CO Offset in PM

Gary Z. Whitten, Ph.D.

Smog Reyes

16 November, 2006

The VOC Offset from CO

- Two Key Issues Today:
  - Reactivity of CO relative to VOC
    - Studies show MIR under-represents CO
  - Reduction of CO from fuel oxygen
    - Idea for adapting off-cycle effect in PM

Reactivity of CO relative to VOC

- European reactivity ratio about 10 to 1
  - 4000 reaction chemistry, trajectory model
- EPA has reported 15 to 1 for mobile VOC
  - Exhaust (as used in PM) somewhat higher
- MIR predicts 66 to 1 (48 to 1 in old PM).
- ARB study 39 to 1 based on SIP grid model instead of high-NOx box-model used for MIR's.

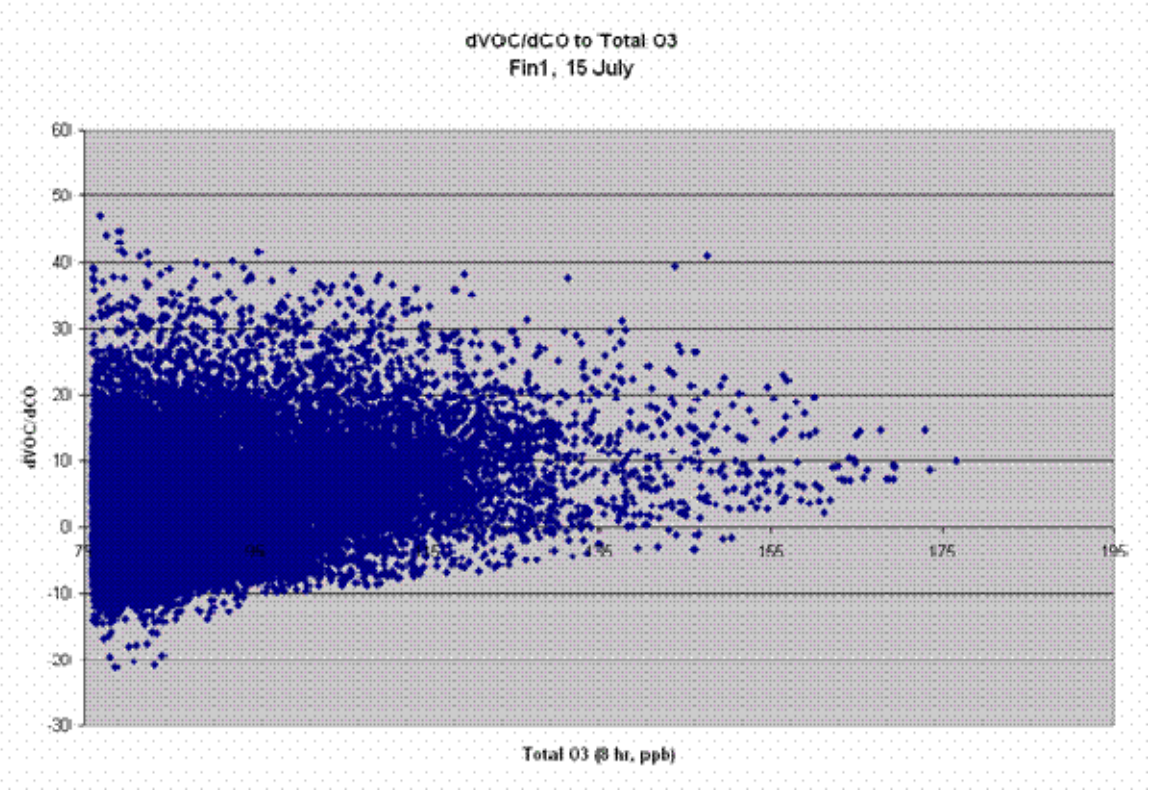
MIR uses box model

- MIR's are based on average of 39 cities
  only 4 of which are in California
- Extra NOx is added to give negative response to incremental NOx
  - i.e. ozone decreases when NOx is increased
- Several grid model studies have tested the MIR factors.
  - Agreement good except CO and ethane

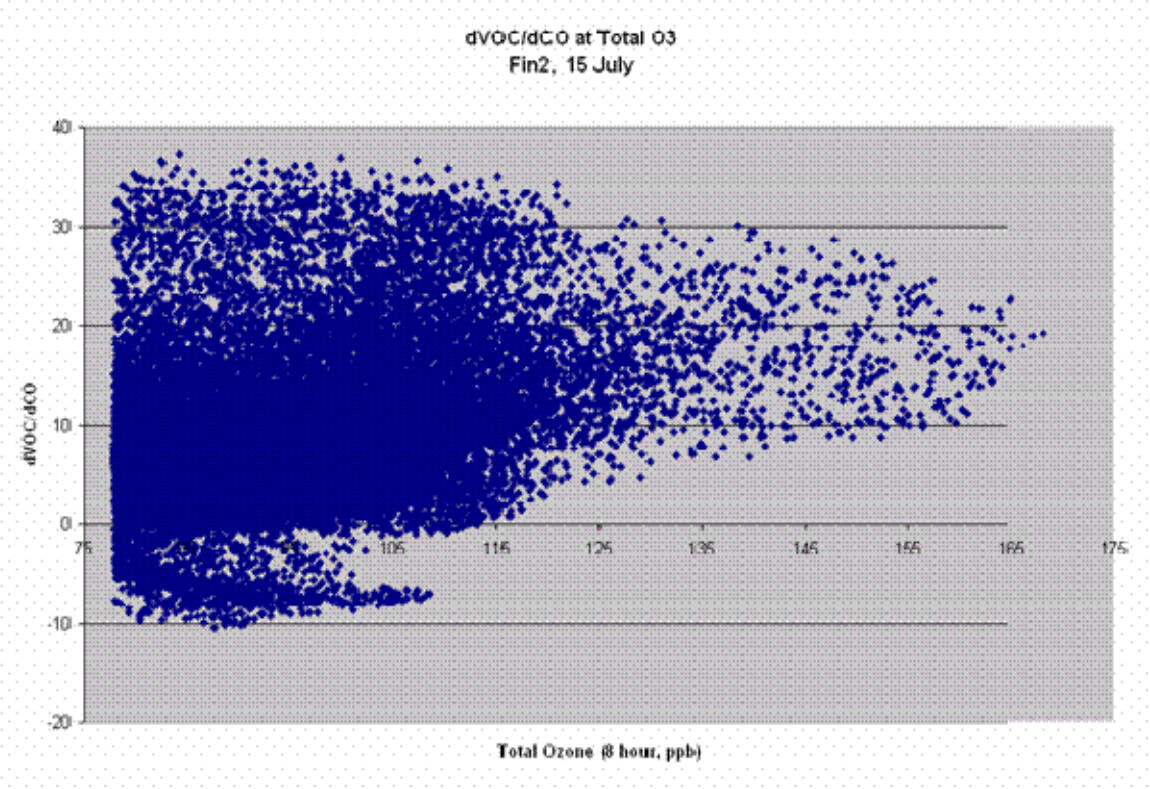
consistent bias for CO seen by MIR-inventor Carter

- Carter, Tonnessen, and Yarwood (2003) specifically state on page 56:
- “For most model species the EKMA [MIR type] results are surprisingly close to the comparable regional relative reactivity metrics given the significant differences in the types of models and scenarios employed.….
- However, there are some consistent differences in EKMA vs. regional relative reactivities for certain model species. Perhaps the most significant is the ***consistent bias*** for the EKMA scales towards predicting lower relative reactivities for the slower reacting species, specifically CO, ethane and to a lesser extent PAR.”

Carter et al. ’03, Revisited, Midwest and South



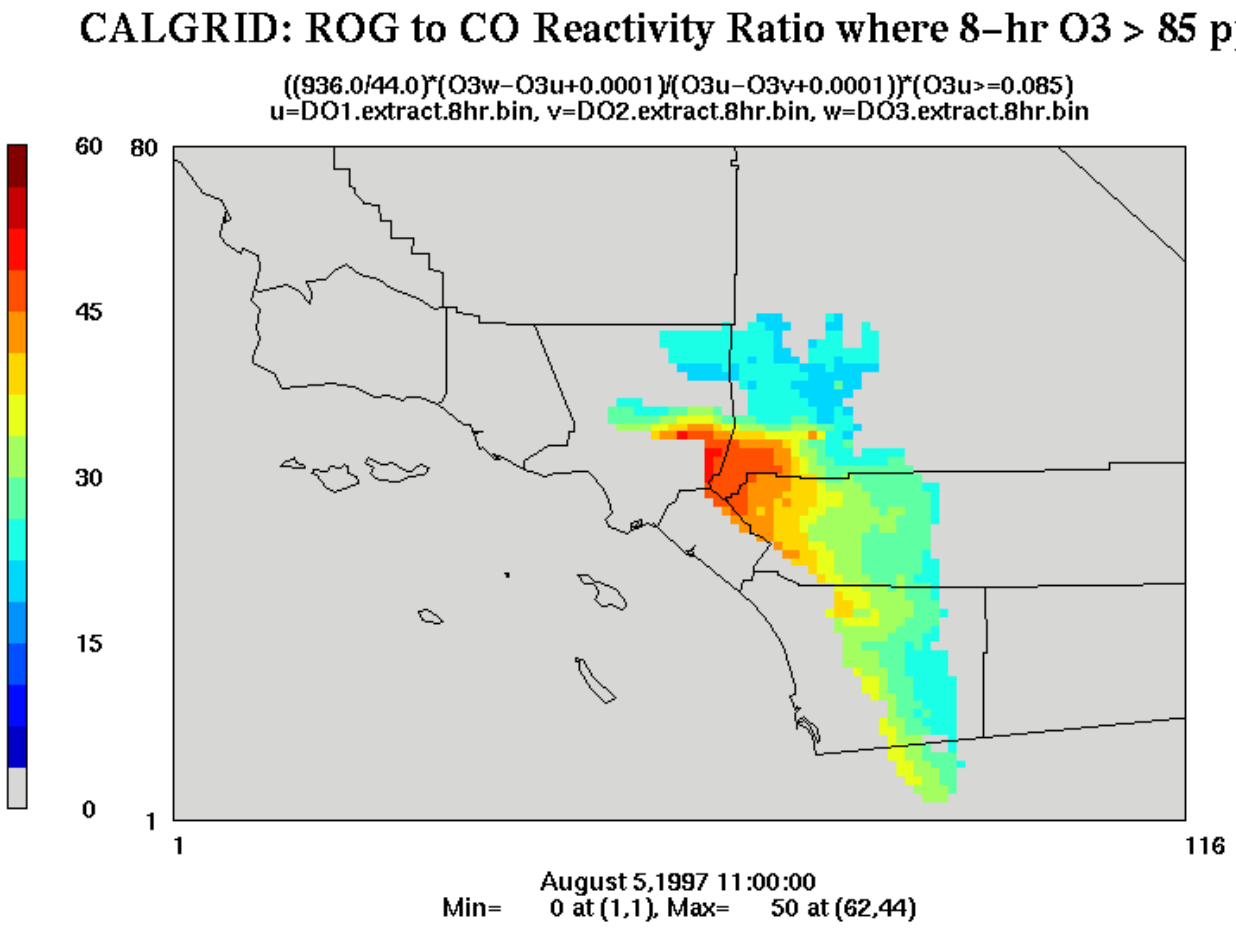
Carter et al. ’03, Revisited, Northeast



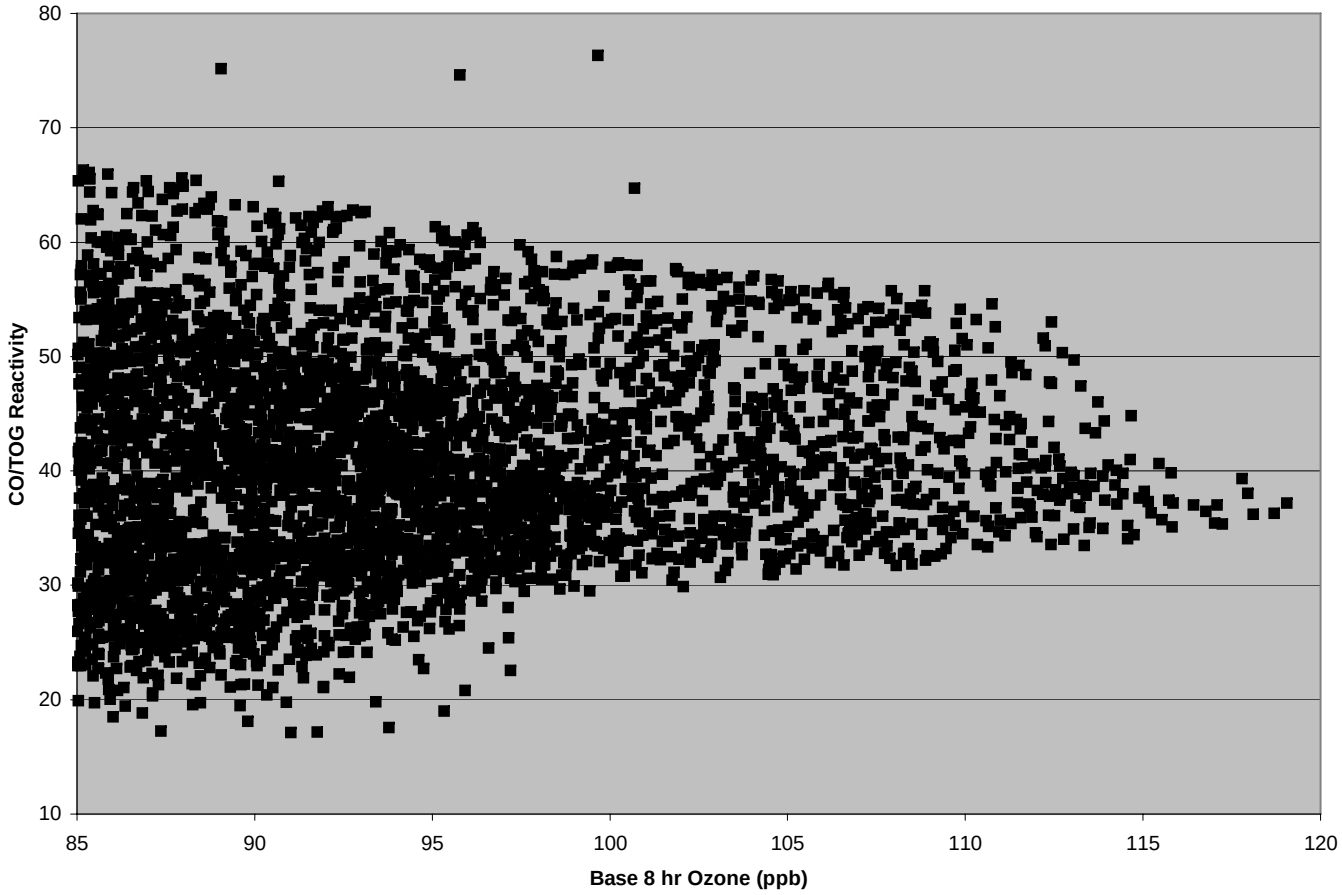
ARB Grid Study

- Saw 39 to 1 at ozone max.
- Did not report other sites.
- Smog Reyes reran ARB model to expand analysis.

ROG to CO Reactivity Ratio for 8-hour Ozone



VOC to CO Reactivity -- ARB



Reduction of CO from oxygen

- In 1999 PM ARB applied 2.8 factor to FTP for aggressive driving credit to all tech groups even though data available only for Tech 4.
- Data on Tech 5 aggressive driving does exist since 2001 (Alliance US06), but will probably not be released.

Reduction of CO from oxygen

- Note: App. G base is 4995 tons per day.
  296.44 tons CO reduced is 5.933%.

Table5. Calculations of CO Reductions Base on FTP and REPO5 Emissions

	81-85 MY	86 to 90 MY	91 to 95 MY	95 to 05 MY	Total
% CO Reduction per wt. % Oxygen	-5.07%	-4.76%	-1.35%	0.00%	
WT. % Oxygen Increased (1.0)	1.00	1.00	1.00	1.00	
Weighted / FTP COMP	2.8	2.8	2.8	2.8	
Adjusted CO Reductions	-101.08	-156.01	-39.35	0.00	-296.44
Ozone Reduction from CO Reductions	-7.08	-10.92	-2.75	0.00	-20.75

New PM uses FTP only

- Factors other than oxygen now incorporated for CO using FTP-only data with statistical model similar to PM for VOC and NOx.
- ARB has remarked that a method to address off-cycle (i.e. aggressive) impact is unknown.
- The 1998 California ethanol study did test off-cycle and the results were the basis for the 2.8 factor in the old PM.

1998 CA Ethanol Study

- Two fuels used.
  - A CaRFG2 with 11% MTBE
  - An E10 blended to the same CARBOB
- Assuming 10% ethanol and 11% MTBE give equal dilution, then main differences are RVP and fuel oxygen percent.
  - RVP does not impact exhaust at low RVP.
- Therefore, a nearly orthogonal comparison for just fuel oxygen (T50 may need study).

New Idea for Off-cycle

- Rather than a 2.8 factor times FTP as in old PM, use an addition to FTP.
  - Rather than apply to all techs as in old PM, use for Tech 4 and maybe Tech 3, but should have data for Tech 5.
- Revisiting 1998 study suggests an addition of about 5% to FTP % impact for fuel oxygen between 2 wt.% and 3.5 wt.%.
- More refined analysis may change this 5% estimate up or down somewhat.