ENVIRONMENTAL CHAMBER STUDIES OF VOC SPECIES IN ARCHITECTURAL COATINGS AND MOBILE SOURCE EMISSIONS

South Coast Air Quality Management District
Contract No. 03468

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Outline

- Objectives
- Current Status
- Candidate VOCs for study

OBJECTIVES

Ambient Surrogate – NO_x Evaluation Experiments

- Evaluate ”Base Case” for reactivity studies
- Evaluate mobile source emission reactivity

Environmental chamber studies of architectural coatings VOCs

- Supplement CARB project
- Funding for at least 3 types of VOCs
- Probable focus on glycols or other VOCs relevant to water-based coatings

Obtain PM formation data in conjunction with these and the CARB reactivity experiments

- PM measurements with reactivity runs involve relatively small incremental cost
- Supplemental EPA earmark funding will cover needed PM characterization work

Evaluate potential utility of UCR EPA chamber for “availability” studies

CURRENT STATUS

Ambient surrogate evaluation

- Experiments will be determined after analysis of results of extensive series of surrogate experiments from EPA OBM study.

Chamber Studies of Architectural Coatings VOCs

- Candidate compounds will be discussed at RRAC meeting
- Initial experiments will use same base case as used for petroleum distillates for CARB project

PM Formation Data

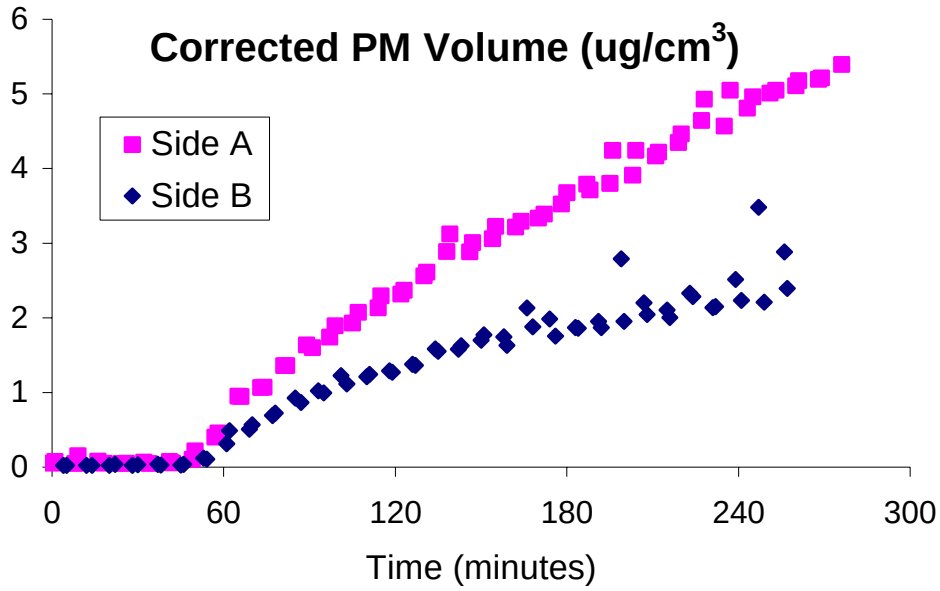
- Some PM data obtained in conjunction with petroleum distillate reactivity study
- The two reactors do not give the same PM results. This is being investigated
- A “chamber model” for PM formation needed

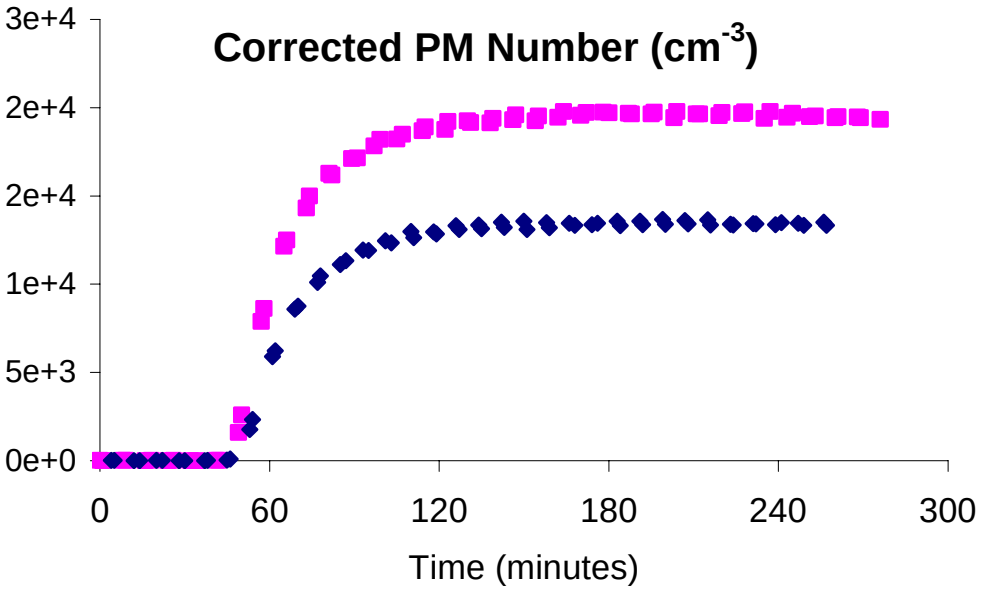
Availability Studies

- RRWG projects are currently focused on modeling, not experiments.

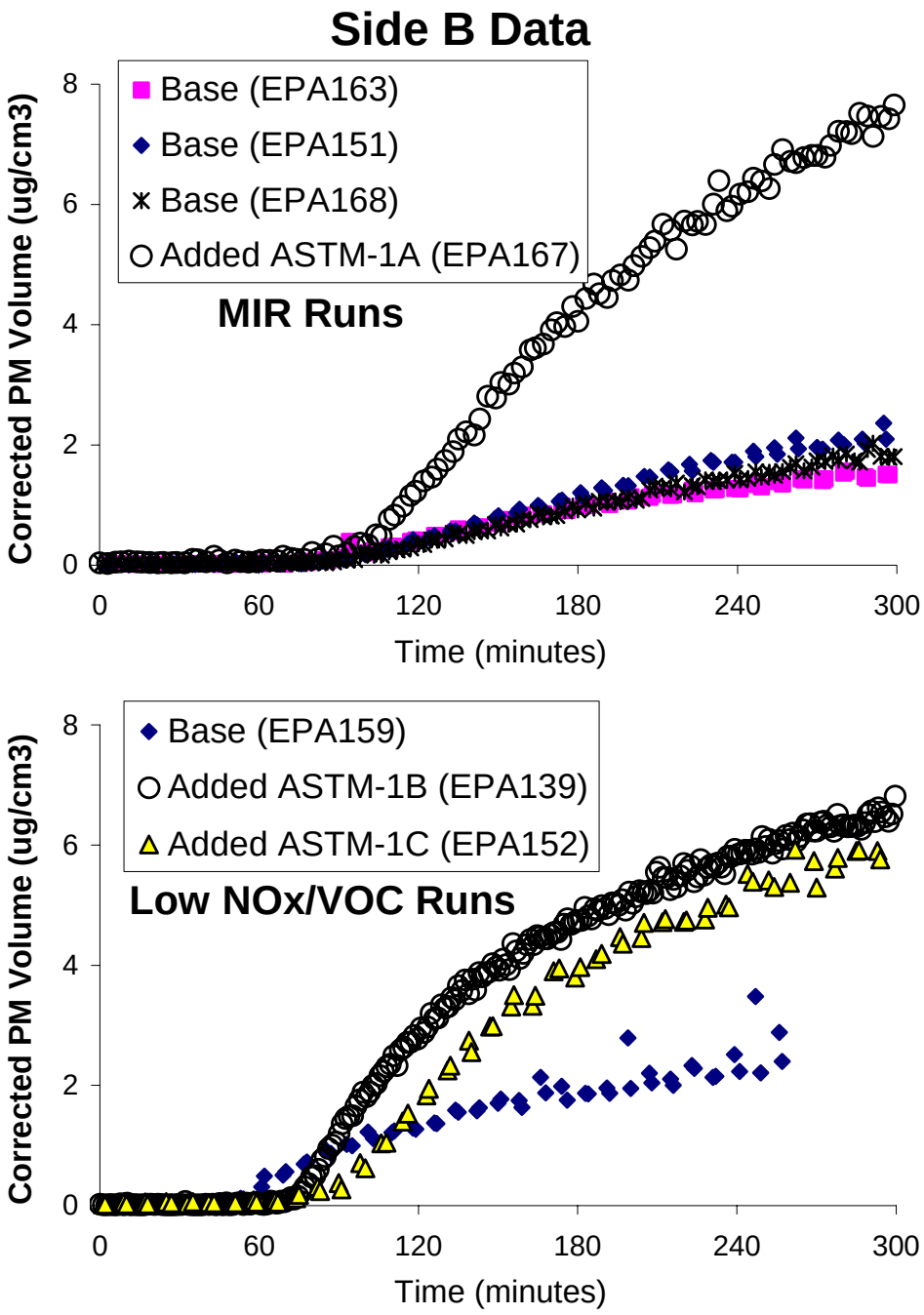
PM SIDE INEQUIVALENCY PROBLEM

(Same base case ROG and NO_x mixture on both sides. O_3 and other gas-phase data are same)





BASE CASE REPRODUCIBILITY AND EFFECTS OF PETROLEUM DISTILLATES



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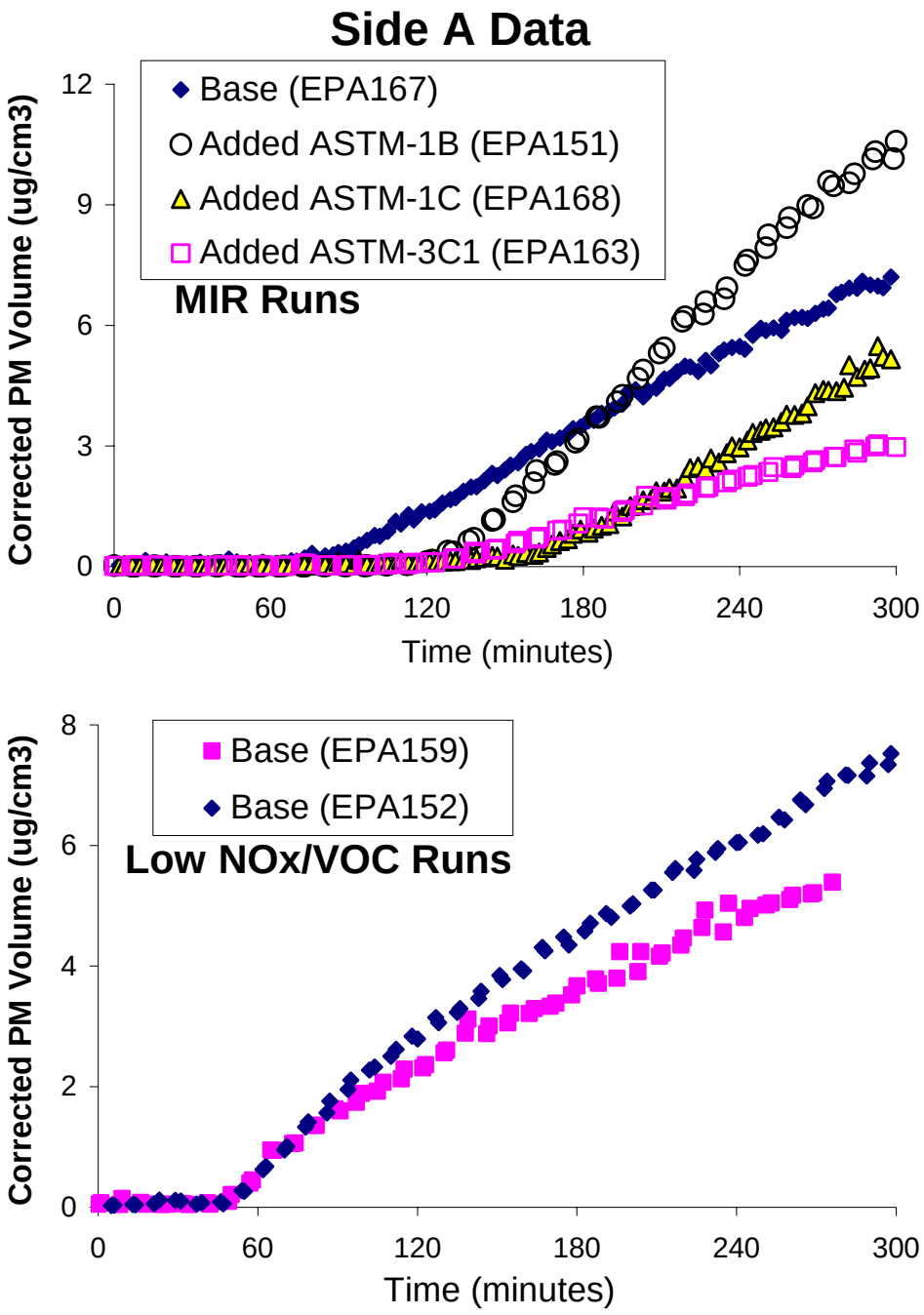

POTENTIAL CANDIDATES FOR SCAQMD COATINGS VOC REACTIVITY PROJECT

(From CARB list)

Ethylene Glycol

- Not studied previously because of volatility and analytical difficulties
- Mechanism not considered uncertain but rate constant not verified

Propylene Glycol

- Studied previously but not using UCR EPA chamber
- Mechanism not considered uncertain and already experimentally verified

Additional Naphtha or Mineral Spirits Solvents (Bin 7 or 10)

- Determination of materials to study should await results of analysis of CARB experiments

POTENTIAL CANDIDATES FOR SCAQMD COATINGS VOC REACTIVITY PROJECT

(From CARB list, continued)

Methanol

- Studied previously but not with full set of base case conditions and with current chambers.
- Mechanism not considered uncertain and probably sufficiently experimentally verified

2-(2-Butoxyethonxy) Ethanol

- No previous chamber studies, but Atkinson et al measured rate constants and major product yields
- Product yields used to refine estimates of SAPRC-99 mechanism generation system
- Mechanism not considered uncertain except perhaps overall nitrate yield

Benzyl Alcohol

- Currently represented using mechanism of toluene, *which is probably incorrect.*
- Most uncertain mechanism of compounds or mixtures listed

POTENTIAL CANDIDATES FOR SCAQMD COATINGS VOC REACTIVITY PROJECT

(From CARB list, continued)

2-Butoxy Ethanol

- Previously studied in chamber experiments
- Atkinson et al measured rate constants and major product yields. Used to refine estimates of SAPRC-99 mechanism generation system
- Nitrate yields measured by Shepson et al. in good agreement with chamber reactivity data.
- Mechanism considered to be well established.

Aromatic 150 (Bin 23)

- Extrapolated mechanisms for high molecular weight aromatics are highly uncertain
- Data will be good complement to study of Aromatics 100 for CARB

UPDATED CHEMICAL MECHANISMS FOR AIRSHED MODEL APPLICATIONS

Proposal to the California Air Resources Board

OBJECTIVES

Update base SAPRC-99 mechanism to be consistent with current data and theories

Improve aromatics mechanisms to be more consistent with chamber data and other results.

Conduct chamber experiments most needed to reduce mechanism uncertainties

Develop **systematic methods to condense mechanisms** for airshed models (goal to provide practical alternatives to CB4)

Implement **updated chlorine chemistry** in mechanism

I**mplement** updated detailed and condensed **mechanisms in airshed model**