

REACTIVITY SCALES AS COMPARATIVE TOOLS FOR CHEMICAL MECHANISMS: SAPRC-07 vs MCM

Dick Derwent
rdscientific, Newbury, United Kingdom

Presentation to Reactivity Scientific Advisory Committee
Air Resources Board, Sacramento
March 2009

COMPARISON OF SAPRC-07 AND MCM v3.1

Reactivity values represent a simple way of comparing chemical mechanisms

Reactivity values compress a great deal of atmospheric chemistry into a single number that reflects the ability of an organic compound to form ozone.

By comparing reactivity values from the MIR and POCP scales, it should be possible to evaluate the SAPRC-07 and MCMv3.1 chemical mechanisms

MASTER CHEMICAL MECHANISM

- Widely used detailed chemical mechanism in Europe
- Available on the web:

<http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html>

- near-explicit representation of the atmospheric degradation of up to 175 organic compounds and their contribution to ozone formation.
- available as stoichiometric reactions with full search and chemistry facilities

PHOTOCHEMICAL TRAJECTORY MODEL PTM

- The MCMv3.1 has been implemented inside the PTM to calculate reactivity scales for multi-day ozone episodes across Europe
- The PTM is a moving box trajectory model
- Assumes complete and instantaneous mixing in the vertical up to the top of the atmospheric boundary layer
- Treats emissions, deposition, atmospheric chemistry, aerosol formation both inorganic and organic

REACTIVITY SCALES

Incremental reactivity

- this is the increase in ozone ΔO_3 in ppb divided by the fractional increase in the emissions from that source category:

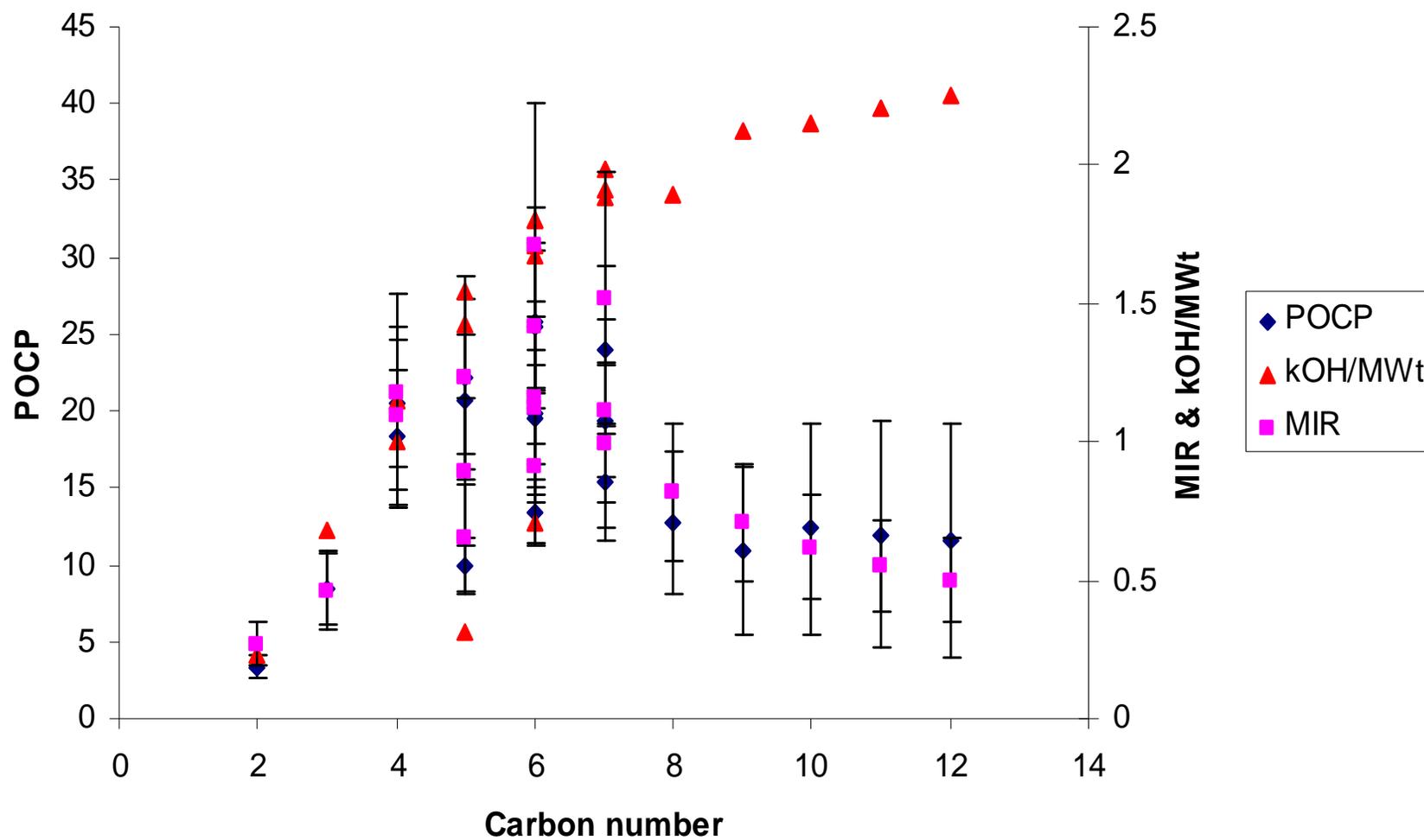
$$IR_i = \frac{\Delta O_3}{\frac{\Delta VOC_i}{VOC}}$$

Incremental reactivities depend on the environmental conditions and are not geophysical quantities

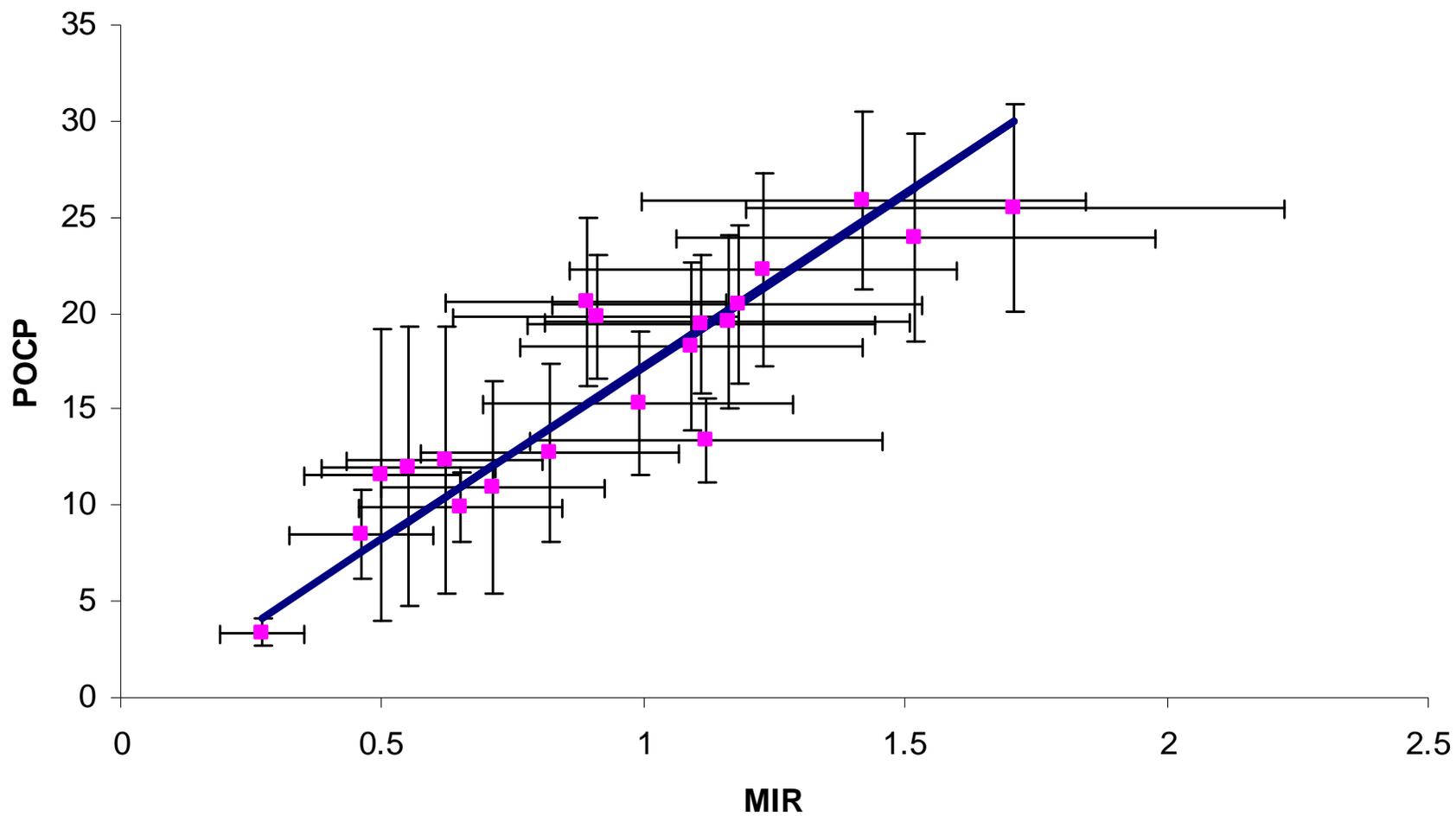
DETERMINATION OF REACTIVITY SCALES FOR CALIFORNIA CONDITIONS

- MIRs are determined using SAPRC-07 for California conditions
- POCPs were determined using the PTM and background scenarios for 'Average US', 'Los Angeles', 'San Diego', 'San Francisco', 'Sacramento' using data supplied by US EPA (Baugues 1990)
- NO_x emissions were scaled to produce the maximum ozone increments for an additional injection of ethylene
- POCPs are presented as indices relative to ethylene =100

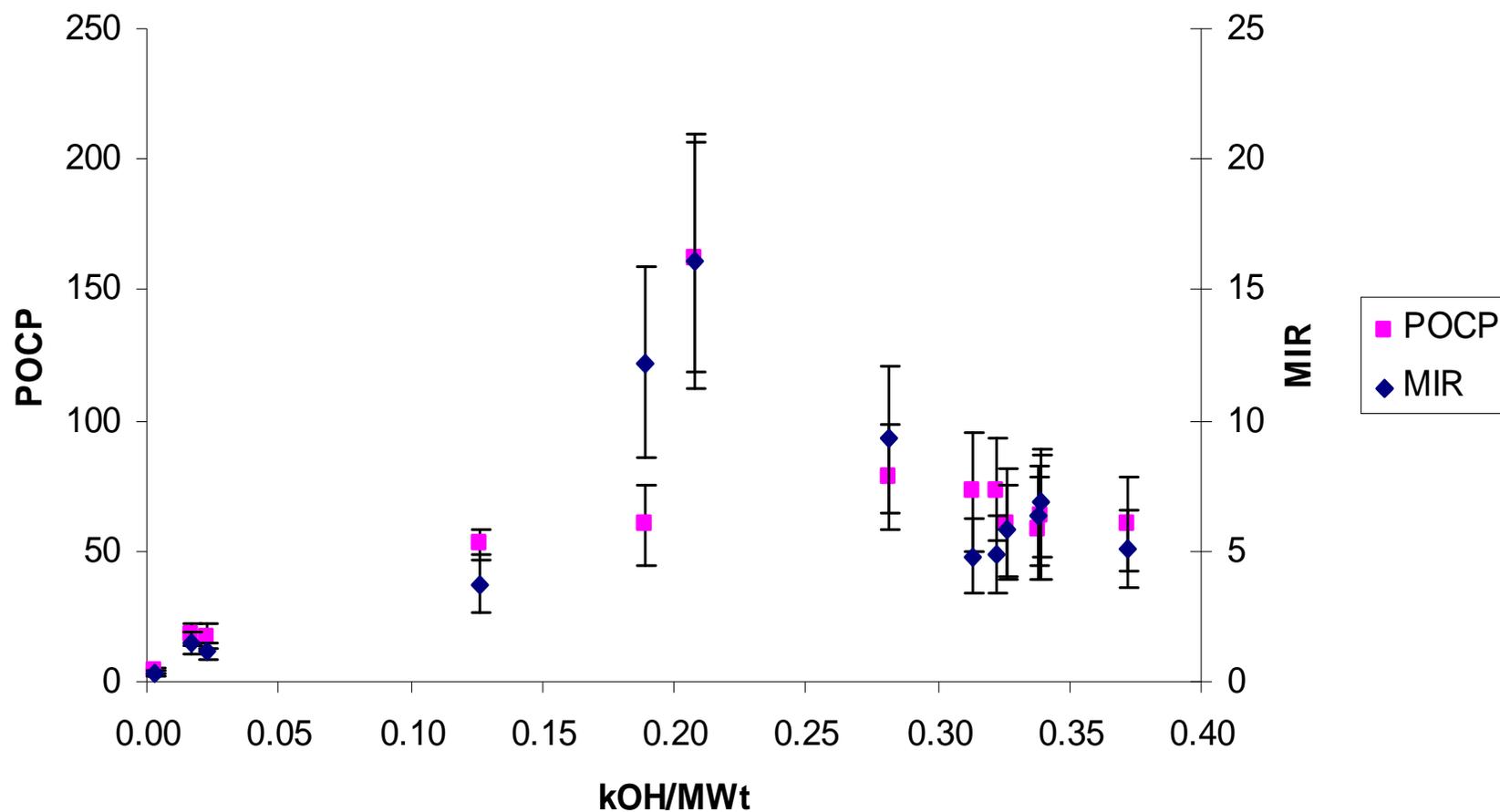
MIR AND POCP REACTIVITIES FOR THE ALKANES COMPARED WITH THOSE FROM THE k_{OH} REACTIVITY SCALE



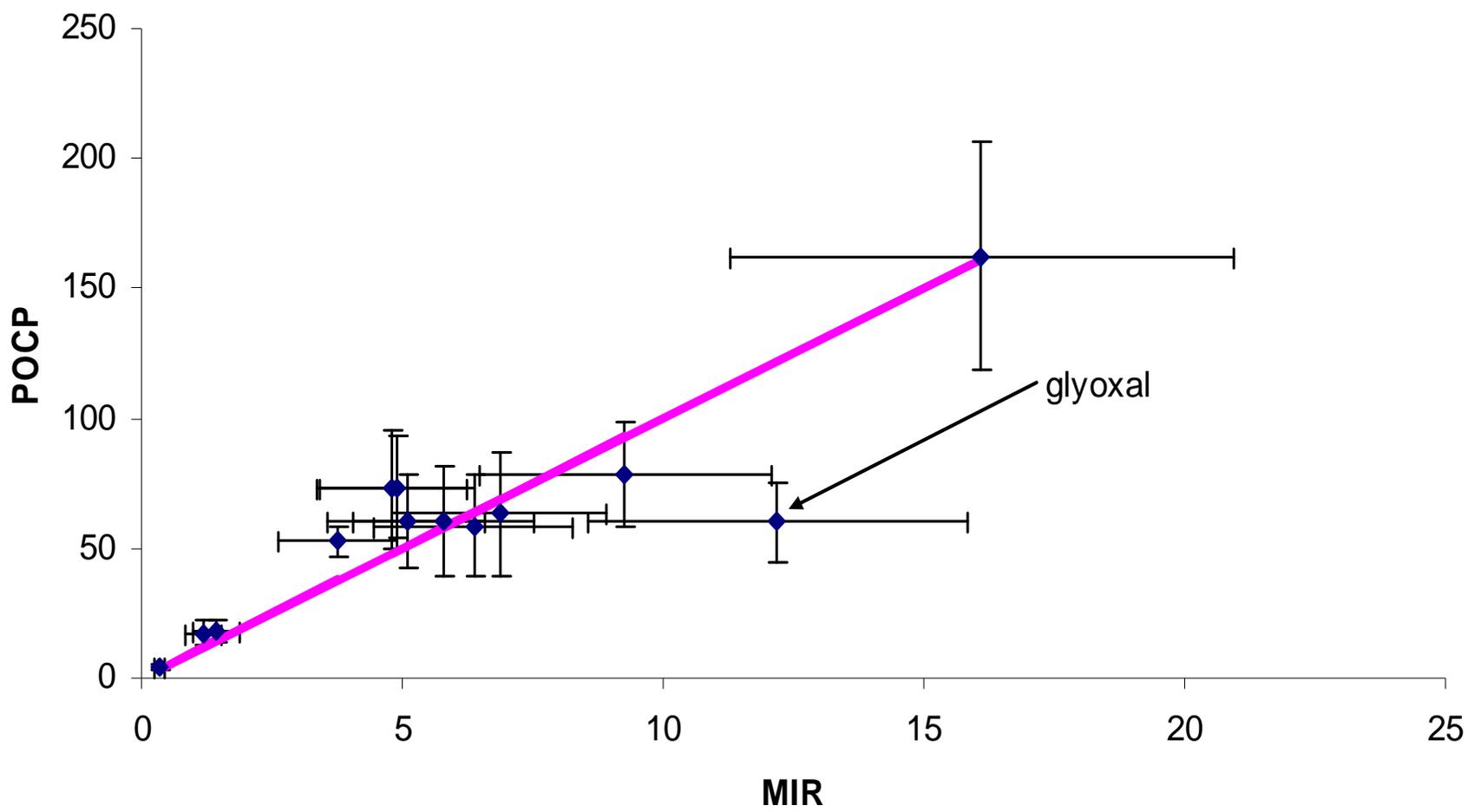
COMPARISON OF MIR AND POCP SCALES FOR ALKANES



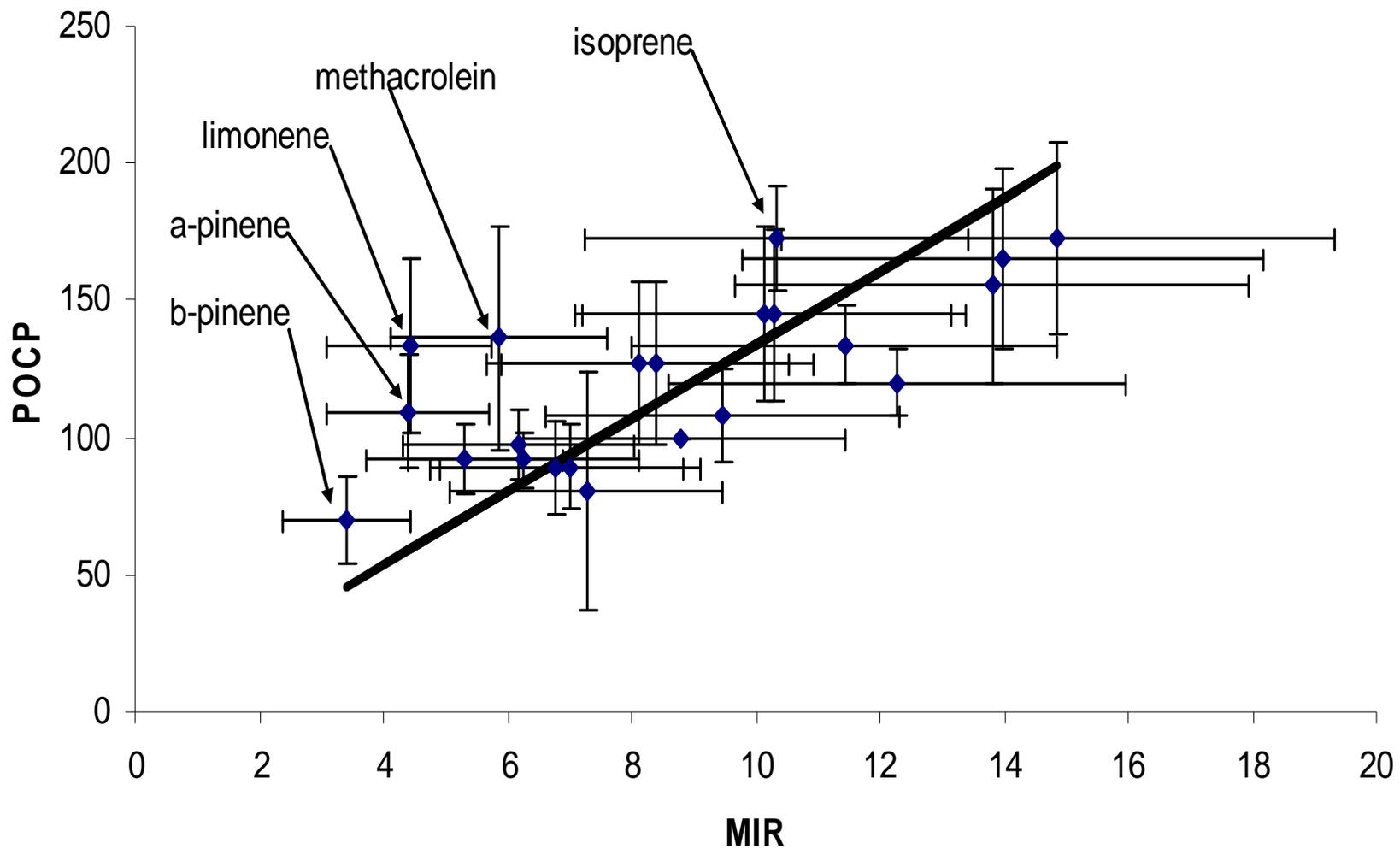
MIR AND POCP REACTIVITIES FOR THE ALDEHYDES AND KETONES COMPARED WITH THOSE FROM THE k_{OH} REACTIVITY SCALE



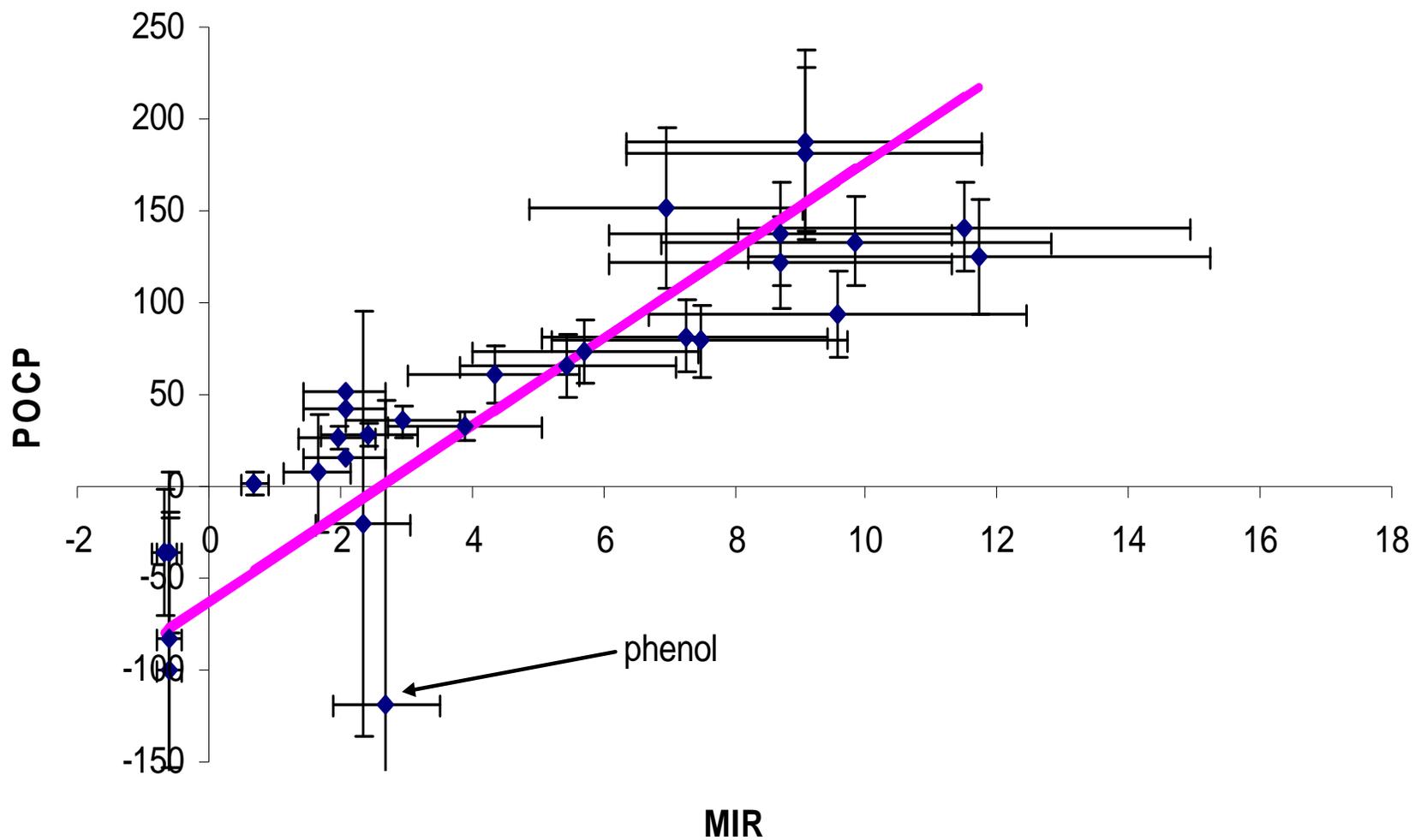
COMPARISON OF MIR AND POCP SCALES FOR ALDEHYDES AND KETONES



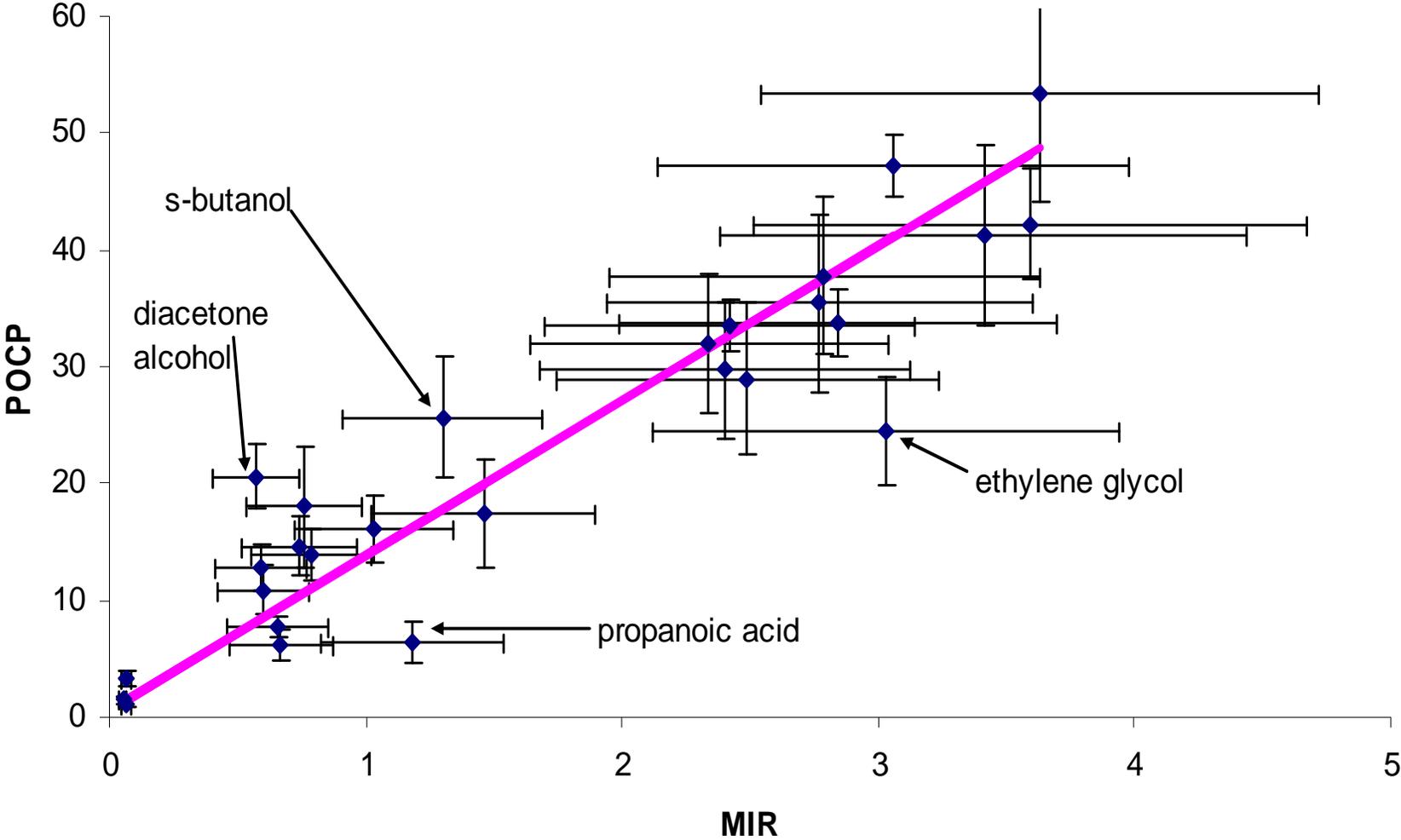
COMPARISON OF MIR AND POCP SCALES FOR ALKENES



COMPARISON OF MIR AND POCP SCALES FOR AROMATICS



COMPARISON OF MIR AND POCP SCALES FOR OXYGENATES



CONCLUSIONS

- The large measure of agreement between the MIRs and POCPs over such a large number of organic compounds could not have been fortuitous
- The SAPRC-07 and MCMv3.1 have represented the available chemical mechanistic data in a consistent manner despite altogether different approaches
- There appear to be a few inconsistencies remaining to be resolved but they are unlikely to have any policy significance

CONCLUSIONS

- Detailed atmospheric chemistry mechanisms are vital for robust policy formulation with respect to organic compounds and ozone formation.
- The SAPRC-07 and MCMv3.1 detailed chemical mechanisms appear to have generated consistent reactivity scales, MIR and POCP scales, respectively under California conditions.
- Both detailed mechanisms appear to have represented the available understanding of the degradation of a large range of organic compounds in a consistent and rigorous manner.

CONCLUSIONS - ALKANES

- Alkoxy radical isomerisation must be consistently described between SAPRC-07 and MCMv3.1 otherwise mechanistic reactivities would not agree for the alkanes

CONCLUSIONS - ALKENES

- Degradation to the first carbonyl reaction product must be consistently treated by SAPRC-07 and MCMv3.1
- The representation of the degradation of the surrogate carbonyl reaction products in SAPRC-07 appears to be consistent with the near-explicit treatment in MCMv3.1
- Differences are found between MIRs and POCPs for isoprene, methacrolein, α -pinene, β -pinene and limonene

CONCLUSIONS - CARBONYLS

- Kinetic reactivity is well represented by both SAPRC-07 and MCMv3.1
- Both mechanisms give a consistent picture of reactivity across this class of organics
- Differences are found for glyoxal which remain unexplained

CONCLUSIONS - AROMATICS

- Large differences were expected for this class of organics because of inadequacies in basic understanding of mechanistic issues
- These were not found and SAPRC-07 and MCMv3.1 agreed very closely
- This agreement is most heartening
- Differences were found for phenol which is a potent NO_x sink

COCONCLUSIONS - OXYGENATES

- Close agreement between SAPRC-07 and MCMv3.1 with esters less reactive compared with ethers
- Differences were found for diacetone alcohol, s-butanol, propanoic acid and ethylene glycol