Environmental Impacts of Capture

8th IEAGHG International CCS Summer School - 6th-12th July 2014.
University of Texas at Austin

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- Nitrosamine and nitramine
- Atmospheric degradation
- Capture plant
- Limits for nitrosamines and nitramines in air and drinking water
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- Nitrosamines and nitramines in the media (Norway)
- Status
- Conclusion
- Further reading

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THE NORWEGIAN STATE ENTERPRISE FOR CARBON CAPTURE AND STORAGE

Gassnova will contribute to promoting solutions and results that can make CCS an effective measure for reducing CO_2 emissions

- **CLIMIT programme**
- **CO_2 Technology Centre Mongstad**
- **CCS projects**
- **Advisory functions**

Background: Amine Emission

2006: Kårstø - plan for capture from CCGT, 1 million ton CO_2 per year:

- Emission of 1 – 4 ppm amines => 40 – 160 ton per year

2008: First literature and worst case assessment:

- Release of maximum 24 tonne amine per year (1 mill ton CO_2 per year)
- Assumptions:
  - Literature data: 2% of amines convert to nitrosamines
  - Instantaneous conversion at stack exit and no further degradation

2009: First time in the national Norwegian news:

Copyright: www.tu.no

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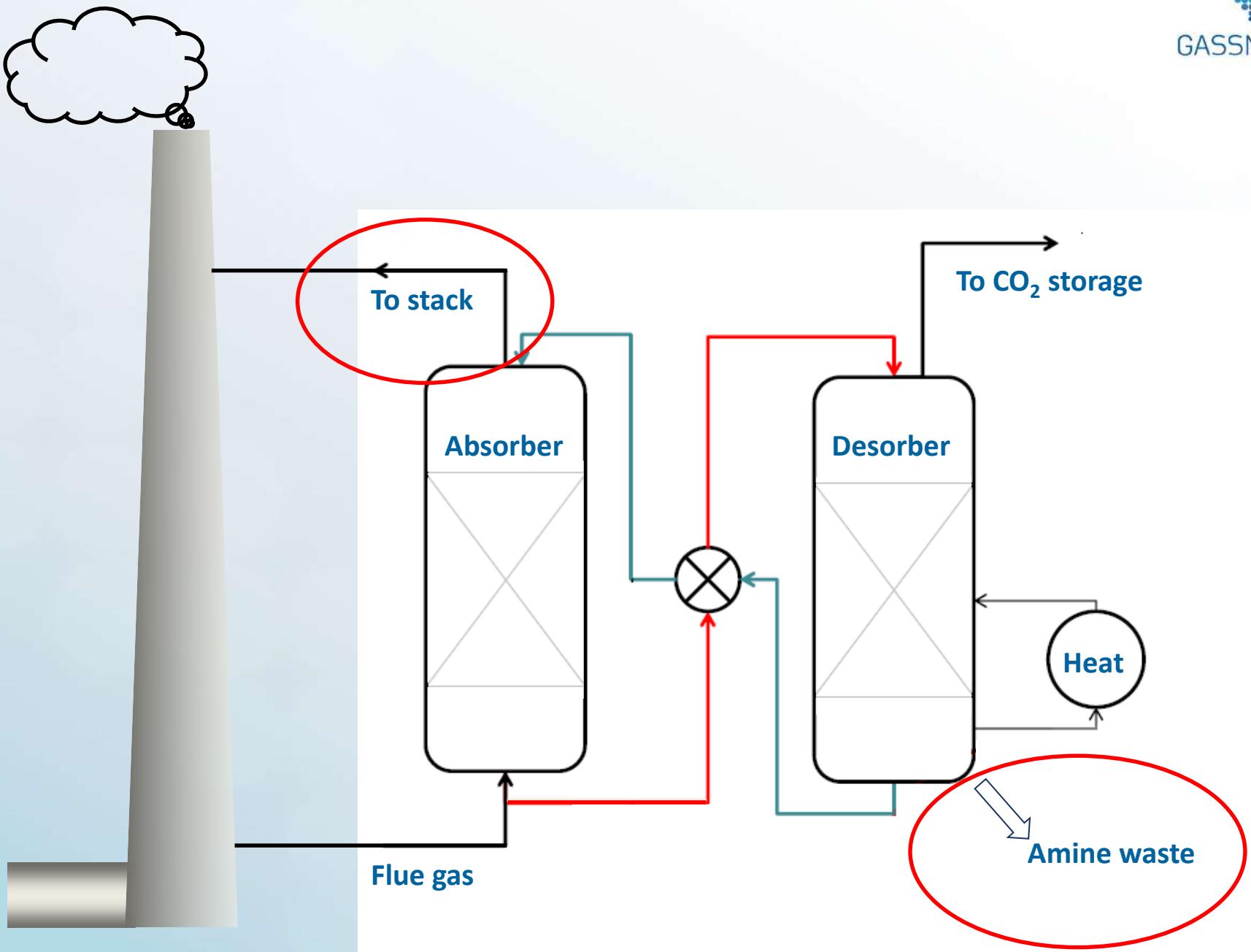
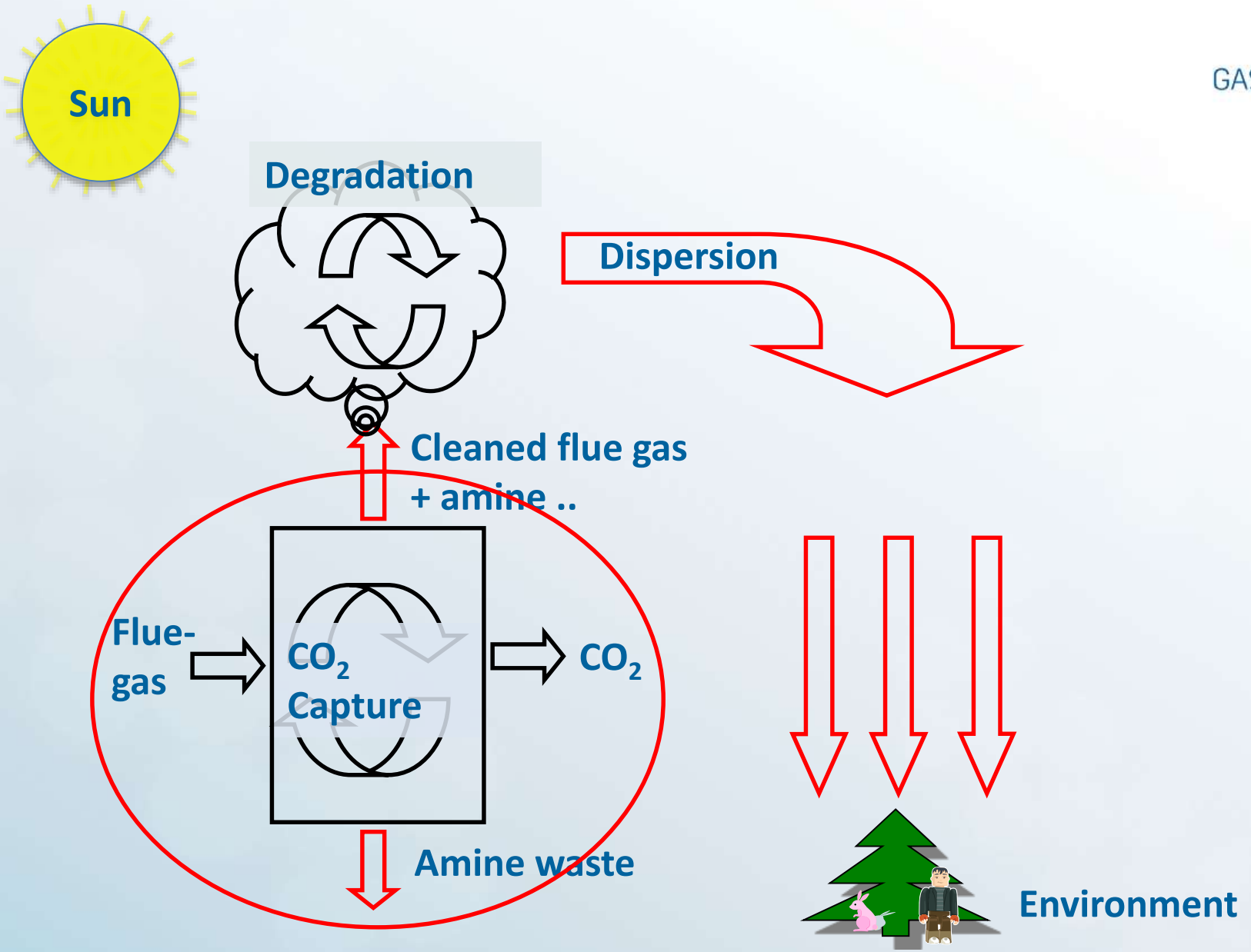

To stack
To CO_2 storage
Absorber
Desorber
Heat
Flue gas
Amine waste


Sun
Degradation
Dispersion
Cleaned flue gas
+ amine ..
Flue-
gas
CO_2
Capture
CO_2
Amine waste
Environment

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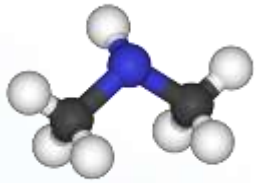
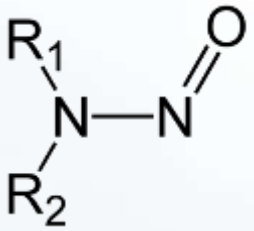


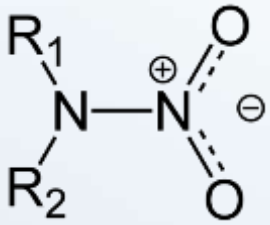
DEGRADATION COMPONENTS OF SPECIAL INTEREST:

- NITROSAMINES AND NITRAMINES

- ***N*-nitrosamines, R_1R_2N-N=O, represent a large and diverse family of synthetic and naturally occurring compounds. Approximately 90% of the 300 nitrosamines tested have shown carcinogenic effects in bioassays and laboratory animals.**



- ***N*-nitramines, R_1R_2N-NO_2, are structurally related to *N*-nitrosamines. Due to this similarity there has been a general interest in the potential mutagenicity and carcinogenicity of the nitramines. A few carcinogenicity studies are available, most of which concern *N*-nitrodimethylamine. The nitramines seem in general to be less potent than the corresponding nitrosamines.**



Source: http://mn.uio.no/ada and wikipedia.com

ATMOSPHERIC DEGRADATION

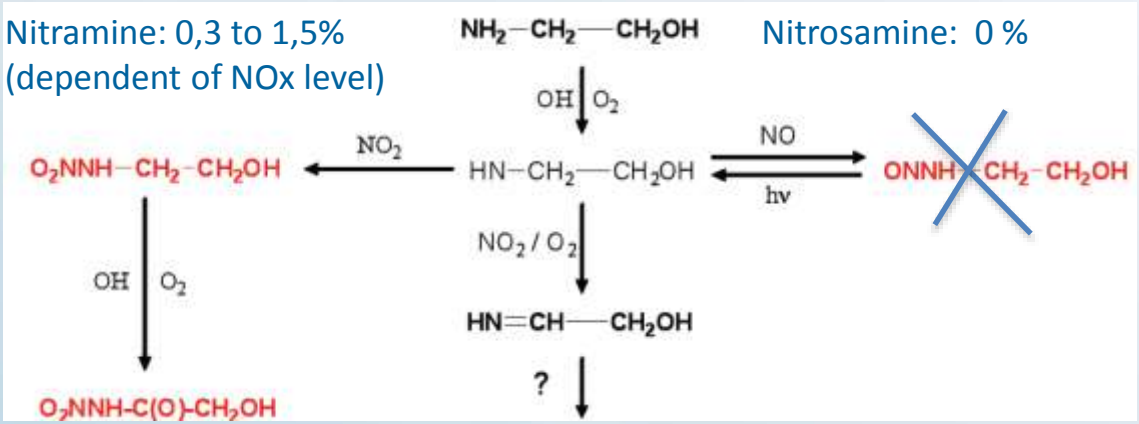
EUPHORE, Valencia

2 x 200 m^3 chambers

Degradation during daytime: OH oxidation chemistry

- This may end in nitrosamines and nitramines

Example MEA - hydrogen abstraction from the amino group:



Source: Nielsen et.al. , Atmospheric chemistry of 2-aminoethanol (MEA), GHGT 10
Se also: Nielsen at.al. Atmospheric chemistry and environmental impact of the use of amines in carbon capture and storage (CCS). Chem. Soc. Rev., 2012, 41, 6684-6704.

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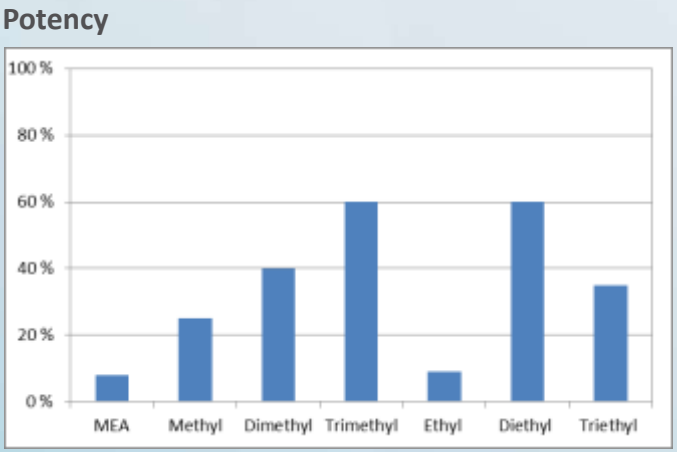
ATMOSPHERIC FORMATION, DESTRUCTION AND DISPERSION

- **The ADA programme provided relevant experimental data:**
  - Photo-oxydating experiments in Valencia (Euphore)
  - MEA, methyl-, dimetyl-, trimethyl-, ethyl-, diethyl, triethyl-amine and piperazine
  - Basis for modelling other amines
- **Vendor amines have also been tested in Valencia**

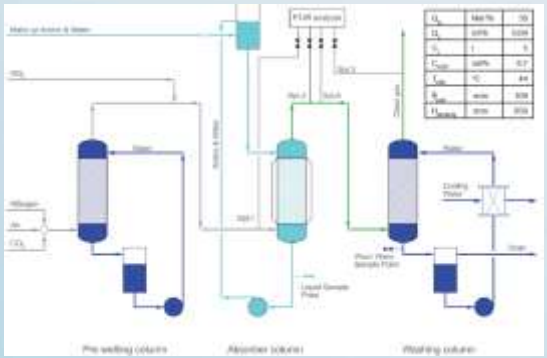


http://mn.uio.no/ada

CAPTURE PLANT (1)

- **Amine chemistry in capture plant (experimentally):**
  - MEA degradation dependent of oxygen, temperature and NO_X
  - Found: DEA, NDELA, NDMA, NMOR, MMA

- **Methodology used in the technology qualification amine program for Full Scale Capture at Mongstad – CCM (Norway)**
  - Vendors did own tests in small solvent degradation rigs



Source: Fostås et.al, Effects of NOx in the Flue Gas Degradation of MEA, GHGT 10
Se also: Einbu et.al, A new test rig for studies of degradation of CO_2 absorption solvents…, GHGT 11

CAPTURE PLANT (2)

- **Initiatives for emission reduction:**
  - An extra water wash section on top of the absorber
  - High efficiency demisters and filters
  - Acid wash in the final washing section on the absorber top
  - UV treatment of lean amine, wash water or gaseous outlet
  - Amine mist – anti mist operation or filter

- **Sampling and analytical techniques:**
  - Sample, identify and quantify nitrosamines and nitramines
  - Total nitrosamine analysis

- **Results:**
  - Sub ppm in emission
  - Level of detection of 0.1 ppb for amines, nitrosamines and nitramines.
  - Total nitrosamine mass balance

LIMITS FOR NITROSAMINES AND NITRAMINES IN AIR AND DRINKING WATER

- **International values for NDMA:**

		WHO	Health Canada	US EPA
Drinking water	ng/l (10^{-5})	100	40	7
Drinking water	ng/l (10^{-6})		4	0,7

- **Norwegian values**
  - Recommendation from Norwegian Institute of Public Health (NIPH 2011)
  - Based on nitrosodimethylamine (NDMA)
  - Annual average

		nitrosamine + nitramines
Drinking water	ng/l	4
Air	ng/m^3	0,3

Report: http://www.klif.no/nyheter/dokumenter/TCM_FHI-rapport.pdf

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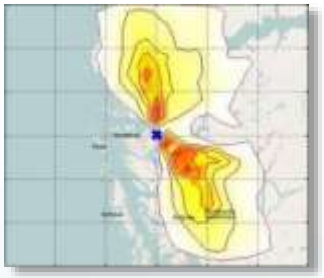

ATMOSPHERIC FORMATION, DESTRUCTION AND DISPERSION

Modelling approach:

- **Instantaneous conversion at absorber exit (first assessment 2008)**
- **Post-processing amine chemistry (discharge permit 2011)**
- **Integrated amine chemistry (current development)**

TCM discharge (2011): Annual average sum of nitrosamines and nitramines.

		NIPH guideline values	MEA Worst case	Likely case
Drinking water	ng/l	4	0,009	0,0022
Air	ng/m^3	0,3	0,52	0,023

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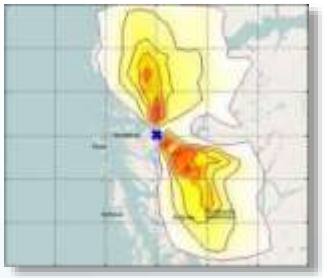

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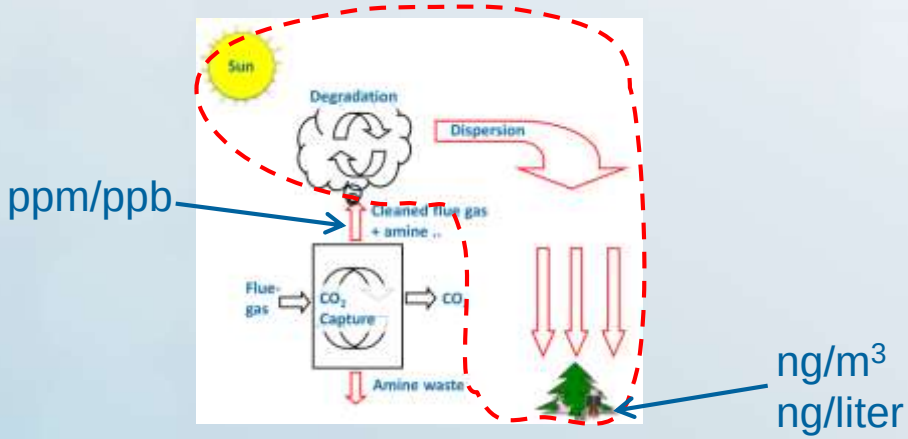
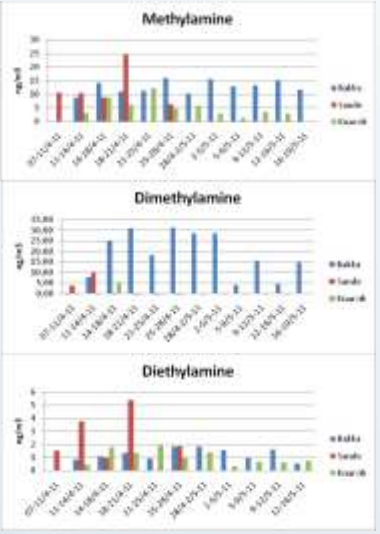


DEPOSITION, EXPOSURE AND TOXICITY

Baseline around Mongstad (by TCM):

- **Air, soil, moss and water**
- **Amine detected**
- **No nitrosamines and nitrosamines detected**
- **Will be monitoring on regular basis**

Amine	Air	Soil	Moss	Fresh water
Methylamine	S	S	S	S
Ethylamine	D	D	D	D
Dimethylamine	S	S	S	S
Diethylamine	S	D	D	D
MEA	D	S	S	S
AMP	D	D	S	D
Piperazine	D	D	D	D



D: detection limit, S: above

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DEPOSITION, EXPOSURE AND TOXICITY

- **Nitrosamine: 90% of the about 300 tested show carcinogenic effects**
- **Nitramines - less data available**
  - Dimetylnitramine 6 x less toxic than corresponding nitrosamine
  - Tested: dimethyl-, methyl-, MEA-, AMP-, piperazine- nitramine
  - Low toxicity levels, but 3 out of the 5 tested positive on genotoxicity

- **Discussion point:**
  - What is the proper risk level (10^{-6} or 10^{-5})
  - Nitrosamine and nitramine evaluated as sum

NITROSAMINES AND NITRAMINES IN THE MEDIA (NORWAY)

- **Debated in public since 2009**
- **Published reports on web and conferences**
- **National and local media discuss:**
  - Nitrosamines, nitramines and atmospheric degradation

February 2011

Copyright: www.nrk.no

March 2011

Copyright: www.aftenposten.no

December 2012

Copyright: www.e24.no

January 2014

Copyright: www.dagbladet.no

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STATUS

Octavius workshop February 13 and 14, 2014 (Press release):

- *Solvent and degradation products emissions should not be a showstopper for the majority of post-combustion CO2 capture processes implemented in industrial facilities*.*

Discharge permits for amine capture plants:

- TCM at Mongstad: Permit given 2011
- CCM at Mongstad terminated, but:
  - *The project would if continued had been able to chose CO_2 capture vendor for Mongstad based on:*
    - *Qualified technology*
    - *Acceptable health and environmental risk*
    - *Competition*

**Press release: http://www.ifpenergiesnouvelles.com/actualites/communiques-de-presse/better-understanding-on-emissions-phenomena-from-co2-capture-processes*

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CONCLUSION

- Uncertainty greatly reduced
- Generated new know-how of high scientific and technical quality
- Developed new methods for sampling and analysis
- Major gaps have been closed in atmospheric fate of emission
- Water phase is sink
- Nitrosamines have short lifetime in the atmosphere
- Toxicity of amine degradation products has been reviewed and tested.
- TCM has got the discharge permit
- CCM has developed a toolbox for technology qualification of amine
- Further work on amine mist

Further reading

Overview article presented at GHGT-11 in Kyoto (2012):

- Health and environmental impact of amine based post combustion CO_2 capture (Gjernes, Helgesen, Maree)

  http://www.sciencedirect.com/science/article/pii/S1876610213001720

TCM studies and research projects :

- http://www.tcmda.com/en/Technology/Environmental-studies/

Full scale CO_2 Capture Mongstad (CCM):

- http://www.gassnova.no/en/ccs-projects/full-scale-mongstad