Sulfur Preconditioning Impacts:
Why Existing Data Understates the Impact of Sulfur on Emissions

SAE Government/Industry Meeting

April 28, 1999

Takafumi Nishikawa, Toshihisa Yamaguchi, Hideki Uedahira
HONDA R&D CO., Tochigi R&D Center
John German, American Honda Motor Co.

Chemistry of Catalysis

- Successful catalysis depends on the formation of labile chemical bonds
- Elements that bond strongly to catalyst sites have the effect of "poisoning" the catalyst
- Sulfur can bond with both precious metal surfaces, especially Pd, and with ceria
- Reactions are very complex and are strongly affected by air/fuel ratio and temperature
- 1997 Report by CE-CERT summarized existing data
  - "Potential for Improved Sulfur Tolerance in Three-Way Automotive Catalysts", Timothy Truex, CE-CERT, Univ. of California-Riverside, November 26, 1997

CE-CERT: Sulfur Interaction with Pd

	Adsorption	Removal
Lean	SO_2 chemisorbs only below 500°C	S_{ad} removal at temperatures >650°C
Stoichiometric	SO_2 dissociatively adsorbed to form strongly adsorbed S_{ad}	
Rich	SO_2 dissociatively adsorbed to form strongly adsorbed S_{ad}	S_{ad} removal at temperatures >750°C

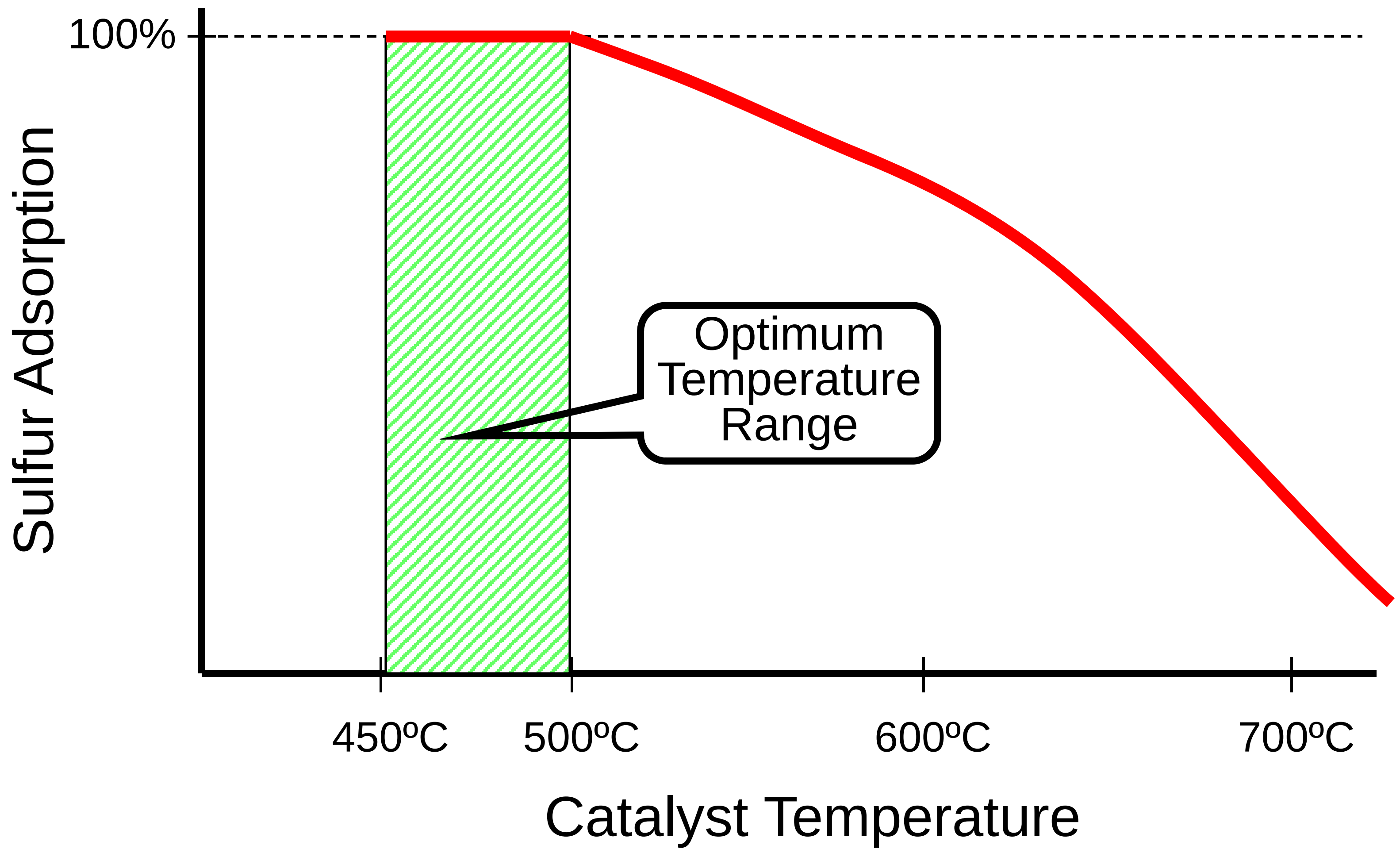
Sulfur migrates into bulk Pd

- Greater sensitivity
- Much slower in reaching equilibrium conditions
- Tendency towards irreversible poisoning

CE-CERT: SO_2 Reactions with Ceria

	Adsorption	Removal
Lean	$Ce_2(SO_4)_3$ formed (reduces catalyst O_2 storage capacity)	$Ce_2(SO_4)_3$ slowly decomposes at temperatures >650°C
Stoichiometric	$Ce_2(SO_4)_3$ formed (reduces catalyst O_2 storage capacity)	
Rich		$Ce_2(SO_4)_3$ rapidly decomposes at temperatures >600°C

Honda R&D Theory of Sulfur Adsorption



Sulfur Conditioning Considerations

- **Sulfur adsorption is depend on catalyst temperature**
- **Catalyst temperature must be below 500ºC for rapid sulfur adsorption**

<u>New Honda Catalyst Conditioning Sequence</u>

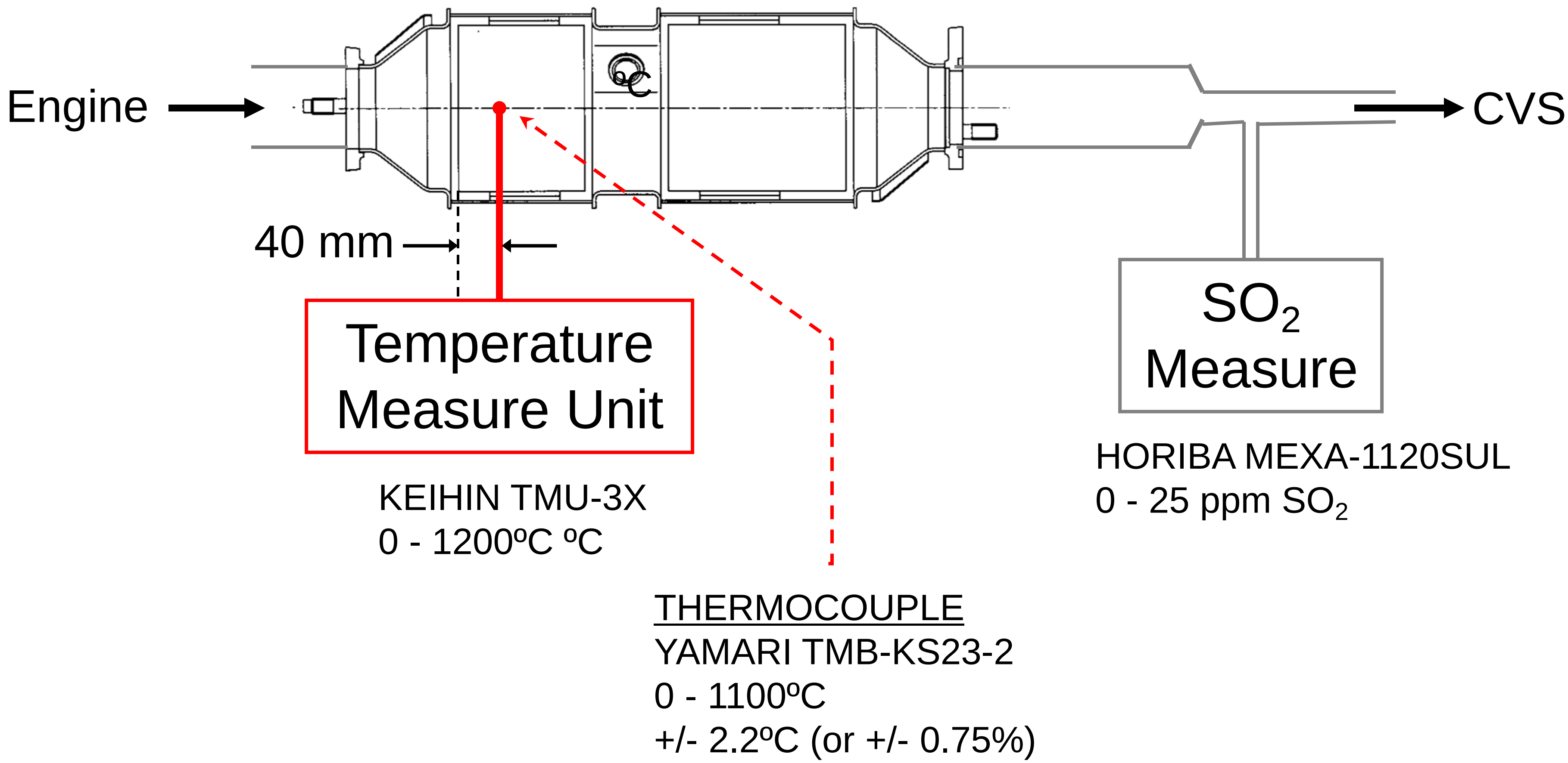
Maintain Catalyst temperature at 450º-500ºC

determined by monitoring catalyst temperature

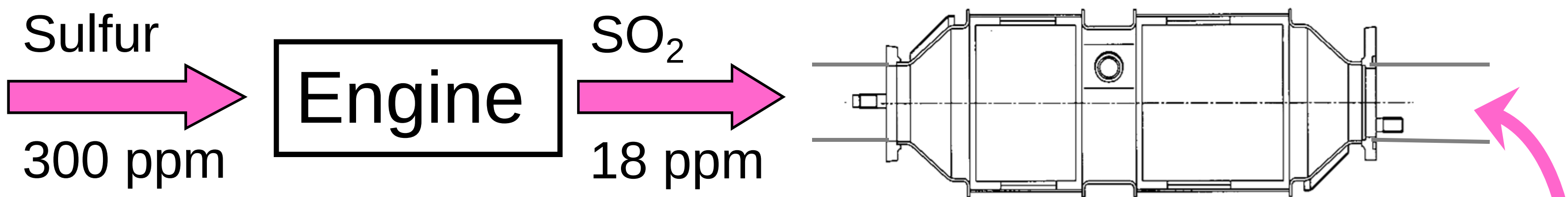
Until full sulfur adsorption

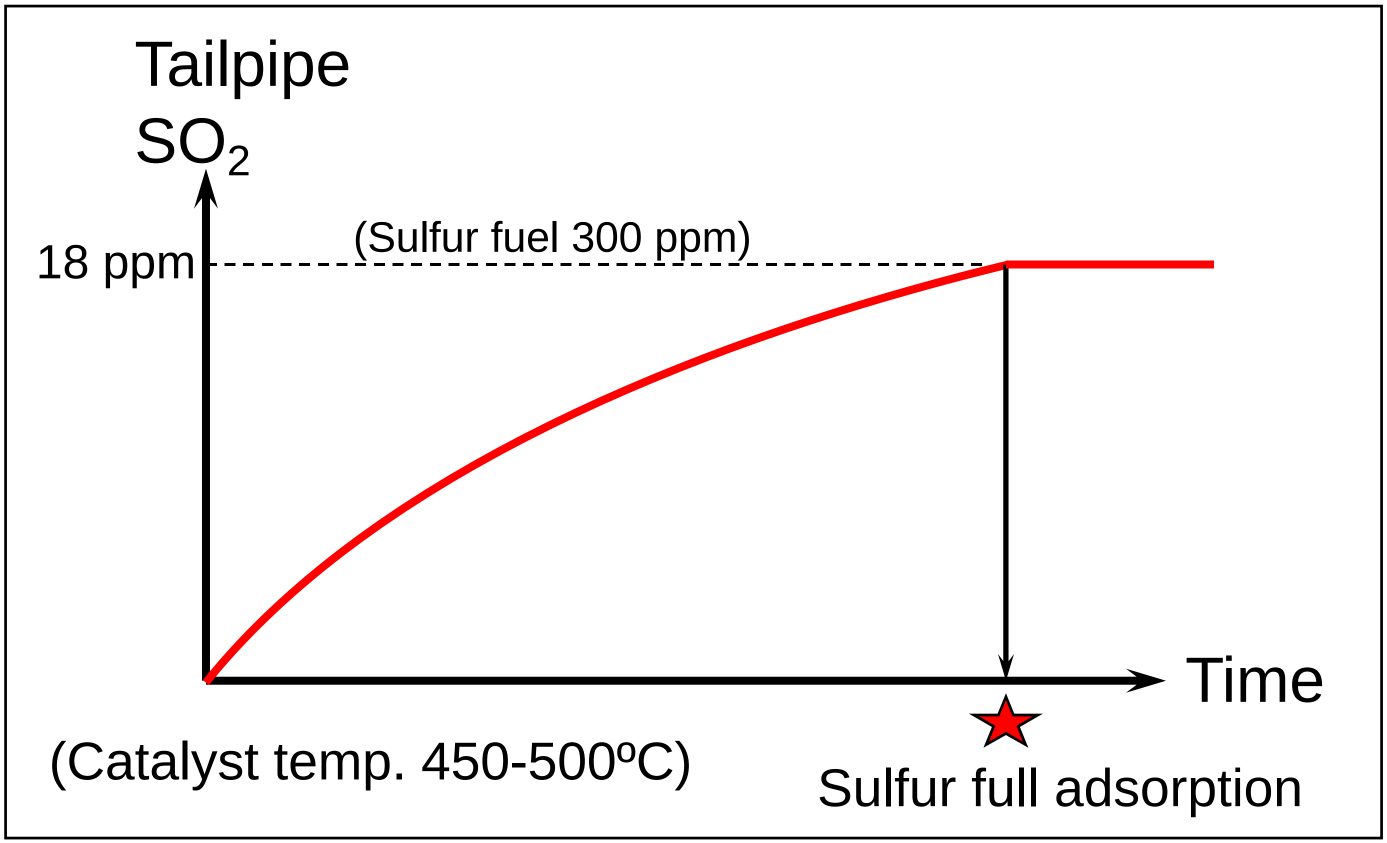
determined by monitoring exhaust SO2

Instrumentation



Honda Sulfur Adsorption Method



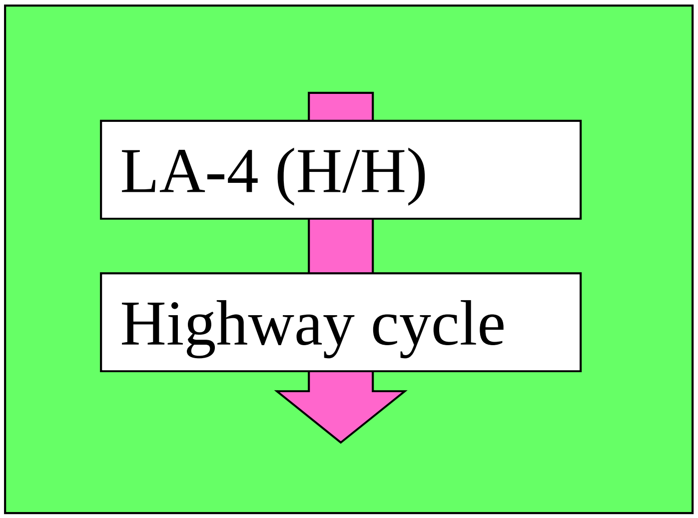


At first, all sulfur is adsorbed, so tailpipe SO_2 is 0 ppm

After full adsorption, tailpipe SO_2 is 18 ppm

Testing on Vehicle #1

EPA Draft Conditioning



Honda Conditioning

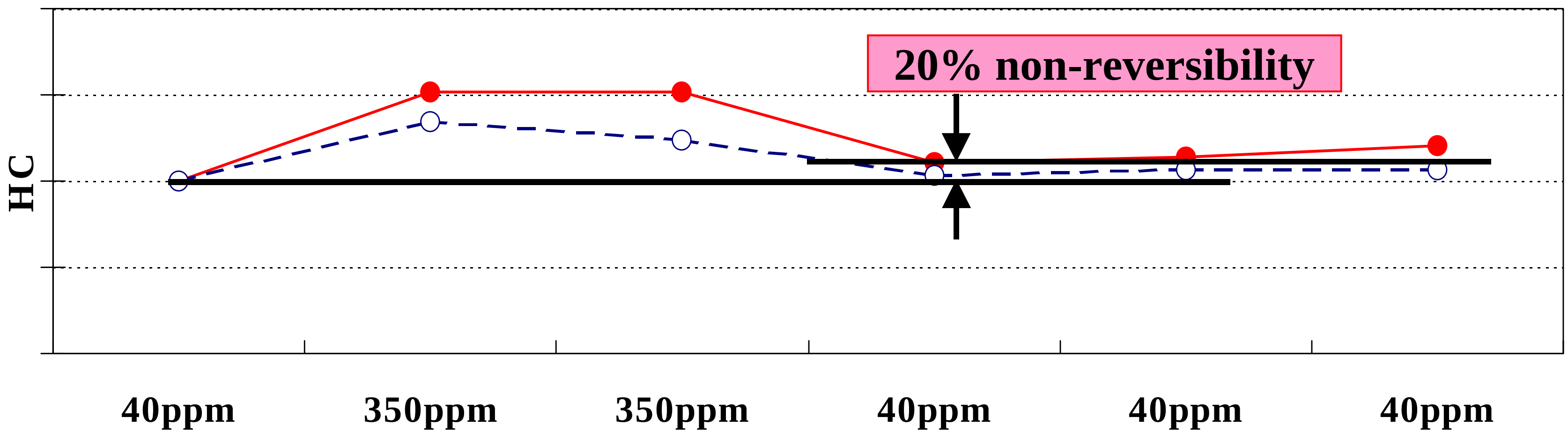
Catalyst temperature:
450º-500ºC

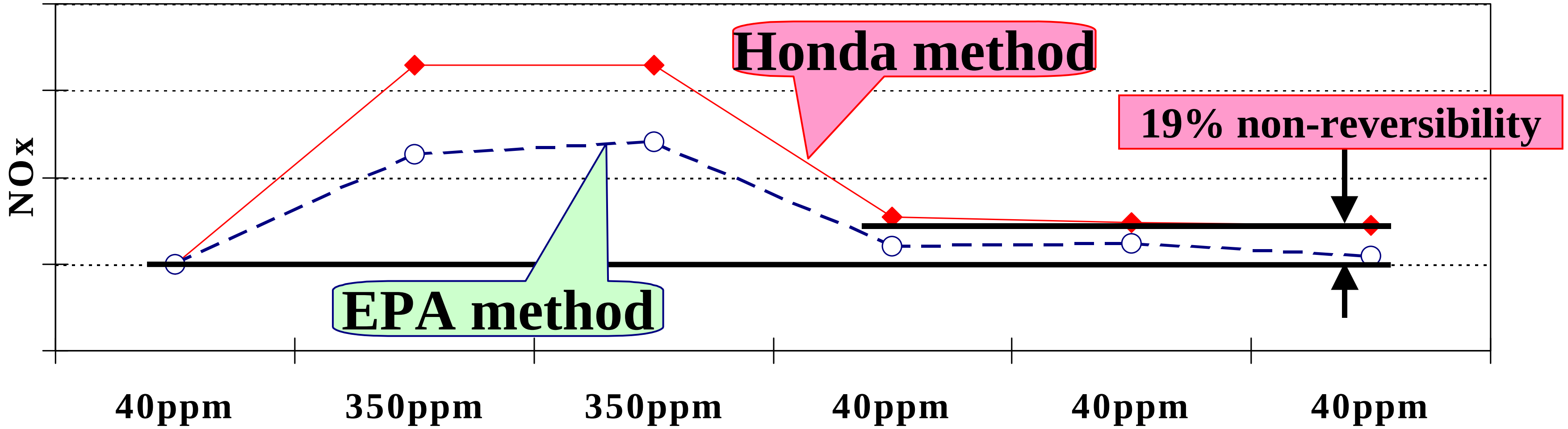
About 35 m/h Cruise

Until full adsorption

- Test sequence:
  - FTP using 40 ppm fuel
  - Conditioning procedure using 350 ppm fuel
  - FTP using 350 ppm fuel
  - Consecutive FTPs using 40 ppm fuel

Vehicle #1: Test Results





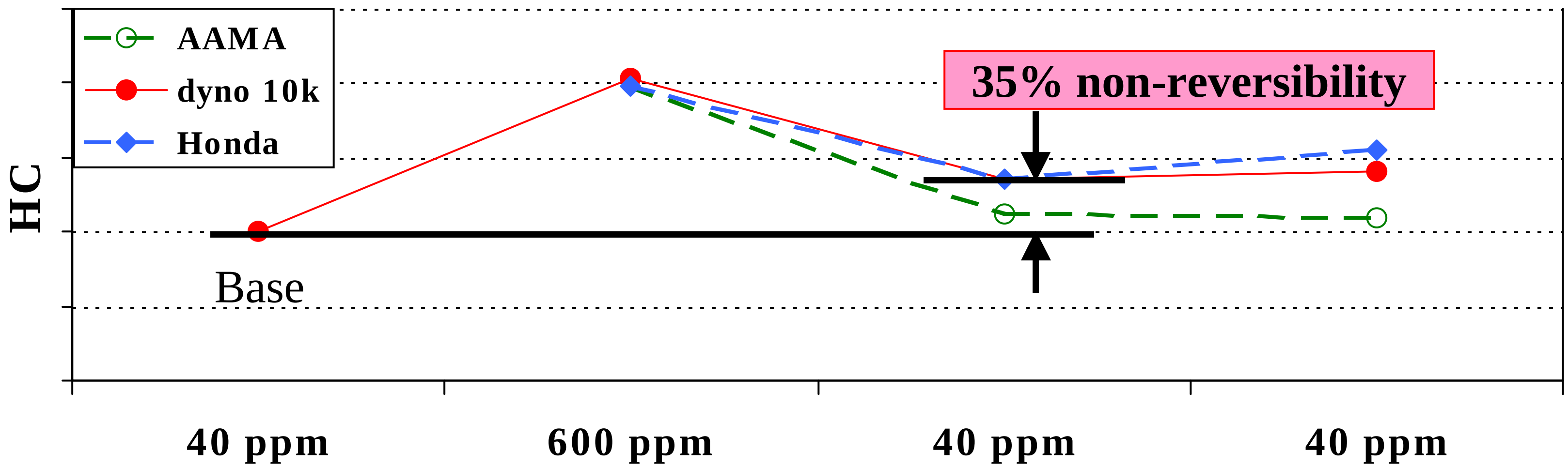
Conclusions for Vehicle # 1

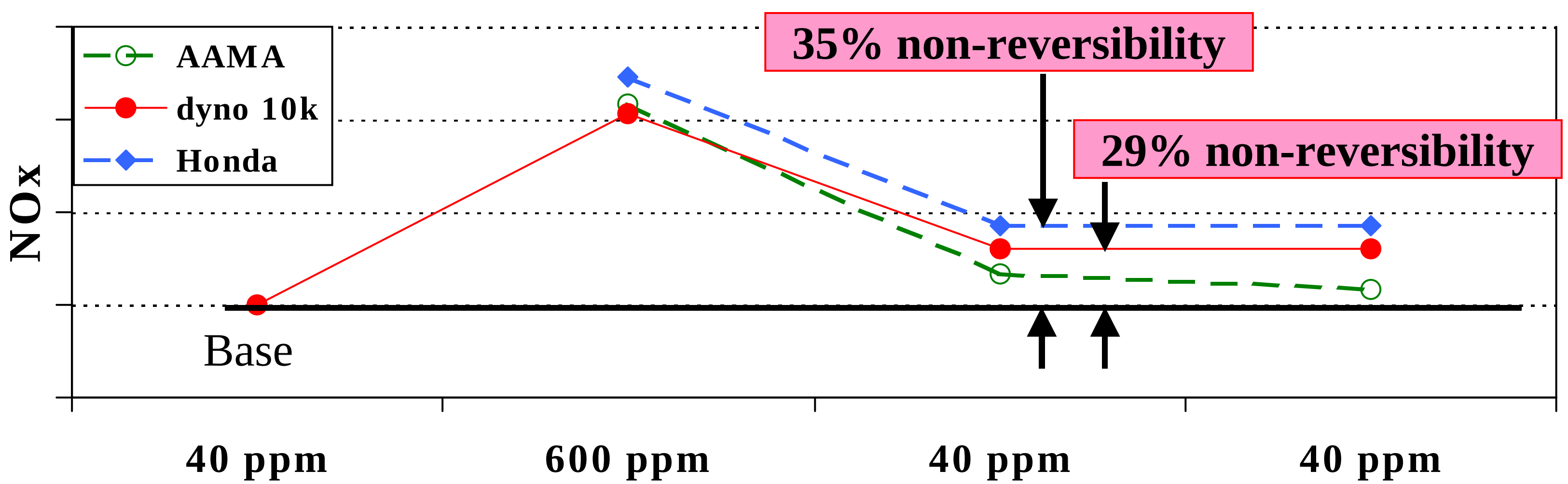
- No sulfur non-reversibility was found using the EPA Draft Conditioning procedure
- Honda conditioning method had higher sulfur sensitivity and about 20% non-reversibility
- EPA's draft sulfur preconditioning method did not load enough sulfur on the catalyst
  - Catalyst temperature was too high on the highway cycle and the preconditioning was too short

Comparison to Extended In-Use Driving

- To evaluate the representativeness of the Honda conditioning method, a second vehicle was run on the dyno for 10k miles representing city-type driving:
  - Mileage accumulation consisted of cruises at different speeds ranging from 25 to 60 mph, interspersed with accelerations
  - Catalyst temperature generally ranged between 500ºC and 600ºC, with temperature spikes as high as 750 ºC
- Test results were compared to:
  - Honda preconditioning method (identical to vehicle #1)
  - AAMA/AIAM preconditioning method (instead of draft EPA)

Test Results on Vehicle # 2





Conclusions for Vehicle # 2

- The 10k dyno conditioning generated sulfur effects similar to the Honda preconditioning method
- The non-reversible sulfur effects on this vehicle were even higher than vehicle #1, both on the 10k dyno and the Honda preconditioning tests
- Although there was some non-reversibility with the AAMA/AIAM preconditioning on this vehicle,
- the AAMA/AIAM method drastically under-predicted the impact of sulfur on reversibility

In-Use versus Preconditioning Conditions

- Average in-use vehicle speeds (EPA's SFTP data):
  - Baltimore: 24.5 mph
  - Los Angeles: 28.3 mph
  - Atlanta: 28.8 mph
- Sulfur preconditioning conditions:
  - LA-4 cycle: 19.7 mph average
  - Highway cycle: 48 mph average
  - Honda's preconditioning procedure: 35 mph cruise
  - Honda's 10k conditioning: 25 to 60 mph cruises/accels
  - Recent EPA road aging: approx. 40 mph average

Conclusions

- In-use, vehicle speeds and, thus, catalyst temperatures are usually low
- Highway cycle, Honda 10k conditioning, and EPA's recent road aging generate higher catalyst temperatures than are usually found in-use
- The LA-4 generates representative catalyst temperatures, but previous test programs did not run enough LA-4 cycles to saturate the catalyst
- Honda preconditioning method uses appropriate catalyst temperatures and ensures saturation
- Existing data likely understate sulfur impacts by a factor of about two