Intra-catalyst Reductant Chemistry in Lean NOx Traps: A Study on Sulfur Effects

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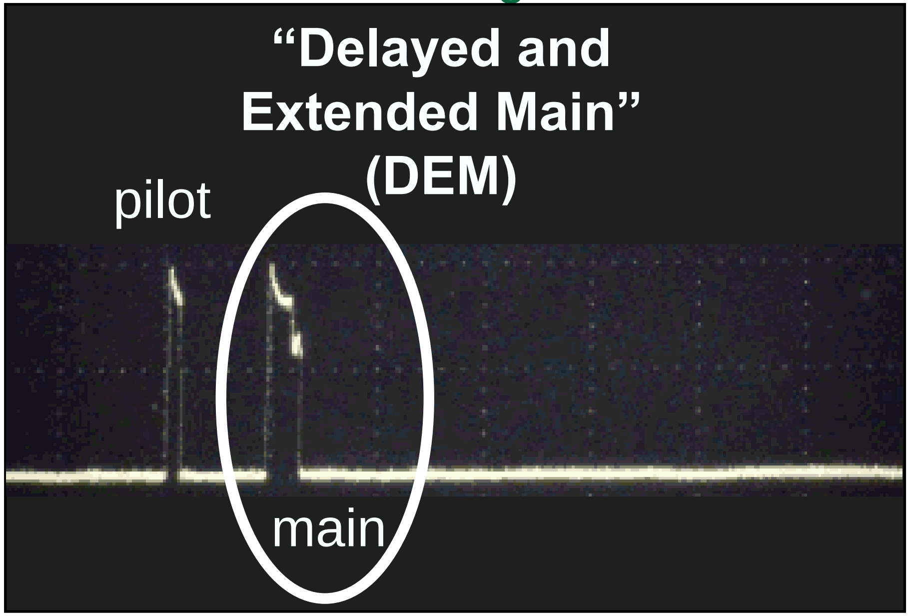
Study Focus Area: Sulfur Effects on Reductant Utilization by Lean NOx Trap Catalysts

- **Lean NOx Trap (LNT) catalysts are effective at reducing NOx from diesel engines but need…**
  - **Periodic "regeneration" (rich exhaust) with suitable reductants**
  - **Durability against negative sulfur effects**
    - **Sulfur degrades performance over time by poisoning NOx sites**
    - **deSulfation (high temperature clean up) recovers lost site activity**

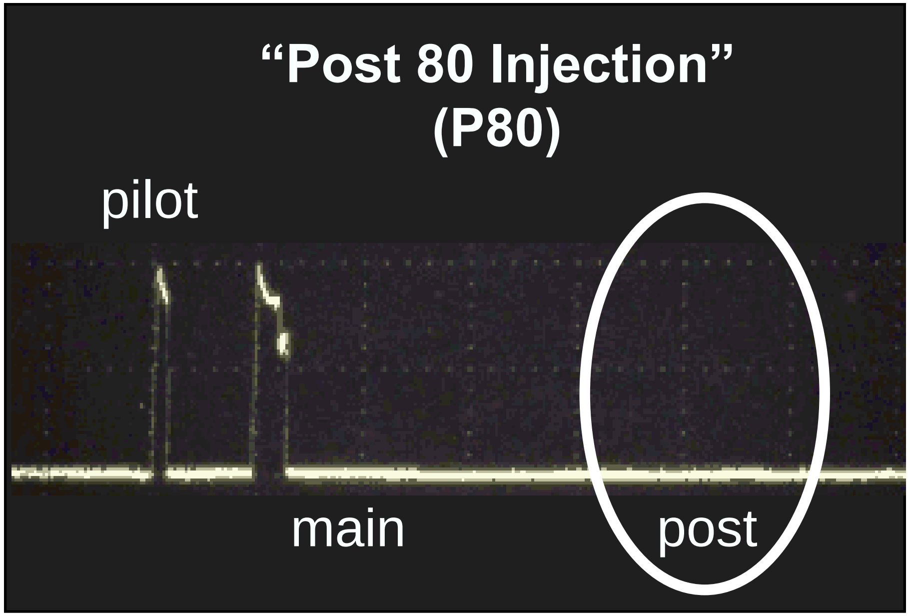
- **ORNL has studied regeneration chemistry on a light-duty diesel engine platform with in-cylinder combustion techniques**
  - **Intra-catalyst sampling has been applied to characterize reductant utilization [SAE 2006-01-1416, SAE 2005-01-3876, SAE 2004-01-3023]**

- **Study presented here focuses on the effects of sulfur on intra-catalyst chemistry during in-cylinder regeneration**

Two engine control strategies for achieving intermittent rich combustion for regeneration of LNT



“Delayed and Extended Main” (DEM)

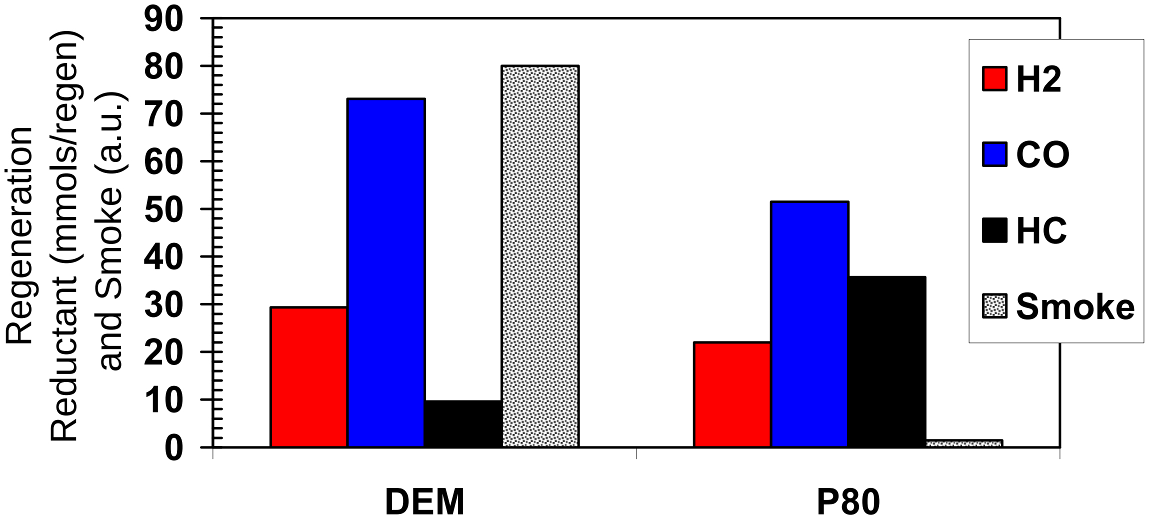


“Post 80 Injection” (P80)

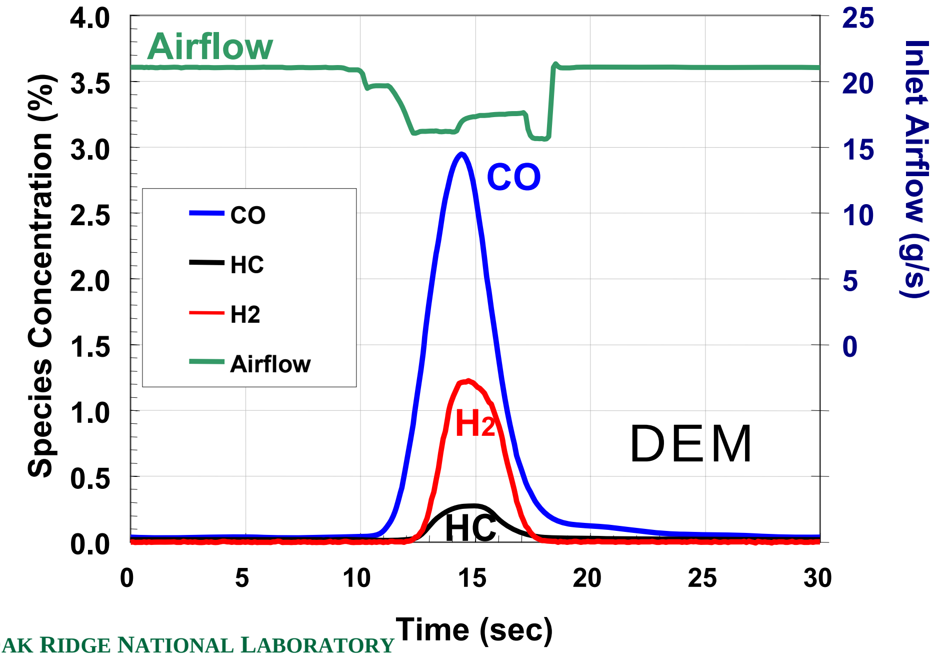
Two LNT Regeneration Strategies Chosen Based on Difference in Chemistry

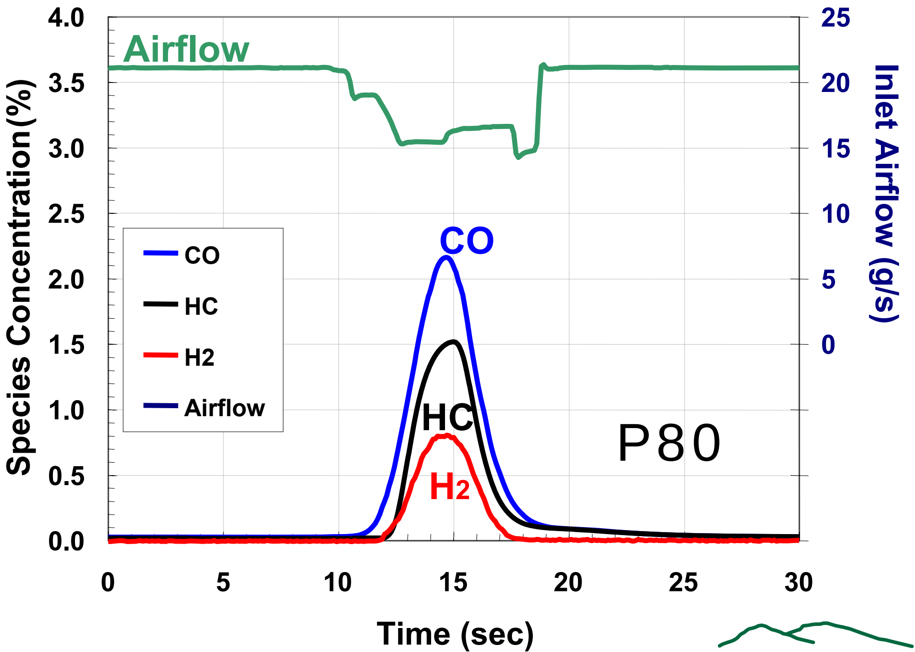
- **Delayed and Extended Main (DEM):**
  - **Throttle for reduced air flow**
  - **Extra fuel injected near main injection timing to achieve rich conditions**
- **Post 80 Injection (P80):**
  - **Throttle for reduced air flow**
  - **Extra fuel injected after main injection later in cycle to achieve rich conditions**

Two engine control strategies for achieving intermittent rich combustion for regeneration of LNT



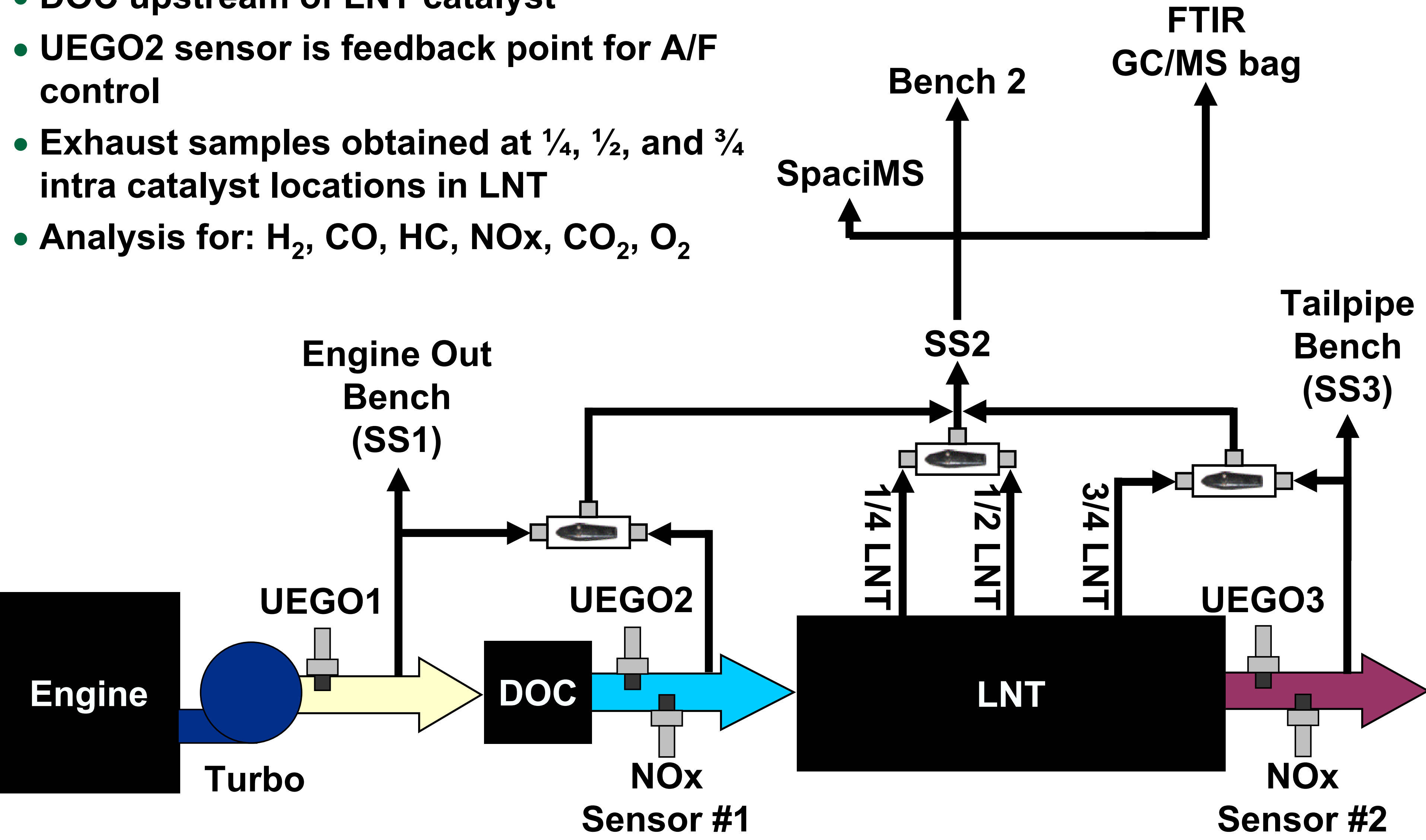
- **Delayed and Extended Main (DEM):**
  - **High H_2 and CO**
  - **Low HC**
  - **High PM**
- **Post 80 Injection (P80):**
  - **Moderate CO and H_2**
  - **High HC**
  - **Low PM**



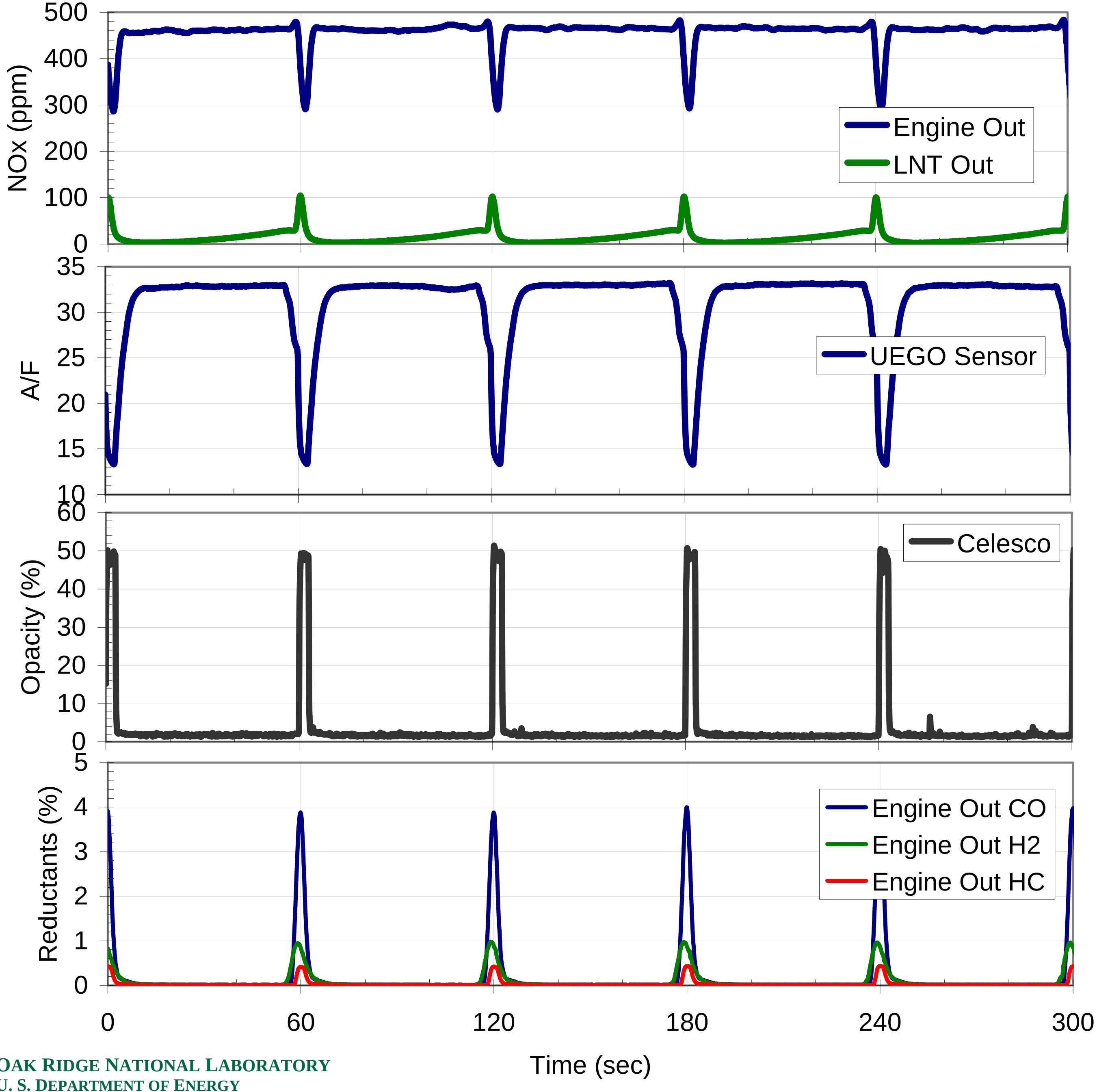


Experimental setup allows full exhaust species characterization throughout the catalyst system

- **DOC upstream of LNT catalyst**
- **UEGO2 sensor is feedback point for A/F control**
- **Exhaust samples obtained at ¼, ½, and ¾ intra catalyst locations in LNT**
- **Analysis for: H_2, CO, HC, NOx, CO_2, O_2**



Exhaust Speciation: DEM Strategy, 60s Cycle (DEM, 60s)



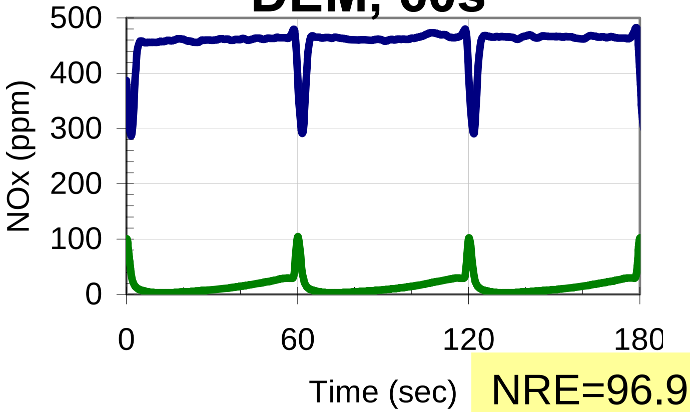
DEM, 60s

- NOx Reduction Efficiency (NRE)=96.9%
- Mean LNT Temp=329ºC
- Minimum A/F=13.5

- 60 second Cycle:
  - 57 seconds Lean
  - 3 seconds Rich

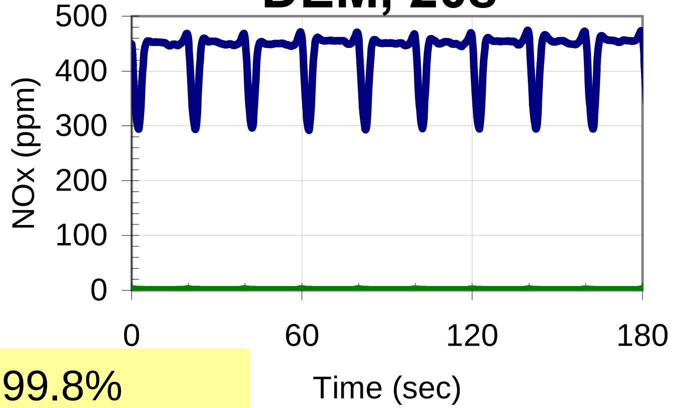
Strategy and Cycle Time Combinations in Study

DEM, 60s



NRE=96.9%
LNT Temp=329ºC
PM(relative)=0.46

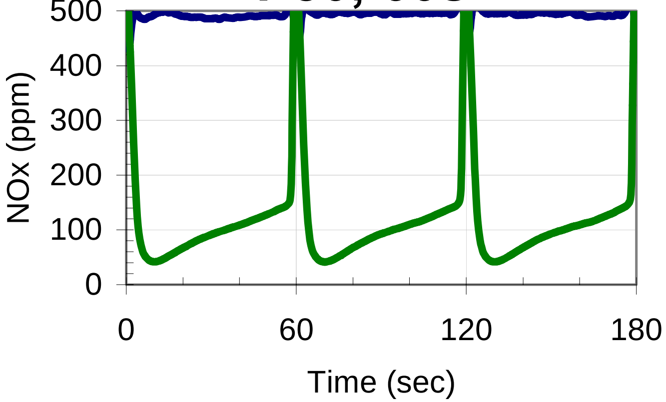
DEM, 20s



NRE=99.8%
LNT Temp=392ºC
PM(relative)=1.0

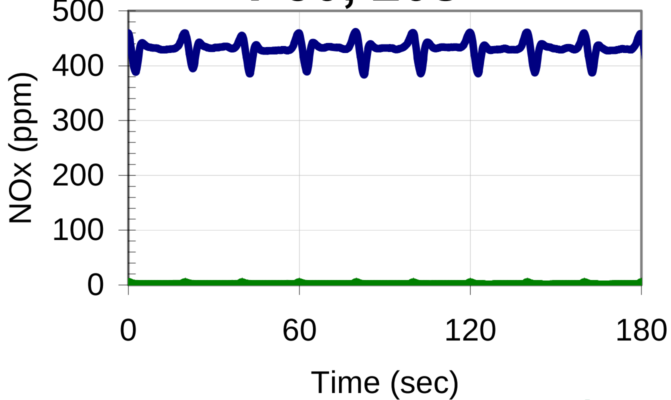
NRE=78.3%
LNT Temp=333ºC
PM(relative)=0.10

P80, 60s



NRE=99.3%
LNT Temp=434ºC
PM(relative)=0.09

P80, 20s



Catalyst chemistry characterized under sulfated and desulfated conditions

Sulfation procedure

- **Degreened in air**
- **BP15 fuel**
- **1% bottled SO_2 at 3.4slpm**
- **Three loading states (fuel S + bottled S)**
  - **3.06g S ≈ 2888 miles**
  - **5.63g S ≈ 5319 miles**
  - **9.63g S ≈ 9087 miles**
- **Full characterization done at each loading state**

Fuel loading

Fuel Flowrate	0.6 g/s
Fuel Economy (assumed)	45 mi/gal
BP 15 Sulfur Content	0.0015%
Fuel Density	0.143 gal/lb
Miles per gram S	944 mi/g
grams S /min	0.00054 g/min

Bottle loading

Molecular Weight of S	32.06 g/mol S
1% SO2 flowrate	3.4 slpm
SO2 concentration	1.00%
S flowrate	0.0486 g/min

	state 1	state 2	state 3
1% SO2 Injected (min)	28	45	60
Injected S (g)	1.35	2.18	2.92
Cumulative Engine S (hrs)	52.8	64.9	98.0
Cumulative Engine S (g)	1.71	2.10	3.18
Running Total S (g)	3.06	5.63	9.63
Equivalent miles	2888	5319	9087

Desulfation procedure

- **Engine based desulfation**
  - **Target 700°C / 14AFR**
  - **Fixed boost to 0kPa**
  - **Use RPM to control airflow**
  - **Control catalyst inlet AFR using in-pipe injection**
- **20 minute desulfation event**

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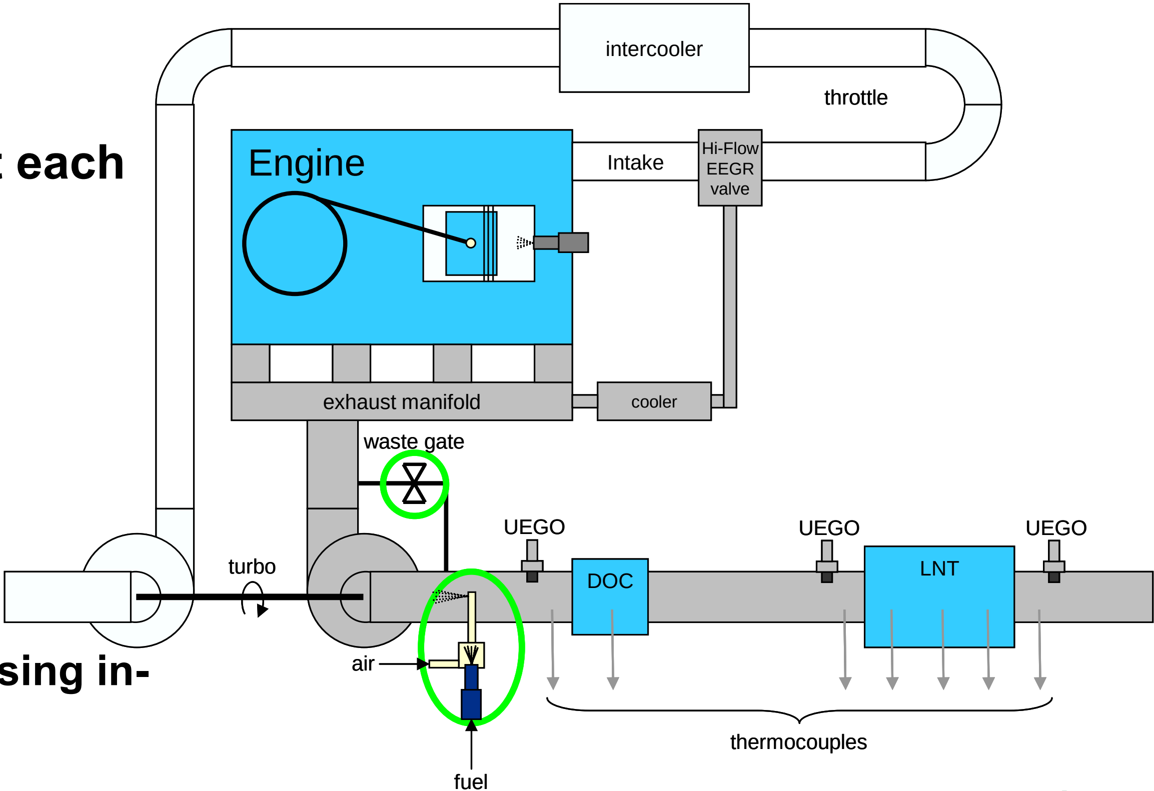
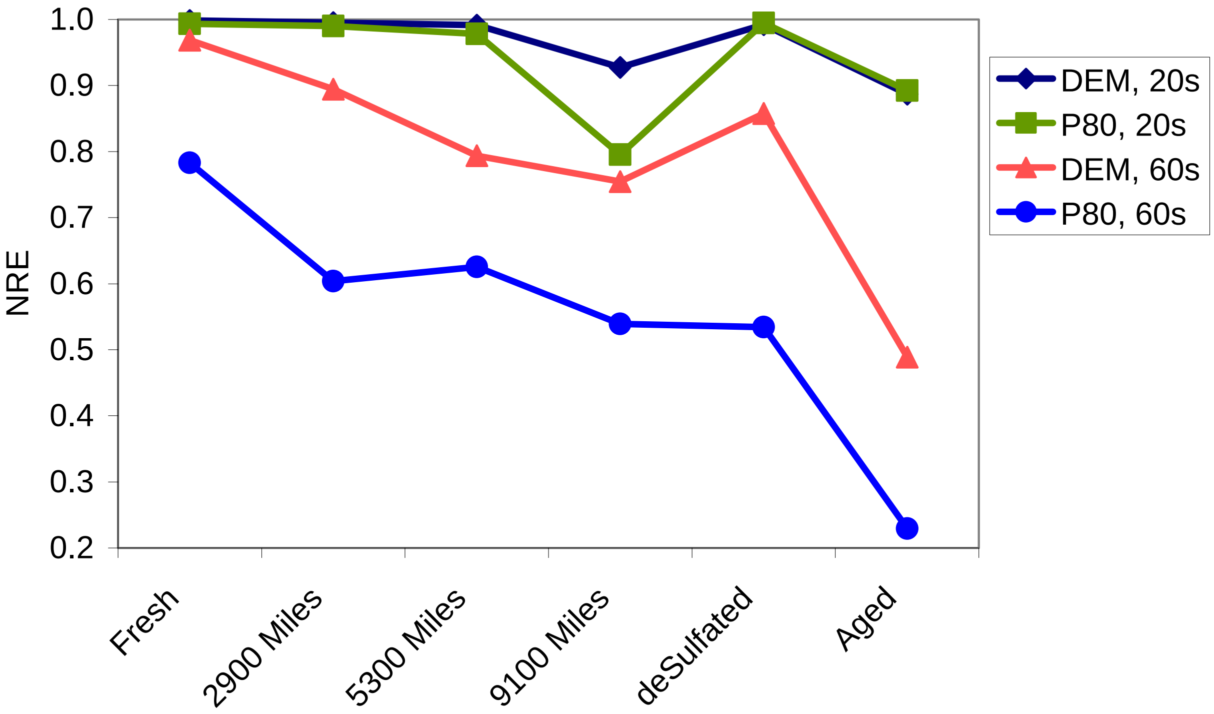
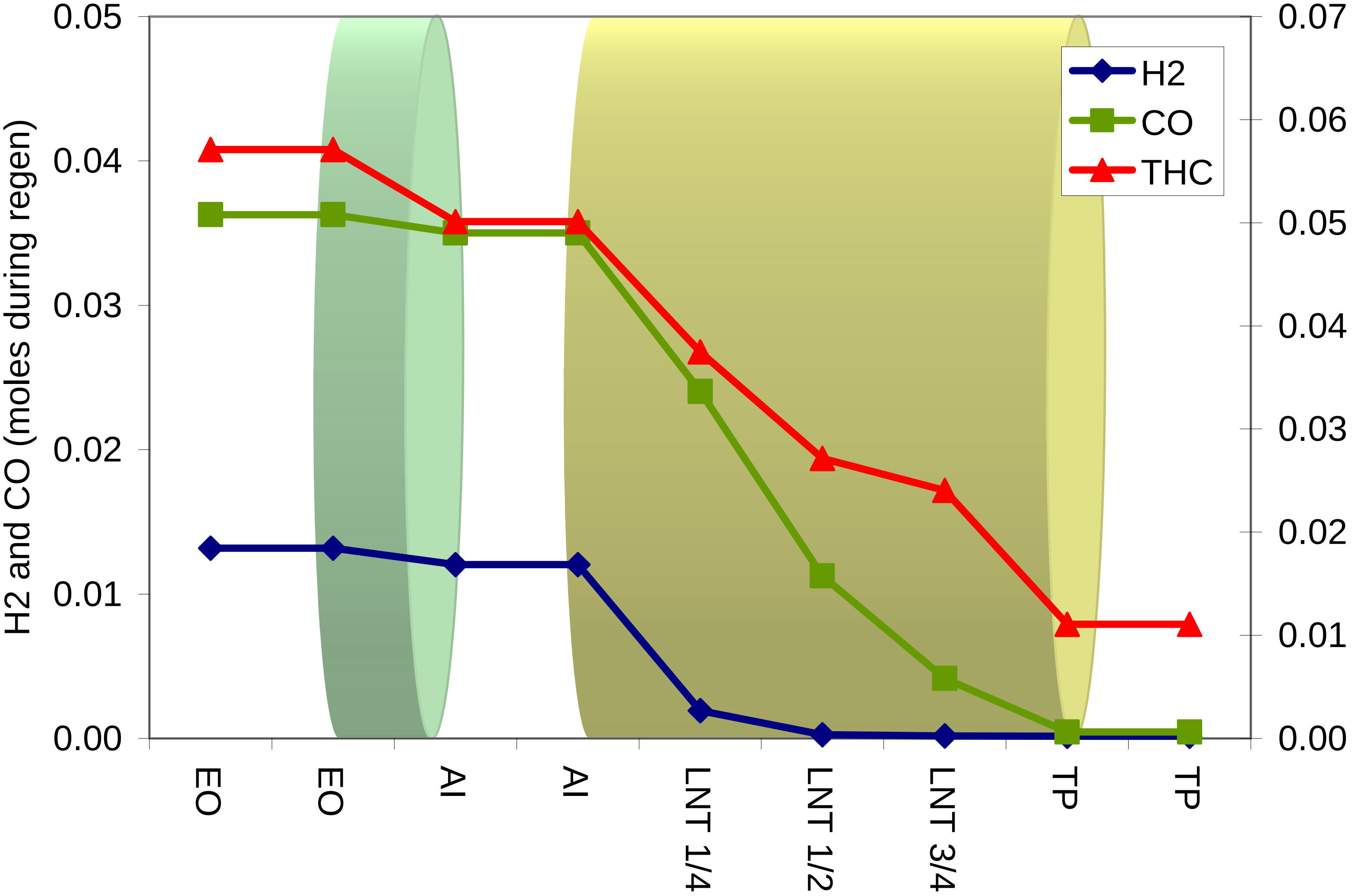


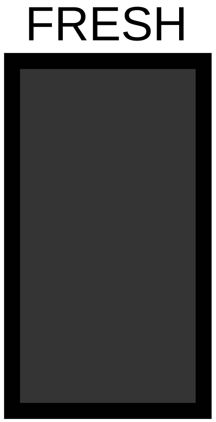
S/deS Effect on Strategy Performance

- **P80 strategies (Higher in HCs, Lower H_2/CO) appear to degrade more with S/deS; Why???**



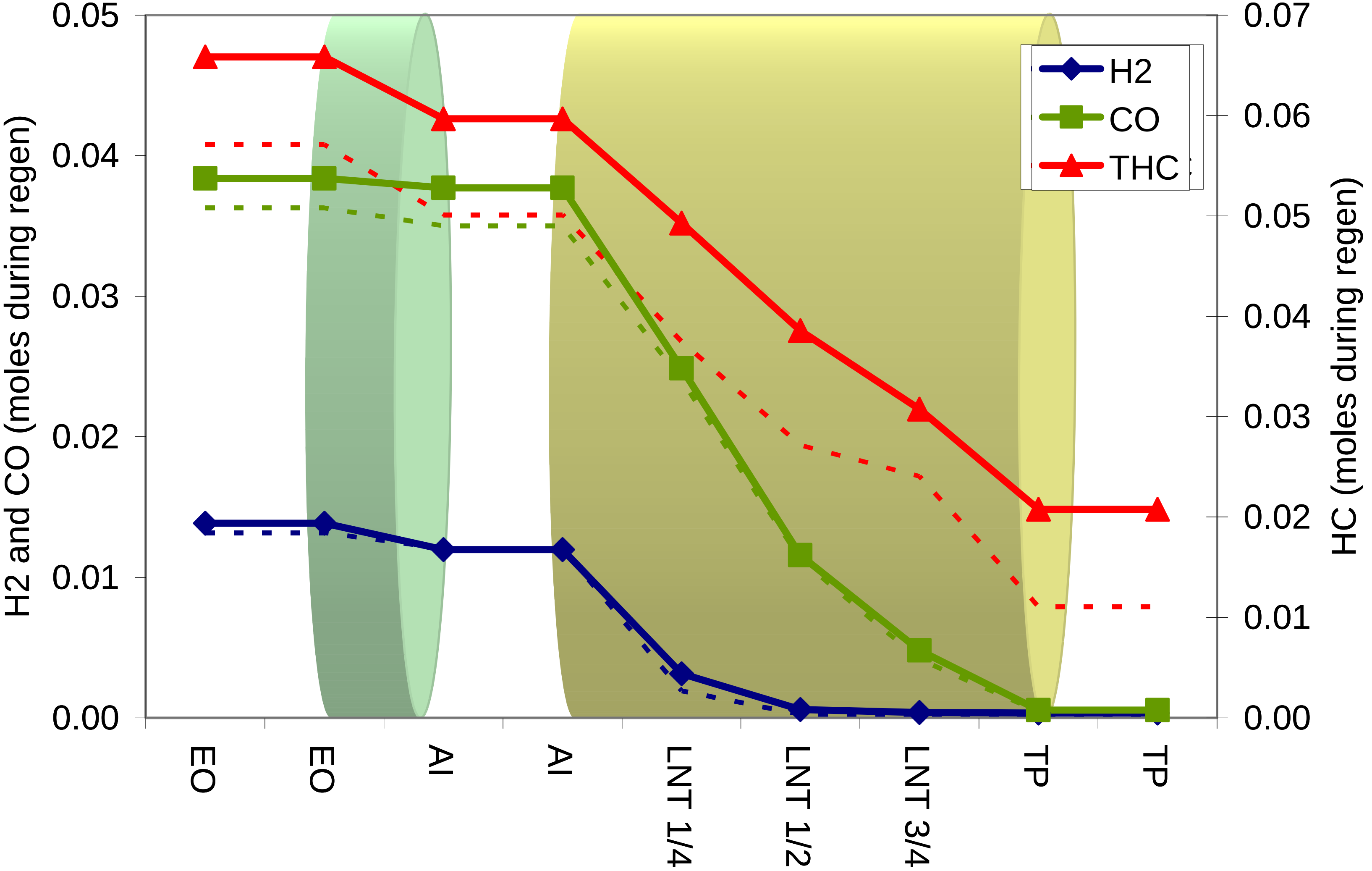
Small downstream shift in reductant utilization with S exposure

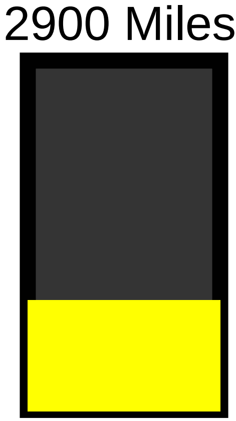




P80, 60s

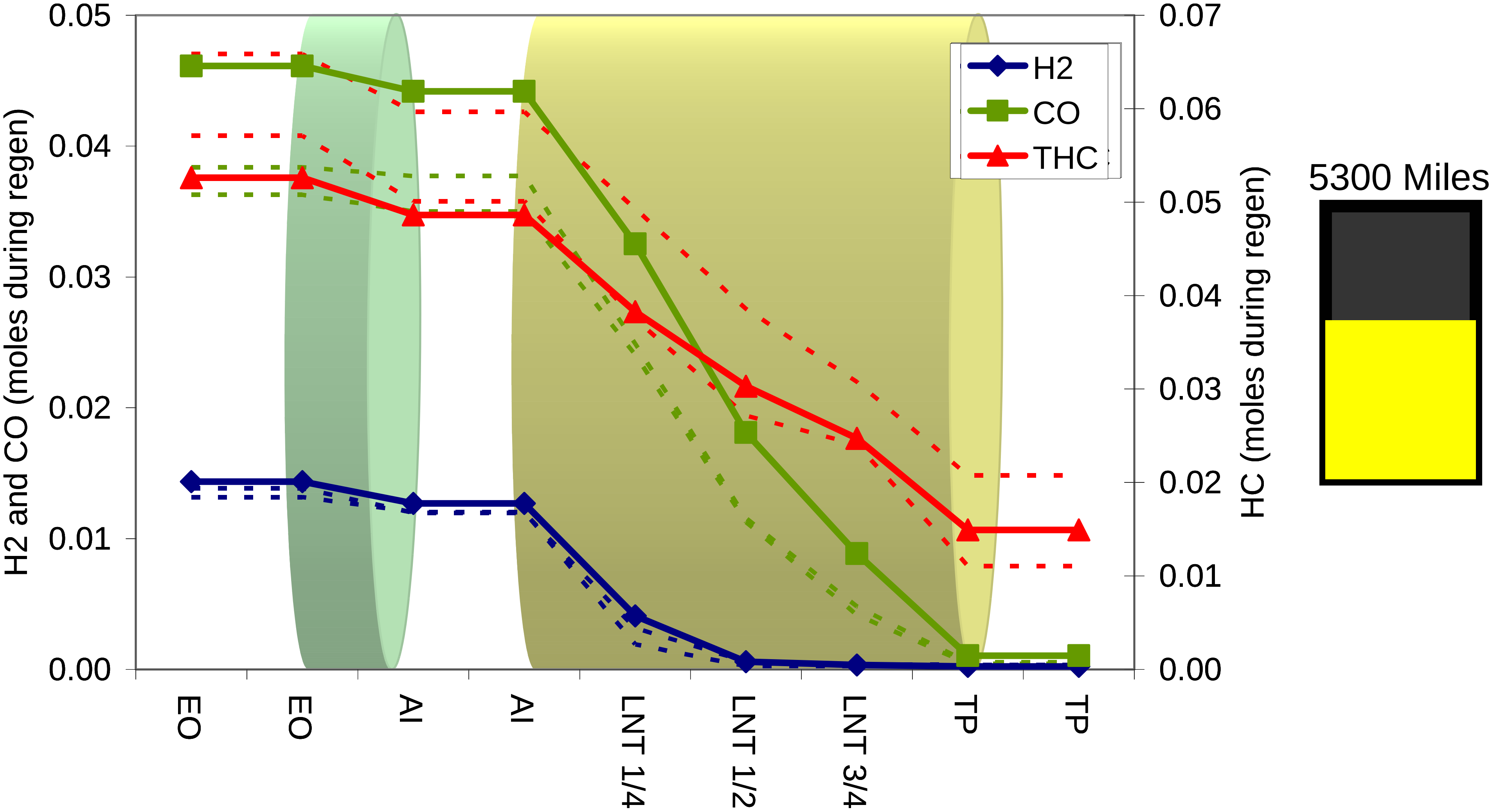
Small downstream shift in reductant utilization with S exposure





P80, 60s

Small downstream shift in reductant utilization with S exposure



P80, 60s

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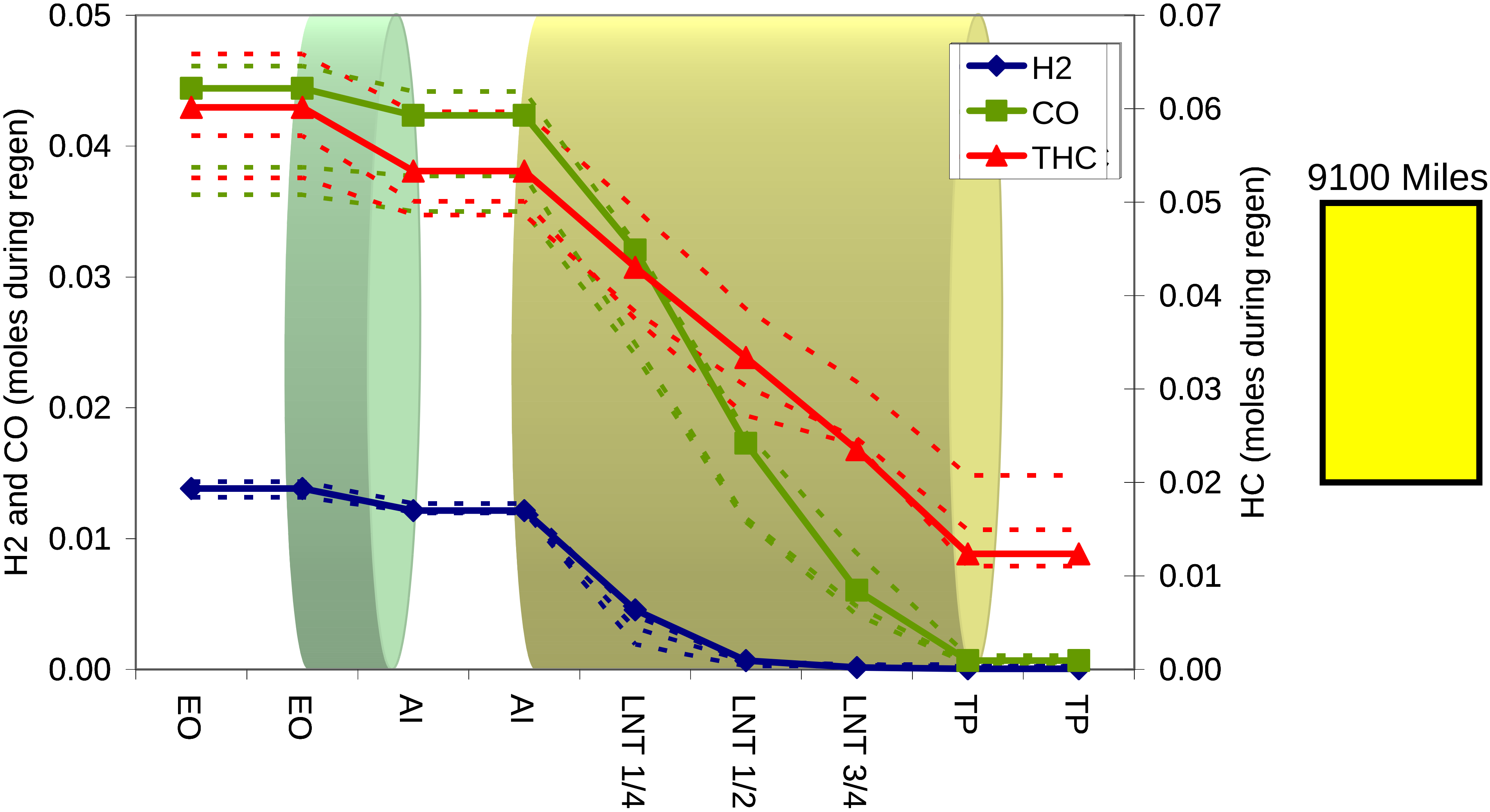
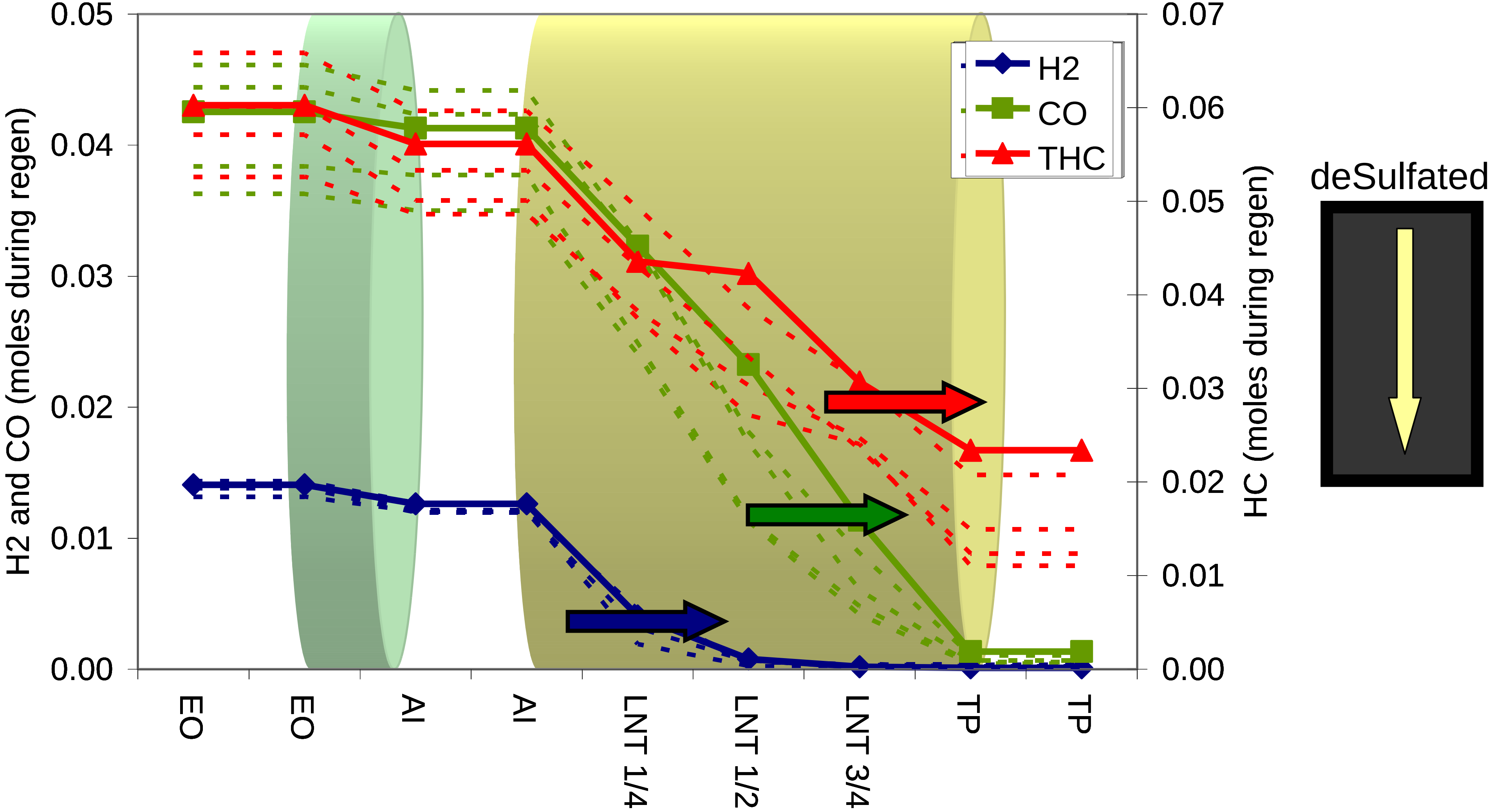


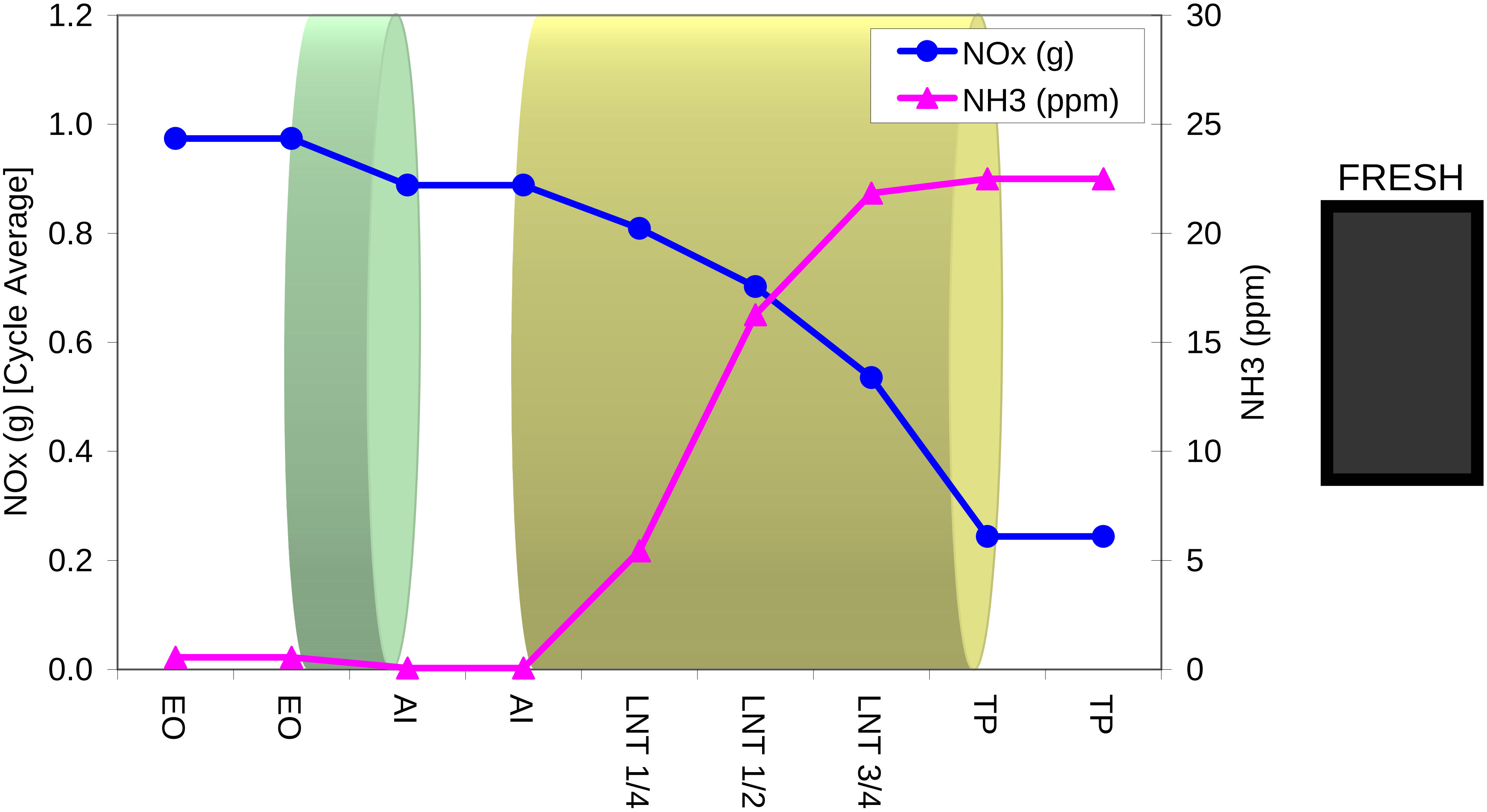
P80, 60s

Small downstream shift in reductant utilization with S exposure



P80, 60s

Significant changes observed in N_2 selectivity with S/deS



P80, 60s

Note: NH_3 and NOx not in same units. EO NOx ~ 500ppm

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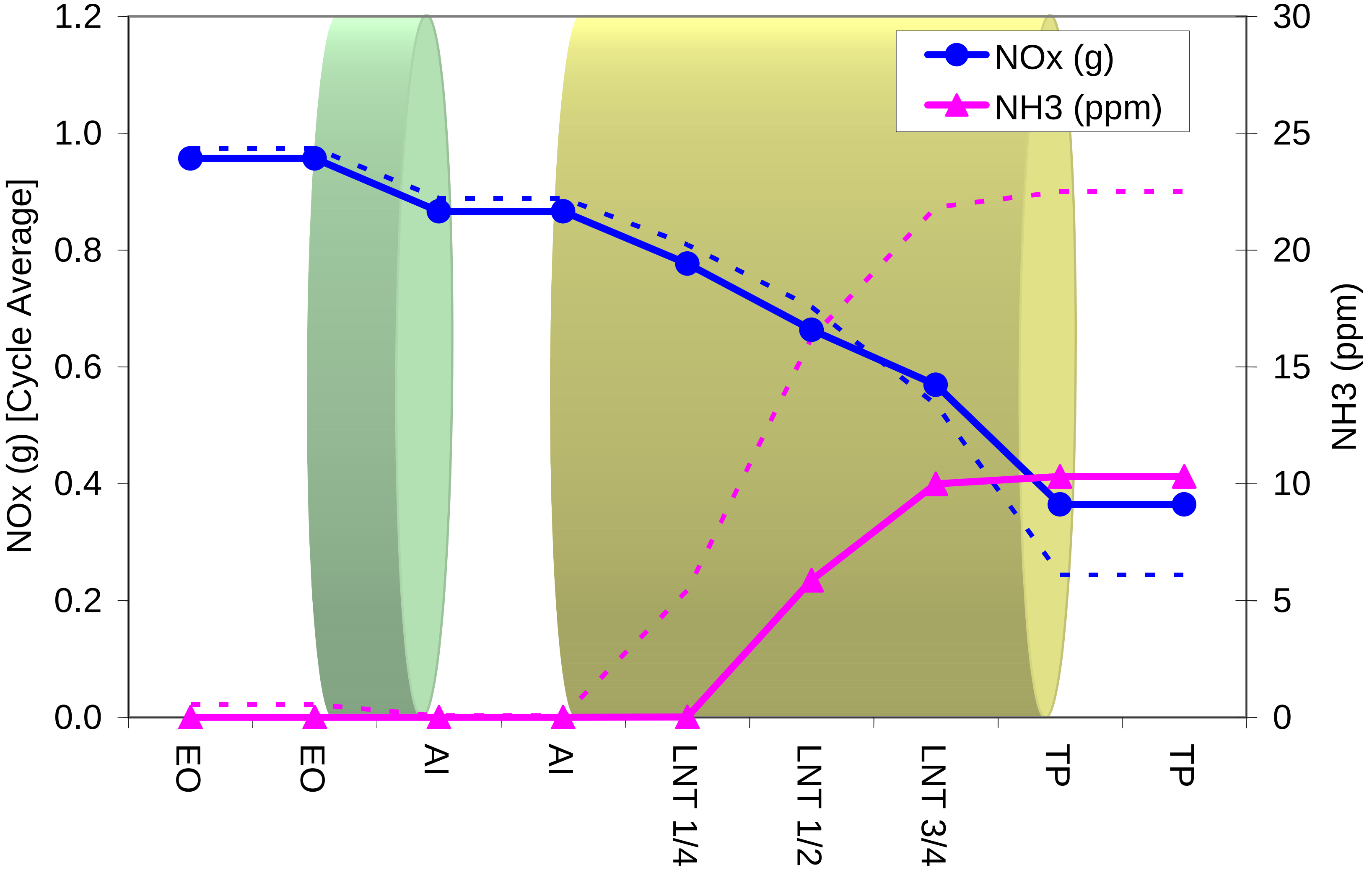

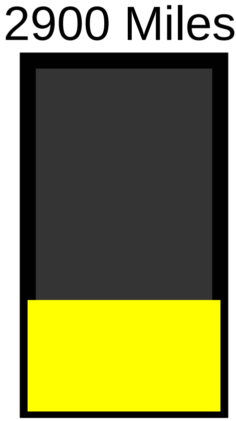

P80, 60s

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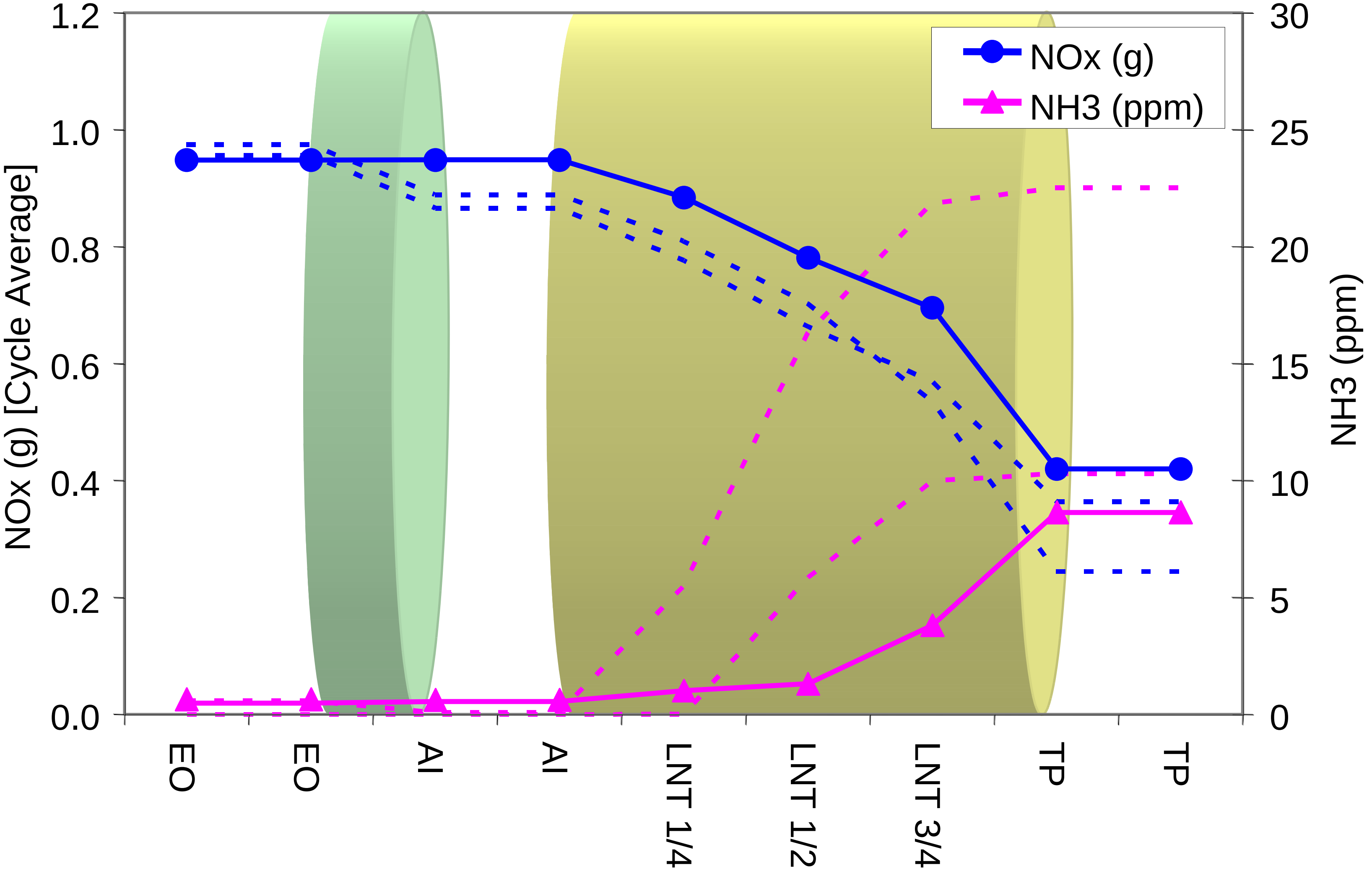

9100 Miles

P80, 60s

Note: NH_3 and NOx not in same units. EO NOx ~ 500ppm

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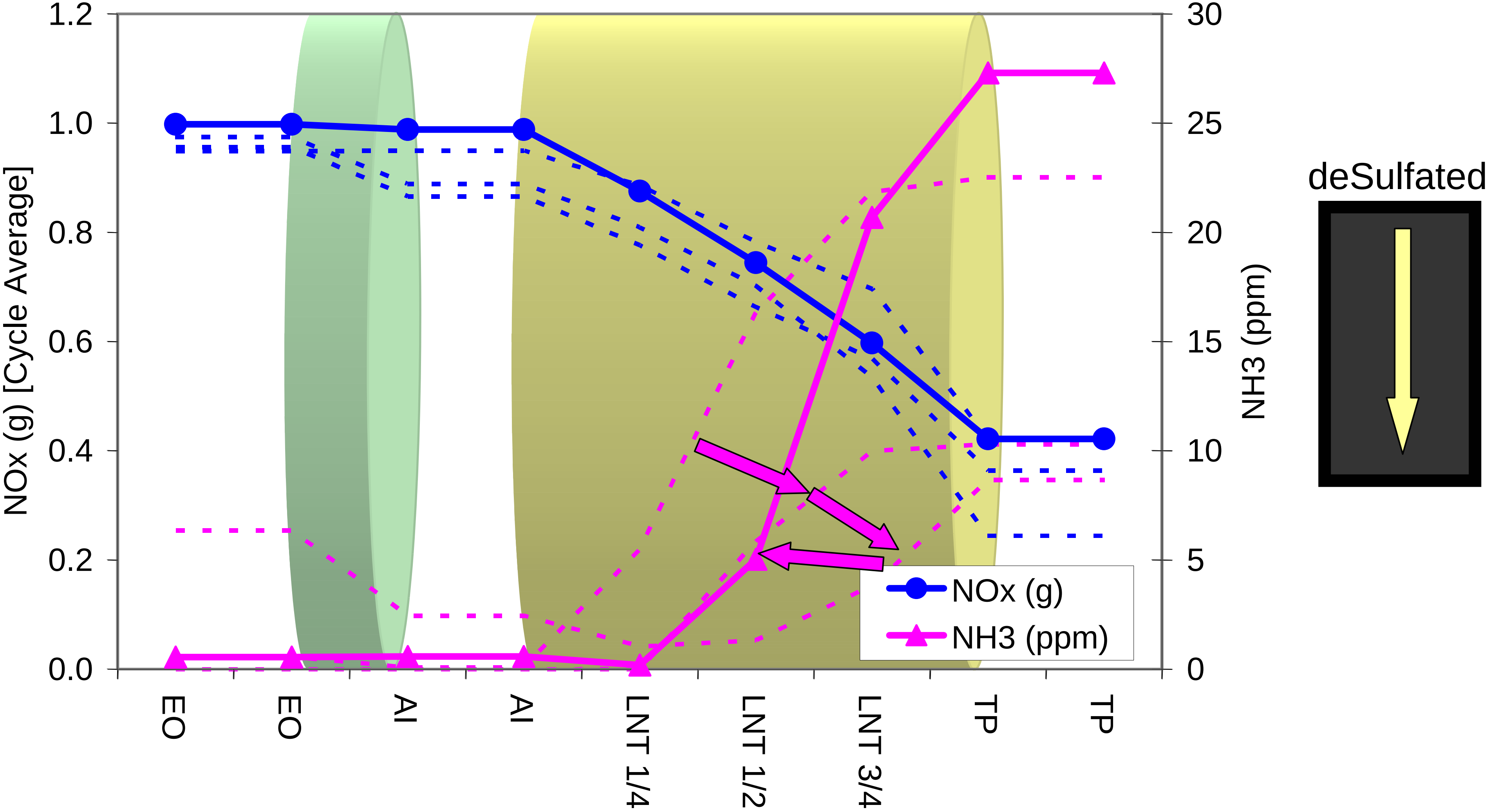
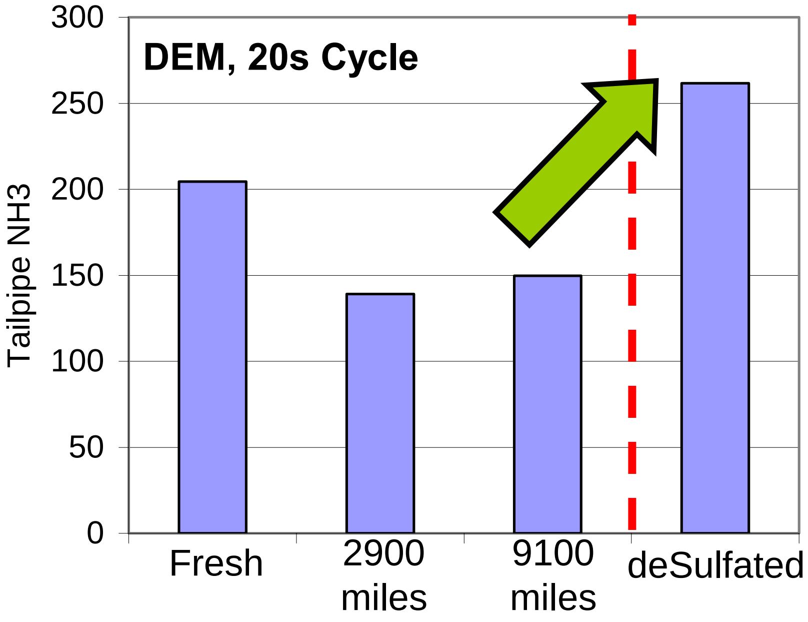
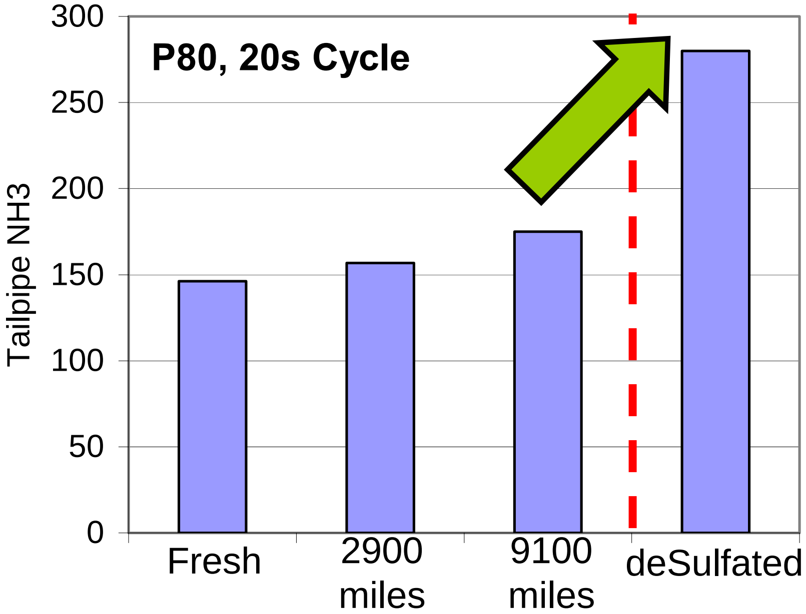


P80, 60s

Note: NH_3 and NOx not in same units. EO NOx ~ 500ppm

NH_3 formation increases after deSulfation





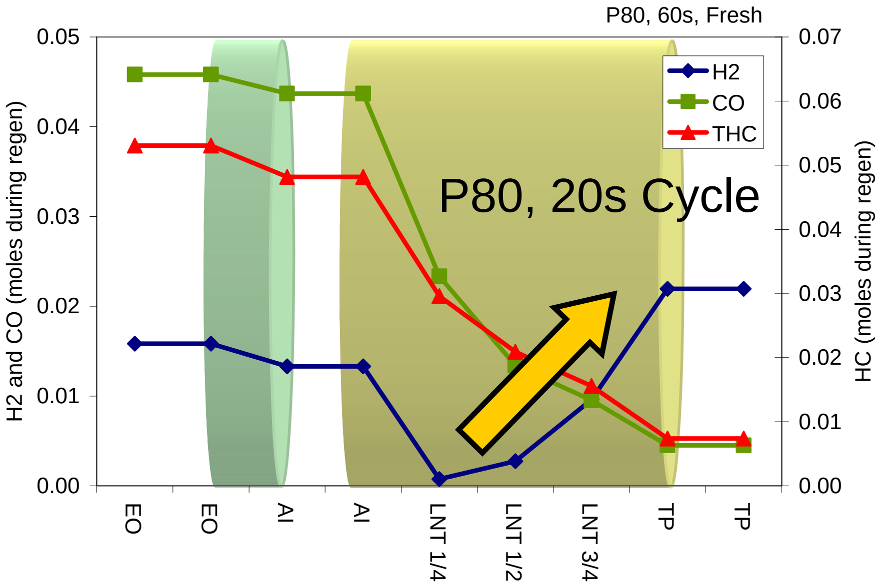
- NH_3 formation after deSulfation was higher for all cases

Potential causes:

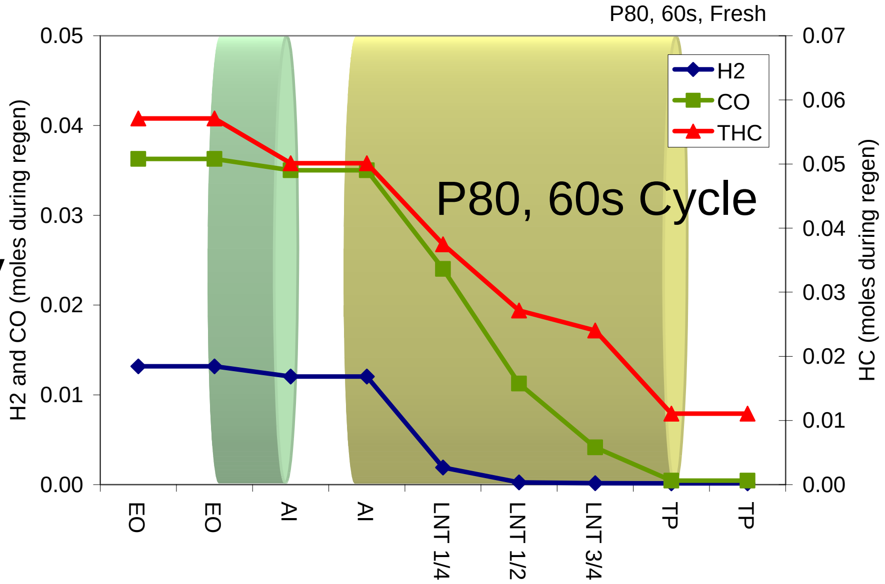
- Sintering of Sorbate
  - suspect thermal sintering of sorbate may be the cause of higher NH_3
  - Castoldi et. al. Report NH_3 formation corresponds with higher sorbate loading (bulk crystallites)
    - L. Castoldi, I. Nova, L. Lietti, P. Forzatti, “Catalysis Today” 96 (2004), pp. 43-52
- Change in Reductant:NOx ratio
  - CLEERS, Pihl, and other work on N_2 selectivity show NH_3 increases with increasing Reductant:NOx ratio
    - Pihl, et.al. SAE 2006-01-3441

H_2 Produced In Catalyst During 20s Cycles

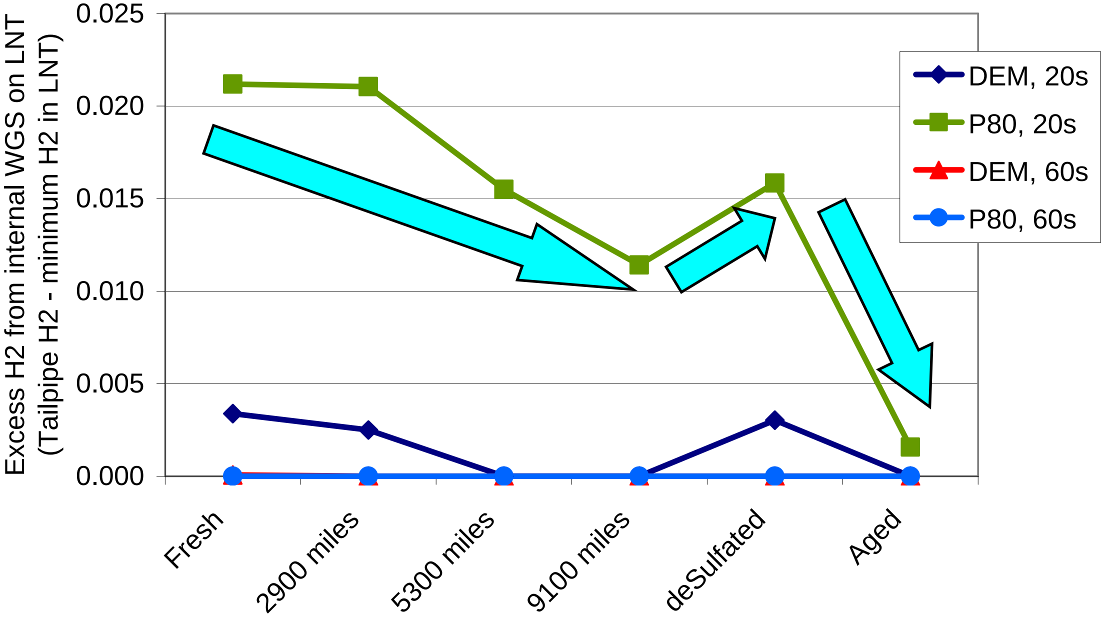
- In 20s cycles, H_2 observed being created in catalyst most likely from reforming reactions (water-gas shift, etc.)



- Same process may occur in 60s data, but H_2 may be consumed immediately for NOx reduction



Catalytic H_2 production: Effect of S/deS



- Increase in catalytic-produced H_2 greater for P80 strategy
- H_2 production degrades with S/deS aging
- LNT performance may degrade more rapidly for strategies that depend on catalyst utilizing HCs from engine

Summary

- **In general, reductant utilization in LNT moved downstream only slightly with S/deS**
  - **Process is consistent; optimism for modeling**

- **NH_3 formation increased after deSulfation process**
  - **Regeneration control strategies must adjust accordingly with age**

- **Strategies with high HC and low H_2/CO (P80) may depend on catalytic H_2/CO production for regeneration**
  - **S/deS degradation of catalytic H_2/CO production may have greater degradation impact on the effectiveness of P80-like strategies**

- **Preparing Paper for SAE Fall Powertrain and Fluids Conference**