The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

PZ pilot campaign at TCM – oxidation due to O_2 and NO_2 in flue gas

PCCC8, Marseille, France

The University of Texas at Austin and Honeywell
Texas Carbon Management Program

September 18, 2025

Presentation outline

- Pilot scale
- TCM flue gases
- Liquid solvent degradation data
  - LC/MS (measured at TCM)
  - Amino acids (measured at UT)
- Gas phase evidence of oxidation
- Modeling NH_3 evolution due to oxidation
- Oxygen measurements
- Conclusions

Pilot facilities scale

Parameter	SRP (UT Austin)	NCCC (Southern Co.)	TCM (Mongstad, Norway)
Size equivalent (MW_{eq})	0.1	1.0	12 (RFCC f.g. at 40,000 kg/hr)
Abs packing height (ft)	20	40	60
Flue gas source	Synthetic	Nat gas boiler	RFCC, MHP (fuel gas boiler)
Flue gas rate (kg/hr)	1,350	3,630	35,800 (RFCC)/45,800 (MHP)
CO_2 capture rate (MT/d)	1.5	6	180 (RFCC)/234 (MHP) @ 96%

Flue gases at TCM

Component	RFCC	MHP
CO_2 (%)	15.7	9.9
O_2 (%)	2.5-3.5	3.8
NO_2 (ppmv)	0.5-1.5	15.7
Total particle no. (TN) (#/cm^3)*	7.9 - 9.5 X 10^4	-

*From Laborelec report (2025).

Degradation data – liquid phase

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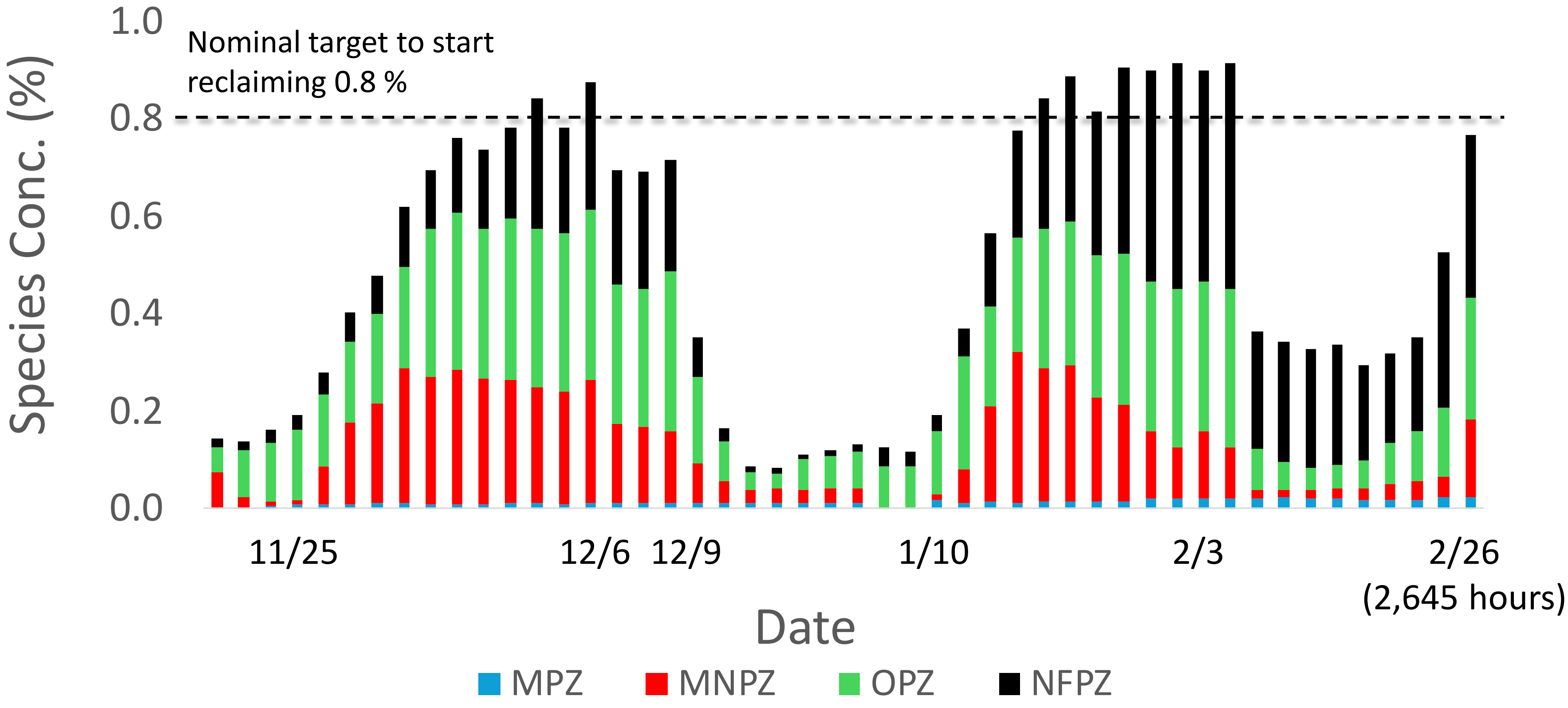
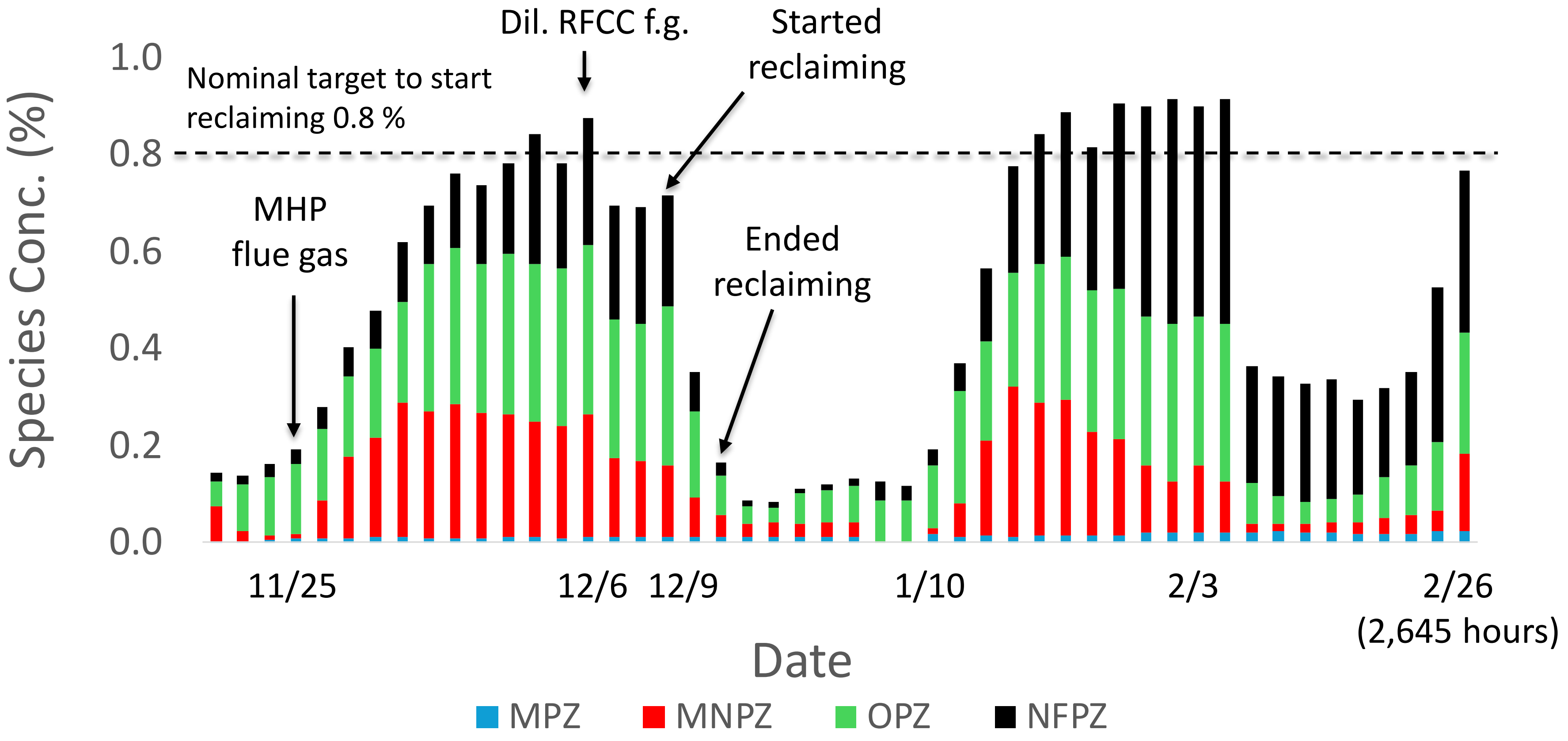
Aggregate oxidation species (%) by LC/MS at TCM



Aggregate oxidation species (%) by LC/MS at TCM



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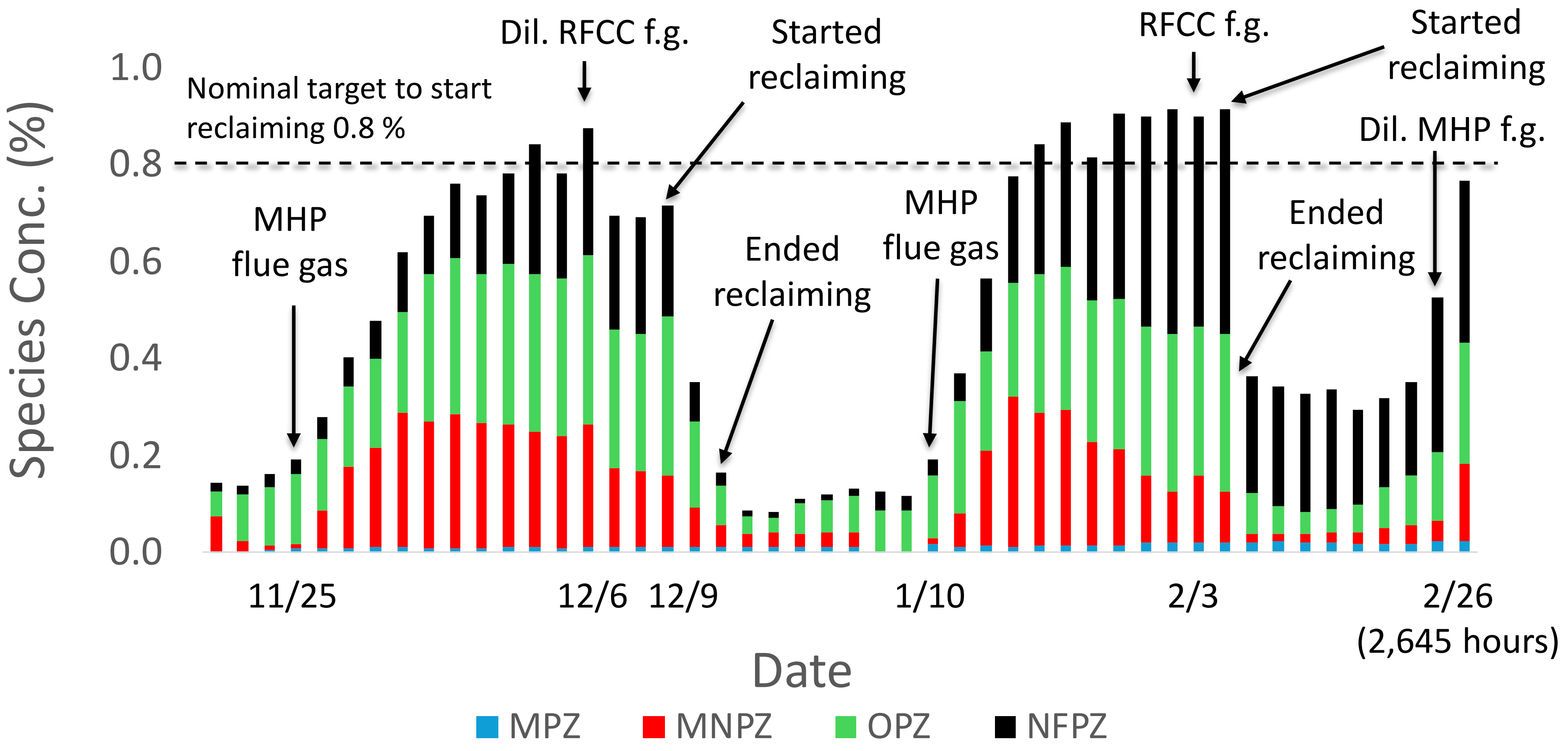

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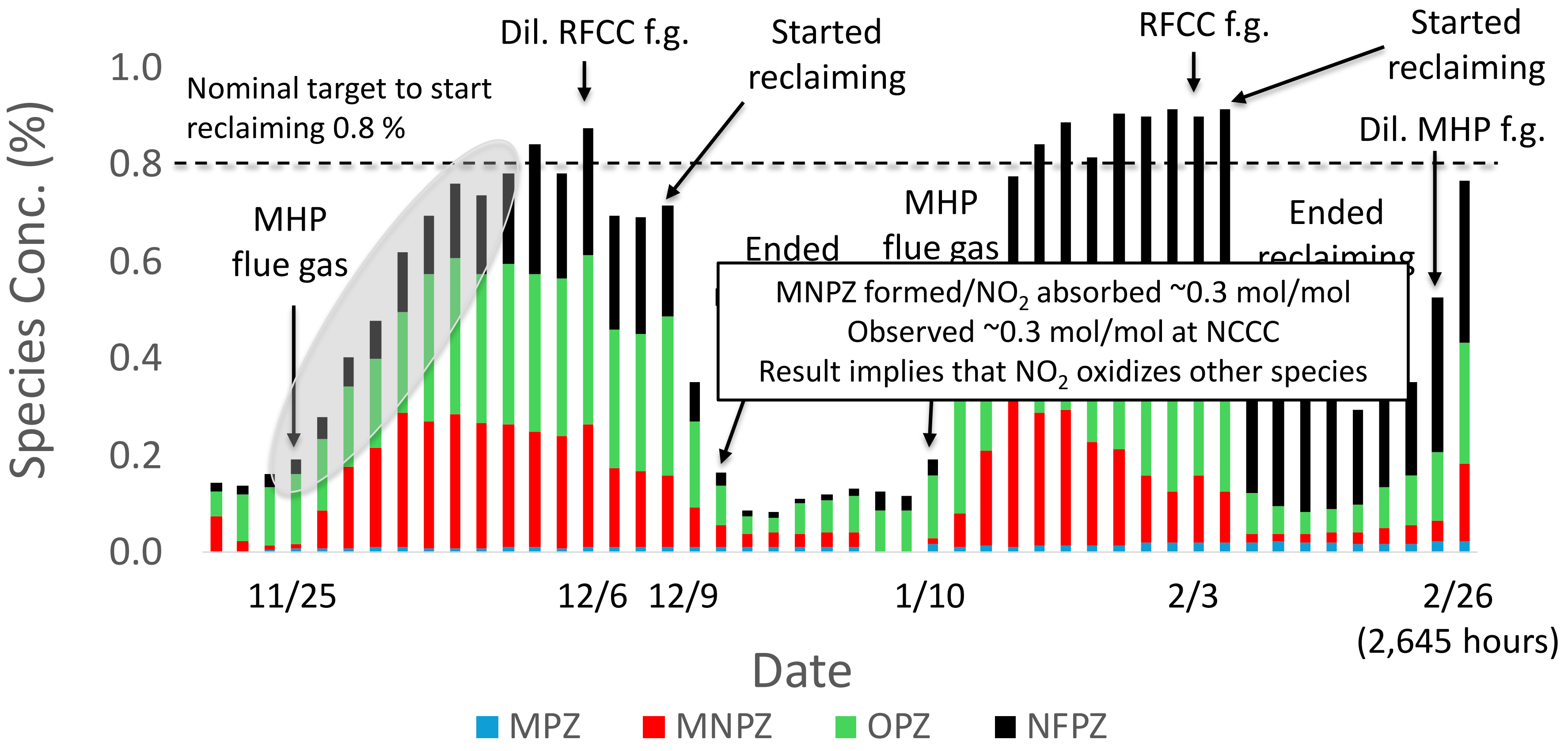


Reactions in the absorber and stripper

Table 1. PZ oxidation by NO_2 at absorber temperature

Type of reactions	Reactions	Numbers
NO_2 absorption	$NO_2 + PZ \rightarrow PZ\cdot + NO_2^-$	(1)
Radical propagation	$PZ\cdot + O_2 \rightarrow PZOO\cdot$	(2)
	$R\cdot + PZ \rightarrow PZ\cdot + P$	(3)
	$R\cdot = PZOO\cdot, PZO\cdot, and \cdot OH$	
	$P = PZOOH, PZOH, and\ H_2O$	
Radical termination	$2PZ\cdot + H_2O \rightarrow PZOH + PZ$	(4)
Organoperoxy dissociation	$PZOOH + PZ \rightarrow 2PZOH$	(5)
	$PZOOH \rightarrow PZO\cdot + \cdot OH$	(6)
Nitrosamine/nitramines generation	$NO + PZ\cdot \rightarrow MNPZ$	(7)
	$NO_2^- + PZ \rightarrow MNPZ$	(8)
	$NO_2 + PZ\cdot \rightarrow m-nitro\ PZ$	(9)

Reactions in absorber and abs packing; plenty of O_2

Ref: Chen, C. and Rochelle, G.T. Amine Oxidation Catalyzed by NO_2, 16th International Conference on Greenhouse Gas Control Technologies, Lyon, France, October 23-27, 2022.

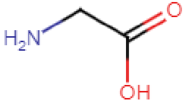
Table 2. MNPZ generation and decomposition in the stripper (high temperature)

Type of reactions	Reactions	Numbers
Nitrosation	$NO_2^- + H^+ + PZ \rightarrow MNPZ$	(10)
MNPZ thermal decomposition	$MNPZ + 0.5\ H_2O \xrightarrow[base,\ \Delta]{} PZOH + 0.5\ N_2O$	(11)

Reactions in stripper; absence of O_2

Amino acids

TCM lean sample (hydrolyzed) total amino acids



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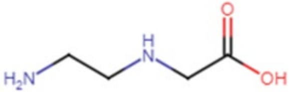

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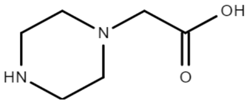

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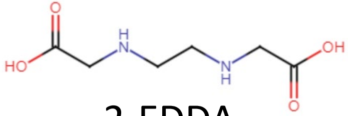

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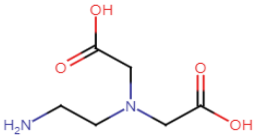

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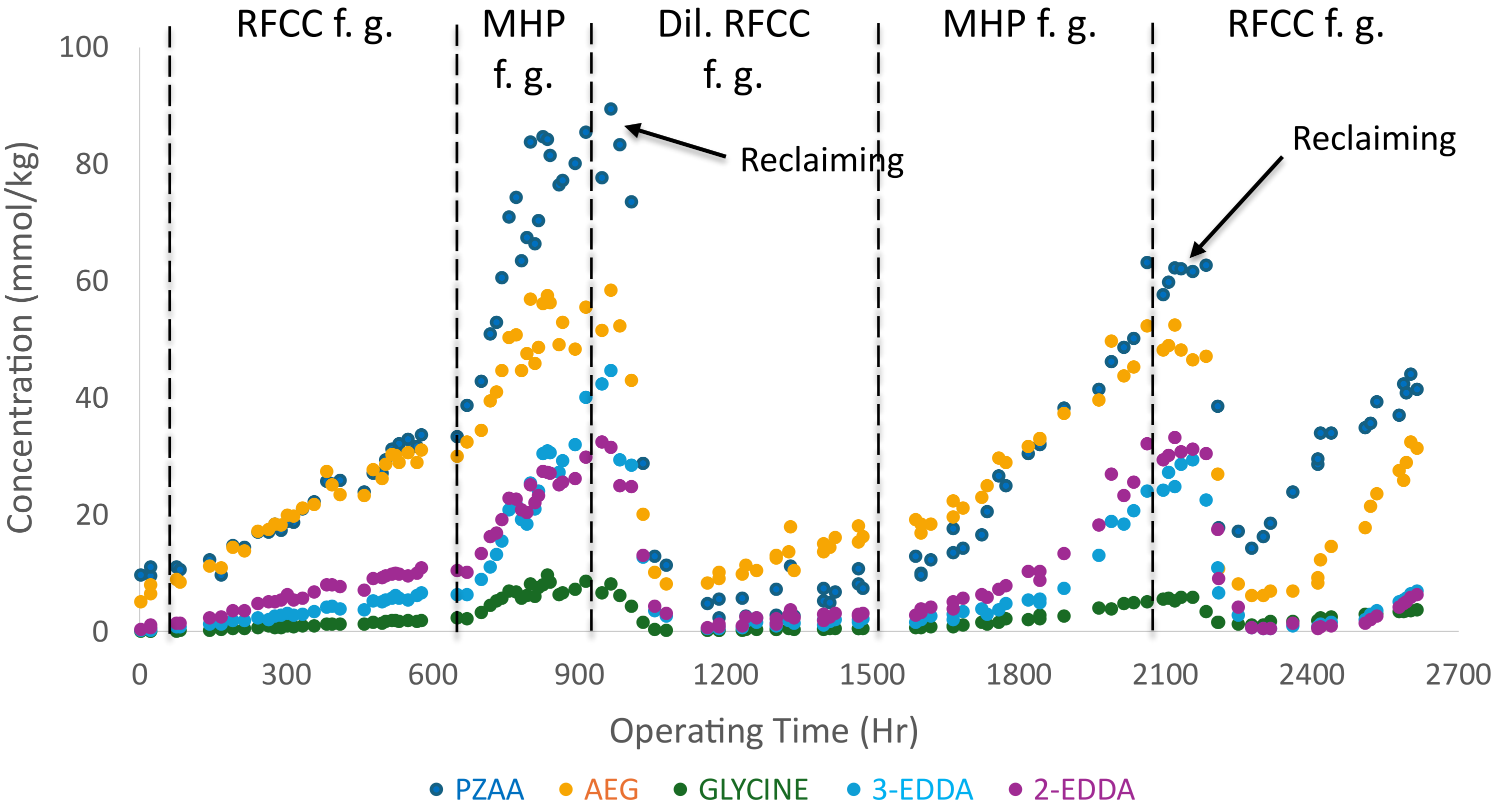
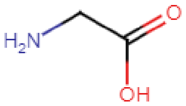


TCM lean sample (hydrolyzed) total amino acids



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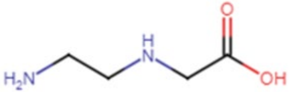

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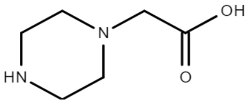

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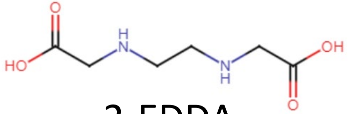

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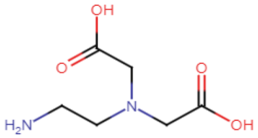

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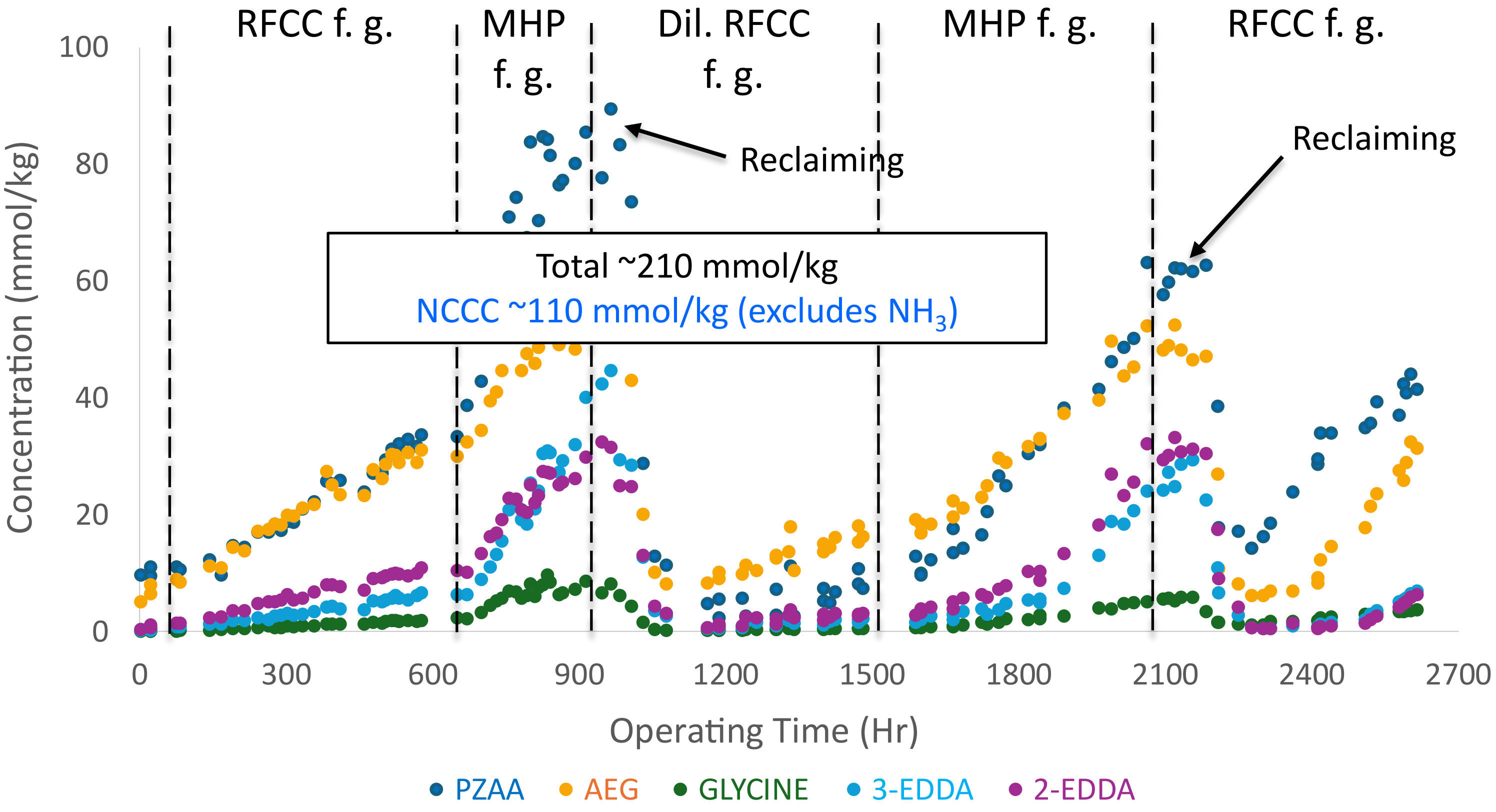
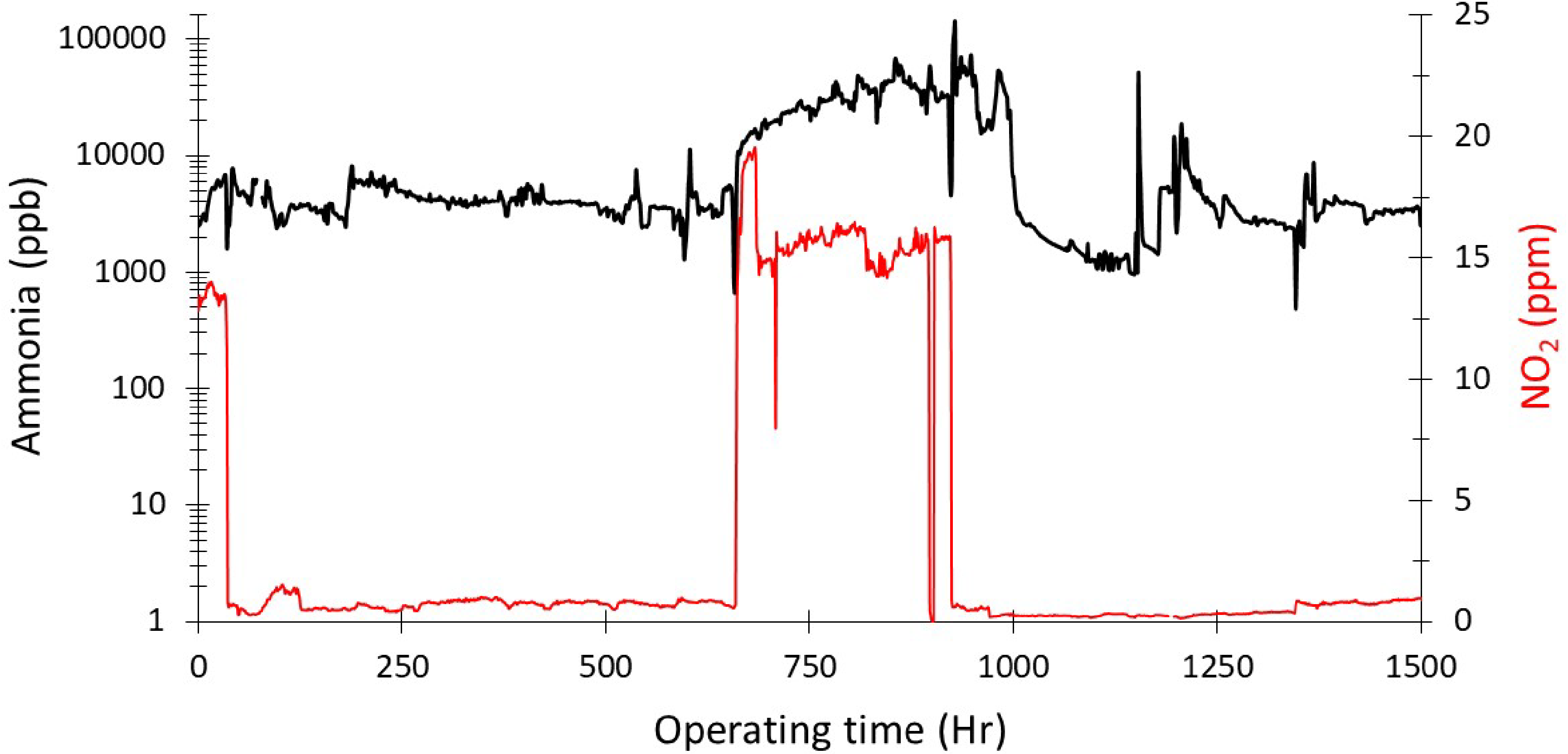


Gas phase evidence of oxidation

NH_3 (FTIR) response to NO_2 at TCM



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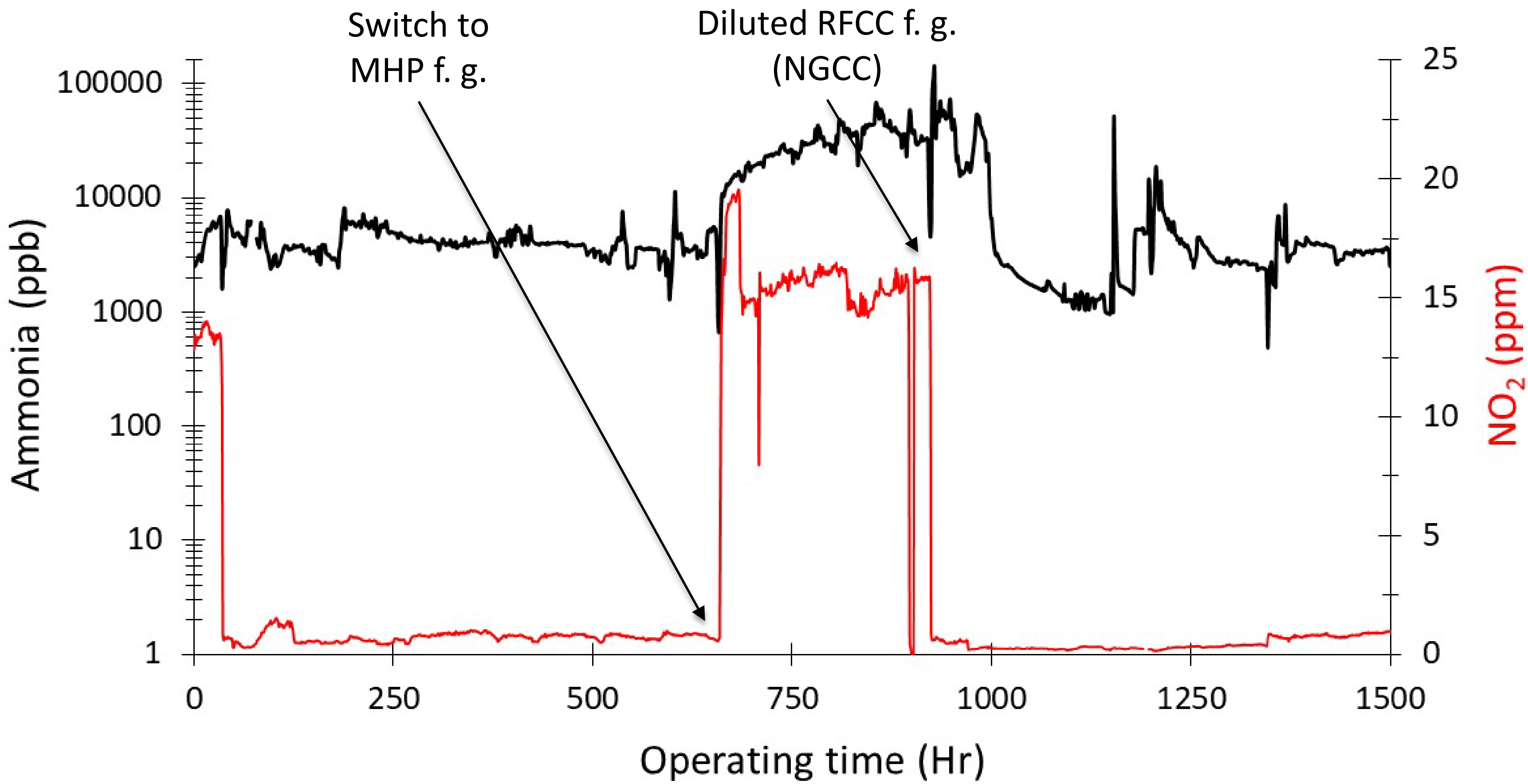


Modeling NH_3 response to NO_2

Steady state run periods modeled

Gas	Start Time	End Time	Total time (d)	Avg O_2 (%)	Avg NO_2 (ppm)	Mols NH_3/Mols NO_2
RFCC	11/5	11/14	10	3.1	0.7	5.2
RFCC	11/18	11/25	8	3.1	0.8	3.7
RFCC	12/30	1/7	8	2.9	0.9	3.8
MHP	11/25	12/6	12	3.8	15.3	1.7
MHP	2/26	2/26	2	3.7	17.0	1.0
Dil-RFCC	12/20	12/24	5	16.0	0.4	7.6
Dil-RFCC-2	12/24	12/30	7	9.4	0.8	4.0
Dil-MHP	1/7	1/21	15	13.8	5.5	1.2
Dil-MHP	2/20	2/22	3	13.4	6.3	1.1

(a) Data sets represent steady state conditions
(b) No weighting based on run duration in model
(c) Included NH_3 in CO_2 stream; <5% but ~9% when P_{str} lowered for reclaiming

Modeling NH_3 response to NO_2

$$\left.mols\ NH_3\middle/mols\ NO_2\right. = 0.01[O_2]_{avg} + 4.4[NO_2]_{avg}{}^{-0.48} - 0.44$$

Where: $[O_2]$ (%) & $[NO_2]$ (ppm)

Key takeaways:

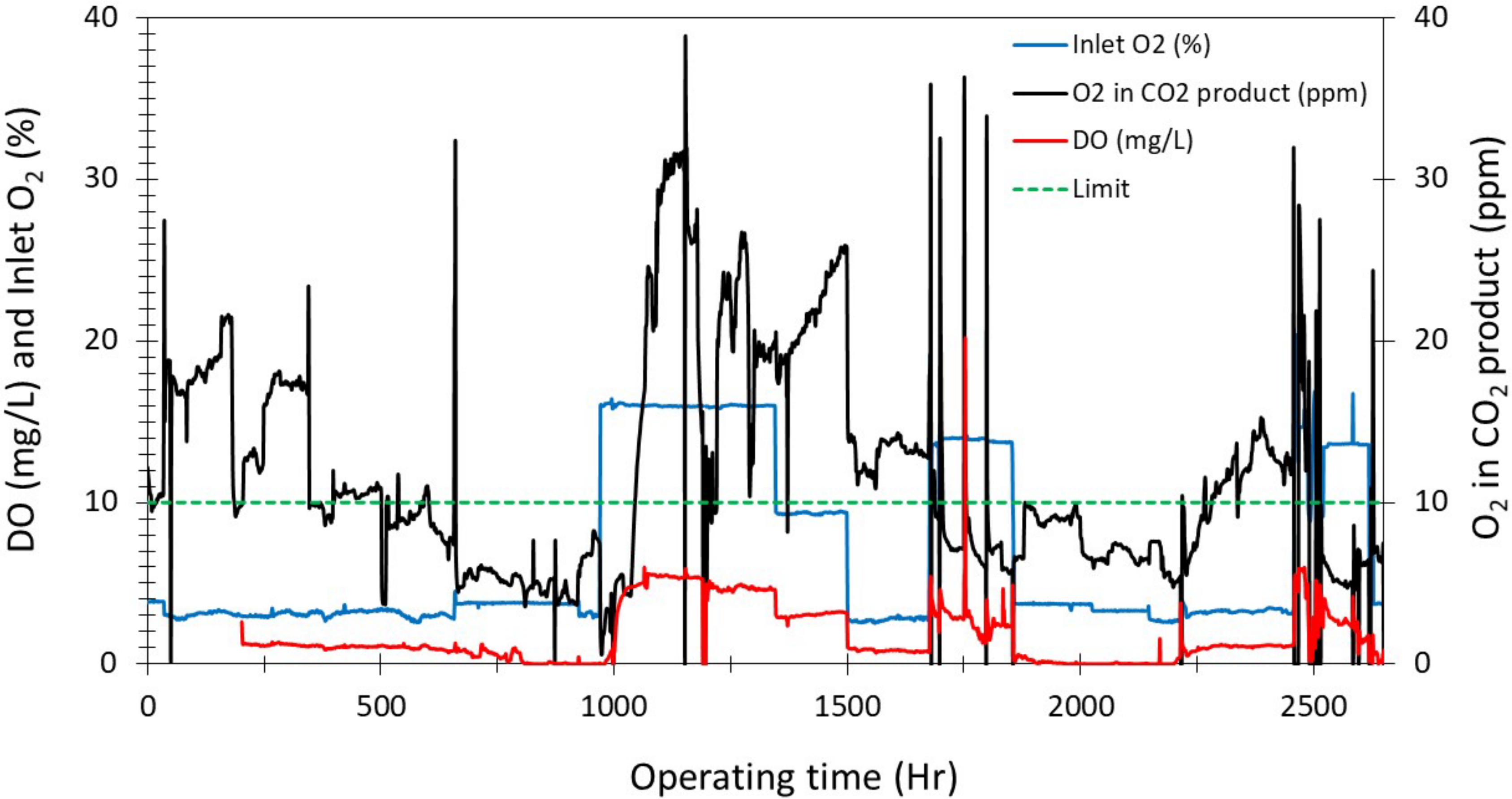
(1) Relationship between cumulative mols NH_3/mols NO_2 and $[NO_2]_{inst}$ obeys power law

(2) Flue gas O_2 concentration has little bearing on model results – indicates the model over-simplifies the chemistry

(3) Modeling oxidation should account for accumulation and oxidation of amino acids

Oxygen measurements

NH_3 (FTIR) response to NO_2 at TCM



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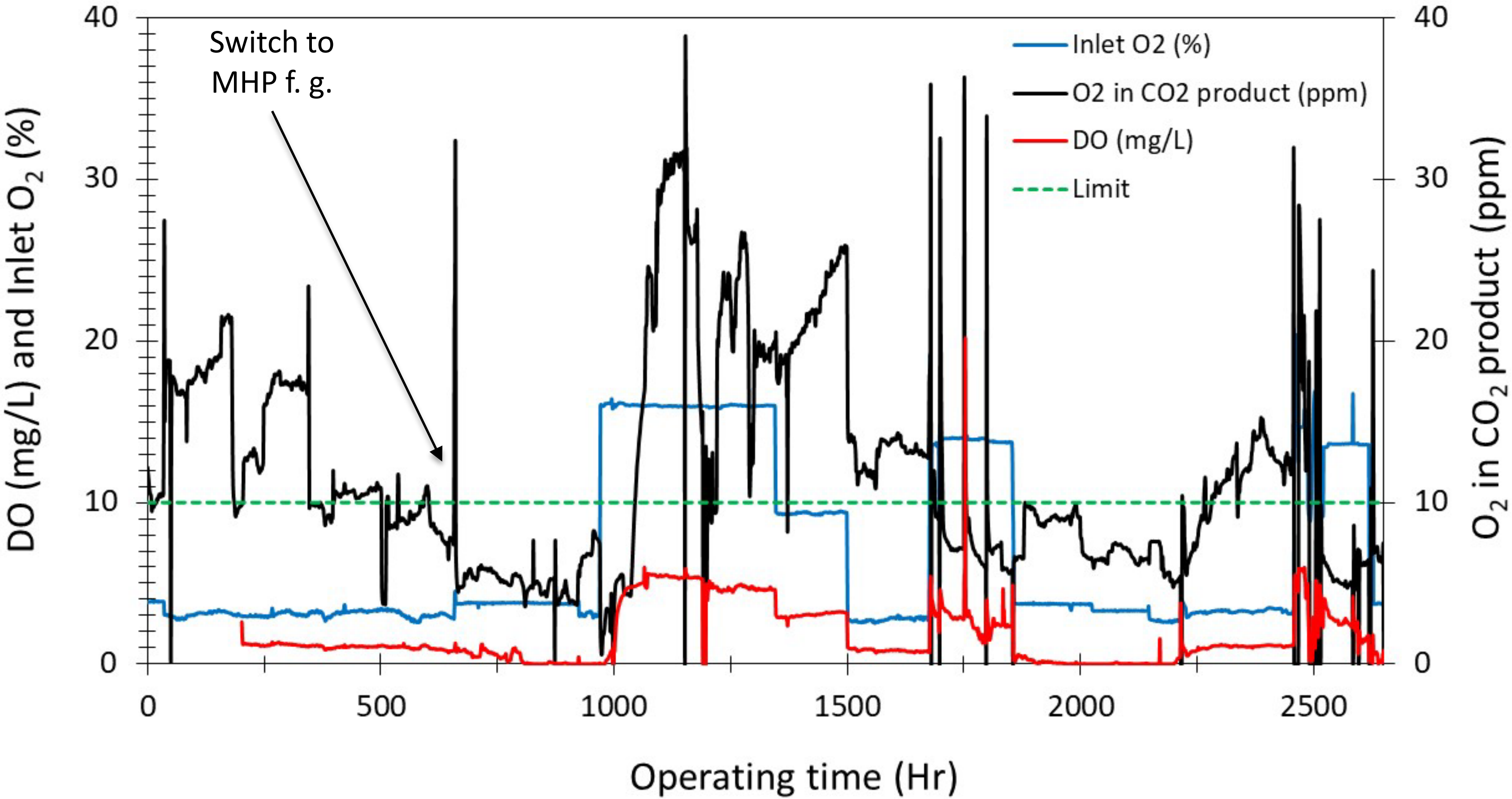

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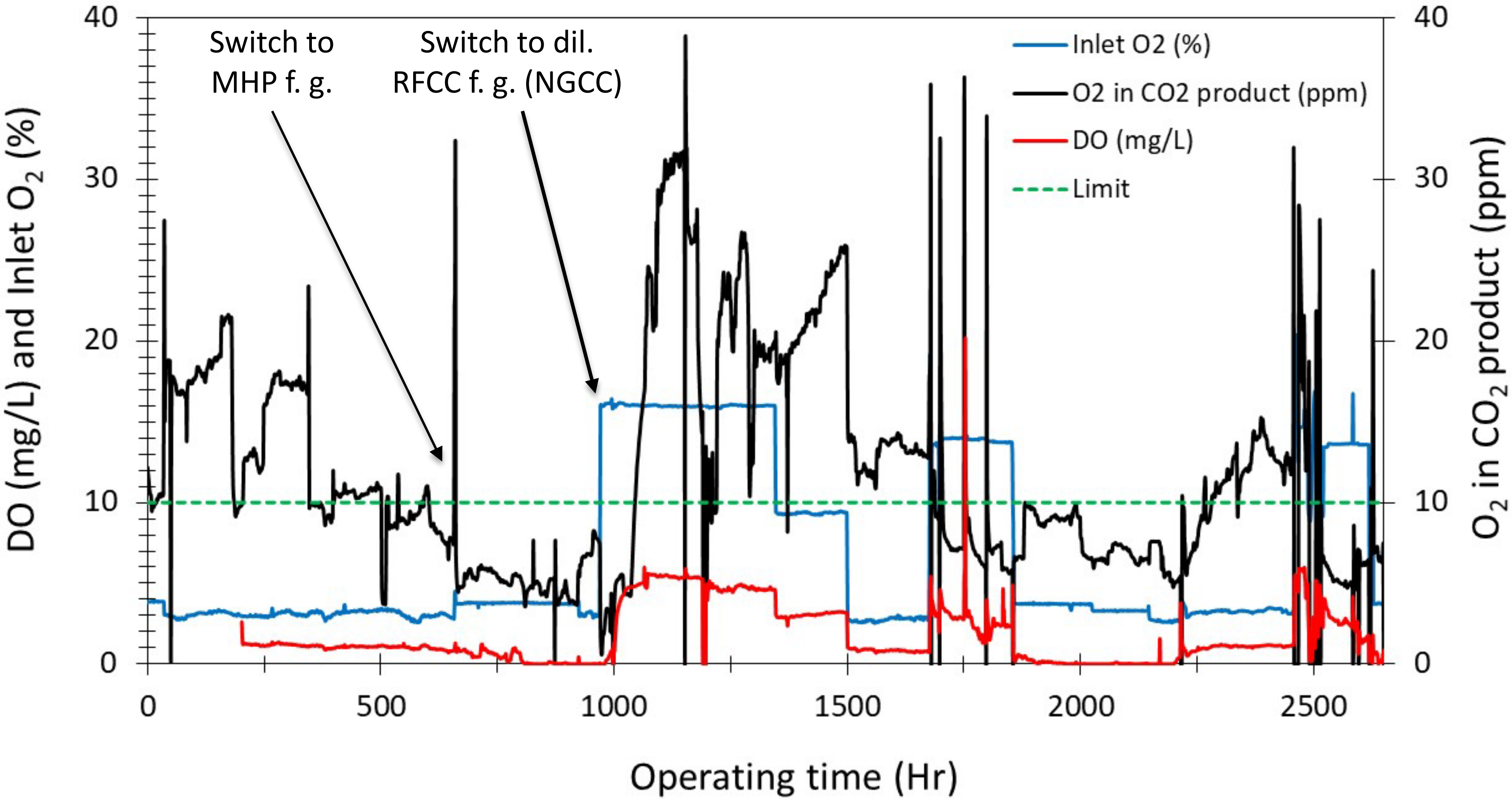

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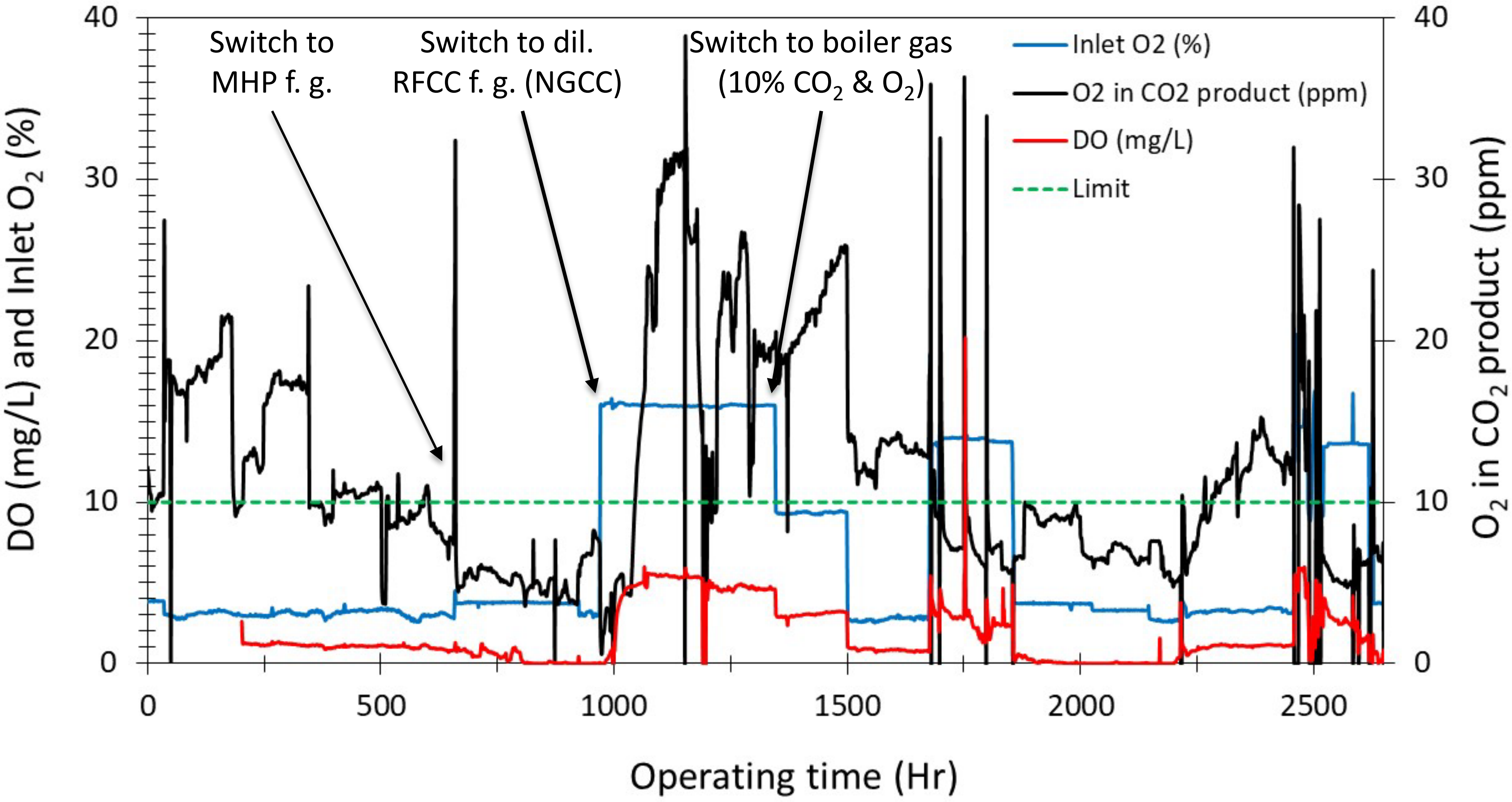

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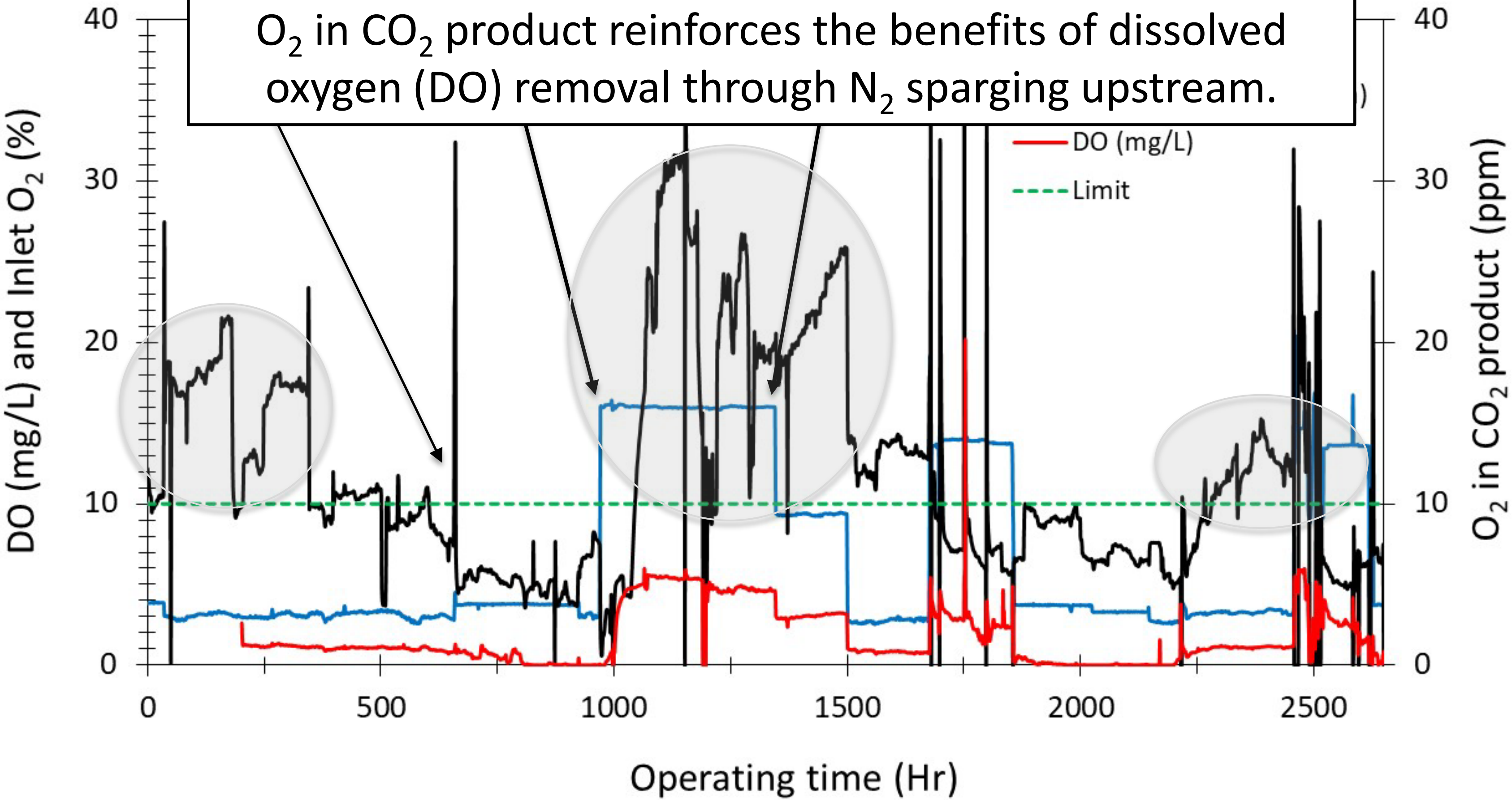
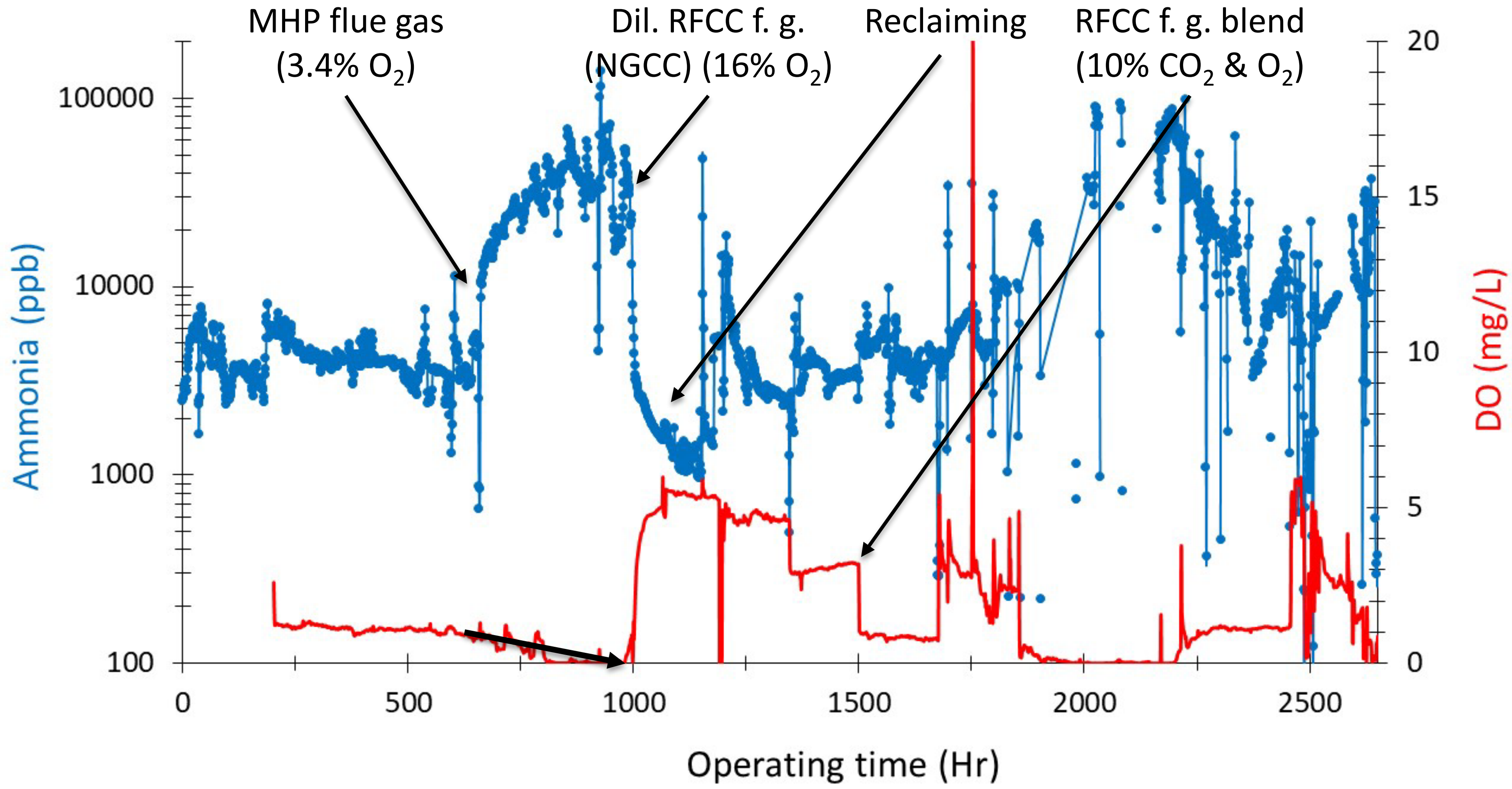
NH_3 (FTIR) response to NO_2 at TCM

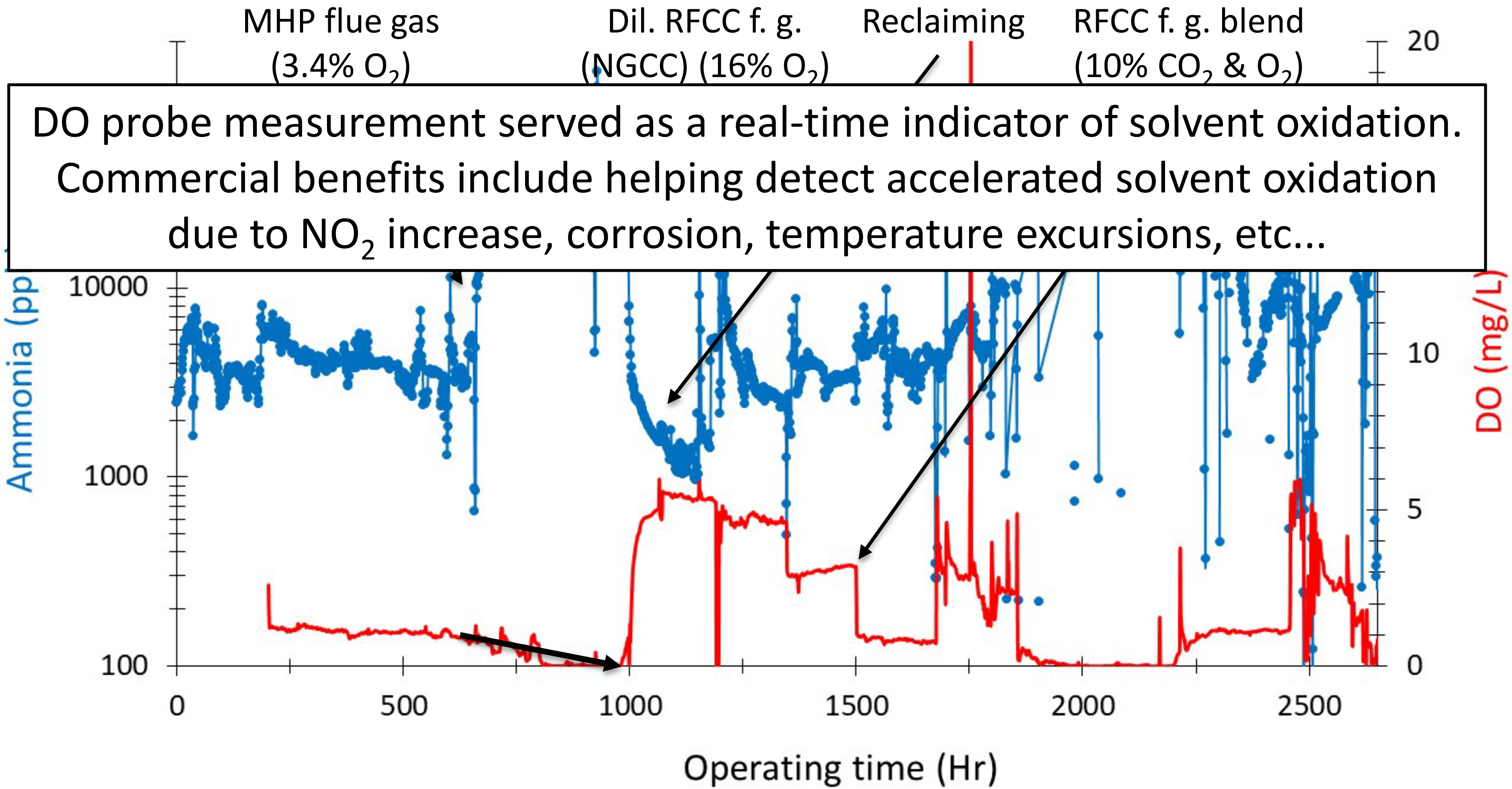
O_2 in CO_2 product reinforces the benefits of dissolved oxygen (DO) removal through N_2 sparging upstream.



DO and NH_3 (FTIR) at TCM



DO and NH_3 (FTIR) at TCM



DO probe measurement served as a real-time indicator of solvent oxidation. Commercial benefits include helping detect accelerated solvent oxidation due to NO_2 increase, corrosion, temperature excursions, etc...

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Conclusions

- MHP flue gas with 16 ppm NO_2 accelerated formation of amides, amino acids, and MNPZ
- Mols MNPZ formed/mols NO_2 absorbed ~0.3
- NO_2 accelerated evolution of NH_3
  - Modeled the ratio using steady state run periods
  - Model may be improved by accounting for amino acids
- Oxygen measurements
  - O_2 >10 ppm in CO_2 product when not depleted before stripper; supports argument for DO stripping in absorber
  - DO measurement is a useful real-time tool for monitoring solvent health

Acknowledgements

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US Department of Energy

Technology Centre Mongstad

Disclaimer

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One author of this paper consults for a process supplier on the development of amine scrubbing technology. The terms of this arrangement have been reviewed and approved by the University of Texas at Austin in accordance with its policy on objectivity in research. One author also has financial interests in intellectual property owned by the University of Texas that includes ideas reported in this paper.

Questions?

Project participants

Party	Person	Role
NETL	Krista Hill	Project Manager
Texas Carbon Management Program (TxCMP)	Dr. Gary Rochelle Dr. Fred Closmann	Principal Investigator Project Manager
Honeywell	Carl Stevens Nathan Lozanoski Ramiro Roman	Technology development
University of Oslo	Armin Wisthaler Tomas Mikoviny	Gas phase measurements (TOF-MS)
TCM	TCM Team	Pilot implementation

TCM solvent

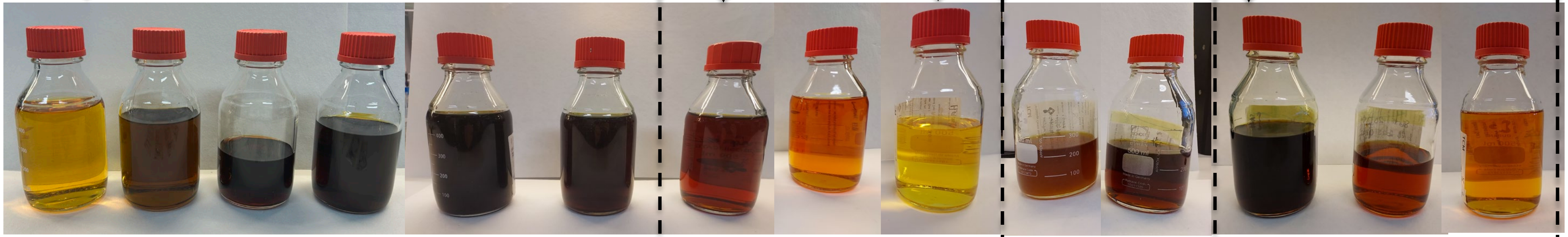
Switch to MHP (high NO_2)

Start recl.

After recl.

MHP f.g. (high NO_2)

Start recl. (2/4)

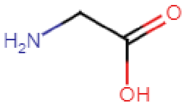


11/25 11/29 12/2 12/4 12/9 12/9 + 20 h 12/10 12/11 12/17 1/27 1/30 2/5 2/6 2/10

After reclaiming

2/15 through 2/17

TCM lean sample (unhydrolyzed) free amino acids



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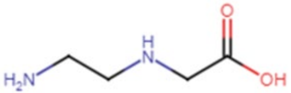

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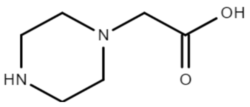

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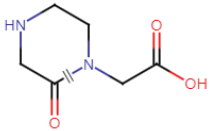

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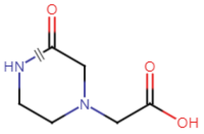

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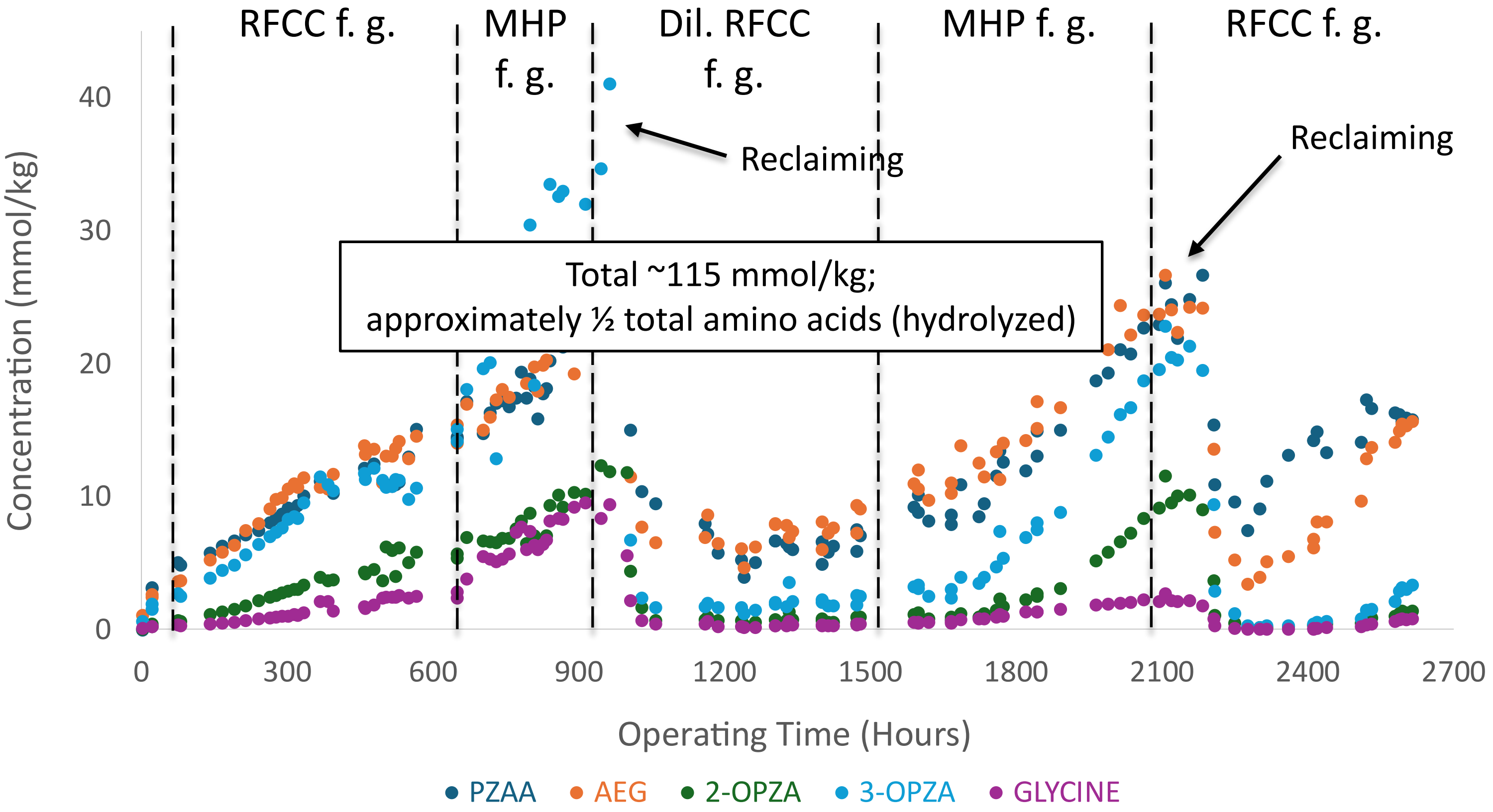
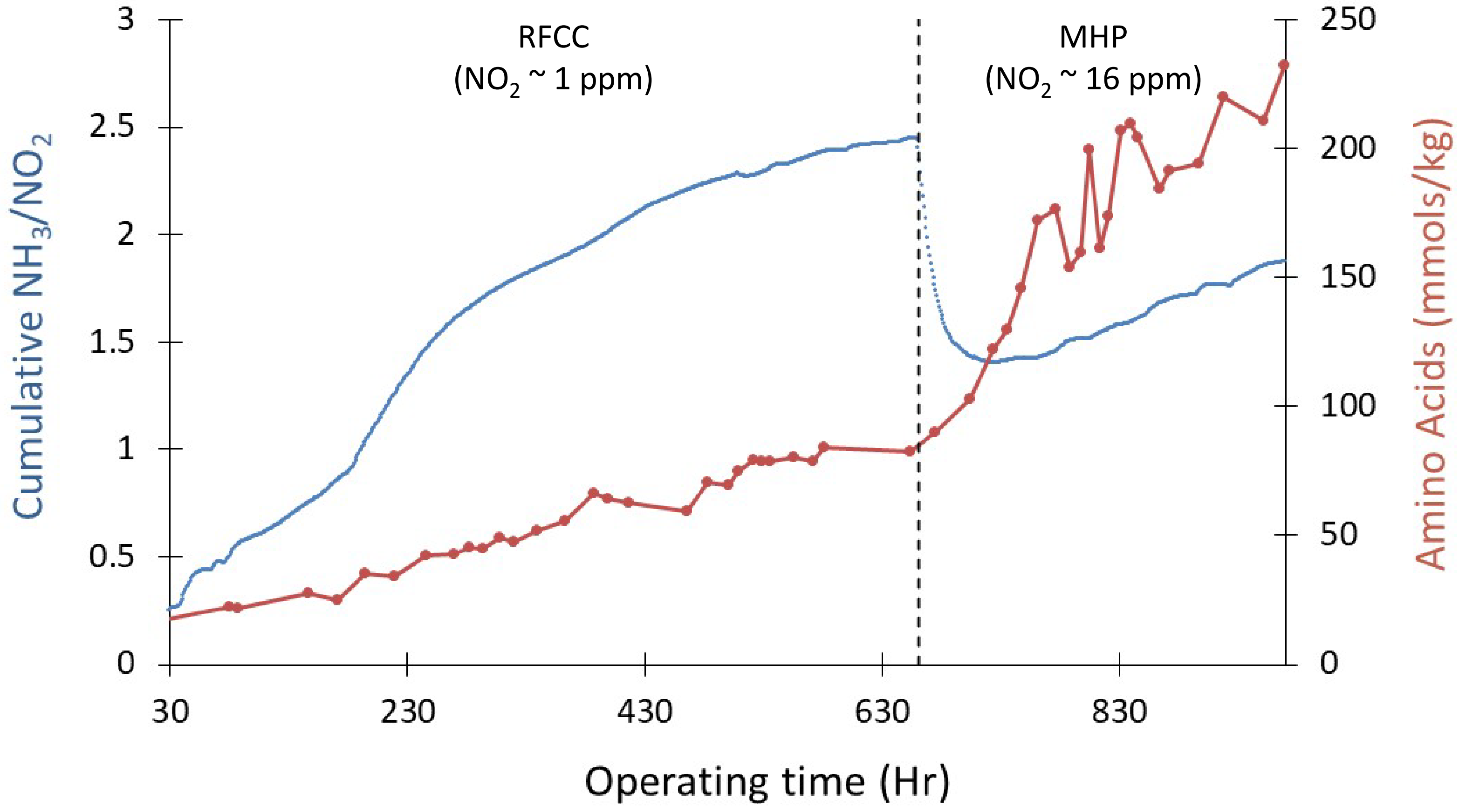
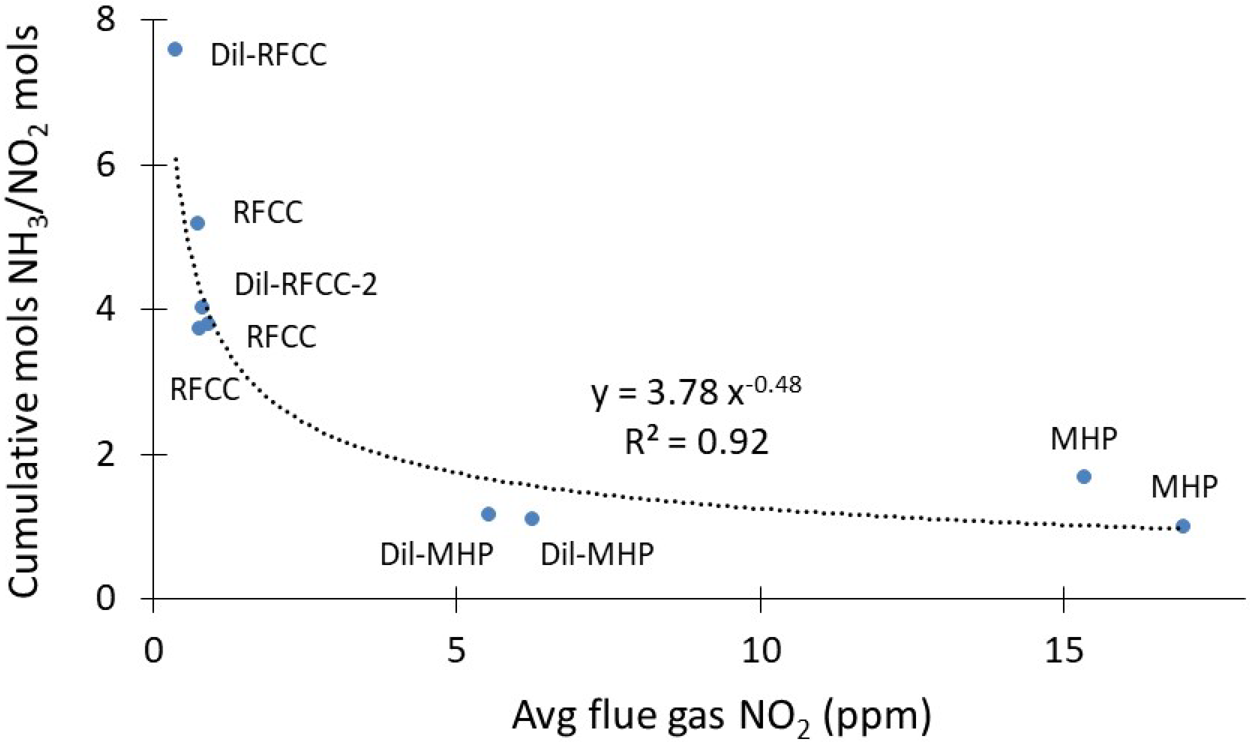


NH_3/NO_2 and amino acids at TCM



Modeling NH_3 response to NO_2



Relationship between cumulative mols NH_3/mols NO_2 and $[NO_2]_{inst}$ obeys power law.

Oxidation species (mmol/kg) by LC/MS at TCM