EVALUATION OF ATMOSPHERIC IMPACTS OF SELECTED COATINGS VOC EMISSIONS

CARB Contract Number 00-333

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Summary of Progress through
June 2002

Outline of Presentation

- Status of preparation of UCR EPA Chamber
- Progress on interfacing a total carbon analysis method to direct reactivity measurements.
- Results of reactivity analysis of petroleum distillates studied by Censullo et al (2002)
- Ongoing Work

Note: Current information about project available at http://www.cert.ucr.edu/~carter/coatings/

STATUS OF PREPARATION OF UCR EPA CHAMBER

Essentially all instruments to be used have been acquired, but some still being evaluated

Enclosure and temperature control systems are completed and perform satisfactorily. Some formaldehyde and NO_x offgasing observed.

Preliminary experiments were conducted with a large “pillow bag” and blacklights. Data indicate background low enough for low NO_x experiments

Argon arc light is now operational, but not with final spectrum. Performance being evaluated

Final spectral filter may be delivered in July

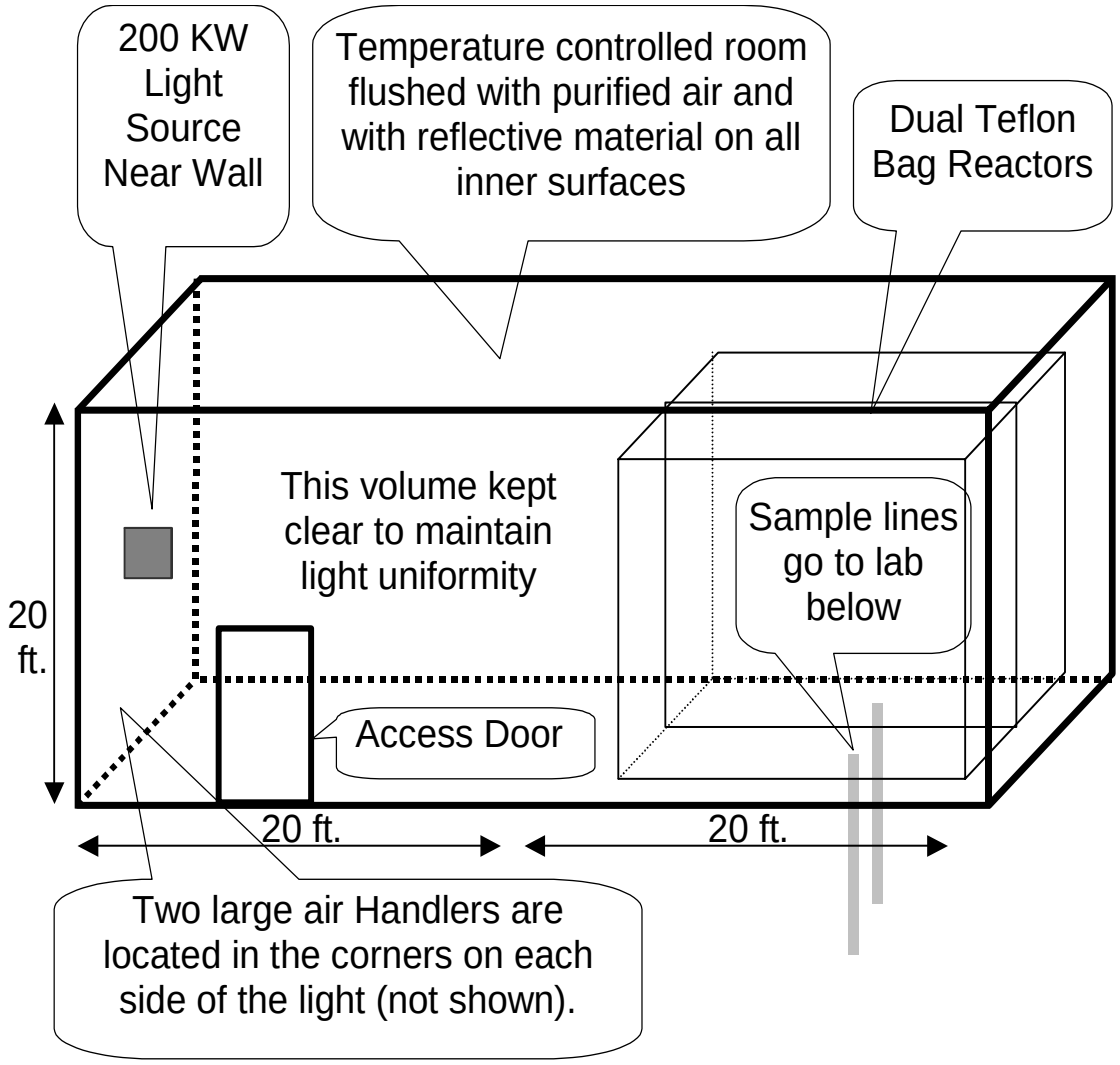
Construction is underway on final chamber configuration and mixing and injection systems. Process taking longer than expected

Now looks like first experiments with final configuration may be conducted in July

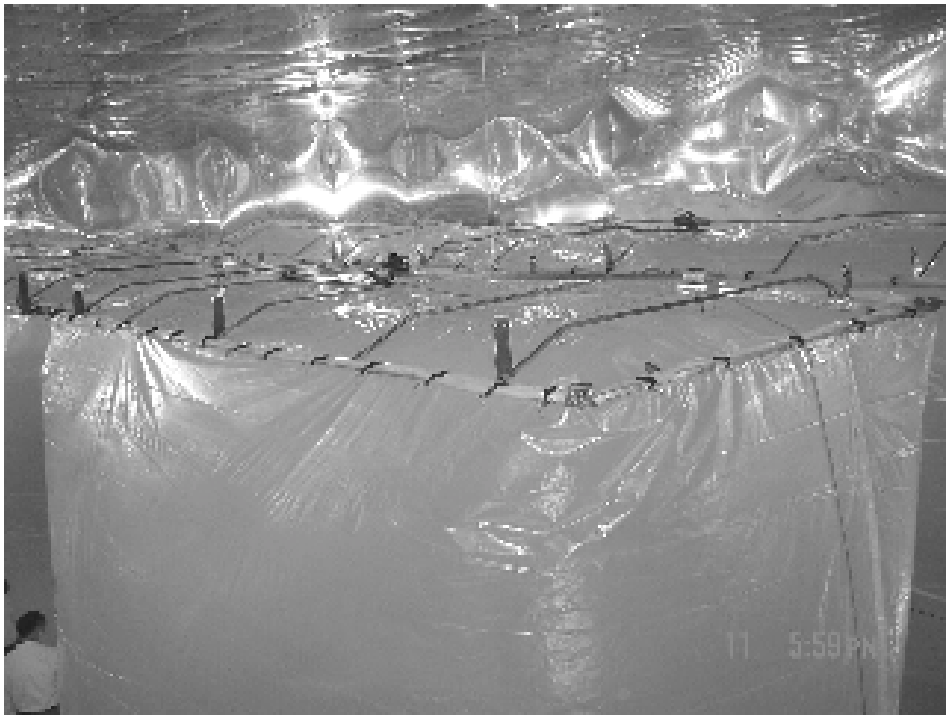
Draft QA plan, data processing procedures, and standard operating procedures developed

Current information about project available at http://www.cert.ucr.edu/~carter/epacham/

DIAGRAM OF CHAMBER ENCLOSURE AND REACTORS



PROTOTYPE REACTOR



MEASUREMENT OF DIRECT REACTIVITY

Background

Direct reactivity measures the O_3 formed directly from the VOC's reactions. Such measurements could reduce mechanism evaluation ambiguities

A plug flow HONO photolysis system has been developed for direct reactivity measurements

Such measurements have potential to provide reactivity data at lower cost than chamber runs

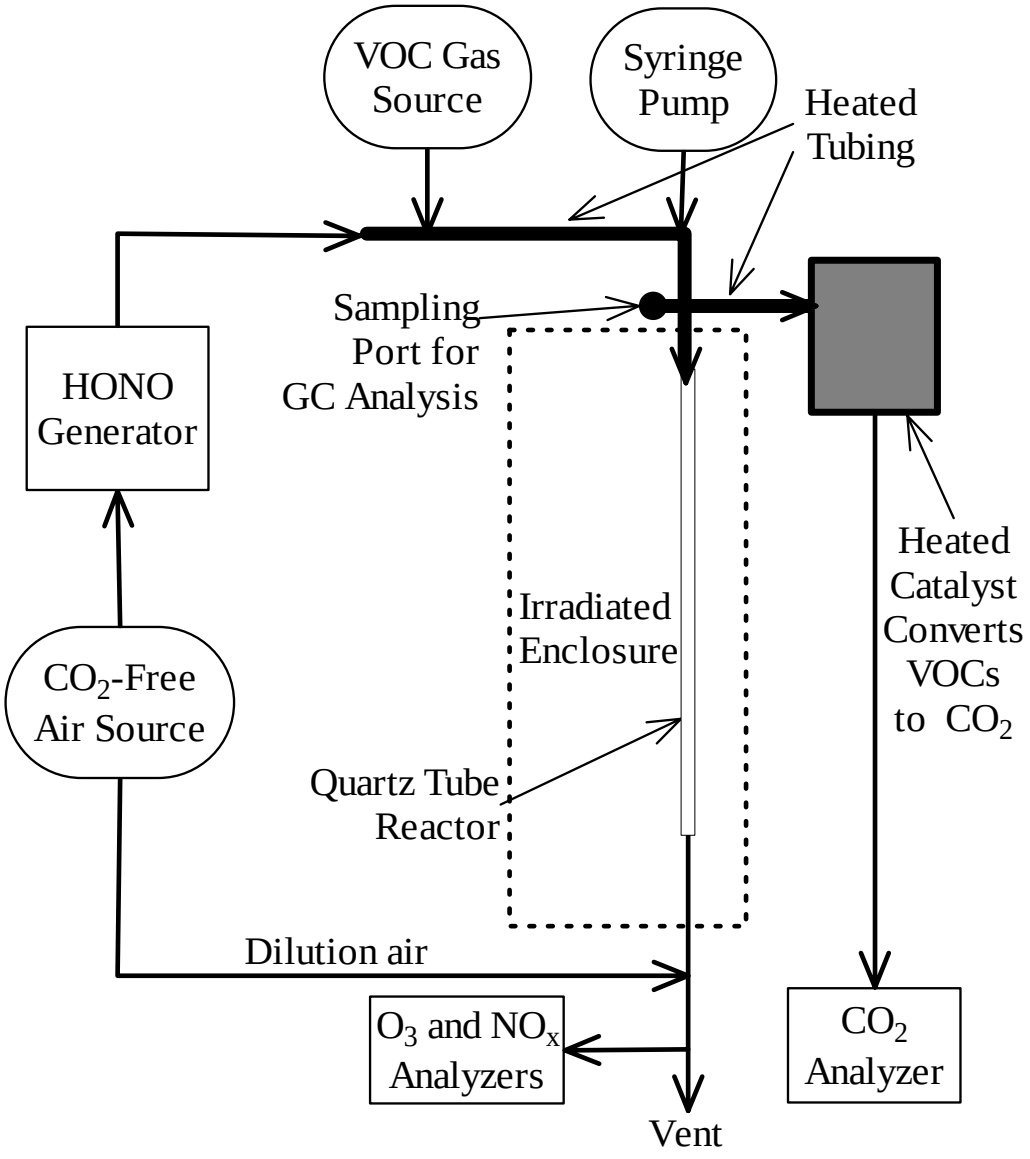
The current system works well for high volatility compounds suitable for GC analysis, but not for low volatility compounds or complex mixtures

Interfacing the system with a total carbon analysis method should reduce the cost and may permit use with lower volatility compounds

Current Objectives

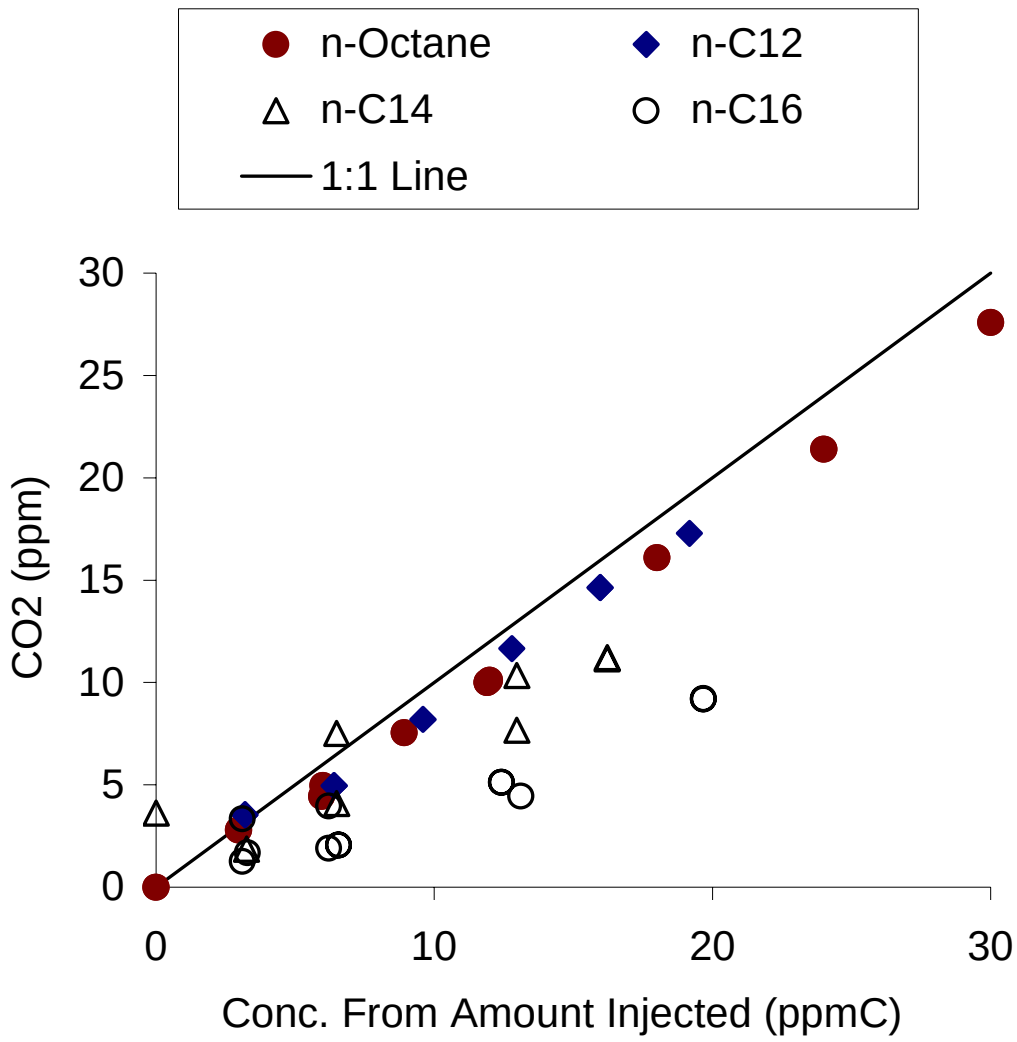
- Develop total carbon analysis method that can be interfaced to existing system
- Improve low volatility injection procedures
- Evaluate performance with high and low volatility compounds and petroleum distillates

DIAGRAM OF PLUG FLOW SYSTEM MODIFIED FOR TOTAL CARBON ANALYSIS



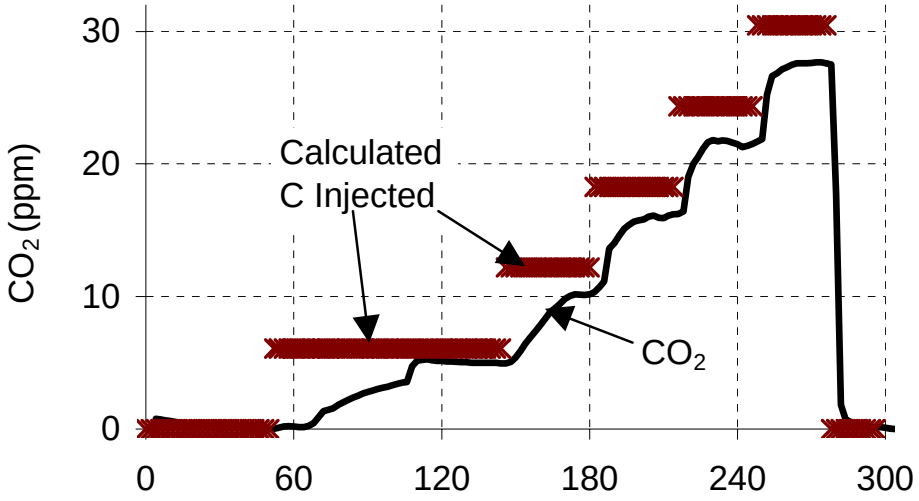
- Catalyst from air purifier for Byron Model 15, heated to ~370^{o}C.
- Sub-ppm sensitivity CO_2 analyzer funded by ACC gift

COMPARISON OF CONCENTRATIONS DERIVED BY CO_2 CONVERTER WITH CALCULATED AMOUNTS INJECTED

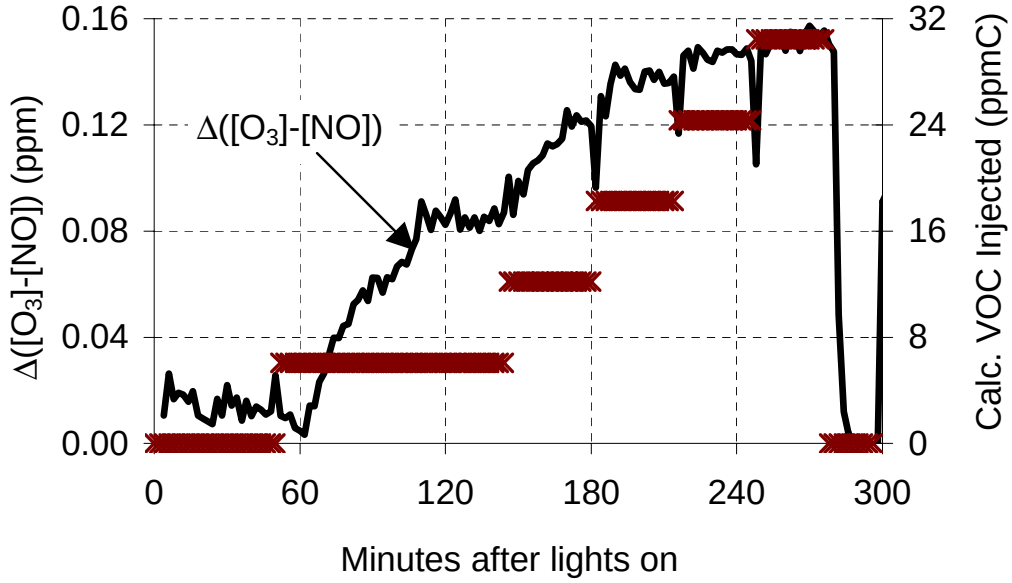


RESULTS OF EXPERIMENT WITH N-OCTANE USING CO_2-BASED CARBON ANALYSIS

VOC INJECTED AND MEASURED CARBON



$\Delta([O_3]-[NO])$



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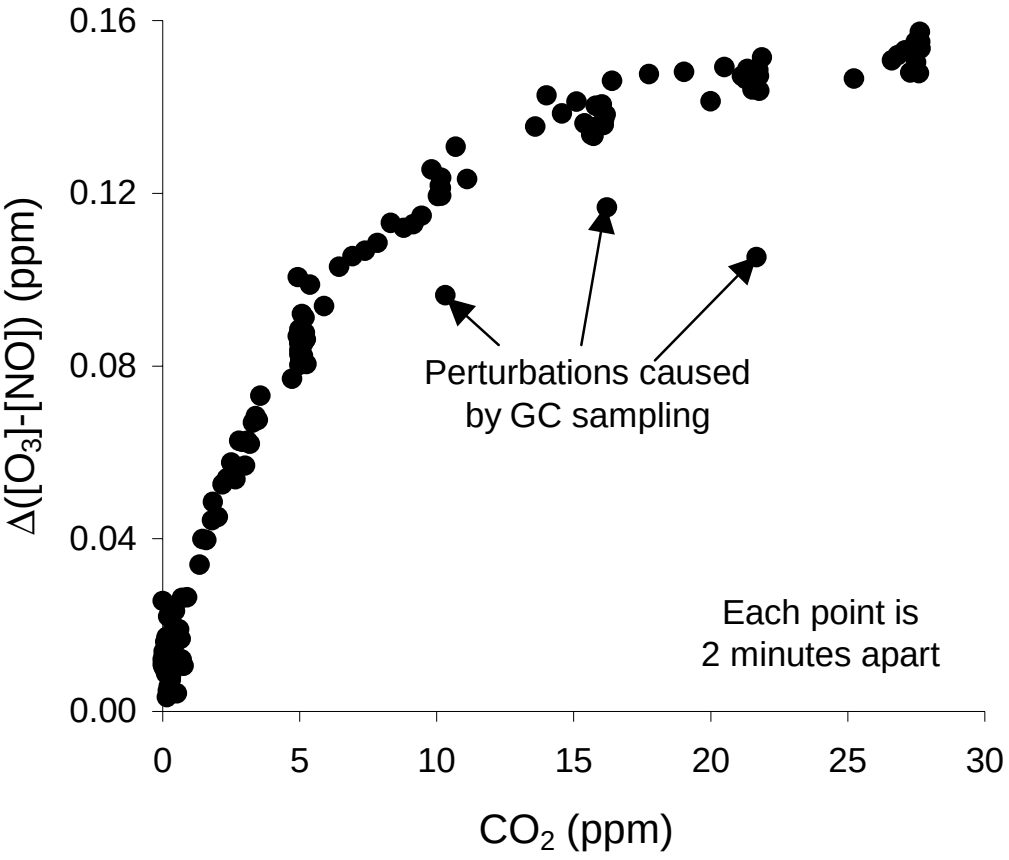
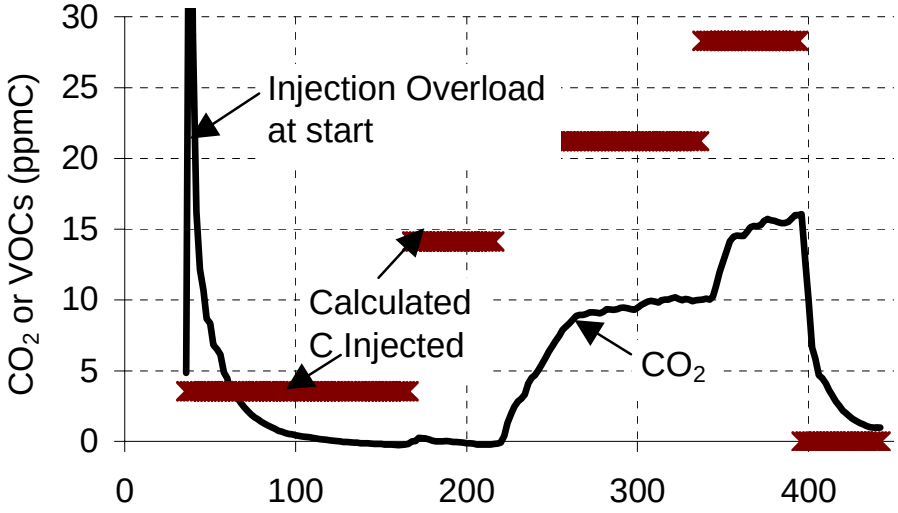


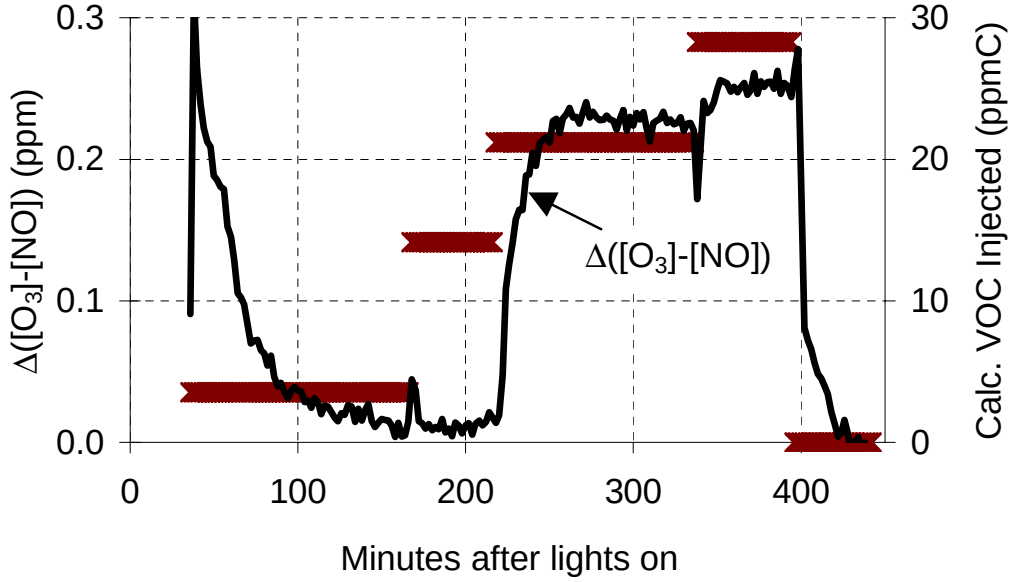
- CO_2 data in good agreement with n-octane analysis by GC
- Results in fair agreement with model predictions. (Not shown because conditions not yet fully characterized for modeling)

RESULTS OF EXPERIMENT WITH MINERAL SPIRITS "B" USING CO_2-BASED CARBON ANALYSIS

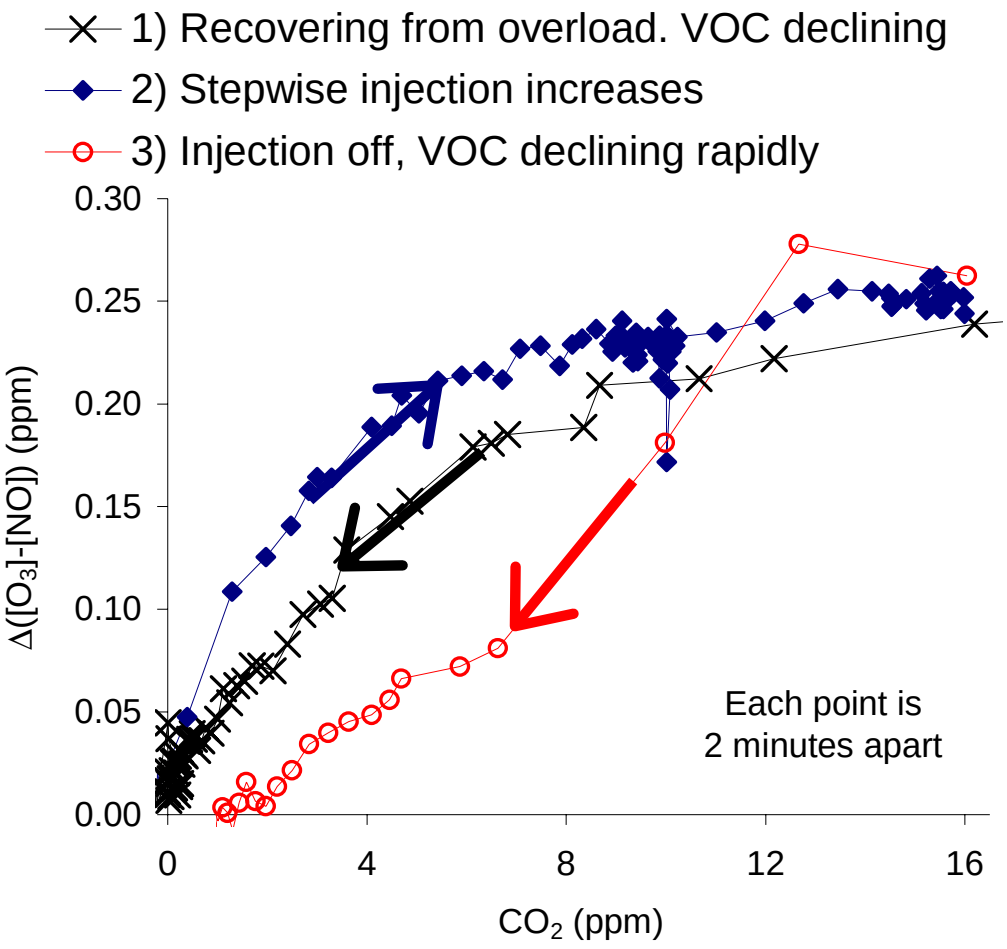
TOTAL CARBON AND VOC INJECTED



Δ([O3]-[NO])



RESULTS OF EXPERIMENT WITH MINERAL SPIRITS "B" USING CO_2-BASED CARBON ANALYSIS



- MS "B" contains primarily C_{11}-C_{14} alkanes
- CO_2 response is higher compared to $\Delta([O_3]-[NO])$ response when VOC is declining compared to when VOC is increasing

SUMMARY OF STATUS AND CURRENT PLANS FOR DIRECT REACTIVITY MEASUREMENT WORK

Catalytic combustion with CO_2 analysis works well in experiments with higher volatility compounds, eliminating the need for GC analysis

However, current combustor system apparently has hang-up for lower volatility compounds and needs to be improved

Use of smaller catalytic combustor with shorter inlet system and higher temperature is being investigated

Once the combustor system is improved, it will be used to evaluate how to improve syringe pump injection system for low volatility compounds

REACTIVITY ANALYSIS OF PETROLEUM DISTILLATES STUDIED BY CENSULLO ET AL.

Compositional data obtained for 41 types of petroleum distillates

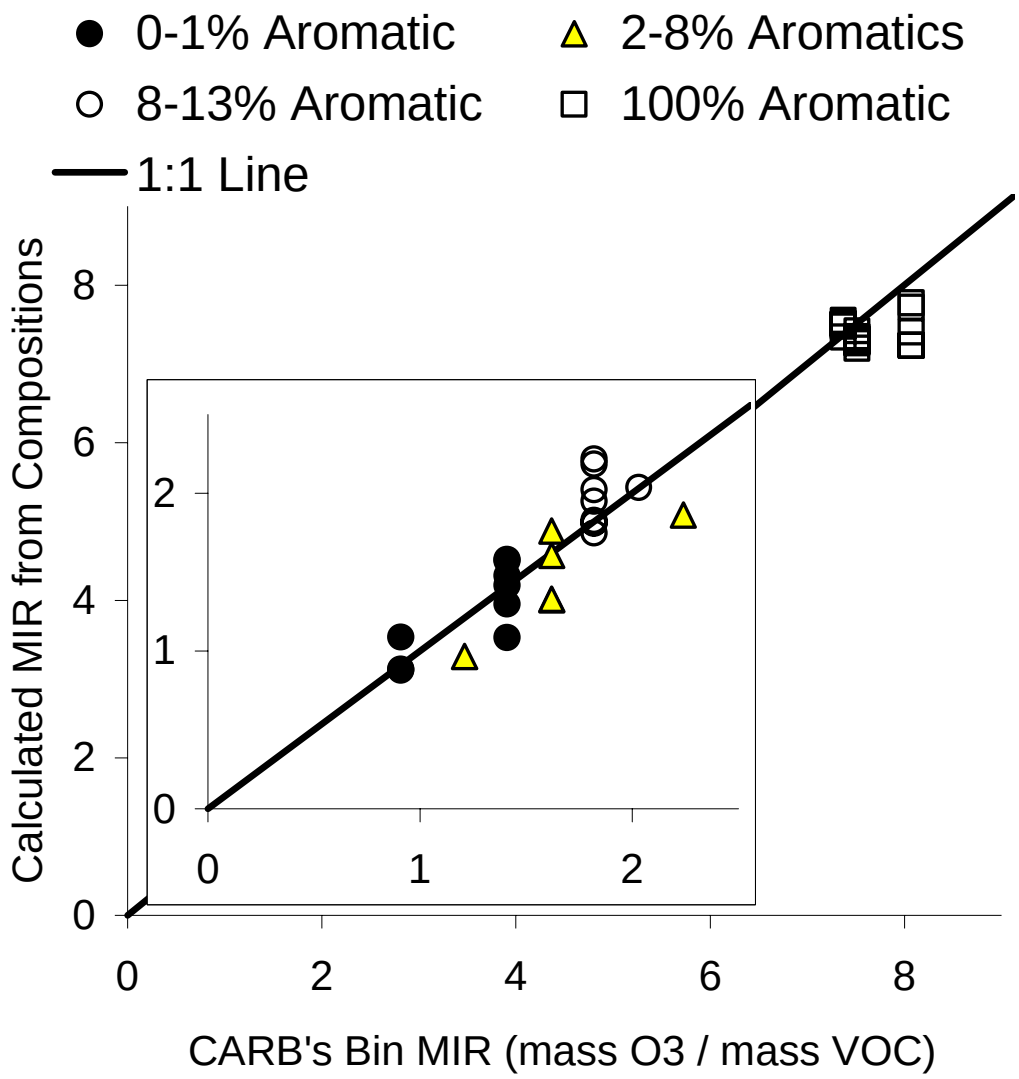
- 9 types with ≥99% alkanes (Bins 6, 11)
- 6 types with 2-8% aromatics (Bins 4, 9, 14)
- 10 types with 8-23% aromatics (Bins 10, 15)
- 16 types with 100% aromatics (Bins 21 - 23)

Two methods used to compute MIRs from the compositional information:

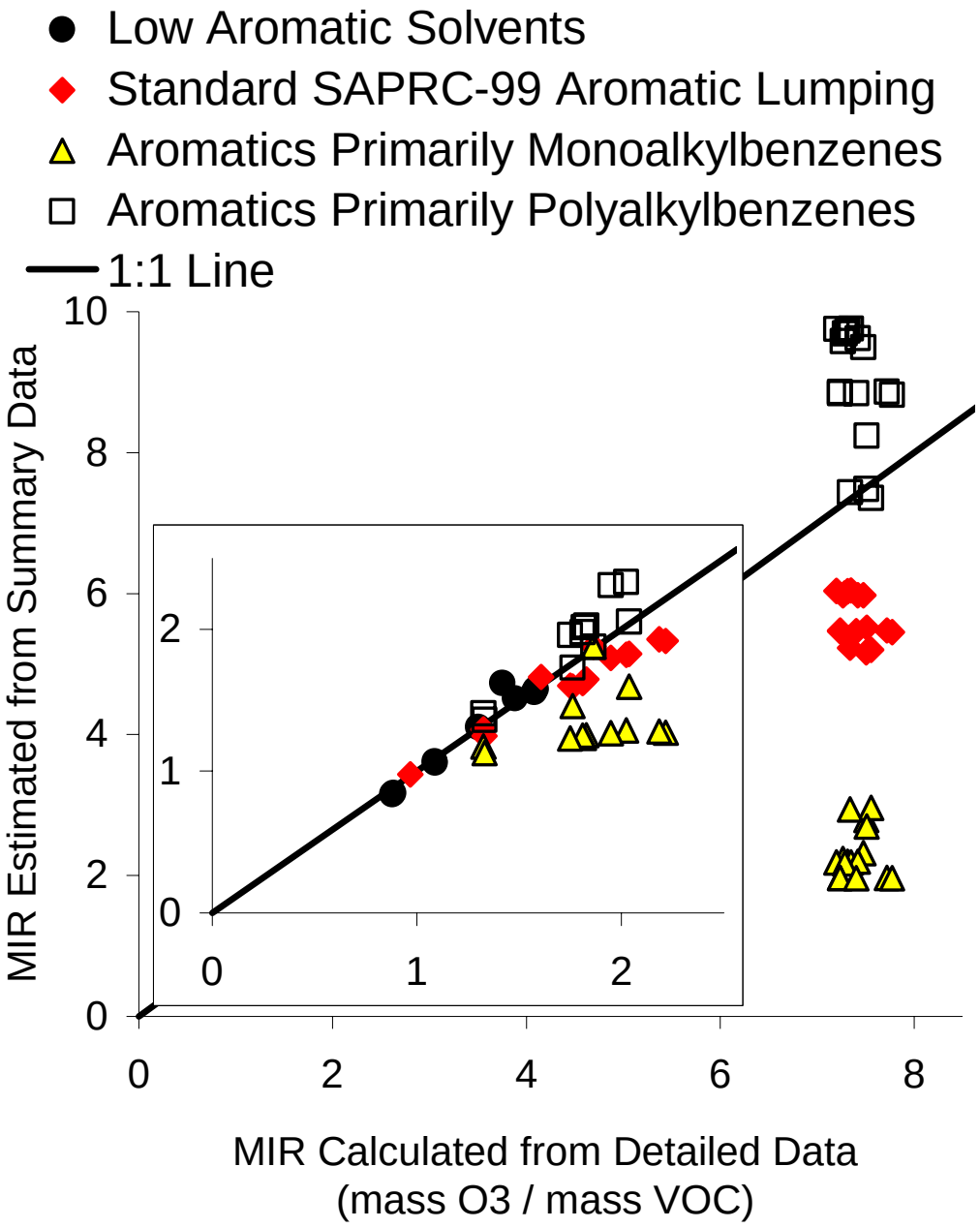
- Based on detailed GC analysis (using generic types only for unspeciated branched and cyclic alkanes)
- Based only on generic type (n-, iso-, or cyclic alkane or aromatic) and carbon number data

Computed MIRs are compared with MIR's derived using CARB's binning method

COMPARISONS OF MIRs DERIVED FROM DETAILED SPECIATION DATA WITH MIRs ESTIMATED USING CARB's BIN METHOD



COMPARISON OF MIRs DERIVED FROM GENERIC TYPES WITH MIRs DERIVED FROM DETAILED SPECIATION DATA



SUMMARY OF TYPES OF AROMATICS IN AROMATIC-CONTAINING SOLVENTS ANALYZED BY CENSULLO ET AL

Aromatic Type	Wt. Percent of All Solvent Aromatics	
	Total	No Chamber Data
Monoalkyl Benzenes	9%	3%
Dialkyl Benzenes	44%	17%
Tri- and poly Alkylbenzenes	41%	21%
Indans, Naphthalenes and Tetralins	6%	4%
Unknown	0.3%	0.3%
Total	100%	46%

Aromatics with no chamber data have uncertain reactivities because aromatic mechanisms have to be adjusted to fit chamber data

SUMMARY OF RESULTS OF ANALYSIS OF CENSULLO ET AL DATA

CARB's binning method performs reasonably well in predicting MIRs derived from Censullo et al's compositional data

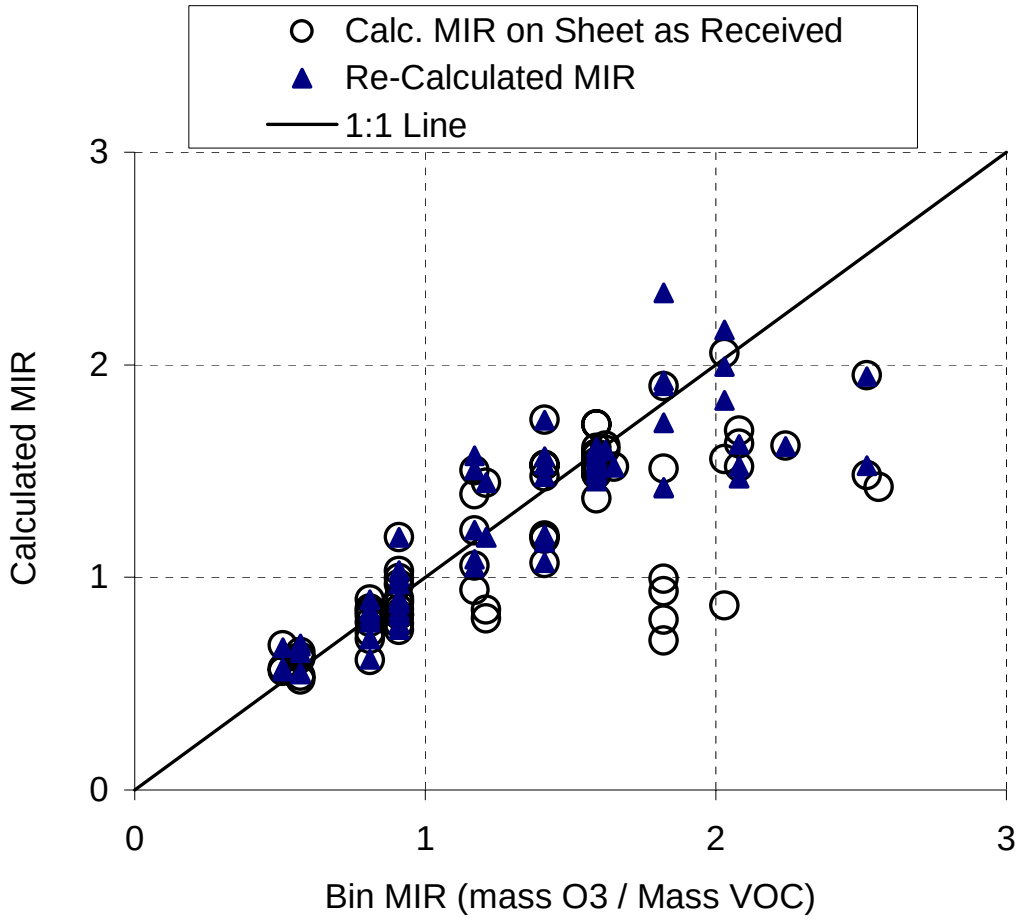
Generic type analysis may be sufficient to estimate reactivities for all-alkane solvents, but not for high aromatic solvents

SAPRC-99 representation of unspeciated aromatics may underestimate reactivities of aromatic constituents in petroleum distillates

Most aromatics in these petroleum distillates are di- to polyalkyl benzenes

Almost half of the aromatic mass in these petroleum distillates has no chamber data and therefore very uncertain reactivities

COMPARISONS OF CALCULATED AND BIN MIRs FOR HYDROCARBON SOLVENTS DATA PROVIDED BY THE ACC



- Data for 78 aliphatic hydrocarbon solvents provided (aromatics <20%)
- Re-calculated MIRs are preliminary. Need information on aromatic carbon number dist.
- Some inconsistencies with ACC MIR values

ONGOING WORK

Chamber Experiments

Complete construction of UCR EPA chamber and begin characterization

Continue evaluating analytical instrumentation

Work with RRAC in selecting petroleum distillates for experiments

Direct Reactivity Measurement

Attempt to improve total carbon analysis system for use with low volatility compounds

Attempt to improve injection system

Use C_{12} – C_{16} n-alkanes and selected mineral spirit samples for evaluation

Reactivity Evaluation of Pet. Distillates

Compile data for additional samples as they become available

Develop standard spreadsheet format and reactivity and uncertainty analysis procedures