Measuring air emissions and hazardous solvent impurities

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Presented to DOE workshop
June 8, 2023

Needs for additional stack & ambient measurements

Are nitrosamine emissions negligible?

Can amine be reduced to <0.1 ppm?

How do aldehyde emissions vary with what?

- 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

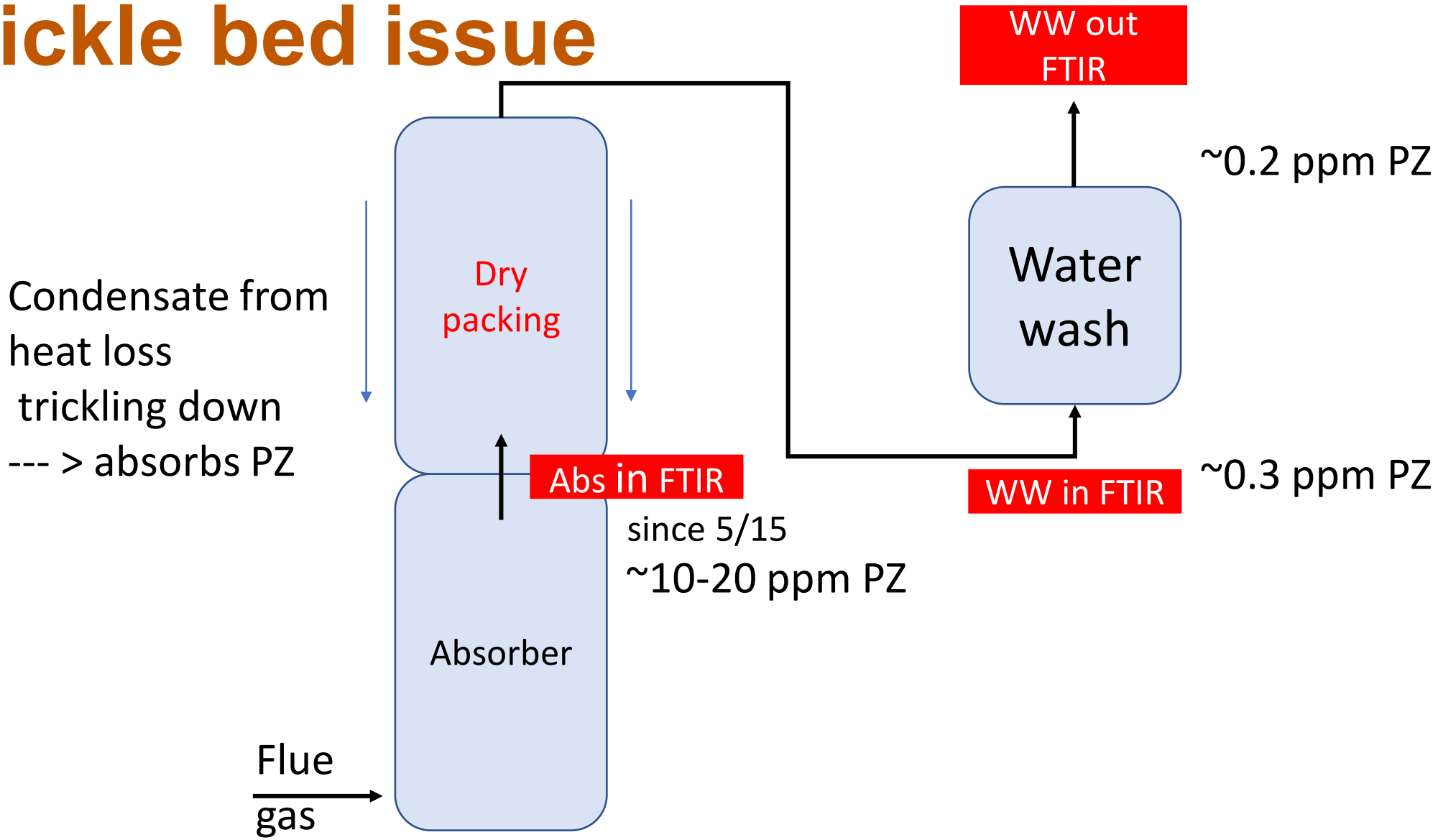
Does nitrosamine, aldehyde, or Cr make solvent spills hazardous?

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

FTIR at NCCC
Trickle bed issue



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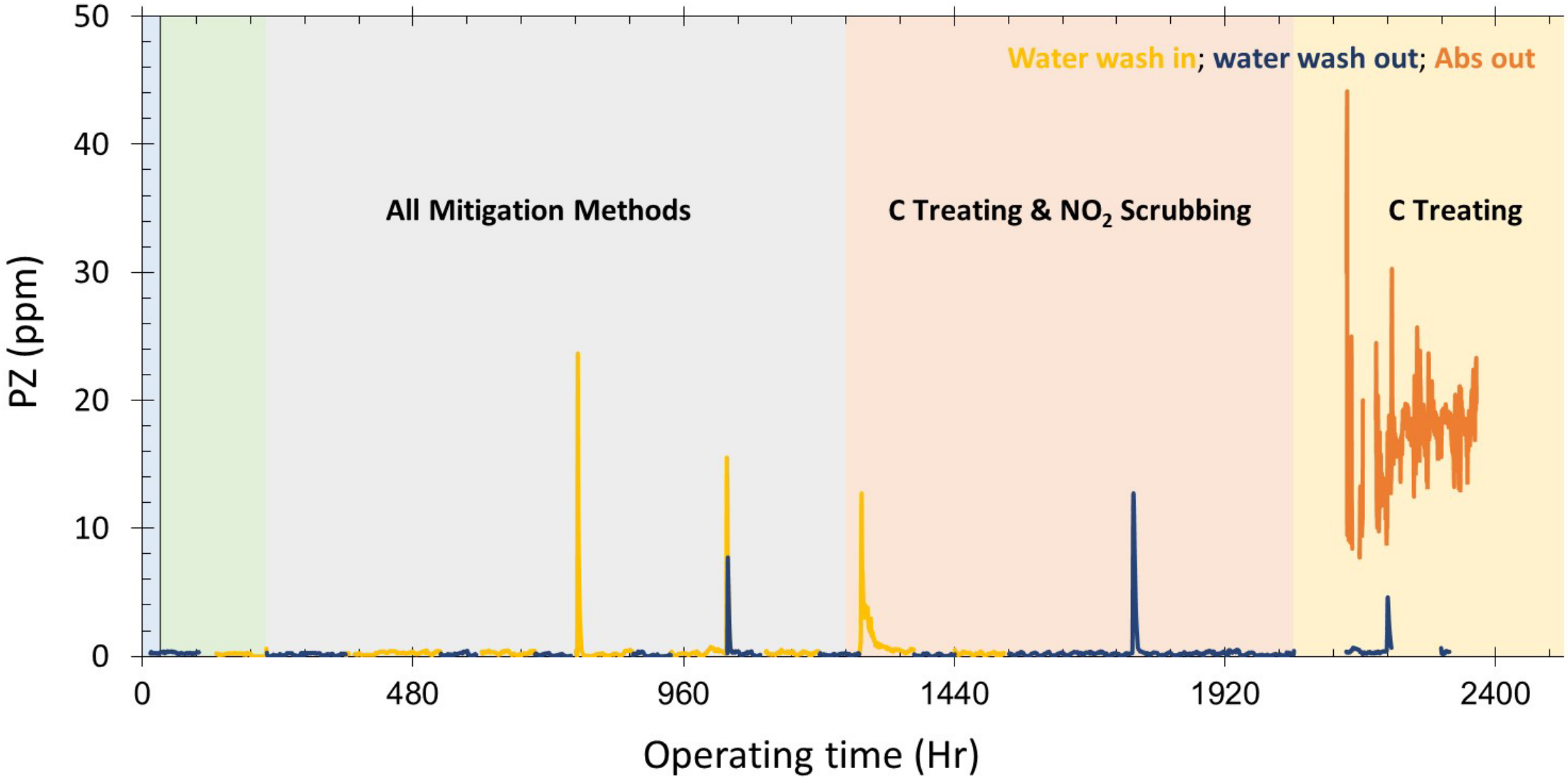
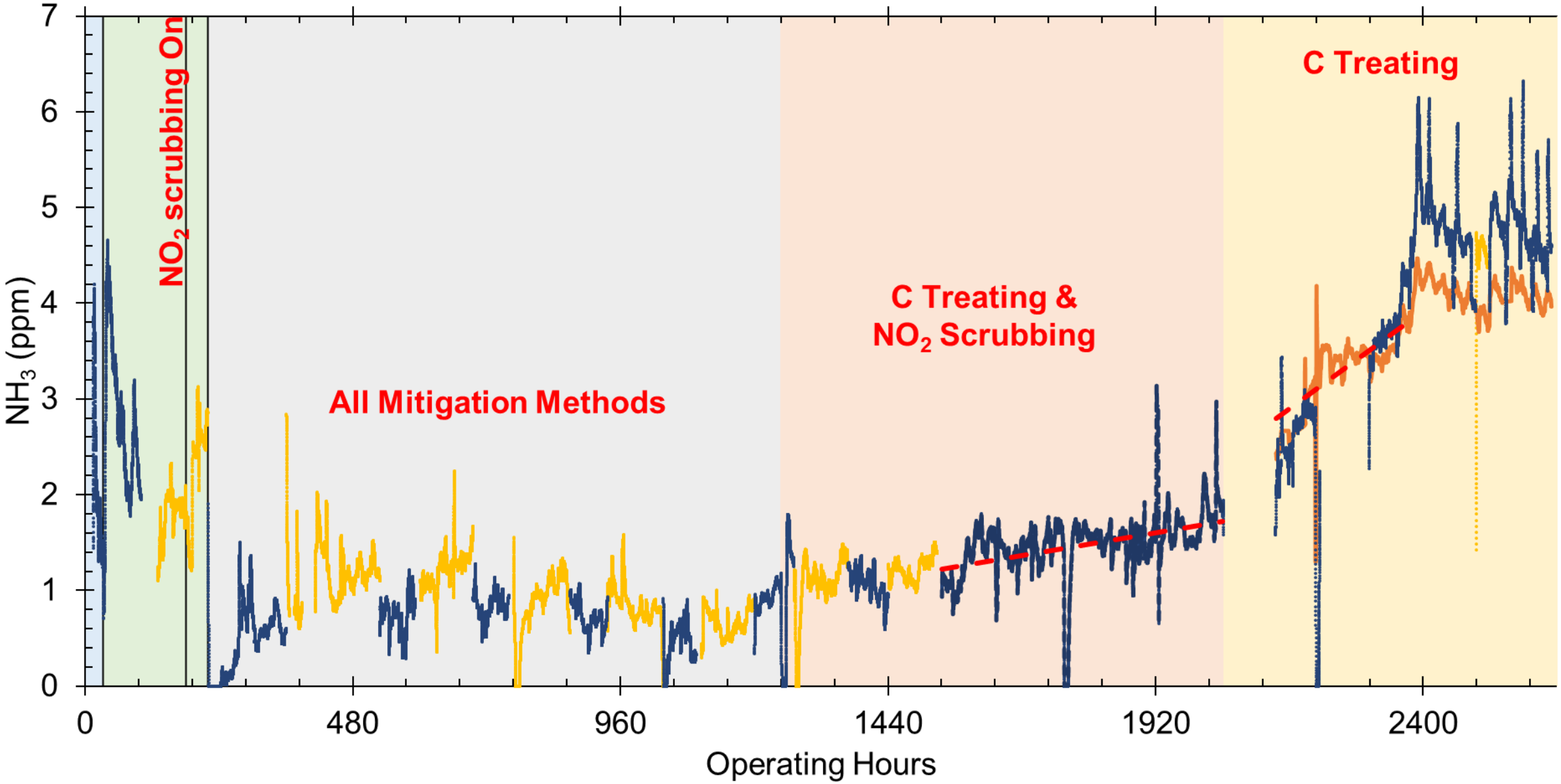
PZ by FTIR at NCCC (2023)

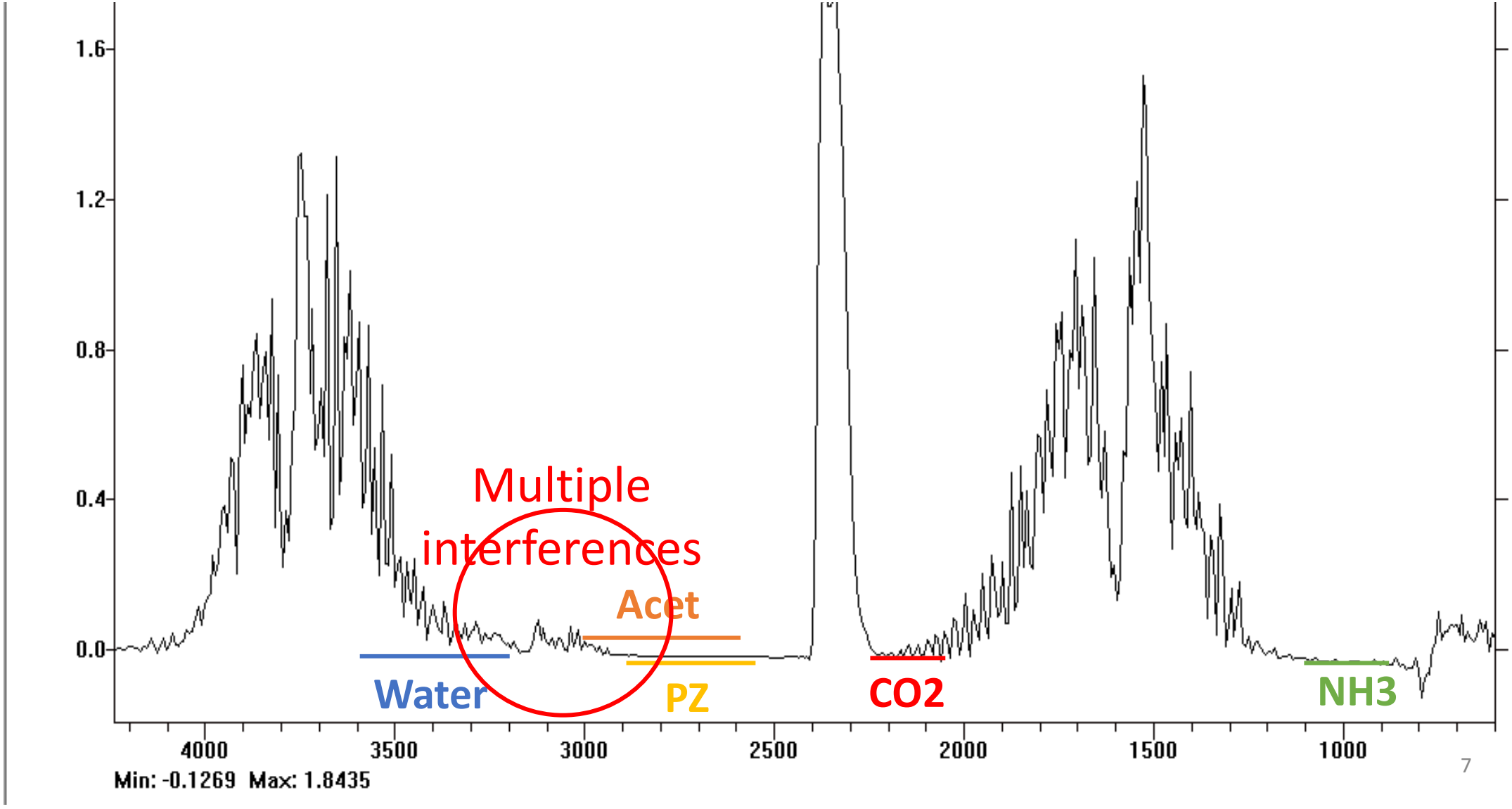


Ammonia by FTIR at NCCC 1st used by Goff (2004)



FTIR regresses multicomponent spectra

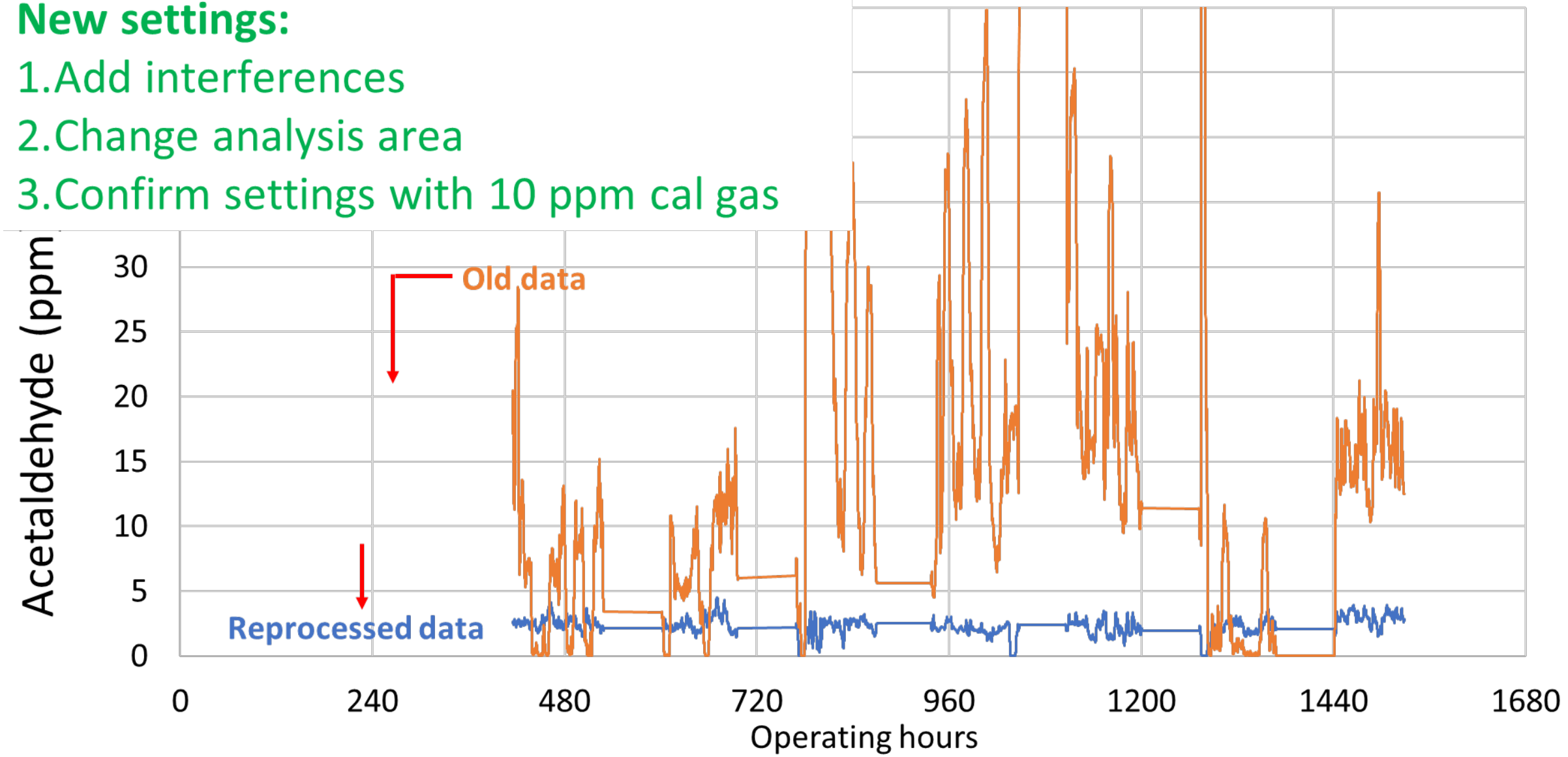
Gas at 180°C, 5 l/min, includes vaporized aerosol



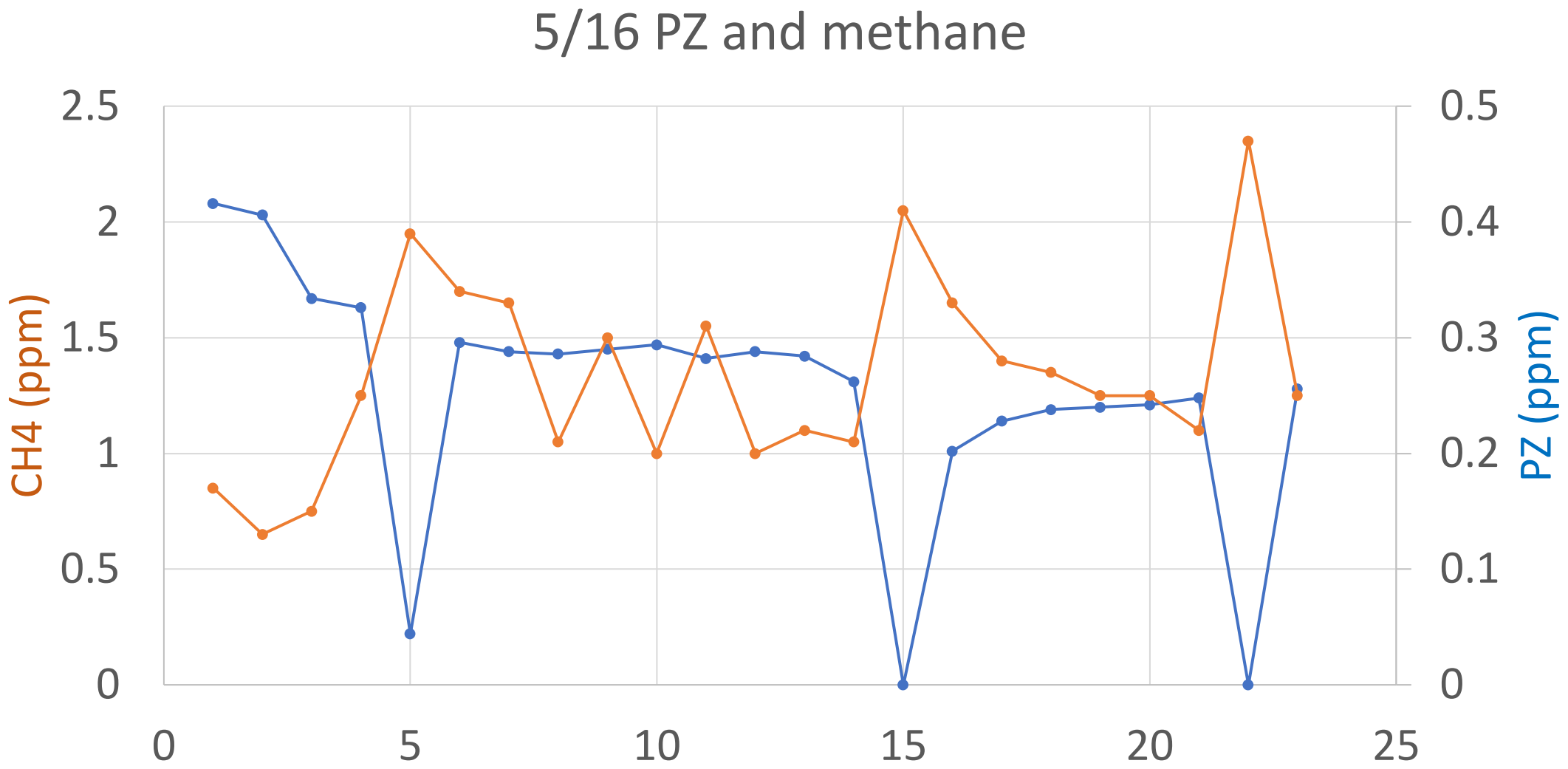
Acetaldehyde: Spectra interference

New settings:

1. Add interferences
2. Change analysis area
3. Confirm settings with 10 ppm cal gas



PZ & CH_4: Spectra interference



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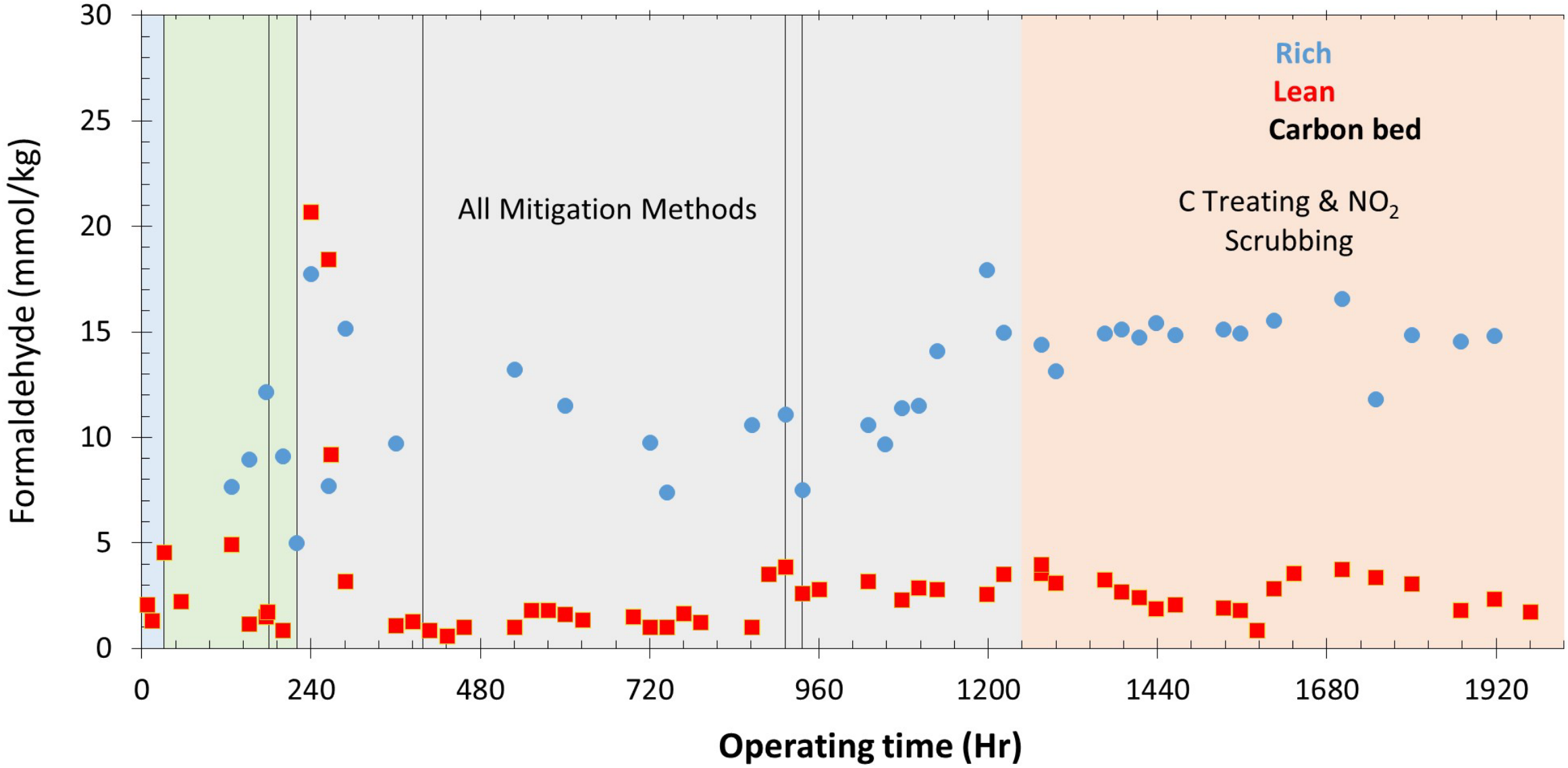
Formaldehyde by HPLC at NCCC (2023)



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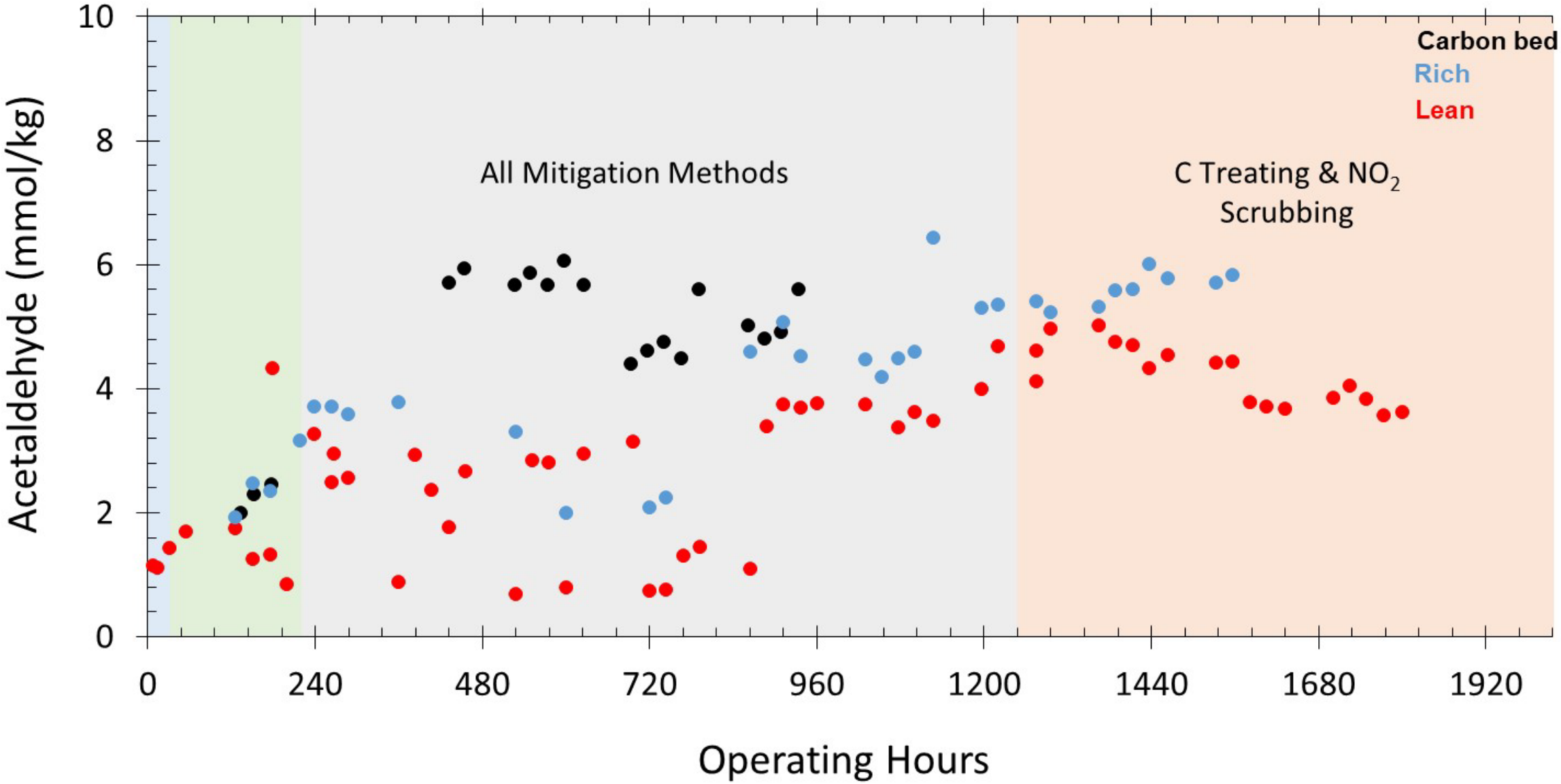
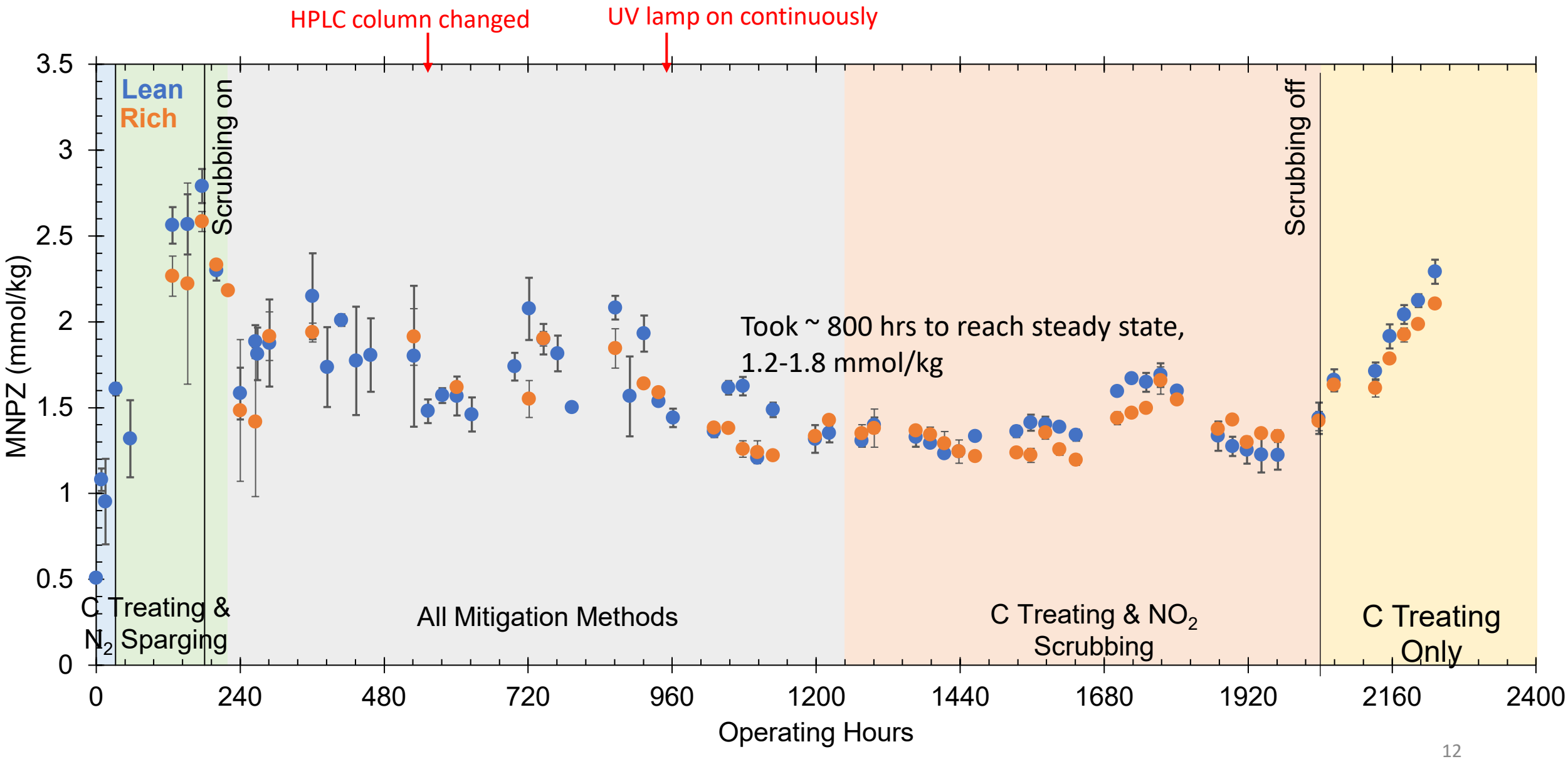
Acetaldehyde by HPLC at NCCC (2023)



Mononitrosopiperazine at NCCC (2023) by HPLC



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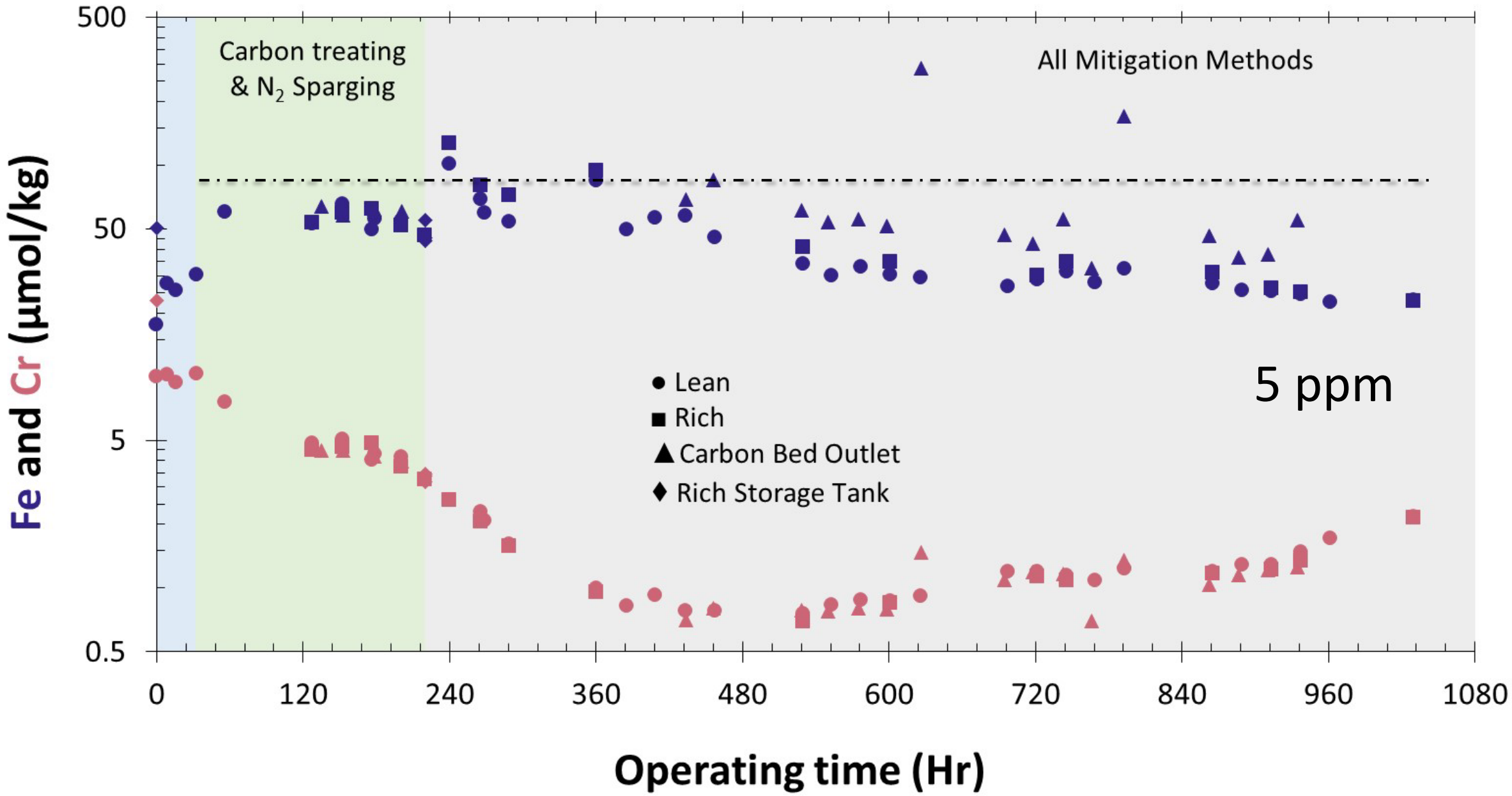
Iron and chromium by ICPMS



Recommendations for Analytical Support

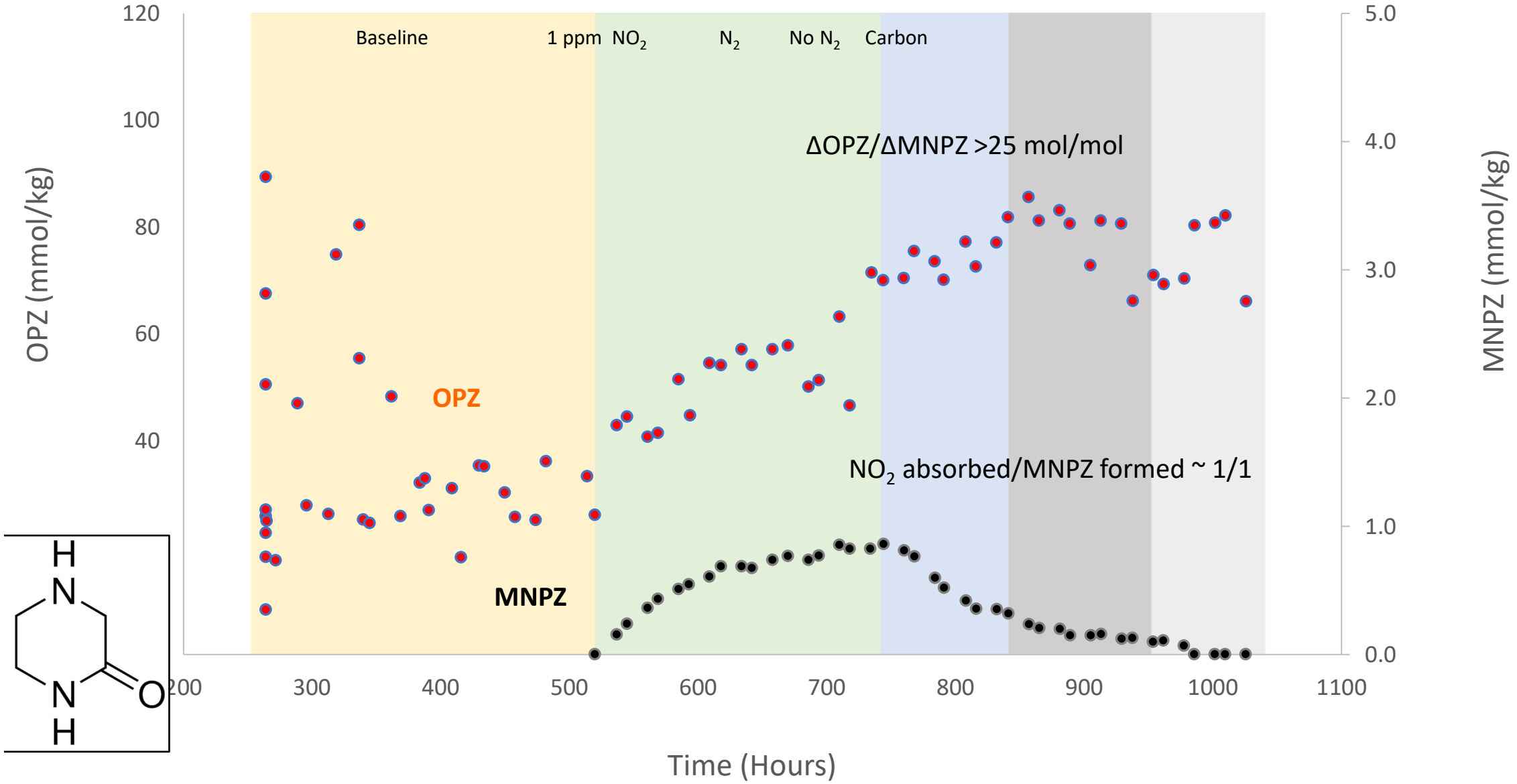
- Gas Analyses
  - Intermittent by PTR-TOF-MS and by Batch Gas Sampling
  - Continuous by FTIR if sensitivity is adequate
- Liquid Analyses
  - Metals by ICPMS
  - Aldehydes by HPLC with DNPH
  - Specific nitrosamines by HPLC

Backup slides

FTIR in current NCCC campaign

Locations	CO_2 product line	Absorber out	Water wash in	Water wash out
Components	Water CO_2 PZ NH_3 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	FTIR at the CO_2 line was moved to measure Abs out on 5/15		Share the same FTIR	

Oxopiperazine (OPZ) & mononitrosopiperazine (MNPZ) at SRP



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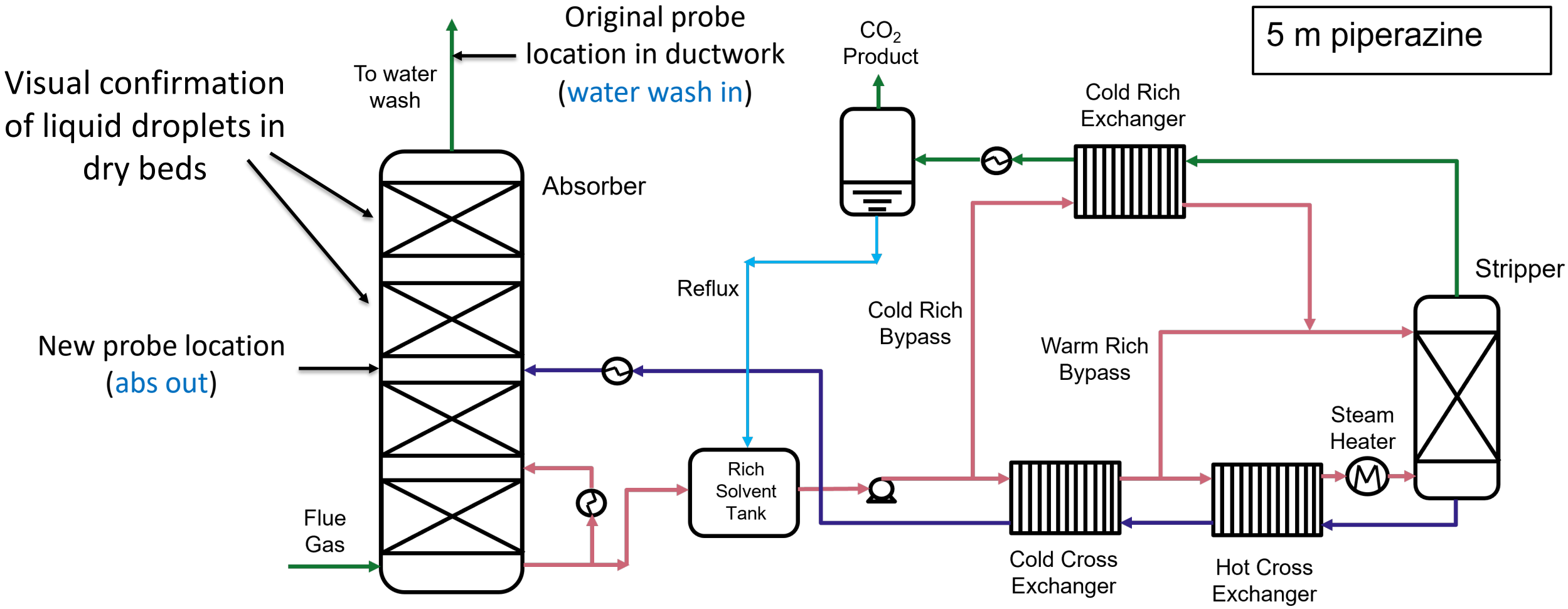
PZ by FTIR, sampling pts



Spectra interference

Calcmet - [Analysis Information - UT-Austin-2022.LIB]

File Edit View Measure Options Tools Window Help

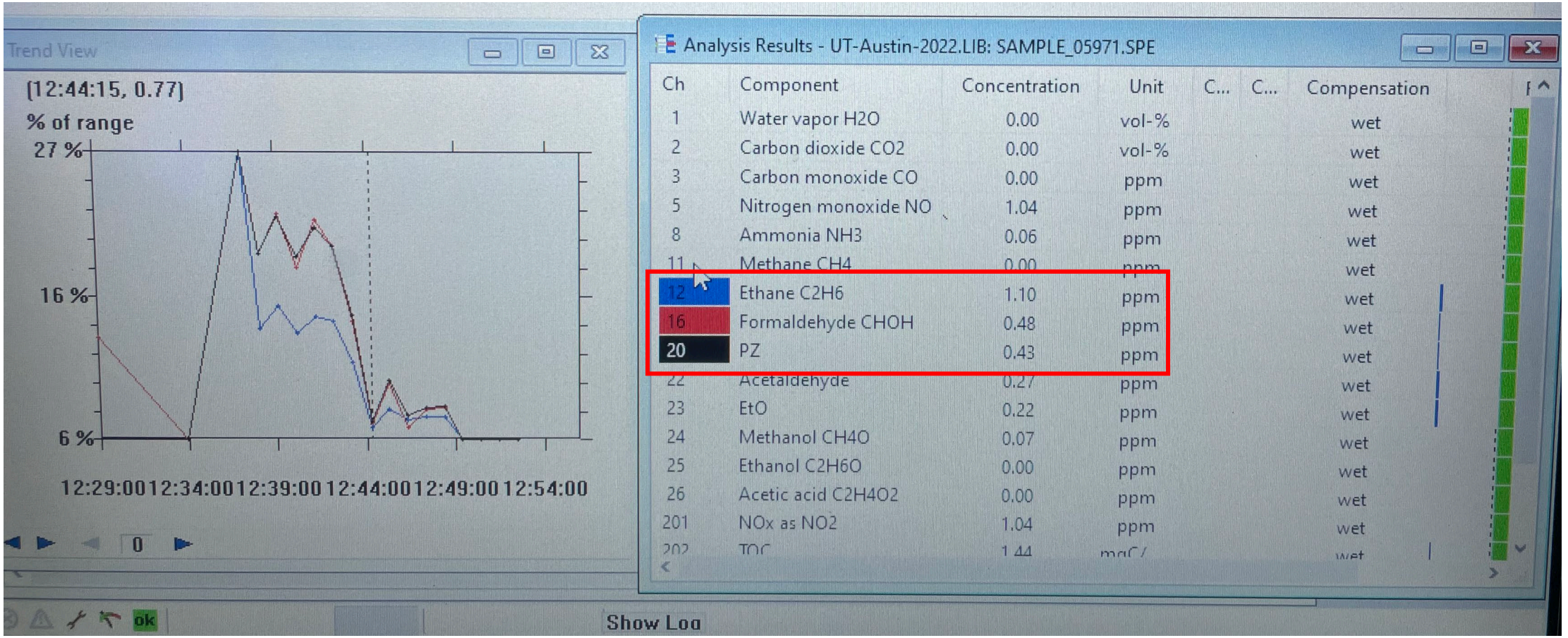
1s 5s 20s 1M 3M

Ch	Component	Compensation	Display	Ch(A)	Ch(M)	References	Interferences	Measuring ran...	Analysis area 1	Analysis area 2	Analysis area 3
1	Water vapor H2O	wet	Always	-	-	22	2	0 - 30	-	-	3200 - 3401 (1.0)
2	Carbon dioxide CO2	wet	Always	-	-	10	2	0 - 25	-	2065 - 2245 (1.0)	-
3	Carbon monoxide CO	wet	Always	-	-	5	2	0 - 500	-	2000 - 2200 (1.0)	2540 - 2590 (1.0)
5	Nitrogen monoxide NO	wet	Always	-	-	4	3	0 - 200	-	1875 - 2138 (1.0)	-
8	Ammonia NH3	wet	Always	-	-	2	4	0 - 50	895 - 1100 (1.0)	-	-
11	Methane CH4	wet	Always	-	-	3	3	0 - 100	-	-	2600 - 3200 (1.0)
12	Ethane C2H6	wet	Always	-	-	2	3	0 - 50	-	-	2600 - 3200 (1.0)
16	Formaldehyde CHOH	wet	Always	-	-	2	3	0 - 50	-	-	2550 - 2850 (1.0)
20	PZ	wet	Always	-	-	6	9	0 - 100	-	2550 - 2890 (1.0)	-
22	Acetaldehyde	wet	Always	-	-	5	9	0 - 100	-	-	2600 - 3000 (1.0)
23	EtO	wet	Always	-	-	3	10	0 - 100	-	-	2850 - 3200 (1.0)
24	Methanol CH4O	wet	Always	-	-	3	10	0 - 100	-	-	2725 - 3150 (1.0)
25	Ethanol C2H6O	wet	Always	-	-	2	10	0 - 100	-	-	2700 - 3100 (1.0)
26	Acetic acid C2H4O2	wet	Always	-	-	2	9	0 - 100	-	1800 - 2200 (1.0)	-
201	NOx as NO2	wet	Always	-	-	C	1	0 - 200	-	-	-
202	TOC	wet	Always	-	-	C	3	0 - 50	-	-	-
221	Ambient pressure	N/A	Always	-	-	S	-	150 - 1150	-	-	-
226	Cell temperature	N/A	Always	-	-	S	-	0 - 200	-	-	-

➡ Residuals are low at this moment, data have a certain reliability

Spectra interference

Injection 0.5-2 ppm PZ in Nitrogen…



Aldehydes by HPLC: +DNPH to detect with UV