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– catching our future



Nitrosamine formation in the CESAR1 solvent

PCCC-8, Marseille, France – September 18th, 2025

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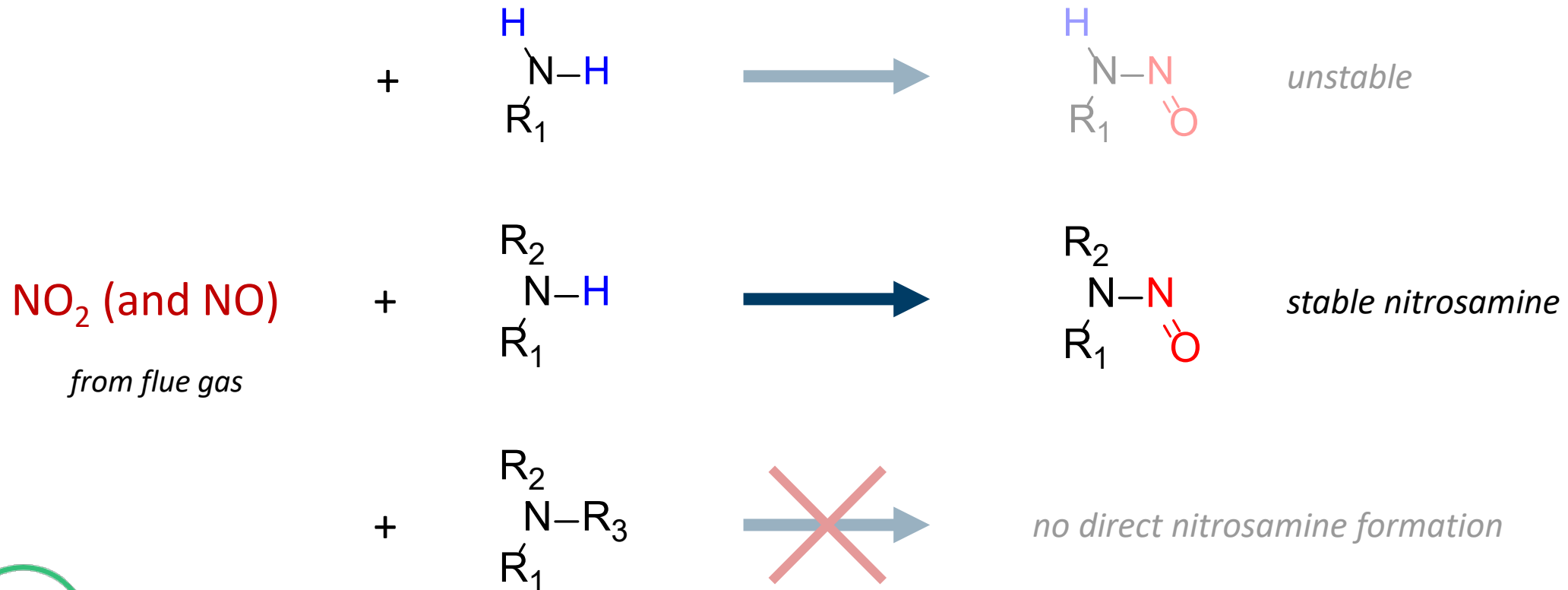


The CESAR1 solvent

AMP	PZ
2-amino-2-methylpropane-1-ol	piperazine
3 m / 27 wt% (aq.)	1.5 m / 13 wt% (aq.)
Sterically hindered, primary amine.	Cyclic secondary diamine.
 <chem>CC(C)(C)NCO</chem>	 <chem>C1CCNCCN1</chem>



Nitrosamine formation



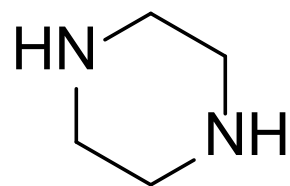


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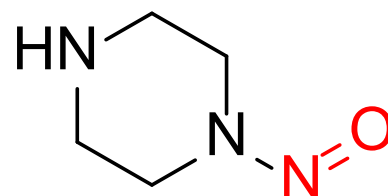
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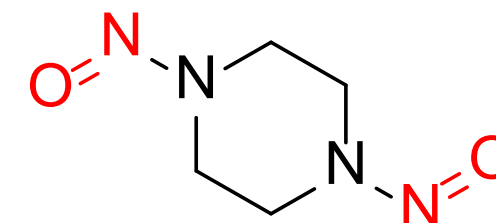
Nitrosamines in CESAR1



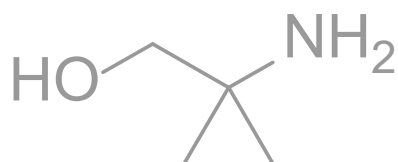
PZ



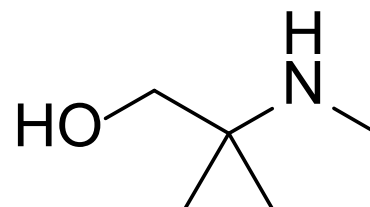
MNPZ



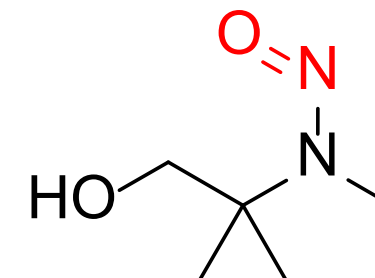
DNPZ



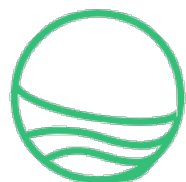
AMP



MAMP



NMAMP



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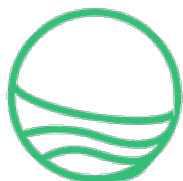
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Analytical methodology

- LC-MS
 - Chromatographic separation
 - Two-dimensional mass spectrometry
 - Analytical standards with known purity
 - 2-5% uncertainty
- Total nitrosamine (TONO) analysis
 - Treatment with HCl and CuCl in closed vial at 70°C:
Nitrosamine $\rightarrow\rightarrow$ NO $\cdot$ (g)
 - Headspace analysis on GC-NCD (single peak)
 - Calibration with NDMA
 - Uncertainty 5-10%



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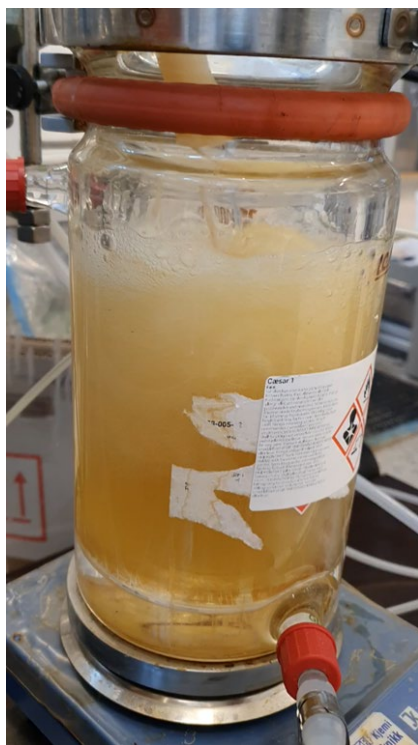
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Three types of samples

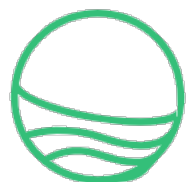
Lab scale oxidation



Tiller pilot campaign



TCM pilot campaign

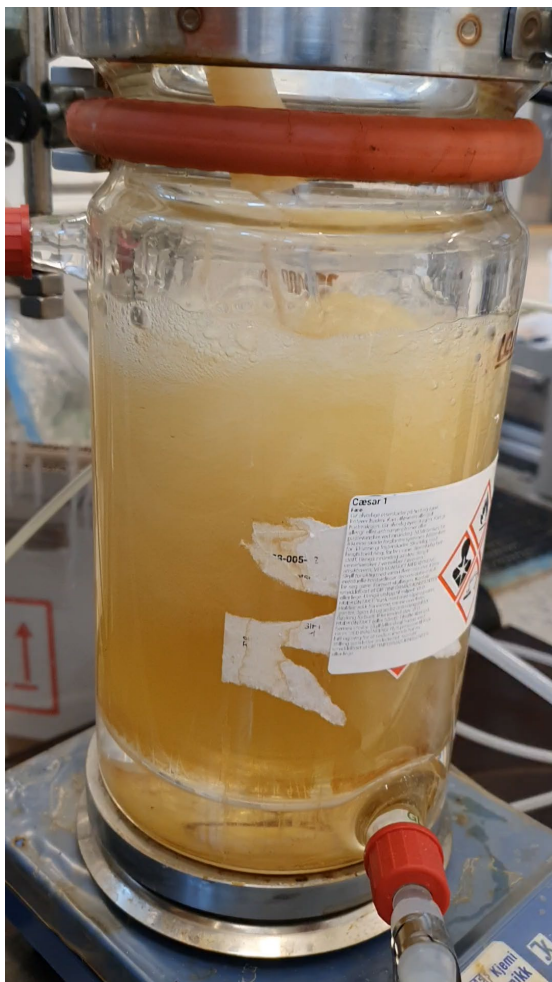


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Nitrosamine formation in the absence of NO_2



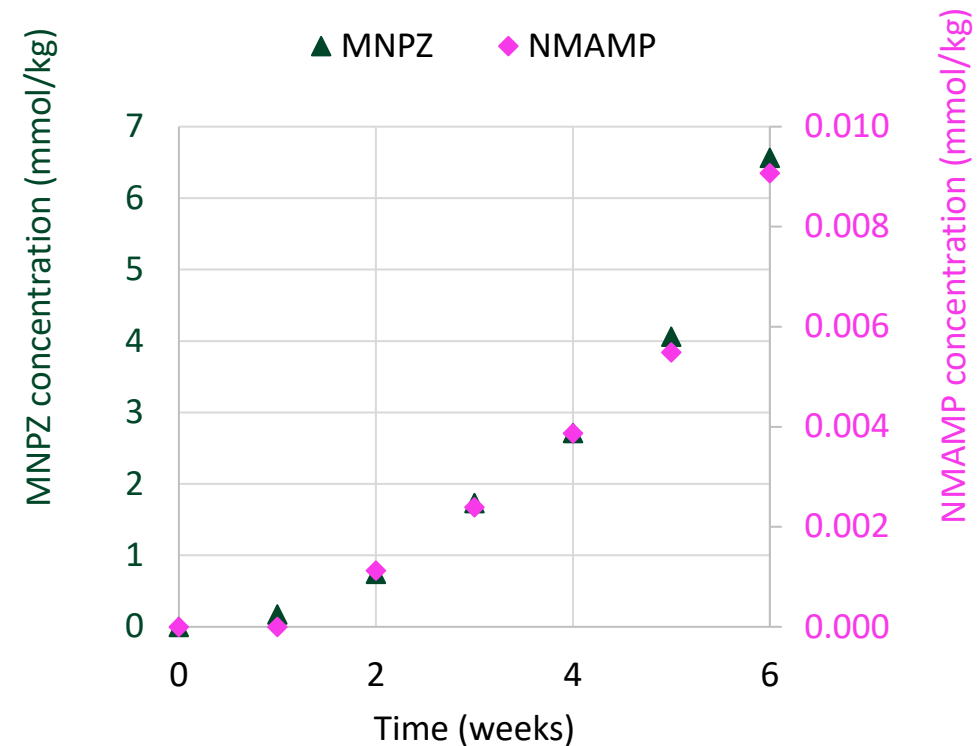
60°C

0.4 mol_{CO₂}/mol_N

21% O₂, 78% N₂, 1% CO₂

50 L/min gas recirc.

6 weeks



Nitrosamines formed during pilot campaign at Tiller

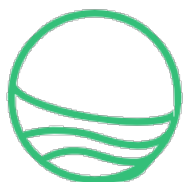


CESAR1

solvent campaign

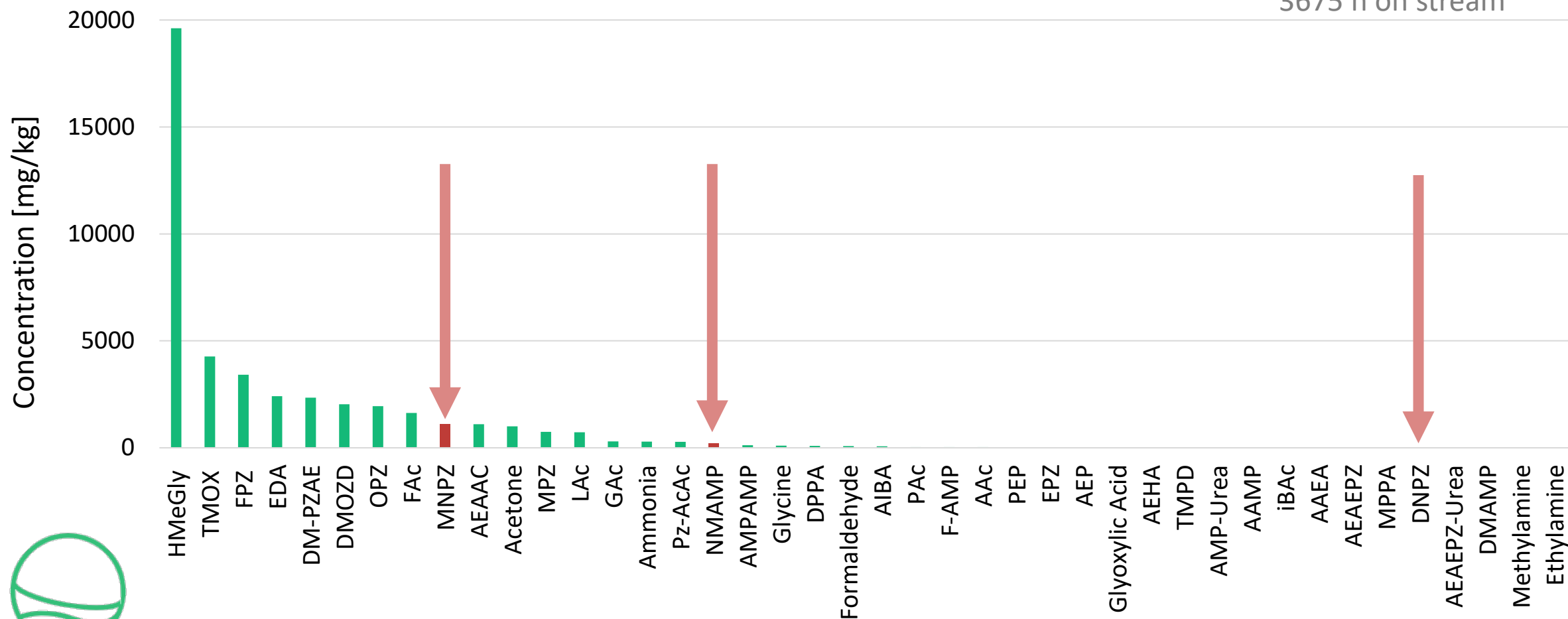
2024-2025

4136 h on stream

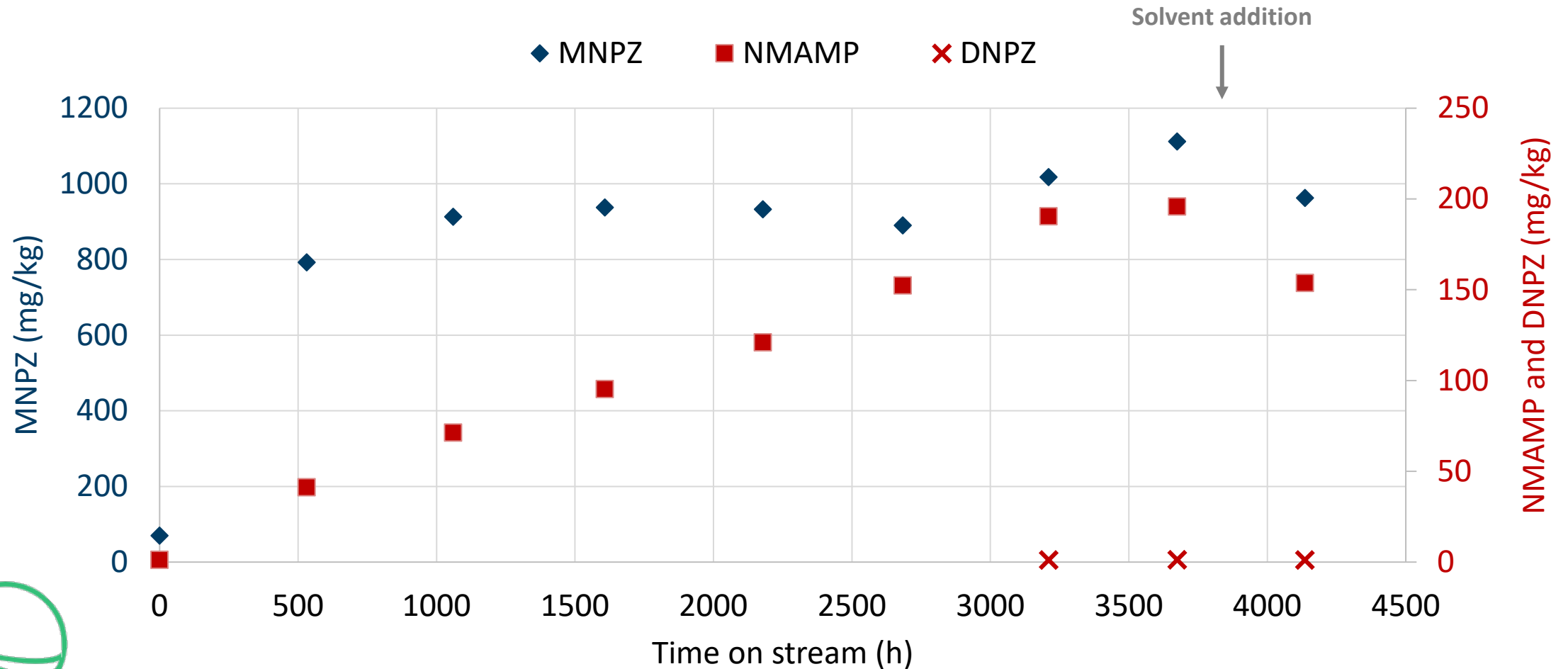


Nitrosamines formed during pilot campaign at Tiller

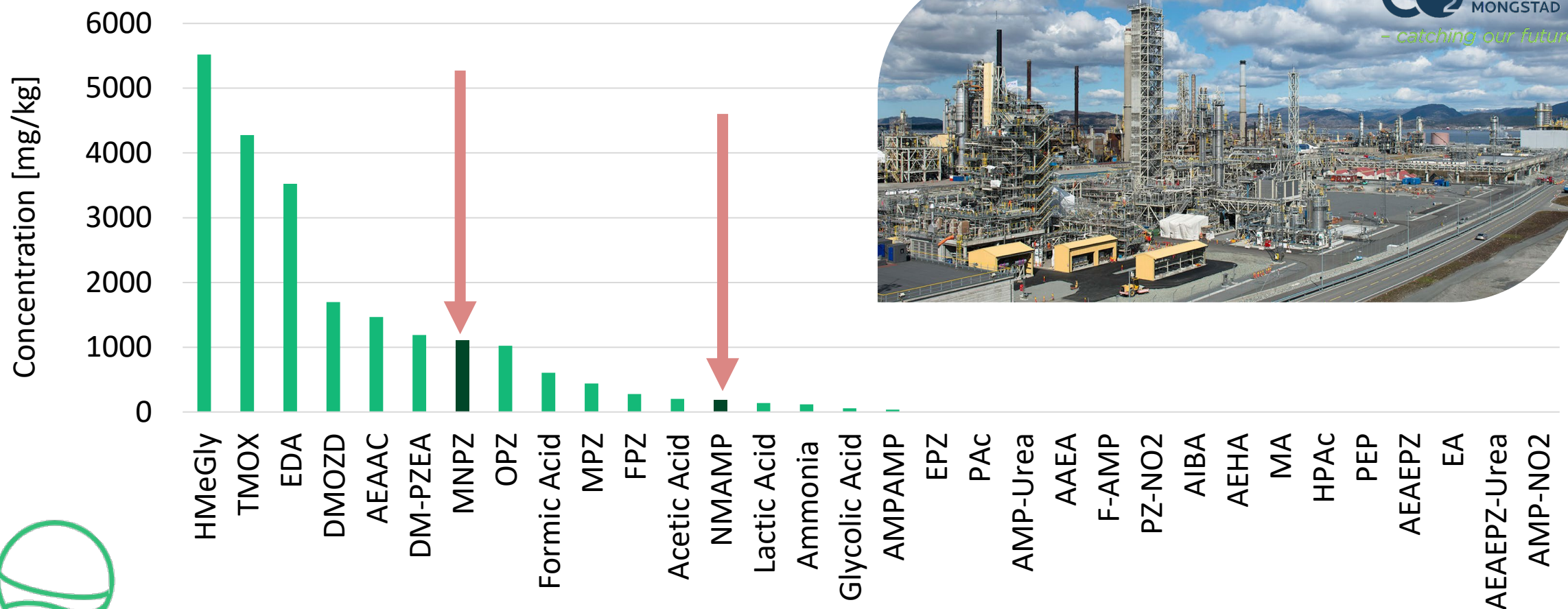
3675 h on stream



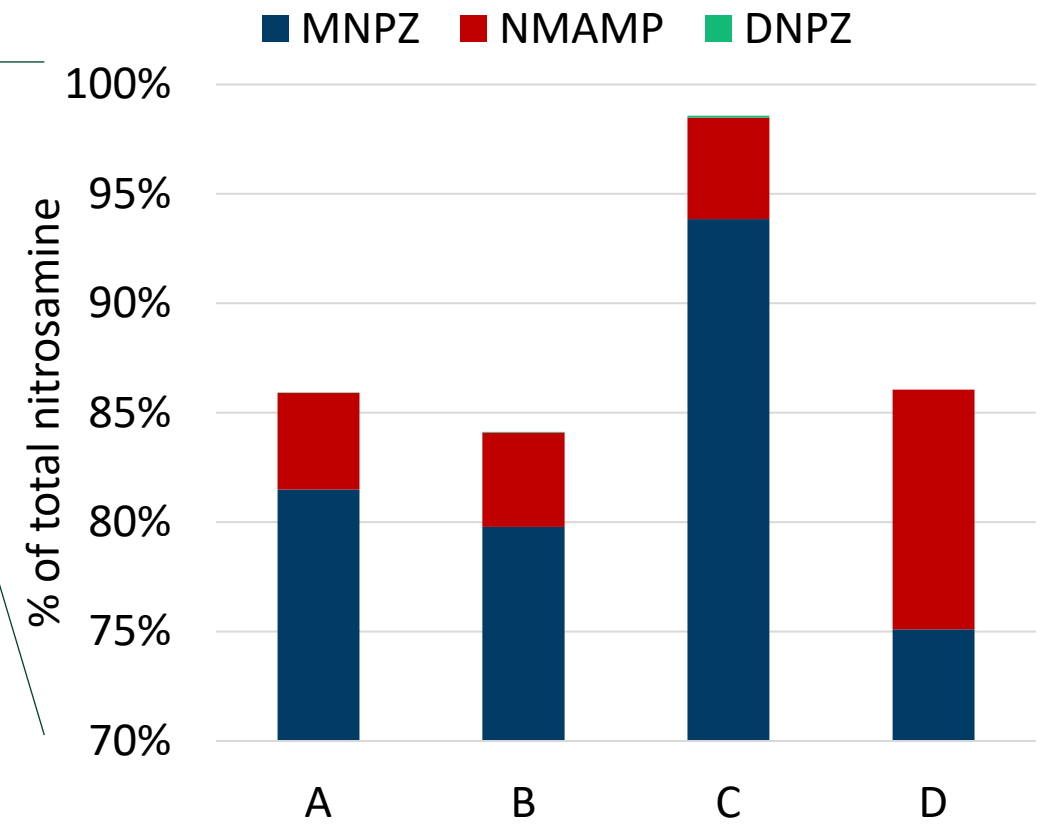
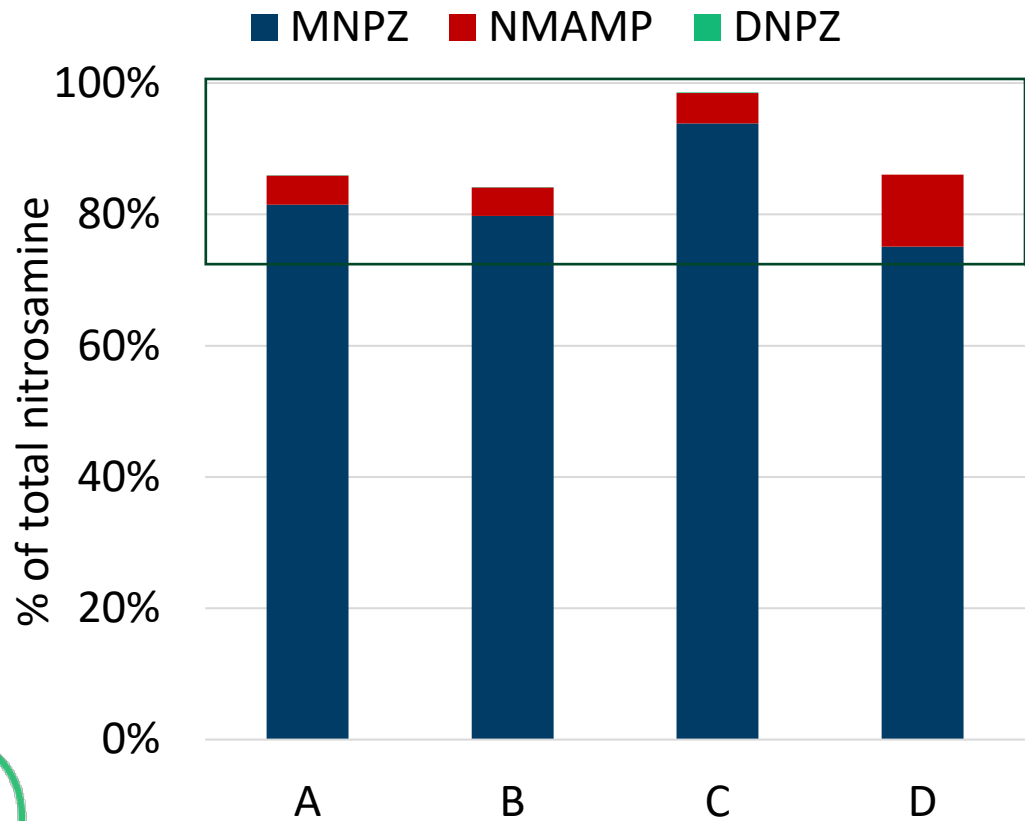
Nitrosamines formed during pilot campaign at Tiller



Nitrosamines formed during pilot campaign at TCM



Amount of TONO accounted for





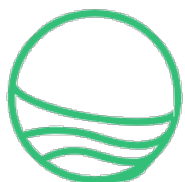
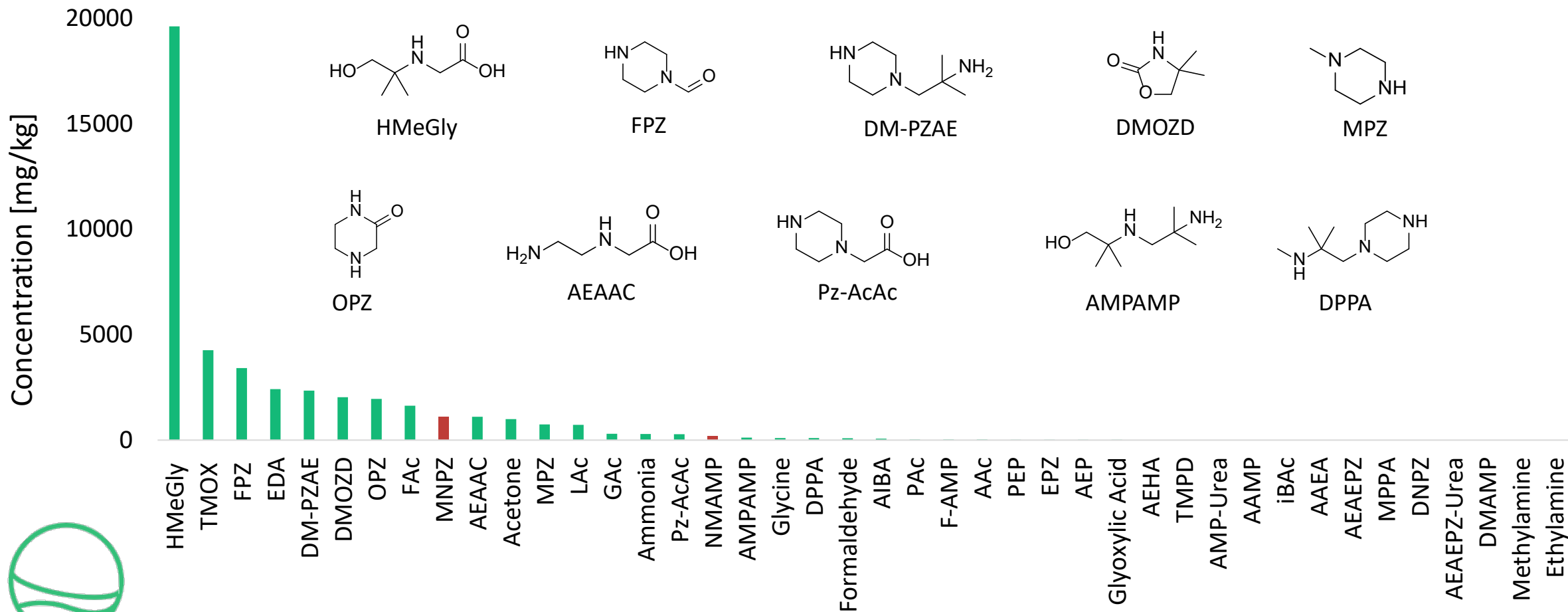
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Secondary amine degradation compounds



3675 h on stream



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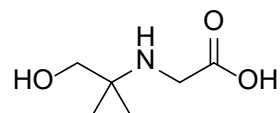
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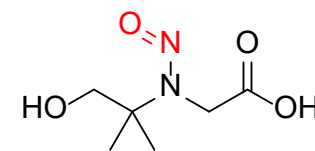
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New nitrosamines

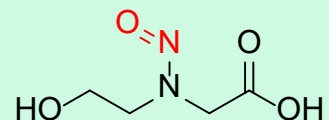


HMeGly

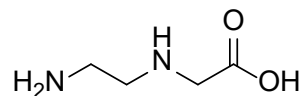
nitrosation



N-nitroso HMeGly

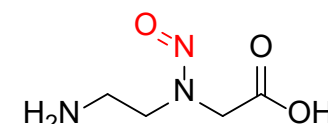


N-nitroso HEGly is the main nitrosamine to form in MEA.

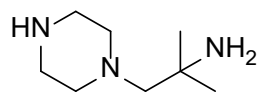


AEAAC

nitrosation

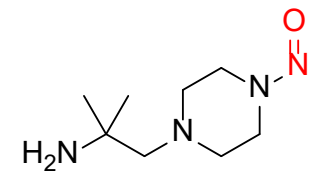


N-nitroso AEAAC

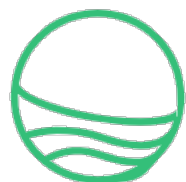


DM-PZAE

nitrosation



N-nitroso DM-PZAE



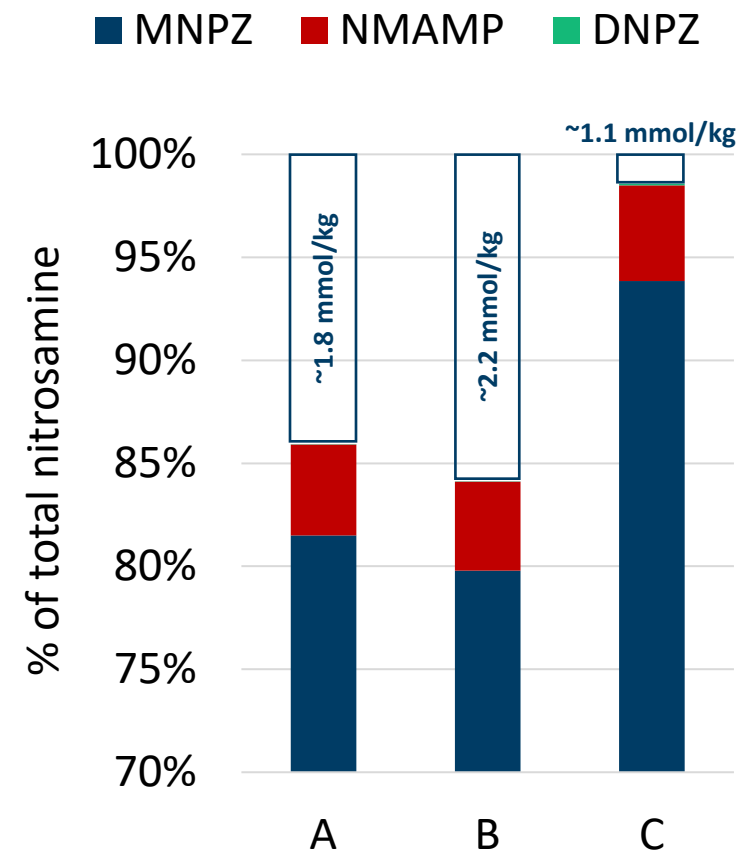
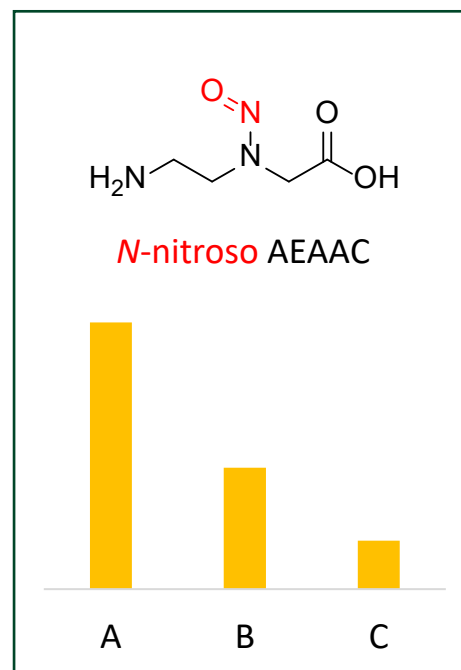
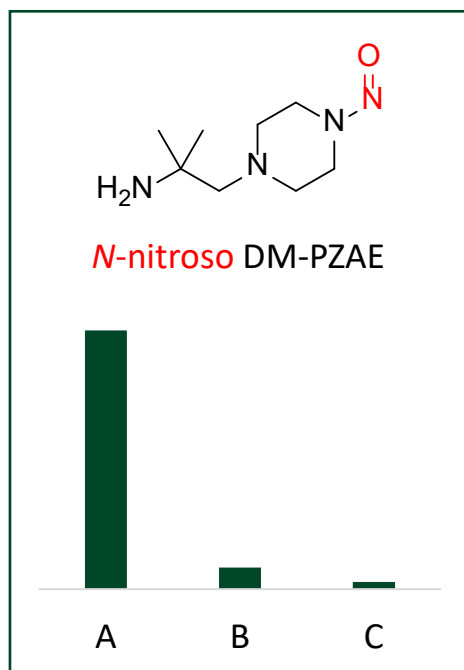
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First steps towards closing the nitrosamine knowledge gap

Signal intensity ~30x higher in N-DM-PZEA than N-AEAAC





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Summary, conclusions and future work



Nitrosamines may form also in the absence of NO_x

Some of the most abundant known degradation compounds of CESAR1 are nitrosamines

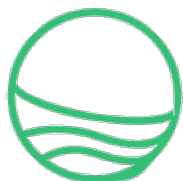
- **MNPZ**, NMAMP, (DNPZ present but not abundant)

Additional nitrosamines exist

- N-DM-PZEA and N-AEAAC confirmed
- N-HMeGly highly likely
- Further degradation compound-based nitrosamines possible

All nitrosamines that form in CESAR1 (and other amines) should be identified

- Properties of new nitrosamines will need to be studied



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QUESTIONS? Thank you!

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