# Measuring air emissions and hazardous solvent impurities

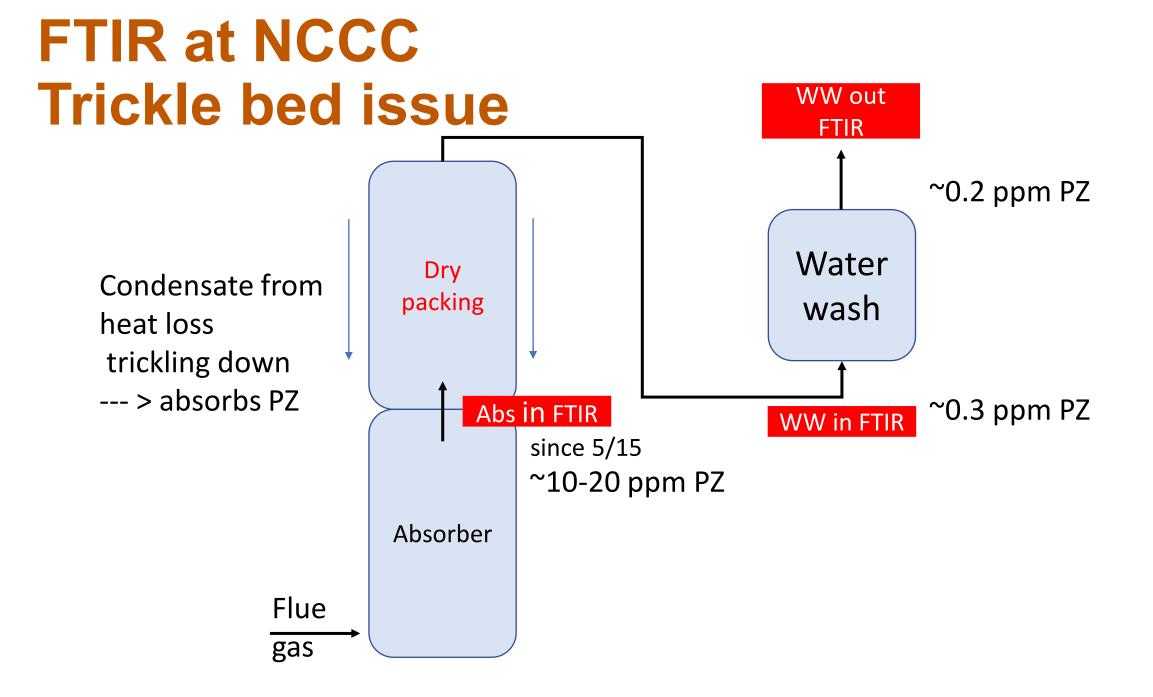
Gary T. Rochelle Texas Carbon Management Program Department of Chemical Engineering University of Texas at Austin Presented to DOE workshop June 8, 2023 Needs for additional stack & ambient measurements <u>Are nitrosamine emissions negligible?</u> <u>Can amine be reduced to <0.1 ppm?</u> <u>How do aldehyde emissions vary with what?</u>

- Continuous FTIR provides amine/ammonia values >1 ppm
  - \$150k/systemMay be useful for aldehydes
  - Used at NCCC, TCM, SRP, Tiller, etc.
- Batch adsorbent tube sampling provides greater sensitivity for many components; most suppliers use this at NCCC, etc.
- Proton Transfer Reaction/Time Of Flight/Mass Spectrometry
  - >1 ppt, can also monitor ambient air for amines and nitrosamines
  - \$600k/machine, several are available for ambient use in US
  - Used at TCM and other sites in Europe for source analysis by U Oslo
    - will be used at NCCC this summer.
  - PTR/TOF/MS should be used intermittently at all testing sites in U.S.

#### Liquid Phase Methods

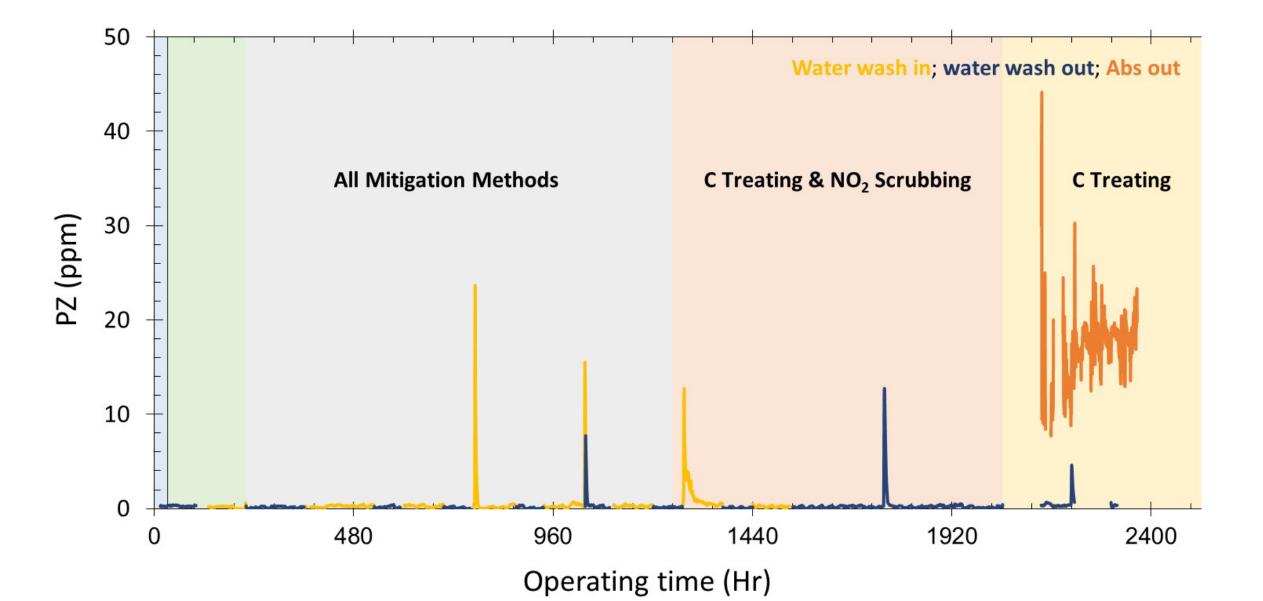
Does nitrosamine, aldehyde, or Cr make solvent spills hazardous? Are aldehyde emissions correlated with liquid phase aldehydes? How do dissolved aldehydes vary with conditions?

- Aldehydes by HPLC
- Nitrosamine by HPLC
- Metals by ICPMS ppb

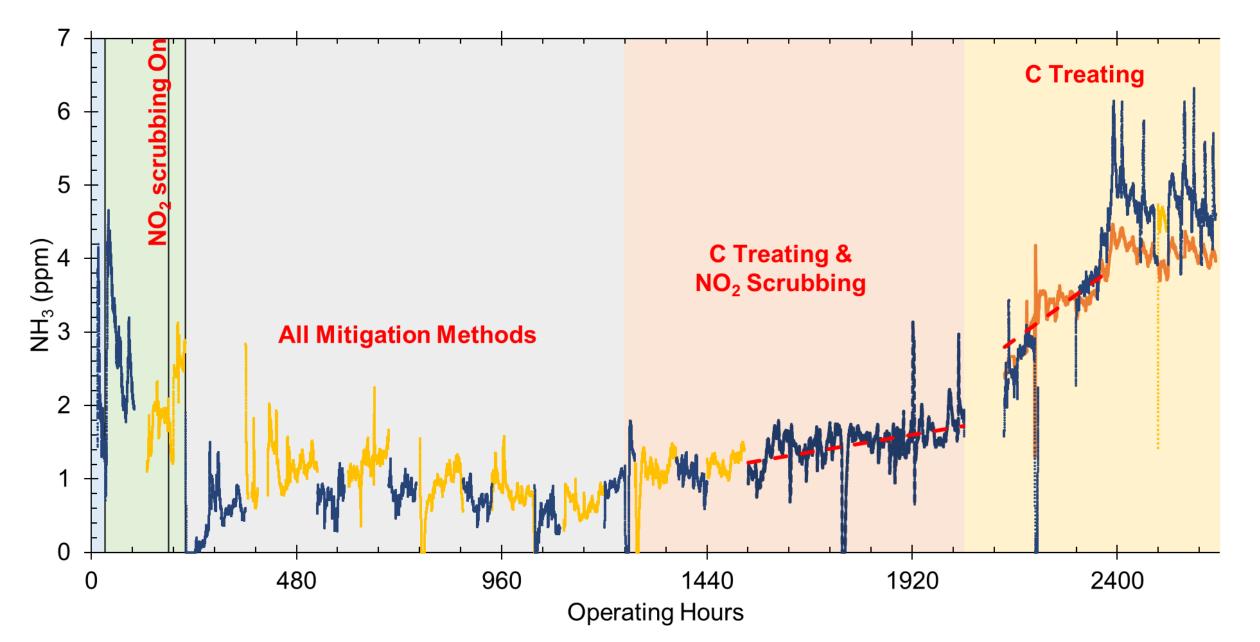




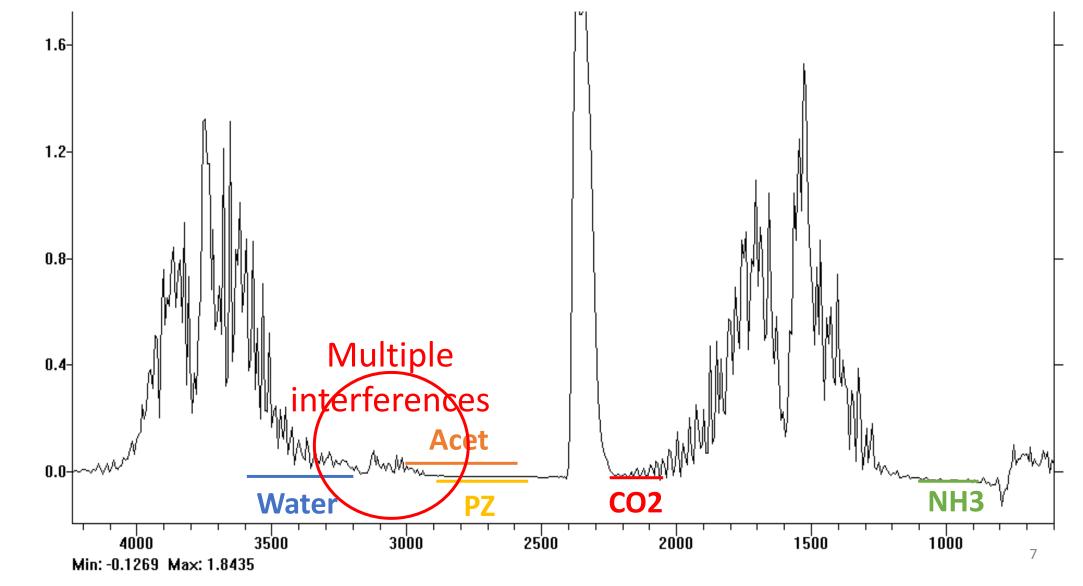
## PZ by FTIR at NCCC (2023)



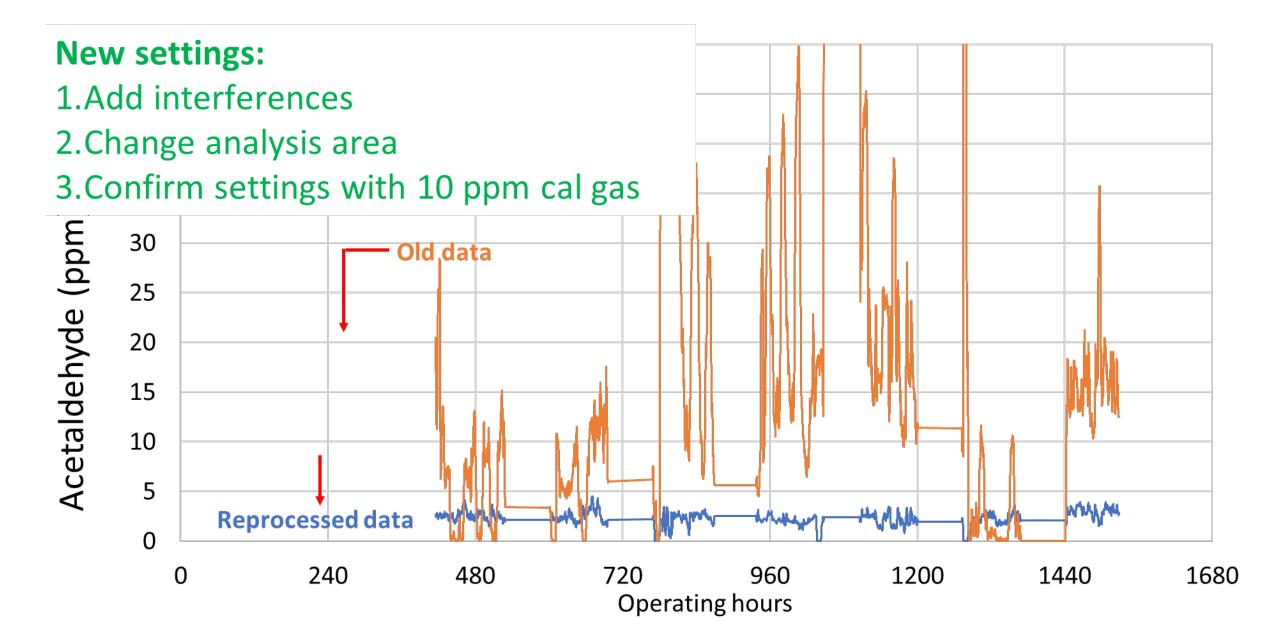
#### Ammonia by FTIR at NCCC 1<sup>st</sup> used by Goff (2004)



#### **FTIR regresses multicomponent spectra** Gas at 180°C, 5 I/min, includes vaporized aerosol

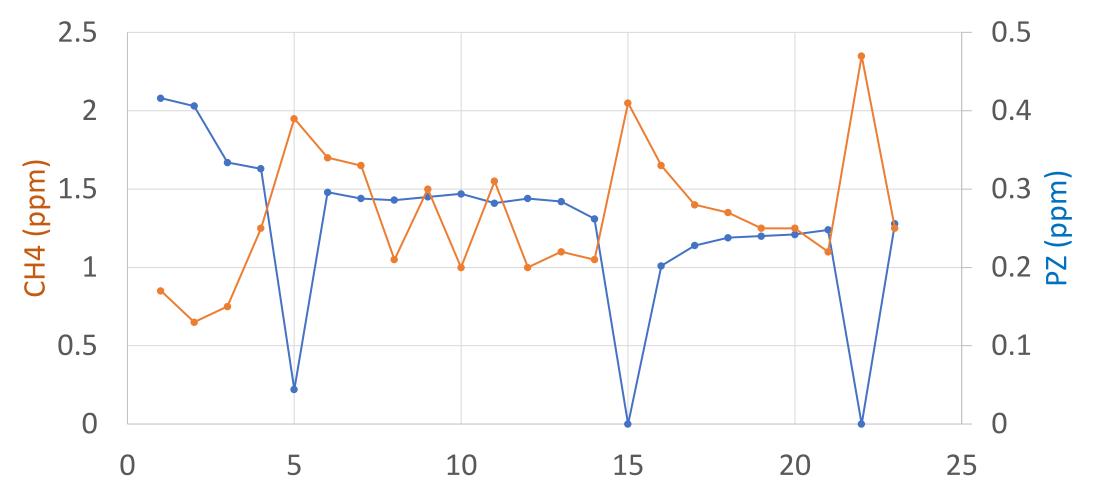


#### Acetaldehyde: Spectra interference

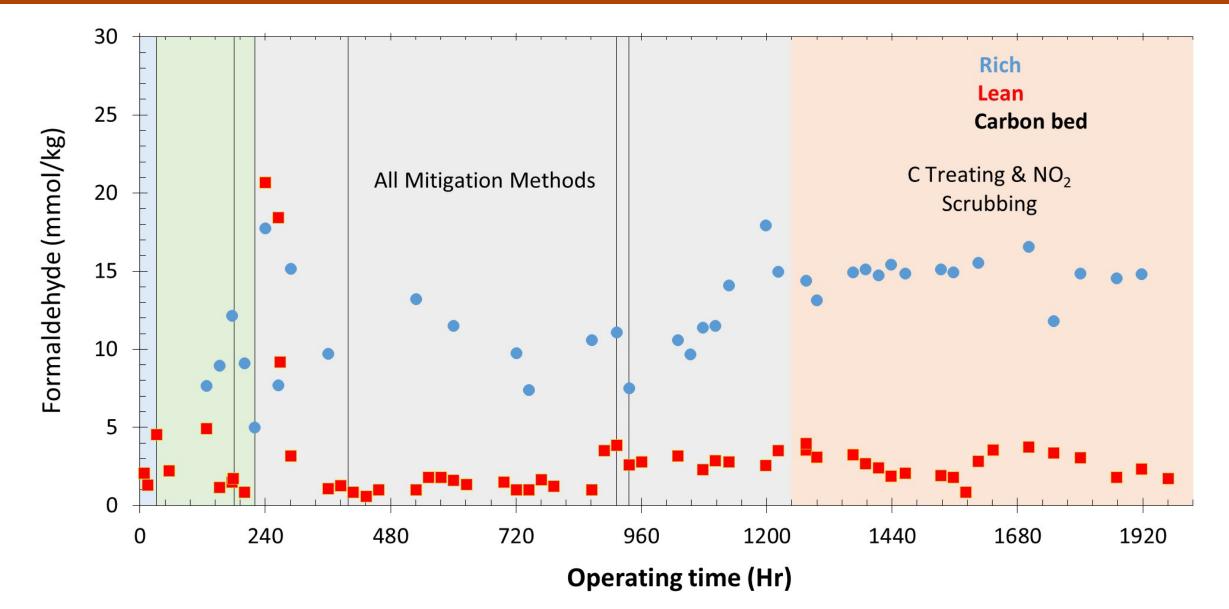


#### **PZ & CH<sub>4</sub>: Spectra interference**

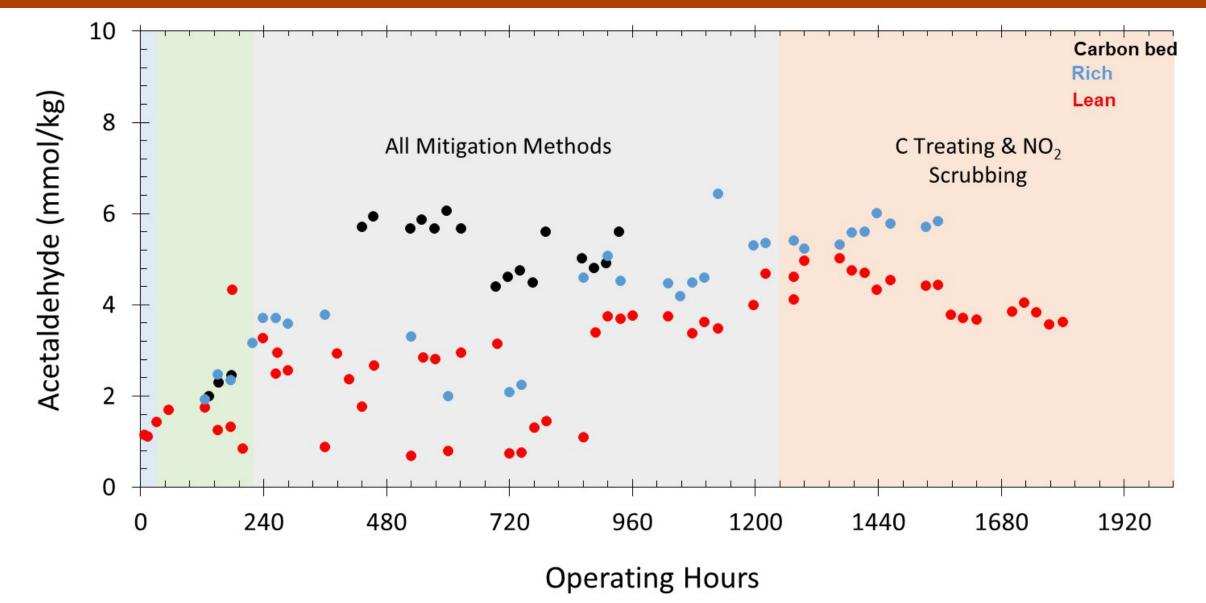
5/16 PZ and methane







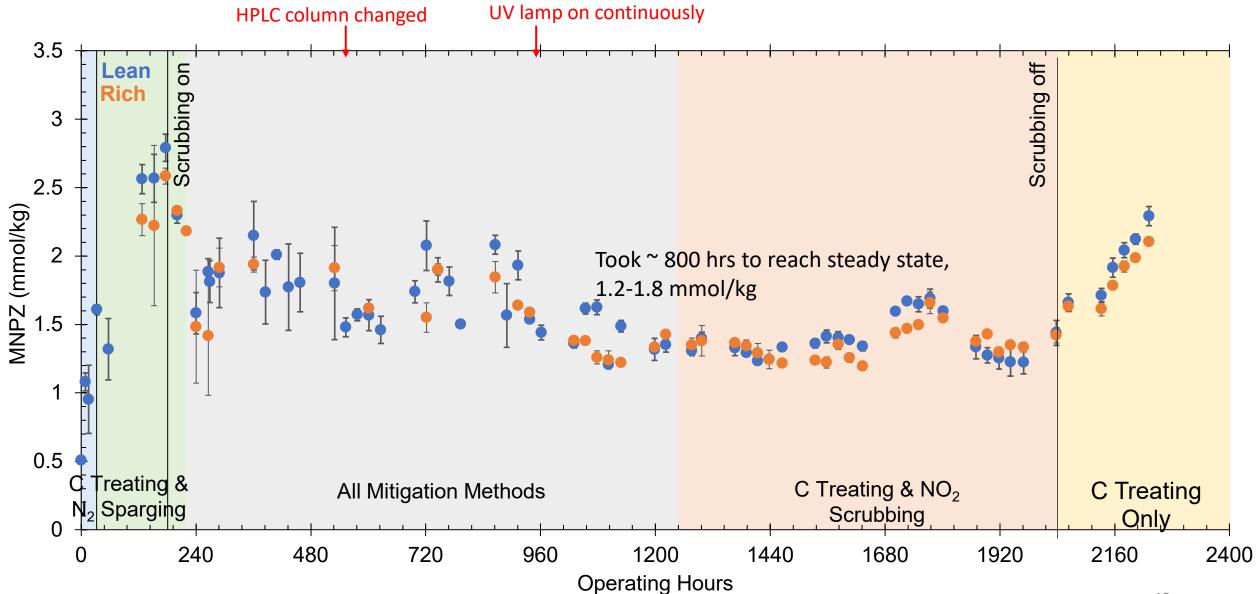




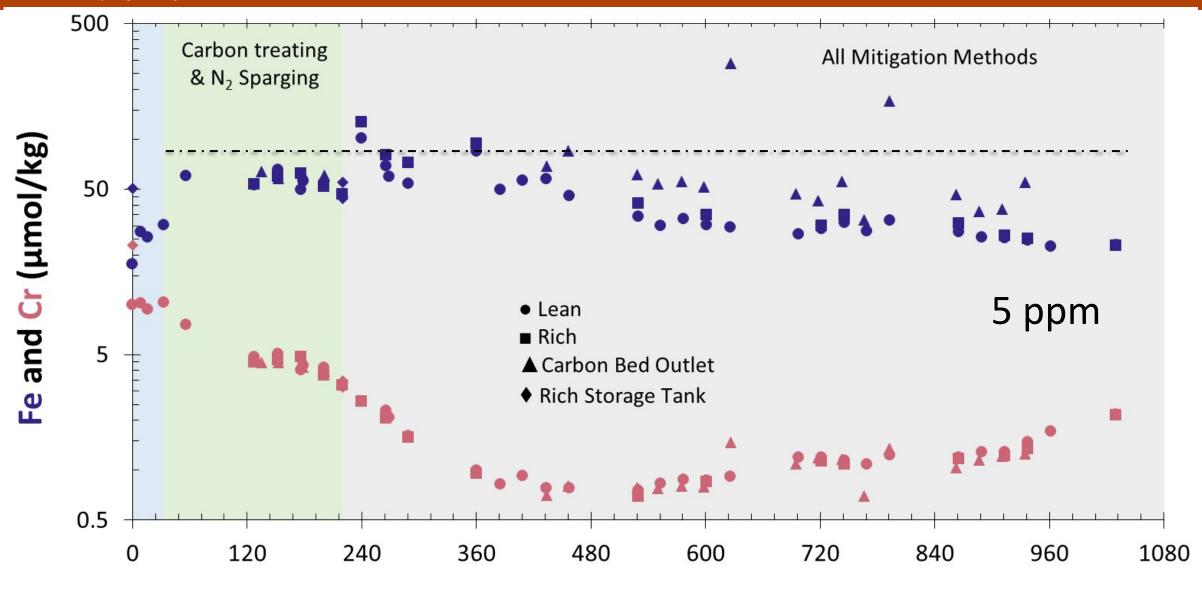
The University of Texas at Austin McKetta Department of Chemical Engineer

of Chemical Engineering

### Mononitrosopiperazine at NCCC (2023) by HPLC



# Iron and chromium by ICPMS



The University of Texas at Austin

McKetta Department

Cockrell School of Engineering

of Chemical Engineering

**Operating time (Hr)** 



# **Recommendations for Analytical Support**

- Gas Analyses
  - Intermittent by PTR-TOF-MS and by Batch Gas Sampling
  - Continuous by FTIR if sensitivity is adequate
- Liquid Analyses
  - Metals by ICPMS
  - Aldehydes by HPLC with DNPH
  - Specific nitrosamines by HPLC

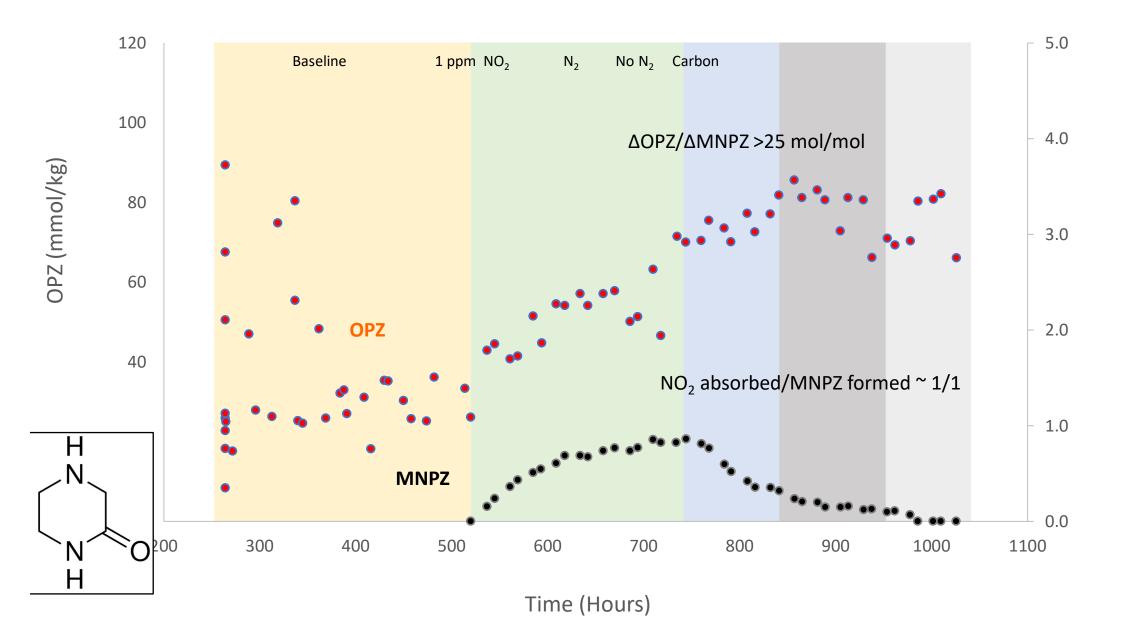


# **Backup slides**

# **FTIR in current NCCC campaign**

Locations	CO <sub>2</sub> product line	Absorber out	Water wash in	Water wash out	
Components	Water CO <sub>2</sub> PZ NH <sub>3</sub> Acetaldehyde		Water $CO/CO_2$ $NO/NO_2$ PZ $NH_3$ Formaldehyde Acetaldehyde $CH_4/C_2H_6$ EtO $CH_3OH/C_2H_5OH$ Acetic acid	→Zero	
Note		ine was moved to s out on 5/15	Share the same FTIR		

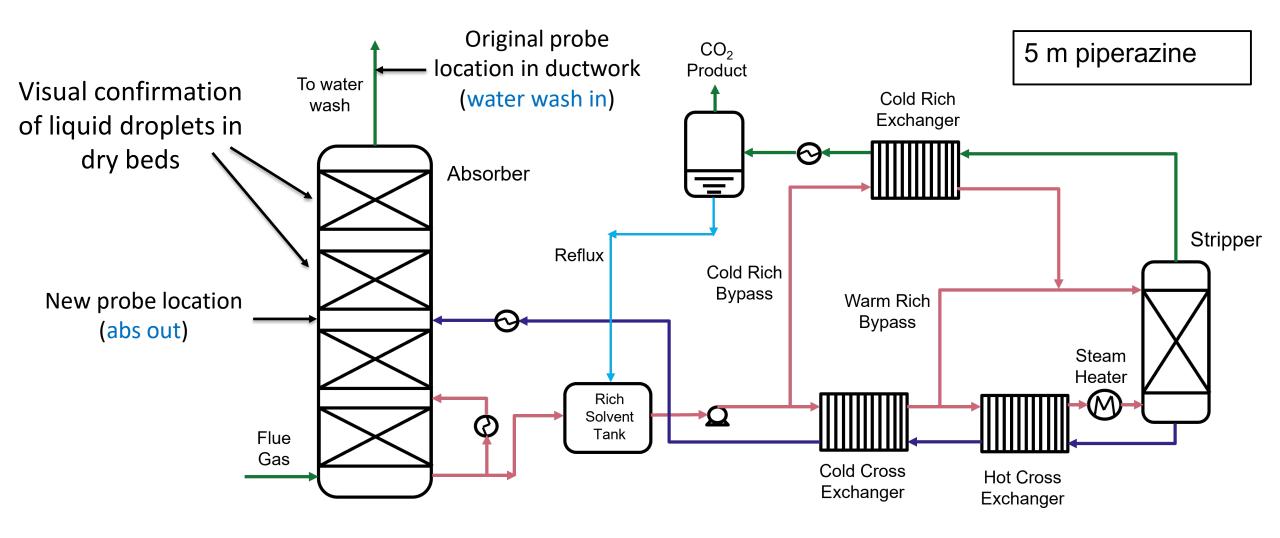
#### Oxopiperazine (OPZ) & mononitrosopiperazine (MNPZ) at SRP



MNPZ (mmol/kg)



# PZ by FTIR, sampling pts



## **Spectra interference**

cmet - [Analysis Informatio	on - UT-Austin-202	22.LIB]							-	$\Box$ $\times$
lit View Measure Op	tions Tools Wi	indow Help								
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Component	Compensation	Display	Ch(A)	Ch(M)	References	Interferences	Measuring ran	Analysis area 1	Analysis area 2	Analysis area 3
Water vapor H2O	wet	Always	-	-	22	2	0 - 30	-	-	3200 - 3401 (1.0)
Carbon dioxide CO2	wet	Always	-	-	10	2	0 - 25	-	2065 - 2245 (1.0)	-
Carbon monoxide CO	wet	Always	-	-	5	2	0 - 500	-	2000 - 2200 (1.0)	2540 - 2590 (1.0)
Nitrogen monoxide NO	wet	Always	-	-	4	3	0 - 200	-	1875 - 2138 (1.0)	-
Ammonia NH3	wet	Always	-	-	2	4	0 - 50	895 - 1100 (1.0)	-	-
Methane CH4	wet	Always	-	-	3	3	0 - 100	-	-	2600 - 3200 (1.0)
Ethane C2H6	wet	Always	-	-	2	3	0 - 50	-	-	2600 - 3200 (1.0)
Formaldehyde CHOH	wet	Always	-	-	2	3	0 - 50	-	-	2550 - 2850 (1.0)
PZ	wet	Always	-	-	6	9	0 - 100	-	2550 - 2890 (1.0)	-
Acetaldehyde	wet	Always	-	-	5	9	0 - 100	-	-	2600 - 3000 (1.0)
EtO	wet	Always	-	-	3	10	0 - 100	-	-	2850 - 3200 (1.0)
Methanol CH40	wet	Always	-	-	3	10	0 - 100	-	-	2725 - 3150 (1.0)
Ethanol C2H6O	wet	Always	-	-	2	10	0 - 100	-	-	2700 - 3100 (1.0)
Acetic acid C2H4O2	wet	Always	-	-	2	9	0 - 100	-	1800 - 2200 (1.0)	-
NOx as NO2	wet	Always	-	-	С	1	0 - 200	-	-	-
TOC	wet	Always	-	-	С	3	0 - 50	-	-	-
Ambient pressure	N/A	Always	-	-	S	-	150 - 1150	-	-	-
Cell temperature	N/A	Always	-	-	S	-	0 - 200	-	-	-
	dit View Measure Op Component Water vapor H2O Carbon dioxide CO2 Carbon monoxide CO Carbon monoxide CO Nitrogen monoxide NO Ammonia NH3 Methane CH4 Ethane CH4 Ethane C2H6 Formaldehyde CHOH PZ Acetaldehyde EtO Methanol CH4O Ethanol C2H6O Acetic acid C2H4O2 NOx as NO2 TOC Ambient pressure	dit View Measure Options Tools Will   Image: Second s	Image: ComponentComponentComponentImage: ComponentImage: Component <td>dit View Measure Options Tools Window Help   Image: Image:</td> <td>dit View Measure Options Tools Window Help   Image: Second Second</td> <td>dit View Measure Options Tools Window Help   Image: Second Line Secon</td> <td>dit View Measure Options Tools Window Help   Image: Component Image: Component Component Component Component Always - - 22 2   Carbon dioxide CO2 wet Always - - 22 2 2   Carbon monoxide CO wet Always - - 10 2   Carbon monoxide CO wet Always - - 4 3   Ammonia NH3 wet Always - - 4 3   Methane CH4 wet Always - - 2 3   Formaldehyde CHOH wet Always - - 2 3   PZ wet Always - - 2 3   PZ wet Always - - 2 3 3   PZ wet Always - - 2 3 10   Methanol CH40 wet Always - - 3 10 3</td> <td>View Measure Options Tools Window Help   Image: Component Component Component Component Normal Stress Ch(A) Ch(M) References Interferences Measuring ran   Water vapor H2O wet Always - - 22 2 0 - 30   Carbon dioxide CO2 wet Always - - 10 2 0 - 25   Carbon monoxide CO wet Always - - 4 3 0 - 200   Nitrogen monoxide NO wet Always - - 4 3 0 - 200   Ammonia NH3 wet Always - - 4 3 0 - 200   Methane CH4 wet Always - - 4 3 0 - 200   Methane CH6 wet Always - - 2 4 0 - 50   PZ wet Always - - 2 3 0 - 100   Acetaldehyde wet Always - - 5 9 0 - 1</td> <td>dit View Measure Options Tools Window Help   Image: Second Second</td> <td>it View Measure Options Tools Window Help   Image: Second Second</td>	dit View Measure Options Tools Window Help   Image:	dit View Measure Options Tools Window Help   Image: Second	dit View Measure Options Tools Window Help   Image: Second Line Secon	dit View Measure Options Tools Window Help   Image: Component Image: Component Component Component Component Always - - 22 2   Carbon dioxide CO2 wet Always - - 22 2 2   Carbon monoxide CO wet Always - - 10 2   Carbon monoxide CO wet Always - - 4 3   Ammonia NH3 wet Always - - 4 3   Methane CH4 wet Always - - 2 3   Formaldehyde CHOH wet Always - - 2 3   PZ wet Always - - 2 3   PZ wet Always - - 2 3 3   PZ wet Always - - 2 3 10   Methanol CH40 wet Always - - 3 10 3	View Measure Options Tools Window Help   Image: Component Component Component Component Normal Stress Ch(A) Ch(M) References Interferences Measuring ran   Water vapor H2O wet Always - - 22 2 0 - 30   Carbon dioxide CO2 wet Always - - 10 2 0 - 25   Carbon monoxide CO wet Always - - 4 3 0 - 200   Nitrogen monoxide NO wet Always - - 4 3 0 - 200   Ammonia NH3 wet Always - - 4 3 0 - 200   Methane CH4 wet Always - - 4 3 0 - 200   Methane CH6 wet Always - - 2 4 0 - 50   PZ wet Always - - 2 3 0 - 100   Acetaldehyde wet Always - - 5 9 0 - 1	dit View Measure Options Tools Window Help   Image: Second	it View Measure Options Tools Window Help   Image: Second



# **Spectra interference**

#### Injection 0.5-2 ppm PZ in Nitrogen...

end View	E Ana	alysis Results - UT-Austin-202	22.LIB: SAMPLE_0	5971.SPE	
(12:44:15, 0.77)	Ch	Component	Concentration	Unit	C C Compensation
% of range	1	Water vapor H2O	0.00	vol-%	wet
27 %	2	Carbon dioxide CO2	0.00	vol-%	wet
-	3	Carbon monoxide CO	0.00	ppm	wet
- //	5	Nitrogen monoxide NO	1.04	ppm	wet
	8	Ammonia NH3	0.06	ppm	wet
	11	Methane CH4	0.00	ppm	wet
16 %-	12 -5	Ethane C2H6	1.10	ppm	wet
- / MAII -	16	Formaldehyde CHOH	0.48	ppm	wet
	20	PZ	0.43	ppm	wet
	22	Acetaldehyde	0.27	ppm	wet
	23	EtO	0.22	ppm	wet
6%	24	Methanol CH4O	0.07	ppm	wet
	25	Ethanol C2H6O	0.00	ppm	wet
12:29:0012:34:0012:39:0012:44:0012:49:0012:54:00	26	Acetic acid C2H4O2	0.00	ppm	wet
	201	NOx as NO2	1.04	ppm	wet
	202	TOC	1 44	maC/	wet

#### Aldehydes by HPLC: +DNPH to detect with UV

