Background

Amine based post combustion CO_2 capture is considered to be the most mature of the capture technologies available today. The technology is based on washing the flue gas with a solvent that captures CO_2. Thus, a small fraction of this solvent will be released through the stack together with the cleaned flue gas. This release may cause environmental concerns both directly and indirectly through subsequent solvent degradation into other substances in the atmosphere. The expected emissions of amines, additives and their degradation products with flue gas stream and waste product streams are continued concerns for the deployment of full scale CO_2 post combustion capture using amines.

There is a clear lack of understanding in the characteristics of the used solvent and their degradation products, which are an additional concern. From the global prospective, it is clear that the activities in relation to this topic are limited and there is a clear need for cooperation and knowledge exchange between the different institutes.

The "Environmental Impact of Post Combustion Capture" workshop was held, primarily to share information on the environmental effects of using chemical solvents for the capture of CO_2 associated with conventional combustion based fossil fuel fired power stations.

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- An opportunity for the different active groups to meet and to discuss the related environmental issue,
- To build the basis for a future detailed IEAGHG study on environmental impact of the post combustion capture and be the first activity for follow up workshops or symposiums.

The workshop was organised by the IEAGHG in partnership with Gassnova SF, Norway. The objective was to bring together researchers and industry involved in post combustion capture of carbon dioxide to discuss the expected environmental impact of large scale deployment of this technology, the current ongoing activities in relation to this topic and to share knowledge, experience and future plans.

This report contains summaries of the presentations on a variety of developments including updates on amines, use of ammonia as a solvent, ionic liquids, solid sorbents, pilot plant and demonstration projects, modelling activities and environmental impacts of post combustion capture. In addition, the overall meeting evaluation and the major learning points from the meeting are summarised at the end of the report.

2 Programme

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- Post combustion capture life cycle analysis and general environmental impact.
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- Atmospheric chemistry and dispersion.
- Effects and impact on the environment.

3 Presentations Summaries and Discussion

3.1 Welcome and introduction, Klaus Schöffel, Gassnova SF, Mohammad Abu Zahra, IEAGHG

The meeting was opened by Klaus Schöffel, who welcomed the delegates on behalf of Gassnova the host, extended thanks to the delegates, sponsors and speakers of the workshop for sharing their knowledge of the work currently undertaken around the world on the environmental impact of amine emissions during CO_2 post combustion capture and hoped that the workshop would be beneficial, and include meaningful discussions.

Mohammad Abu Zahra welcomed the delegates on behalf of IEAGHG and hoped for a fruitful and interesting workshop. Following this Mohammad gave a short introduction to the IEAGHG, explaining the background of the programme and its members and sponsors. The background and origination of the workshop was explained, touching briefly on the main aims of the workshop and the reasons for international activity in the environmental impact of amine emissions during CO_2 post combustion area. The interest of the workshop was high. Some 70 delegates from 15 countries joined the programme with more than 40% of the delegates coming from Norway.

Mohammad thanked the sponsors for the financial support of the workshop and the organising team from Gassnova and IEAGHG for their efforts.

3.2 Amine to air-problem description, Svein Knudsen, NILU

Svein discussed a worst case study for a possible amine plant in Norway and identified challenges due to possible reactions between the amine, flue gas and air. The importance of a holistic understanding of the whole reaction chain/emission system was emphasised. That starts from the amine being specified and supplied until the reaction products are seen in the emissions to air and/or water with the possible biological consequences and waste production/disposal.

Detailed knowledge about the different elements in the reaction is currently missing. For instance the chemical processes in the air, water, soil and transport between these compartments as well as effects on nature are uncertain. Also, the level of emissions needs to be quantified. Moreover, there is a need to distinguish between accumulating and non-accumulating toxic substances and the more long term acute toxic substances. The critical environmental loads relating to toxicity need to be found to ensure an acceptable risk level. Further, the global consequences of these releases need to be evaluated to be able to put CCS in context. Possible consequences of accidental releases also have to be looked into.

The knowledge concerning environmental loads caused by the different substances needs to be understood to find environmentally friendly amines. For this, necessary critical loads, methodologies and tools to test the amines and evaluate their environmental impacts need to be in place. It is probably not the mother amine that causes the problem and one single CCS plant is not expected to have a major influence.

3.3 Flue gas degradation of amines, Steinar Pedersen, Statoil

Steinar presented work on the flue gas degradation of amines, which is part of a current research program managed by Statoil. Considering the current status of the degradation products; CO_2 and O_2 degradation are well described, but on NO_x degradation there is hardly any related work being reported. Therefore, the scope of this program was defined to identify the degradation products generated in the absorber and decide on the emissions to air and water. To be able to perform the research Statoil needed to develop methods for sampling and analyses.

A simple test rig without a stripper was used for the testing. The test protocol was briefly presented in the seminar, which depends on varying the flue gas and solvent composition, gas/liquid ratio, absorber reaction conditions, water wash conditions and stripper conditions. All these parameters were varied to be able to get a better understanding of the influence caused by, among others; the amount of O_2, CO_2, NO_x and the degree of water wash.

The results showed that ammonia is the primary degradation product of MEA and its' production is strongly correlated with NO_x concentration in the flue gas. Moreover, the tests concluded that there was a correlation between the amount of NO_x and nitrosamine formation. Nitrosamines were found with NO_x levels between 25 - 50 ppm, but without NO_x, no nitrosamines were detected. Temperature dependence was tested in a separate autoclave experiment and showed that increasing the temperature enhances the formation of nitrosamines. Experiments were not designed to run under real process conditions, but were used to show what type of compounds can be formed. Water wash showed a good effect on reducing the MEA slip, while MMA (monomethylamine) passed more or less unaffected through the water wash.

The solvents used for CO_2 capture need to be evaluated or replaced at intervals to be able to control the formation of harmful compounds. In addition, the solvent degradation problems could be reduced by reducing the NO_2 in the flue gas with some monitoring and control techniques.

3.4 Environmental impacts of emissions from post combustion CO_2 capture, Moetaz Attalla and Merched Azzi, CSIRO

Attalla and Azzi from CSIRO presented their different test programmes, facilities and ongoing activities. CISRO is carrying solvent and emissions research programme with the objectives to; understand the oxidative mechanisms of amine degradation, understand the fate of slipped amines and amine degradation products, determine whether amines form nitrosamines and under which conditions, develop appropriate solution-based mitigation strategies and to understand the environmental impact of amine slip. CSIRO performs complete tests of the whole emission chain. Different amines are tested in lab scale absorption/desorption unit. Nitrosamines were not found with primary amines. However, the mono- and di-nitroso derivatives of piperazine were detected in a 15 wt % solution exposed to synthetic flue gas. The researchers also detected the nitramine derivative of piperazine, in addition to the nitroso derivative of DEA, in solutions exposed to synthetic flue gas. The thermal and ultraviolet stability of the nitroso piperazine derivatives were also explored. The researchers showed the nitroso piperazine's thermal stability at stripper conditions (approximately 160 °C) and typical propensity to degrade upon exposure to ultraviolet light.

The need for better understanding of the chemistry of degradation under real flue gas conditions was stressed. In addition, emissions' monitoring for both parent amine and degradation products is a necessity for extended operation of the solvent. Moreover, the effectiveness of current de-NOx technologies needs to be evaluated and determined.

The photo-degradation of MEA was presented as a study case, which was tested in the CSIRO smog chamber facilities and the dispersion of the releases is evaluated in Air Quality Models (AQM). It was shown that the smog chamber could be used for photo degradation of MEA and that the experiments could be performed in a controlled and repetitive way. This project is in its final stages and the presented results in this workshop were preliminary and no conclusions have been drawn at this stage.

The primary emissions need to be clearly defined together with meteorology/topography to have a clear input to the Air Quality Models (AQM). The chemical transformation of the substances found in the smog chamber is an important input to the model. The AQM needs to be run several times with representative data for all seasons and will define the secondary products such as ozone’s, aerosols and other air toxics, which will lead to dry and wet deposition.

3.5 Atmospheric chemistry of amines: a critical element of EPRI’s research on the environmental impacts of future electric sector emissions, Eladio Knipping, EPRI

The objectives of the research programme on health and environmental impacts of EPRI are to evaluate the potential human health and environmental impacts related to the future combustion-based generation options and to provide the designers and engineers with the knowledge to be able to mitigate environmental problems early in the development process.

To be able to achieve this EPRI has systematically screened all the possible problems and gathered information on the emission control already known. Moreover, to get an understanding of the experience so far, field measurements on relevant plants were planned for. EPRI has evaluated amines in air and particles and concluded that amines will remain connected to particles. Further exploration of particles and products is planned started in 2010.

In this work, it was found that oxidation of tertiary amines formed significant aerosol whereas oxidation of secondary or primary amines did not form significant aerosol. Major emphases were made on the importance to gather data for risk and vulnerability assessments, toxicological studies, field experiments, chamber experiments and chemical mechanism and model development.

3.6 Atmospheric Degradation of Amines (ADA): Gas phase photo-oxidation of 2-aminoethanol (MEA), Claus Nielsen, University of Oslo

The atmospheric gas phase photo oxidation of MEA was studied at the European Photochemical Reactor (EUPHORE) in Valencia. The objective was to identify the atmospheric photo-oxidation products of MEA under relevant NO_X conditions.

Aerosol formation was tested using experiments with 100-700 ppbV MEA, which resulted in an increase in total aerosol mass up to 230 µg/m^3. The observed chamber aerosol mainly consisted of secondary organic salt particles and to a lesser extent non-salt organics. These particles resemble ethanolammonium nitrate, but there are clearly other compounds present.

It was found that the major products (> 80 %) in the photo-oxidation were formamide and formaldehyde, of which the latter has a short atmospheric lifetime. Minor products (<10%) were the short-lived amino acetaldehyde and the longer-lived 2-oxo acetamide. Nitrosamines from MEA were not detected in any of the experiments. On the other hand, a small amount of the MEA nitramine was identified and quantified.

The full results were presented in a report and now available from http//ada.nilu.no

3.7 Emission measurements at Dong's pilot plant for CO_2 capture in Esbjerg-EU project CESAR, Eirik da Silva, SINTEF-CESAR

The CESAR project aims for a breakthrough in the development of low-cost post-combustion CO_2 capture technology to provide economically feasible solutions, with a major objective to demonstrate a CCS technology with a capture cost of 15 Euro per tonne CO_2. The CESAR project was built on the findings from the CASTOR project and is using the pilot plant in Esbjerg as a demonstration facility. The Esbjerg pilot plant was built in 2005 with a capacity of 5000 m^3/h or 1 tonne CO_2/h. The pilot plant was designed based on the commercial CO_2 capture technology using MEA solvent and an absorption unit with the height of 34.5 m and 1.1 m diameter.

A test with MEA was performed during the spring of 2009. Emission sampling was carried out after a test run time of 700-800 hours. Standard measurements in and out of the absorber were performed and pH in the wash water was measured. It was stated that it was a challenge to get representative samples. Standard analytical reference methods (ISO, VDI, MEL, etc) were used for the chemical analysis.

The chemical analysis targeted various interesting compounds in both the gas and liquid phases (e.g. MEA, DEA, Aldehydes, and Ammonia). The results from the emission measurements 1 are shown in the table below.

Compound	Unit	Inlet absorber	Outlet absorber	Outlet absorber after water wash
MEA	mg/Nm^3	<0.1	0.7	<0.3
DEA	mg/Nm^3	<0.2	<0.3	<0.2
Formaldehyde	mg/Nm^3	<0.1	0.7	<0.1
Methylamine	mg/Nm^3	<0.2	<0.3	<0.2
Acetamide	mg/Nm^3	<0.6	<1.0	<1.0
Ammonia	mg/Nm^3	<0.1	23	20

The tests found the formation of ammonia and degradation products in the wash water treatment and proved that the water wash works well in reducing the amount of MEA and formaldehyde in the emitted flue gas. The detected degradation products in both the liquid and gaseous phases were typical of oxidative degradation of MEA.

The bubble cap has a positive effect on the emissions by reducing the amount of MEA and formaldehyde in the flue gas leaving the absorber. The absorber column has an overall positive environmental effect by reducing the amount of metals, dust and SO_2 in the emitted flue gas.

New tests with alternative amines will start in the spring of 2010.

3.8 Information requirements for the environmental impact assessment (EIA) process, Fredrik Weidemann, Norwegian Pollution Control Authority (Klif)

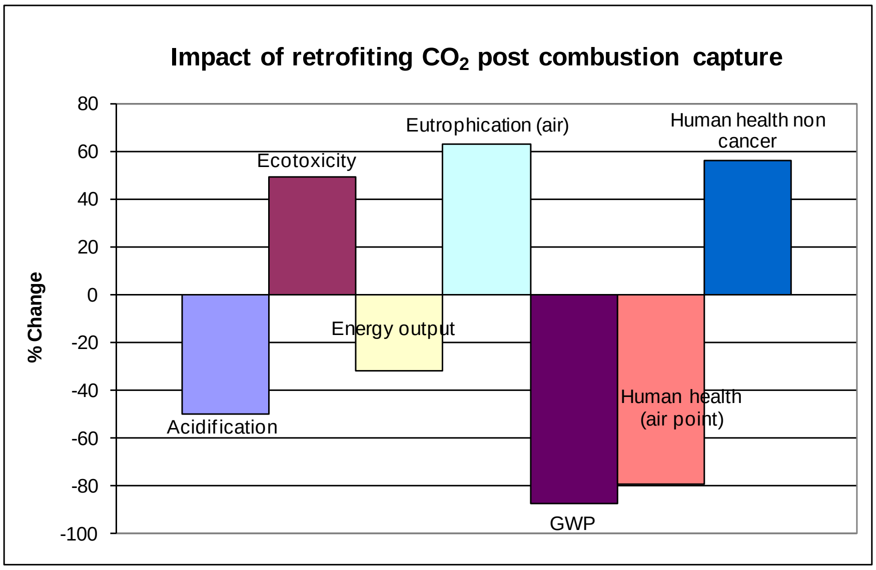
A thorough description of the formal public process connected to obtaining discharge permits for post-combustion amine plants in Norway was given by Fredrik Weidemann from Klif. Klif welcomes CCS but works actively to avoid introducing new environmental problems. Therefore, an environmental impact assessment is needed to quantify and qualify the description of all emissions; describe the receipt (air, water and ground); describe the distribution and deposition of the emitted substances; evaluate the possible degradation products and study the impact of these emissions and products on the environment and public health.

It was stated that the issued Environmental Impact Assessments (EIAs) on post-combustion capture in Norway being evaluated by Klif have been uncompleted due to limited information about solvent composition, degradation products and environmental impact data. It is the technology vendor's responsibility to convey this information to the site owner which in turn will present it to the authorities as part of the EIA report. In Norway information about health and environmental risks shall be publicly available. All chemicals imported and used in Norway must be registered in the "Product Register". Limited access to confidential information is an option. The EIA work shall be based on existing information, however, lacking information shall be identified and necessary research initiated. A question was raised who is responsible for carrying out research to fill the data gap. The site owner is responsible towards the authorities, but the technology owner must contribute with technology and solvent specific research. From the audience it was mentioned that a thorough program on amine HSE evaluations has just recently been initiated by GassnovaSF/Statoils Mongstad full scale capture project which is now in planning.

3.9 Environmental impacts of post combustion capture: Case study of SaskPower's Boundary Dam Power Station, Jitsopa Suebsiri, University of Regina

This presentation was based on a life-cycle assessment (LCA) approach to evaluate the environmental impact of post-combustion carbon capture. A LCA study of CCS system consisting of coal mining, an 882 MW power plant with post-combustion capture, CO_2 transport and CO_2 EOR operations and storage has been completed. Three scenarios were studied: i) Power plant without capture, ii) retrofit of 1 out of 6 units (150 MW out of 882 MW) with CO_2 capture and iii)carbon capture for the whole power plant. The detailed results were presented with graphical comparison of the three scenarios (see example overleaf).

It was identified that the energy consumption for capture and storage was estimated to 33 % of the total output of the power plant. Different impact assessment methods (TRACI, CML, EDIP) were used to illustrate that impact categories can give different results with different methods. Thus it is important to use more than one method when studying LCA impact assessment and to carefully interpret and communicate the results of such a study.



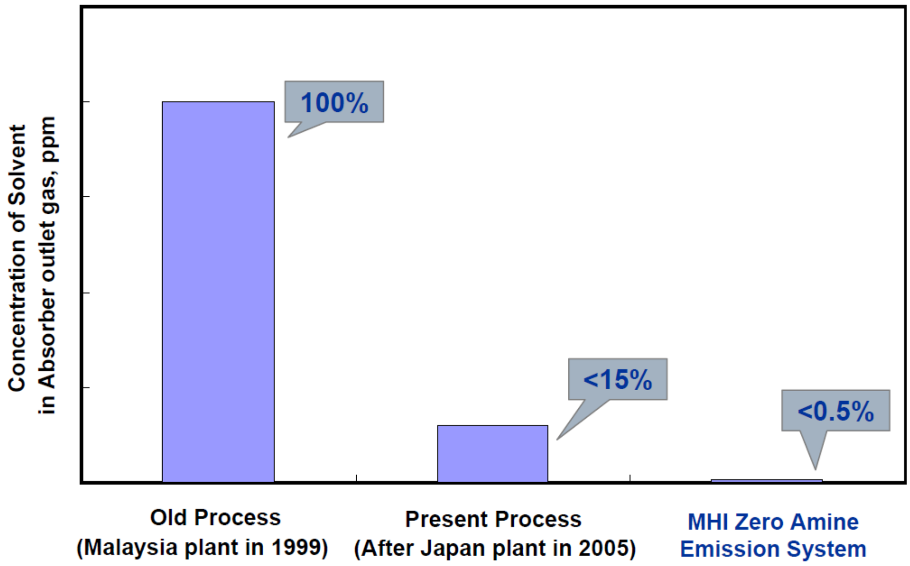
3.10 Comparison of emission profile between conventional amine and amino acid based systems, Henk Trap, TNO

Henk introduced his presentation on how we as humans perceive risk. Those small constituents which we do not see and have very limited knowledge about are often believed to be the ones subject to the highest risk. This is highly valid also for amines, amino acids and their degradation products. This is because of the lack of knowledge about what happens with the chemicals in the process and after they have been emitted and also the toxicity of all these different chemical compounds.

Sensing techniques, both online and off-line, were presented. The importance of sampling and analysis techniques was stressed because what is found during sampling and analysis of chemical compounds is highly dependant on the techniques applied. A specific 3D plot of analysis results based on MEA with a GCxGC-ToF-MS was presented as a promising method for analysis of minor constituents in the emission amine based CO_2 capture. The announced comparison between amines and amino acids was not successful due to lack of data primarily for the amino acid salts-based solvents. However, the tools to find the missing data are available as soon as the search for data is initiated.

3.11 MHI amine emission control technology, Takashi Kamijo, Mitsubishi Heavy Industries

The MHI's reference CO_2 capture plants, research activities and experiences from commercial plants were presented. In 1994 MHI introduced an optimized packing and demister technology in the absorber column washing section. In the period 1999 to 2008, MHI installed nine commercial plants with this technology, all of them running with the proprietary KS-1 solvent. In 2003, an improved proprietary washing system was developed. They are able to reach 1 ppmv of amine emission, 1.5 ppmv of degradation products and no mist emission with this technology. Also other emission compounds are low. MHI have, however, seen the need for further reduction of amine emissions and have under development a new technology where they introduce a special reagent in the final washing stage in the top of the absorber. A liquid stream subject to waste water treatment is then produced. The target for this new technology (MHI zero amine emission system), which has been tested in pilot scale since 2009 and is expected to be commercial within two years, is to fall below 0.1 ppmv amine and 0.2 ppmv degradation products in the treated off gas. MHI also informed that they have under construction a 500 tonne per day demo plant in the US. The comparison of amine emissions data using MHI technologies with time scale from 1999 is shown in the figure below.



3.12 Econamine FG+ process: recent advances in emissions control, Satish Reddy, Fluor

Fluor has experience from 35 industrial size plants used for producing CO_2 from natural gas for the food industry. The solvent used is Monoethanolamine (MEA).The absorber has advanced internals and the last washing section is used for cooling the off gas to reduce the amine slip. Their largest plant in Bellingham with a capacity of 100,000 tonne/year CO_2 (now dismantled due to limited market for the product), was designed for 1 ppmv amine emission in the flue gas. At present Fluor is developing a new and advanced scrubbing system which will reduce the emission by one order of magnitude. However, these systems with lower emissions can result in a minor increase of OPEX. In addition, the pressure drop will increase with 15-20 mbar. This technology will be tested in 2011 in a unit now under construction connected to a coal-fired power plant at Wilhelmshaven, in cooperation with the German energy producer E-ON. Fluor is also improving the reclaimer waste production and disposal. They can offer two different reclaimer waste treatment technologies, one based on incineration and the other based on ion exchange.

Satish in his presentation stressed the need for the authorities to set target levels of amine emissions, and then vendors can endeavour to design systems to meet this target.

3.13 Emission measurement and analysis from mobile CO_2 capture test facility, Oscar Graff, Aker Clean Carbon

The company Aker and its subsidiaries were presented together with the history of carbon capture within the company. Aker Clean Carbon (ACC) is involved in extensive R, D&D programmes including among others, Mongstad, BigCO2 and SOLVit. Moreover, their Mobile Test Unit (MTU), being 20% of the Esbjerg testing facility, has now been run in three different campaigns using MEA as the primary solvent; one at Risavika in Norway connected to a gas-fired turbine (4% CO_2) and two consecutive ones (12% CO_2) at Longannet in Scotland downstream a coal-fired power station.

Representative sampling to be able to measure emissions at the top of the absorber is challenging but has been improved over the three campaigns. A special focus has been on the formation of nitrosamines and other emission products. No nitrosamines were measured at Risavika, while at Longannet (MTU emission campaign 3) such compounds were identified in 4 out of 10 test runs. Analysis of the supplied amine revealed that unused industrial grade amine contained nitrosamine. Moreover, the ammonia was detected in low levels in Risavika campaign (below 5 ppm and in higher levels at Longannet (>50 ppm).

In this presentation, Oscar discussed the sampling and analytical methods as important parameters in receiving realistic and reliable results. Having the emissions compounds at very low levels will make detecting and analysing them very challenging. In addition, the use of different sampling and analytical methods will result in different results. Emission control has been improved by introducing acid to the final washing stage at the absorber top. It was announced that the Tiller test facility in Trondheim, Norway is to be opened in April 2010.

As a conclusion from the technology vendors' presentations it can be stated that the vendors are ready to introduce amine emission reduction measures. They are waiting for a target value from decision makers, i.e. the authorities and site owners.

The workshop was closed and concluded by Mohammad Abu Zahra/IEAGHG, who thanked the delegates and the presenters for their contribution in making this workshop a full success. In addition, Mohammad summarised the major learning points, and knowledge gaps, which requires further attention.

4 What have we learned from the environmental impacts of amine emissions during post combustion capture workshop?

The major learning knowledge, points of discussion, which were raised during the meeting and require further attention, could be summarised as follow:

- The focus of the current environmental impacts activities is mainly on the conventional MEA as a chemical solvent
- Strong opinion was presented from authorities that the available information on the environmental impacts are not enough and more knowledge will be required before allowing capture large-scale deployment
- Evaluating the problem should start with studying the capture process, identify the hot spots and quantify the expected emissions components
- The amine and chemical emissions problem needs to be identified more clearly
- The measured levels/values of emissions should be put in perspective and compared with the safe acceptable levels of emissions
- Quantifying the effect of NO_x and O_2 under real operation conditions is required
- Measuring and quantifying the major emissions and degradation products (e.g. mother solvent, ammonia, formamides, formaldehydes, acetamide, Nitrosamines and nitramines) from the capture plant is very important, and should be done using standardised equipment and procedures
- Special attention needs to be given to the degradation products quantities and composition
- Developed emissions related regulations are missing
- Definition of the emissions level of toxicity and acceptable levels is required
- Emissions measurement and evaluation tools and chemical sampling and analytical techniques require major focus
- A question needs to be answered, if the current available technologies for deep removal of chemicals are sufficient or do we need more improved technologies?
- Pilot plants tests using real flue gases and online measurements for chemical emissions are essential
- It is important not to send fraudulent message to the outside world that there is an environmental impact issue
- Major technologies providers are confident that they have efficient technologies for deep amine removal and cleaning but extra costs might apply

5 Workshop evaluation

5.1 Participants

More than 65 registrants, representing 15 countries – 40% from Norway.

Comments:

- There was clear interest in joining the workshop and the number of participants was limited to the capacity of the venue. This increasing interest in the environmental impact of post combustion capture makes it one of the important topics to focus on in our future activities on post combustion capture.

5.2 Workshop programme

The programme covered different aspects of environmental impacts of post combustion capture and amine emissions. The programme was balanced by introducing experimental results and modelling activities. In addition, the chemical emissions regulations and the development lines of the amines deep removal technologies were discussed.

Comments:

- For the future meeting, it is important to increase the focus on the pilot plant activities and real condition experimental measurements.
- Next meeting should keep track of the development of the chemical emissions regulations and to continue monitoring the new generation technologies for deep removal of chemicals.

6 Next Meeting(s)

The environmental impact of post combustion capture and amine emission is a very important topic. Therefore, there is a general consensus to continue working on such a topic and to monitor the regulations and technologies development lines. However, it was agreed to integrate the environmental impact workshop activities within the international capture network, which will be extended to a full post combustion capture conference and will be held in the spring of 2011.

The nature of the environmental impact session within the post combustion capture conference will be decided on depending on the submitted abstracts and size of interest in this topic. After this first conference, the environmental impact sessions will be evaluated and the option of having it in a separate network will be re-evaluated.

7 Thanks and Acknowledgements

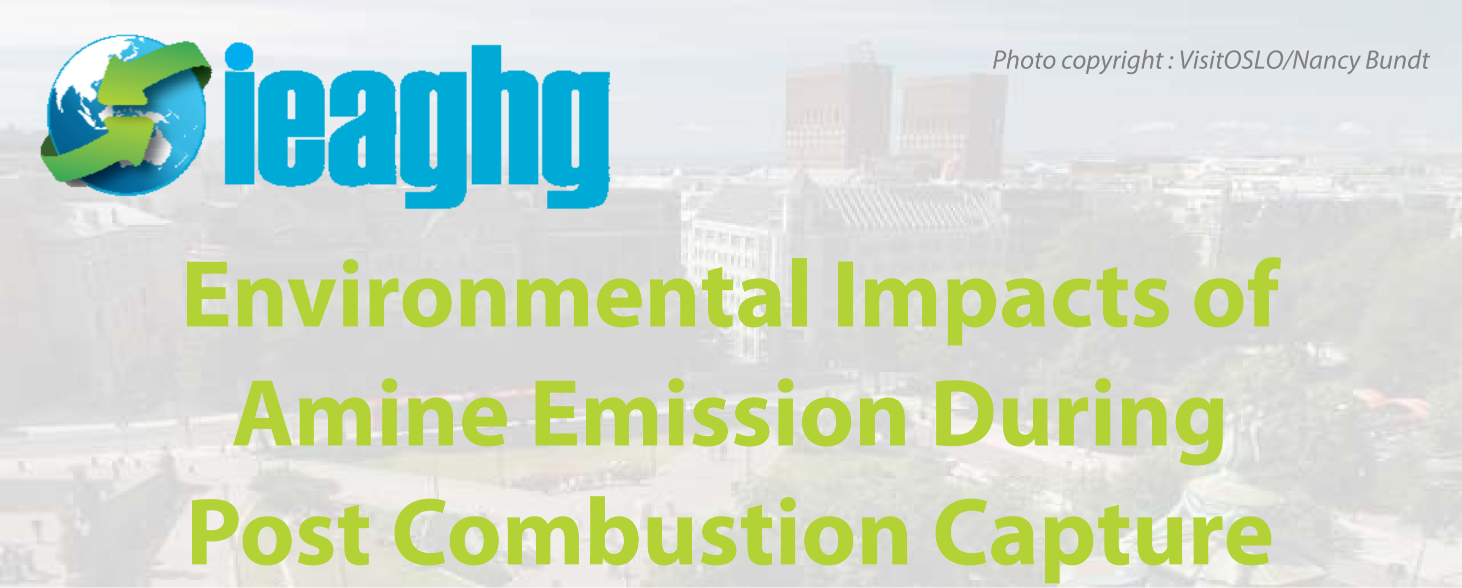
IEAGHG coordinators and all participants wish to thank Erik Gjernes and Klaus Schöffel and the staff of Gassnova for all their hard work in hosting and sponsoring the meeting. Also Statoil are acknowledged for the splendid dinner.

Laila Iren Helgesen and Ola Vebjørn Halden from Gassnova are acknowledged for their help during the workshop for the purpose of preparing this report.

8 Contacting the Co-ordinator

IEAGHG together with Gassnova organised and co-ordinated this workshop. Queries about the workshop or copies of this report can be obtained by contacting:

Mohammad Abu Zahra mohammad.abuzahra@ieaghg.org, Erik Gjernes eg@gassnova.no or mail@ieaghg.org.



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Environmental Impacts of Amine Emission During Post Combustion Capture

16th February 2010

Folketeateret, Oslo, Norway

Organised by
IEAGHG

Hosted by
Gassnova SF

Sponsored by

GASSNOVA

Statoil

16th February 2010

08:30	**Registration and Coffee**
09:00	**Welcome & introduction;** Mohammad Abuzahra/Klaus Schöffel, IEAGHG/Gassnova SF
09:25	Amines to air - problem description; Svein Knudsen, NILU
09:50	Flue gas degradation of amines; Steinar Pedersen, Statoil
10:15	Environmental impacts of emissions from post combustion CO_2 capture; Moetaz Attalla and Merched Azzi, CSIRO
10:40	**Coffee Break**
11:00	Atmospheric chemistry of amines: a critical element of EPRI's research on the environmental impacts of future electric sector emissions; Eladio Knipping, EPRI
11:25	ADA: Gas phase photo-oxidation of 2-aminoethanol (MEA); Claus Nielsen, University of Oslo
11:50	Emission measurements at Dong's pilot plant for CO_2 capture in Esbjerg - EU project CESAR; Eirik da Silva (SINTEF), CESAR
12:15	**Lunch Break**
13:15	Information requirements for the environmental impact assessment (EIA) process; Fredrik Weidemann, Norwegian Pollution Control Authority (SFT)
13:40	Environmental impacts of post-combustion capture: Case study of SaskPower's Boundary Dam Power Station, Saskatchewan, Canada; Anastassia Manuilova, University of Regina
14:05	Comparison of emission profile between conventional amine and amino acid based systems; Henk Trap, TNO
14:25	MHI amine emission control technology; Takashi Kamijo, Mitsubishi Heavy Industries
14:45	**Coffee Break**
15:00	Econamine FG+ process: recent advances in emissions control; Satish Reddy, Fluor
15:20	Emission measurement and analysis from mobile carbon capture test facility; Oscar Fr. Graff, Aker Clean Carbon
15:40	Workshop discussion and closing; Mohammad Abuzahra/Klaus Schöffel, IEAGHG/Gassnova SF
16:00	**Workshop Close**

ATTENDEE LIST

Environmental Impacts of Amine Emission During Post Combustion Capture

16th February 2010, Folketeateret, Oslo, Norway

Name, Organisation	
Mohammad Abu Zahra, IEAGHG	Jan Lambrichts, The Dow Chemical Company
Colin Alie, Environment Canada	Angela Mangiaracina, ENEL s.p.a
Henrik Andersen, Statoil	Sara Mcgowan, Vattenfall Research & Development AB
Moetaz Attalla, CSIRO	William Mitch, Yale University
Merched Azzi, CSIRO Australia	Helle Mostad, Statoil
Otto Morten Bade, Aker Clean Carbon	Takashi Nakamura, JAPAN NUS Co., Ltd.
Randi Bjørklund, Aker Clean Carbon	Sissel Nepstad, TCM DA
Andy Booth, SINTEF Materials and Chemistry	Claus Nielsen, CTCC, University of Oslo
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Odd G Brakstad, SINTEF Materials and Chemistry	Nader Padban, Vattenfall Research & Development AB
Eirik Da Silva, SINTEF Materials and Chemistry	Steinar Pedersen, Statoil ASA
Deepak Deshpande, Shell Technology Norway	Sandra Persson, Rintekno AB
Christian Dye, NILU	Scott Randall, NILU
Lars Ingolf Eide, Research Council of Norway	Satish Reddy, Fluor Corporation
Olav Falk-Pedersen, TCM DA	Bernd Schallert, E.ON Engineering
Erik Gjernes, Gassnova SF	Klaus Schöffel, Gassnova SF
Kazuya Goto, Research Institute of Innovative Technology for the Earth	Jae-Goo Shim, Korea Electric Power Research Institute
Oscar Fr. Graff, Aker Clean Carbon	Merethe Sjøvoll, Statoil
Ola Vebjorn Halden, Gassnova SF	Ole Kristian Sollie, Det Norske Veritas
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Karl Anders Hoff, SINTEF Materials and Chemistry	Vibeke Talstad, Statoil
Richard Hotchkiss, RWE npower	Linda Tangen, Statoil RD
Jon Hovland, Tel-Tek	Nathalie Thybaud, ADEME
Takashi Kamijo, Mitsubishi Heavy Industries Ltd.	Henk Trap, TNO
Matthias Karl, NILU, Norwegian Institute for Air Research	Frederik Weidemann, Climate and Pollution Agency
Atsushi Kato, Mitsubishi Heavy Industries Europe, Ltd.	Armin Wisthaler, University of Innsbruck
Eladio Knipping, Electric Power Research Institute	Kristina Wittmeyer, TCM DA
Svein Knudsen, NILU	Markus Wolf, ALSTOM Power Switzerland
Satish Kumar, Abu Dhabi Future Energy Company (MASDAR)	Petra Zapp, Forschungszentrum Juelich

Workshop on Environmental Impact of Amine Emission During Post Combustion Capture

Introduction

Dr. Mohammad Abu Zahra

IEA Greenhouse Gas R&D Programme

IEA Greenhouse Gas R&D Programme

A collaborative research programme founded in 1991

Aim: Provide members with definitive information on the role that technology can play in reducing greenhouse gas emissions.

Producing information that is:

- *Objective, trustworthy, independent*
- *Policy relevant but NOT policy prescriptive*
- *Reviewed by external Expert Reviewers*
- *Subject to review of policy implications by Members*

IEA GHG is an IEA Implementing Agreement in which the Participants contribute to a common fund to finance the activities. Funding approx 2.5 million $/year.

IEA GHG Members

IEAGHG Activities

- **Studies (>120)**
- **Communications**
- **Facilitating and focussing R&D activities**
- **International Research Networks**
  - *CO_2 storage (Risk assessment, Well bore integrity, Monitoring)*
  - *CO_2 capture (Post-combustion, Oxy-fuel combustion, High temperature solids looping)*

Why a workshop on environmental impact of post-combustion capture?

- The environmental impact of CO_2 post combustion capture is a continued concern for the full scale deployment
- There is little information on the chemical emissions problem and its technical solutions
- Limited related activities and a clear need for co-operation and knowledge exchange

Aims of the workshop

- To give an overview of the current on-going environmental impact activities
- A starting point to define gaps of knowledge and R&D areas of interest
- An opportunity for the different active groups to meet and to discuss the related environmental issues
- To build the basis for a future detailed IEAGHG study on environmental impact of post combustion capture.

Agenda

- Morning session

09:00 – 10:40	11:00 – 12:15
Welcome & Introduction – IEAGHG/Gassnova Amines to air – NILU Flue gas degradation of amines – Statoil Environmental impacts of emissions from PCC – CSIRO	Atmospheric chemistry of amines – EPRI ADA: Gas phase photo-oxidation of MEA – UOS Emissions measurements at Dong's pilot plant – Statoil

- Afternoon session

13:15 – 14:45	14:45 – 16:00
Information required for EIA – SFT Environmental impact of PCC – UOR Emissions from amine and amino acid based systems – TNO MHI amine emission control technology - MHI	Econamine FG^+ process – Fluor Emissions measurement and analysis – ACC Closing and discussion – IEAGHG/Gassnova

Where to go from here?

- **A report of the meeting including the presentations will be distributed**
- **An IEAGHG study “Evaluation of Available Technologies for Deep Removal of Amines” will be issued**
- **Questionnaire:**
  - *Do we need any further specified meetings focusing on environmental impact? Or it could be combined with other capture activities?*
  - *If so, how should they be organised?*
  - *What topics should be included?*

Please share your opinion in person here or respond later on by email

IEAGHG study - Objectives

- **To identify and quantify the sources of chemical emissions in the CO_2 post-combustion capture process**

- **To identify the gaps of information particularly in the characteristics of any chemical release (includes speciation) that could be carried over in the bulk gas released from the absorption tower.**

- **To review current best available technologies to allow deep removal of these chemicals from the bulk flue gas emitted from the capture process.**

- **To review any HSE considerations in dealing with any possible emissions of these chemicals that could be carried over to the released bulk gases.**

Acknowledgements

- Thanks to Gassnova for hosting and sponsoring the workshop
- Statoil for their support and sponsoring the dinner
- All speakers and participants
- Gassnova staff, especially Erik Gjernes and Klaus Schöffel

Thank you

General - *www.ieaghg.org*

CCS - *www.co2captureandstorage.info*

GHGT-10

19th – 23rd September 2010 Amsterdam
www.ghgt.info/ghgt10.hmtl

Amines to air
Problem description

Svein Knudsen

Senior research scientist

NILU

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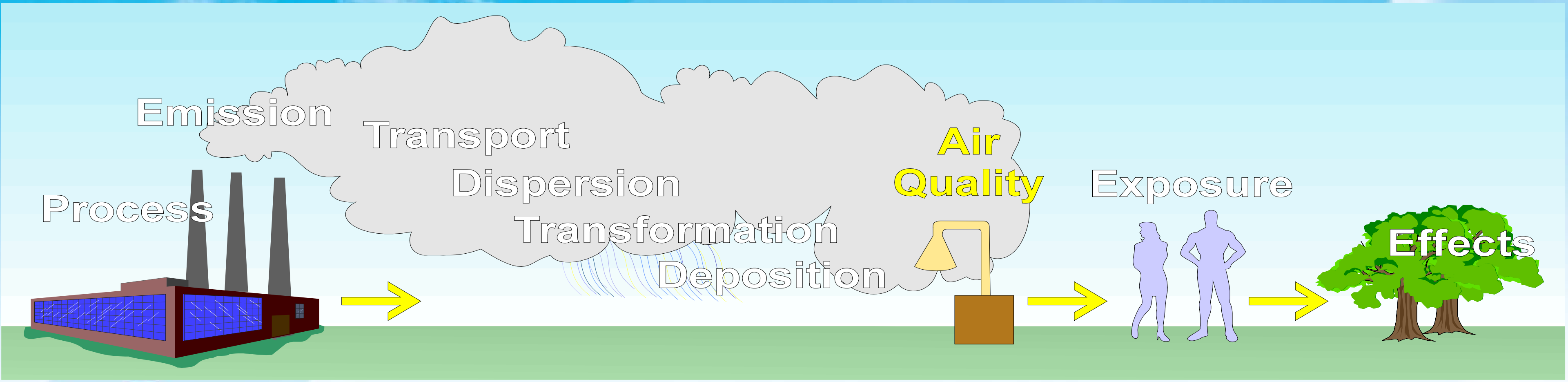
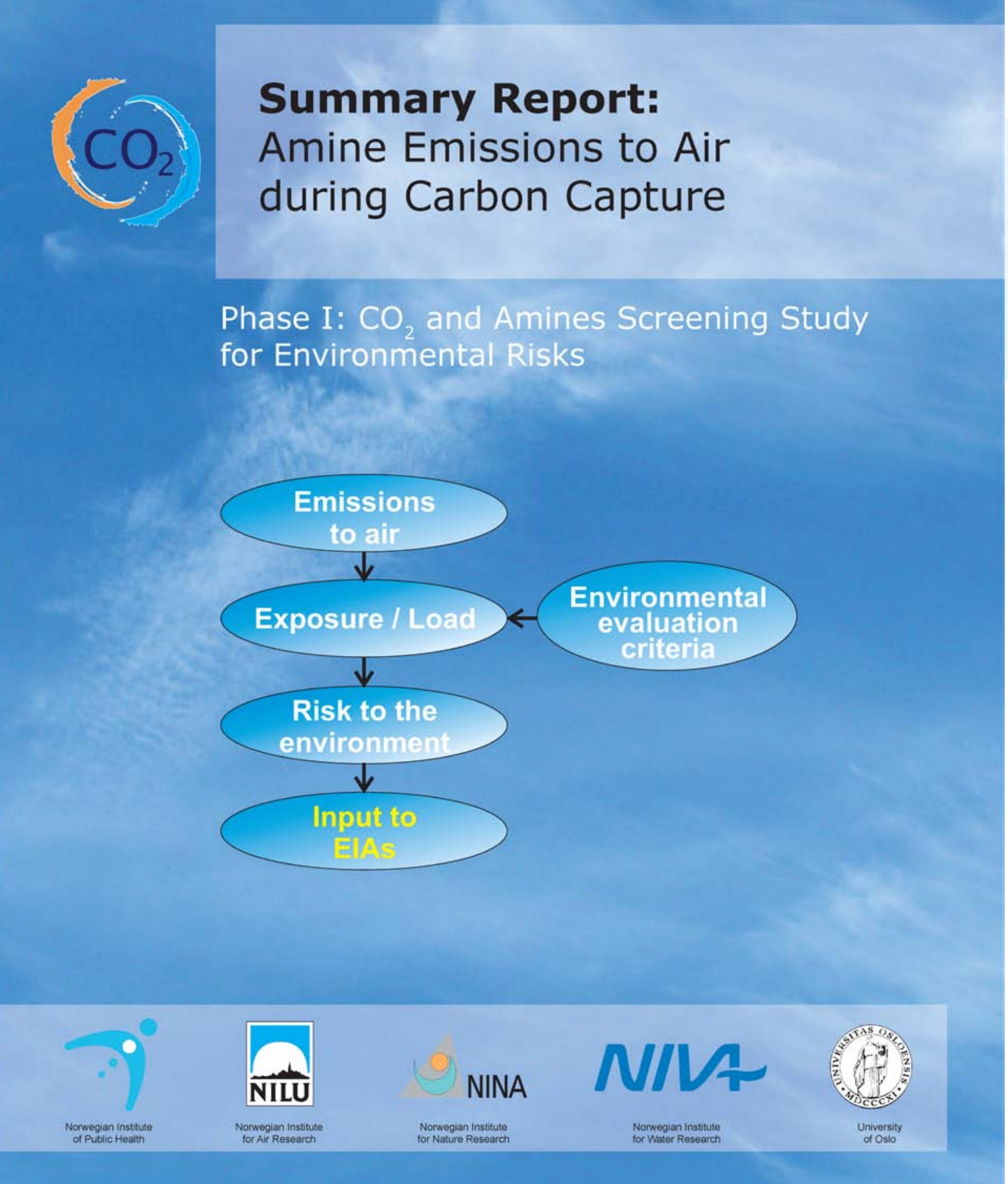


Content

- A bit of history
- Past, current and future projects
- Problem overview
- Conclusions



CO_2

Summary Report:
Amine Emissions to Air during Carbon Capture

Phase I: CO_2 and Amines Screening Study for Environmental Risks

Emissions to air

Exposure / Load

Environmental evaluation criteria

Risk to the environment

Input to EIAs

Norwegian Institute of Public Health

NILU
Norwegian Institute for Air Research

NINA
Norwegian Institute for Nature Research

NIVA
Norwegian Institute for Water Research

University of Oslo

Reports available at http://co2.nilu.no

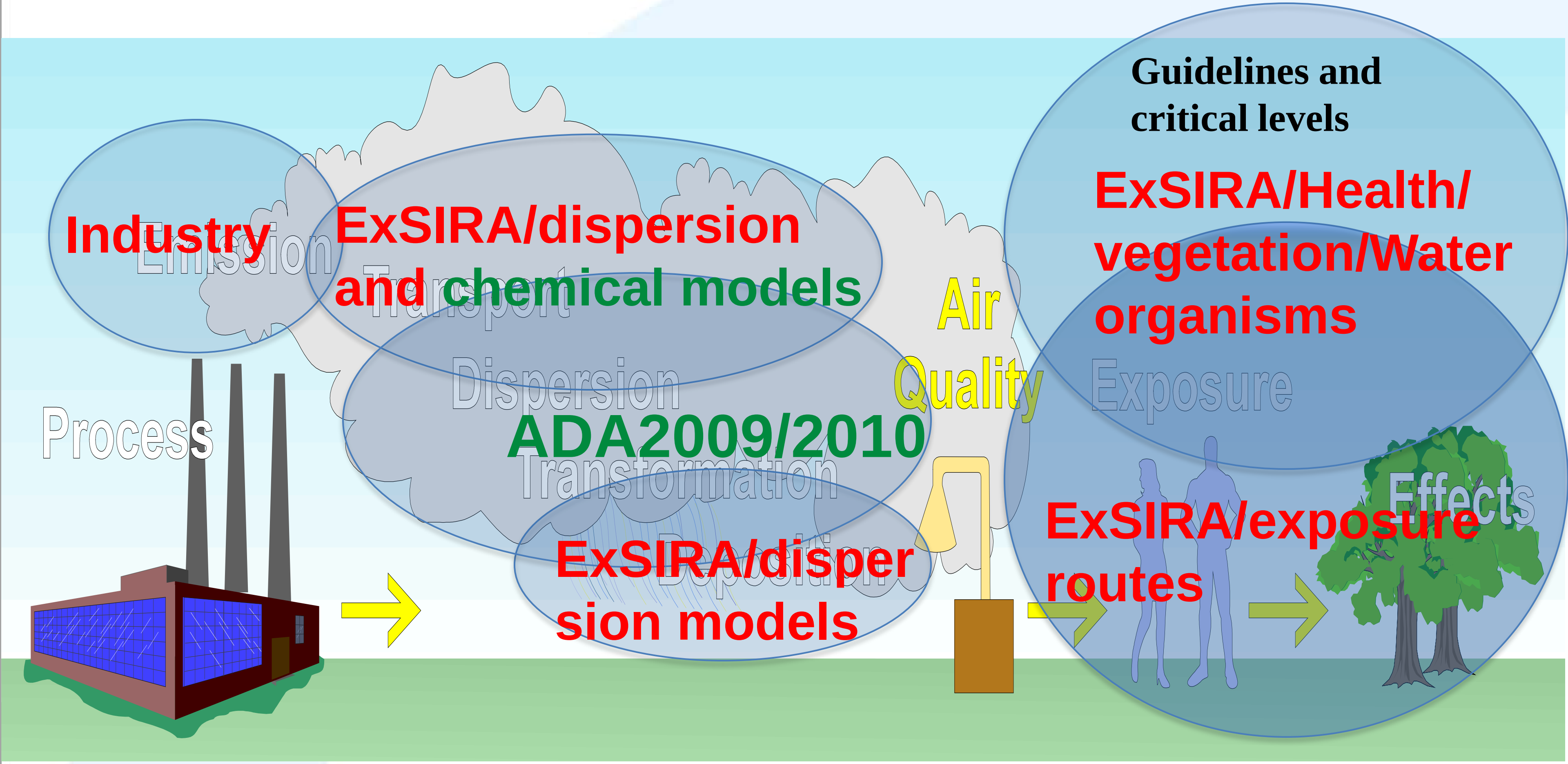
GASSNOVA

StatoilHydro

Chemically produced compound potentially more toxic than the mother amine

Worst case show that there can be problems connected to emissions of amines to air

Project in pipeline and funded projects



Guidelines and critical levels

Industry

ExSIRA/dispersion and chemical models

ADA2009/2010

ExSIRA/dispersion models

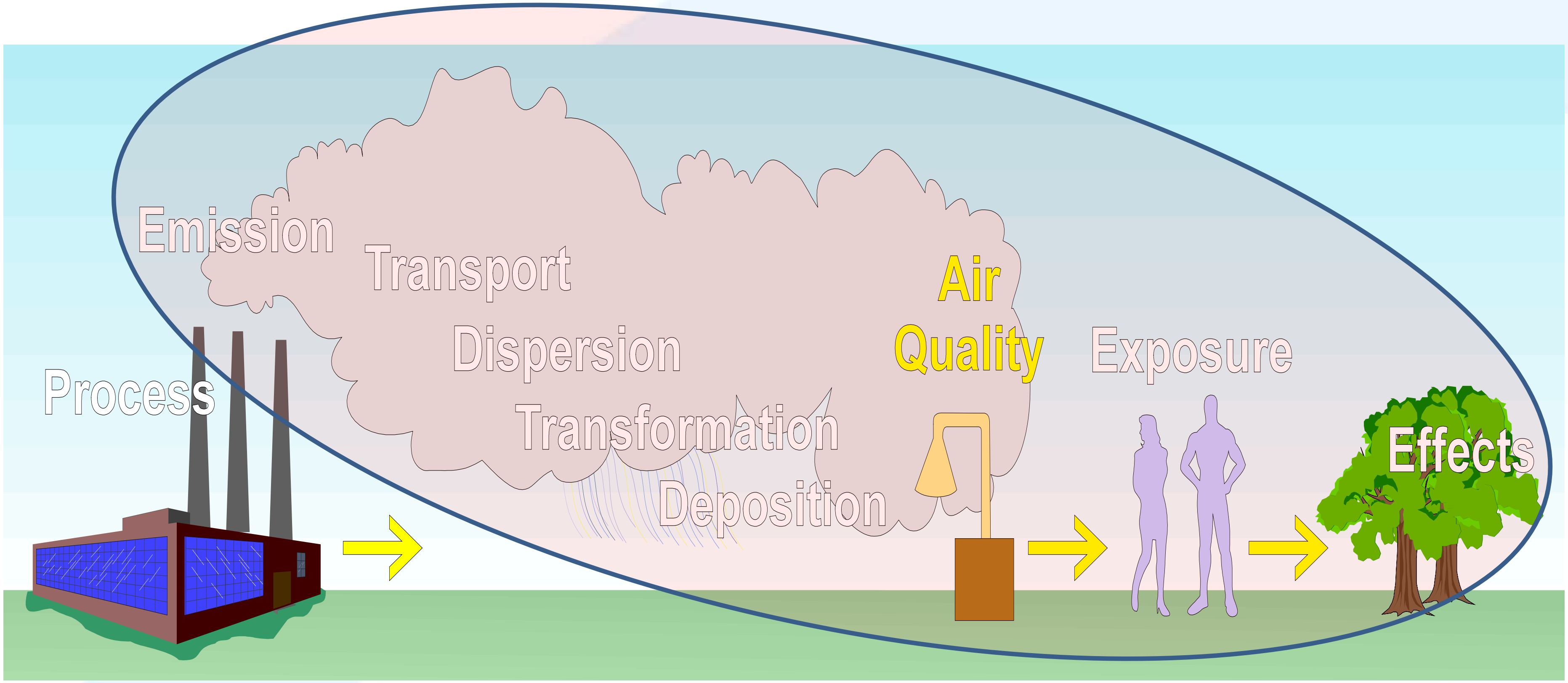
ExSIRA/Health/vegetation/Water organisms

ExSIRA/exposure routes

Holistic understanding emissions to the environment

- Production (large scale)
- Transport (leaks and vapour recovery)
- Use for CCS and other processes (Refineries)
- Disposal

System insight



Emission

Transport

Dispersion

Transformation

Deposition

Process

Air Quality

Exposure

Effects

System insight

- Integrated processes
- Understand development with time
  - Long residence time and toxic (problem)
  - Short residence time and non toxic (no problem)
- Need sufficient knowledge to have holistic understanding
- Understanding of exposure route necessary to evaluates effects

Important processes

- Emissions (Critical for fate)
- Dispersion coupled to chemistry (concentration)
- Chemical processes
  - Air (gas, rain and particles)
  - Water
  - Soil
- Transport between matrixes
- Effects dependent on dose and response (toxicity)
- Global, regional and local understanding

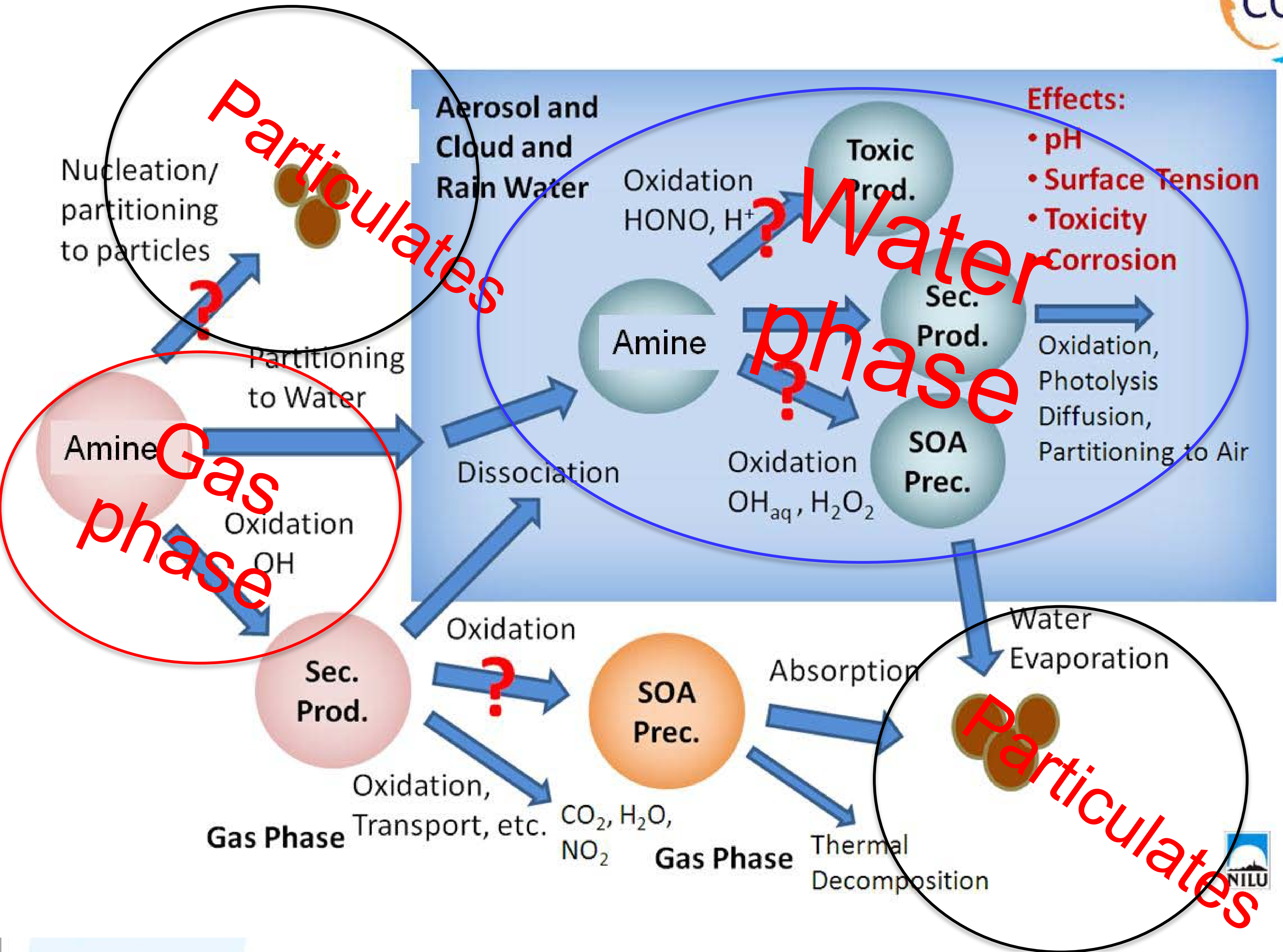
Emissions (later speakers will cover this)

- No good open information
- Probably the majority is mother amine but surely others as well
- Effects depend on complexity of emissions
- The effects will make the limits for possible emissions and the need for cleaning devices
- Accidents

Need quantification

Dispersion/ Chemistry (later speaker)

- Dispersion and chemistry needs to be solved together
- Sources and sinks need to be included
- Needs chemical identification and quantification
- Complicated



Particulates

Nucleation/ partitioning to particles

?

Aerosol and Cloud and Rain Water

Oxidation HONO, H^+

?

Toxic Prod.

Water phase

Effects:

- **pH**
- **Surface Tension**
- **Toxicity**
- **Corrosion**

Amine

Sec. Prod.

?

SOA Prec.

Oxidation, Photolysis Diffusion, Partitioning to Air

Partitioning to Water

Amine

Gas phase

Oxidation OH

Dissociation

Oxidation OH_{aq}, H_2O_2

Sec. Prod.

Oxidation

?

SOA Prec.

Absorption

Water Evaporation

Particulates

Oxidation, Transport, etc.

Gas Phase

CO_2, H_2O, NO_2

Gas Phase

Thermal Decomposition

Critical load/ Toxicity/environment and human health

- Need to investigate mother amine (largest emission)
- Need to look into chemical produced substances (smaller emissions/production)
- Critical/safe levels of exposure
- Toxicity (short to long term)
  - Human health
  - Vegetation
  - Water organisms

Exposure depends on Toxicity and Load

- Possible that the substances are not stable and travels from emissions to vegetation and becomes nutrients

NEED INVESTIGATION

- Possible that there is a bottle neck where one or more substance are stable and that the residence time is long

NILU

Accumulation

Is there a stop on the road to destruction?

- **Air**
- **Water**
- **Soil**
- **Vegetation**
- **Humans**
- **Organisms**

If yes: the impact might be large if toxic

If no: Impact is normally smaller, need more toxicity to get same effect

Conclusions

- Choice of amine can improve the environmetal friendliness of CCS
- Environmental evaluation is important for technological development
- Need to establish:
  - Critical loads
  - Methodology and tools
  - Environmental routs to evaluate impacts
- Problem probably not the mother amine
- To do the right choice information is needed
- One plant of CCS is probably not a problem

Thank you for the attention!!

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www.nilu.no

Flue gas degradation of amines

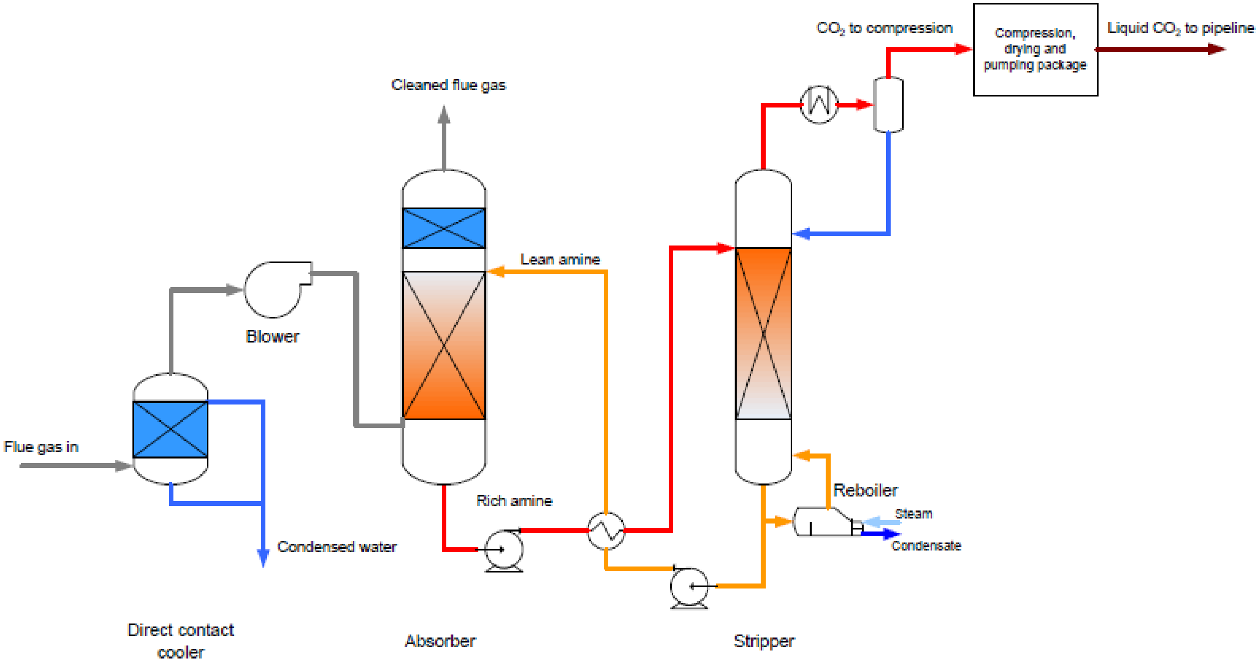
Steinar Pedersen, Merethe Sjøvoll, Berit F. Fostås; Statoil ASA

IEA GHG workshop in Oslo 16th February 2010

Outline

- Amine Process and Environmental Risks
- Solvent Evaluation Requirements
- Flue Gas Degradation of Amines Project
- Aminox™ Test Rig
- Experimental
- Results
- Solutions

Amine process and environmental risks



- Flue gas degradation of amine solvent
- Emission to atmosphere of amine and degradation products
- Atmospheric degradation of emitted compounds

Solvent evaluation requirements

Amine solvent testing
Process degradation
Sampling
Analytical methods
Degradation products

Pilot/Full scale testing
Emission sampling
Emitted compounds
Emitted amounts

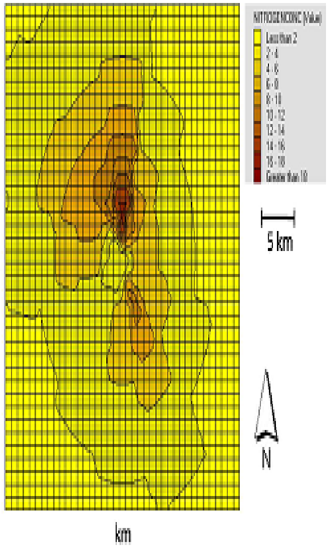
http://www.co2cesar.eu/

Atmospheric degradation
Fate of emissions
Degradation products

http://ada.nilu.no/ http://euphore.es/

Toxicity testing
Safe level - assessment

Dispersion modelling
Exposure pathways
Exposure levels



http://co2.nilu.no/

Vendor information required for health and environmental risk assessment

Flue gas degradation of amines project

Current status:

- CO_2 and O_2 degradation - well described
- NOx degradation - hardly any work reported

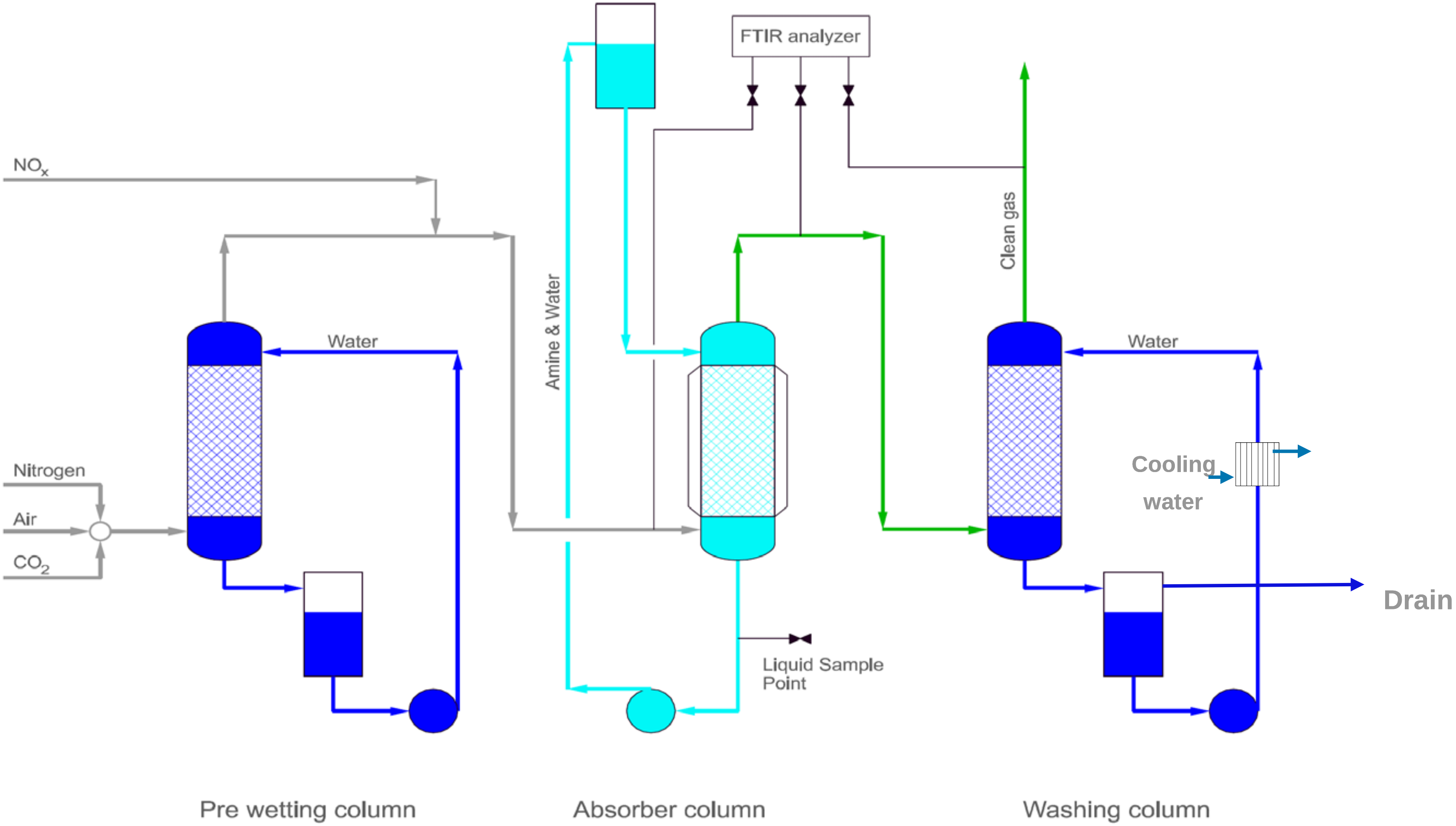
Project objectives:

- Potential process formation of harmful compounds
- Absorber slip of volatile compounds
- Effect of water wash
- Emission simulations
- Sampling and chemical analysis

Project output:

- Identification of degradation products
- Methods for sampling and measurement

The Aminox™ test rig



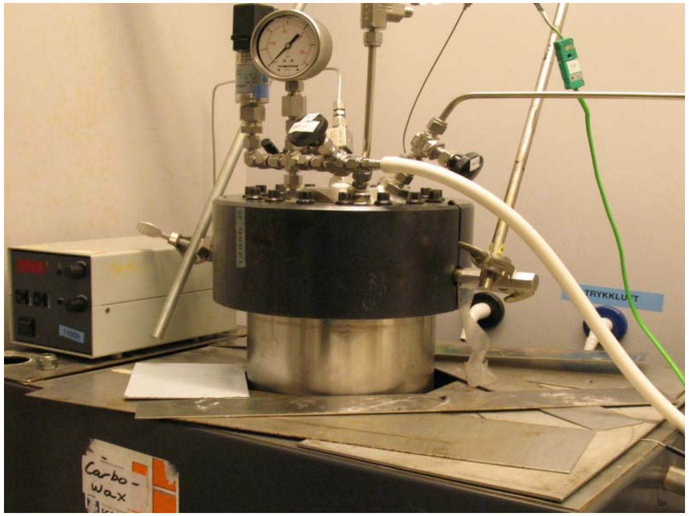
Statoil

Experimental

- Variables
  - Flue gas and solvent compositions
  - Gas/Liquid ratio
  - Absorber reaction conditions
  - Water wash conditions
  - Stripper conditions (lab scale autoclave)
- Sampling
  - Liquid samples, solvent and wash water samples
  - Gas sampling, on-line FT-IR, (on-line MS)
- Chemical analysis
  - IC
  - Potentiometric titration
  - LC-MS fingerprint
  - GC-MS
- Designed experiments and multivariate data analysis

Testing procedure

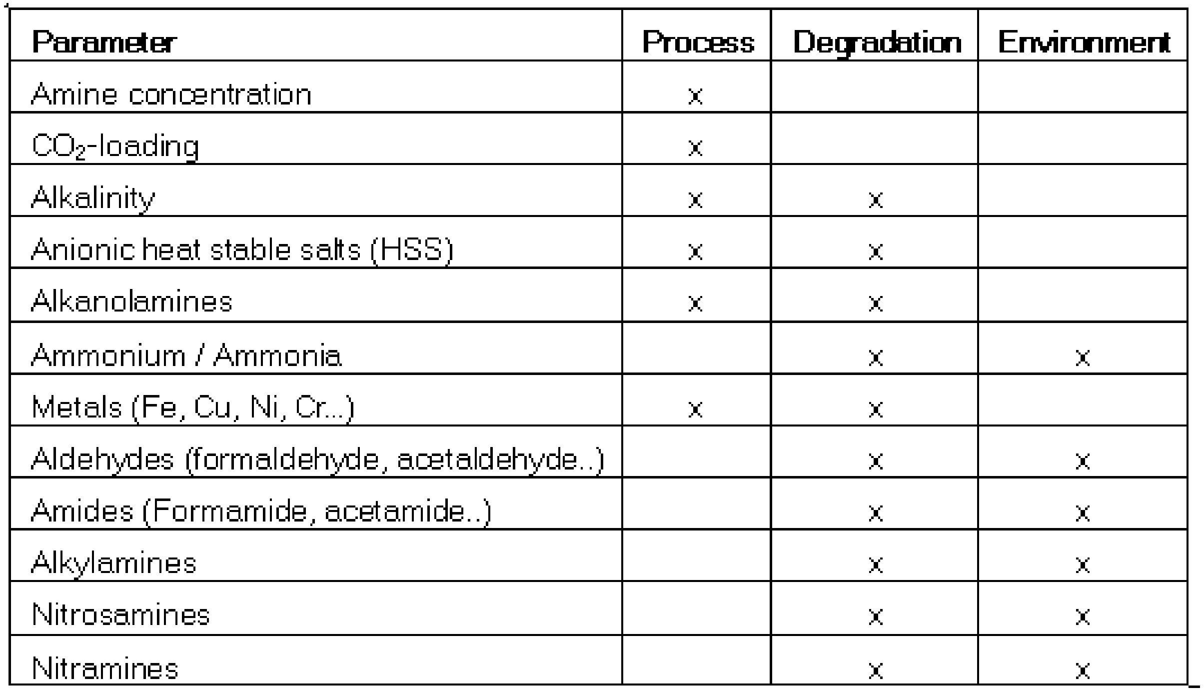
- CO_2 absorption to target loading
- Degradation at set flue gas composition
- Autoclave degradation
- Sampling and analysis at selected intervals
- Continuous FT-IR online monitoring



Aminox Parameter	**Unit**	**Level**
MEA	w%	30 - 40
Gasflow, wet	Nm^3/h	40
Liquid flow	l/min	0.7
L/G (mole based)		1.3
Temperature	°C	44
CO_2	vol%	3.5
H_2O	vol%	6.7
O_2	vol%	0-14
NOx	ppm	0-100
Time	h	95

Autoclave Parameter	**Unit**	**Level**
Pressure	bara	3 - 4
Temperature	°C	120
Time, degradation	h	24-50

Analytical parameters

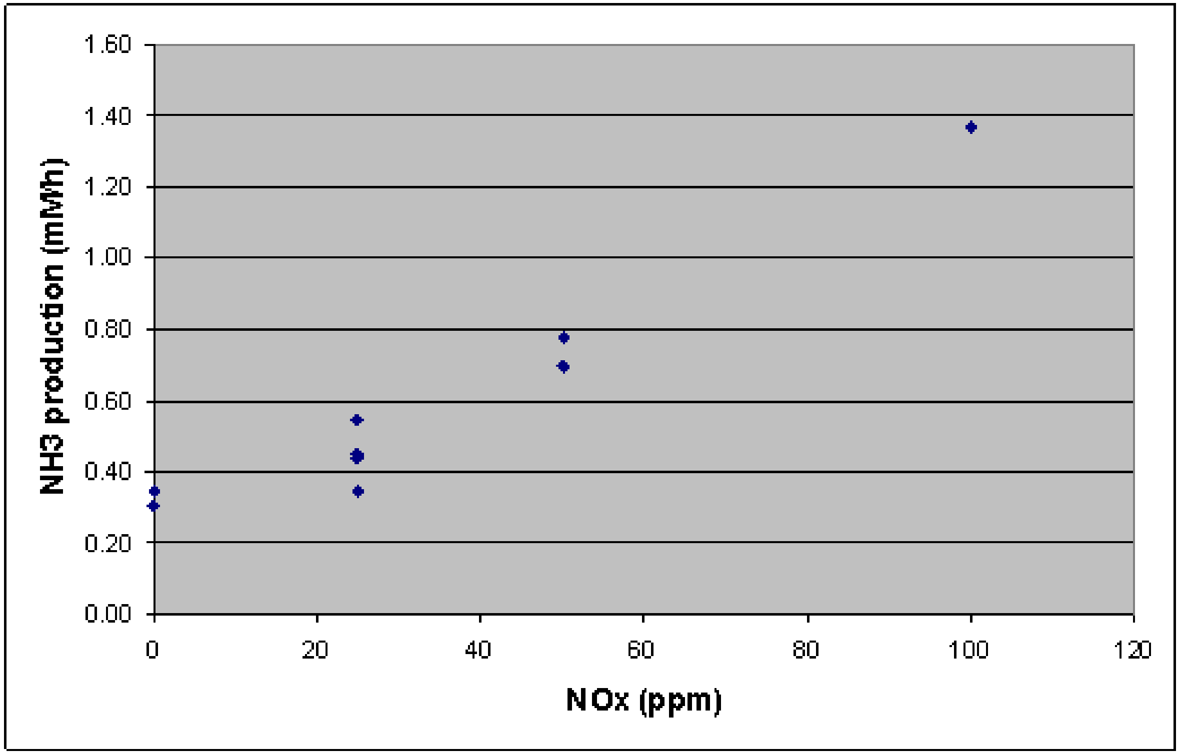


Parameter	Process	Degradation	Environment
Amine concentration	x		
CO_2-loading	x		
Alkalinity	x	x	
Anionic heat stable salts (HSS)	x	x	
Alkanolamines	x	x	
Ammonium / Ammonia		x	x
Metals (Fe, Cu, Ni, Cr...)	x	x	
Aldehydes (formaldehyde, acetaldehyde..)		x	x
Amides (Formamide, acetamide..)		x	x
Alkylamines		x	x
Nitrosamines		x	x
Nitramines		x	x

Special focus to clarify formation and emission of these environmental compounds

- Methods are established
- Known degradation products are identified and quantified
- Relevant degradation rates are observed

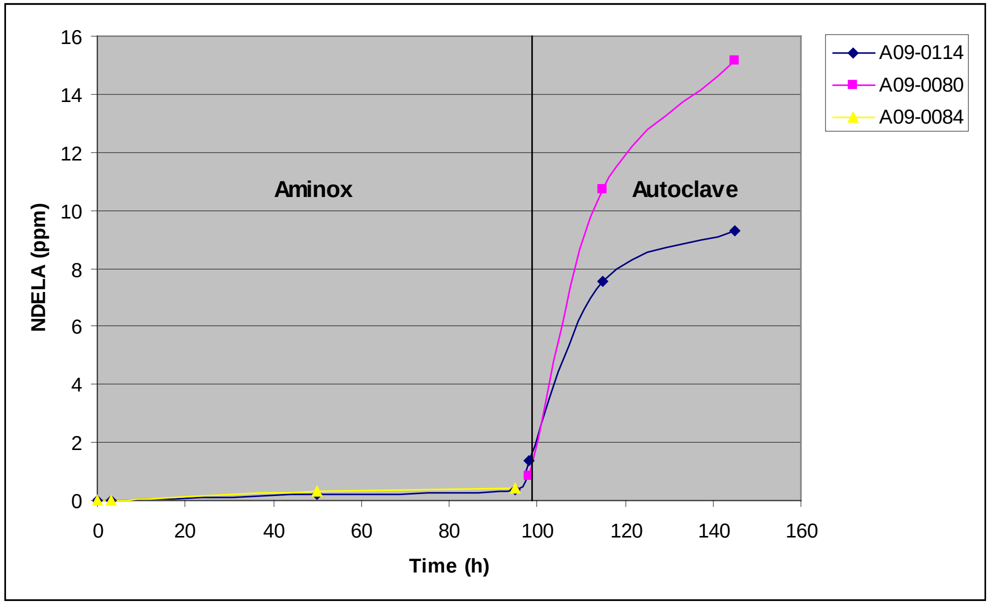
Degradation rates

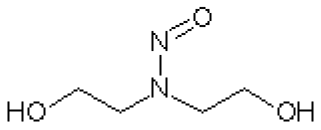


50% of MEA would be degraded after one year testing, given a constant rate at 50 ppm NOx exposure

- Ammonia is the primary degradation product of MEA
- Ammonia production is strongly correlated with NOx-concentration in the flue gas

Potential nitrosamine formation

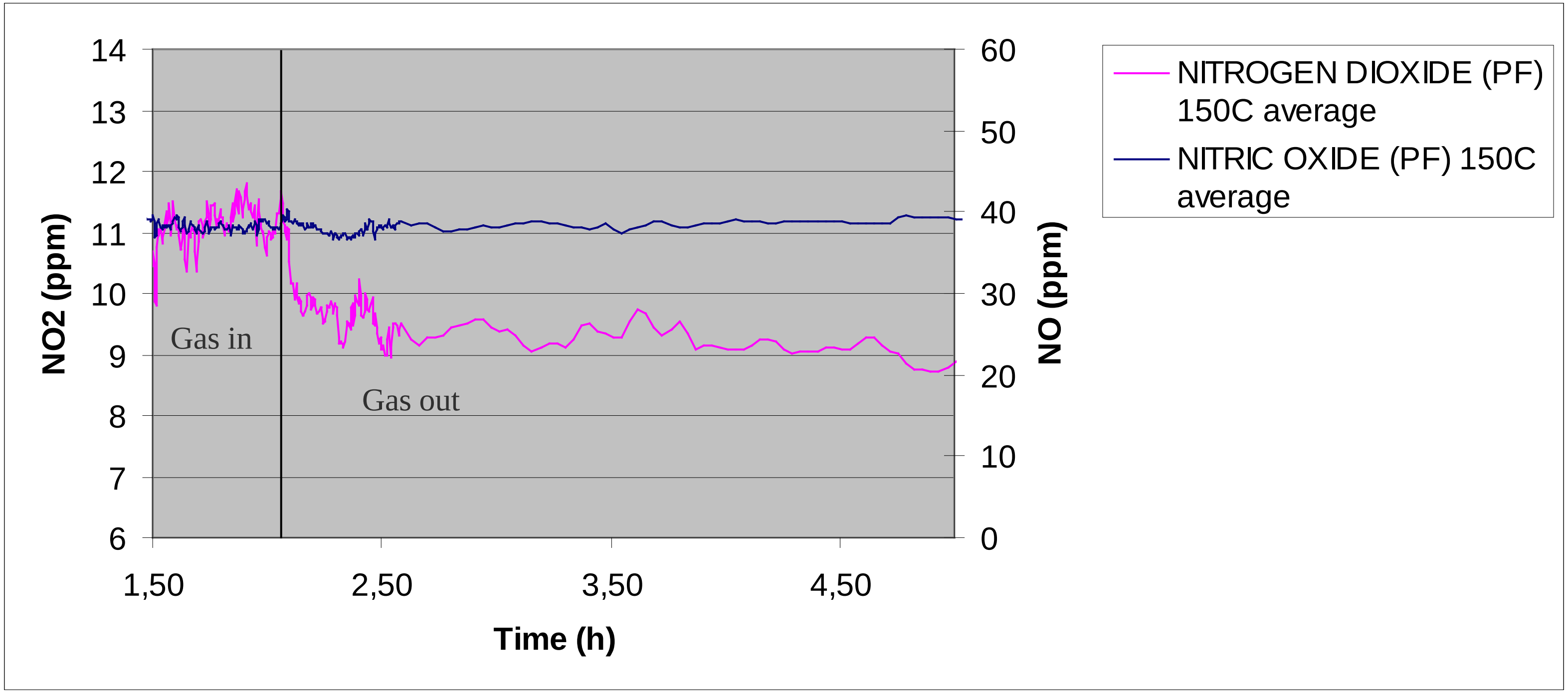




NDELA

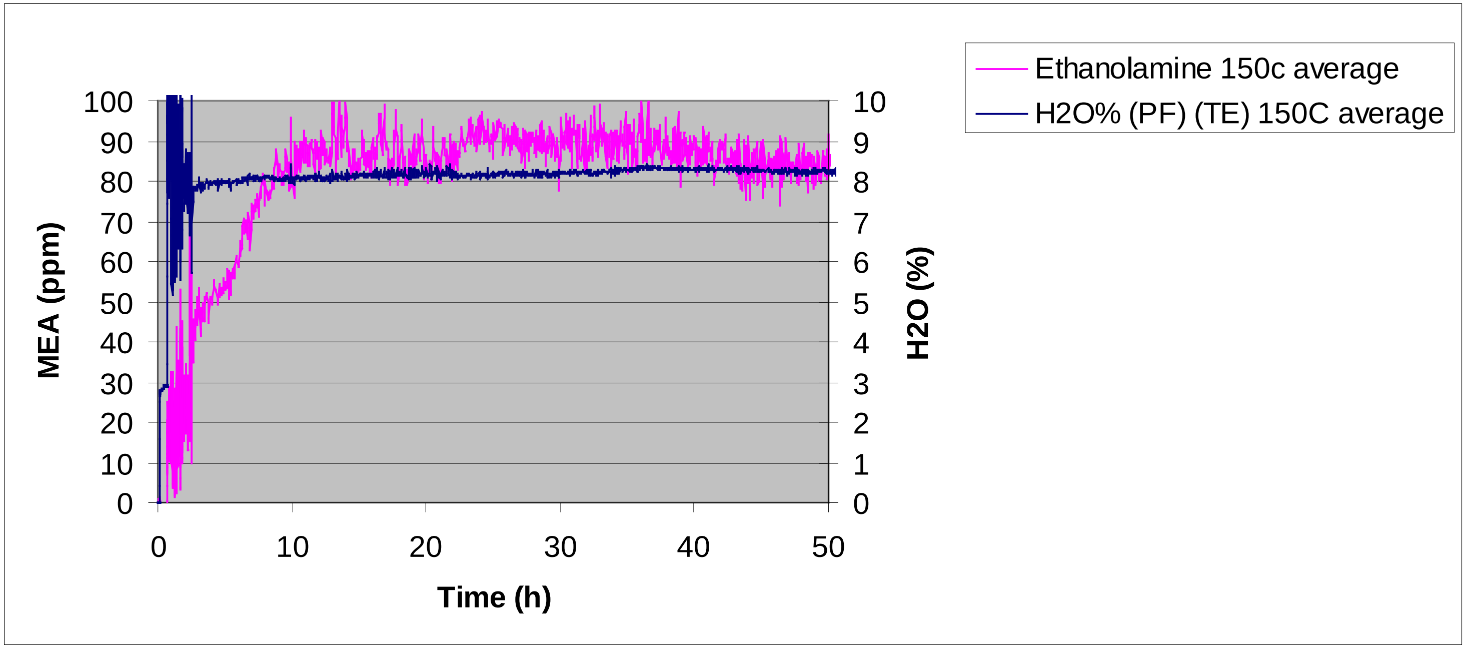
- Results indicate ~ 0.5 ppmw Nitrosamine NDELA in all samples exposed to NOx (25-50 ppmv)
- In samples without NOx exposure nitrosamines could not be detected
- Formation rate is very low at Aminox conditions, much higher rates are seen in the Autoclave
- MEA as a primary amine is not expected to form a stable nitrosamine
- NDELA may form from DEA (DEA is an impurity or a result of NOx induced degradation of MEA)
- In wash water samples ~ 10 ppbw NDELA was found

NO_2 absorption from flue gas



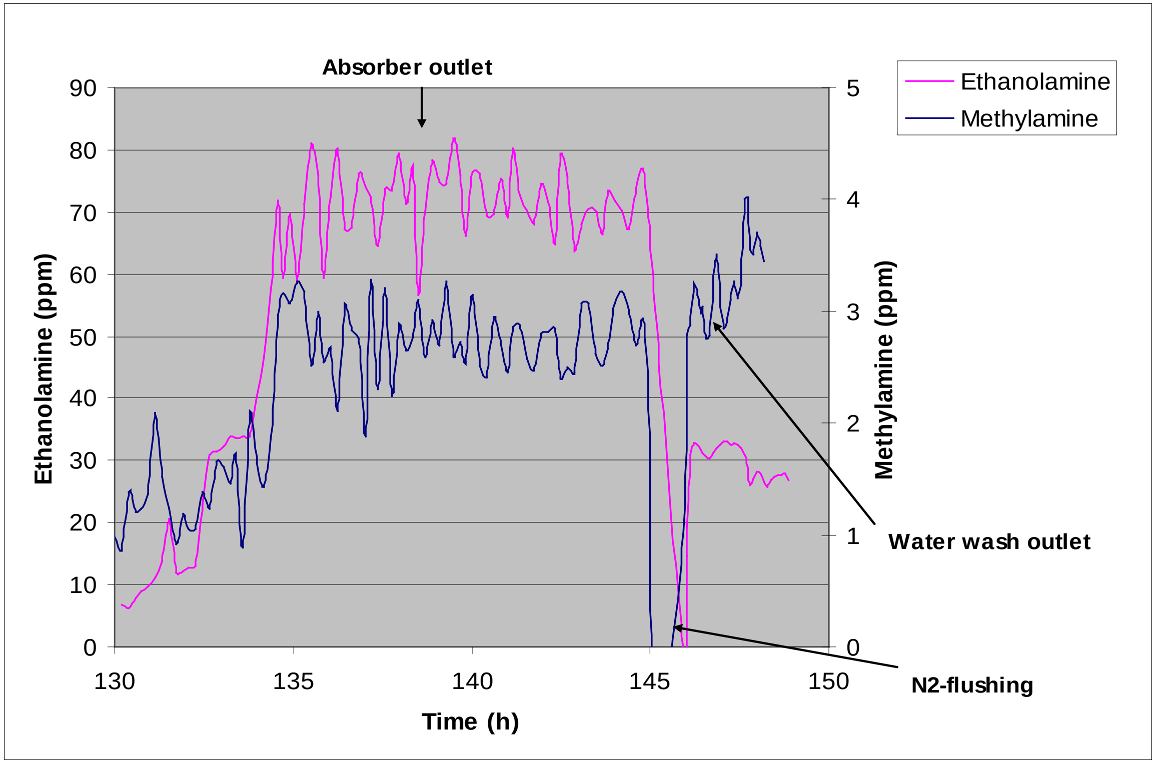
- NO is oxidised to NO_2 in the absorber inlet
- About 20% of NO_2 is absorbed into the liquid phase

MEA slip from absorber



- MEA measurements are demanding
- Strong adsorption to sampling tube surface and partitioning to water
- Long sampling intervals are needed for representative measurements
- MEA mass balance closure > 90% was achieved

Methylamine slip from absorber



Highly volatile methylamine may form nitramines to a large extent in the atmosphere, Pitts and Hanst reported in the 70’s

- Methylamine is observed in levels about 2 – 4 ppmv

Proposed solutions

- Solvent evaluation
- Solvent replacement at intervals to control harmful compounds
- Avoid NO_2
- Monitor and control the process and the emissions
- Environmental monitoring

Thank you

The Flue Gas Degradation of Amines project are supported by Gassnova’s Climit Program.

Flue gas degradation of amines

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Roger Dahl, Nina Aas, Ingvar Eide, Gunhild Neverdal, Toril Berg
Bodil Thorvaldsen, John Arild Svendsen, Steinar Pedersen.
Henrik Solgaard Andersen; Project Manager

www.csiro.au

Environmental Impacts of Atmospheric Emissions from Amine-based Post-Combustion CO_2 Capture

Coal Portfolio

Moetaz Attalla and Merched Azzi

16th February 2009

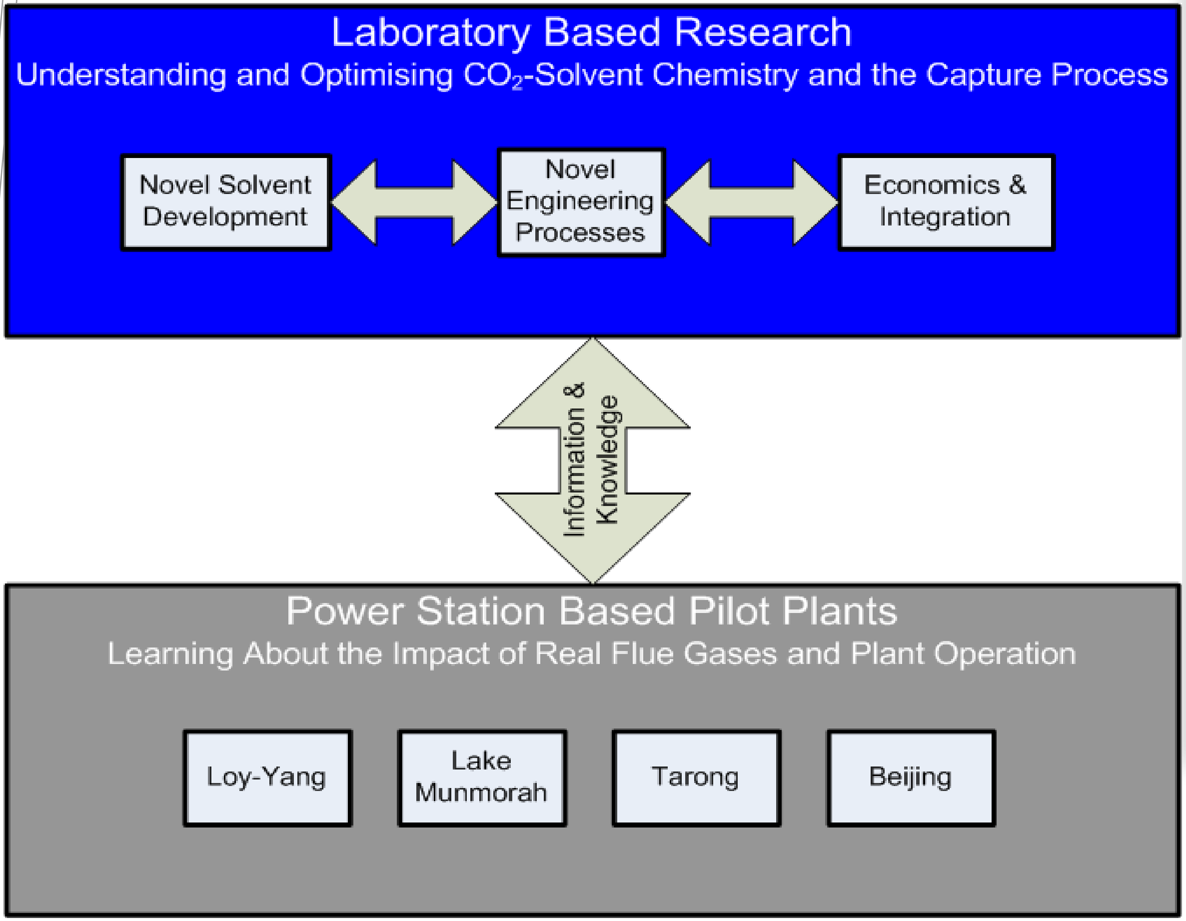
CSIRO Energy Centre

CSIRO’s Energy Research At Newcastle

- Renewable Energy Systems
  - Solar Thermal
  - Vibration Energy Harvesting
  - Organic Photovoltaics
- Improving Energy End Use
  - Distributed Energy
  - Self Learning Smart Agent Technologies
  - Energy Storage
- Carbon Capture and Storage
  - Geosequestration (ECBM,..)
  - Post Combustion Capture Technologies

CCS - The science challenges

- CSIRO’s PCC research is unique in its integrated program of solvent development, process improvement and process operation



Laboratory Based Research

Understanding and Optimising CO_2-Solvent Chemistry and the Capture Process

Novel Solvent Development ↔ Novel Engineering Processes ↔ Economics & Integration

Information & Knowledge

Power Station Based Pilot Plants

Learning About the Impact of Real Flue Gases and Plant Operation

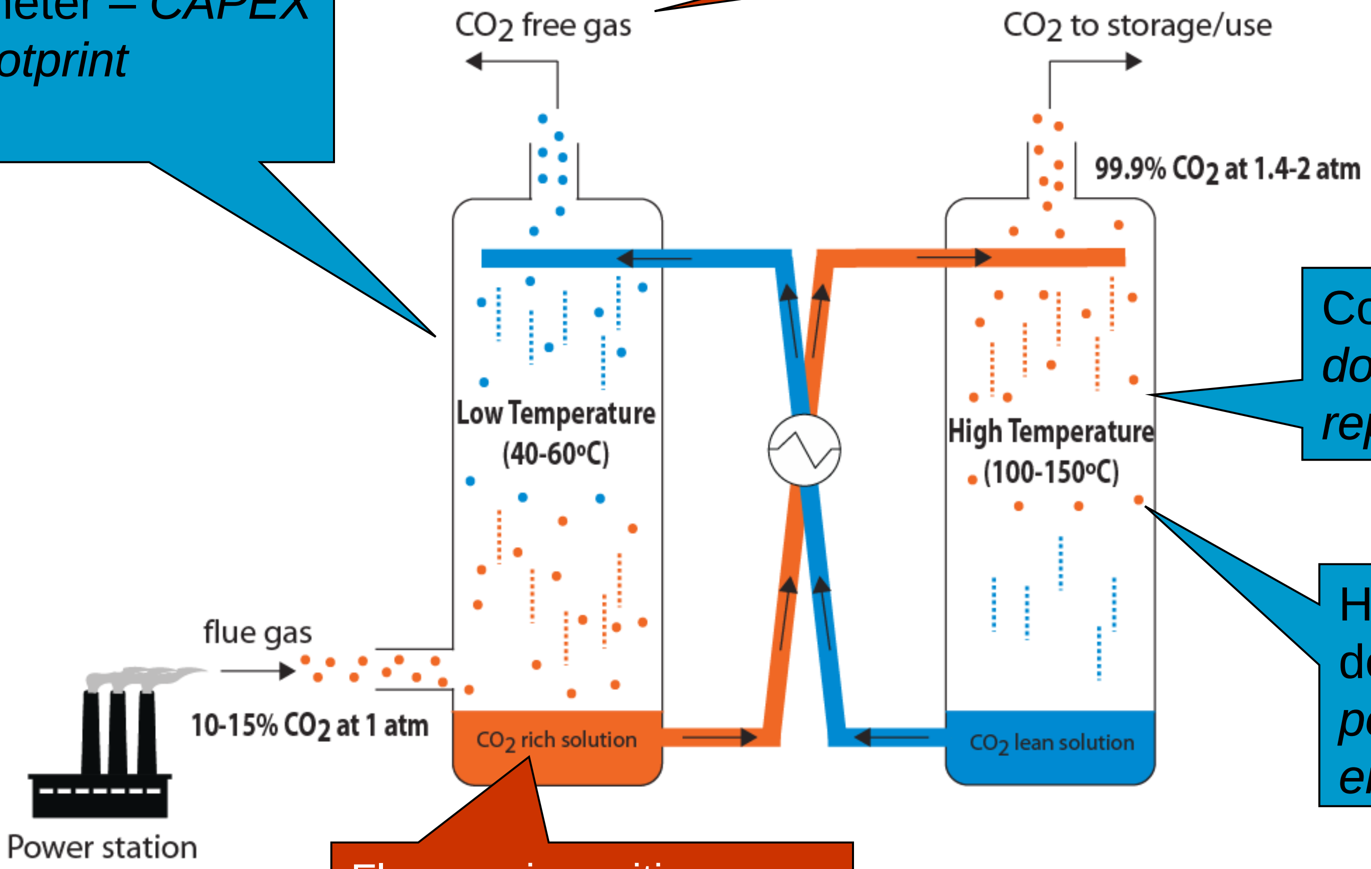
Loy-Yang

Lake Munmorah

Tarong

Beijing

The Scientific Challenges…….



Column height & diameter – *CAPEX & footprint*

Atmospheric emissions – *environmental impacts*

Corrosion – *plant downtime and repair*

Heat for desorption – *power station energy penalty*

Flue gas impurities – *solvent degradation*

Identifying potential impacts when solvent-based carbon capture is deployed….

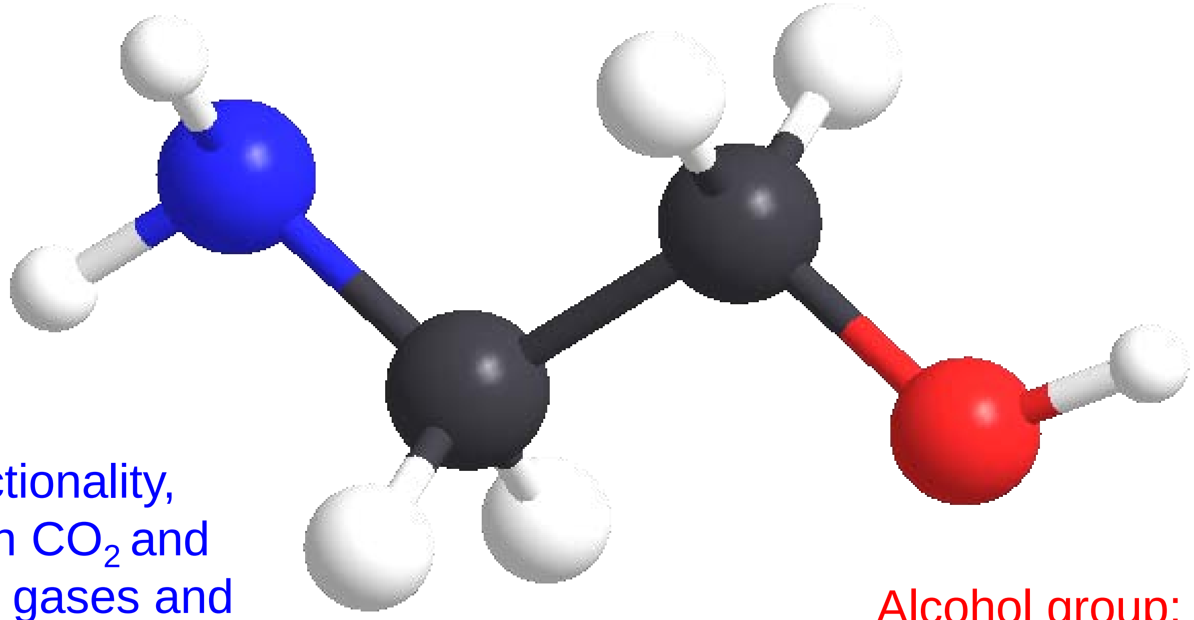
- Solvent-based carbon capture plants using amines can mitigate stationary-source CO_2 emissions, However……

- What are safe levels of exposure to amines and their degradation products?
- What happens when there is amine "slip" from the capture plant
- What is the atmospheric fate of the lost amine molecules?
- Are they deposited close to the emission source, or does atmospheric chemistry convert them into deleterious molecules, harmful to people and the environment?
- How can we develop safe levels or environmental thresholds for amines?
- How much amine can be "released" to the environment before authorities need to act?
- Do secondary and tertiary amines form stable nitrosamines under PCC operating conditions (potent mammalian carcinogens)?

Current Capture Technology - Alkanolamines

Monoethanolamine (MEA)

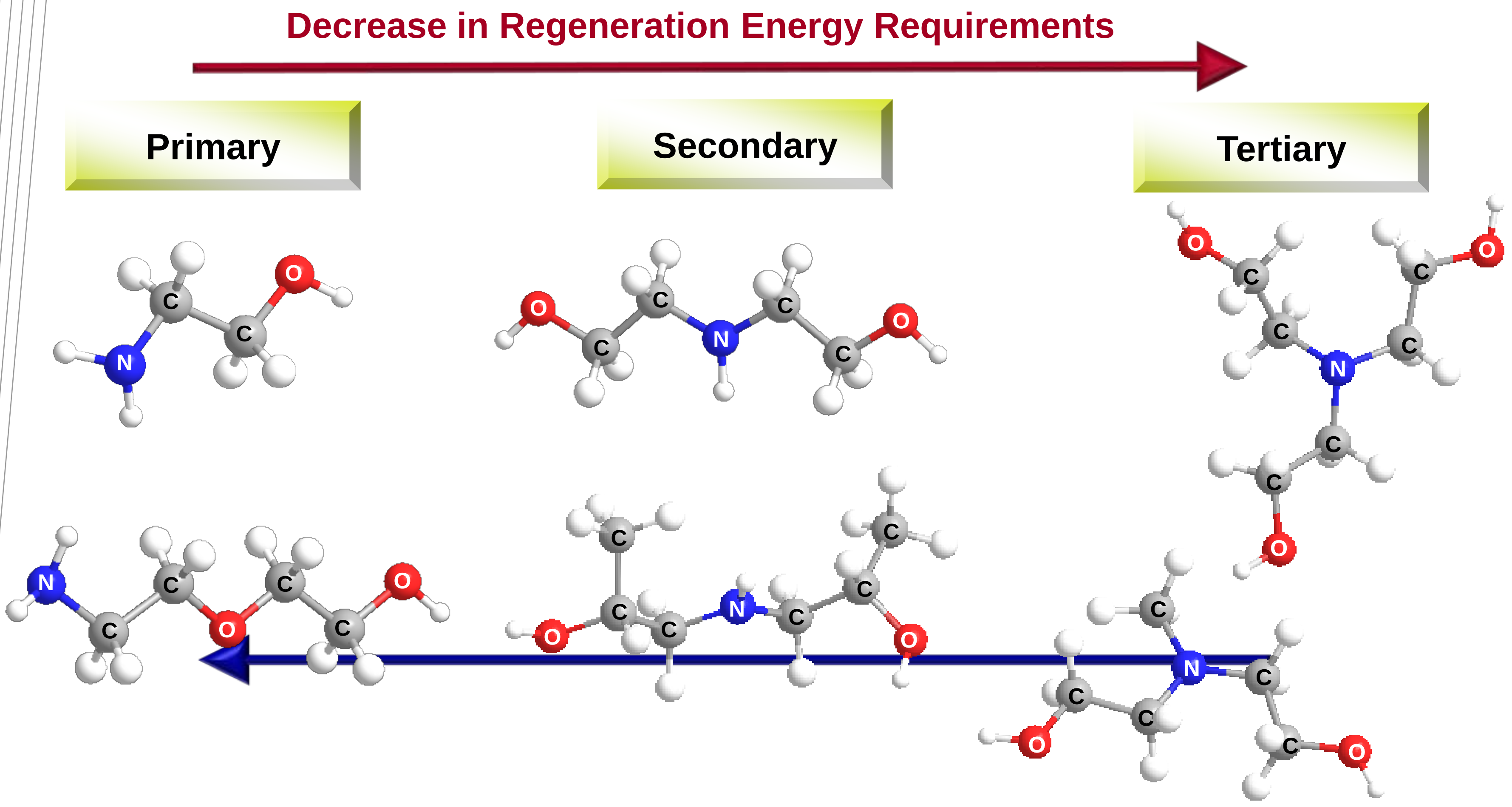
Short carbon chain:
simple, reduces cost of
amine



Nitrogen:
basic functionality,
reacts with CO_2 and
other acid gases and
acts as a Brønsted
base

Alcohol group:
reduces volatility
increases solubility

Conventional Amines



Decrease in Regeneration Energy Requirements

Primary

Secondary

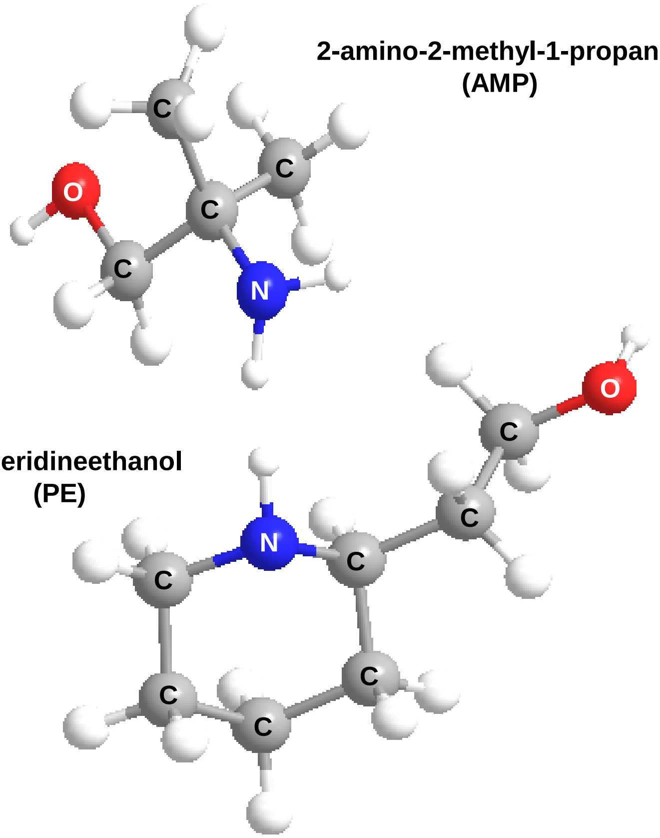
Tertiary

Increase in Reaction Rate

Environmental impacts of amine-based CO_2 capture...... Attalla and Azzi

Enhanced Amines

Sterically-Hindered Amines



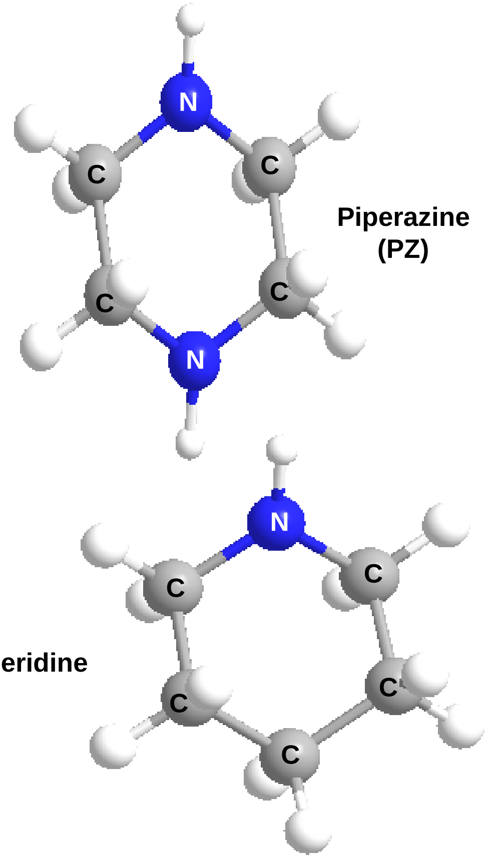
2-amino-2-methyl-1-propanol
(AMP)

2-piperidineethanol
(PE)

Lower Regeneration Energies

Environmental impacts of amine-based CO$_2$ capture...... Attalla and Azzi

Heterocyclic Amines



Piperazine
(PZ)

Piperidine

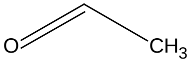
Enhanced CO$_2$ Absorption

Degradation Products for MEA

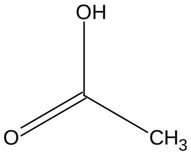
Absorber side

ammonia 1.2.3 NH_3

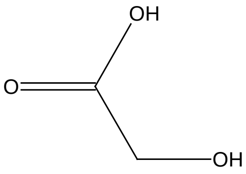
acetaldehyde 2



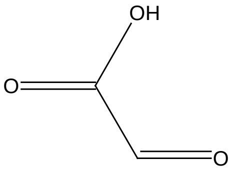
acetic acid 1.2.3



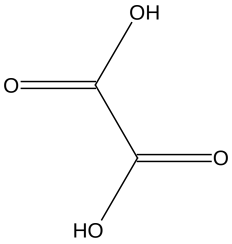
hydroxyacetic acid 1.2.3.5

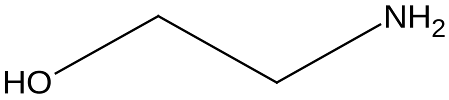


oxoacetic acid 1.2.3.5

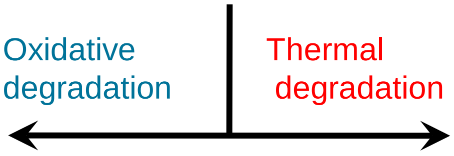


ethanedioic acid 1.2.3.5





2-aminoethanol, MEA



Oxidative degradation

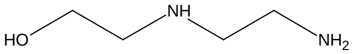
Thermal degradation

[O_2]

>200° C

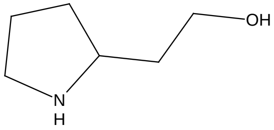
Fate in the Troposphere:

1. assists particle aggregation
2. undergoes photochemical reactions
3. undergoes acid rain forming reactions
4. can form nitrosamines
5. ultimate fate is unknown



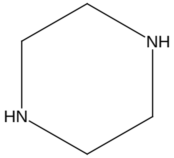
1.2.4.5

2-[(2-aminoethyl)amino]ethanol



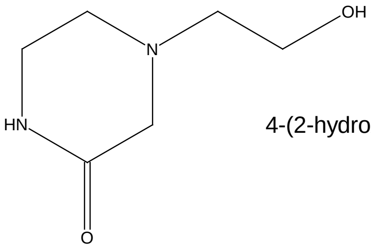
2-(pyrrolidin-2-yl)ethanol

1.2.4.5



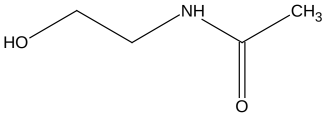
piperazine

1.2.4.5



4-(2-hydroxyethyl)piperazin-2-one

1.2.4.5



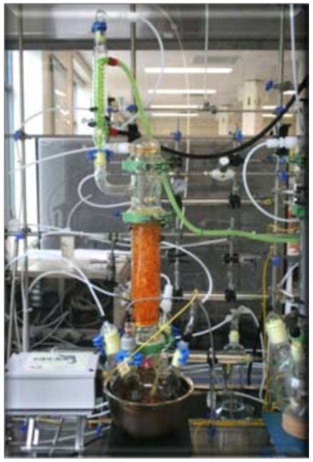
N-(2-hydroxyethyl)acetamide

1.2.4.5

Key Research Program: Solvents and Emissions

Key programme currently being undertaken at the Energy Centre, Newcastle. We seek to:

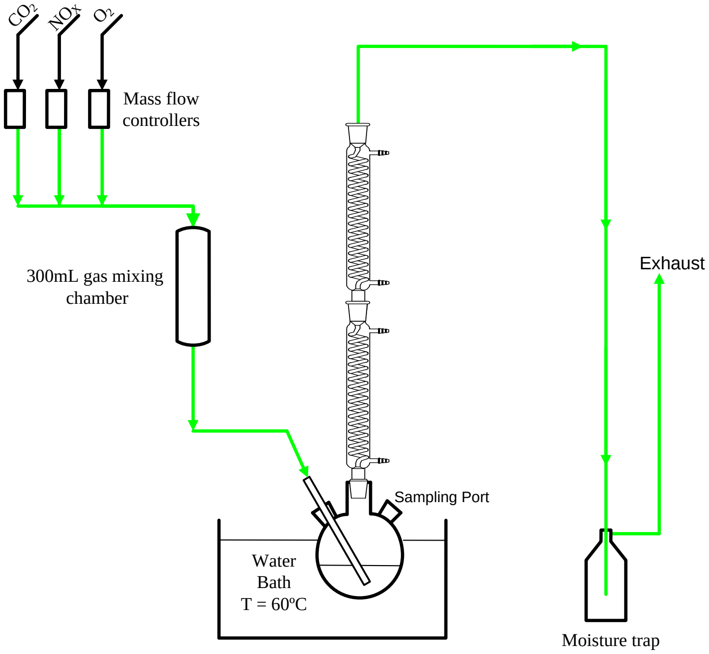
1. understand oxidative mechanisms of amine degradation in the capture plant and under controlled laboratory conditions
2. understand the fate of ‘slipped’ amine and amine degradation products in the troposphere and biosphere
3. determine whether amines form nitrosamines under absorber or stripper conditions or in the atmosphere
4. develop appropriate solution-based mitigation strategies
5. understand the environmental impact of amine slip



Experimental

Reaction Conditions:

Temperature 60 C
CO_2 13 %
O_2 5%
NOx 0.8 %
N_2 81%
PZ15%wt/wt
Run time 30 Hours



ATR-FTIR
UV-Vis
GC-MS
API-MS

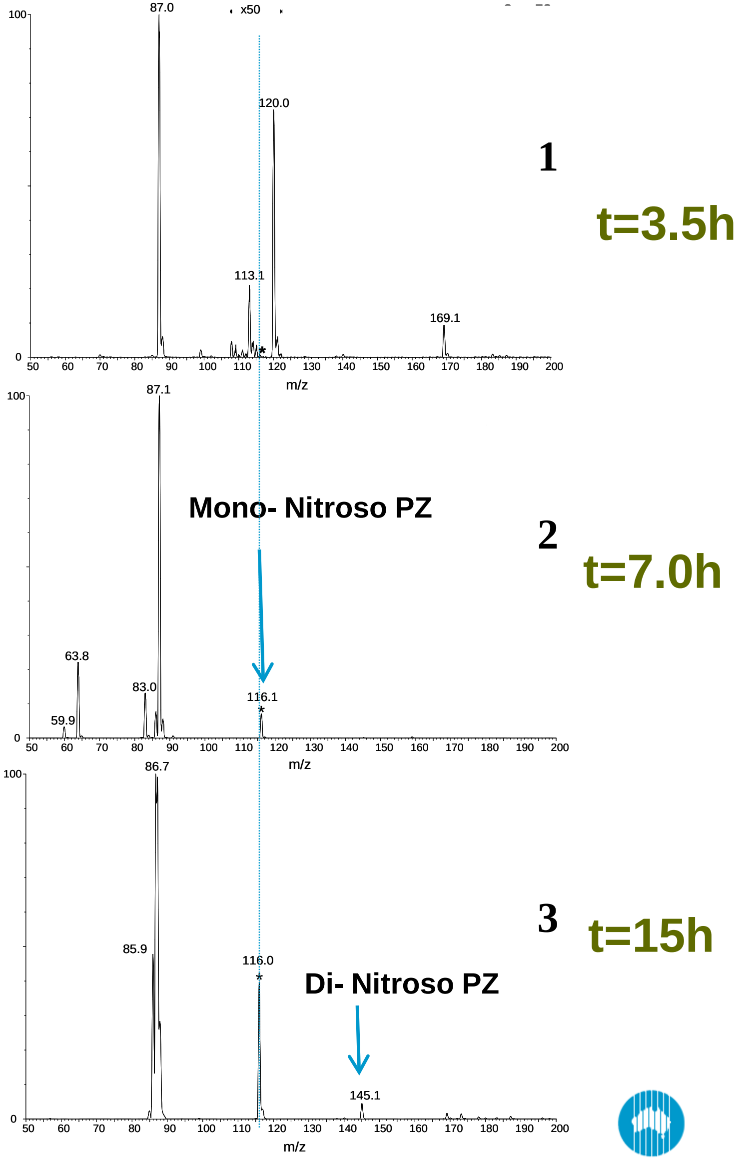
Most probable NOx chemistry

- NOx and water leads to Nitric (HNO3) and Nitrous Acid (**HONO)** formation under ambient conditions:
- **HONO** is a nitrosating agent
- NOx in the flue gas under typical absorber conditions
- $NO + NO_2 + H_2O \rightarrow$ **2 HONO**
- **HONO** + $HOCH_2CH_2NHR_1 \rightarrow$ **$HOCH_2CH_2NR_1$-N=O** + H_2O

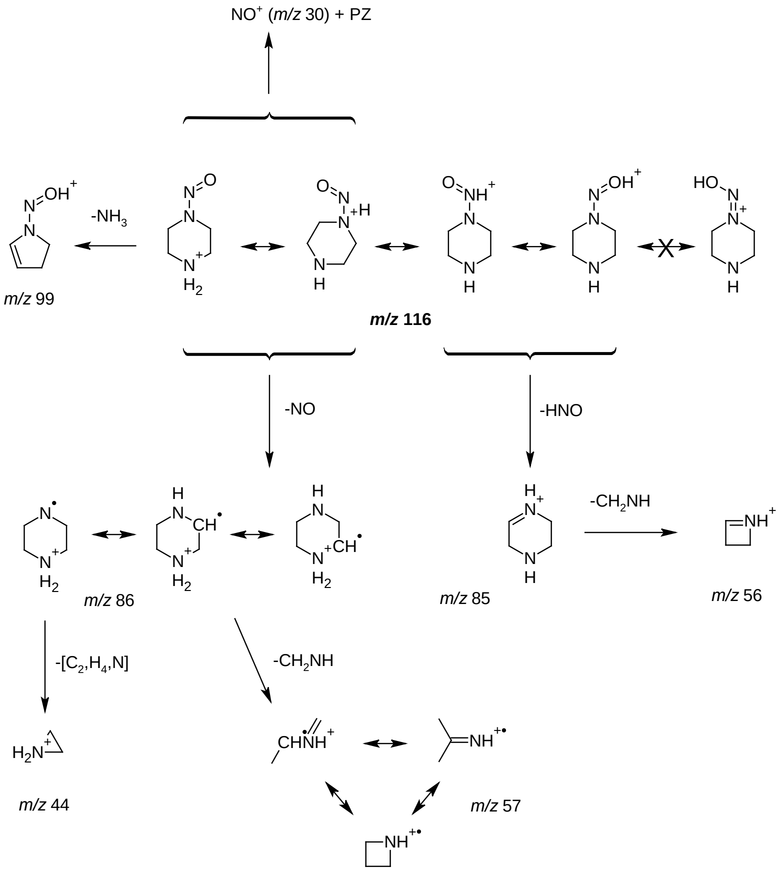
Nitrosamine formation from piperazine

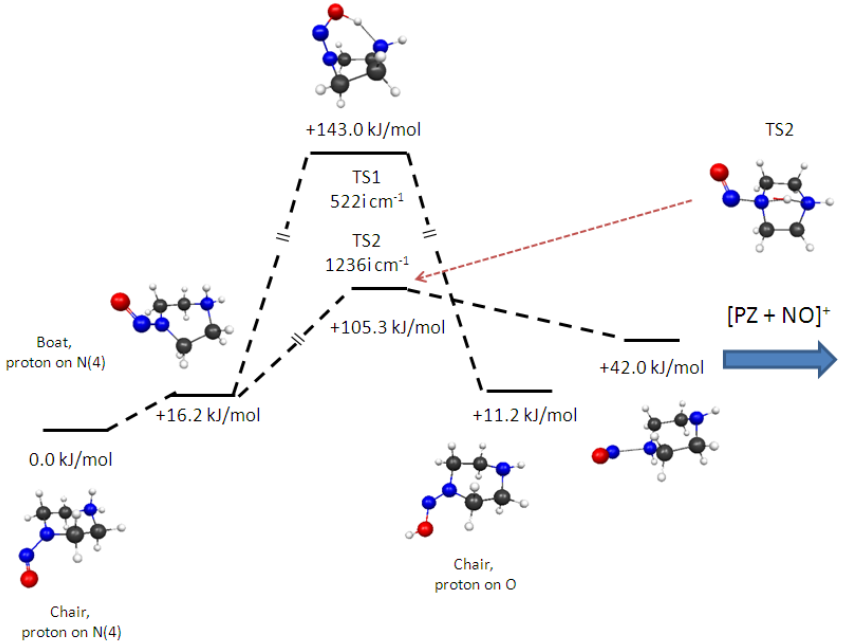
- Under controlled 'Absorber' conditions, in the laboratory, we have observed the formation of N-nitrosopiperazine, N-oxopiperazine and piperazine nitramine

CO_2 loaded PZ solution (LHS)
After exposure to synthetic flue gas (RHS)



We need to understand gas-phase chemistry to quantify N-nitrosopiperazine.......

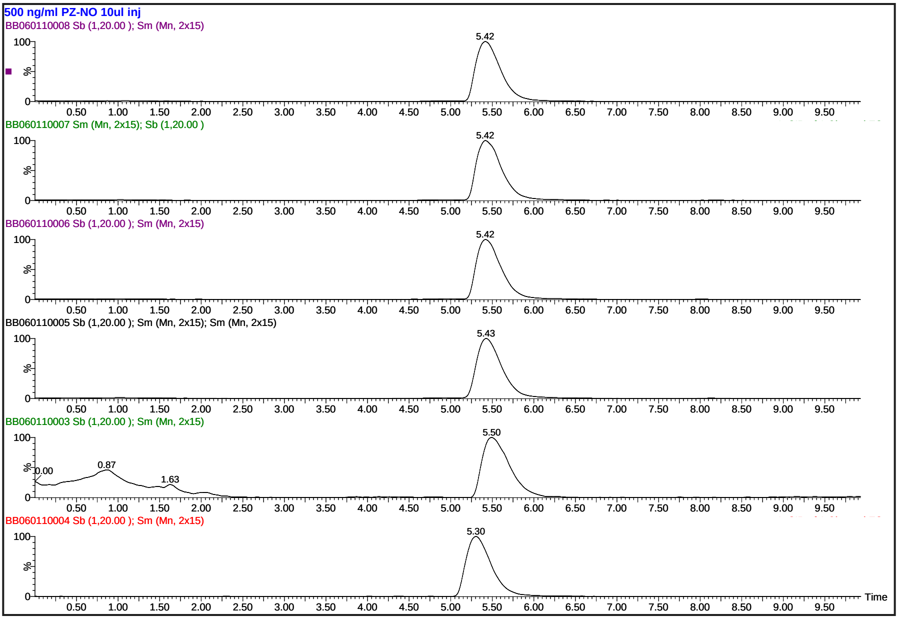




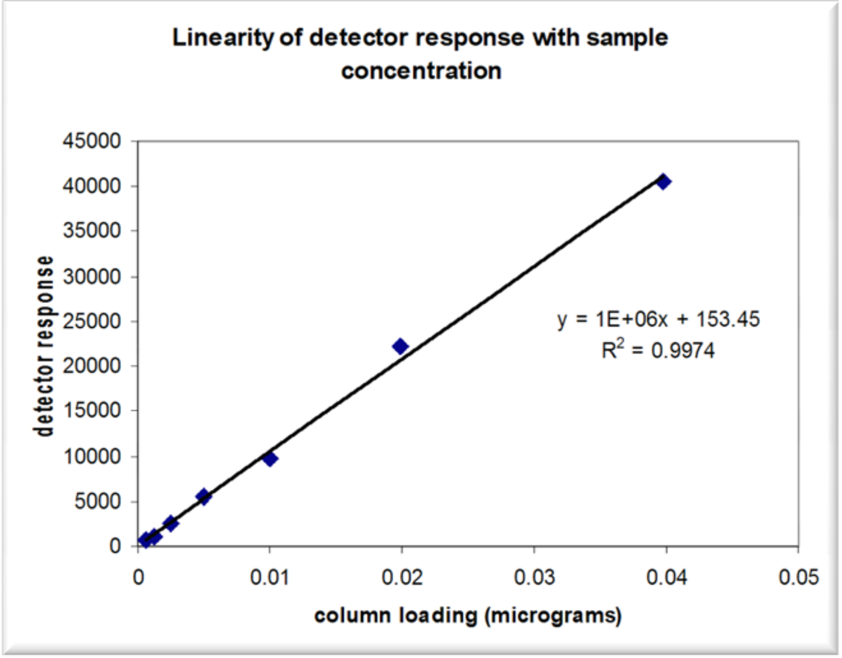
- The ratio of the product peaks at m/z 85, 86 is sensitive to MS conditions because of pre-dissociative isomerisation
- In simple terms, the ion can isomerise before falling apart
- Solution.......use multiple peaks to quantify

Quantifying

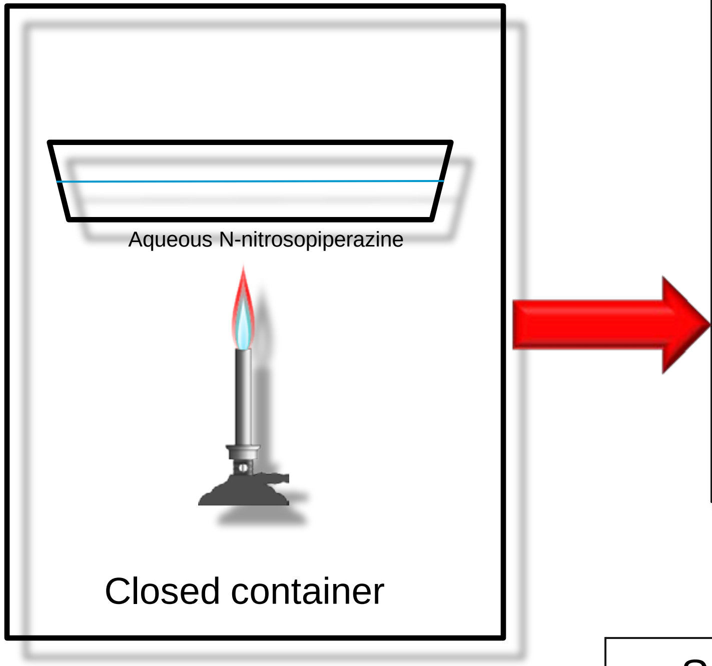
Injection reproducibility at 5 ng with Multiple Reaction Monitoring:

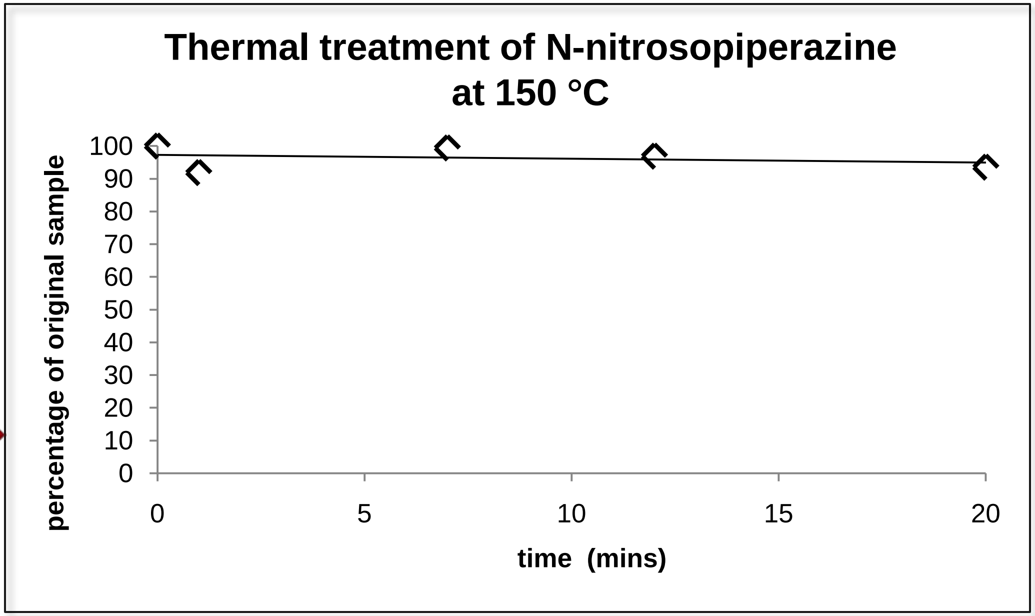


Detector response is linear over 3 orders of loading magnitude.........



Effect of Thermal Treatment

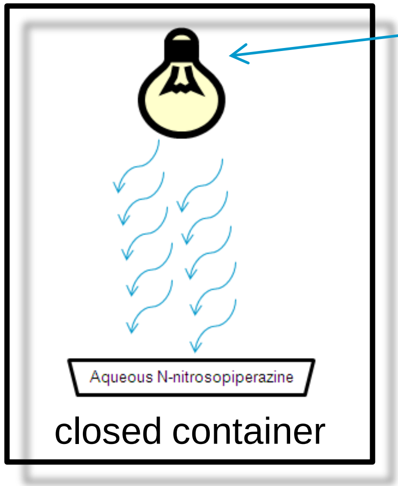


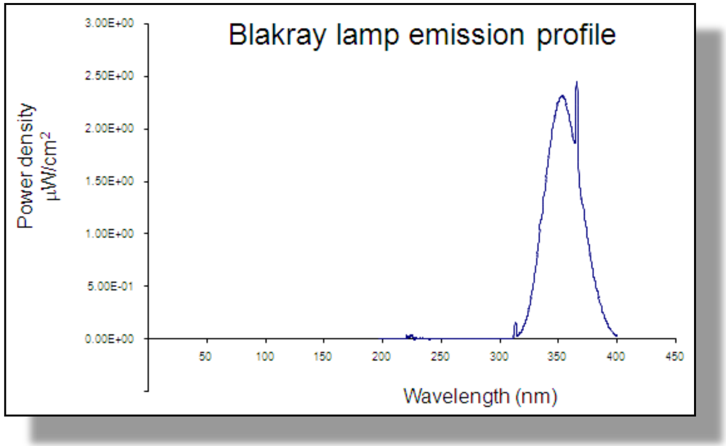


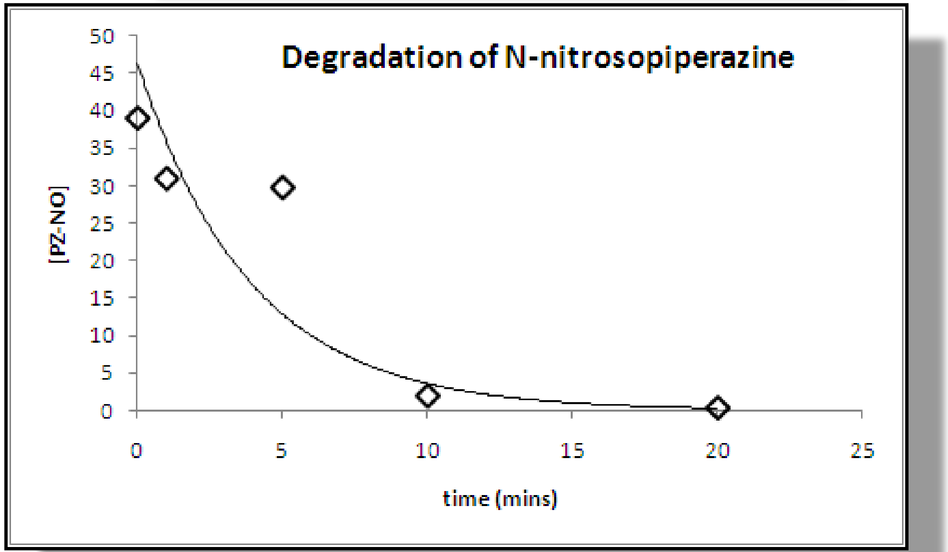
- Solution sampled at regular intervals for analysis
- No thermal degradation observed even after exposure of the same sample to 160 °C for an additional 30 mins

UV light photolysis

Broadband UV light source

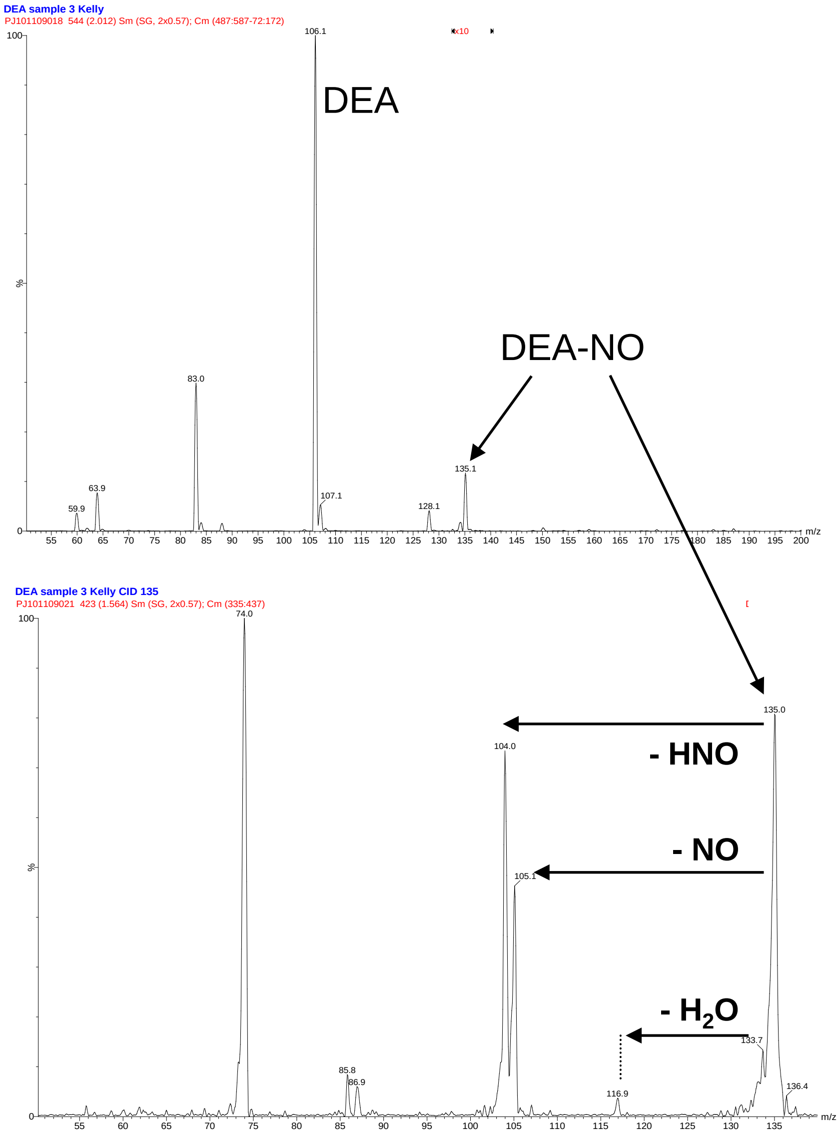






- **Solution of N-nitrosopiperazine**
- **No agitation**
- **Sampled at regular intervals**
- **Broadband UV light source**

Diethanolamine (DEA)



Reaction Conditions:

Temperature 60 °C

CO_2 13 %

O_2 5%

NOx 0.8 %

N_2 81%

Run time 8 Hours

DEA 30%wt/wt

Conclusions and Recommendation

- Oxidative and thermal degradation studies have been carried out in the past have not taken into account ***all*** flue gas contaminants
- Presented case study and other studies indicate that ***secondary amines*** are reactive in the presence of NOx to form nitrosamines and other nitro products.
- Need to better understand the chemistry of degradation under flue gas conditions such as laboratory and pilot plant.
- Solvent development and selection as well as mitigation strategies needed to reduce formation of products of environmental concerns.
- Emissions monitoring for both parent amine and degradation products is a necessity for extended operation of the solvent.
- Need to determine the effectiveness of current de-NOx technologies

Current and future work at CSIRO

Realistic lab based data and analytical procedures:

Oxidation and thermal degradation experiments carried out under controlled conditions

Low level analytical procedures

Pilot plant samples from exhaust and liquor

Long term operational data

Smog chamber simulations will be carried out to:

Identify the major pollutants produced by the photo-decomposition of the flue gas compounds of the absorber under selected ambient conditions

Identify the major chemical reactions pathways responsible for the MEA oxidation

Develop the appropriate chemical mechanism required to simulate the oxidation of MEA

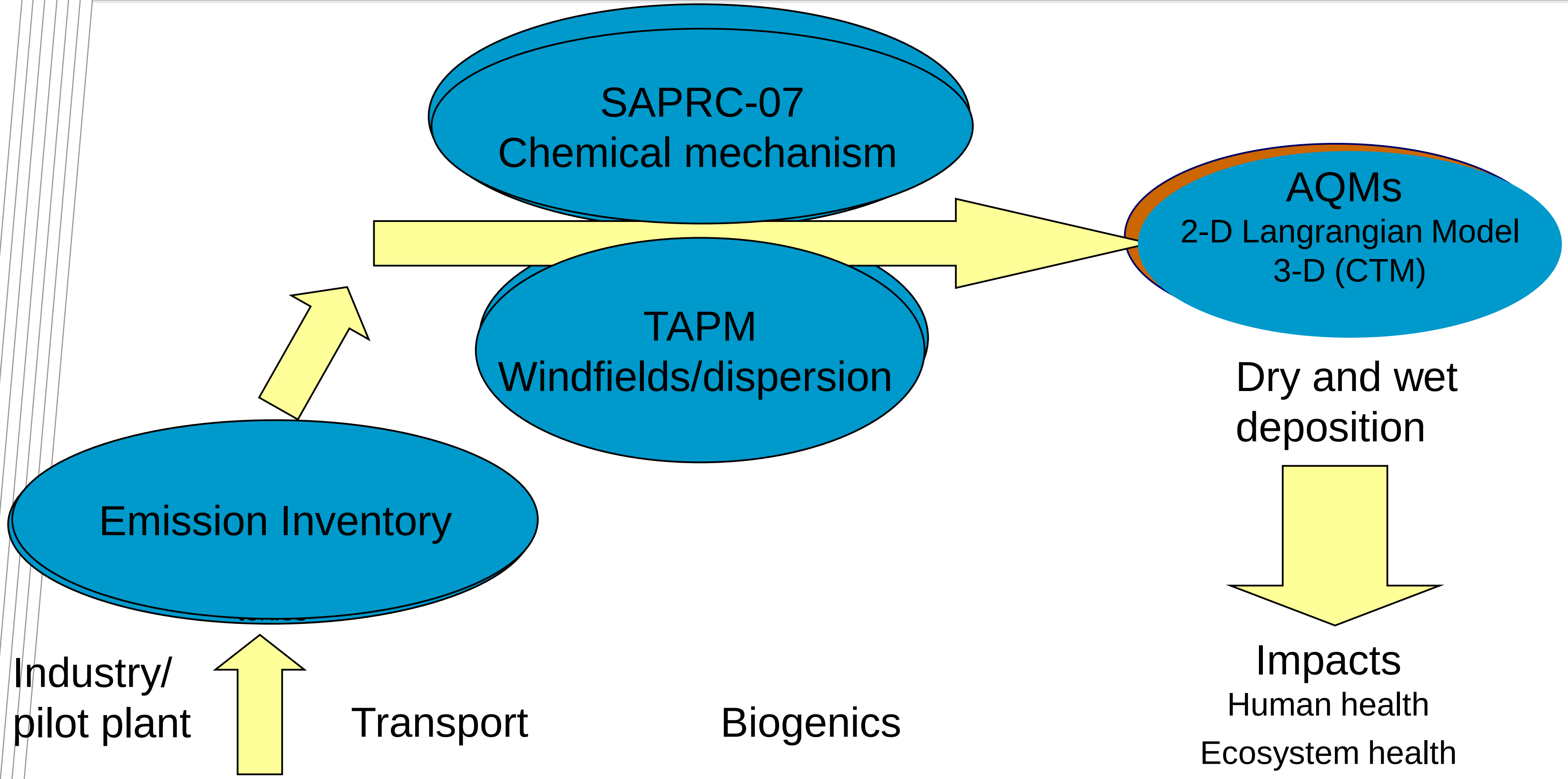
Airshed modelling to determine the potential environmental impact of using amine solution for CO_2 capture

Embedded the modified chemical mechanism into the airshed model

Simulate different atmospheric scenarios to assess the potential impact of the new CO_2 capture process

Determine the trade off between CO_2 capture and local and regional air quality

CSIRO expertise in the whole range of issues



SAPRC-07
Chemical mechanism

AQMs
2-D Langrangian Model
3-D (CTM)

TAPM
Windfields/dispersion

Dry and wet deposition

Emission Inventory

Impacts
Human health
Ecosystem health

Industry/
pilot plant

Transport

Biogenics

- ***What would be the impact of changing emissions profiles ?***

Air Quality Models (AQMs)

- AQ modelling is used to describe the spatial and temporal distribution of pollutants resulting from the interactions between emissions, meteorology, atmospheric concentrations, deposition, and other factors.
- The representation of the chemical transformations has been one of the most challenging tasks for AQ modelling.
- Additional complexity will arise from amine emissions to the atmosphere.
- The atmospheric chemistry of amines is still not well understood and further research is required to better understand this.

Sources of Data

Data from :

1. the CSIRO carbon capture pilot plants
2. The CSIRO solvent degradation laboratory
3. other overseas facilities (if available)
4. the CSIRO smog chamber facility
5. the analytical laboratories

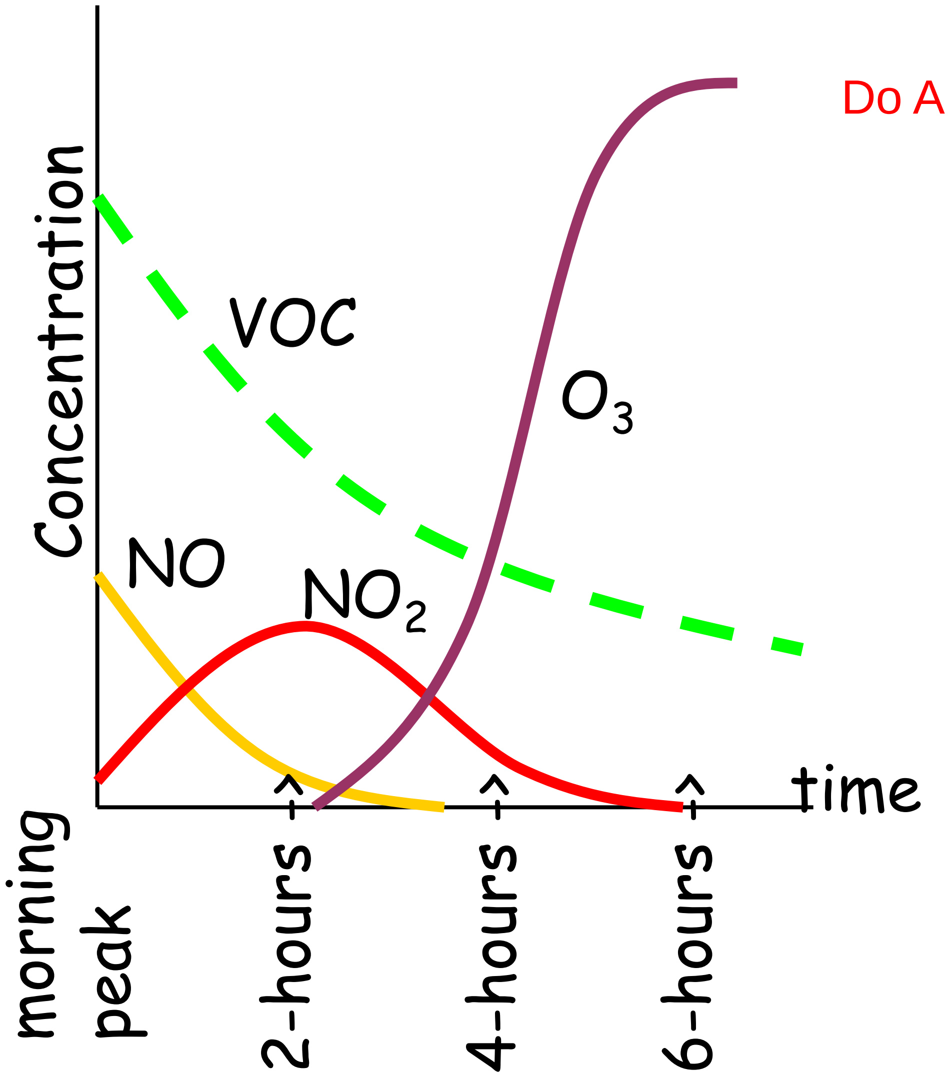
are used to develop the appropriate understanding required for elucidating the atmospheric chemistry of amines and other reactive compounds.

Relevant CSIRO research expertise

- Experimental and apparatus design to accommodate for different types of experiments.
- Collection, interpretation and modelling of data obtained from our experimental facilities including the CSIRO smog chamber.
- Trace, gas-phase organic carbon analysis.
- Air quality and numerical modelling.
- Atmospheric chemistry mechanism development.
- Determination of VOC reactivity and aerosol forming potential and yields.
- Emission, volatility and fate study capability
- Development of air quality models.
- Reactivity and environmental impact assessments.

Chemistry of Reactive Organic compounds

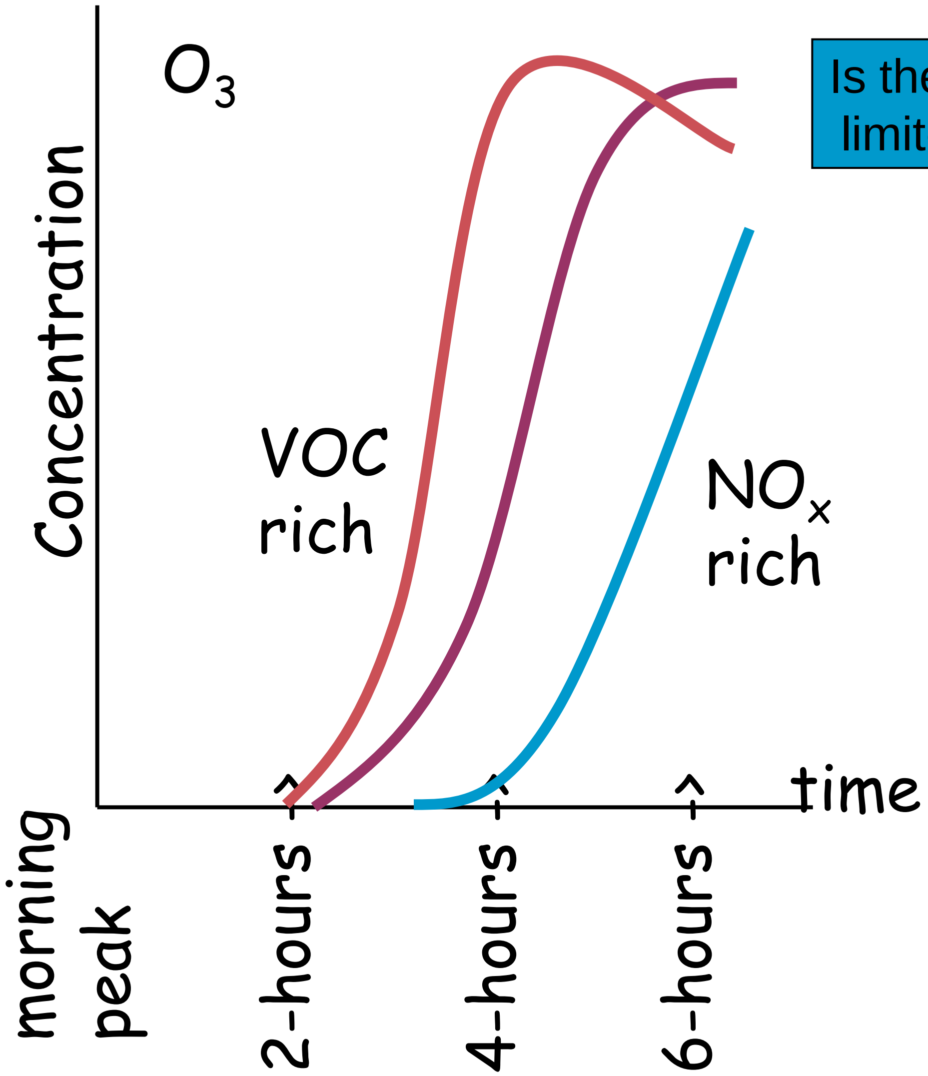
VOC + NO_x (+ sunlight) → Ozone + (other) Smog Products



Do Amines act as VOCs?

Regimes for PCS formation

VOC + NO_x (+ sunlight) → Ozone + (other) Smog Products



Is the production of oxidants limited by NOx or by VOC ?

The CSIRO smog chamber facility

The smog chamber is an 18 m^3 Teflon-lined enclosure with UV lamps at both ends to simulate sunlight.

The chamber is filled with clean air and dosed with NOx and VOC to simulate ozone and secondary organic aerosol formation in the atmosphere.

Dedicated instruments track the concentrations of;

- Ozone
- NOx
- Particles
- VOCs

Advantages of the smog chamber approach

- Simulations can be performed under well specified and controlled conditions appropriate for a selected airshed.
- The results from the chamber experiments can be used to refine the photochemistry to accommodate different ambient air quality modelling scenarios.
- Targeted photooxidation of products of emissions from amine plants such as NH_3, acetaldehyde, formaldehyde and acetone can be investigated.

Case Study

Study of MEA

photo-degradation using the CSIRO smog chamber

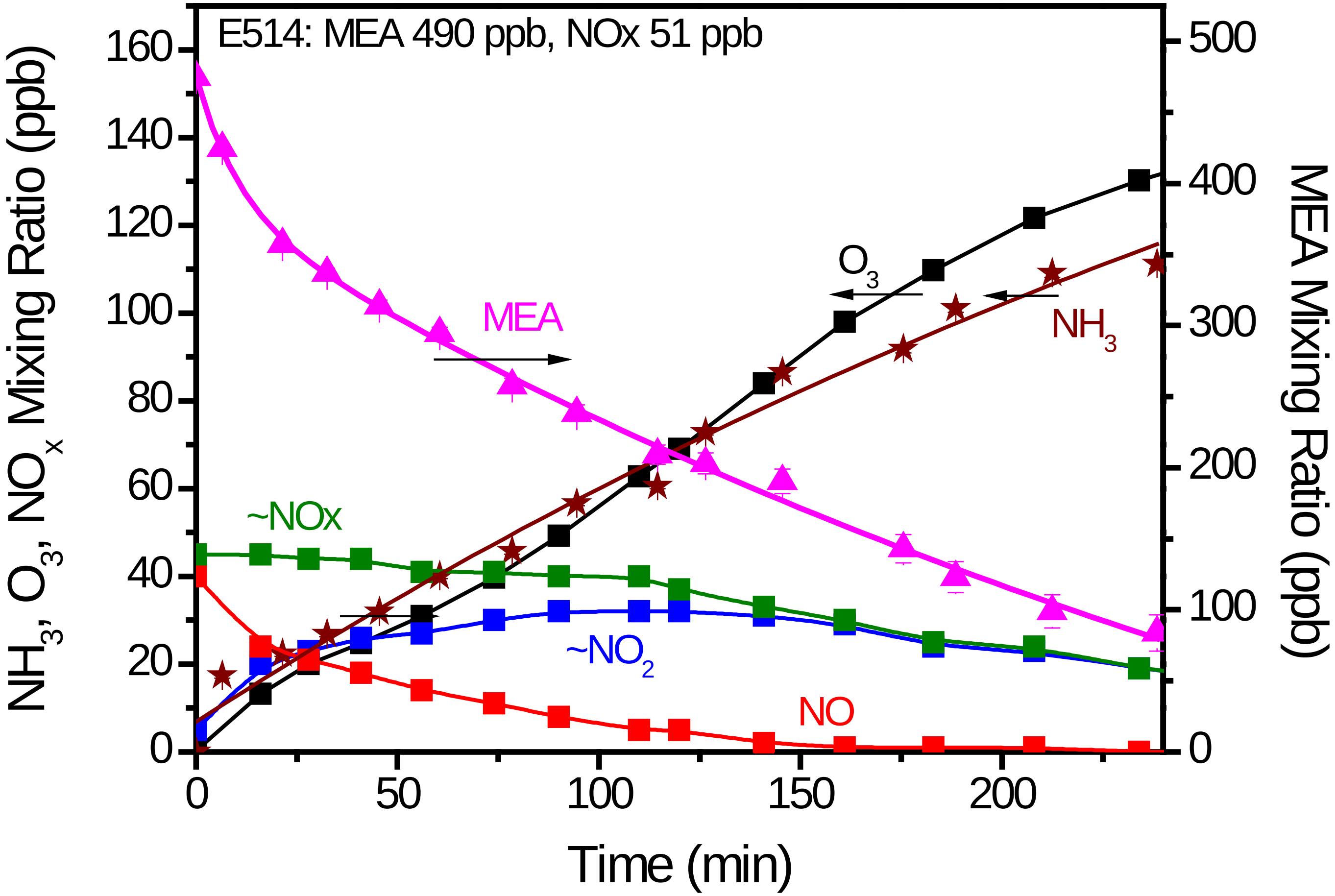
Experimental matrix: Initial concentrations

NO_X Mixing Ratio ±5%	MEA Mixing Ratio ±10%	
(ppb)	167	500
50	6.7	20
150	2.2	6.7
450	0.7	2.2

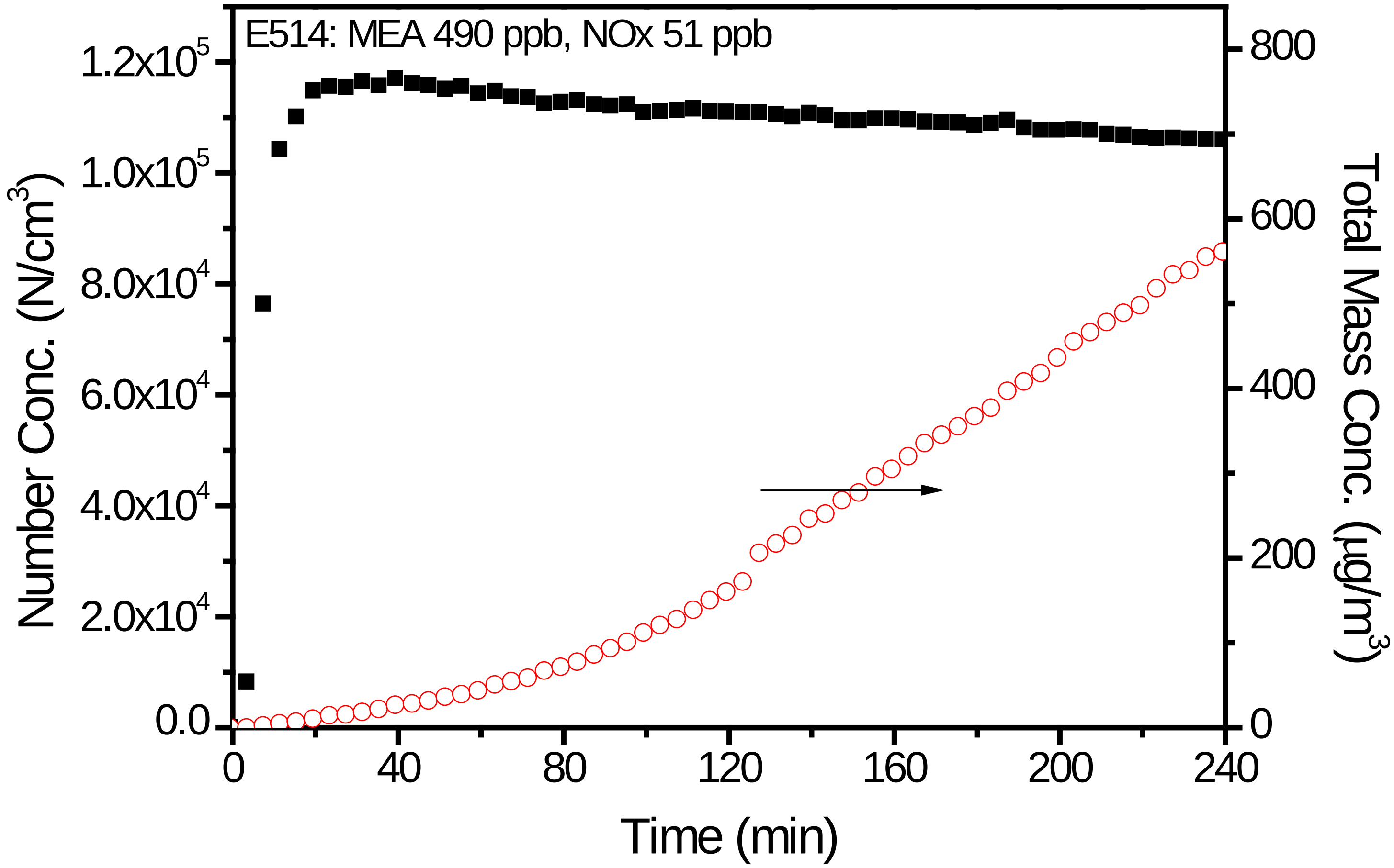
Project status and comments

- The project is being performed in Sydney, Australia in association with Norsk Energi and Gassnova.
- The project is in its final stages.
- Validation, interpretation and modelling are still progressing.
- Results presented here are preliminary.
- Analyses of carbonyls and nitroso-products is still in progress.
- No conclusions have been drawn at this stage.

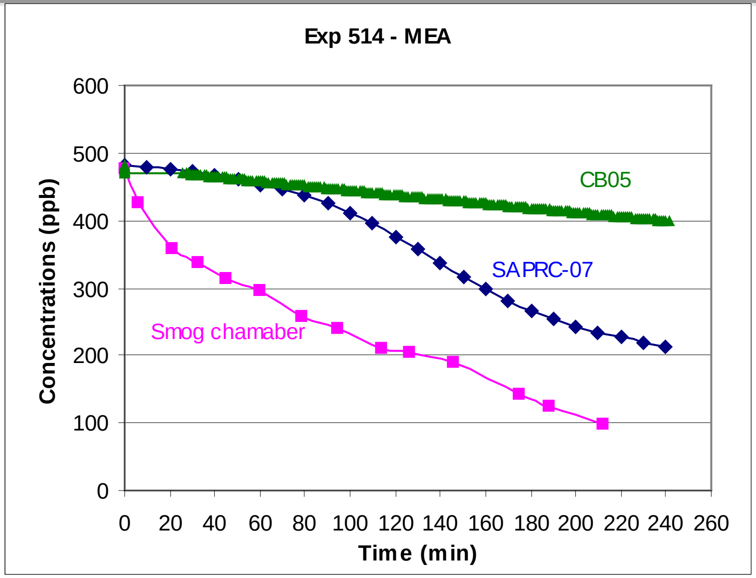
Smog chamber results VOC/NOx = 20

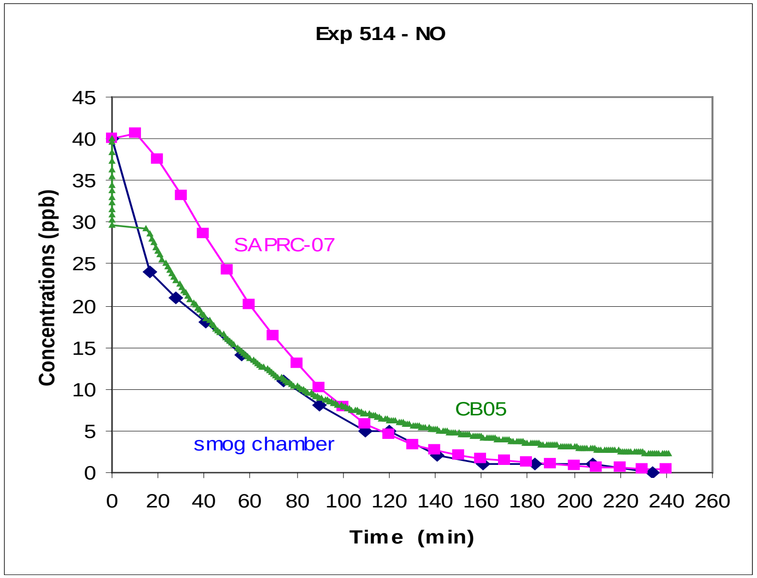


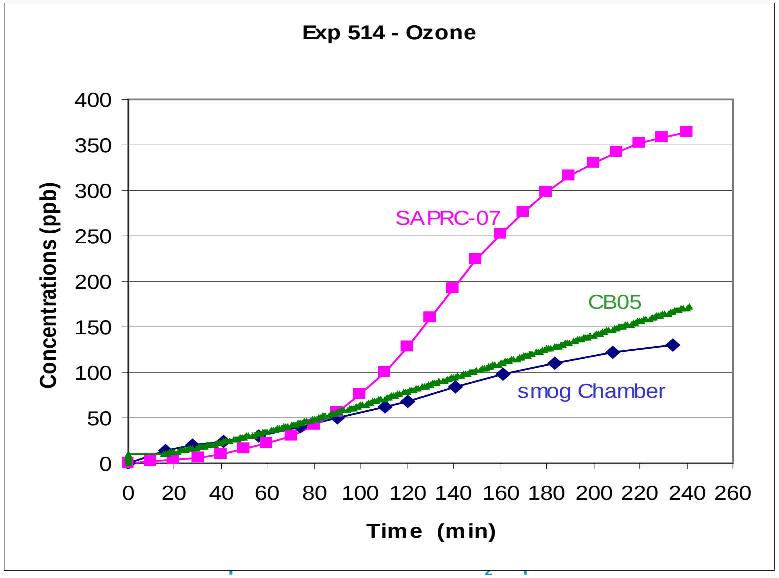
SOA formation (VOC/NOx = 20)



SAPRC-07 simulations (VOC/NOx = 20)



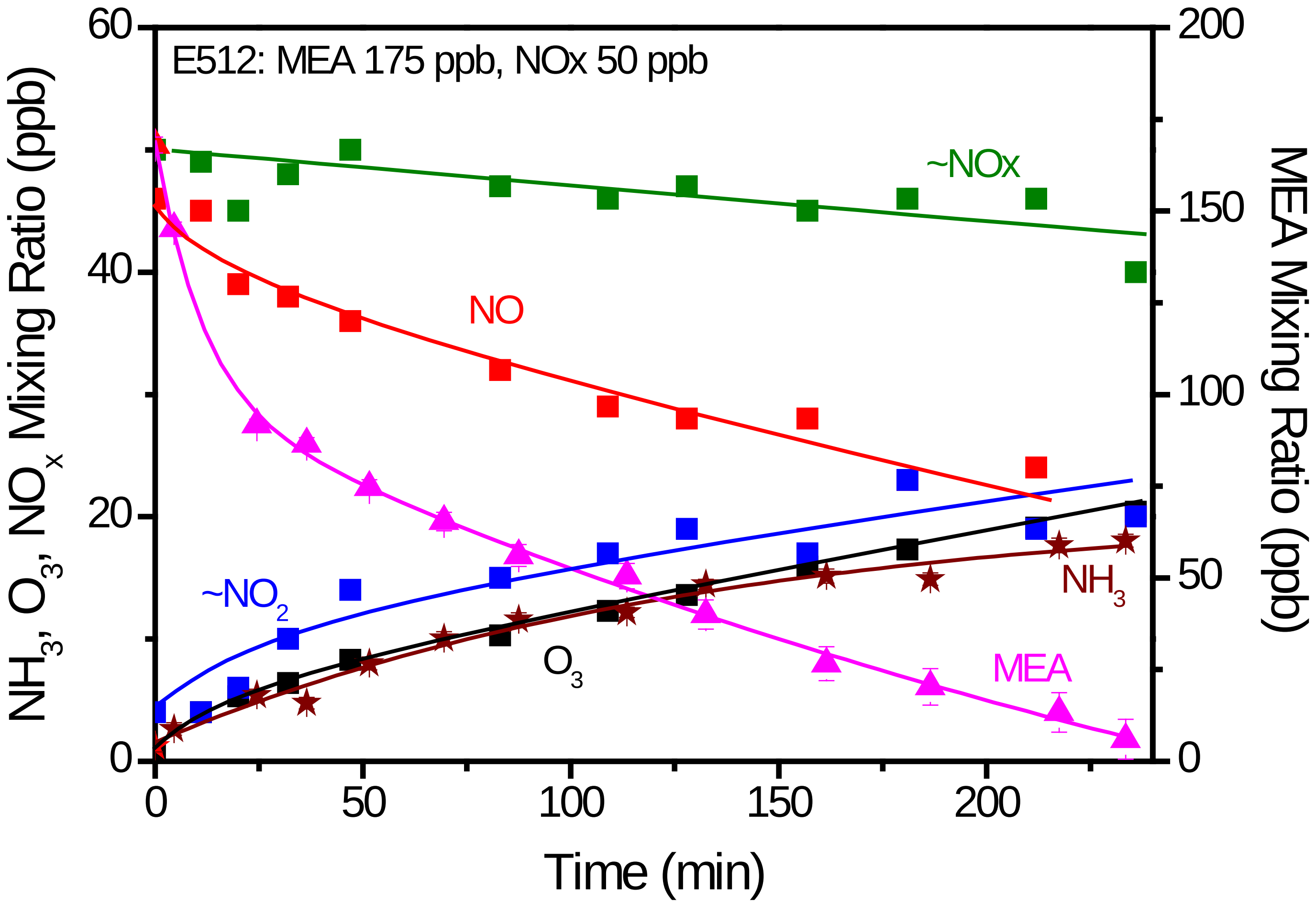




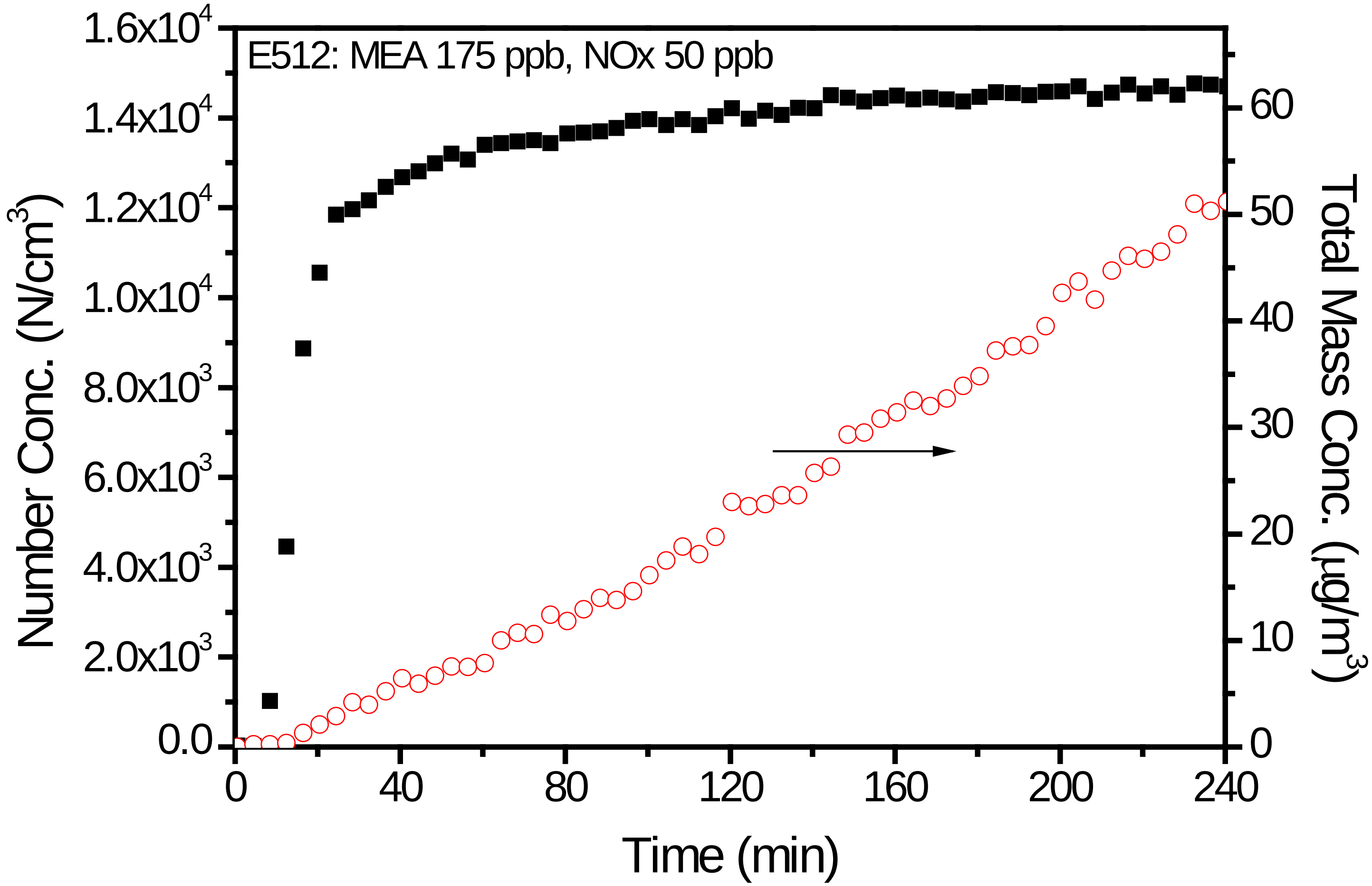
- The formation of NH_3 is an unexpected finding of this study.

- Deficiency in MEA and O_3 is probably due to the unaccounted for consumption of MEA by SOA and NH_3 formation.

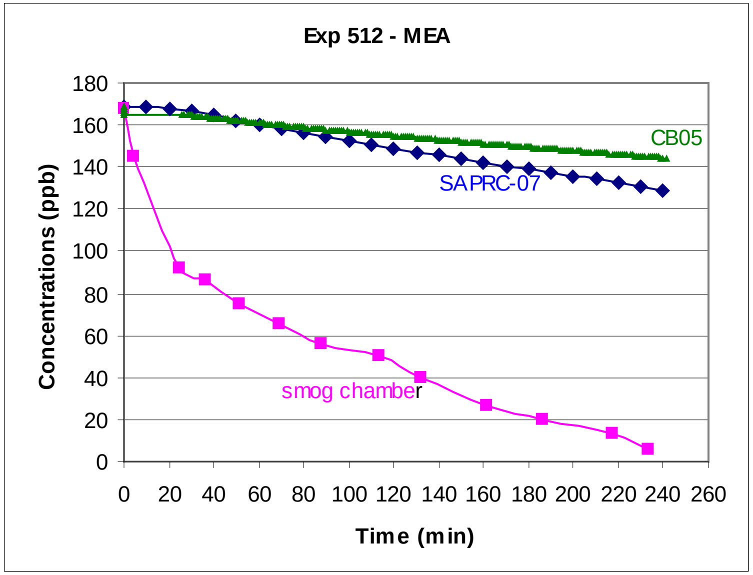
Smog chamber results (VOC/NOx = 6.7)

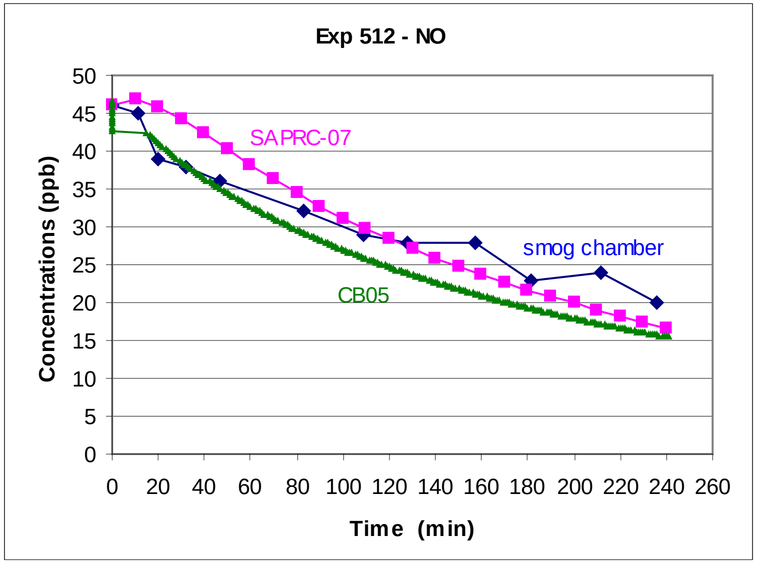


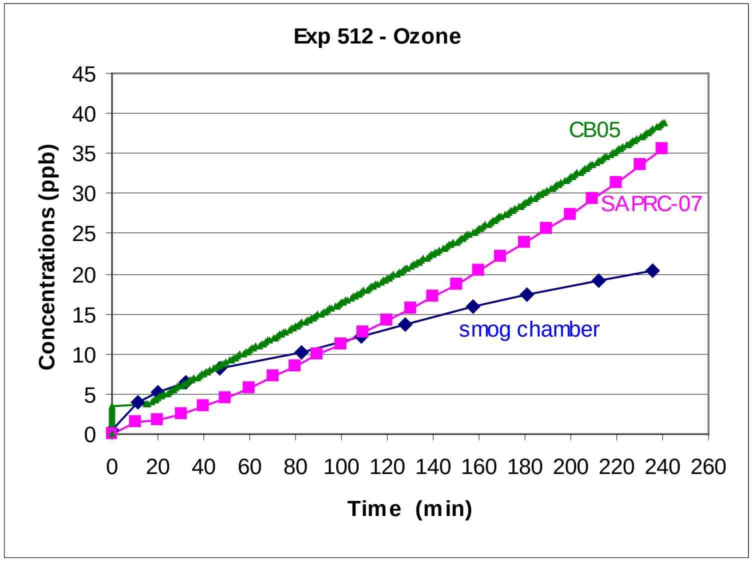
SOA formation (VOC/NOx = 6.7)



SAPRC-07 simulations (VOC/NOx = 6.7)


Exp 512 - MEA


Exp 512 - NO


Exp 512 - Ozone

- The formation of NH_3 is an unexpected finding of this study.

- Deficiency in MEA and O_3 is probably due to the unaccounted for consumption of MEA by SOA and NH_3 formation.

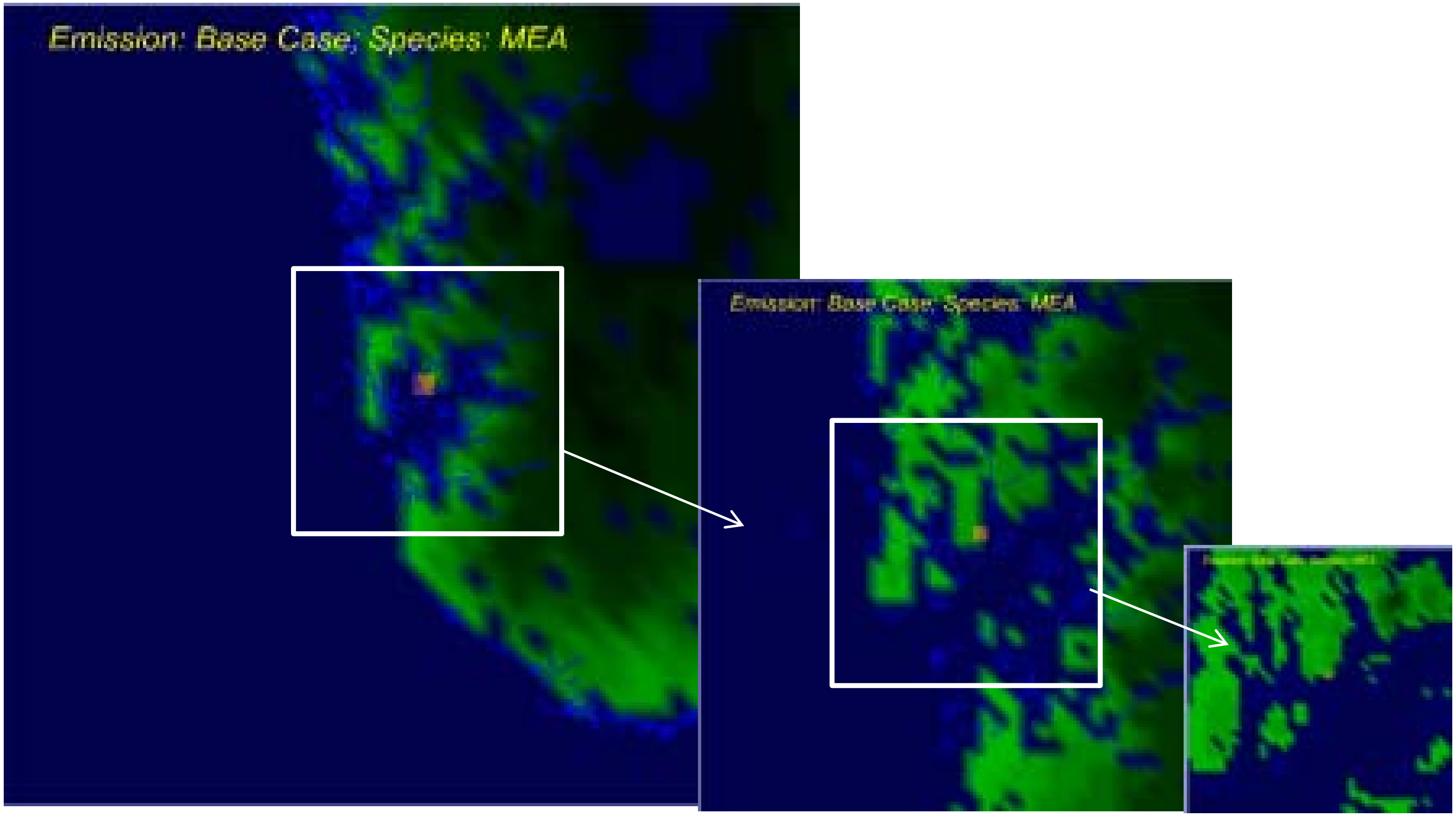
Modelling of Selected Point Source in Norway – Case Study

- 2-dimensional Lagrangian Reactive Wall Model for high resolution.
- 3-dimensional chemical/transport model for regional modelling TAPM/CTM.

Modelling of Selected Point Source in Norway – Case Study Using (TAPM/CTM)

- TAPM-CTM is a coupled 3-D meteorological-chemical transport dispersion model.
  - Prognostic meteorological model (primitive equation; incompressible; non-hydrostatic)
  - Chemical transformation modelled using the CB05 mechanism
  - CB05 extended to include MEA chemistry (derived from smog chamber modelling)
  - ISORROPIA used to model NH_3NO_3 and $NH_3(SO_4)_2$ production
  - Secondary organic aerosols also modelled.
  - Triple nested grid- 9 km; 3 km; 1 km.
  - Regional air emissions inventory (VOC, NOx, CO, SO_2, NH_3 and PM)
  - Detailed industrial inventory (VOC, NOx, CO, SO_2, NH_3, PM and MEA)

Triple nested grid- 9 km; 3 km; 1 km

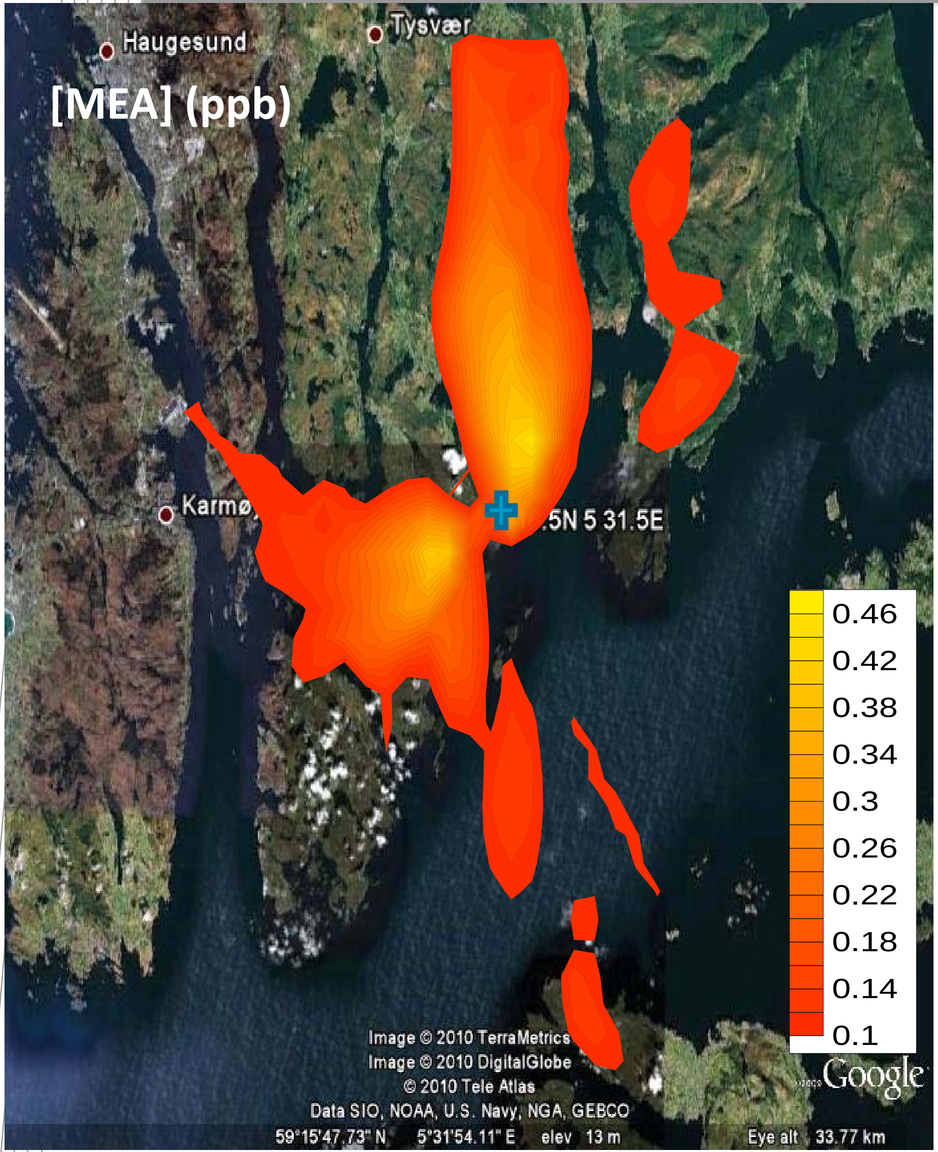


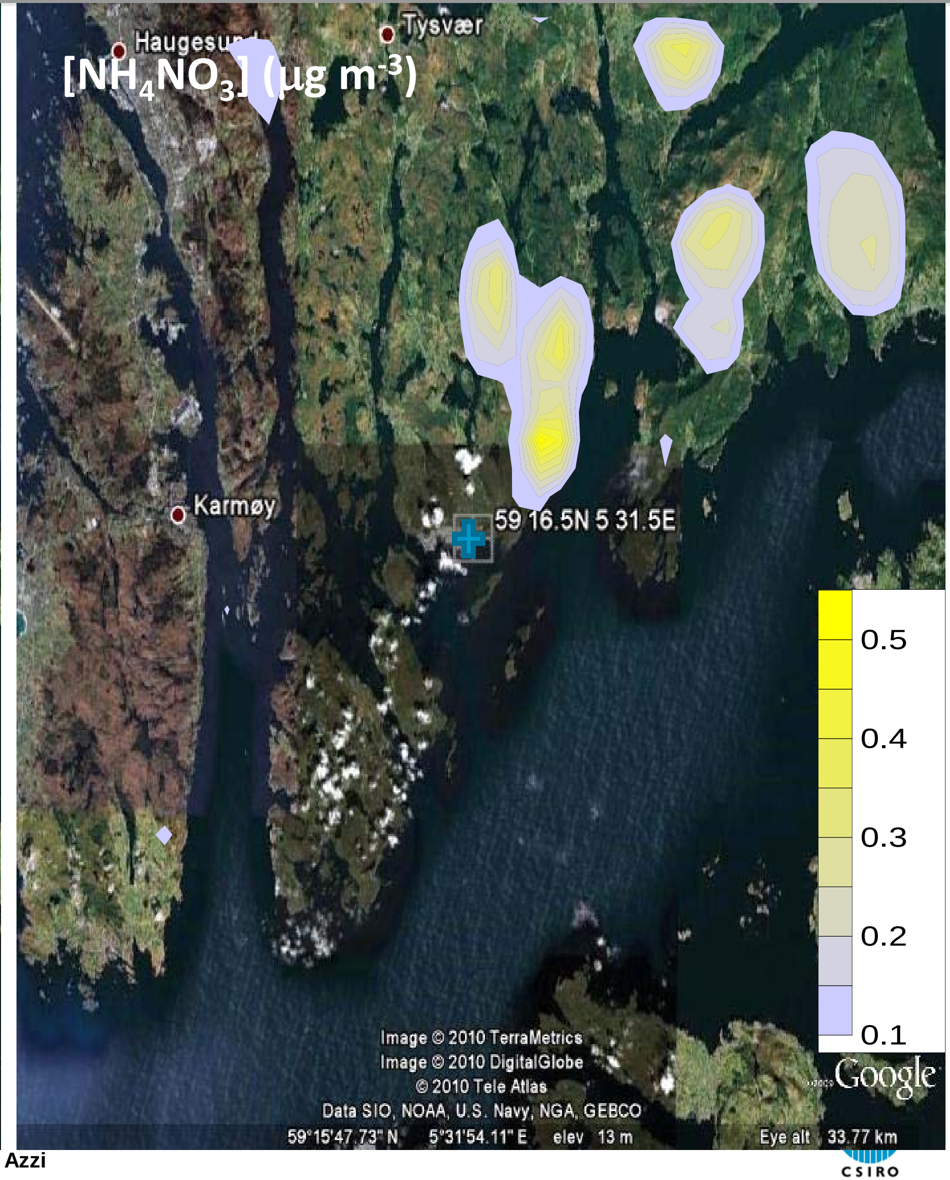
Scenario Case Study

In the example here,

- VOC,NO_x and SO_2 data spatially distributed on 4km gridded population data base. VOC speciated on CB05 organic classes.
- We built a biogenic (VOC&NO_x) and point source (NOx, MEA, NH3) inventories
- We ran TAPM-CTM on 4-nested grids for a week. The outer grid (not shown in the slide) was 27 km spacing and was used for nesting into a global meteorological analysis
- TAPM-CTM has been run for one week. Shown are the peak 1-h concentrations of MEA and ammonium nitrate.

Predicted Peak 1-hr Concentrations of MEA & NH_4NO_3





Preliminary conclusions

- MEA is a photochemical smog precursors that can be limited by NO_x or MEA. There is urgent need to assess the importance of ROC in the process.
- Using diethylamine, the nitrosodiethylamine were detected
- Capability to measure nitrosamines and other nitro-compounds are still progressing
- Ability of SAPRC-07 and CB05 to simulate the limited smog chamber experiments revealed the importance of NH_3 and SOA in the process of MEA decay.
- Chemical reaction modelling is progressing
- Dispersion and deposition estimates is progressing

Recommendations

- The atmospheric photo-oxidation of amines destined for use in PCC should be studied to elucidate the major chemical reaction pathways.
- The speciation and lifetimes of new chemical products of concern need to be determined.
- Simulation experiments should be carried out over a range of ambient conditions (in terms of NO, NO_2, VOC and NH_3 concentrations).
- The urgent development of semi-empirical techniques is required in order to predict the formation of major secondary pollutants.
- The development of more complete, amine-inclusive, atmospheric chemical mechanisms is required for use in air quality models.
- It is important to develop a method for the chemical speciation of the formed SOA during chemical reactions.

Acknowledgments

- We would like to thank the IEA and Gassnova for organising the Workshop.
- We also extend our thanks to Norsk Energi and Gassnova for funding the smog chamber work and CSIRO for project support.
- Special thanks to Anne Tibbet, Dennys Angove and Phil Jackson

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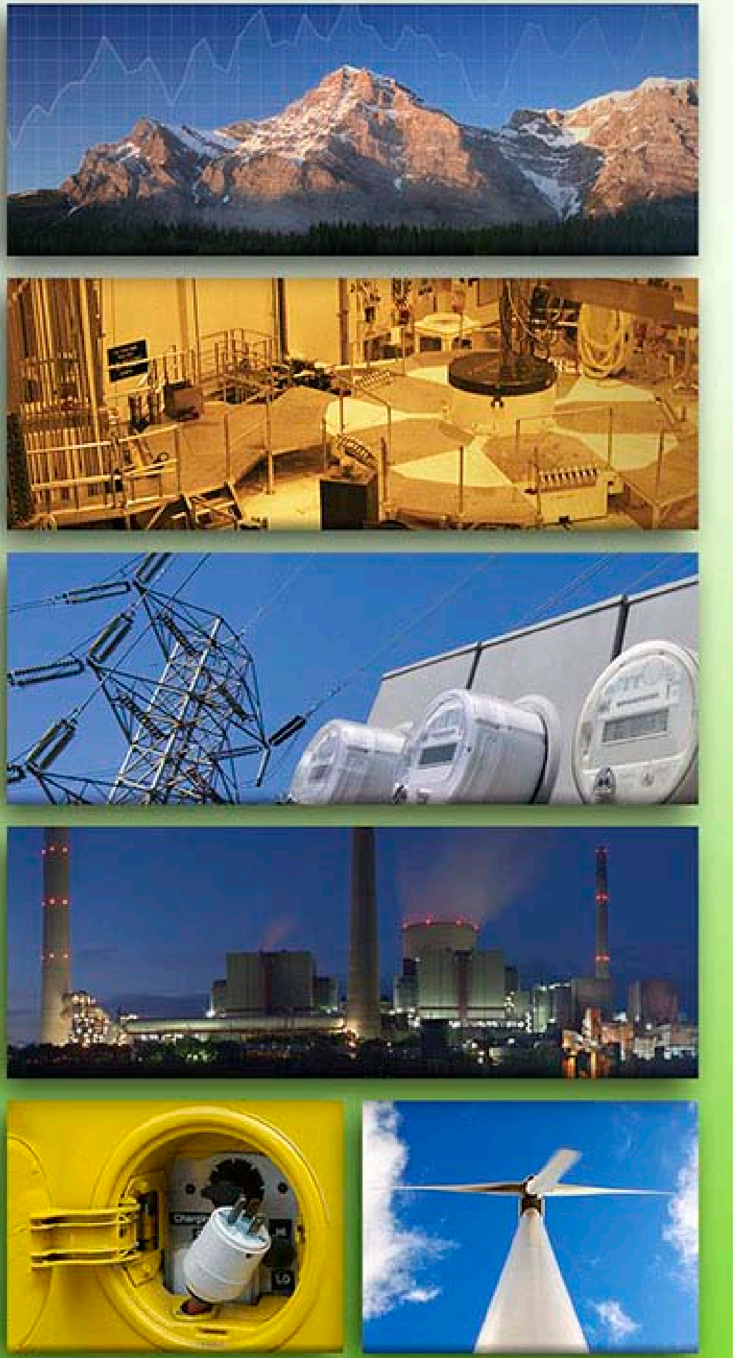

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Atmospheric Chemistry of Amines

EPRI Strategic Research Program on Health and Environmental Impacts of Future Power Plant Emissions

Eladio M. Knipping, Ph.D.
Senior Technical Manager, Environment

Environmental Impact of Amine Emission During Post Combustion Capture
February 16, 2010

Program Objective

- Overall Objective: Evaluate the potential human health and environmental impacts related to the future combustion-based generation options, including emerging
  - fuels,
  - plant designs, and
  - emissions controls.

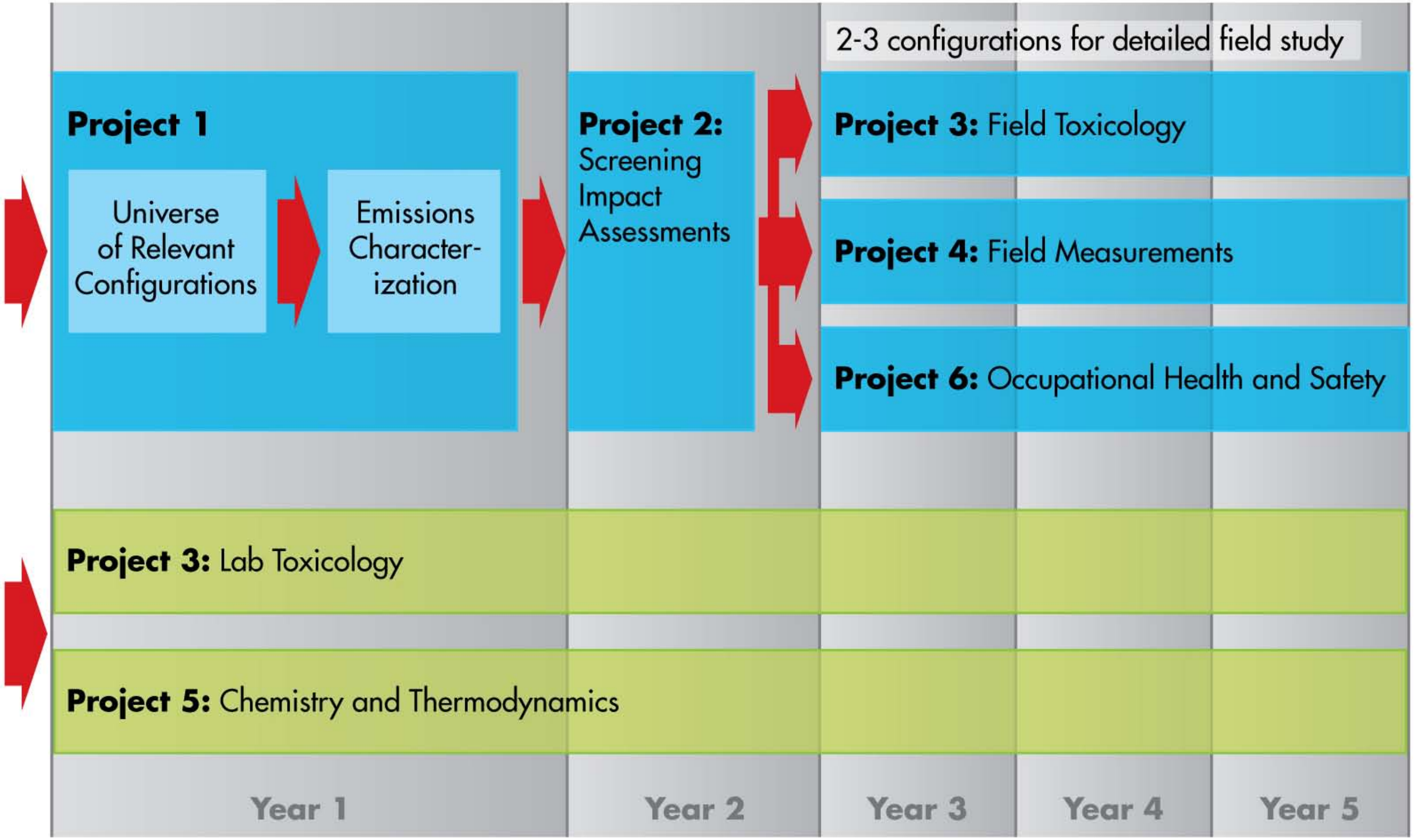
- Provide designers and engineers with the opportunity to mitigate health/environmental concerns early in the development process.

- Increase likelihood of optimal tradeoffs between economic and environmental performance while avoiding costly back-end measures.

Program Scope

Controls/ Designs/ Fuels

Basic Laboratory Science and Modeling



2-3 configurations for detailed field study

Project 1

Universe of Relevant Configurations

Emissions Characterization

Project 2: Screening Impact Assessments

Project 3: Field Toxicology

Project 4: Field Measurements

Project 6: Occupational Health and Safety

Project 3: Lab Toxicology

Project 5: Chemistry and Thermodynamics

Project 1: Parameter Identification and Information Gathering

- Define most prevalent designs, fuels, and controls in 2030

- Develop short list of 20 configurations

- Characterize emissions:
  - Conventional pollutants
  - Novel process-related materials
  - Fugitive emissions

- Provides a preliminary projection of a future combustion-based generation fleet and its potential emissions for use in a screening-level impact assessment (Project 2)

Projected Emissions Controls in 2030

- **NOx:** Will continue to be dominated by SCR, SNCR and LNB installations. Also included two multi-pollutant control systems.
- **Mercury:** Currently dominated by sorbent injection processes; trend will continue.
- **PM:** Likely to be driven almost entirely toward fabric filters (particle size and sorbent considerations).
- **SO_2:** Four dry FGD technologies, 5 wet alkaline solution/slurry systems, 1 amine based process, 3 ammonia-based FGD systems.
- **CO_2:** Biggest unknown. Most likely: several amine-based systems and the two leading ammonia-based technologies.

Project 3: Toxicology Studies

- Laboratory toxicology studies using rodents to evaluate interactions between plant emissions and other atmospheric constituents
- Field toxicology studies to examine the impact of advanced controls and fuels.
- Build upon EPRI-funded “SPHERES” Program: Secondary Particle Health Effects Research
- Finalizing research design
- Exposures to begin later in 2010

Project 4: Field Measurement Studies

- Emissions measurements: flue gas and fugitive emissions

- Ambient measurements: at ground-level downwind of the plant

- Chemicals of interest:
  - SO_2, NOx, PM…
  - Metals
  - Organics
  - Trace elements
  - N-containing compounds, including amine degradation products

Project 5: Chemistry and Thermodynamics Studies

- Laboratory studies: Smog chamber experiments with important constituents of future power plant emissions

- Modeling studies focused on key chemicals related to the future generation fleet

Technical Progress: Project 5
Atmospheric Chemistry of Amines

- Amines are of toxicological interest, but not enough is known about their chemistry in the atmosphere

- Completed Project: “Secondary Organic Aerosol from Aliphatic Amines”

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CALIFORNIA INSTITUTE OF TECHNOLOGY 1891

Secondary Aerosol From Aliphatic Amines

S.M. Murphy, A. Sorooshian, J.H. Kroll, N.L. Ng, P. Chhabra, C. Tong, J.D. Surratt, E.M. Knipping, R.C. Flagan, and J.H. Seinfeld

Open-access manuscript published in Atmospheric Chemistry and Physics (2007)

Emission Sources

- Animal husbandry
  - 0.15±0.06 Tg/yr (Schade and Crutzen, 1995)
  - 100's of ppb of various amines observed in gas phase near source (Rabaud et al., 2003)
  - **Significant uncertainty remains**

- Automobile exhaust
- Marine sources
- Industrial sources
  - Used as catalyst and for H_2S removal

- **CO_2 capture**

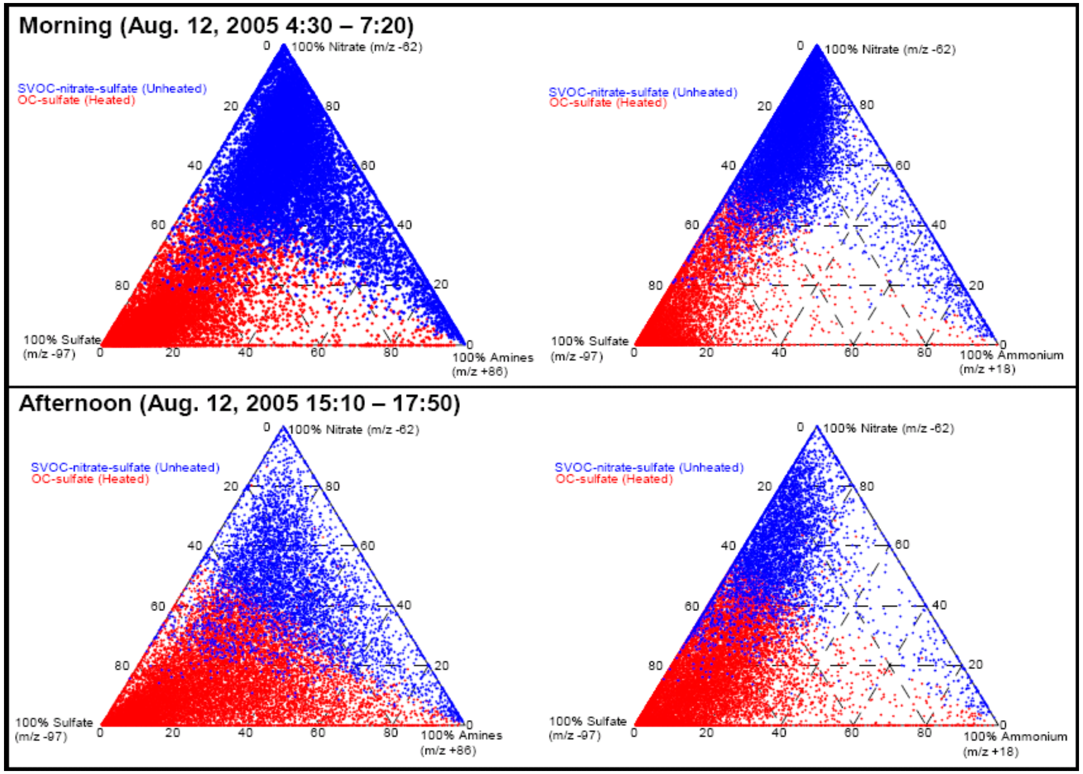
Detection in Atmospheric Aerosols

- Field studies detecting amines (all results indicating amines are from online mass spectrometry results)

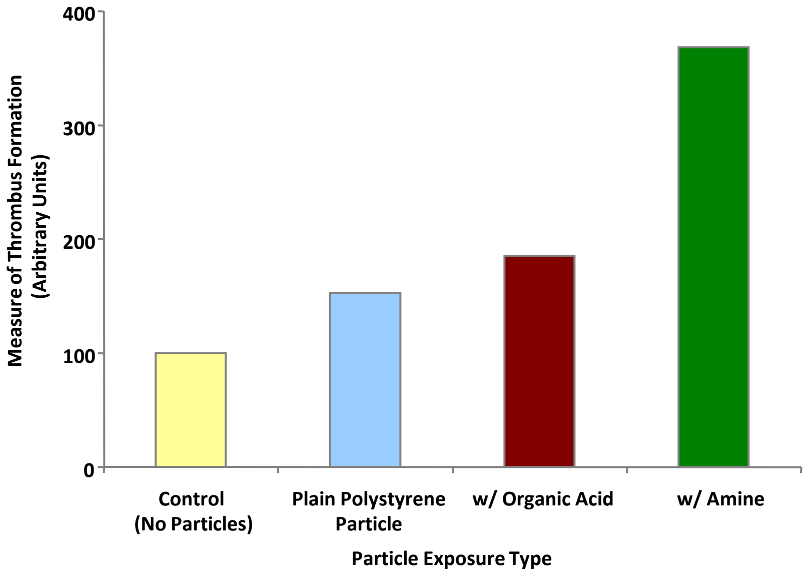
Murphy *et al.*, 1997	Idaho Hill, CO
Angelino *et al.*,2001	Riverside, CA
Tan *et al.*, 2002	Toronto, CAN
Phares *et al.*, 2003	Houston, TX

Detection in Atmospheric Aerosols II

- Field studies suggest that amines can constitute an appreciable portion of organic mass in PM samples and can be important PM components in urban, rural and remote regions: Beddows *et al.*, 2004; Mace *et al.*, 2003; Makela *et al.*, 2001; McGregor and Anastasio, 2001; Neff *et al.*, 2002; Simoneit *et al.*, 2003



Adverse Health Effects: Evidence from Toxicology



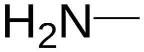
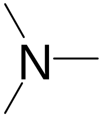
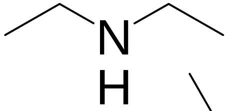
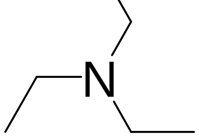
- Toxicology studies have demonstrated that particles containing amines cause adverse health effects [Hammoir et al., *Toxicol. Appl. Pharmacol.*, 2003].

- For example, the intratracheal installation of inert particles coated with amines in hamsters resulted in a **significant** increase (nearly 4 times) in the occurrence of blood clots compared to the control group; in contrast, effects of carboxylic acids were statistically **insignificant** [Nemmar et al., *Am. J. Respir. Crit. Care Med.*, 2002].

Amines in the Atmosphere: Environmental Effects

- Nitrogen deposition
  - Wet or dry deposition
  - Can lead to increased nutrient loadings and low DO levels

Aliphatic Amines Investigated in this Study

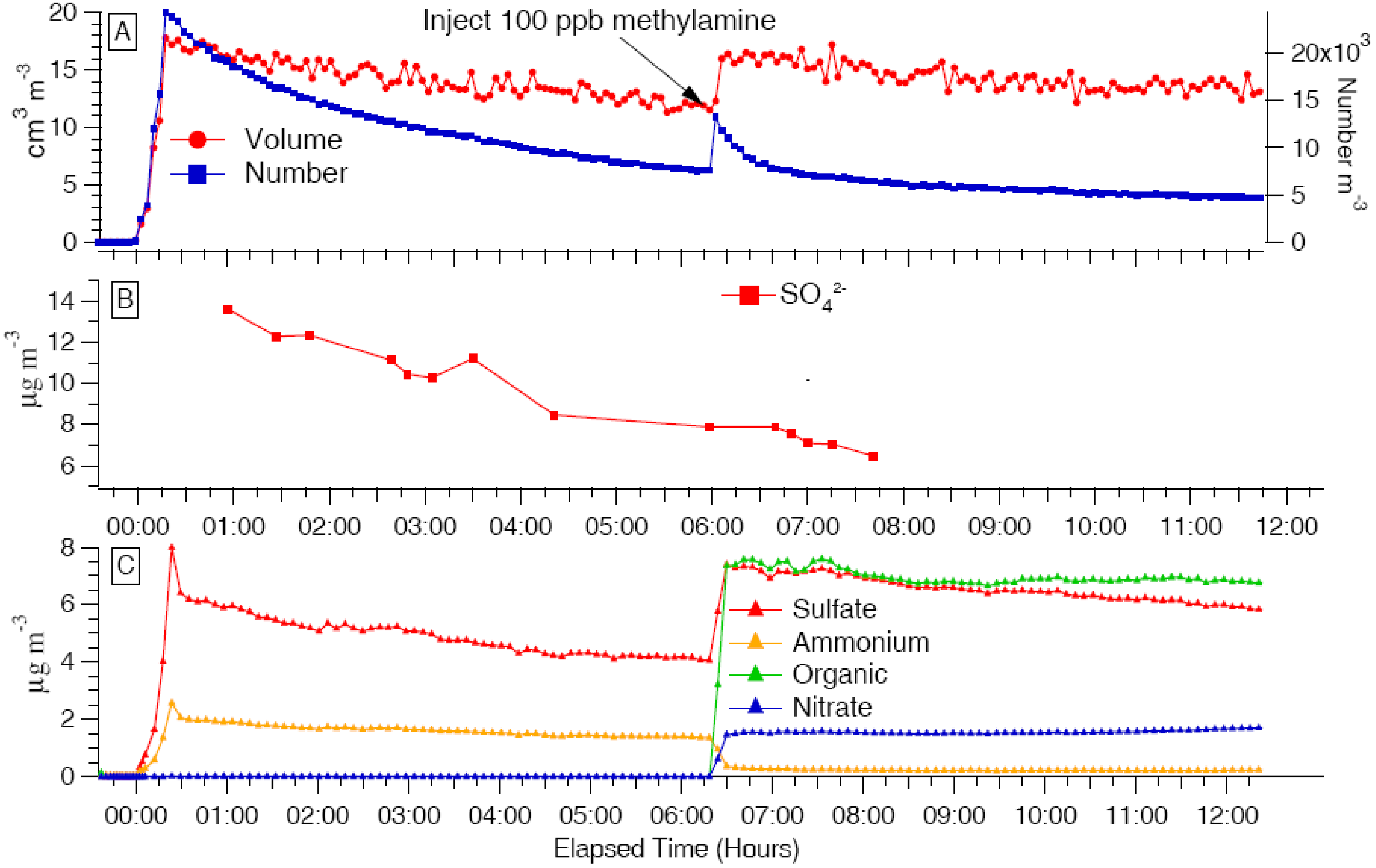
Name (Abbr.)	Structure	Est. Global Emissions* Gg N yr $^{-1}$ (NH_3 = 23,300)
Methylamine (MA)		24 ± 15
Trimethylamine (TMA)		108 ± 30
Ethylamine (EA)		
Diethylamine (DEA)		
Triethylamine (TEA)		
Monoethanolamine (MEA)		

* from animal husbandry operations (Schade and Crutzen, 1995)

One of Few Atmospheric Bases

- Similar to ammonia, amines can form aminium nitrate and aminium sulfate salts
  - $NR_{3\,(g)} + HNO_{3\,(g)} \leftrightharpoons NR_3HNO_{3\,(s)}$
  - $2NR_{3\,(g)} + H_2SO_{4\,(g)} \leftrightharpoons (NR_3H)_2SO_{4\,(s)}$
  - $Kp = p_{NR_3}p_{HNO_3}$

Aminium Sulfate displacing Ammonium Sulfate



Uncertainty in Thermodynamics Leads to Uncertainty in K_p

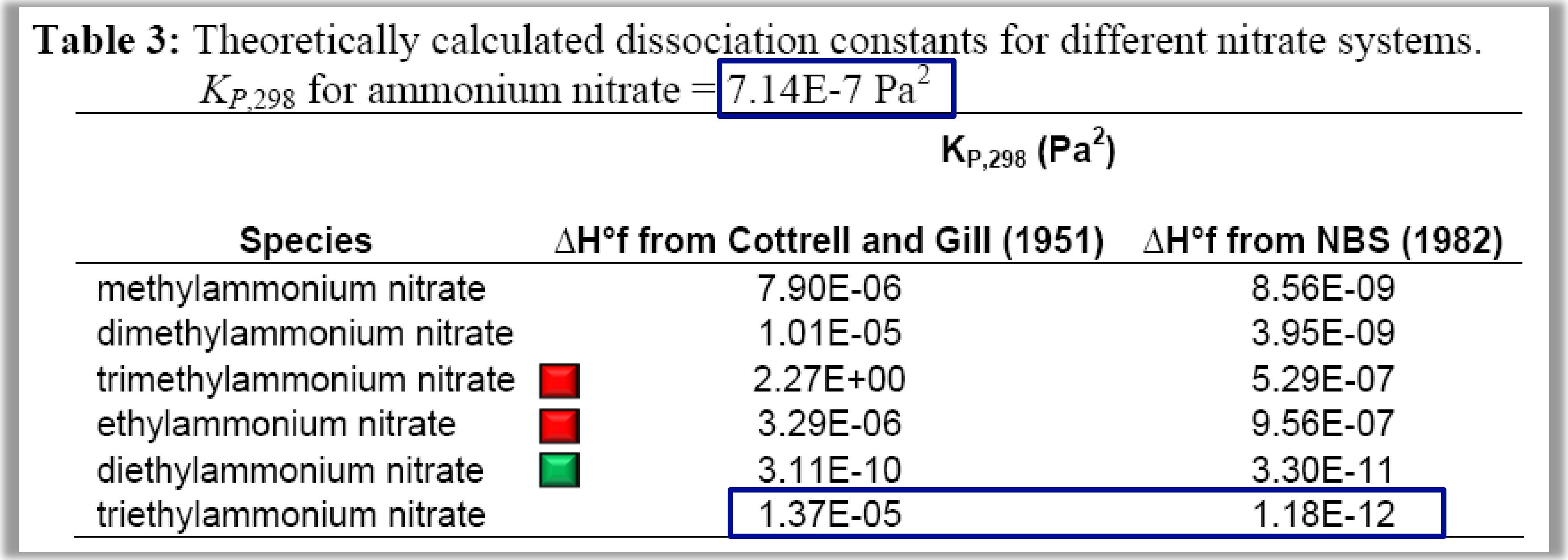


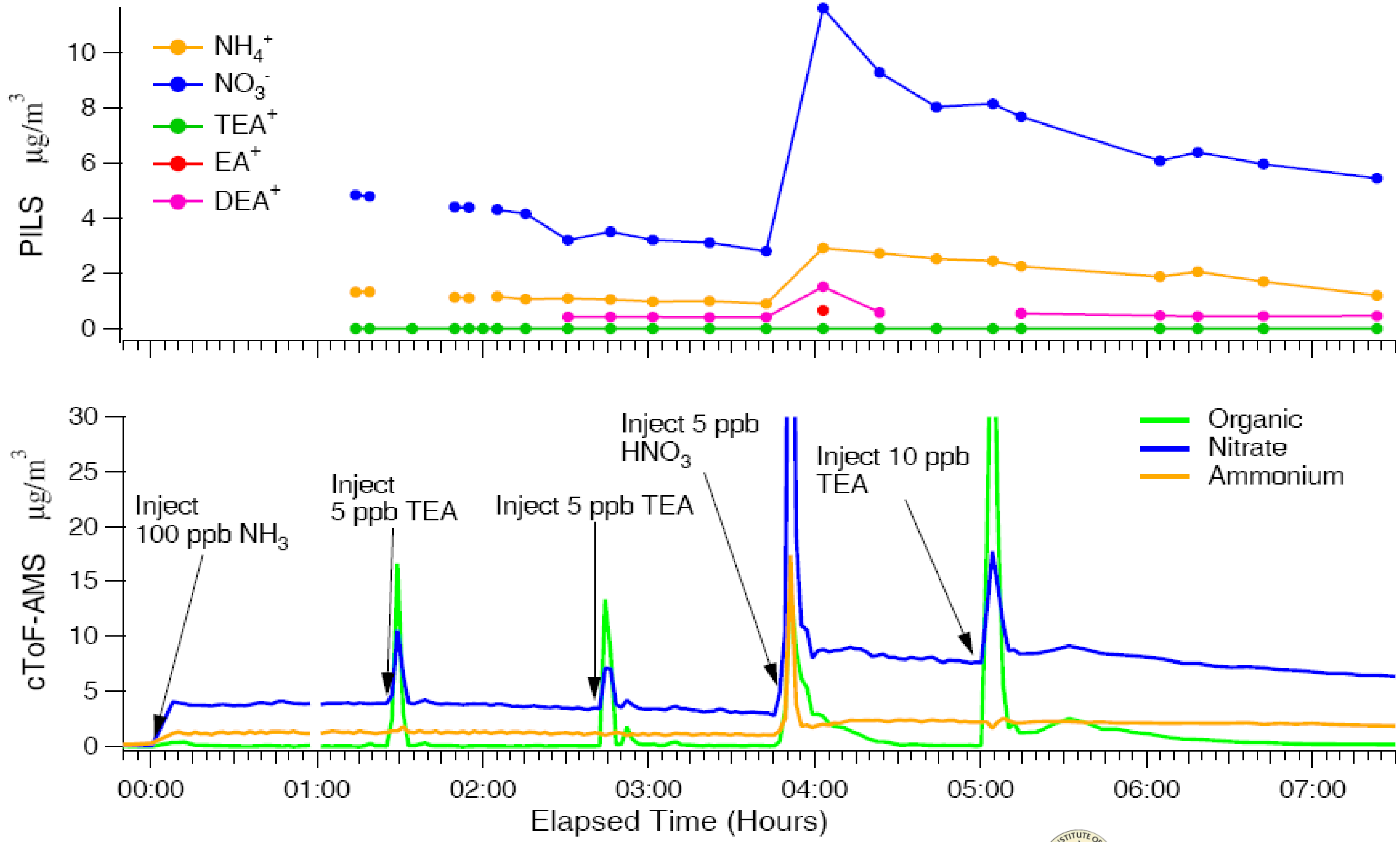
Table 3: Theoretically calculated dissociation constants for different nitrate systems.

$K_{P,298}$ for ammonium nitrate = 7.14E-7 Pa^2

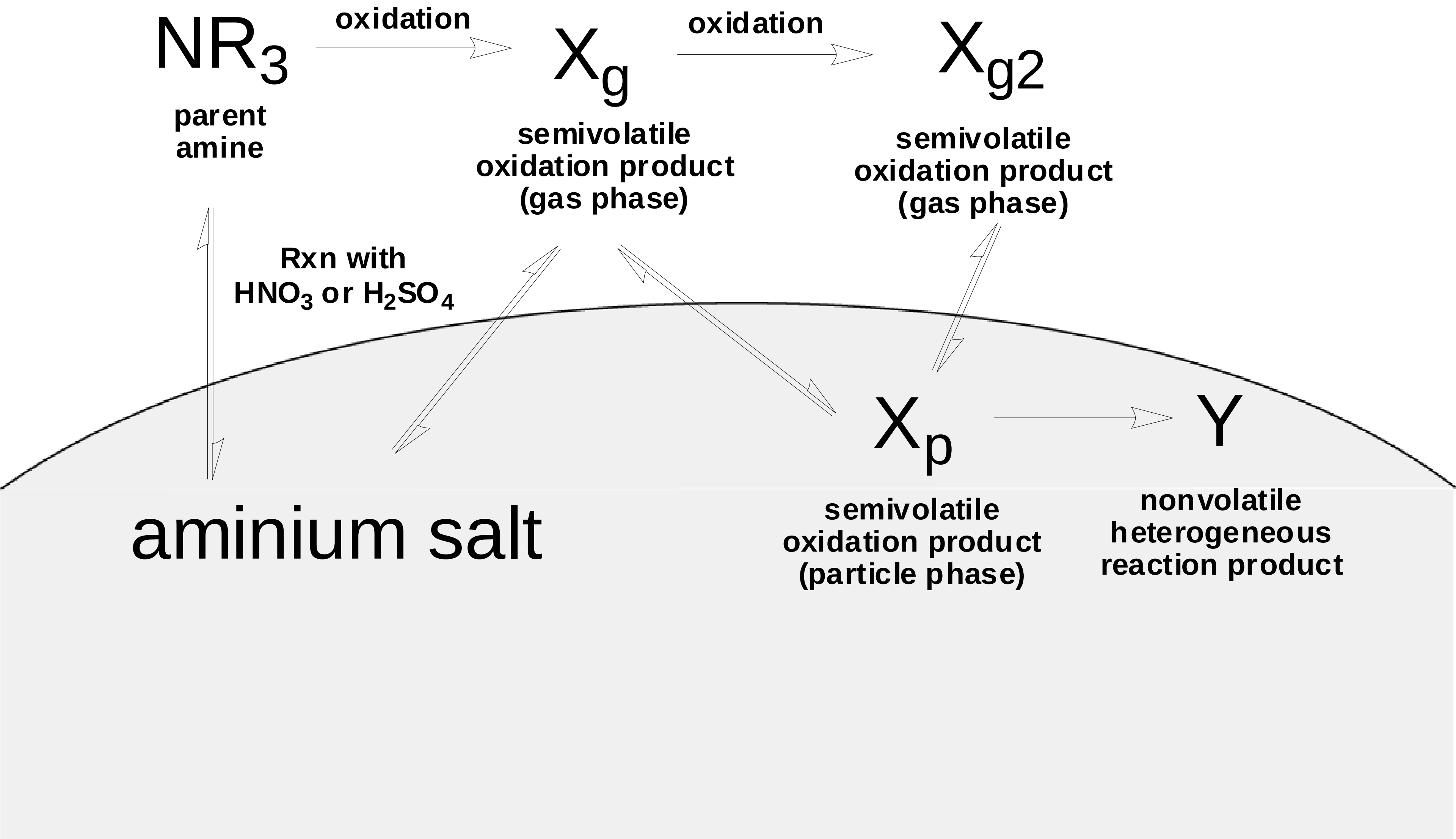
Species	$K_{P,298}$ (Pa^2) ΔH°f from Cottrell and Gill (1951)	ΔH°f from NBS (1982)
methylammonium nitrate	7.90E-06	8.56E-09
dimethylammonium nitrate	1.01E-05	3.95E-09
trimethylammonium nitrate 🟥	2.27E+00	5.29E-07
ethylammonium nitrate 🟥	3.29E-06	9.56E-07
diethylammonium nitrate 🟩	3.11E-10	3.30E-11
triethylammonium nitrate	1.37E-05	1.18E-12

Experimental Approach to Estimating K_p for TEA

TEA Cannot Displace Ammonium from Equilibrated Ammonium NITRATE Particles Unless at High Concentrations or Excess Nitric Acid Exists



Non-Salt Secondary Aerosol Formation Mechanisms



NR_3

parent amine

oxidation

X_g

semivolatile oxidation product (gas phase)

oxidation

X_{g2}

semivolatile oxidation product (gas phase)

Rxn with HNO_3 or H_2SO_4

X_p

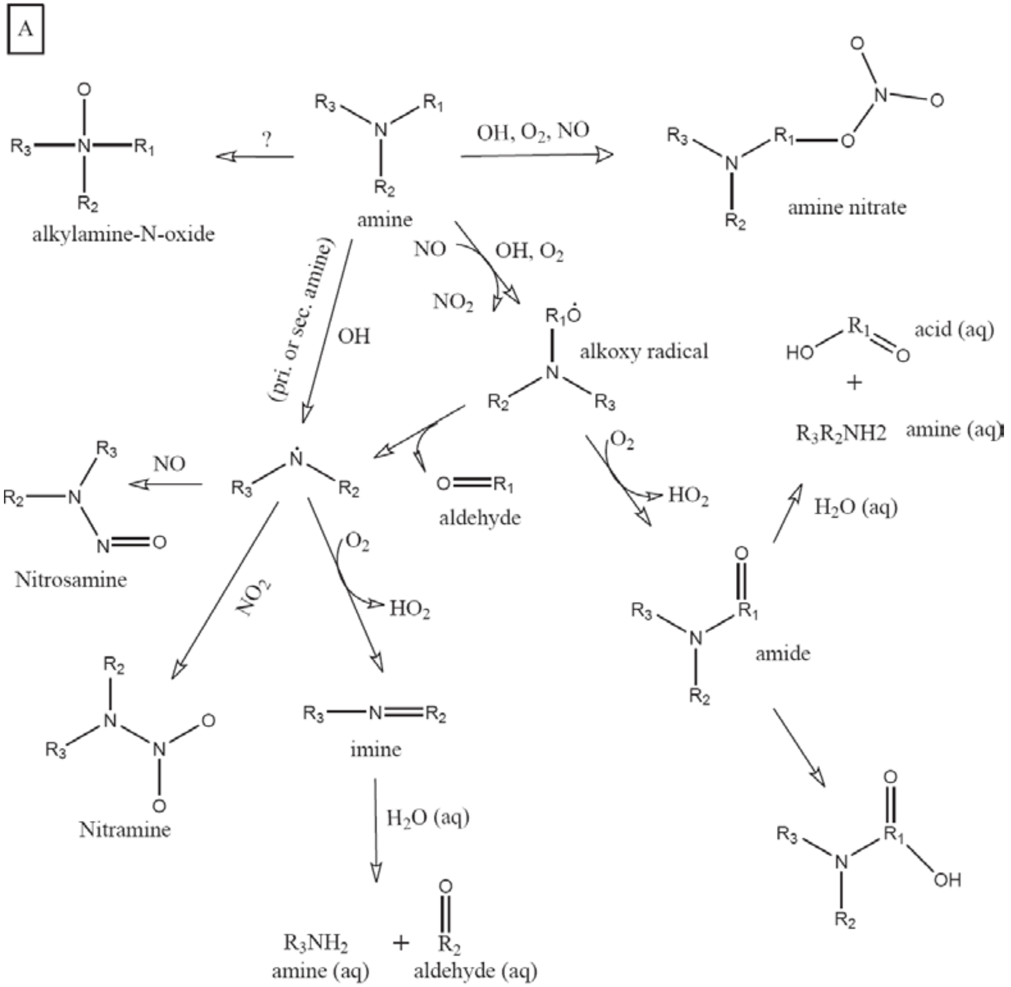
Y

aminium salt

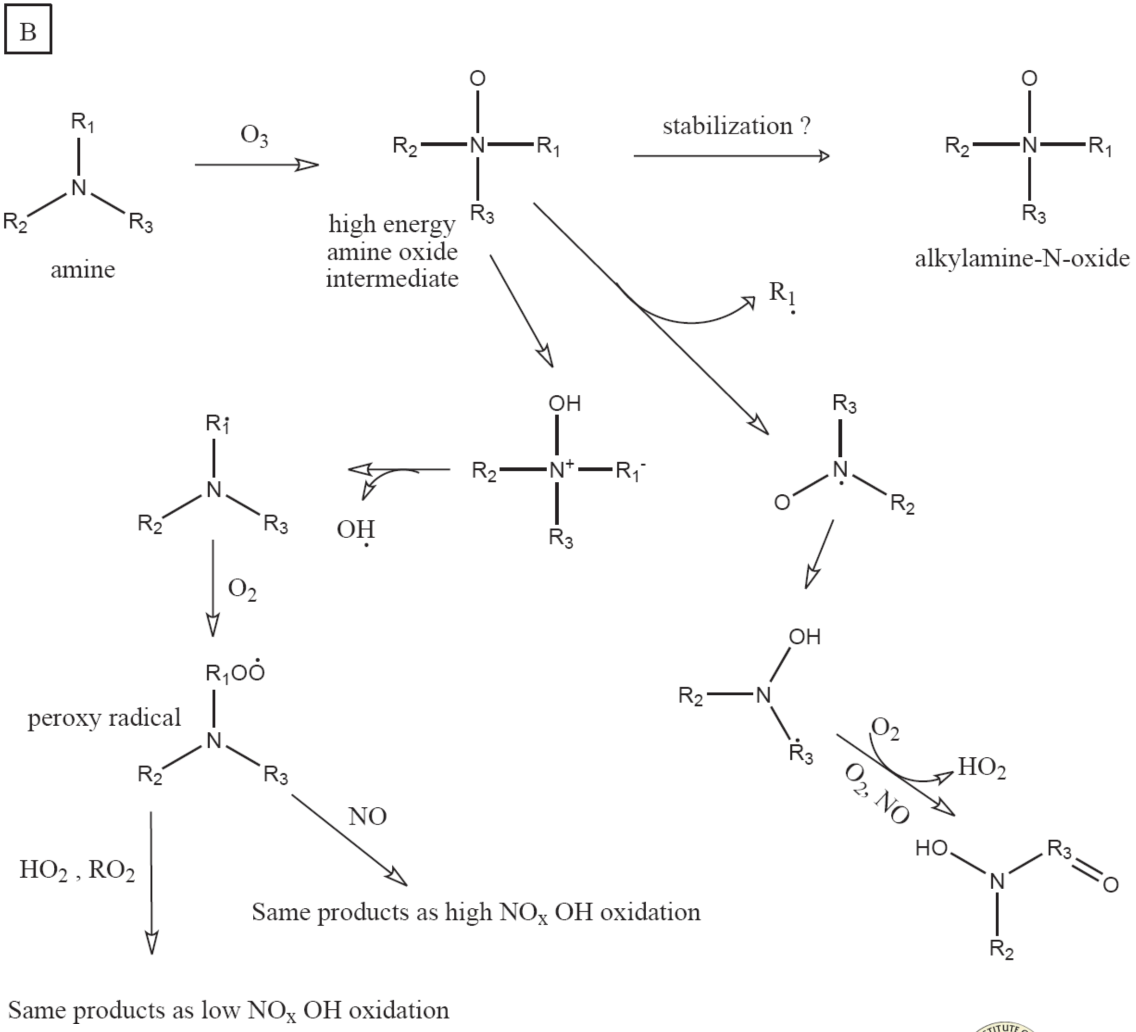
semivolatile oxidation product (particle phase)

nonvolatile heterogeneous reaction product

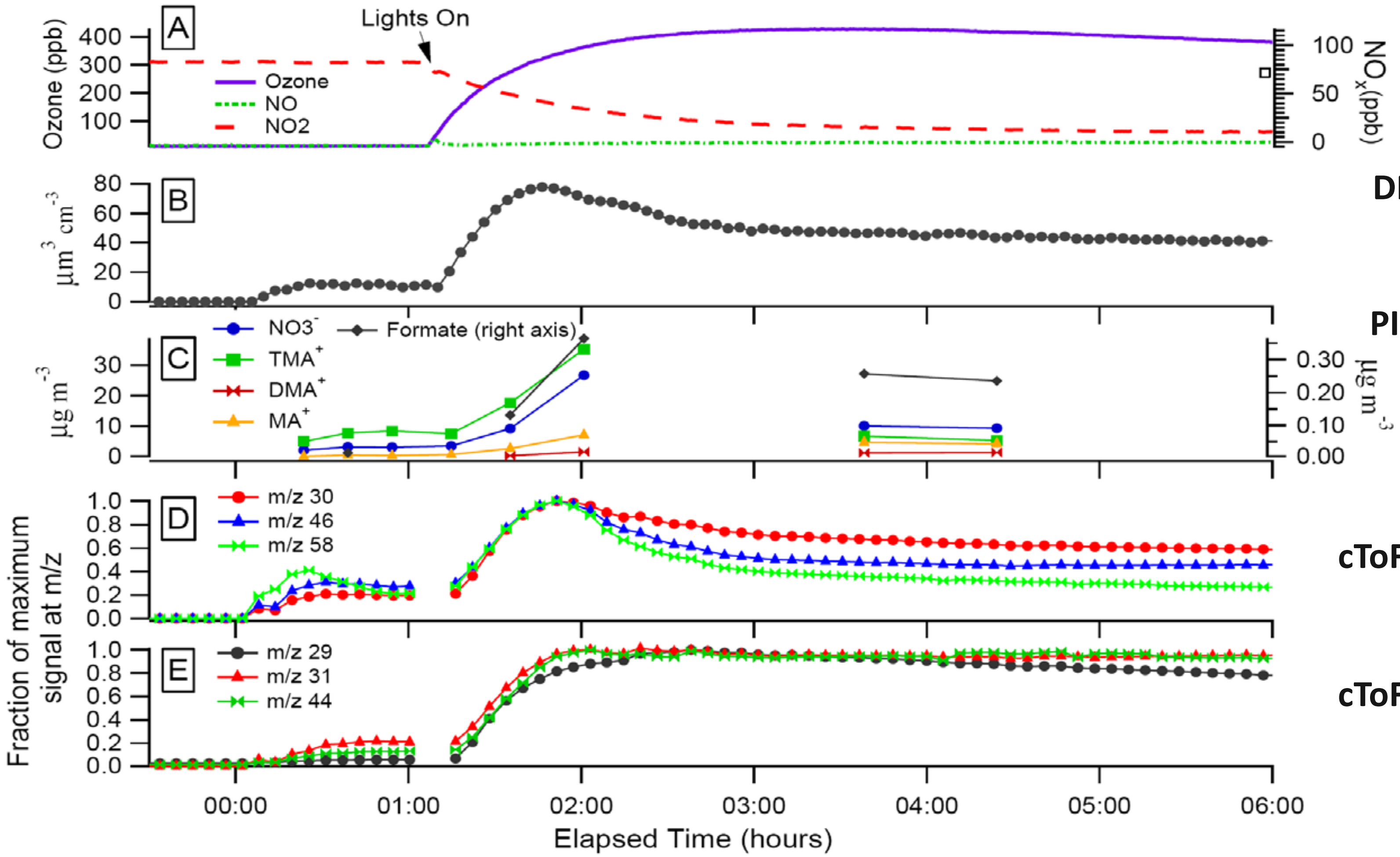
OH Oxidation With NO_x



Ozone Oxidation



Trimethylamine Photooxidation



Gas Phase

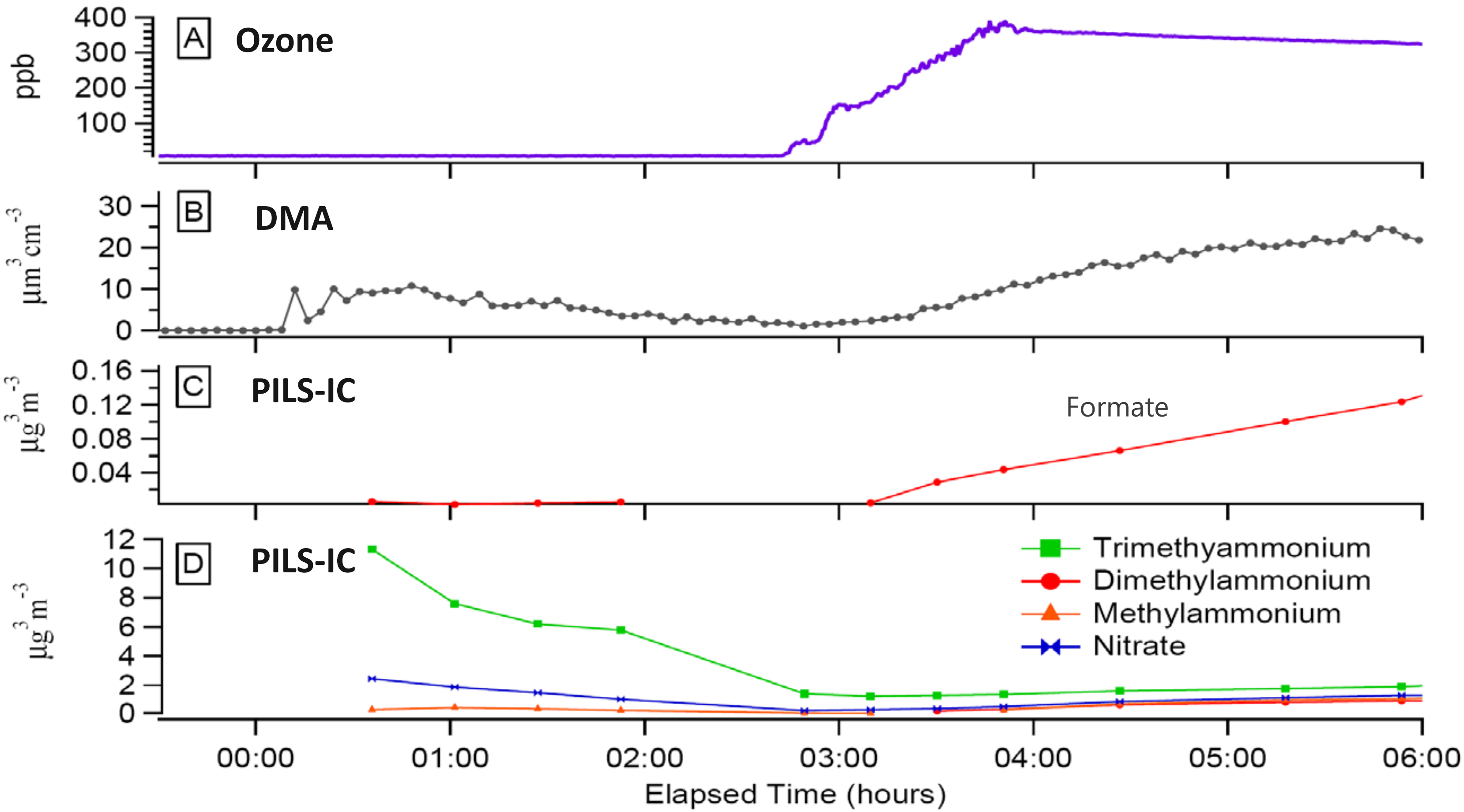
DMA

PILS-IC

cToF-AMS

cToF-AMS

Trimethylamine Ozonolysis



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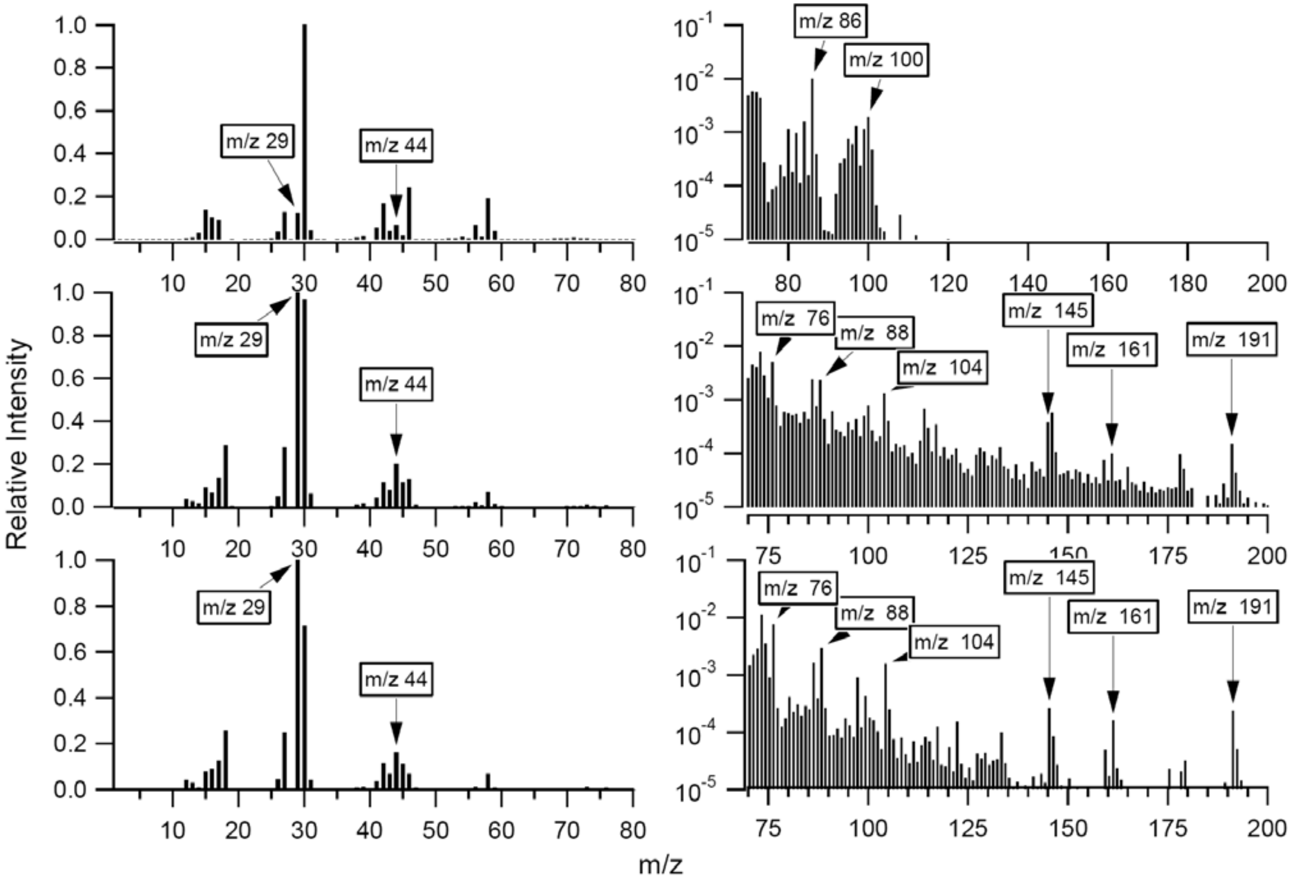
Spectra of Aerosol from TMA

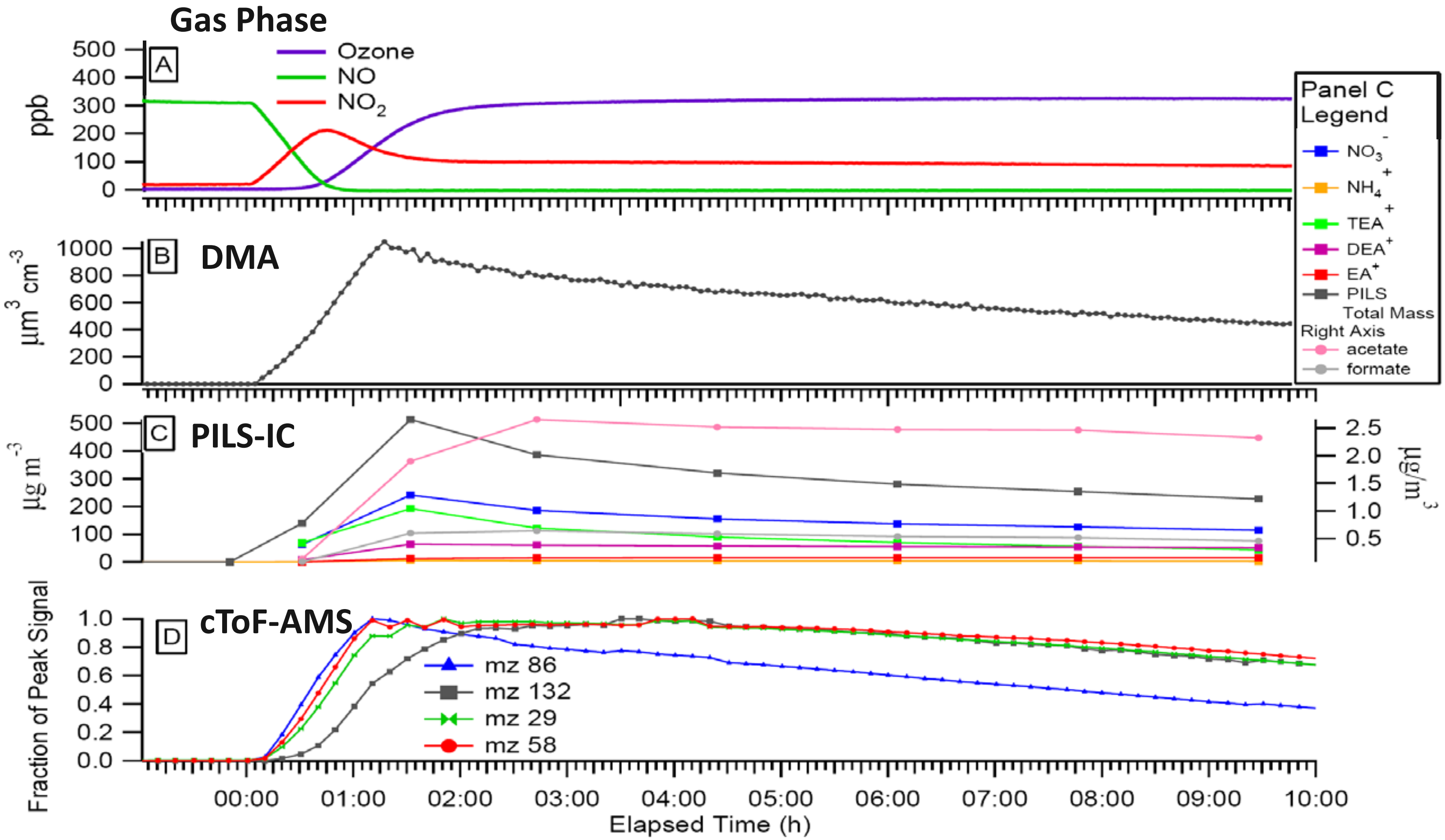
$HN(CH_3)_3NO_3$

$TMA+OH+NO_x$

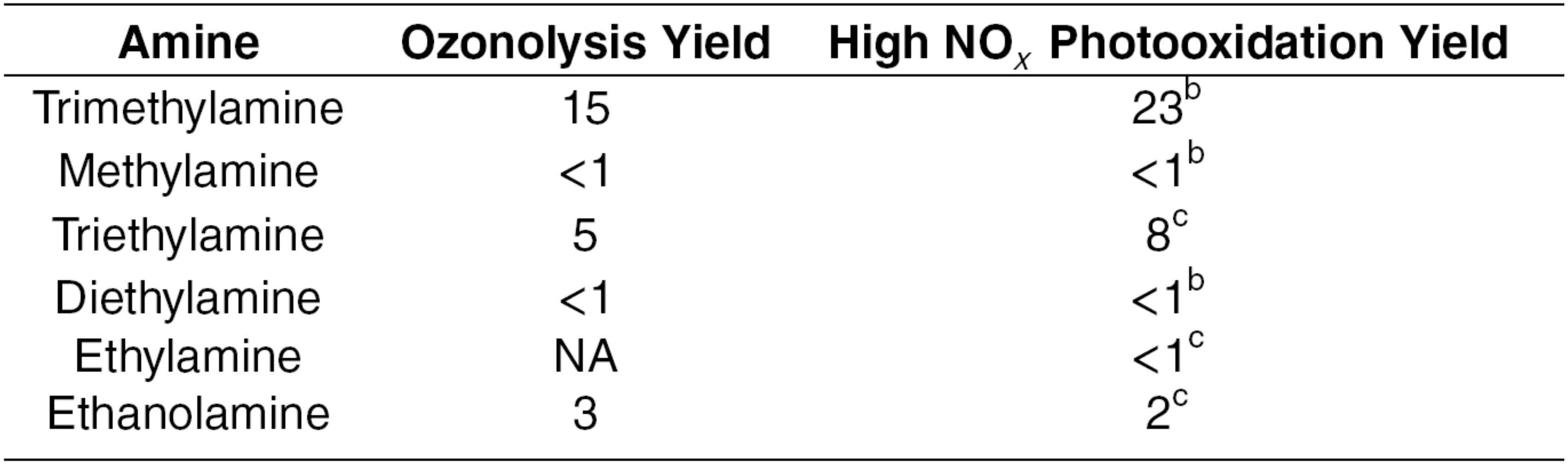
$TMA + O_3$



Triethylamine Photooxidation



Yield Summary



Amine	Ozonolysis Yield	High NO_x Photooxidation Yield
Trimethylamine	15	23^b
Methylamine	<1	$<1^b$
Triethylamine	5	8^c
Diethylamine	<1	$<1^b$
Ethylamine	NA	$<1^c$
Ethanolamine	3	2^c

Conclusions

- Amines form secondary aerosol through a complex mixture of salt formation and oxidation.
- Aminium salt formation is perhaps the dominant atmospheric aerosol formation mechanism, though the **thermodynamics remain uncertain** (better characterization needed).
- In this study, oxidation of tertiary amines formed significant aerosol whereas oxidation of secondary or primary amines did not form significant aerosol.
- To date, most field evidence is mass spectrometry based.
  - This study shows that PILS-IC is an effective means of measuring aminium salts.

Technical Progress: Project 5
Atmospheric Chemistry of Amines

- Amines are of toxicological interest, but not enough is known about their chemistry in the atmosphere

- Completed Project: "Secondary Organic Aerosol from Aliphatic Amines"

- Project in Progress: *"The Thermodynamic Properties and Gas/Aerosol Partitioning of Atmospheric Amines"*
  - Increase knowledge of the thermodynamic properties of amines, and include amines in a gas-particle partitioning model that includes other atmospheric constituents

Many Questions:
Perhaps Answers are in this Room!

- Data for screening risk assessments
- Toxicological studies
- Field experiments
- Chamber experiments
- Chemical mechanism and model development

A very timely workshop!

Together…Shaping the Future of Electricity

CESAR
Enhanced Separation & Recovery

Statoil

Emission measurements at Dong’s pilot plant for CO_2 capture in Esbjerg

EU Project CESAR

Prepared by N. Aas, Statoil; presented by E. da Silva, Sintef

Overview

- Background to the CESAR project
- Dong's facilities in Esbjerg
- MEA campaign and emission sampling
- CASTOR/CESAR pilot plant flow diagram
- Compounds of interest
- Results from the emission measurements
- Results from the liquid analysis
- Conclusions
- Acknowledgement

Background to the CESAR project

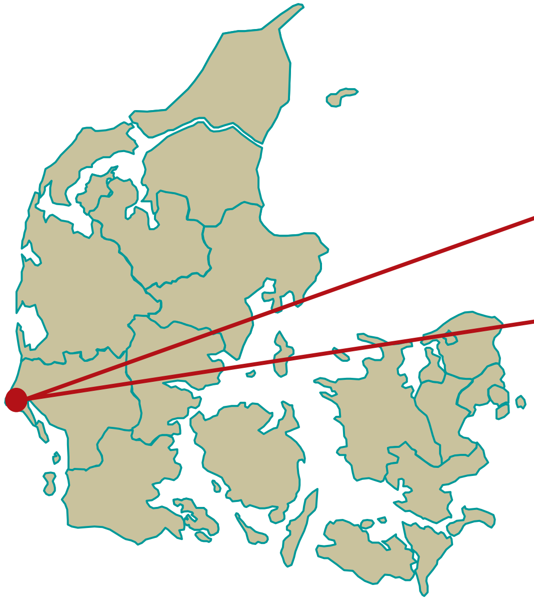
- CESAR aims for a breakthrough in the development of low-cost post-combustion CO_2 capture technology to provide economically feasible solutions for both new power plants and retrofit of existing power plants which are responsible for the majority of all anthropogenic CO_2 emissions.

  The primary objective is to decrease the cost of capture down to 15 €/tCO_2.

- CESAR builts on the findings from CASTOR.

Esbjerg Power Station (ESV)

CESAR
Enhanced Separation & Recovery



- 400 MW_e pulverized bituminous coal
- High dust SCR $deNO_x$ plant
- 3 zones cold-sided ESP
- Wet limestone FGD (saleable gypsum)

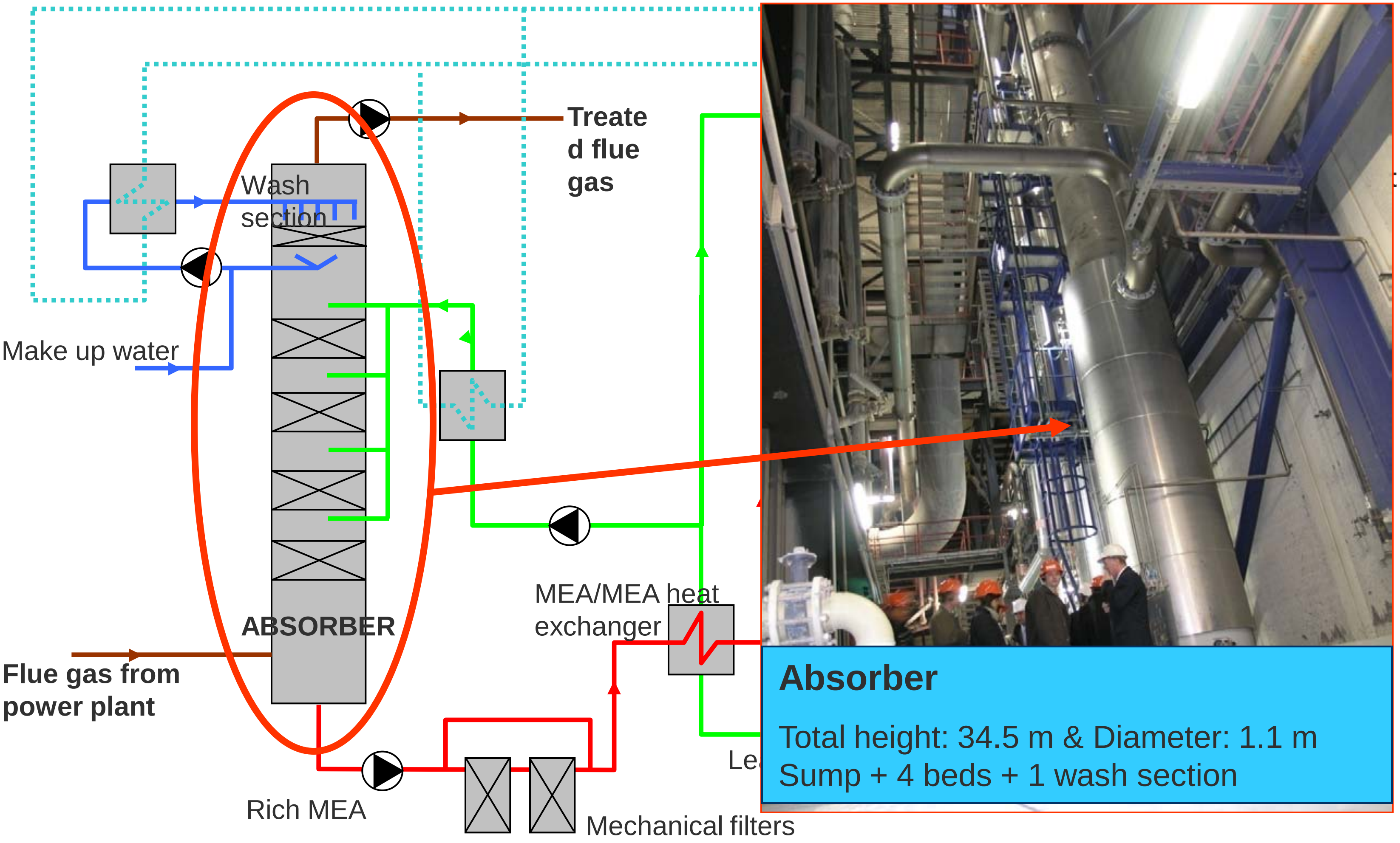
CASTOR Pilot Plant Specifications

CESAR
Enhanced Separation & Recovery

- Pilot plant erected and commissioned during 2005
- Design of pilot plant based on a commercial CO_2 production plant (MEA)
- Pilot plant operates on a slip stream taken directly after the wet FGD
- Design flue gas conditions: ~47°C saturated, <10 ppm SO_2, <65 ppm NO_x, <10 mg/Nm^3 dust

Parameter	*Design value*
Flue gas capacity	5000 Nm^3/h
CO_2 production (at 12% CO_2)	1000 kg/h
Absorption degree	90%
Max solvent flow	40 m^3/h
Max stripper pressure	2 bar_g
Max steam pressure	3.5 bar_g

Esbjerg Pilot Plant Absorber

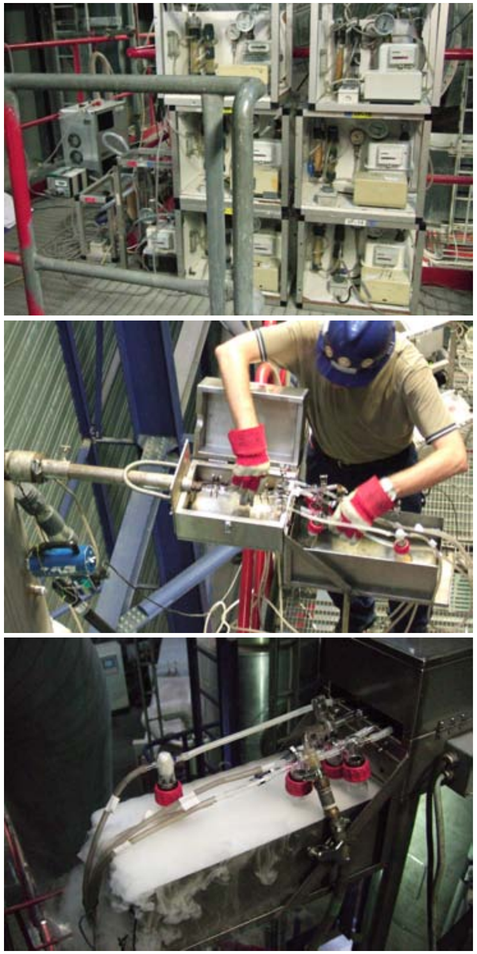


Absorber

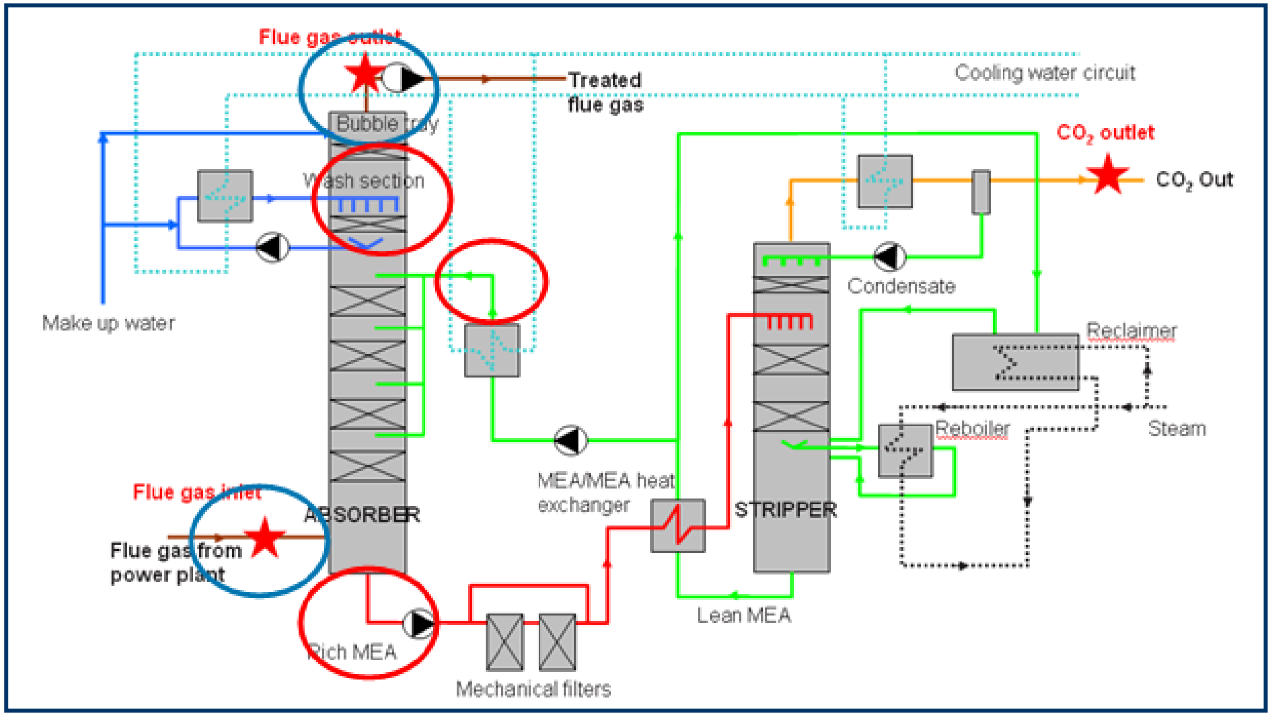
Total height: 34.5 m & Diameter: 1.1 m
Sump + 4 beds + 1 wash section

MEA campaign and emission sampling

- A test campaign using MEA was run during the spring of 2009.
- Emission sampling was carried out on the 10th-11th June, after a test run time of 700 to 800 h.
- Eurofins was responsible for emission sampling and measurements.
- Sampling was done isokinetically using liquid or solid absorbents.
- The analytical methods used for the chemical analysis were standard reference methods (ISO, VDI, MEL etc).



CASTOR/CESAR Pilot Plant Flow Diagram



Blue: gas samples

Red: liquid samples

★: sampling points CASTOR

Compounds of interest

- **Gaseous phase**:
  - MEA, DEA
  - Aldehydes
  - Alkylamines
  - Acetamide
  - Ammonia

  - Flue gas components like H_2O, TOC, VOC
  - Gas velocity measurement
  - Gas volume measurement

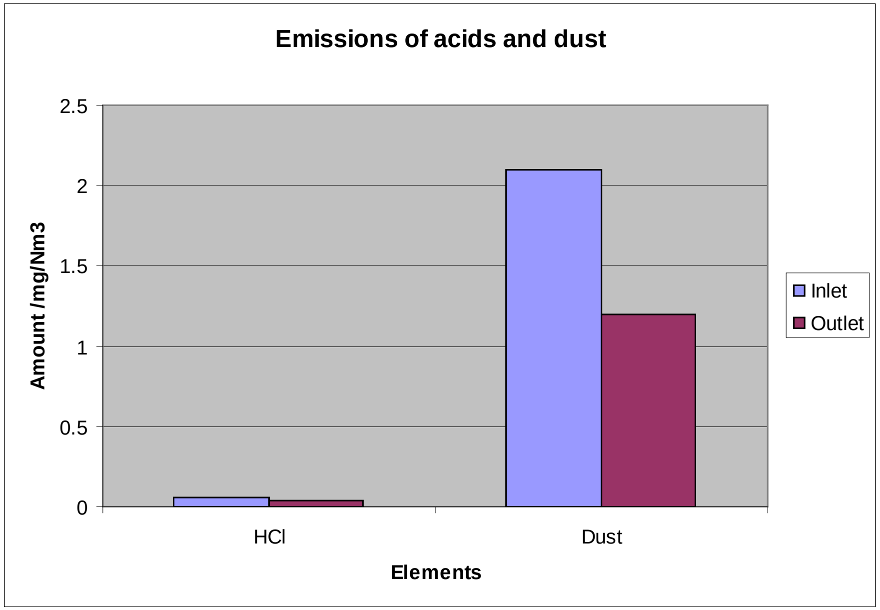
- **Liquid phase:**
  - MEA, DEA
  - Aldehydes
  - Alkylamines
  - Acetamine
  - Ammonia

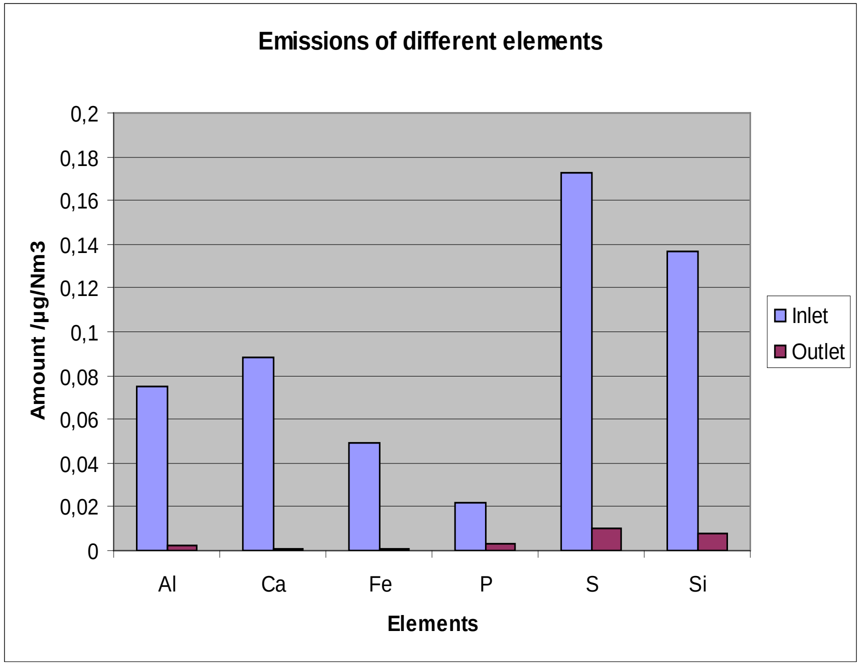
  - pH
  - Metal content
  - Heat stable salts

Results from the emission measurements 1

Compound	Unit	Inlet absorber	Outlet absorber	Outlet abs. after water wash
MEA	mg/Nm3	<0.1	**0.7**	<0.3
DEA	mg/Nm3	<0.2	<0.3	<0.2
Formaldehyde	mg/Nm3	<0.1	**0.7**	<0.1
Methylamine	mg/Nm3	<0.2	<0.3	<0.2
Acetamide	mg/Nm3	<0.6	<1.0	<1.0
Ammonia	mg/Nm3	<0.1	**23**	**20**

Results from the emission measurements 2





Comparison of emissions from CASTOR and CESAR

CESAR
Enhanced Separation & Recovery

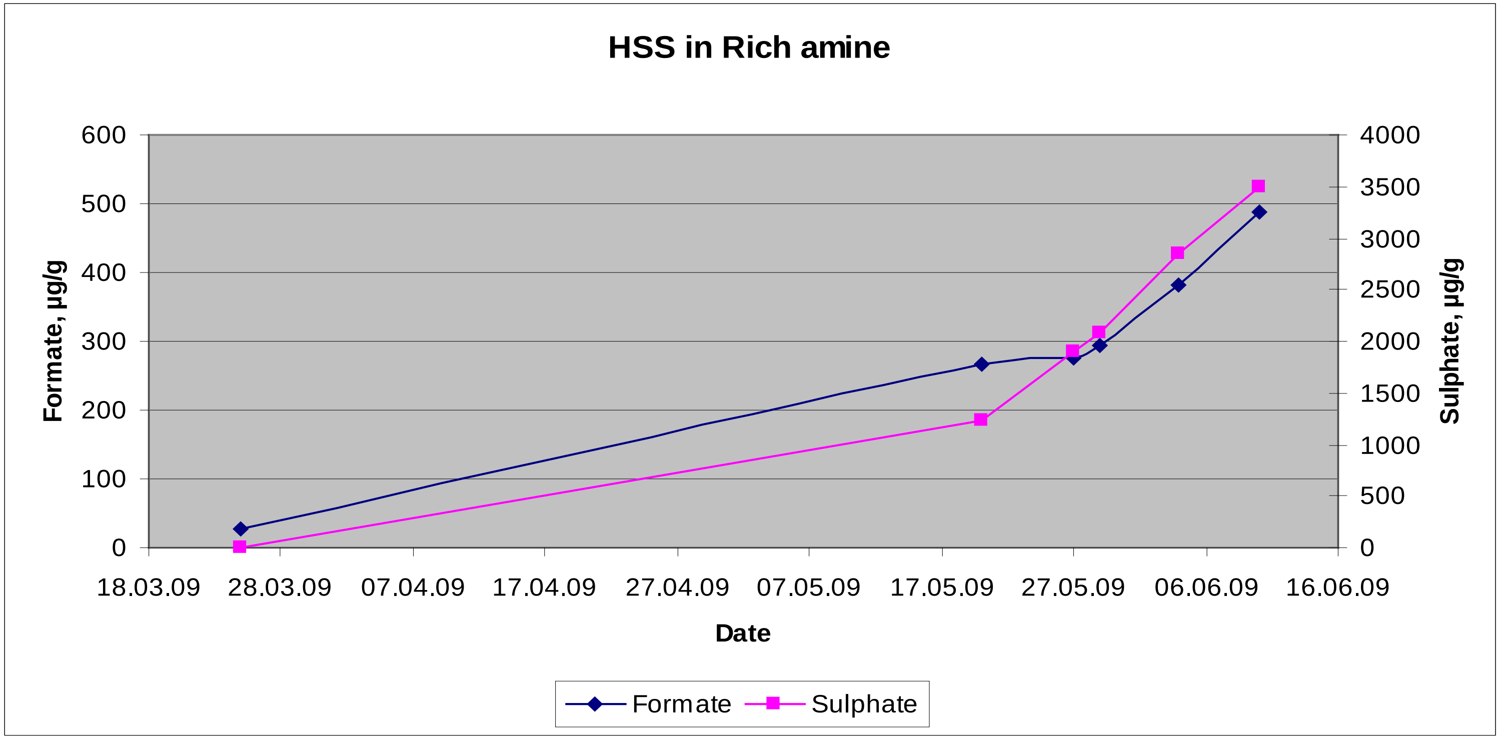
Compound	Unit	CASTOR	CESAR
SO2	mg/Nm3	<0.2	1.5
VOC	mg/Nm3	12	4.1
Ammonia	mg/Nm3	25	23
MEA	mg/Nm3	<0.02	0.7
Formaldehyde	mg/Nm3	0.059	1.1
O2	% dry	7.5	6.9
NOx	mg/Nm3	73	34.4

Results from the liquid analysis 1

Compound	Unit	Wash water
MEA	mg/l	35 000
DEA	mg/l	#
Formaldehyde	mg/l	6.4
Methylamine	mg/l	<0.3

#no measurement due to interference from MEA

Results from the liquid analysis 2



Conclusions

CESAR
Enhanced Separation & Recovery

- Emission measurements have successfully been carried out during the MEA test campaign at the Esbjerg plant.
  - Pioneering work!
- The degradation products typical of oxidative degradation of MEA have been found in both the liquid and the gaseous phase.
- The water wash works well in that it reduces the amount of MEA and formaldehyde in the emitted flue gas.
- The bubble cap has a positive effect on the emissions in that it reduces the amount of MEA and formaldehyde in the flue gas leaving the absorber.
- The absorber has a positive effect on the total emissions as it reduces the amount of metals, dust and SO_2 in the flue gas leaving the absorber.

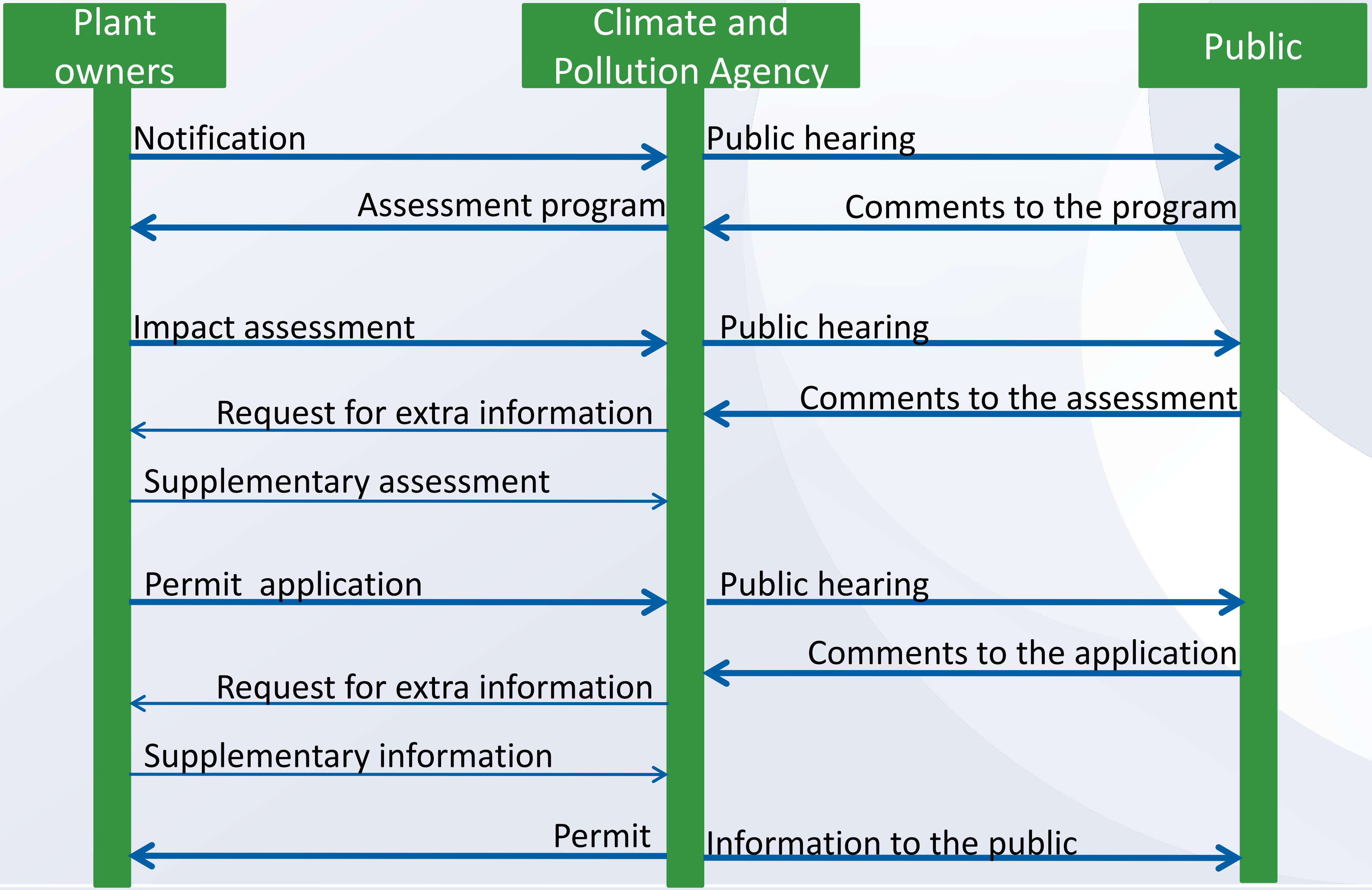
Thank you

CLIMATE AND
POLLUTION
AGENCY

The Impact Assessment Process,

and Information Requests

Fredrik Weidemann



Plant owners

Climate and Pollution Agency

Public

Notification

Public hearing

Assessment program

Comments to the program

Impact assessment

Public hearing

Comments to the assessment

Request for extra information

Supplementary assessment

Permit application

Public hearing

Comments to the application

Request for extra information

Supplementary information

Permit

Information to the public

Scope of Impact Assessment,

in relation to the environment and public health

- Quantitative and qualitative description of all emissions
- Description of the recipient, air, water or ground
- Distribution and deposition of the emitted substances
- Possible degradation products
- Impact of the emissions on environment and public health

Data Input to Impact Assessment

Data related to the environment

- Eco-toxicity
- Degradability
- Bio-accumulation potential

Data related to public heath

- Acute toxicity
- Gene toxicity
- Carcinogenic potential
- Reproductive toxicity
- Toxicity after repeated doses
- Irritation / corrosion
- Sensitisation

Data, Tools and Methods

Data about

- solvents
- emissions
- impacts

Modelling of

- distribution and deposition

Calculation of

- critical loads and emission limits

Information about Solvents

Necessary information about solvents

- The content of amines and additives
- Data about toxicity and eco-toxicity

Information is needed for

- Registration in ECHA, according to REACH (EU)
- Registration in "Produktregisteret", (PR)
  (Composition and classification)
- Preparation of risk assessments analysis on health and environment

The registration to ECHA / REACH and Produktregisteret (PR) is <u>mandatory</u>

LCA of an 882 MW Coal-fired Power Plant with CCS: CO_2-EOR and Storage Option

Anastassia Manuilova
Jitsopa Suebsiri
Malcolm Wilson

Environmental Impact of Amine Emission During Post Combustion Capture
February 16, 2010 @ Oslo, Norway

Introduction

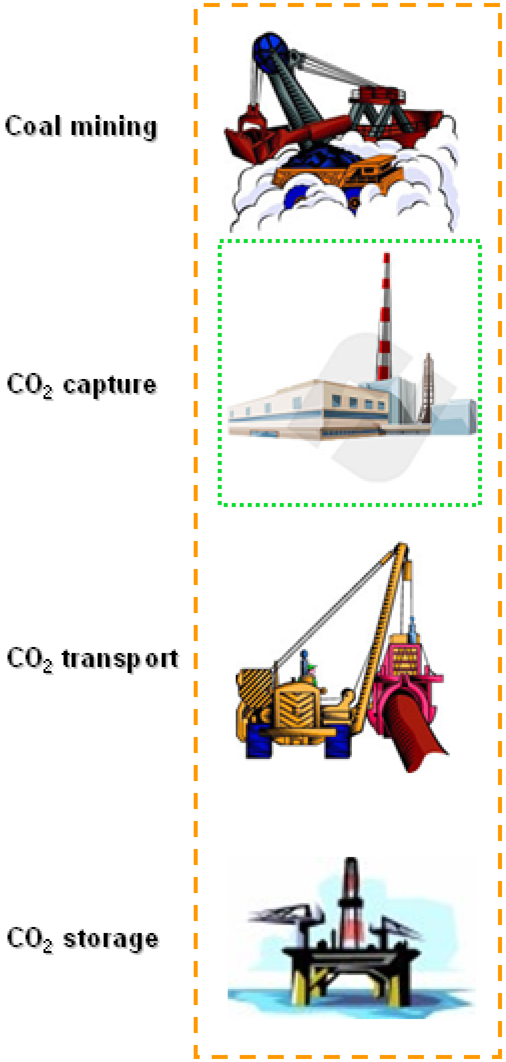
- Background
  - – CO_2 is considered to be the principal greenhouse gas
  - – In order to reduce GHG impact, CO_2 can be captured and stored geologically

- Nature of the problem
  - – Processes should be studied from a life cycle perspective to obtain the total picture and make comparisons to other GHG emissions reduction alternatives

Goal of the study

- Understand implications of Carbon Capture and Storage (CCS) activities
- Study environmental performance of power plant with and without CO_2 capture
- Conduct a LCA study of CCS system consisting of 882MW power plant with a CO_2 post combustion capture unit, CO_2 transport and CO_2-EOR operations and storage, operations at the refinery and product use

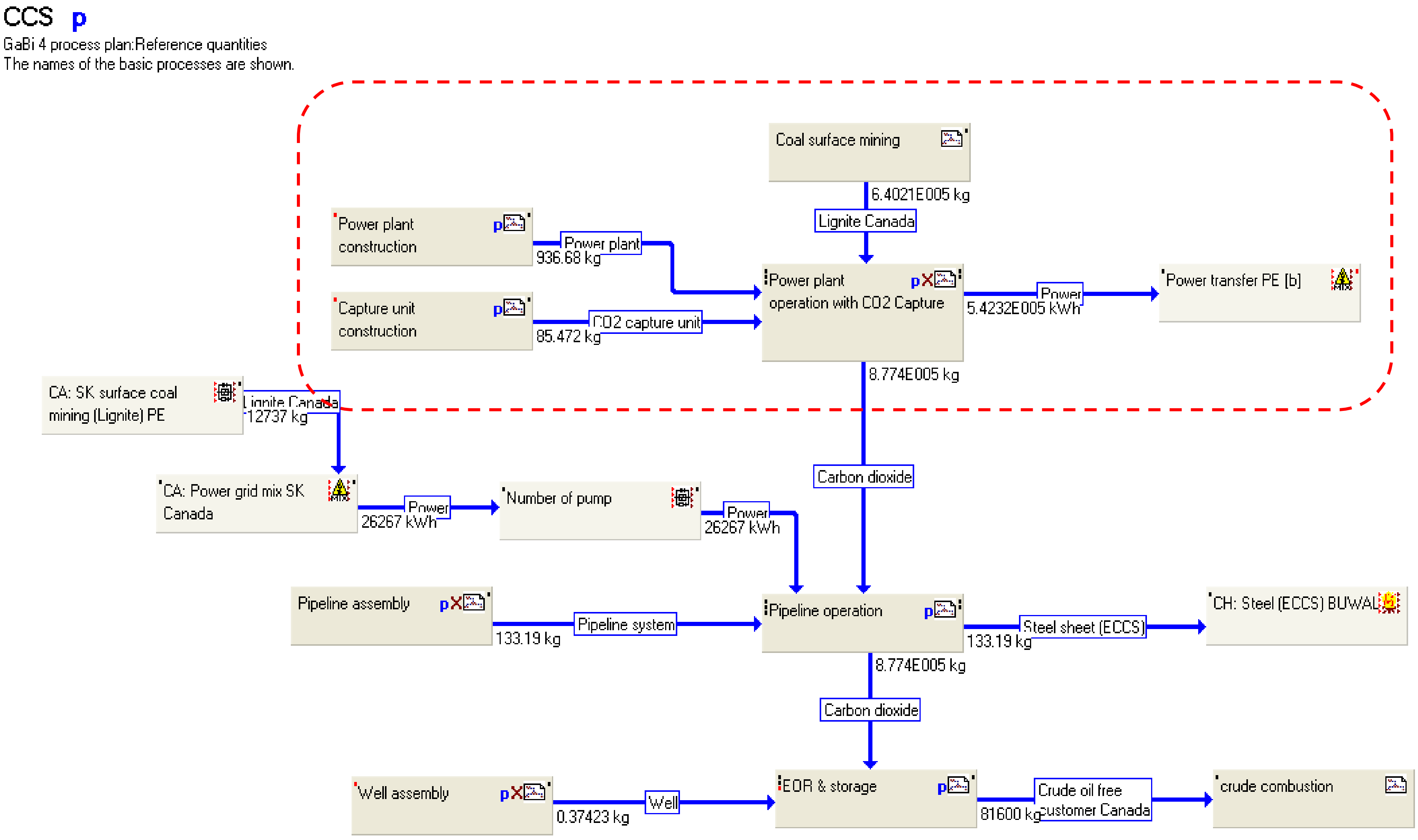
System boundaries



- Coal mining
  - Surface coal mining in Saskatchewan
  - Lignite
- CO_2 capture
  - SaskPower’s Boundary Dam Power Station
- CO_2 transport
  - 100 km pipeline
- CO_2 storage
  - CO_2-Enhanced Oil Recovery, Weyburn oil field

- Functional unit: 1 GJ of energy produced

System boundaries



CCS p

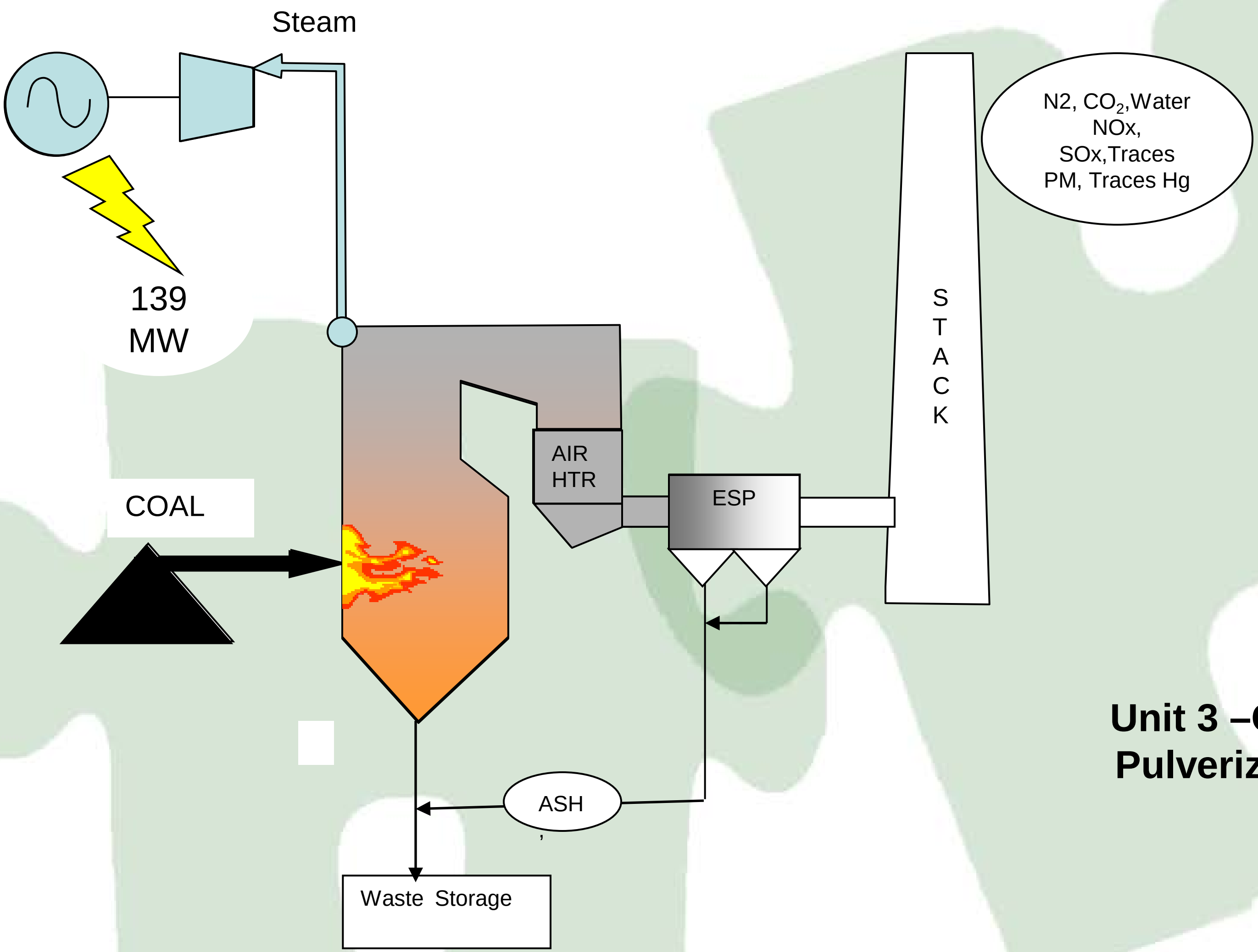
GaBi 4 process plan:Reference quantities
The names of the basic processes are shown.

Boundary Dam Power Station

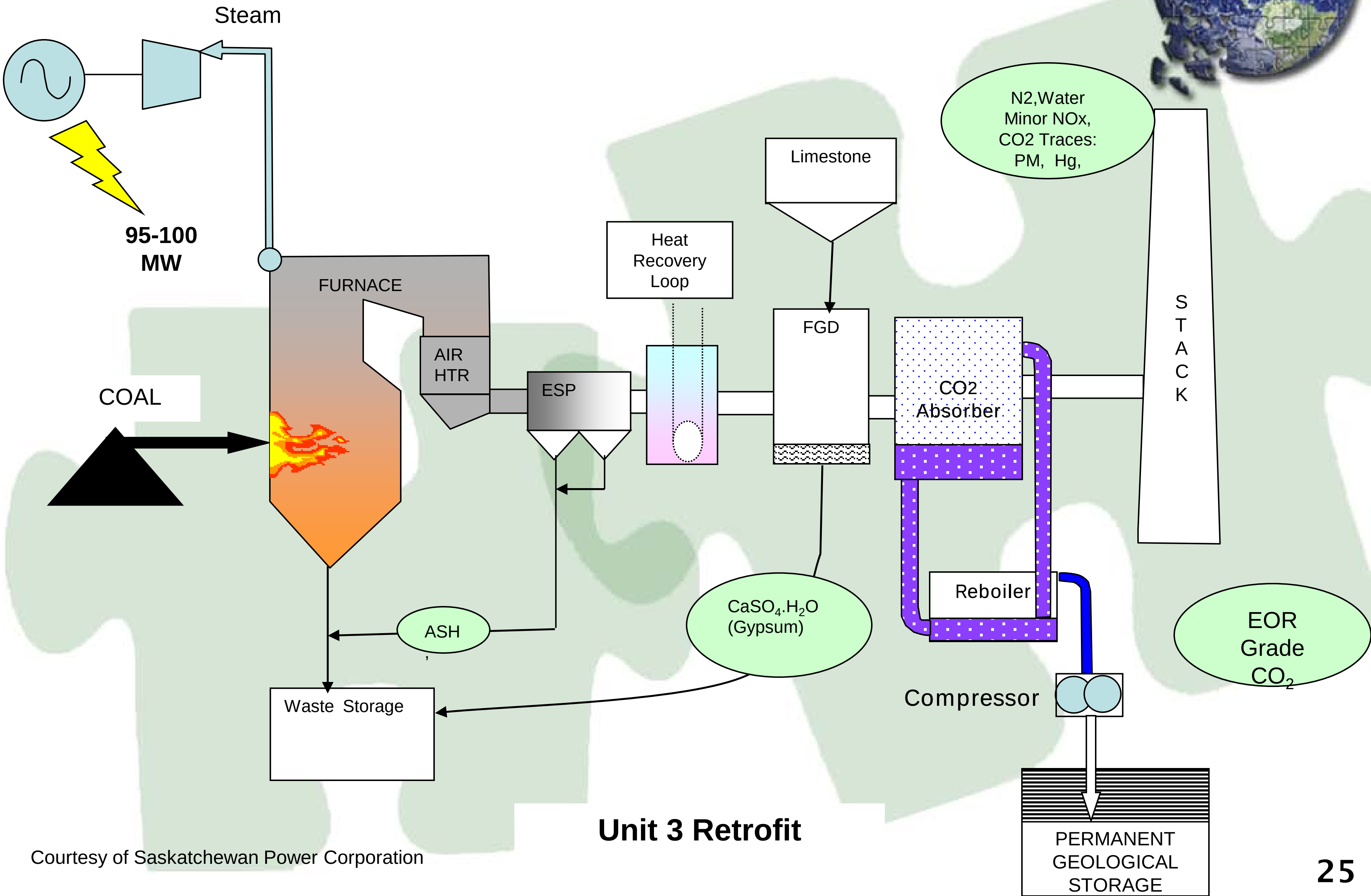
- Capacity: 882 MW
- 6 Units (66;66;150;150;150; 300 MW)
- Retrofit of Unit 3 (150 MW) + FGD and CO_2 post-combustion capture
- In service 2013

Courtesy of Saskatchewan Power Corporation

Unit 3 –Conventional Pulverized Coal Unit



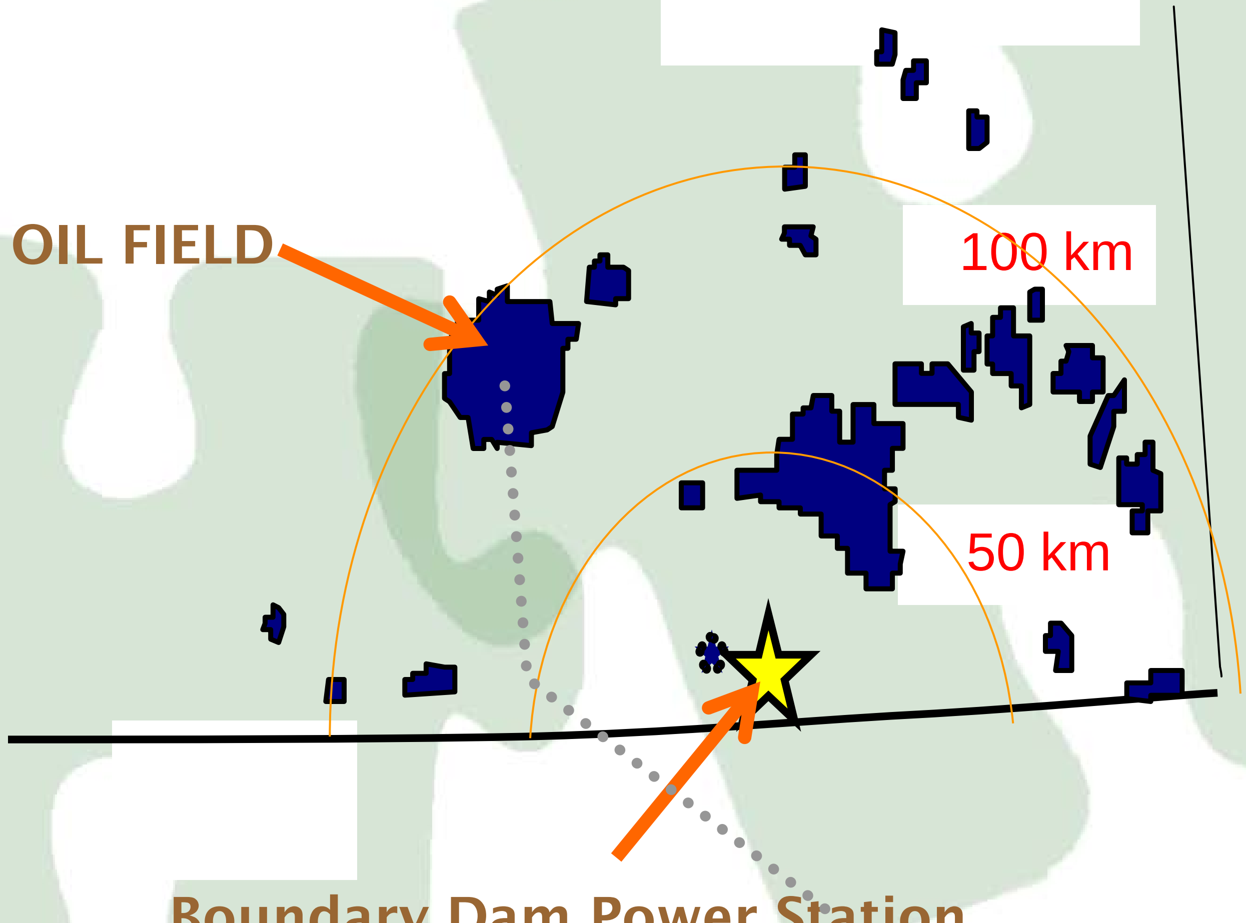
Courtesy of Saskatchewan Power Corporation



Unit 3 Retrofit

Courtesy of Saskatchewan Power Corporation

Storage option: CO_2-EOR



WEYBURN OIL FIELD

Boundary Dam Power Station

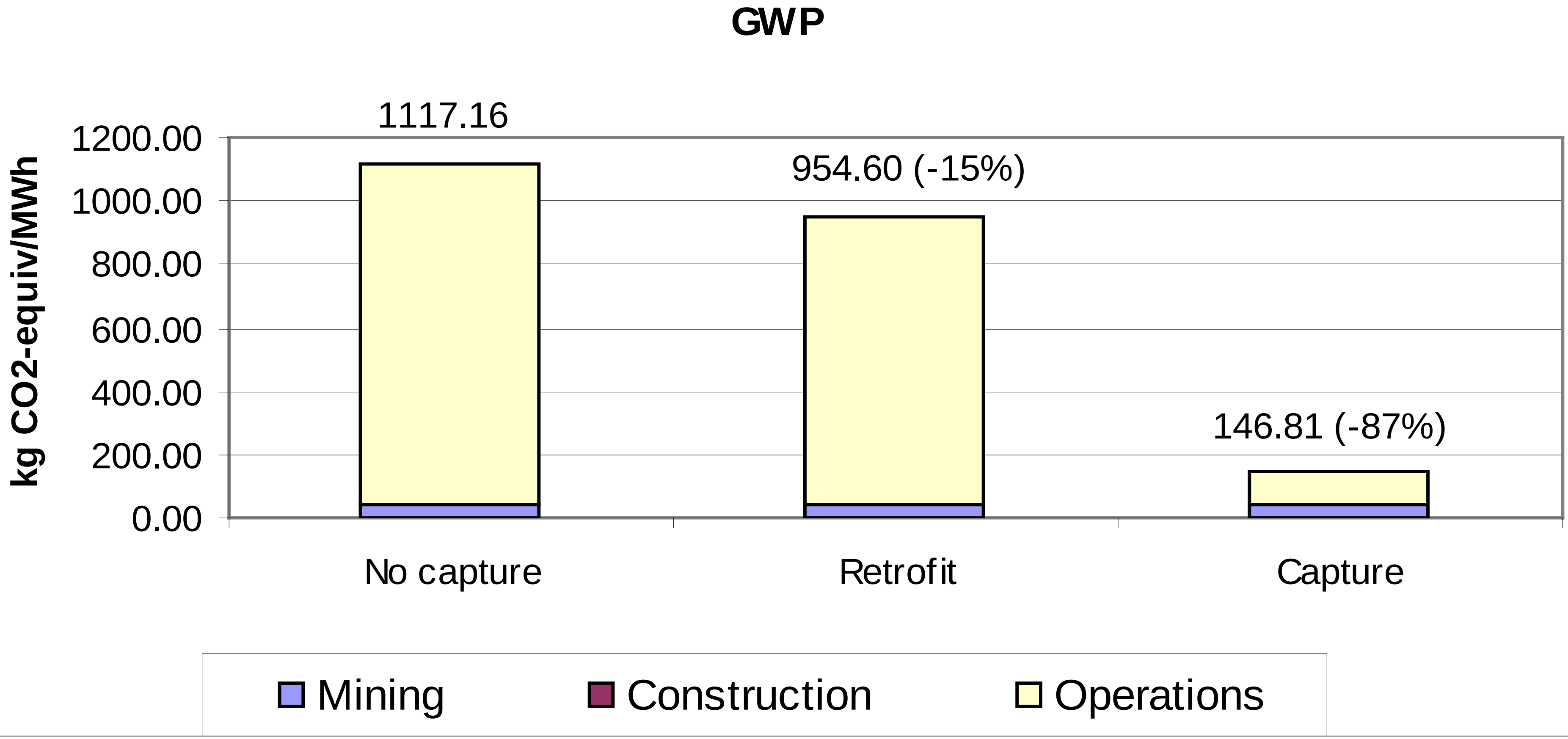
Courtesy of Saskatchewan Power Corporation

Analysis

- Comparison of the following scenarios:
  - Power plant without capture
  - Power plant with unit 3 retrofit: capture (Unit 3 – 150MW)
  - Power plant with capture (all 6 units – 882MW)

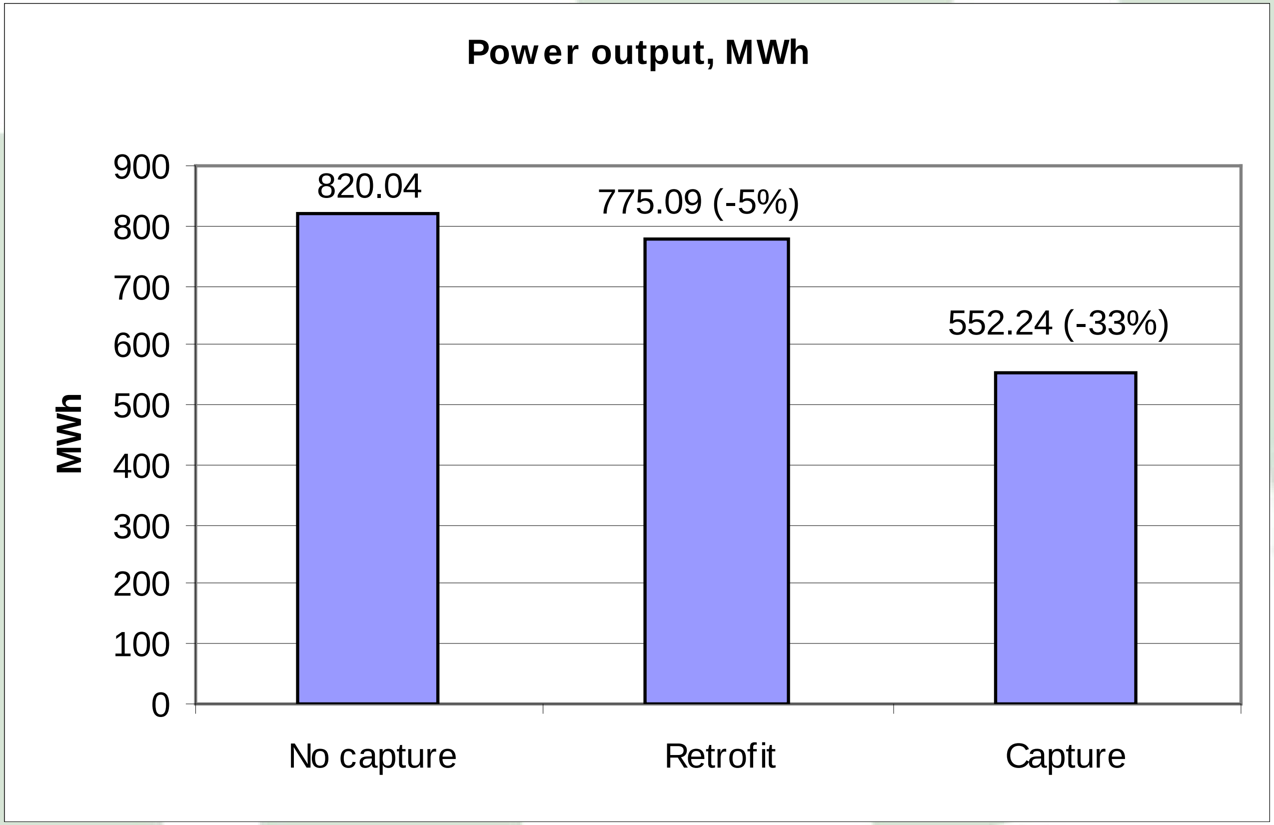
Results

Power plant without capture – Retrofit (capture only from Unit 3 (150 MW)) – Power plant with capture (882 MW)

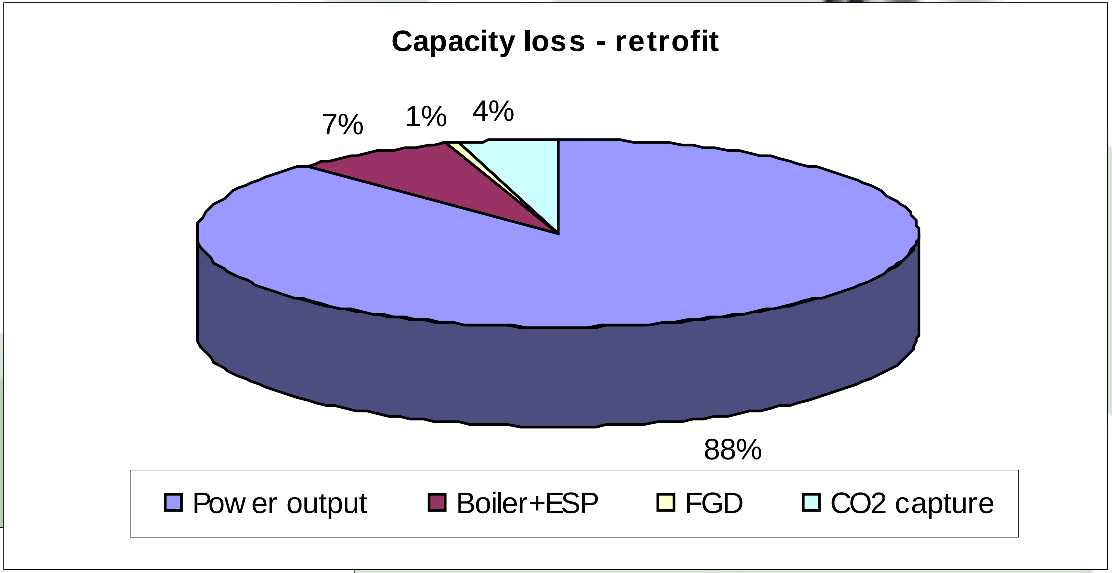


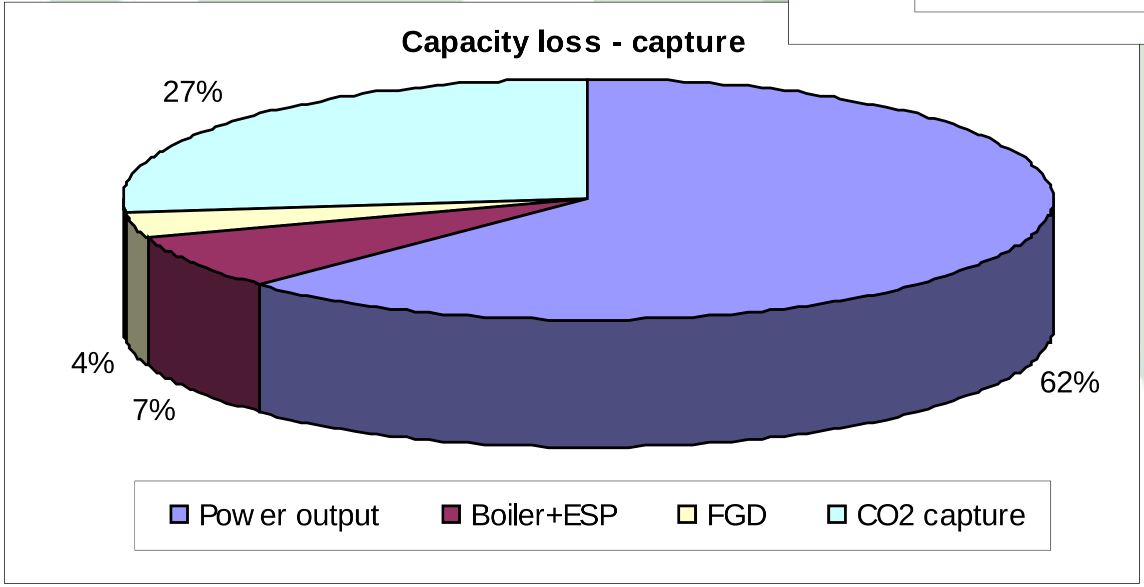
Results

Power plant without capture – Retrofit (capture only from Unit 3 (150 MW)) – Power plant with capture (882 MW)

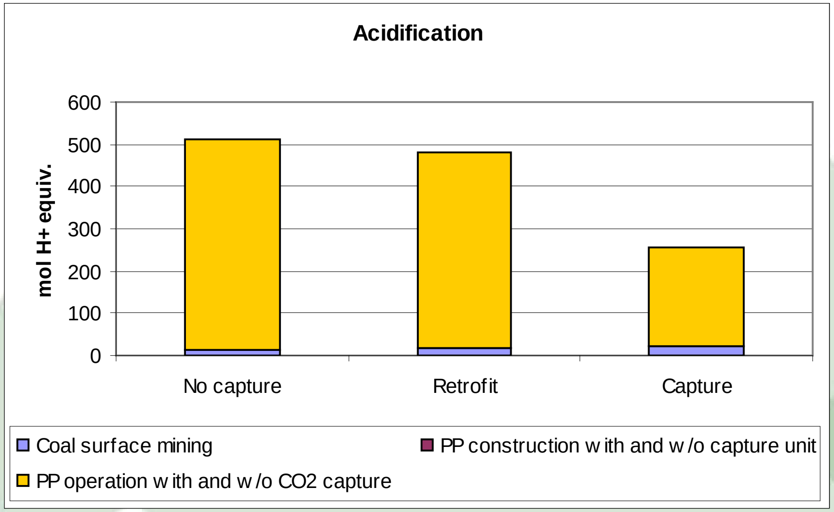


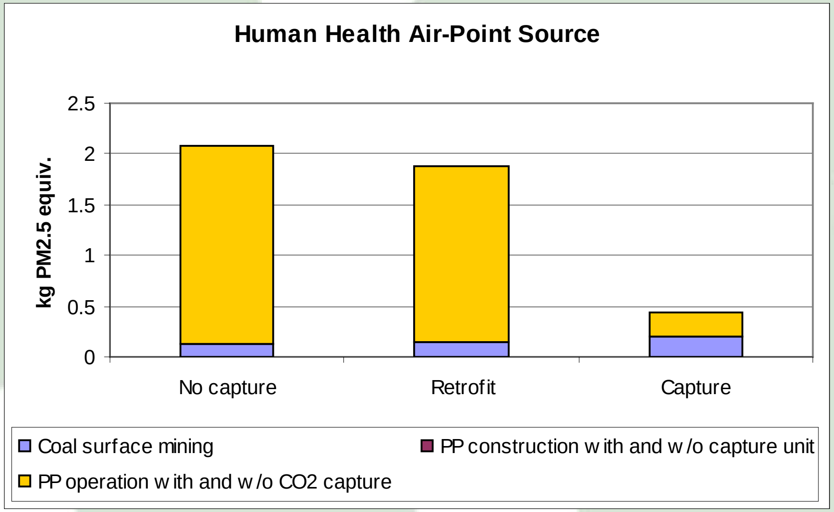
Results – Case 1



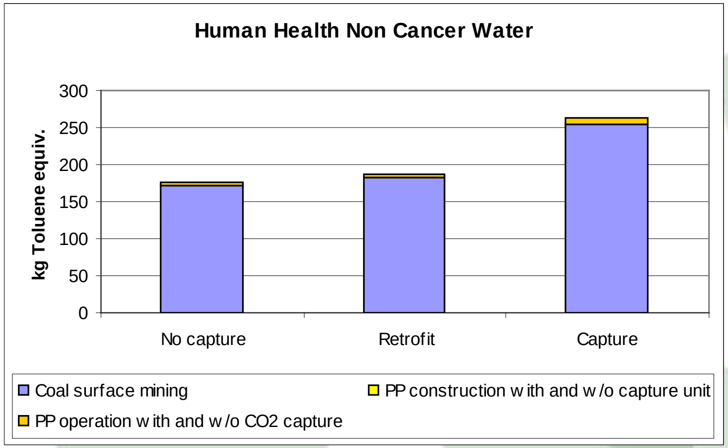


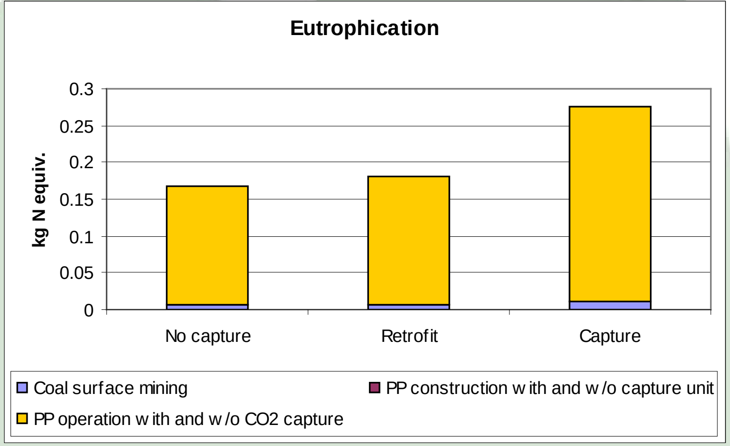
Decrease in other Impacts

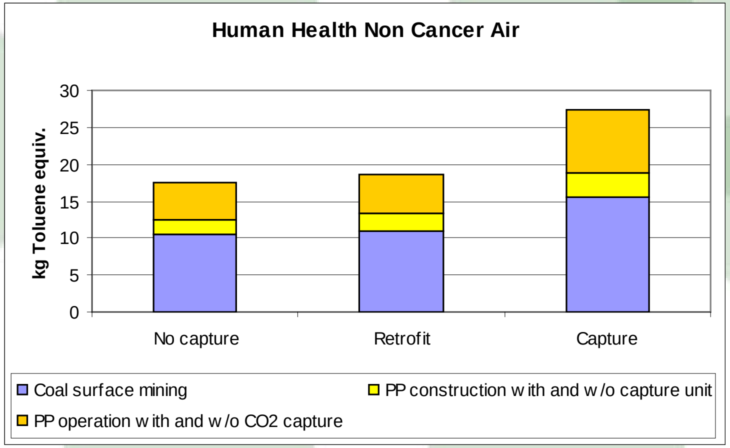


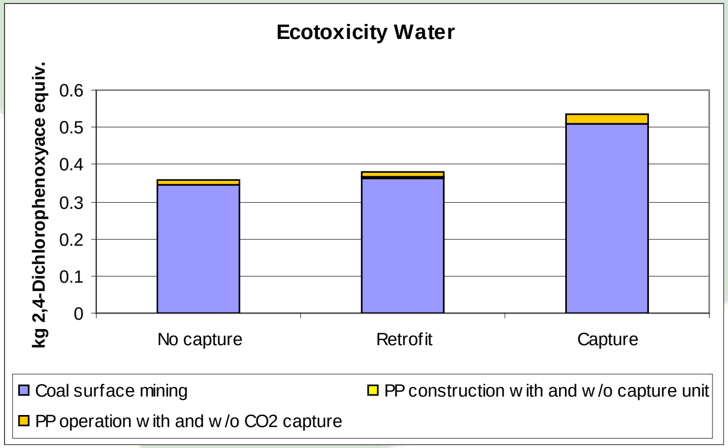


Increase in other impacts

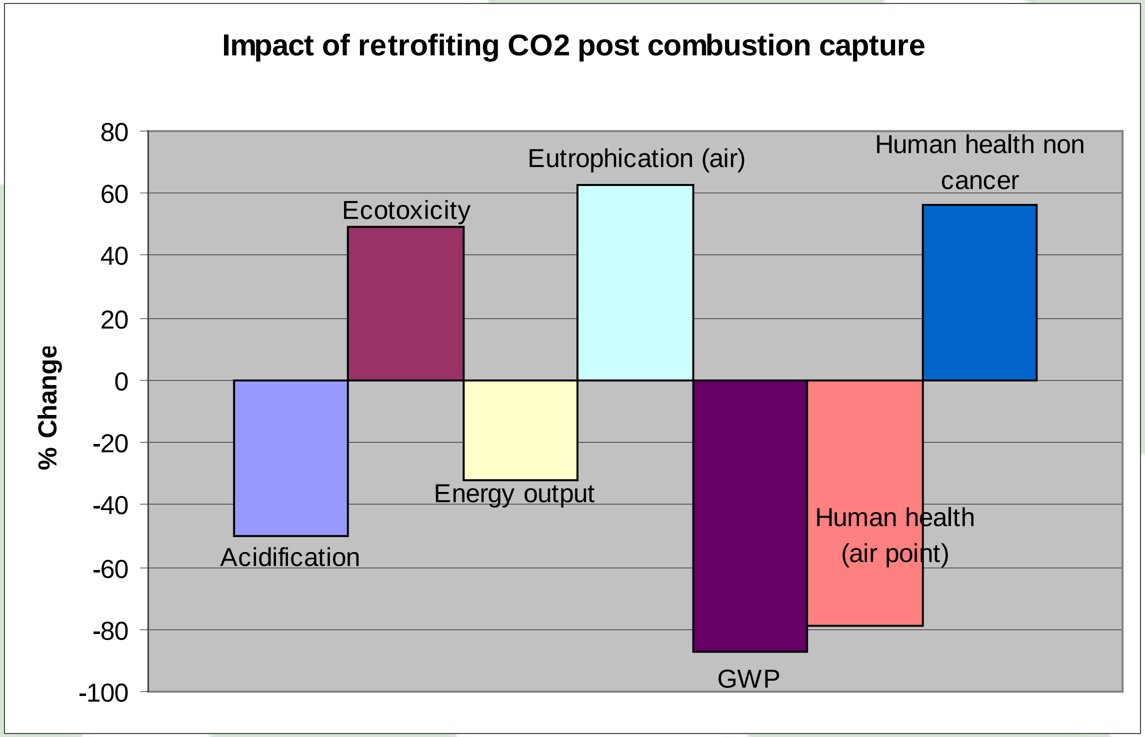




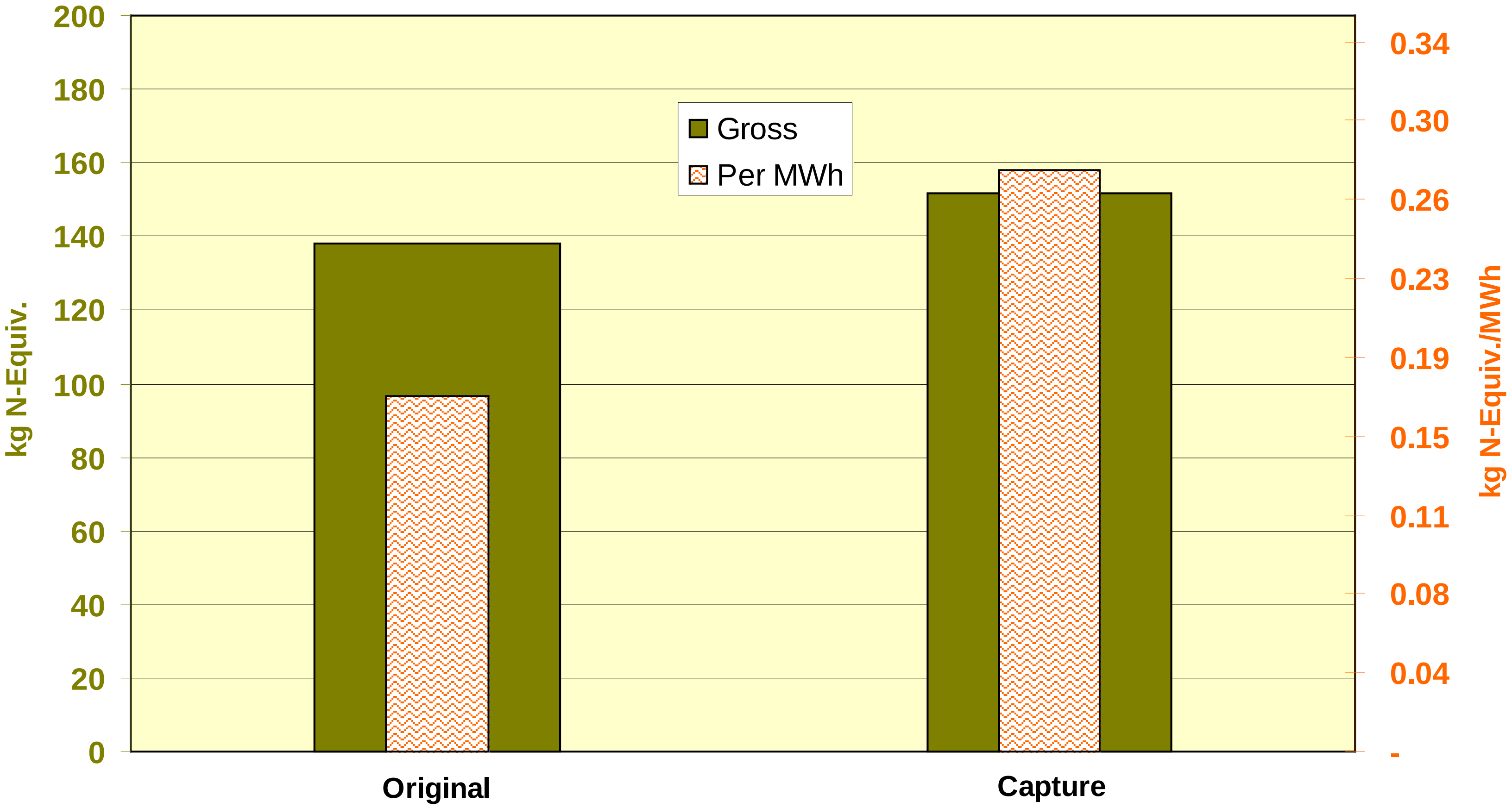




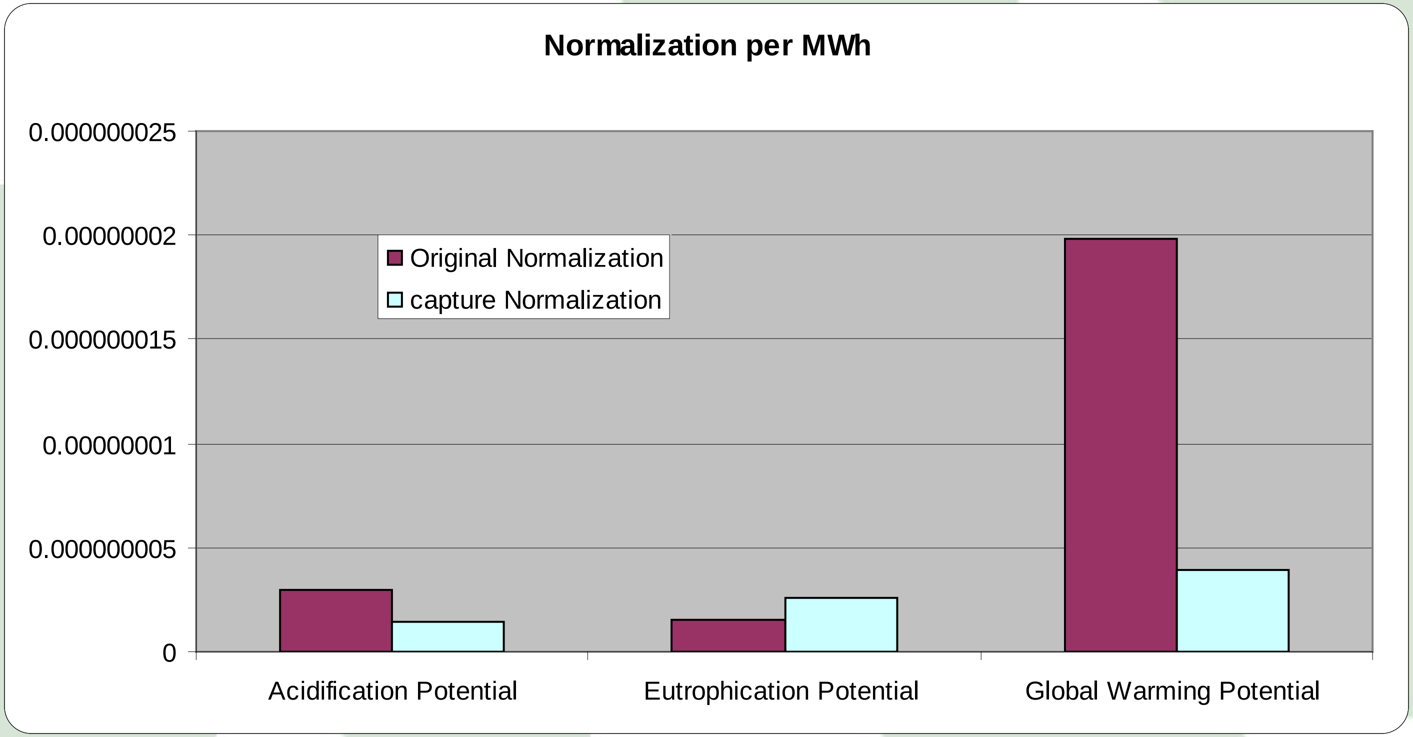
+/- Impacts per MWh



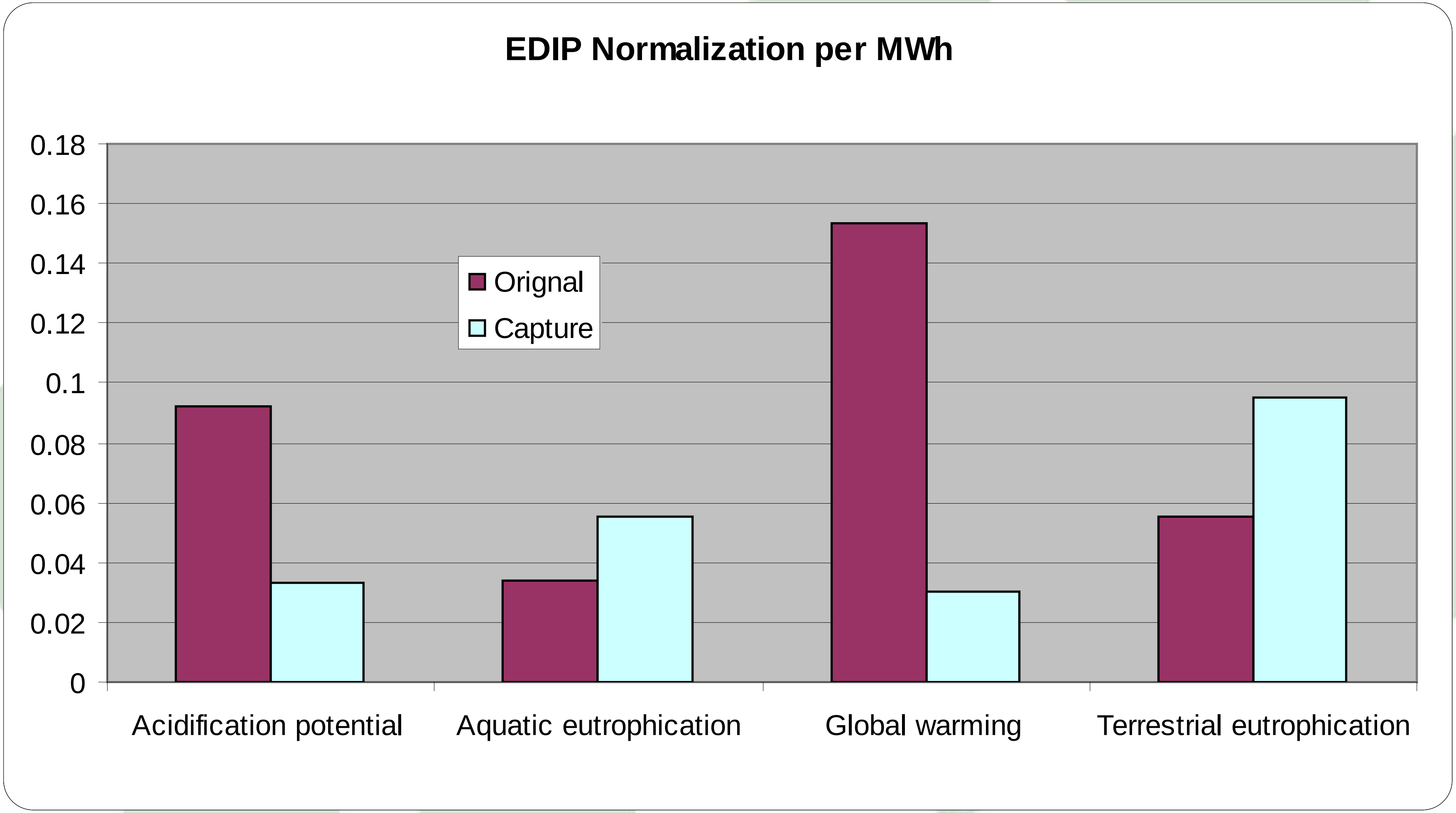
TRACI, Eutrophication [kg N-Equiv.]



CML method


Normalization per MWh
0.000000025
0.00000002
0.000000015
0.00000001
0.000000005
0
Original Normalization
capture Normalization
Acidification Potential
Eutrophication Potential
Global Warming Potential

EDIP method

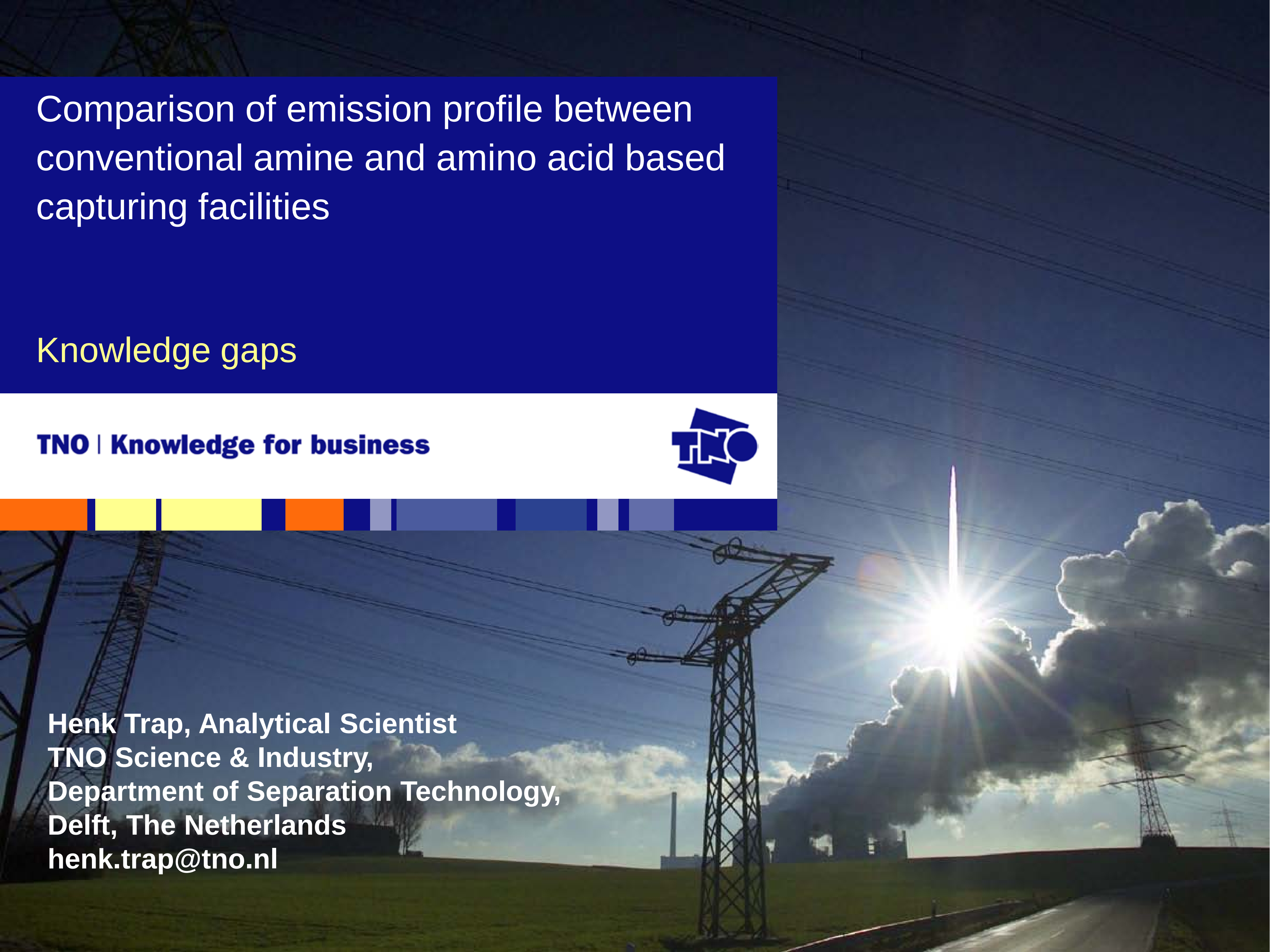

EDIP Normalization per MWh
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Orignal
Capture
Acidification potential
Aquatic eutrophication
Global warming
Terrestrial eutrophication

Thank you

- Financial support
  - IPAC-CO2 www.ipac-CO2.com
  - Office of Energy and Environment at the University of Regina www.uregina.ca/oee

Jitsopa Suebsiri: jitsopa@gmail.com
Anastassia Manuilova: nastenka09@yahoo.com

Thank You



Comparison of emission profile between conventional amine and amino acid based capturing facilities

Knowledge gaps

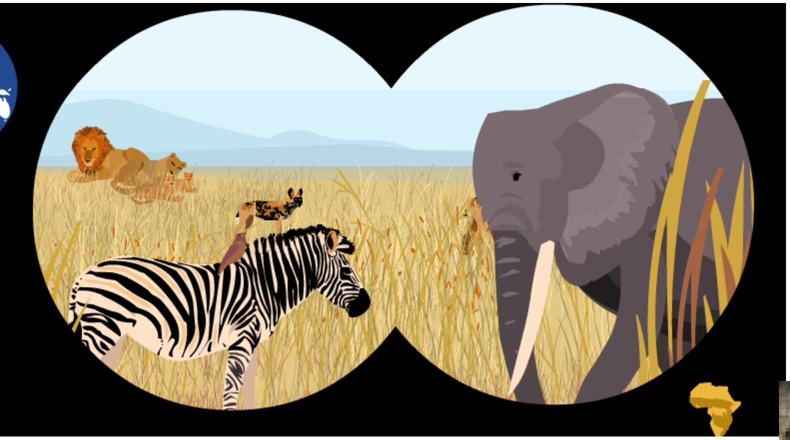
TNO | Knowledge for business

Henk Trap, Analytical Scientist
TNO Science & Industry,
Department of Separation Technology,
Delft, The Netherlands
henk.trap@tno.nl

Scope of the Comparison

- Is it clear what both systems are emitting ?
    - Chemicals, Sensing strategy, Sensing Techniques
- What is the toxicological relevance ? => Impact
- What is the RISK => **chance** X effect (toxicological class e.d.)
- Is it clear what the (degradation) products are ?
- Specific classes
- Emission Profile
- Age of fate of chemicals ?
- Is all this necessary ? Hype effect !

Risk !



Total emission (North America, 2004)

	Canada	Mexico	USA
SO_2 (Mton)	0.62	1.6	9.2
NO_x (Mton)	0.26	0.25	4.0
Hg (kg)	1,986	1,025	44,231
CO_2 (Mton)	128	94	2,178
CO ?	?	?	?
Others	?	?	?

North American Power Plant Emissions, "Secretariat, Commission for Environmental Cooperation"

Chemicals and Chemical classes

- Amines
- Aldehydes
- Permanent gasses (NOx, SO2, SO3, CO, CO2, NH3, O2)
- Acetamines
- Water
- Acids
- HSS (Heat Stable Salts)
- Carbonates, carbamates
- Volatile Organic Components
- Non-volatile organic components
- Volatile and semi- volatile nitrosamines (*) and nitramines(*)
- Tar, dust, fine particles, organometals, etc.

Sensing Strategy

Amine based

- Direct measuring (L.O.D.)
  - Vapour
  - Solvent
  - Waste
  - Company Terrain
  - Environment
- Off-line or indirect measuring (S.I.T.L.)
  - Vapour
  - Solvent
  - Waste
  - Company Terrain
  - Environment

Amino Acid based

- Direct measuring (L.O.D.)
  - Vapour
  - Solvent
  - Waste
  - Company Terrain
  - Environment
- Off-line or indirect measuring (S.I.T.L.)
  - Vapour
  - Solvent
  - Waste
  - Company Terrain
  - Environment

L.O.D.; Limit Of Detection S.I.T.L.; Sky Is The Limit

Sensing Techniques (on-line)

Examples

• Infrared • FT-IR, NIR, FT-NIR	• Amines, Aldehydes, Permanent gasses, Acetamines, Carbonates
• FID (Flame ionization Detector)	• Total Hydro Carbons (THC)

• Chromatography
  • GC-TCD/FID/FPD
  • GC-MS
  • HPLC-UV/ViS
	• Aldehydes, Permanent gasses, VOC’s, Volatile carcinogenic components, non-volatile ..

• Mass Spectrometry • IMS	• VOC’s
• Electrochemical sensors	• Permanent gasses,

Toxicological relevance ? => Impact

- Amines e.g. MEA
  => Permissible exposure limit (PEL) (US); 3 ppm

- Aldehydes e.g. Acrolein, reacts with GSH (enzym)
  => permissible concentration 0.5 µg/kg

- Permanent gasses

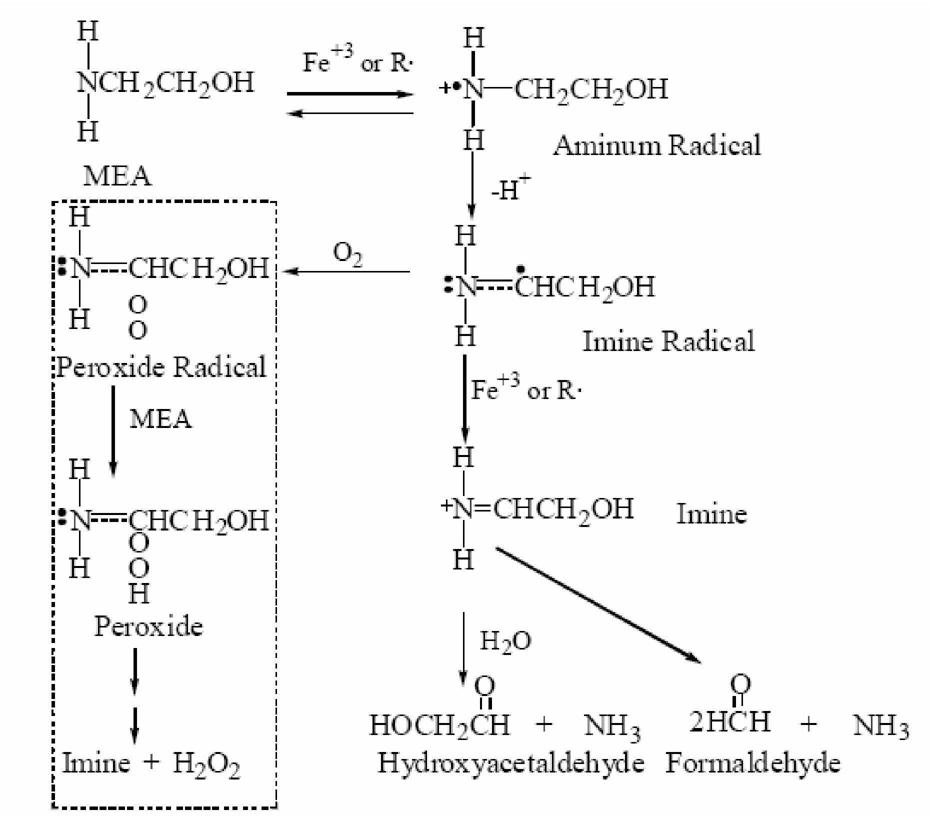
=> NOx	1-10 ppm
=> SOx	2-30 ppm
=> CO	PEL 50 ppm
=> CO2	PEL 5000 ppm
=> NH3	PEL 35-50 ppm

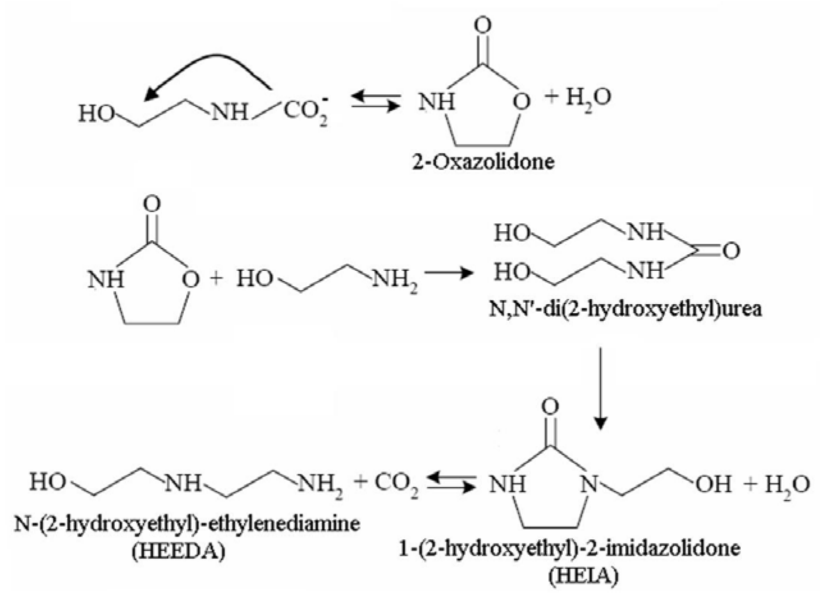
- Acetamines
  => low toxicity, possible carcinogenic

Toxicological relevance ? => Impact

- Acids, e.g. acetic acid and formic acid
- Carbonates, carbamates
  => low toxicity
- Volatile Organic Components => ?
- Non-volatile organic components
  => naphthalene, anthracene?
- Volatile and semi- volatile nitrosamines (*) e.g. NDELA
  => (Class A Carcinogenic), PEL (1 yr) 0.000027 ppm
- Nitramines
  => ….
- HSS
  => Acetate, glycolate, oxalate, thiosulphate, ..
- Tar, dust, fine particles, organometals, etc. => ?

Degradation Products (amine)





Bellona report September 2009 - Amines used in CO2 capture.doc

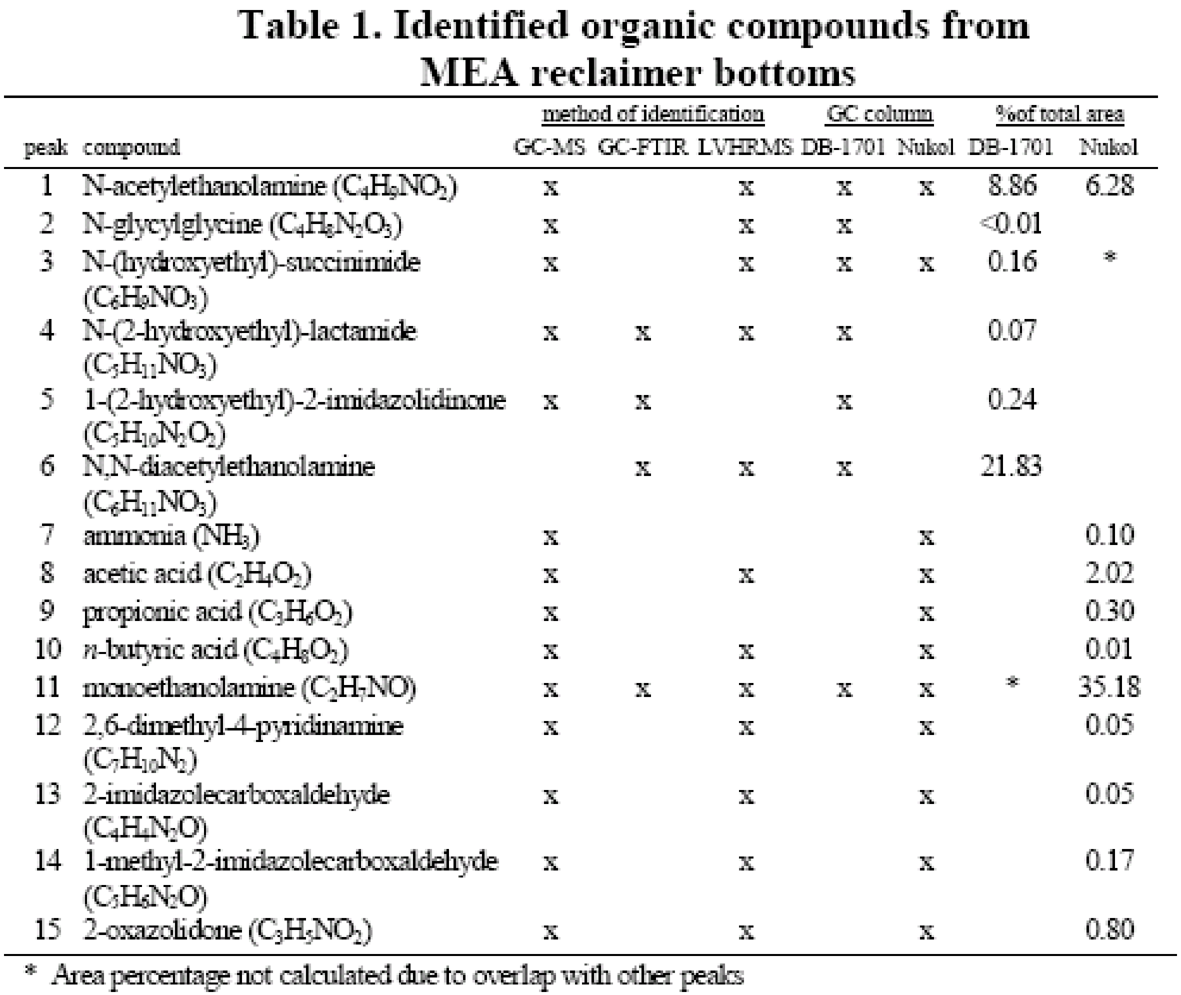


Table 1. Identified organic compounds from MEA reclaimer bottoms

		method of identification			GC column		%of total area	
peak	compound	GC-MS	GC-FTIR	LVHRMS	DB-1701	Nukol	DB-1701	Nukol
1	N-acetylethanolamine ($C_4H_9NO_2$)	x		x	x	x	8.86	6.28
2	N-glycylglycine ($C_4H_8N_2O_3$)	x		x	x		<0.01	
3	N-(hydroxyethyl)-succinimide ($C_6H_9NO_3$)	x		x	x	x	0.16	*
4	N-(2-hydroxyethyl)-lactamide ($C_5H_{11}NO_3$)	x	x	x	x		0.07	
5	1-(2-hydroxyethyl)-2-imidazolidinone ($C_5H_{10}N_2O_2$)	x	x		x		0.24	
6	N,N-diacetylethanolamine ($C_6H_{11}NO_3$)		x	x	x		21.83	
7	ammonia (NH_3)	x				x		0.10
8	acetic acid ($C_2H_4O_2$)	x		x		x		2.02
9	propionic acid ($C_3H_6O_2$)	x				x		0.30
10	*n*-butyric acid ($C_4H_8O_2$)	x		x		x		0.01
11	monoethanolamine (C_2H_7NO)	x	x	x	x	x	*	35.18
12	2,6-dimethyl-4-pyridinamine ($C_7H_{10}N_2$)	x		x		x		0.05
13	2-imidazolecarboxaldehyde ($C_4H_4N_2O$)	x		x		x		0.05
14	1-methyl-2-imidazolecarboxaldehyde ($C_5H_6N_2O$)	x		x		x		0.17
15	2-oxazolidone ($C_3H_5NO_2$)	x		x		x		0.80

* Area percentage not calculated due to overlap with other peaks

Brian R. Strazisar, et.all *Fuel Chemistry Division Preprints* ***2002****, 47(1), 56*

Degradation Products (amino acid)

Sarcosine => Thermal unstable => NH3 forming

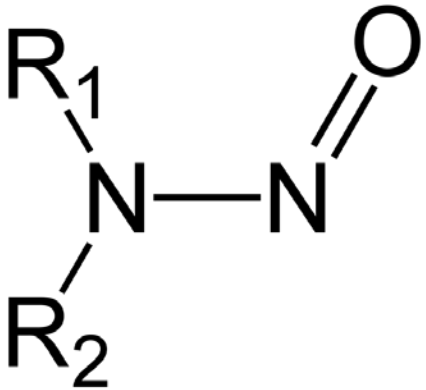
=> HSS

Others

?

Under investigation

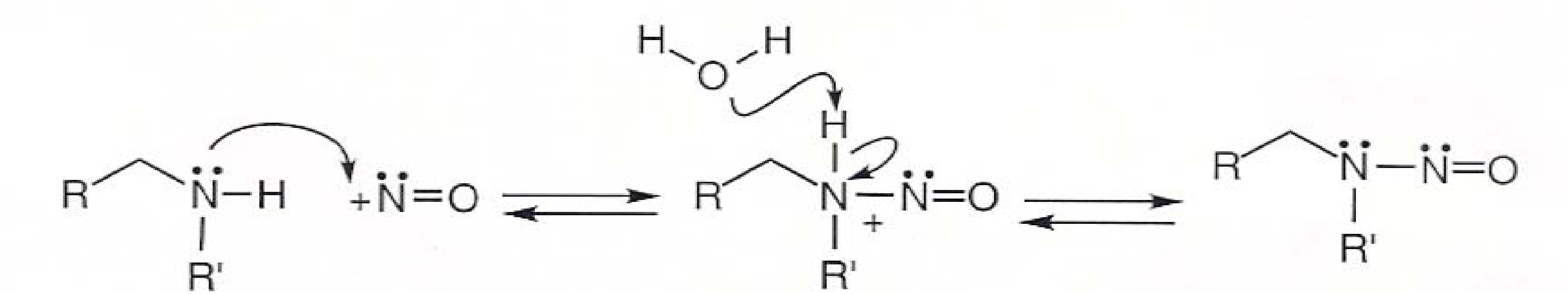
Specific classes
Nitrosamines & Nitramines



Amines and amino acids can be in the presence of NO2 be metabolized to Secondary N-Nitrosamine are persistent and carcinogenic in some situations they can be further metabolized to Nitramines.

Chemistry and reaction mechanism

Two step reaction;
1) radical forming NO,
2) reaction with amine or Amino acid to a Nitrosamine
=> example



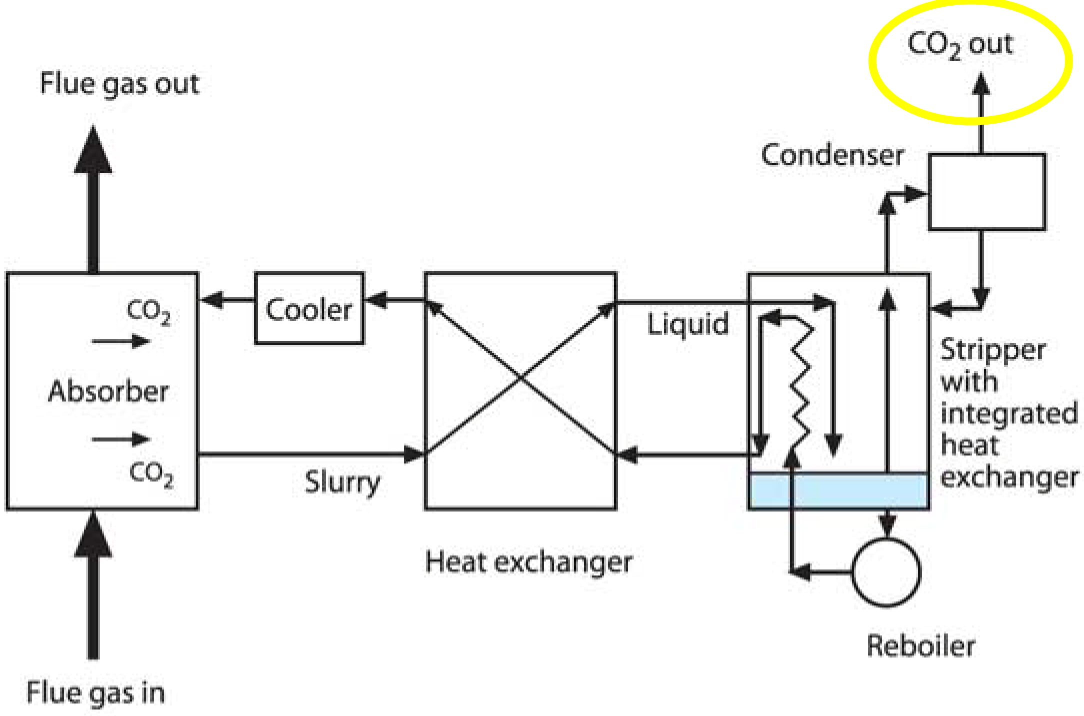
The 'nitrosamine' challenge

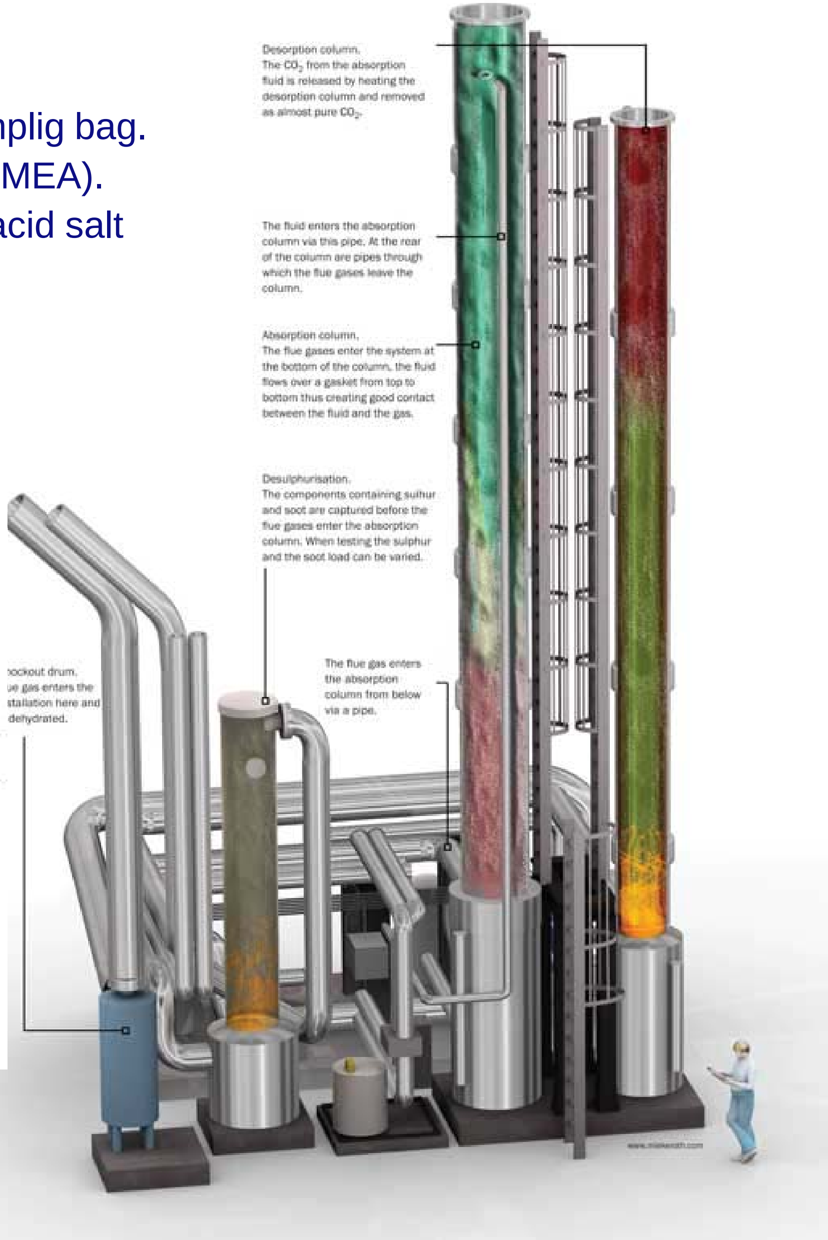
- NOx can act as nitrosation agent in ACIDIC environment –
  => absorber is BASIC
- Primary amines do not form stable nitrosamines –
  => MEA is primary
- Primary nitrosamines decompose rapidly in ACIDIC environment –
  =>absorber is BASIC

Post-combustion CO2 removal, G. de Koeijer, StatoilHydro, 2009

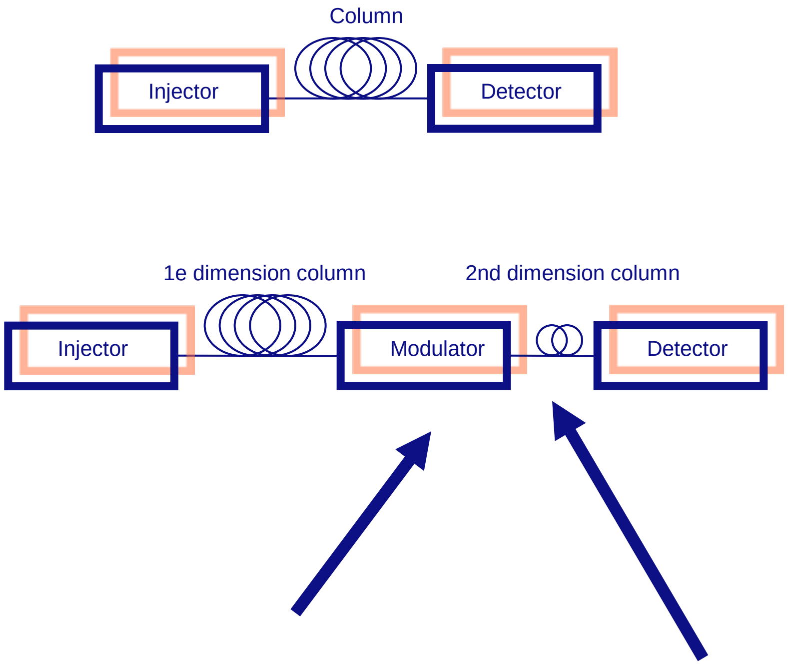
Emission Profile

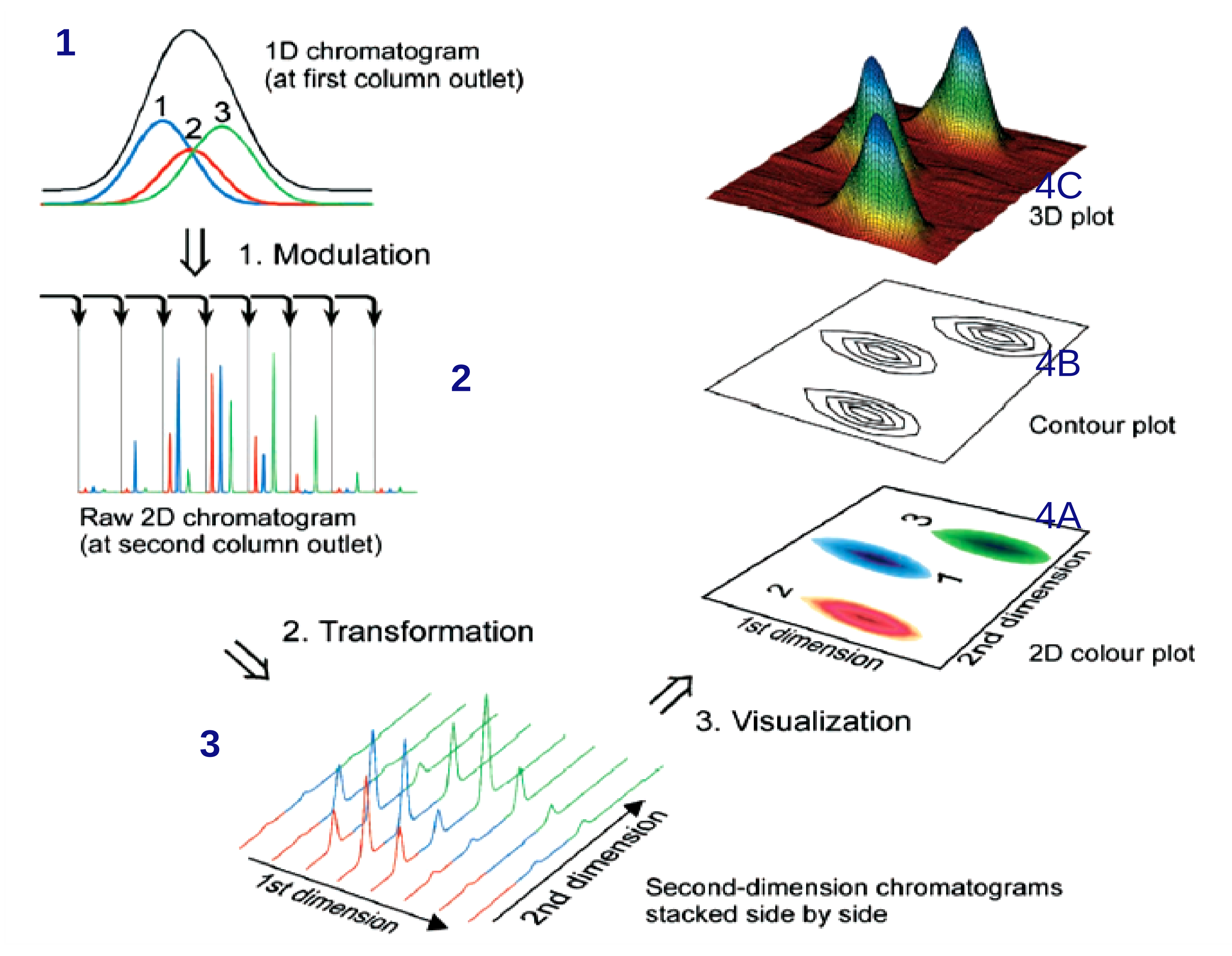
Sampling in the CO2 out pipe by using a Tedlar gas samplig bag.
1st situation after using 1 week an amine based solvent (MEA).
2nd situation after an 8 weeks campaign with an amino acid salt based solvent. Analysis by GCxGC-ToF-MS.

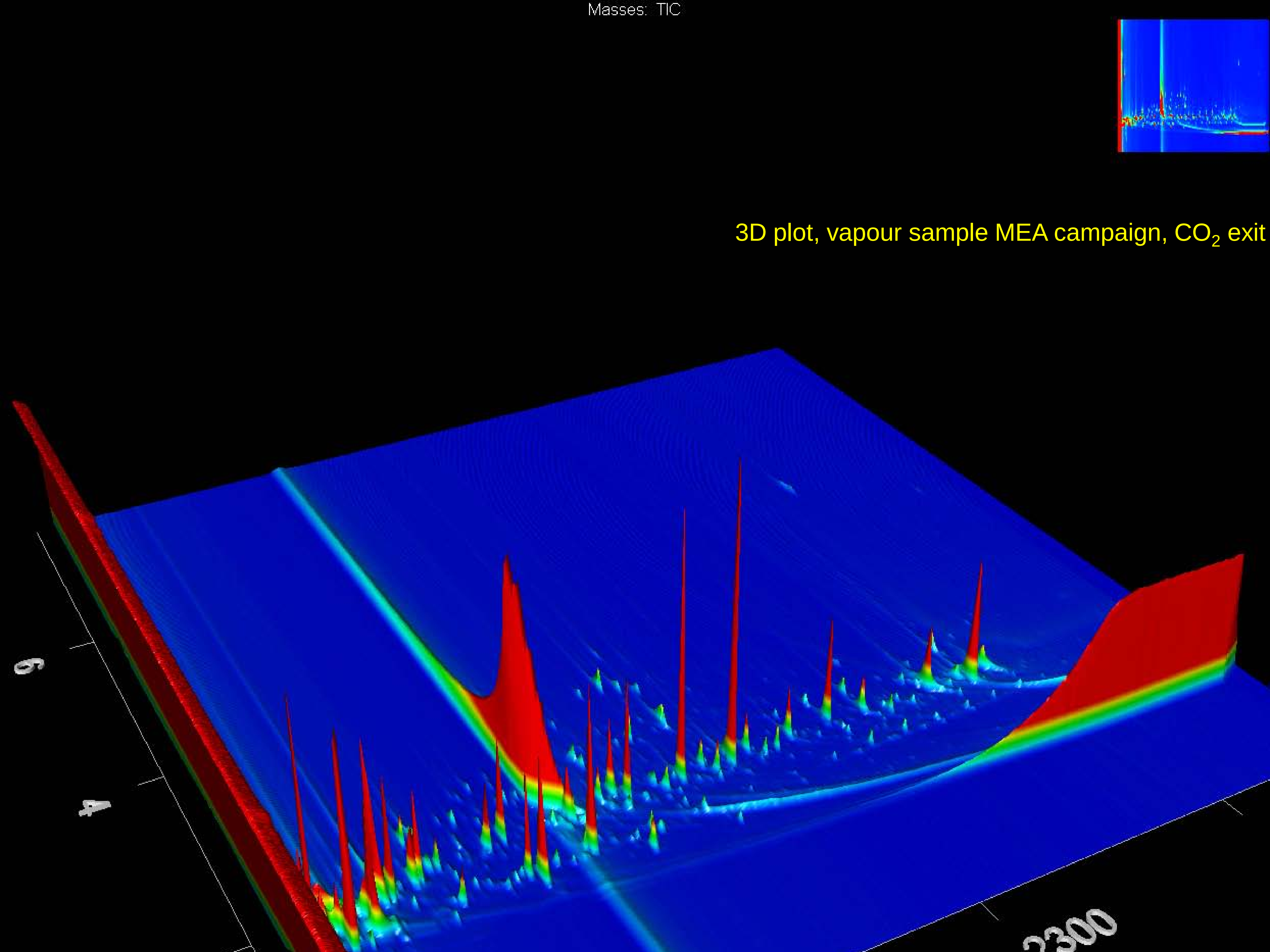




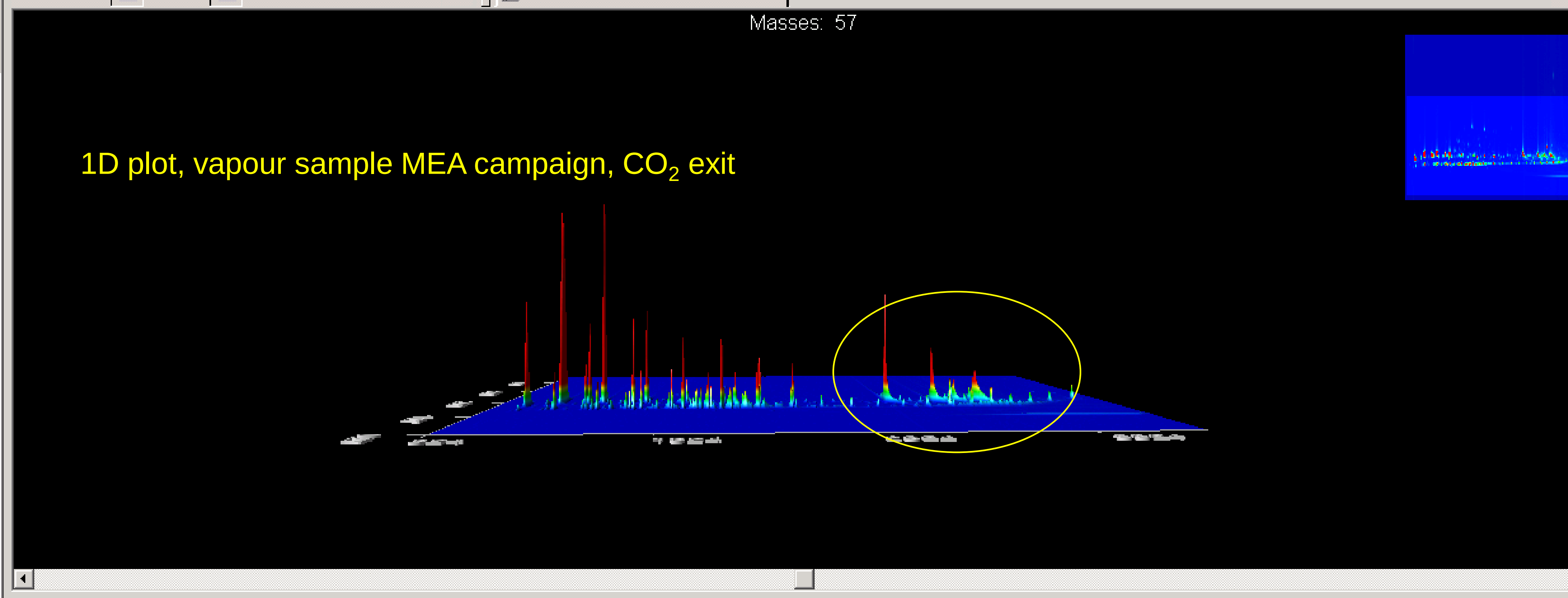
Comprehensive Gas Chromatography (GCxGC)



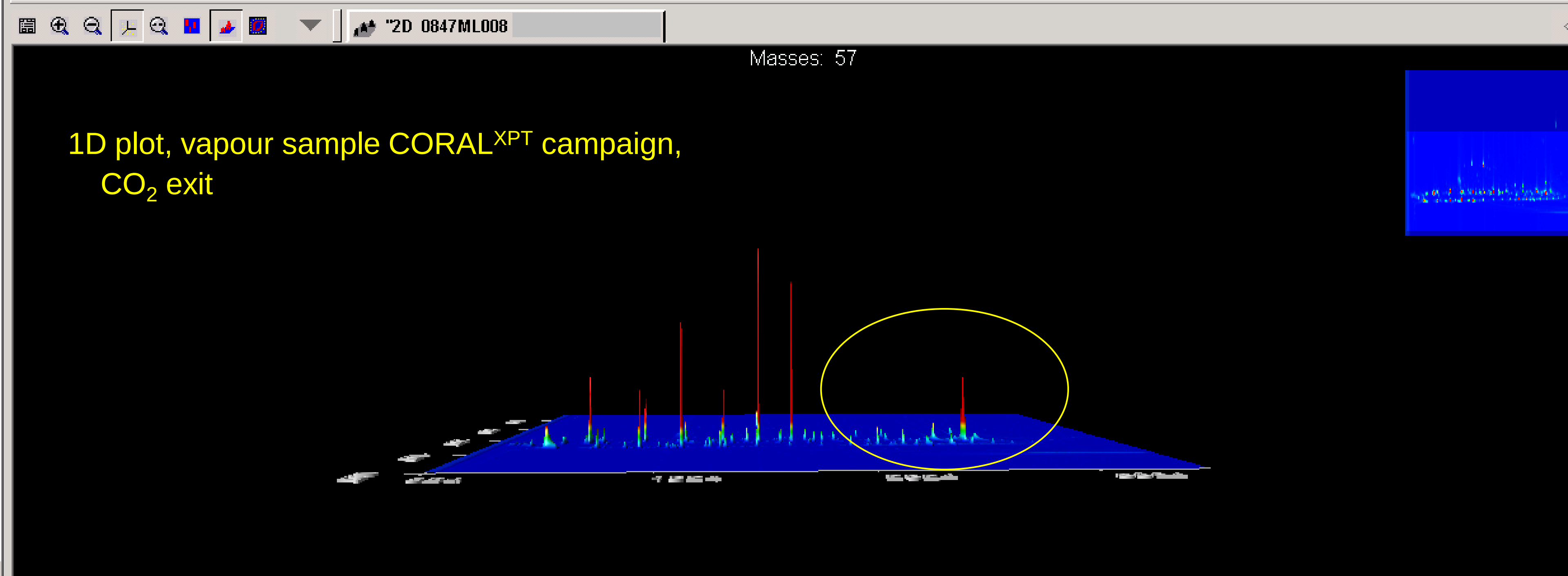

1
1D chromatogram
(at first column outlet)
1
2
3
1. Modulation
2
Raw 2D chromatogram
(at second column outlet)
2. Transformation
3
1st dimension
2nd dimension
Second-dimension chromatograms
stacked side by side
3. Visualization
4C
3D plot
4B
Contour plot
4A
3
1
2
1st dimension
2nd dimension
2D colour plot



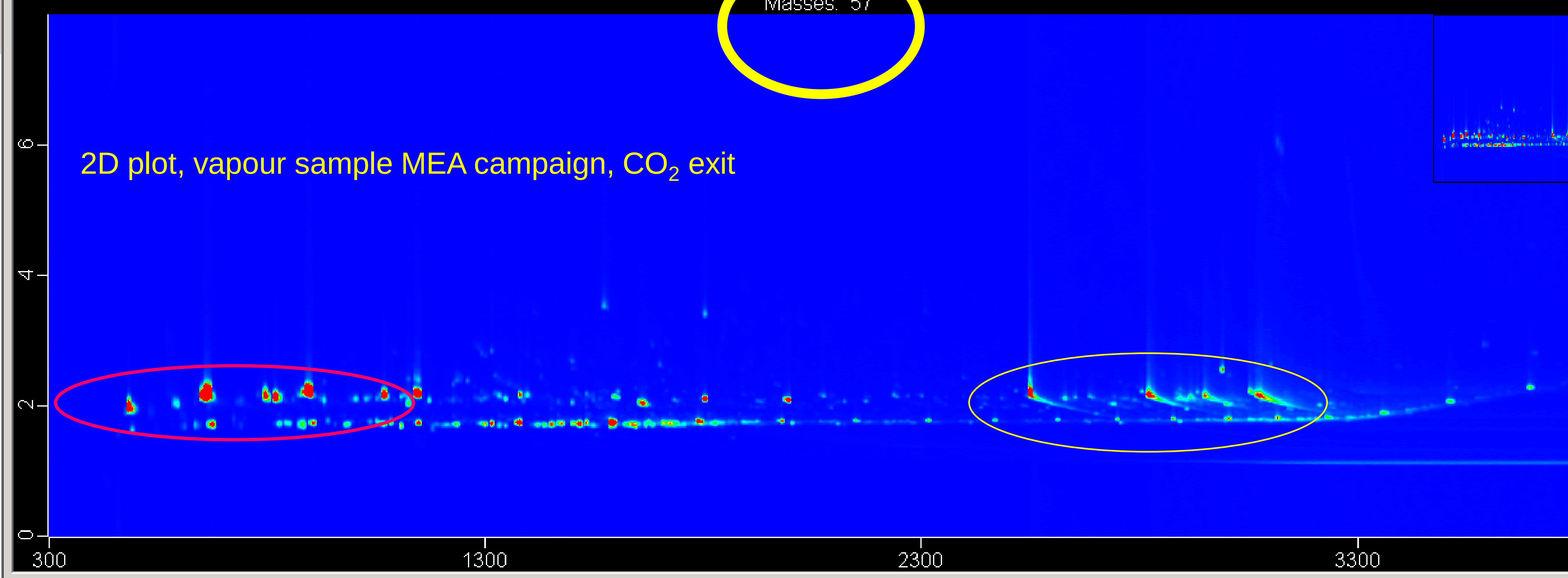
3D plot, vapour sample MEA campaign, CO_2 exit



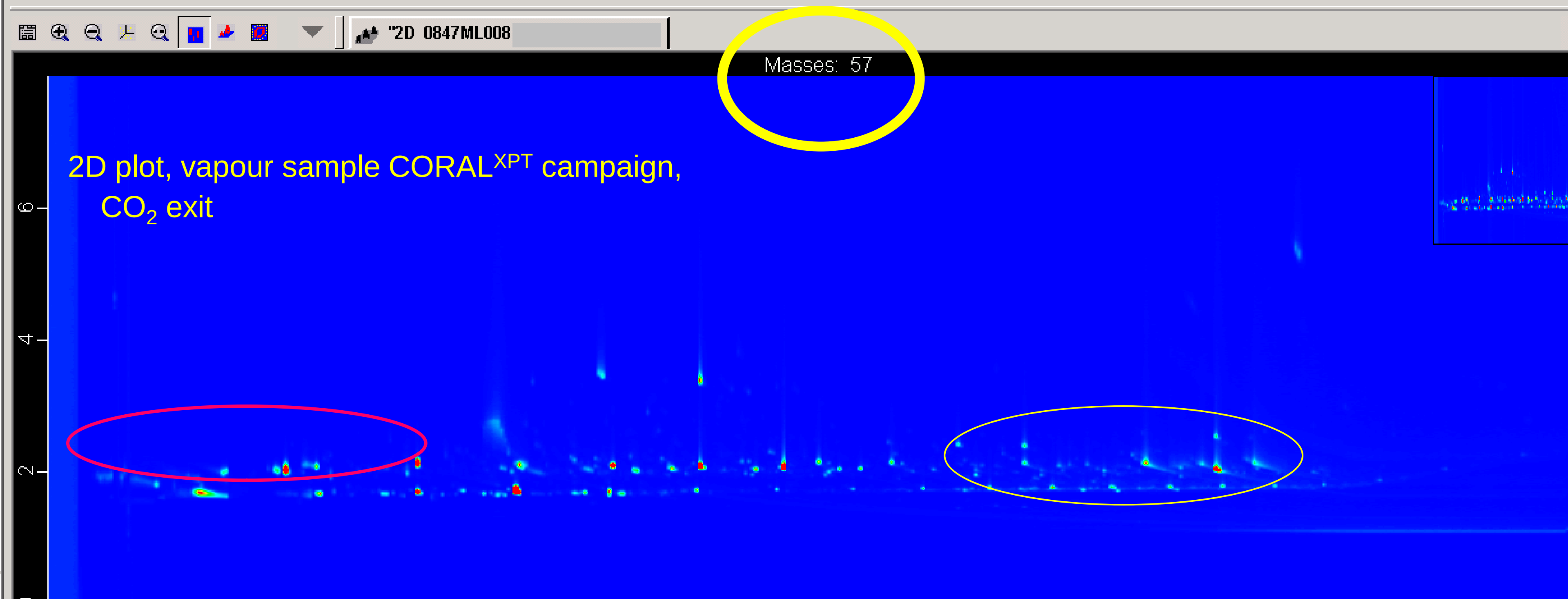
1D plot, vapour sample MEA campaign, CO_2 exit



1D plot, vapour sample CORAL^{XPT} campaign, CO_2 exit



2D plot, vapour sample MEA campaign, CO_2 exit



2D plot, vapour sample CORAL^{XPT} campaign, CO_2 exit

Conclusions

- Comparing facilities is troubled by not looking in the same way
  - Which chemicals, where to look (time effect), how to look (sensing technology)

- More research is needed to investigate degradation products (lab scale) to complete the mass balance.

- Toxicology relevant chemicals should be more investigated in detail (where to find, stability) to optimize countermeasures.

- The age of fate of relevant chemicals in the environment and in waste should be investigated to take into account for the *total* burden of capture facilities.

...THE TOP PRESCRIPTION IS FOR YOUR ARTHRITIS, BUT IT MAY CAUSE A HEART ATTACK. THE SECOND PRESCRIPTION SHOULD PREVENT A HEART ATTACK, BUT IT COULD DAMAGE YOUR LIVER. THE THIRD SHOULD PREVENT LIVER TROUBLE, BUT IT MAY DESTROY YOUR SPLEEN. THE FOURTH PROTECTS THE SPLEEN BUT HAS BEEN KNOWN TO EAT AWAY THE PROSTATE. THE FIFTH.....
©2004 LARRY WRIGHT THE DETROIT NEWS
caglecartoons.com

Econamine FG+^{SM} Process:

Recent Advances in Emissions Control

Satish Reddy

February 16, 2010

FLUOR®

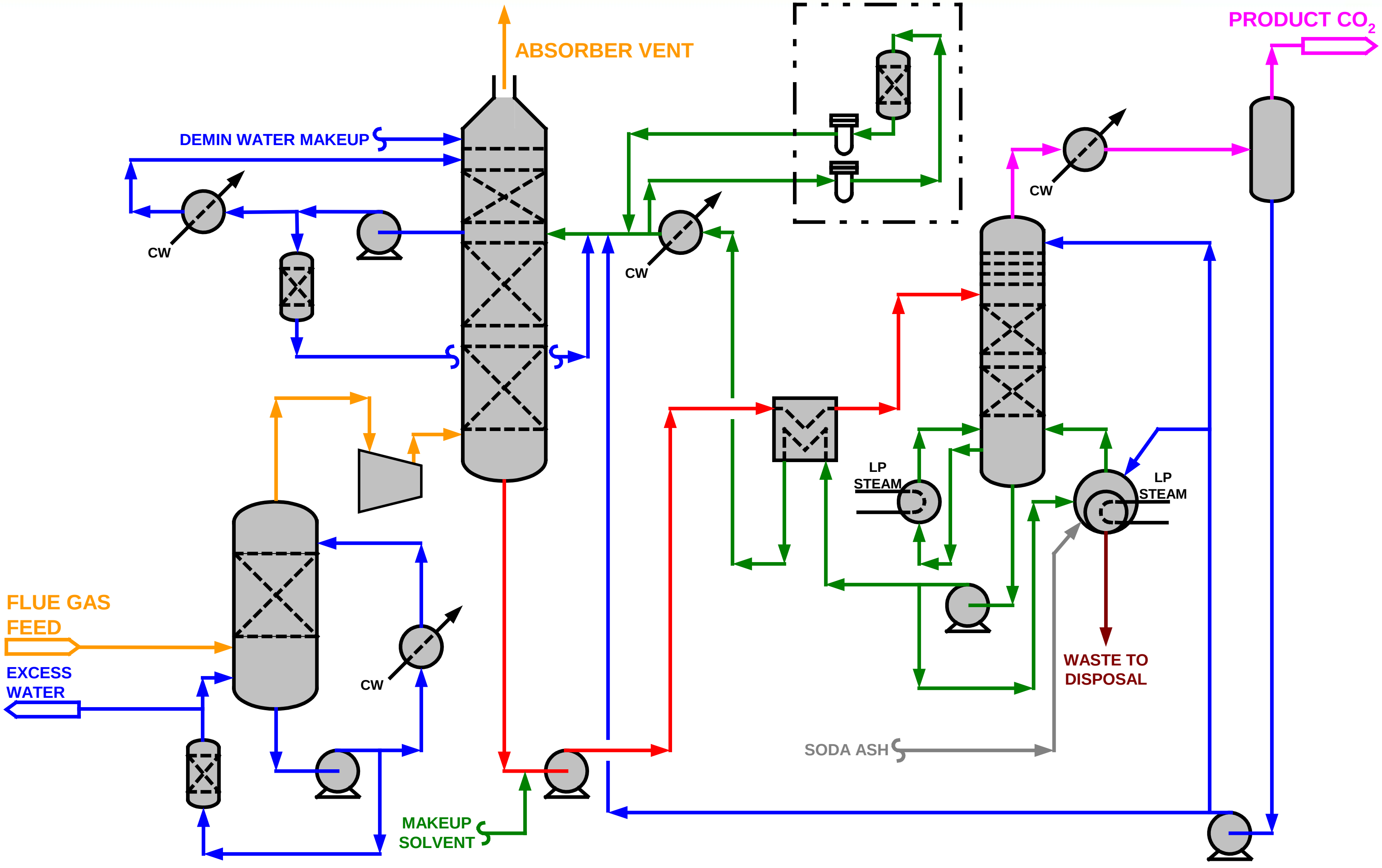
Environmental Impact of Amine Emission During Post Combustion Capture, Oslo

Econamine FG+^{SM} Technology Background

- Econamine FG+^{SM} (EFG+) is Fluor's technology which permits large-scale CO_2 capture from flue gases
- The EFG+ solvent is based on a primary amine

FLUOR®

Simplified Econamine FG+ ^{SM} Flowsheet

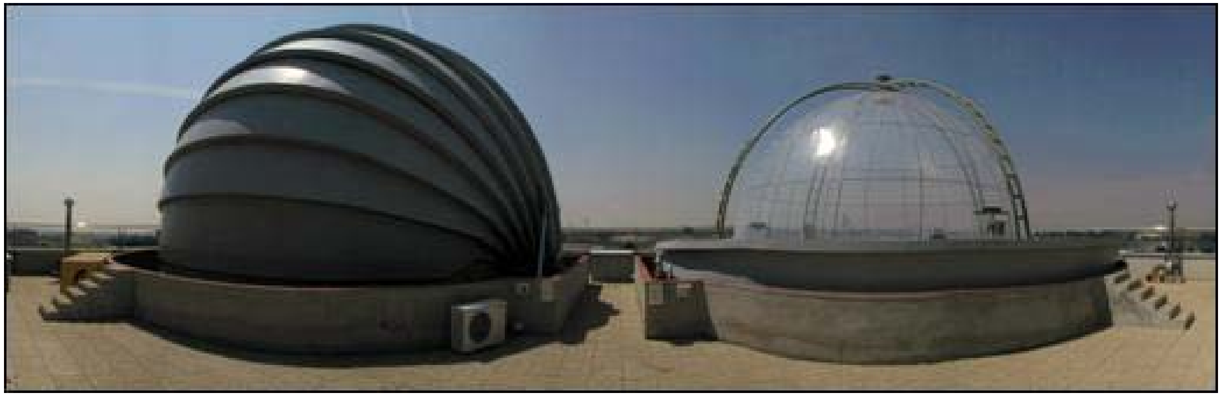


Molecular Modeling Studies

- Over the past two years there has been an increased level of concern regarding amine emissions.
- A molecular modeling study done in Norway has hypothesized that amines react with atmospheric NOx in the presence of ultra-violet (uV) light (sunlight) to form nitrosamines
- The theoretical study assumed 5 ppmv of amine in the spent fluegas
- Nitrosamines are considered harmful to the environment.

Atmospheric Chemistry Test

- The Centro de Estudios Ambientales del Mediterráneo (CEAM), Valencia, Spain is a EU funded Atmospheric Chemistry Studies Center
- Atmospheric chemistry testing with amines is being conducted



- The results of the tests are yet be announced!

Advanced Emission Control System

- The molecular modeling effort has caused a substantial discussion in the CCS community.
- In some countries, there is public anxiety
- For amine based technologies, the best path forwards is to reduce the emission of solvents to the atmosphere
- Fluor’s strategic plan is to demonstrate new plant designs to reduce amine emissions by one order of magnitude

Solvent Emissions from EFG+ plants

- In general, Fluor’s goal has been to minimize stack amine emissions from EFG+ plants.
- At the Bellingham plant, rigorous testing of solvent emissions in the fluegas vent was conducted
- The solvent concentration in the absorber vent was less than 1 ppm (v/v)
- Systems with lower emissions can been designed with a minor increase of OPEX

Further Improvements to Reduce Amine Emissions

- Fluor has developed an advanced scrubbing system, where the solvent concentration in the vent is greatly reduced to around 0.1 to 0.2 ppm (v/v)
- In 2011, the process and equipment to reduce amine emissions will be tested in demonstration plant in Germany
- The fluegas is derived from a coal fired power plant
- The demonstration plant is a result of cooperation between E.ON and Fluor Corporation
- A detailed test plan has been prepared

Target Emissions Levels

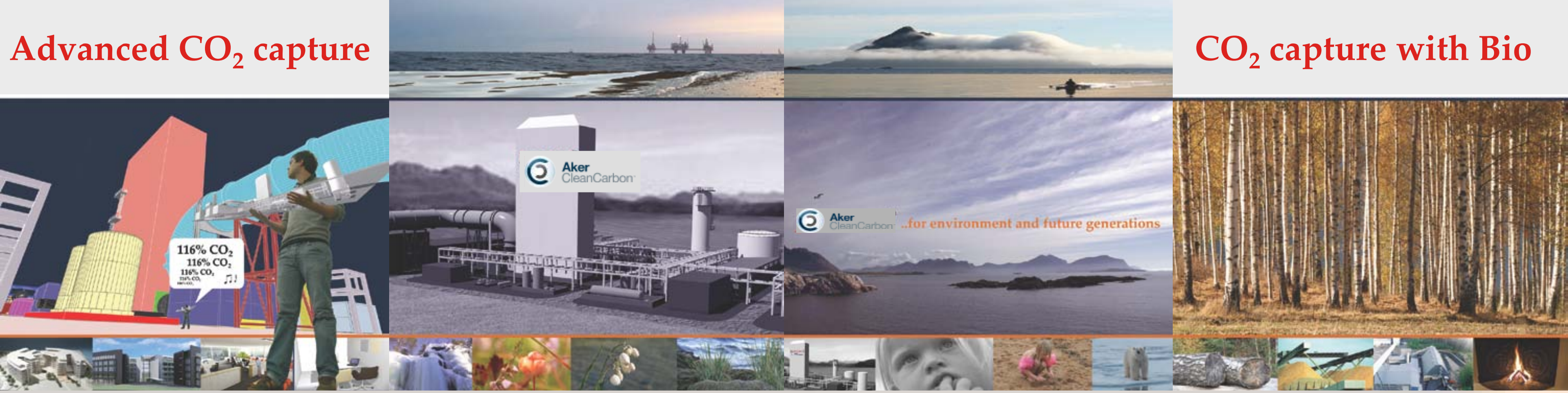
- More efficient scrubbing systems consume more power and/or reagents
- There is a need to design systems that scrub fluegas down to an "adequate" level and to not an arbitrarily low value
- Depending on the environmental impact, the degree of scrubbing (amine concentration) could vary depending on the amine used
- There is a need for the authorities to set target levels for amine emissions. Vendors can endeavor to design systems to meet the target

Reclaimer Waste

- Most amine based CO_2 capture processes require solvent reclaiming
- Depending on the fluegas constituents and the solvent's resistance to degradation a varying amount of reclaimer waste would be produced
- In its current generation technology, Fluor has significantly reduced reclaimer waste production
- Fluor is now focusing on developing methods for reclaimer waste disposal

Questions

Any Questions?



Aker Clean Carbon

- *Emission measurement and analysis from Mobile Carbon Capture Test Facility*

Oscar Fr. Graff

CTO

Oslo, 16 February 2010

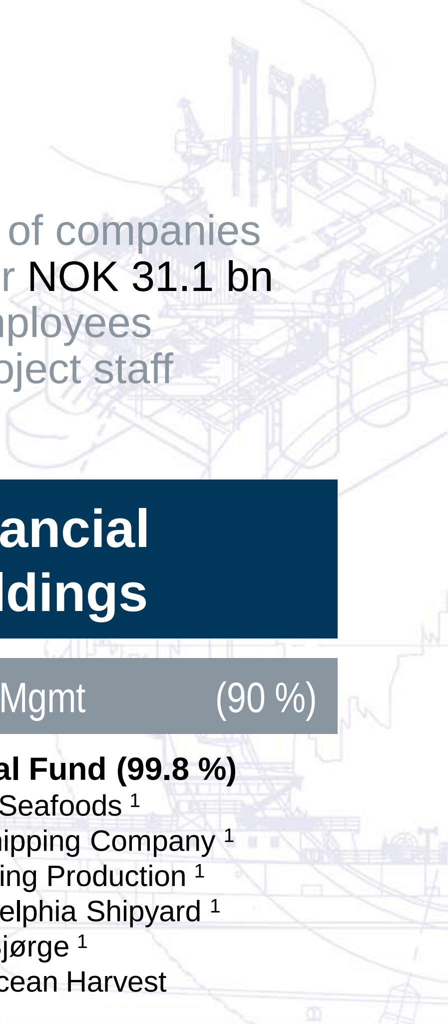
ieaghg

Aker CleanCarbon

This is Aker

Industrial investment company with main interests in **energy, marine** industries and **capital management**

Market value[3] of companies owned by Aker **NOK 31.1 bn**
Number of employees
35,000 incl project staff



Industrial Holdings

Company	Aker ownership
Aker Drilling	(100 %)
Aker Solutions [1]	(24 %)
Det norske [1]	(40 %)
Aker BioMarine [1]	(83 %)
Aker Clean Carbon	(50 %)

Aker ownership in per cent

Treasury
including corporate finance, ship lease etc

Financial Holdings

Company	Aker ownership
Converto Asset Mgmt	(90 %)

Aker Capital Fund (99.8 %)
Aker Seafoods [1]
American Shipping Company [1]
Aker Floating Production [1]
Aker Philadelphia Shipyard [1]
Bjørge [1]
Aker Ocean Harvest

Company	Aker ownership
AAM Abs Return Fund [2]	(20.1 %)

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[1] *Listed on Oslo Stock Exchange*
[2] *Managed by Aker Asset Management*
[3] *As of 30.12.09 (book value for non-listed assets)*

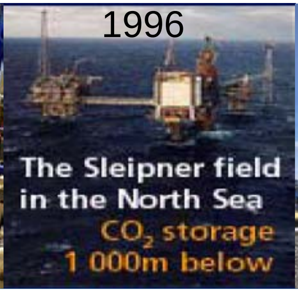
Aker Clean Carbon

- More than 18 years experience and competence within CCS in Aker

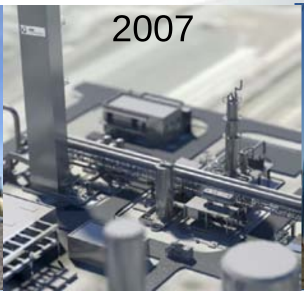
- A focused technology company
  - Core competence within flue gas treatment and CO_2 capture
  - Invested about 300 mill. NOK (33 M€) in technology (own money, last 2 y.)
  - Leading one of the largest R&D programmes in Europe (SOLVit)
  - Operating an advanced mobile test plant
  - Engaged in several CCS projects
  - About 200 engineers in Aker have been engaged in CCS
  - Turn-key supplier of capture plants

- Aker Solutions is our international partner for EPC projects
  - 25 000 employees in 35 countries (Europe, USA/Canada, Asia, Australia)


1996


1996


1998


2007


2008


2011

CCS = Carbon Capture & Storage

part of Aker
Aker CleanCarbon

Aker Clean Carbon in extensive R&D&Q program

R&D Projects = 650 mill. NOK (~80 mill. €)

Technology Centre Mongstad

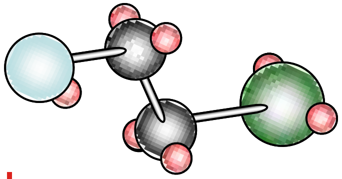
Test rig

Norway

Castor

Denmark

Theoretical



Cleo

RP A203

Mobile plant

Europe

Lab facilities

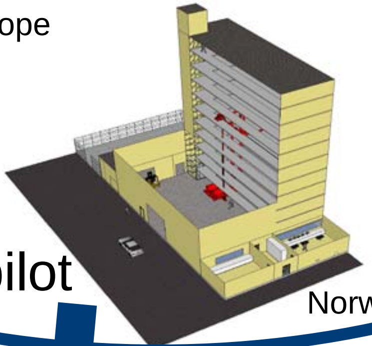
Norway

UK CCS Coal EU Demo

Study & FEED

BigCO2
BigCCS

SOLVit



Tiller pilot

Norway

Kårstø & Mongstad Gas Power

2nd generation MTU

part of Aker
Aker CleanCarbon™

Key to CCS cost reduction:

Selection of optimum solvents (amines + others)

SOLVit – unique R&D programme

SINTEF NTNU Aker CleanCarbon

Ongoing 8 years, 317 MNOK (~40 M€) program:

- Develop, test and select improved solvents
  - Low energy requirement
  - Minimum environmental impact
  - Low corrosion
  - Low degradation
- Advanced simulation model
- World class lab and test facilities
- Mobile test facility (MTU) for industrial sites
- Industrial partners:

e·on SCOTTISHPOWER Energy Wholesale Statkraft

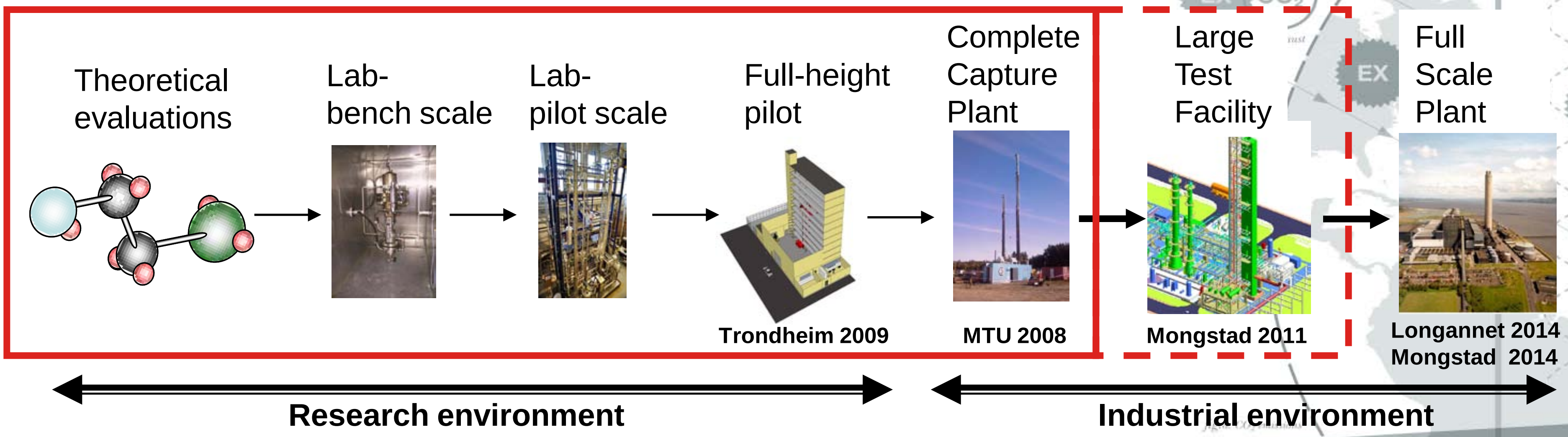
Funded by Gassnova & Climit (NRC)

Sintef/NTNU

Aker CleanCarbon

SOLVit - objectives

- Develop and demonstrate solvents with minimum energy consumption, degradation and lowest possible environmental impact. This is done stepwise and systematic:



Theoretical evaluations → Lab-bench scale → Lab-pilot scale → Full-height pilot → Complete Capture Plant → Large Test Facility → Full Scale Plant

Trondheim 2009

MTU 2008

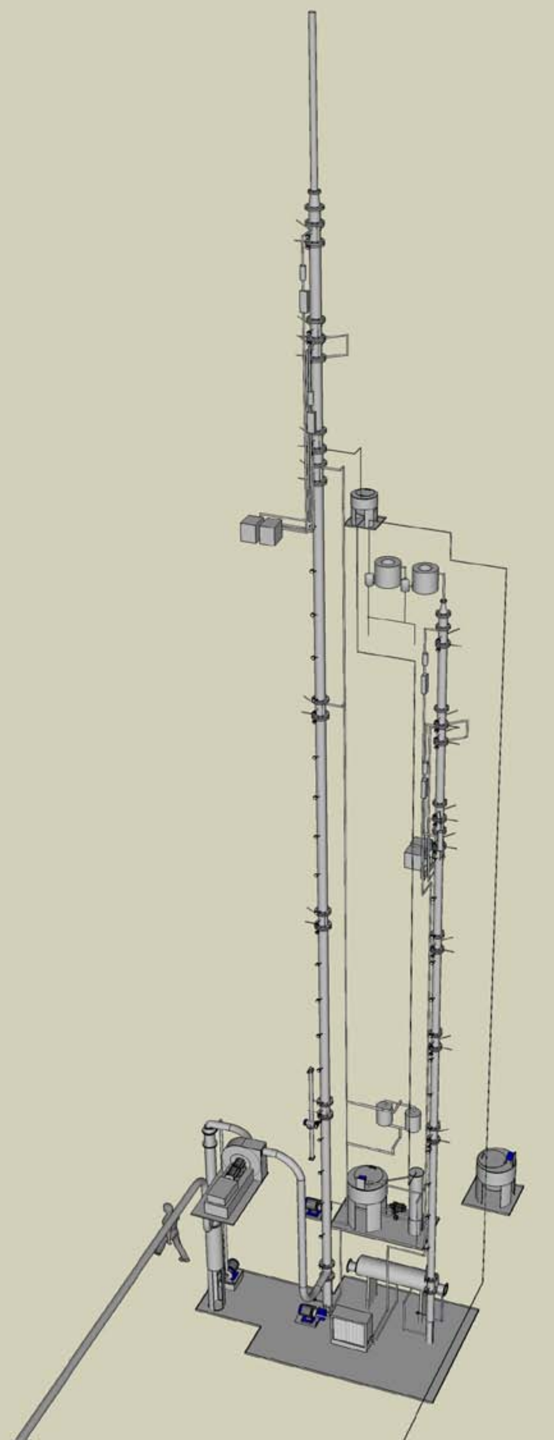
Mongstad 2011

Longannet 2014
Mongstad 2014

Research environment

Industrial environment

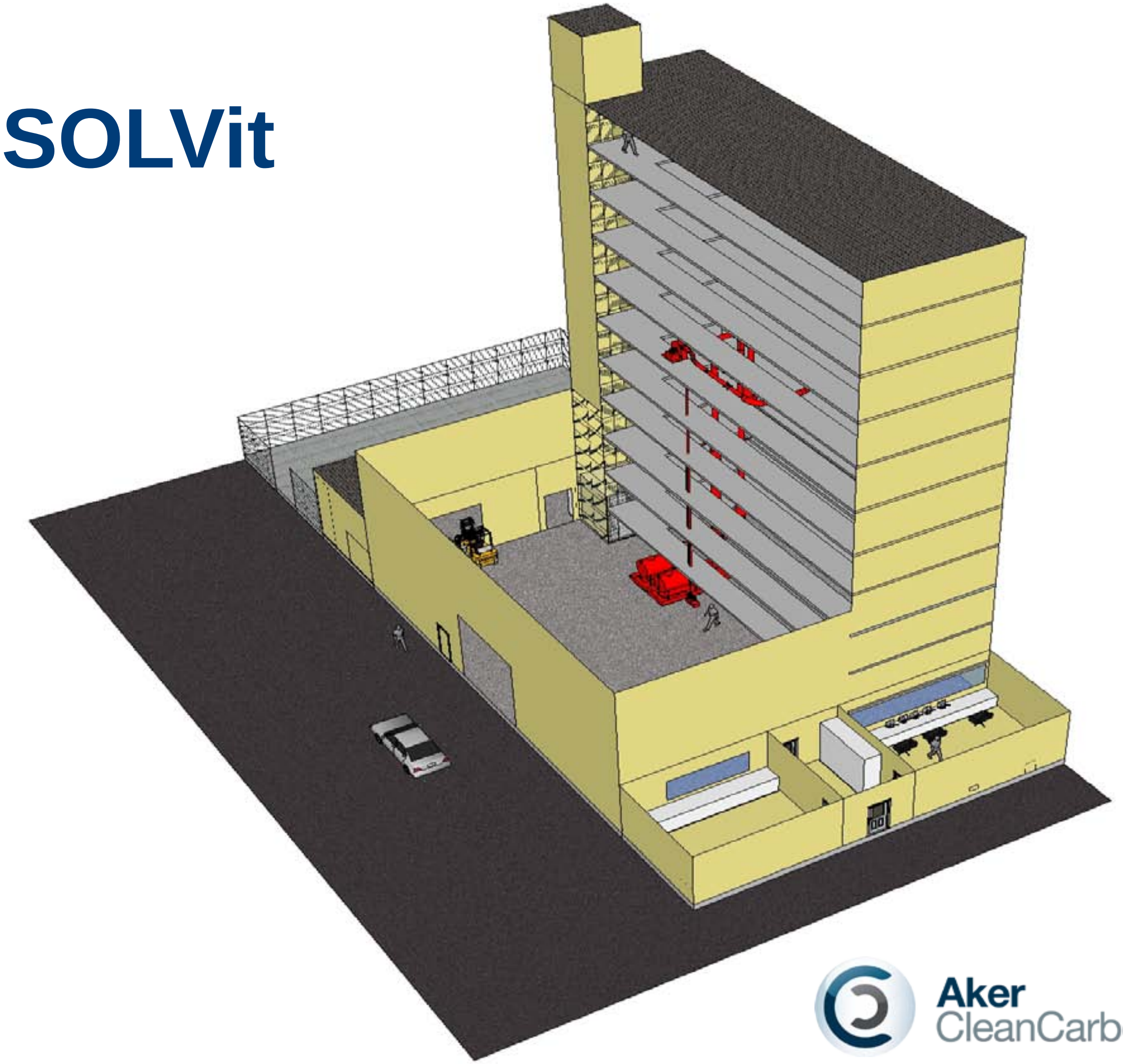
- Demonstration program to transfer experimental data to cost-effective process and plant design
- **World class lab and test facilities in place**



New Tiller Test Rig – 2010

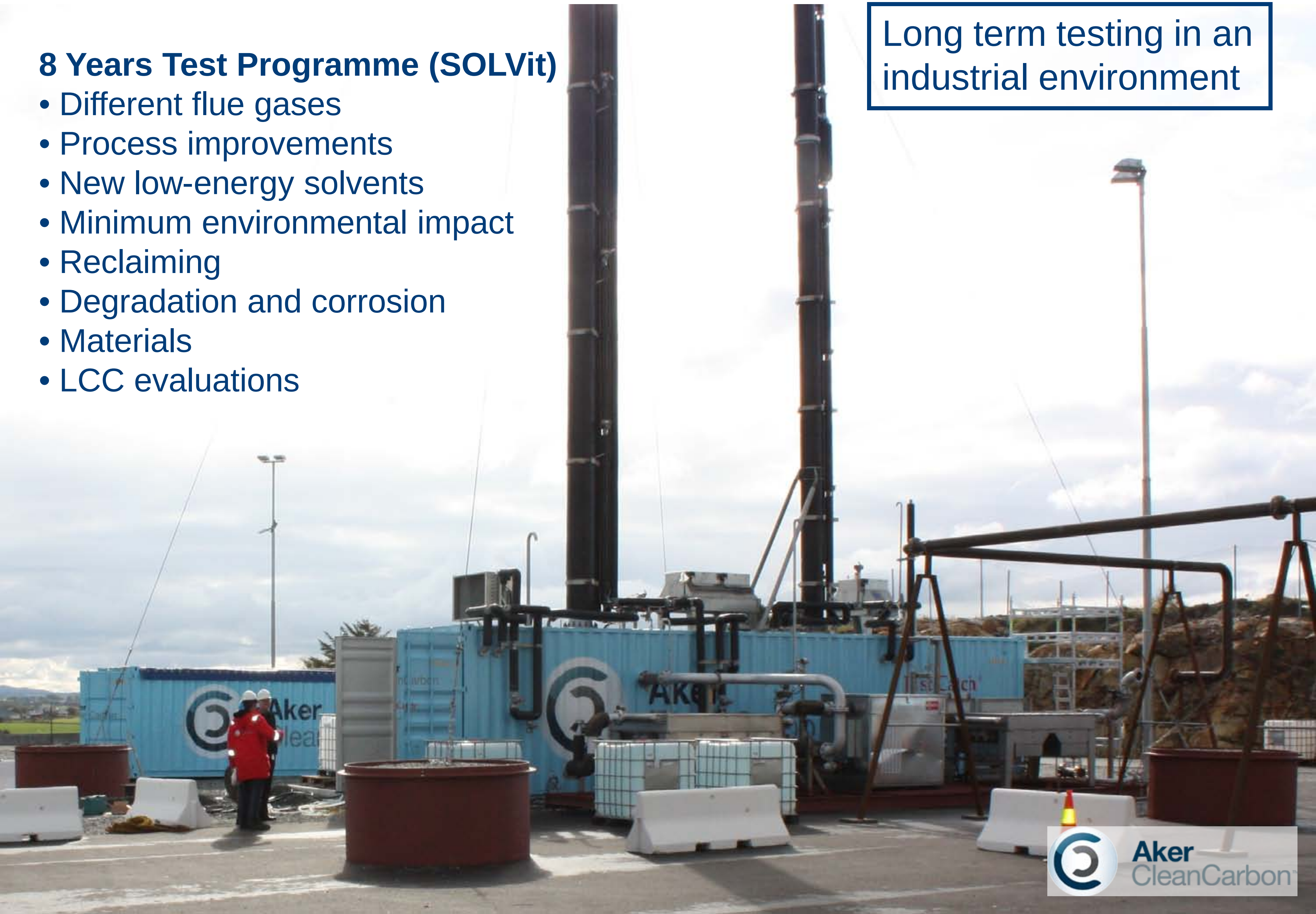
- *ideal for testing and analysis (small-scale)*
- *excellent access to the columns via floors*
- *final testing of chemicals prior to MTU*

SOLVit



Aker CleanCarbon

Advanced mobile carbon capture plant (in operation from 2008)



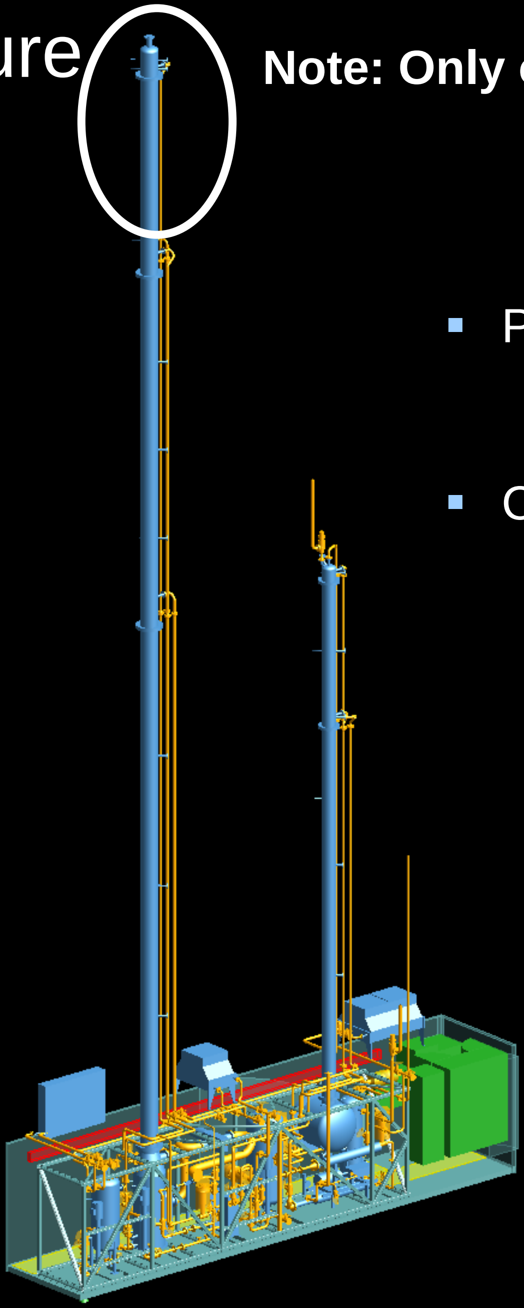
8 Years Test Programme (SOLVit)

- Different flue gases
- Process improvements
- New low-energy solvents
- Minimum environmental impact
- Reclaiming
- Degradation and corrosion
- Materials
- LCC evaluations

Long term testing in an industrial environment

Aker CleanCarbon

Mobile Carbon Capture Facility in operation



Note: Only one water wash section

- Safe operation
- Easy transport & h-up
- Standard container
- Lorry & ship transport
- Industrial flue gases
- Amine flexibility
- Verify design data
- Verify solvent
- Long term testing
- Easy modifications
- Extensive monitoring & analysis

- Process module
  - L= 40 ft, H= 2.6 m
  - Weight= 20 tonnes
- Capacities:
  - Flue Gas: 1000 Am3/h
  - CO_2 capture:
    - Coal Power: 180 kg/h
    - Gas Power: 60 kg/h
    - Composition: 3 -14 %
    - Rate: ~ 85 – 90 %

Aker CleanCarbon

MTU Emission Campaign 1

- Location : Risavika, Norway
- Period : 5 & 6 March 2009
- Solvent : 30 wt% MEA
- Flue gas : 4% CO_2 gas power
- Solvent : 25 days operation
- Company : NILU, Norway

+ 30 m

< 10 m/s

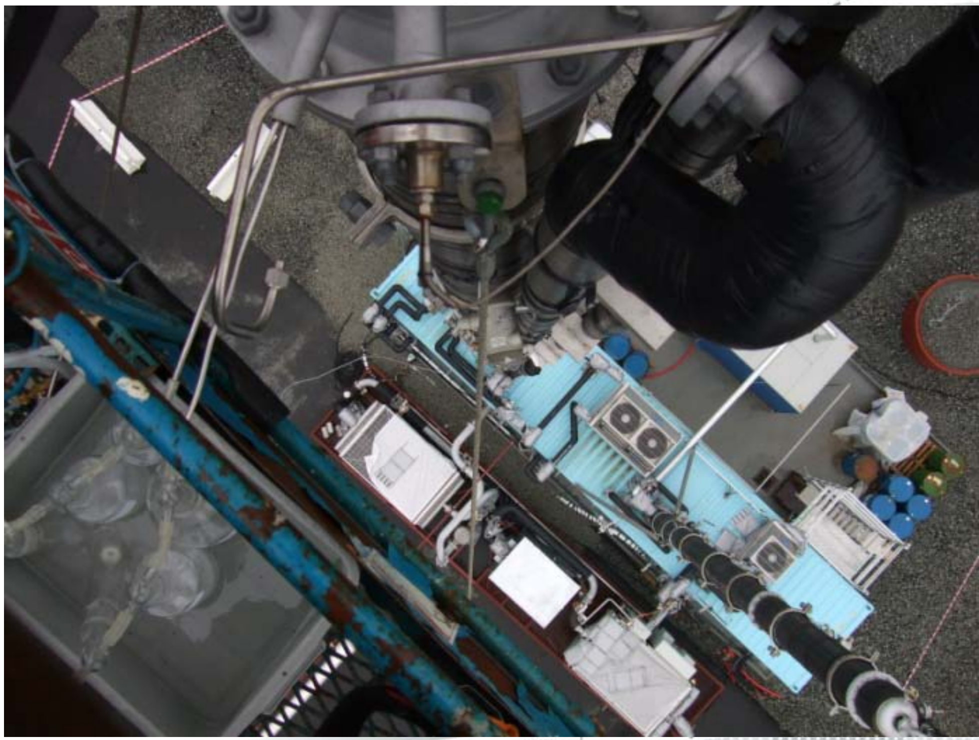
MTU Emission Campaign 1 (NILU)

- Gas sampling
  - Absorber inlet to water wash
  - Absorber top outlet
  - Off-line (none-isokinetic)
  - On-line (FTIR)
- Liquid sampling (manual)
  - Lean MEA
  - Rich MEA
  - Water Wash

MTU Emission Campaign 1 (NILU) - Results

Gas analysis:

- MEA emission: low (ppb level)
- Ammonia: low (below 5 ppm)
- Aldehyds measured
- Amine degradating prod. measured
- No nitrosamines measured



Comments:

1. Offline none-isokinetic sampling gave perhaps underestimated amine values
2. The total number of unknown compounds exceeds the number of those identified (small amounts)

MTU Emission Campaign 2

- Location : Longannet, Scotland
- Period : 15 - 17 September 2009
- Solvent : 30 wt% MEA
- Flue gas : 12% CO_2 coal power
- Solvent : 6 days operation
- Company : SINTEF, Norway

MTU Emission Campaign 2 (SINTEF)

- Gas sampling
  - Absorber top outlet
  - Off-line (isokinetic)
  - On-line (2 x FTIR)
- Liquid sampling (manual)
  - Make-up MEA
  - Lean MEA
  - Rich MEA
  - Wash water

MTU Emission Campaign 2 (SINTEF) - Results

Gas analysis:

- MEA emission: 1 to 4 mg/Nm3
- Ammonia: ~ 50 ppm (2 x FTIR + impinger)
- Aldehyds not analysed
- Amine degradating prod. measured
- Nitrosamines (9 off) not measured

Amine liquid analysis:

- Same nitrosamine as in MEA make-up measured

Comment:
Analysis affected by water condensation
in sampling arrangement

MTU Emission Campaign 3

- Location : Longannet, Scotland
- Period : 4 & 5 November 2009
- Solvent : 30 wt% MEA
- Flue gas : 12% CO_2 coal power
- Solvent : 25 days operation
- Company : Eurofins Miljø, Denmark

MTU Emission Campaign 3 (Eurofins)

- Gas sampling
  - Absorber inlet
  - Absorber top outlet
  - Off-line (isokinetic)
  - On-line (FTIR)
- Liquid sampling (manual)
  - Make-up MEA
  - Lean MEA
  - Rich MEA
  - Wash water
  - DCC water

MTU Emission Campaign 3 (Eurofins) - Results

Gas analysis:

- MEA emission: below detection (0.02-0.03mg/Nm^3)
- MEA emission: FTIR detected amine in one camp.
- Ammonia: above 80 ppm
- Aldehyds measured
- Amine degradating prod. measured
- Nitrosamines (10 off) analysed, 4 measured (sub-µg/Nm^3)

Amine liquid analysis:

- Same nitrosamine as in MEA make-up measured

<u>Comments:</u>

Aker Clean Carbon Emission Control Technology was tested in separate campaign:

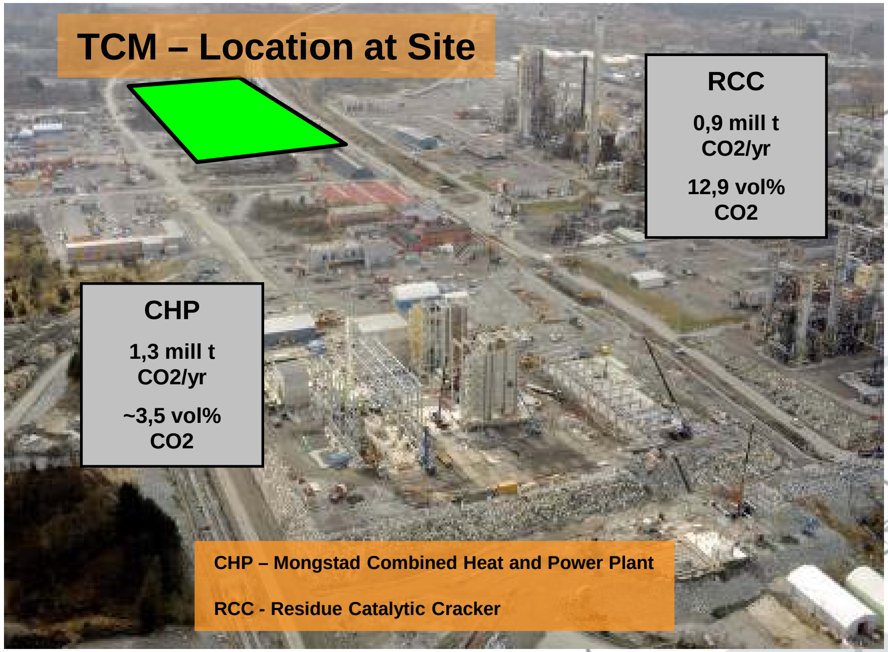
1. Ammonia level dropped well below 5 ppm
2. All of the 4 nitrosamines dropped below detection level (not able to measure)
3. Several patents applied for Emission Control Technology

Applied sampling and analytical methods

- The gas analysis of some of the emissions compounds are challenging, below ppm level
- Different sampling and analytical methods will give different results
- Some sampling methods and analysis are not accredited
- There are several uncertainties in the results
- More test campaigns, analysis and results are needed in order to conclude emission levels

European CO_2 Technology Centre Mongstad

- Aker Clean Carbon has been awarded the contract for the amine plant
- World's most advanced plant
- We shall operate the plant for the first 14 mth's, operating data for remaining period
- We shall test own absorbents
- Scale-up from MTU=45 times
- Reduce cost and risk
- Emission & waste important parts of the test programme
- MTU will operate in parallel with larger amine test plant



TCM – Location at Site

RCC
0,9 mill t CO2/yr
12,9 vol% CO2

CHP
1,3 mill t CO2/yr
~3,5 vol% CO2

CHP – Mongstad Combined Heat and Power Plant

RCC - Residue Catalytic Cracker

- About 100 engineers engaged
- Fabrication at Aker Stord, ~300 workers
- Capacity: 78 000 tons CO_2 per year
- CO_2 removal from gas- and coal power (cracker)
- Start-up: 2011

part of Aker

Aker Stord

Construction work - Amine Test Plant - Mongstad

The preferred partner

Aker CleanCarbon™

part of Aker

UK Competition
ScottishPower Consortium is Short Listed


Longannet
Coal Fired Power Station
2400 MW


1st CC from
Coal in UK

Consortium members:

- Scottish Power
- National Grid
- Shell
- Aker Solutions
- Aker Clean Carbon

UK Competition:

- CO_2 capture from coal fired plant
- Capture: 2 million tons CO_2 per year
- Full chain within 2014
- Capture, transport & permanent storage

Scottish Power Consortium

- 1 of 2 remaining short listed bidders

CCS is good for the **pollutions** and **global warming**!

1950

No treatment

2010

Present treatment. Some Emissions:

Dust: ~ 50 mg
SO_X: 30 - 70 ppmv
NO_X: 30 - 70 ppmv
CO_2: ~ 13 % vol.

CCS

2014?

Carbon Capture. Emissions:

Dust: ÷ 99 %
SO_X: ÷ 99 %
NO_2: ÷ 99 %
CO_2: ÷ 90 %

Coal fired power stations

Aker CleanCarbon

Aker
CleanCarbon™

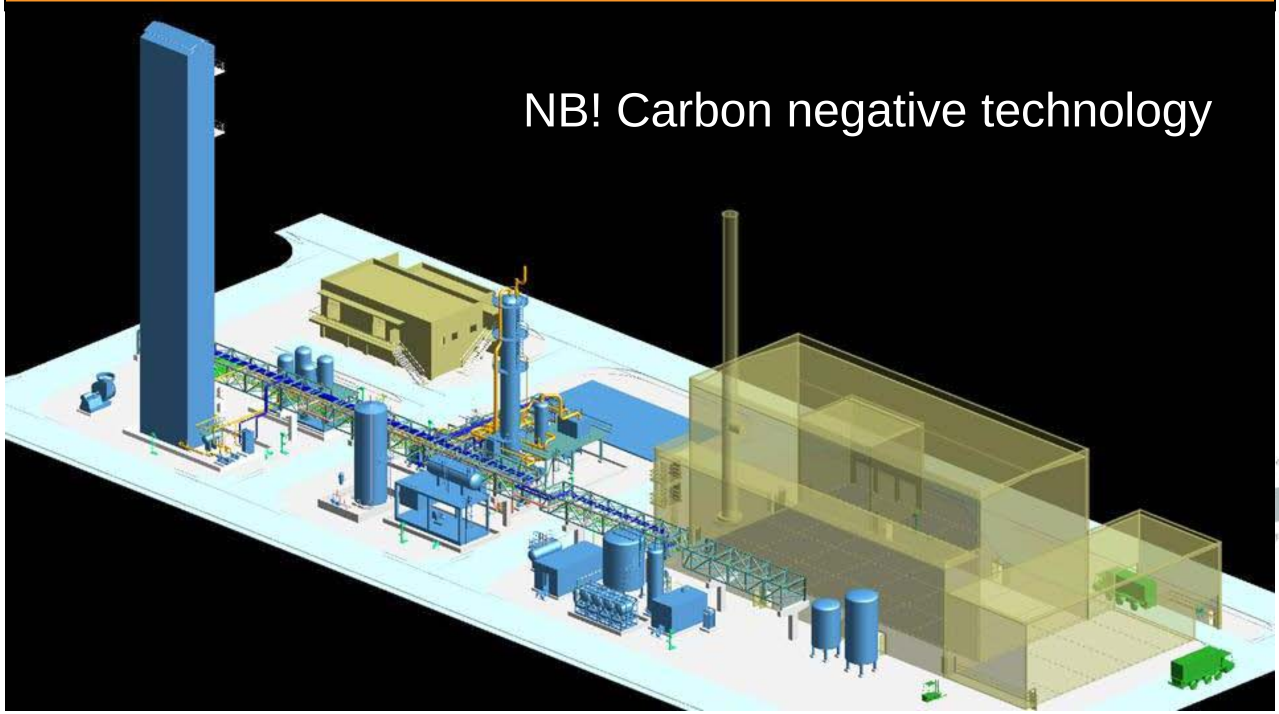
www.akercleancarbon.com

TECHNOPORT
AWARDS 2008

Trondheim
22. oktober 2008

”Innovative Environmental Technology Award 2008”

CO_2 capture plant with integrated bio-energy


NB! Carbon negative technology

http://www.headspin.no/upmedia/TP08/TechnoportsPrisMain03.wmv

The preferred partner

Aker CleanCarbon

part of Aker

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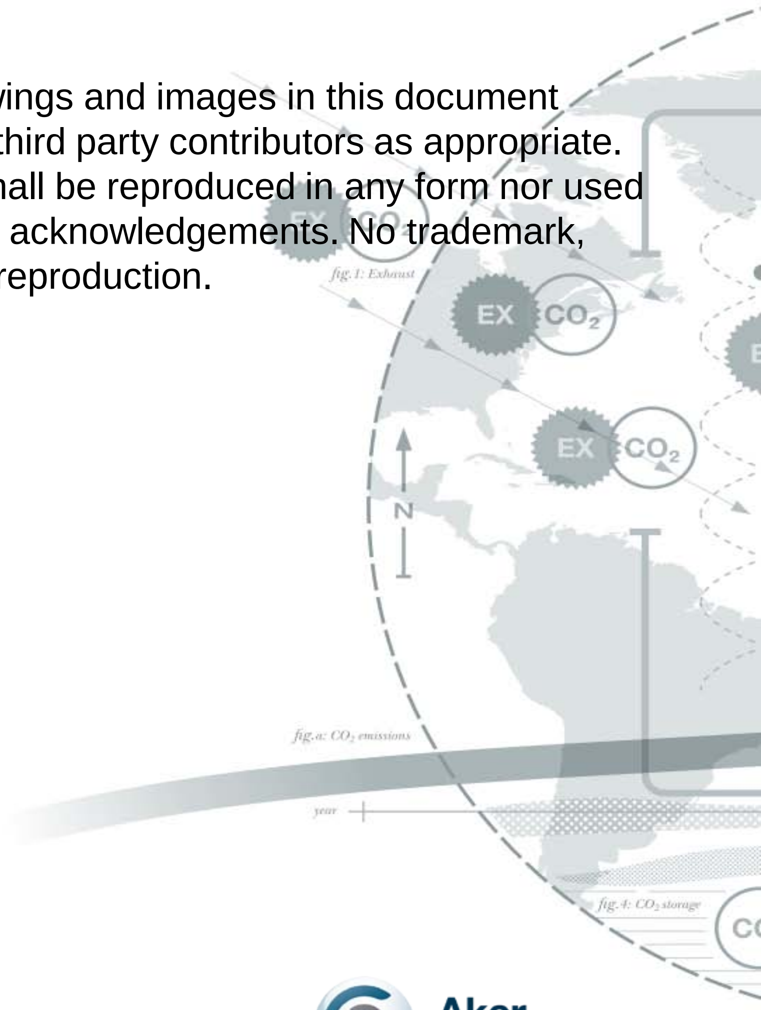
fig.1: Exhaust
EX
CO_2
EX
CO_2
N
fig.a: CO_2 emissions
year
fig.4: CO_2 storage

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