Environmental Fate of Nitramines and Nitrosamines Released as Degradation Products from Post Combustion CO_2-Capture Plants

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SOLV fate

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Transport and transformation
in the atmosphere

Release from amine based PCCS plant

Deposition in terrestrial and aquatic environmental compartments

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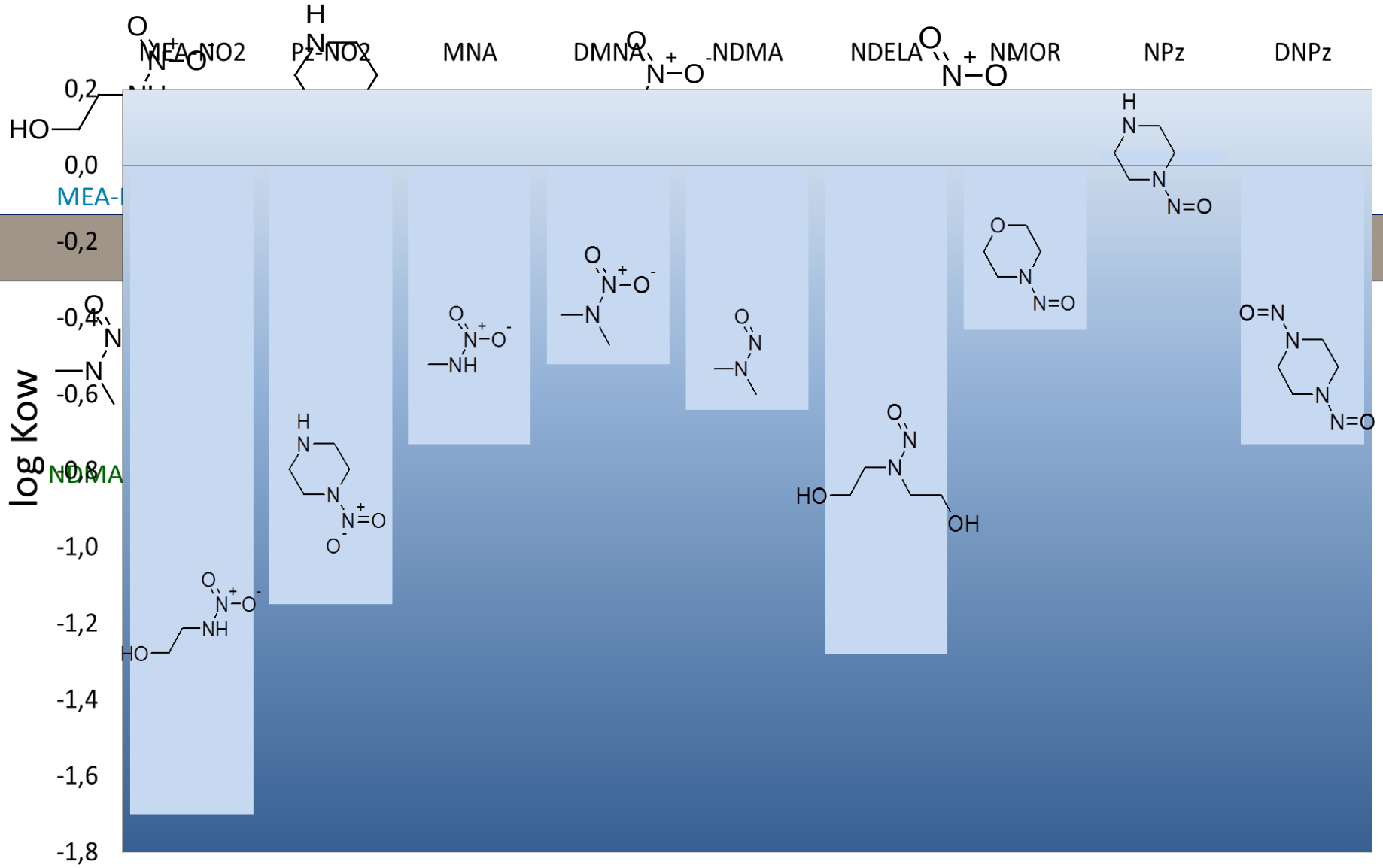
Nitramines


MEA-NO2
Pz-NO2
MNA
DMNA
NDMA
NDELA
NMOR
NPz
DNPz
log Kow
0,2
0,0
-0,2
-0,4
-0,6
-0,8
-1,0
-1,2
-1,4
-1,6
-1,8
MEA-
NDMA

Evaluating environmental fate and effects

Assumptions: Atmospheric release - > wet deposition

Initial deposition site

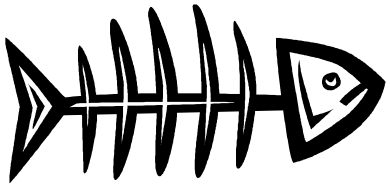
Transport mechanisms

- leaching (rain)
- natural waters (river)

Degradation in "final" or temporary matrices

Yes/No - > Degradation rates

- photodegradation
- biodegradation



Toxicity

- bioavailability
  - drinking water (human)
  - uptake in plants
  - uptake in organisms (including fish etc.)
- uptake mechanisms
- concentration levels

Risk assessment

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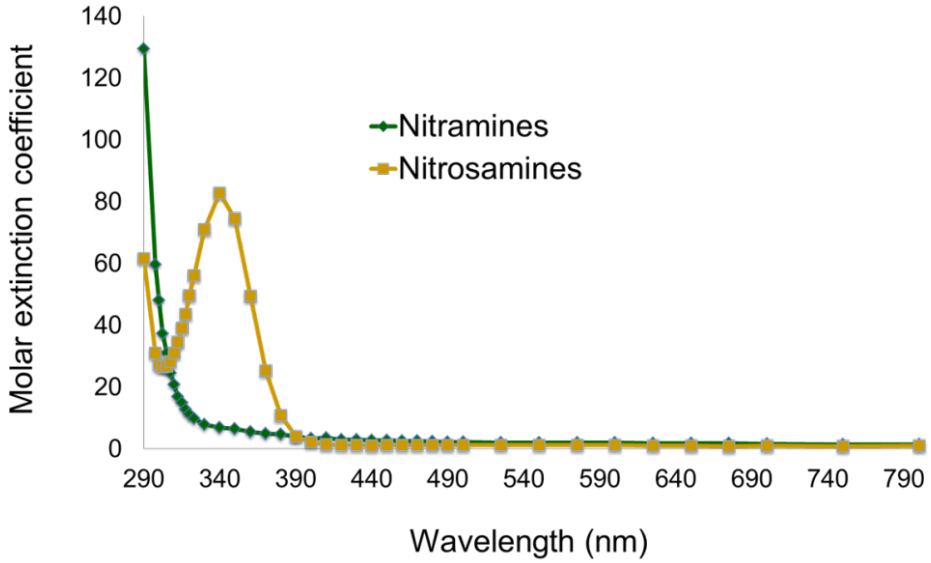
Previous work – Photodegradation in natural sunlight

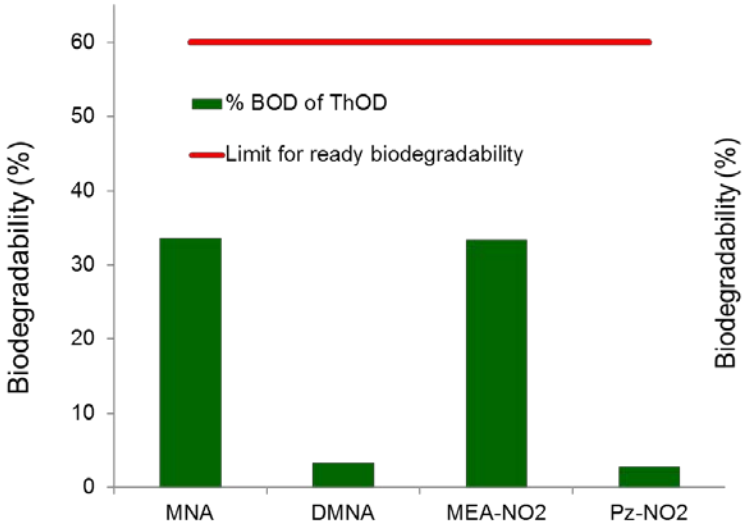


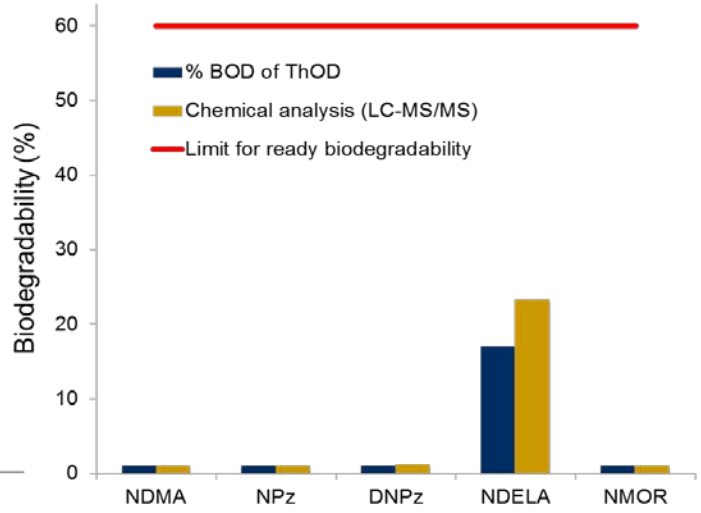
A theoretical and experimental study has looked at the photolytic degradability of nitramines and nitrosamines exposed to natural sunlight

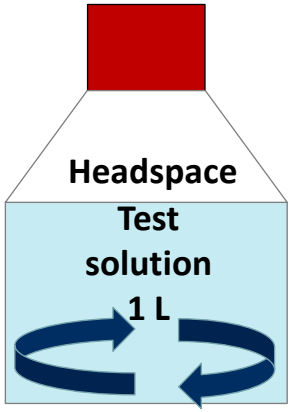
Degradation half-lives of **nitrosamines** were found to be in the range 6-12 minutes

Nitramines showed no potential of photodegradation by sunlight

Previous work – Biodegradability in freshwater



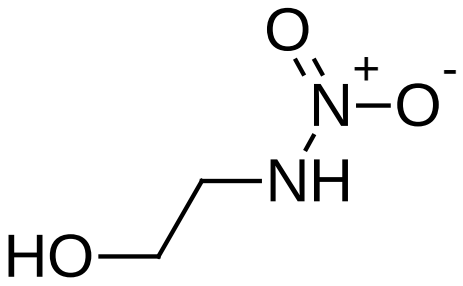
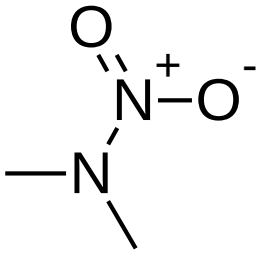
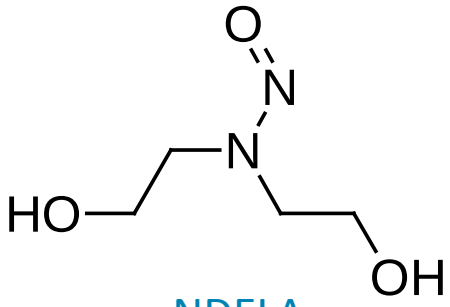
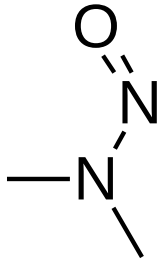




Test of ready biodegradability (OECD) showed that **only nitrosamines and nitramines with –OH groups** had potential to biodegrade in natural freshwater (e.g. drinking water)

Tests at low concentrations revealed a **half-life of NDELA of ~30 days**, regardless of initial concentration (1-100 µg/L).

Selection of compounds for soil and biodegradation study

	Biodegradable in freshwater, Polar	Not biodegradable in freshwater, less polar
Nitramines	 MEA-NO_2	 DMNA
Nitrosamines	 NDELA	 NDMA

Chemical analysis of N-amines

Sample preparation is challenging

– highly water soluble compounds

– some have low boiling point or are otherwise sensitive to heat

Implications:

- preferrable to sample from the water phase in two-phase systems (e.g. soil-water)
- low LODs for analysis necessary
  – avoid pre-concentration step
  – expected environmental concentrations are very low

Analysis by LC –MS/MS QqQ

- Direct injection of water sample
- Deuterated ISTD for quantification

	Ion source	LOQ (ppb)
DMNA	ESI	1
MEA-NO_2	APCI	0.1
NDMA	APCI	1
NDELA	APCI/ESI	1

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Biodegradability under anoxic conditions

Clay as bacteria source

100 mL test units

- wet clay
- sterilized freshwater 1:4
- nutrients
- sterile control units included

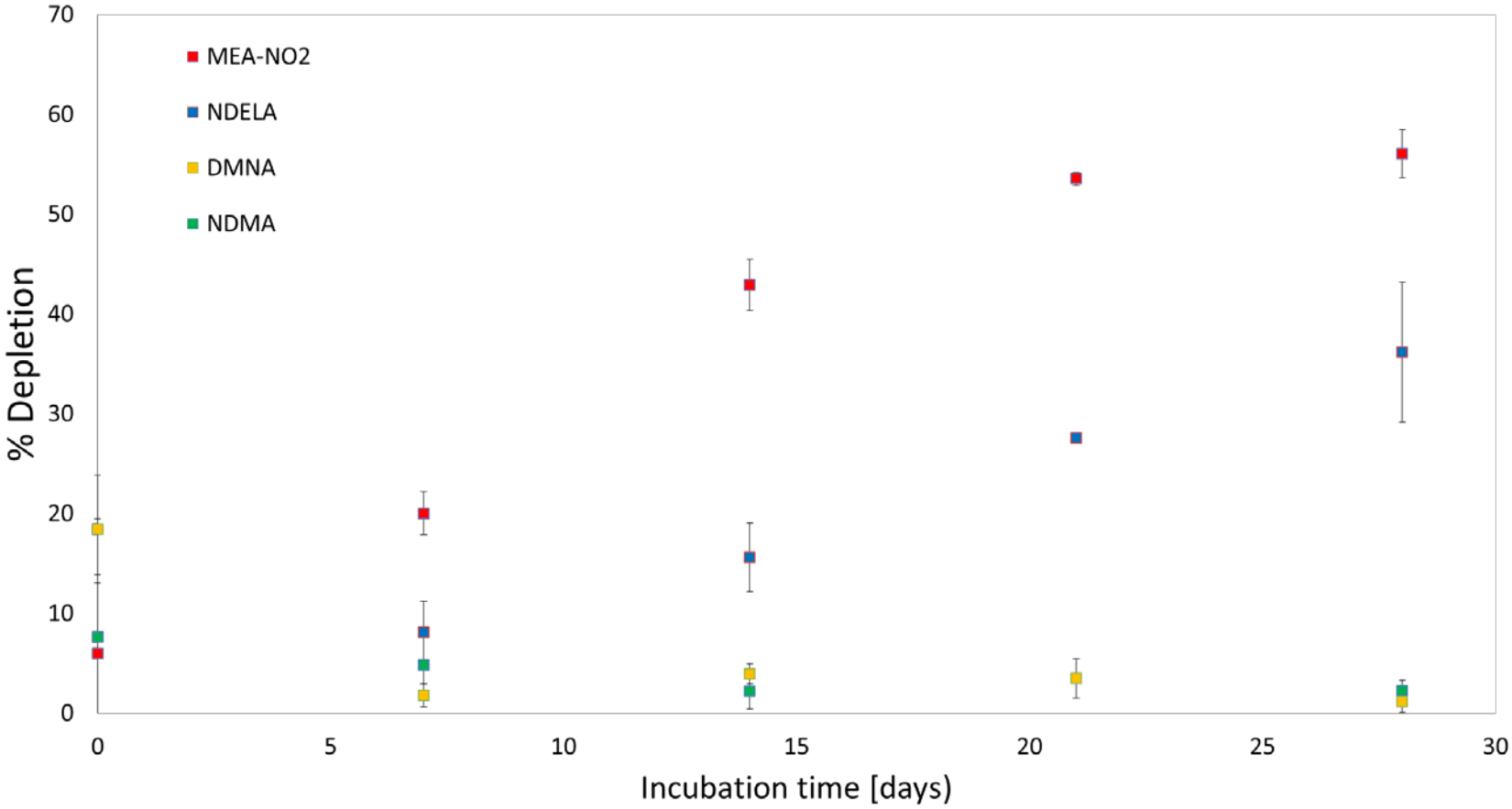
Redox and pH measurements to ensure stabile conditions

Pre-incubation of test units for 26 days prior to experiment start-up

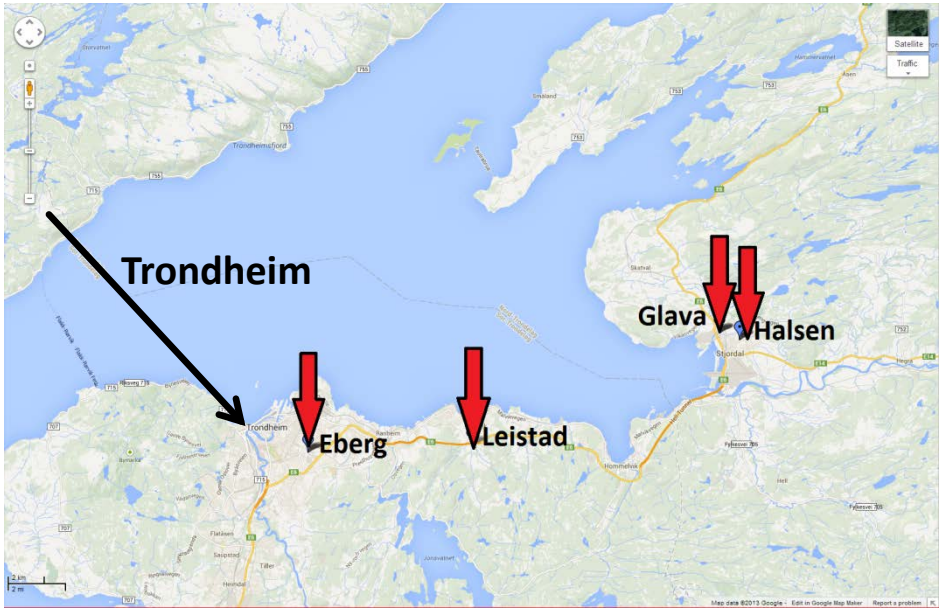
At experiment start-up, the chemical were spike in the samples at initial concentrations of 100 µg/L

Sampling regime: 0, 7, 14, 21, 28 and 56 days

Biodegradability under anoxic conditions



Soil adsorption



Four soil types selected for testing according to OECD 106

Soil	pH (in 0.01 M $CaCl_2$)	Organic carbon content %	Soil texture	Porosity (water content %)
Eberg	6,1	4,5	Fat clay	30
Leistad	6,9	6,1	Loamy clay	29
Halsen	4,6	1,0	Loamy silt	6
Glava	4,5	2,5	Blue clay	24

Soil adsorption

The soil was air-dried and suspended in 0.01 M $CaCl_2$ at a ratio of 1:5

The suspension was sterilized before spiking in the chemical

The solution was shaken for 2-7 days

Adsorption in %:

	Eberg	Halsen	Glava	Leistad
NDMA	< 10	< 10	< 10	< 10
NDELA	< 10	< 10	< 10	< 10
DMNA	< 10	< 10	< 10	< 10
MEA-NO2	< 10	< 10	< 10	< 10

- No adsorption to soil observed
- If nitramines and nitrosamines are deposited in soil, wash out and further transport to groundwater must be expected
- **Soil is not a final sink of *N*-amines**

Biodegradability in soil?

Non-sterilized soil-water samples - > depletion of some test compounds were observed

Not explained by adsorption

Depletion in % (48 hours):

	Eberg	Halsen	Glava	Leistad
NDMA	< 10	< 10	< 10	< 10
NDELA	**76 ± 2**	< 10	< 10	< 10
DMNA	**61 ± 4**	< 10	**48 ± 15**	**15 ± 2**
MEA-NO2	**96 ± 1**	**27 ± 4**	< 10	**37 ± 3**

- May be attributed to biodegradation in soil
- This appear to be a very rapid process
- Needs further investigation

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Summary

Given an atmospheric release of nitrosamines or nitramines, followed by wet deposition

If deposited in freshwater:

- Nitrosamines will degrade rapidly by photolysis
- Nitramines are persistent to photodegradation

If deposited in terrestrial environment (soil):

- Nitrosamines will degrade rapidly by photolysis and be bound in the soil
- → If environmental conditions enable leaching to groundwater or surrounding lakes or rivers, this is likely to occur
- *N*-amines containing –OH groups will be susceptible to aerobic biodegradation and
- It is believed that soil bacteria have been observed to degrade tertiary amines (rapidly)
- This hypothesis need further investigation

- Less biodegradable nitramines may persist in the water and potentially accumulate

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