Proposed Amendments to Tables of Maximum Incremental Reactivity (MIR) Values

ARB Public Workshop

August 4, 2009

California Environmental Protection Agency

Air Resources Board

Current Regulatory Status

- MIRs used for mobile sources & fuels
- Aerosol coatings regulation uses MIRs
- Section 94700: MIR values for ~800 individual VOCs or mixtures
- Section 94701: MIR values for 24 bins of hydrocarbon (HC) solvents

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Why Amend MIR Values?

- Last amended in 2003
- Dr. Carter developed new SAPRC-07 mechanism; MIR changes for VOCs
- Hundreds of new VOCs, with MIRs
- Review of bin values for HC solvents
  - New data on solvent compositions
  - Impacts of new MIR values on bin system

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Scientific Reviews

- Research Screening Committee:
  - Approved SAPRC-07 final report
- SAPRC-07 Peer Review:
  - Evaluated by 4 independent scientists
- Reactivity Scientific Advisory Committee (RSAC):
  - Approved SAPRC-07's scientific basis & resulting MIRs

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What's New for SAPRC-07?

- 1500 Experiments; State-of-Science
- Corrections/modifications to mechanisms
- Distinct VOC mechanisms: 21% additional
- Additions/changes:
  - Aromatic mechanisms
  - Chlorine chemistry
  - Particulate Matter (PM) prediction

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What's New for MIRs?

- Updated mechanism used (scenarios & methodology: same as for SAPRC-99)
- ~300 more VOCs & mixtures of interest
- MIRs calculated for >1100 VOCs
  - >700 VOCs represented explicitly
  - >300 VOCs represented by "Lumped Molecule" method
  - >50 mixtures

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Changes in MIR Values

- Overall, MIRs are Lower: 12 - 13%
  - MIR for Base VOC Mixture: ~ – 5%
  - Average Change, Relative MIRs: ~ – 7%
- 94% of VOCs: MIR change < 30%

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Largest MIR Changes

Compound	MIR: Now	New
3-methoxy-1-butanol	0.97	3.75
2-amino-2-methyl-1-propanol	4.75	-2.57*
2-(chloromethyl)-3-chloropropene	3.13	6.85
1,2-dibromoethane	0.046	0.098
1,2-dichloroethane	0.098	0.21
trans-1,2-dichloroethene	0.81	1.65

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MIR Changes by Class

Chemical Class	Avg MIR Change
Alkanes	-14 ± 6%
Alkenes	-5 ± 9%
Aromatics	1 ± 16%
Aldehydes	-5 ± 8%
Ketones	-12 ± 13%

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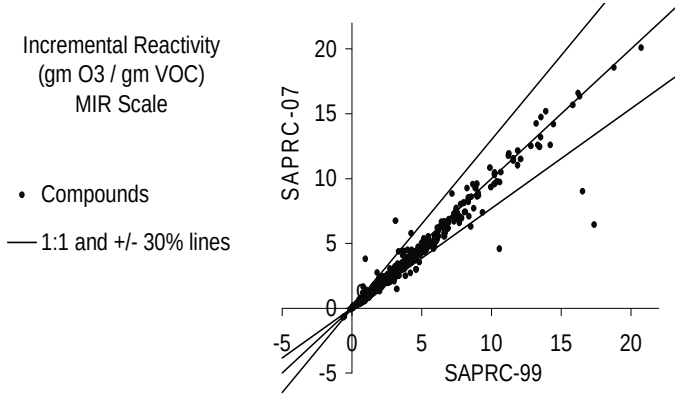
Changes in MIR Scale



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Hydrocarbon (HC) Solvent Bins

- Developed for complex mixtures
- 20 Bins for alkanes (n-, iso-, & cyclo-alkanes)
- 4 Bins for aromatics
- Current bin method:
  - % of n-, iso-, & cyclo-alkanes, aromatics
  - Mean of boiling ranges
  - SAPRC-99 MIR vs. boiling point correlations for each class fraction

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Carter Bin Estimation Method

- Use species composition data for solvents (previously confidential)
- Then use the component MIRs:
  - Boiling Range
  - HC class & carbon #
- Assumptions:
  - Alkane class fractions equally distributed
  - Compositions depend only on carbon #

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Carter Bin Estimation Method - 2

- MIRs evaluated for >100 solvents with composition data
- Bin composition assignments used to update bin MIRs to SAPRC-07
- Change in method:
  - MIRs decrease more for light solvents with cycloalkane content
- Change in mechanism:
  - MIRs for alkane bins (1-20) decrease ~14% (avg)

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HC Bin MIRs: 2000 - 2009

Boiling Point (°F)	80-205			>205-340			>340-460			>460-580		
MIRs	Bin	2000	2009	Bin	2000	2009	Bin	2000	2009	Bin	2000	2009
Alkanes	1	2.08	1.33	6	1.41	1.08	11	0.91	0.63	16	0.57	0.47
n- & iso-Alkanes	2	1.59	1.23	7	1.17	0.95	12	0.81	0.55	17	0.51	0.43
cyclo-Alkanes	3	2.52	1.53	8	1.65	1.34	13	1.01	0.79	18	0.63	0.54
Alkanes: <8% aromatic	4	2.24	1.37	9	1.62	1.35	14	1.21	0.91	19	0.88	0.61
Alkanes: 8-22% arom.	5	2.56	1.47	10	2.03	1.88	15	1.82	1.48	20	1.49	0.89

Boiling Point (°F)	280-290			320-350			355-420			450-535		
MIRs		2000	2009		2000	2009		2000	2009		2000	2009
Pure Aromatic	21	7.37	7.44	22	7.51	7.39	23	8.07	6.66	24	5.00	3.76

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Timeline

- RSAC approved SAPRC-07 mechanism & MIR values: March 25, 2009
- Proposed amendments to tables of MIR values, including HC solvent bins
  - ARB Workshop: August 4, 2009
  - Staff Report: September 17, 2009
  - Exec. Officer (EO) Hearing: November 3, 2009

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We Request Your Help!

- Economic Assessment for Staff Report
  - Cost/Benefit to California Businesses
  - Due August 11
- Missing Chemicals for MIR List?
  - Due today
- Smog Chamber Tests for any VOCs?
  - Due today

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