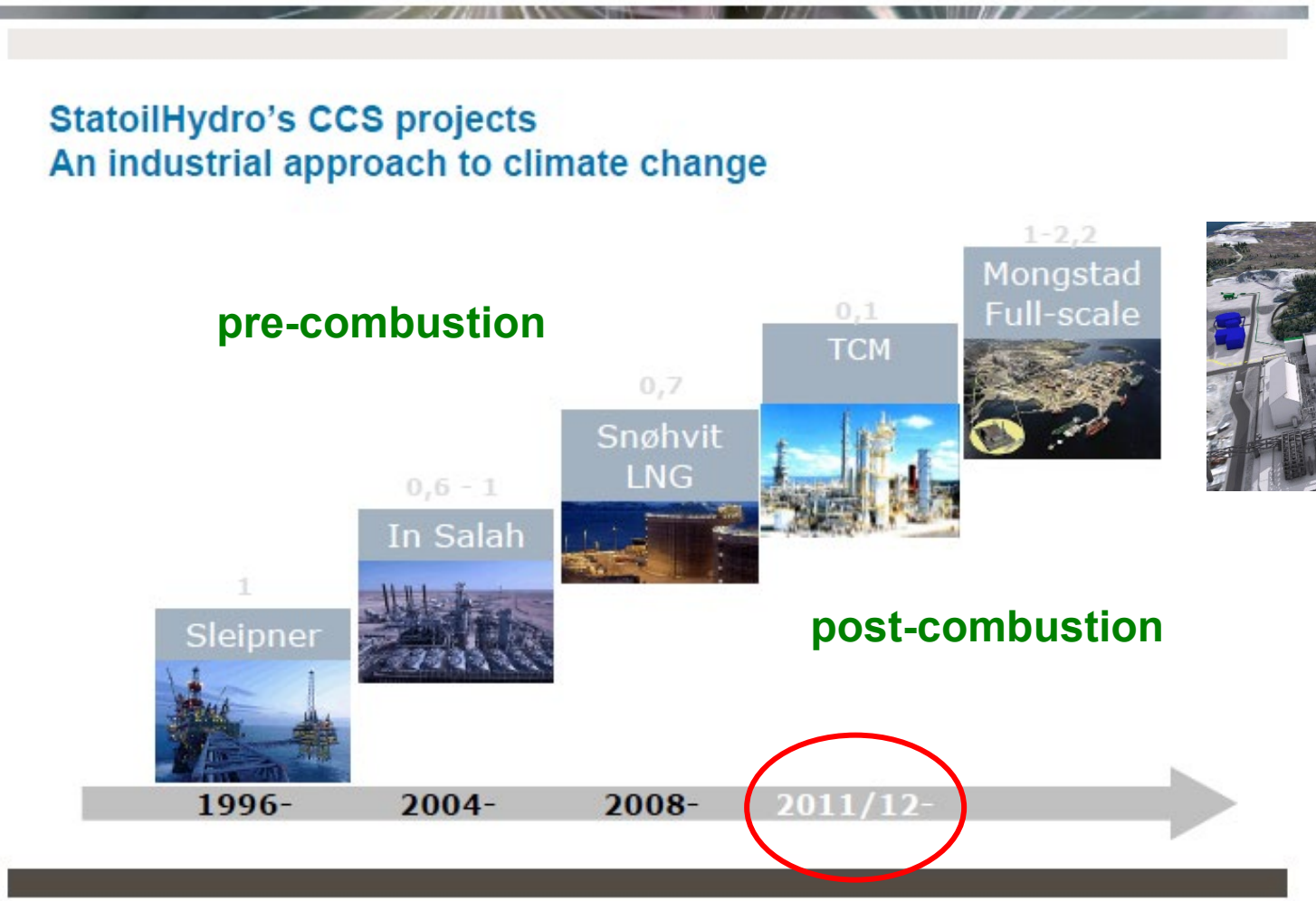
The Total Nitrosamine Method

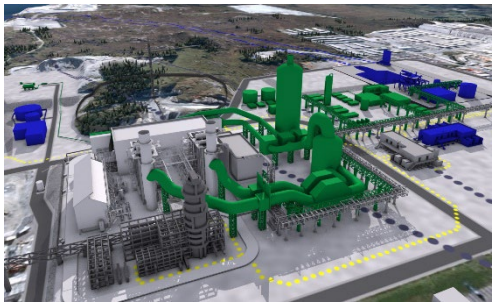
William Mitch, Ning Dai

Stanford University

Mongstad Refinery

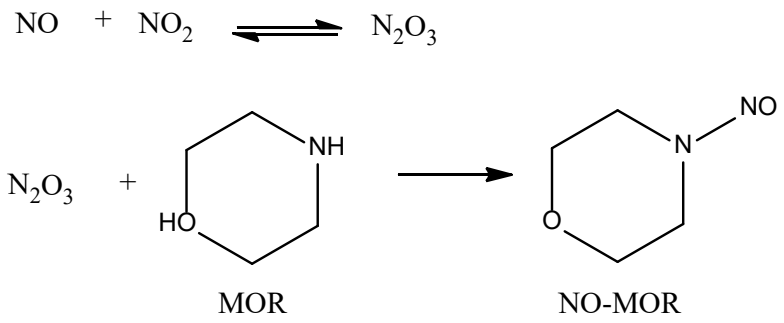
Norwegian Prime Minister: Norway's "Moon Program"



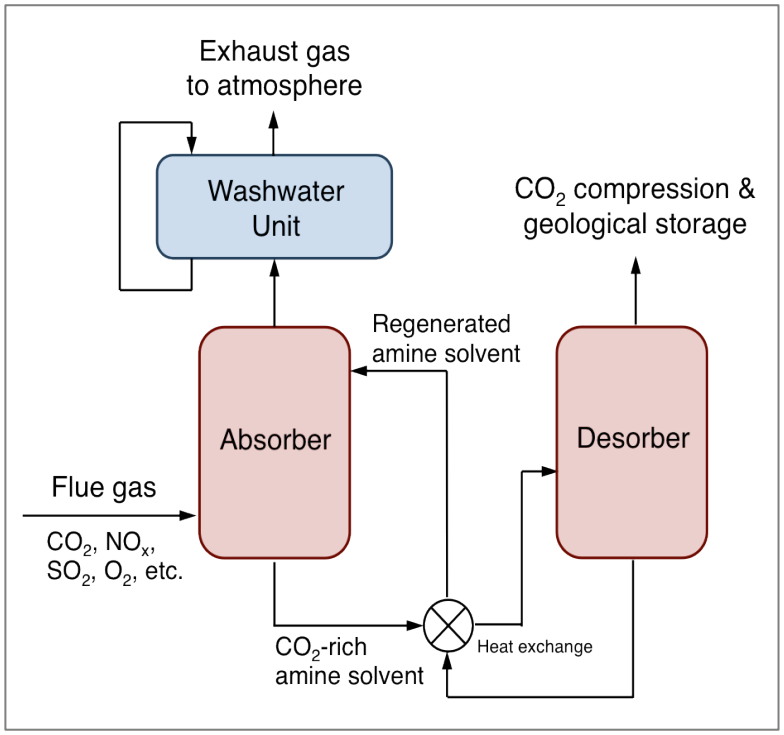


The Problem

Post-Combustion Applications: Exposure to NO_x

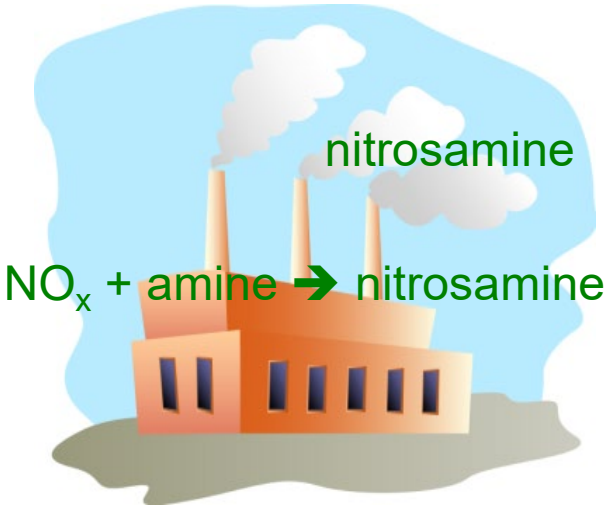


nitrosamine



Nitrosamines are potential carcinogens

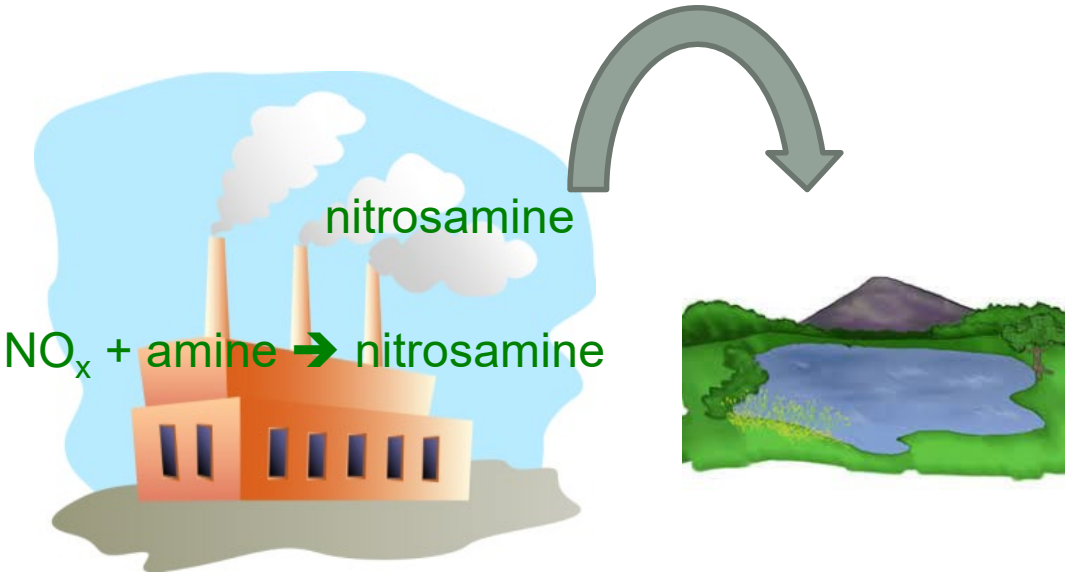
a current focus for drinking water research
on the EPA's radar screen for regulation
affect downwind airsheds or water supplies?

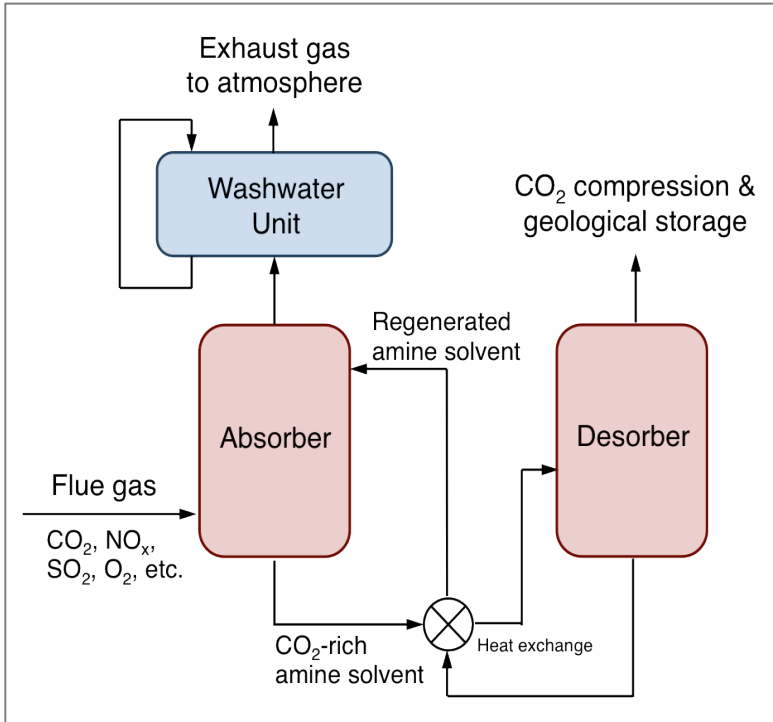


Analysis

Target ➔ washwater

- **Washwater is the "last stop" before release**
- **More concentrated than samples of downwind air or surface waters**
  - **With those samples, need to "re-concentrate" at any rate (e.g., impactors)**
  - **Washwater is already "pre-concentrated" and near equilibrium with atmosphere just downwind**





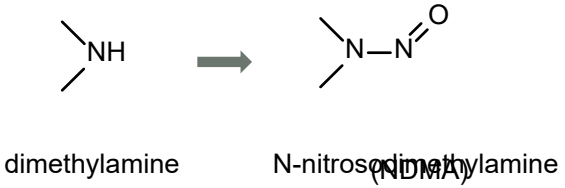
Analytical Challenges

- **Low concentrations matter**
  - **Drinking water regulations near 10 ng/L**

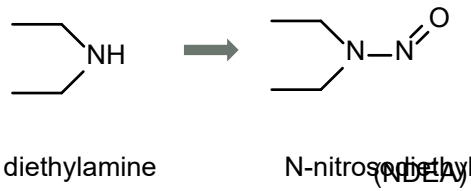
- **Typical analytical approaches for nitrosamines involve mass spectrometry**
  - **Need to concentrate the sample**

  - **Know which nitrosamine to look for**
    - **Dial in a specific parent ion mass**

  - **Each amine forms a specific nitrosamine ➔ need to know amine precursors**



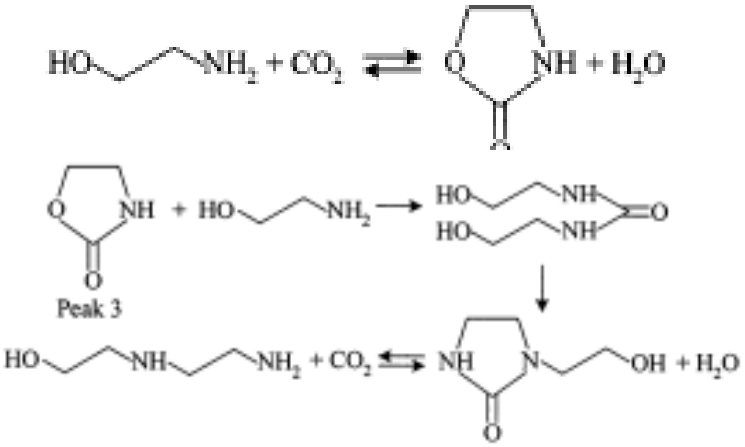
dimethylamine N-nitrosodimethylamine (NDMA)

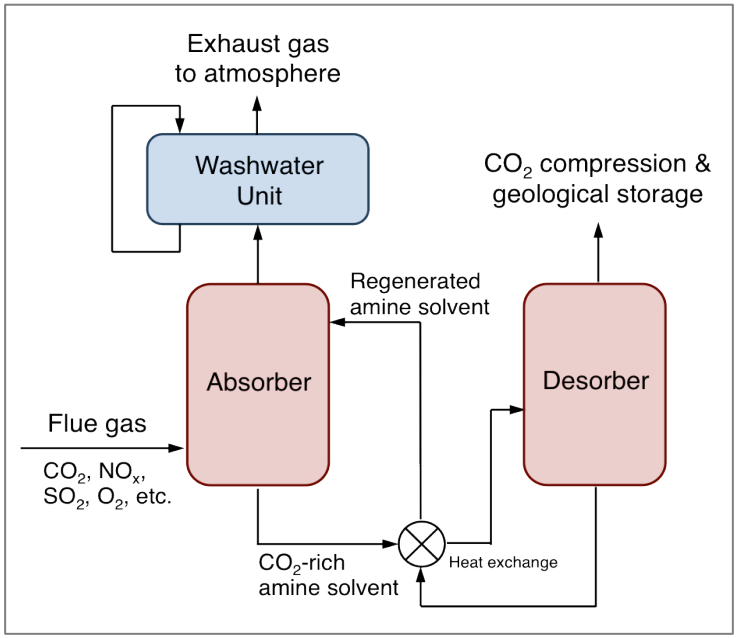


diethylamine N-nitrosodiethylamine (NDEA)

Analytical Challenge

- **Amine precursor structures unclear**
  - **Vendors prefer to keep structures secret**
  - **Harsh conditions in capture units ➔ degrade to new amine precursors**
    - **High pH**
    - **Exposure to reactive oxygen/nitrogen species**
    - **High temperatures in desorber**



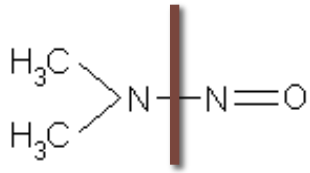


- **May be difficult to predict the nitrosamine to target**

Analytical Solution: Total Nitrosamines (TONO)

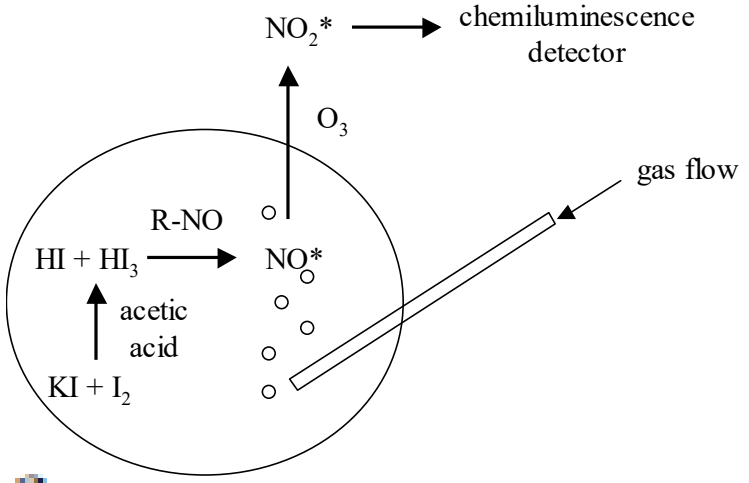
Inject sample into a reaction chamber where N-NO bond is cleaved

Cleavage by acidic triiodide



Measure liberated NO by chemilimunescence

A measure of total nitrosamines on a **molar** basis



Pre-treatment

Nitrite occurs in washwaters

Will yield NO within the reactor

Pre-treat samples with sulfamic acid to destroy

$$NH_2SO_3H + HNO_2 \rightarrow N_2 + H_2SO_4 + H_2O$$

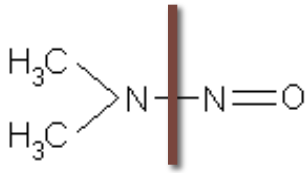
Standard curves made with NDMA

Detection limit 0.03 nmol as NDMA (60 nM for 500 uL injection or 4.4 ug/L as NDMA)

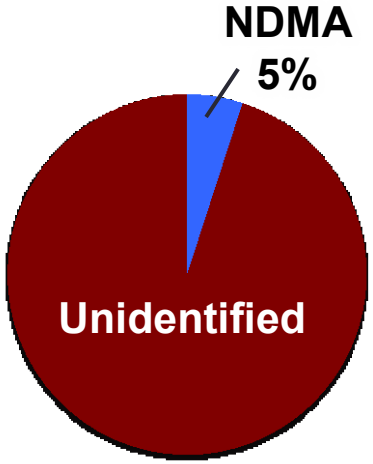
With extraction/concentration ➔ 0.5 nM (37 ng/L as NDMA) for drinking water

Analytical Solution: Total Nitrosamines (TONO)

Benefits



- Can keep amine formulae proprietary
- No need to characterize all of the degradation products
  - One peak – not integrating hundreds of peaks by GC-MS
- No need to synthesize individual nitrosamine products
- Can combine with mass spec to determine what fraction of TONO an individual nitrosamine accounts for
  - Is the specific nitrosamine of interest really important?



TONO adopted for monitoring by Norway

We trained official Mongstad lab in Finland and vendor labs

Analytical Solution: Total Nitrosamines (TONO)

Example

- TONO and mass spec applied to washwaters
  - Primary amine (MEA) solvent
  - Primary amine (AMP)/secondary amine (PZ) combination

Table 2. Aminox Washwater Characteristics

analyte	washwater		unit
	MEA-based	AMP/PZ-based	
MEA	6.8	NA	mM
PZ	NA	2.0	mM
AMP	NA	8.8	mM
pH	10.2	10.7	
nitrite	210	85	μM
nitrate	25	16	μM
formaldehyde	200	140	μM
acetaldehyde	NA	1.3	μM
formate and acetate	1100	72	μM
oxalate	2.3	<1	μM
absorbance at 254 nm	0.4658	0.8400	cm^{-1}
total *N*-nitrosamine	0.73	59	μM
N-nitromonoethanolamine	<0.24	NA	μM
N-nitrosodiethanolamine	0.042	NA	μM
N-nitrodiethanolamine	<0.20	NA	μM
N-nitrosomorpholine	0.12	NA	nM
N-nitrosopiperidine	0.60	NA	nM
N-nitrosodimethylamine	0.55	NA	nM
1-nitrosopiperazine	NA	65	μM
1-nitropiperazine	NA	<3	μM
1,4-dinitrosopiperazine	NA	0.31	μM
1-nitro-4-nitrosopiperazine	NA	3.1	nM
1,4-dinitropiperazine	NA	23	nM

Dai, N.; Shah, A.D.; Hu, L.; Plewa, M.J.; McKague, B.; Mitch, W.A. Environ. Sci. Techr

Importance of Washwater Unit

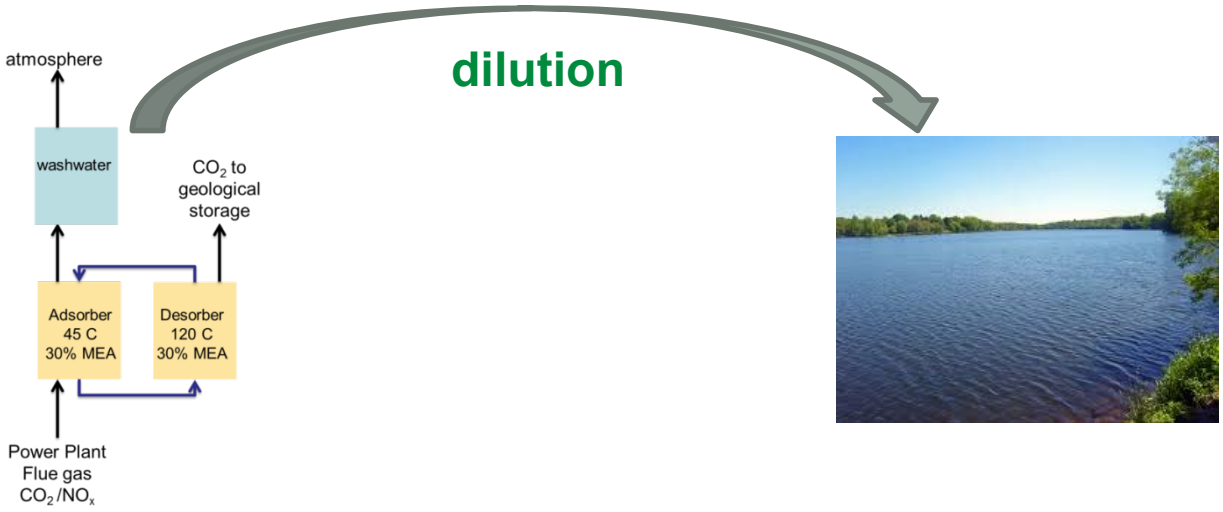
Used to scrub (clean) flue gas before emit

Final barrier between plant and environment

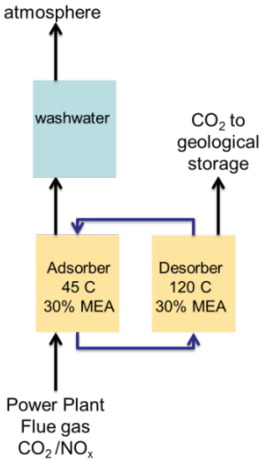
Can't control air quality after this point

Emit mists/aerosols containing contaminants directly to the atmosphere

If in equilibrium with atmosphere, estimate of concentrations in downwind lakes where also equilibrium modified for dilution



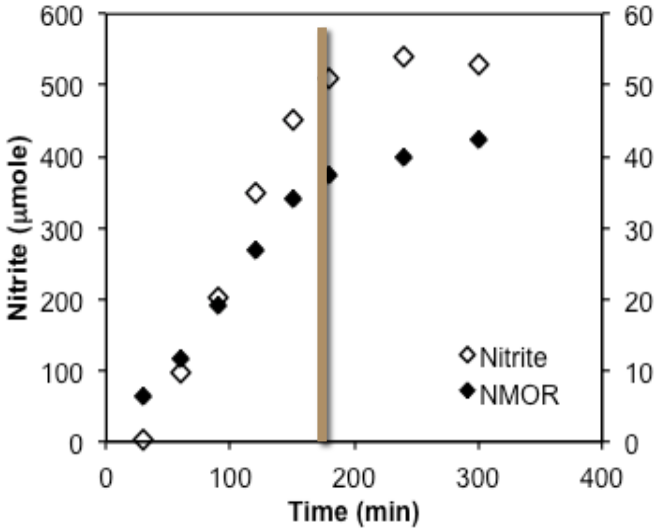
Washwater as a Source, Not a Sink



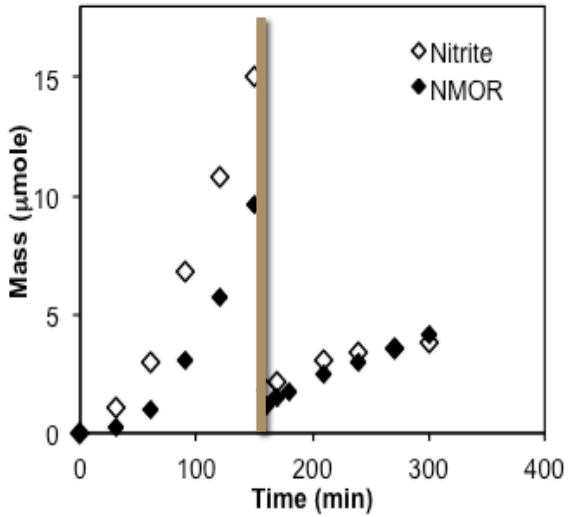
Operate pilot reactor with NOx then

- Change washwater liquid
- Apply NOx-free flue-gas
  - Mass transfer from absorber only source of nitrosamines in washwater

Absorber



Washwater



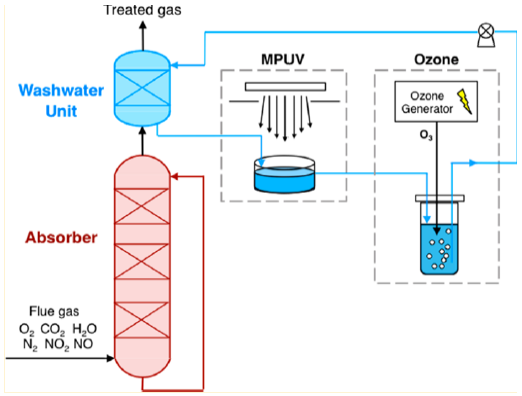
NMOR accumulation rate drops to 20%

- Importance of droplets + volatilization

Accumulation from NOx reactions with amines volatilized into washwater

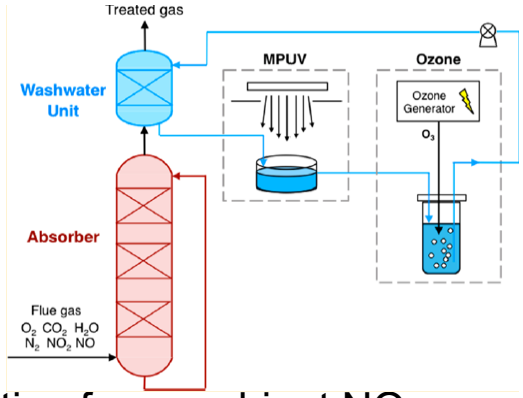
Solutions

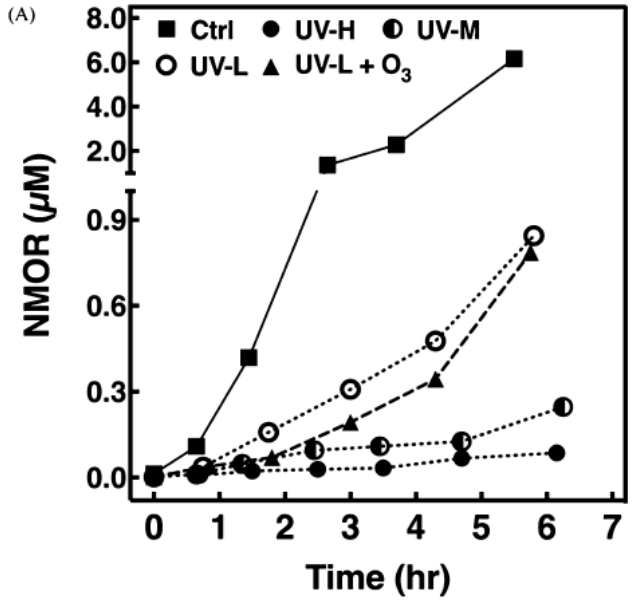
- Nitrosamines are a potential problem
  - Reducing NO_2 can help, but not solve the problem
  - Using primary amines can help, but not solve the problem
  - Beware copper
- Mongstad ➔ place the burden on the vendor to ensure no release of nitrosamines/nitramines
- Washwater is the final barrier
  - Supposed to clean exhaust
  - But serves as a source of nitrosamines via reactions of residual NO with amines accumulating in washwater
- Can we apply *continuous* treatment to washwater to destroy nitrosamines, nitramines and amines?
  - Maintain driving force from gas phase to washwater ➔ washwater as a sink!
- Technologies must be cheap
  - Drinking water a cheap industry
  - ➔ apply drinking water technologies

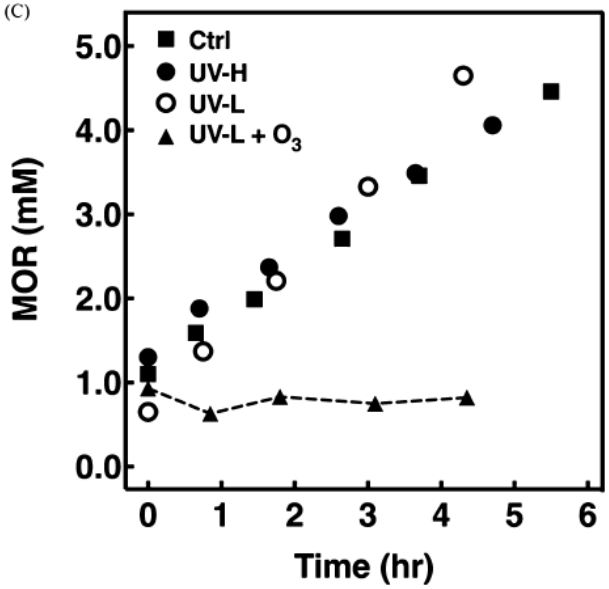


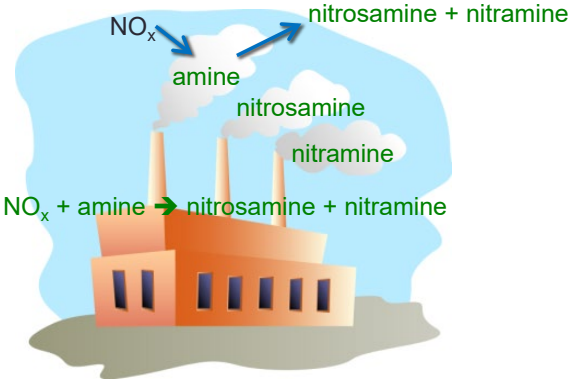
Solutions – Continuous Runs

- UV photolyzes nitrosamines (NMOR) ➔ nitrite and amines
  - Low – 272 mJ/cm^2
  - Medium – 537 mJ/cm^2
  - Hi – 1308 mJ/cm^2
- Ozone oxidizes amines (MOR)
  - Not much effect on nitrosamine control
  - But does control amine accumulation
    - Amine emissions also regulated to prevent formation from ambient NOx









Relevant Publications

Dai, N.; Shah, A.D.; Hu, L.; Plewa, M.J.; McKague, B.; Mitch, W.A. Measurement of nitrosamine and nitramine formation from NOx reactions with amines during amine-based carbon dioxide capture for post-combustion carbon sequestration. Environ. Sci. Technol. 2012, 46, 9793-9801.

Dai, N.; Mitch, W.A. Relative importance of N-nitrosodimethylamine compared to total N-nitrosamines in drinking waters. Environ. Sci. Technol. 2013, 47, 3648-3656.

Dai, N.; Mitch, W.A. Controlling Nitrosamines, Nitramines, and Amines in Amine-Based CO2 Capture Systems with Continuous Ultraviolet and Ozone Treatment of Washwater. Environ. Sci. Technol. 2015, 49 (7), 8878-8886.

Acknowledgements: CO_2 Capture Mongstad (CCM) Project

Norwegian State

Gassnova

GASSNOVA

Statoil

Statoil