INVESTIGATION OF VOC REACTIVITY EFFECTS USING EXISTING REGIONAL AIR QUALITY MODELS

SUMMARY OF PROGRESS
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BY

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OBJECTIVES

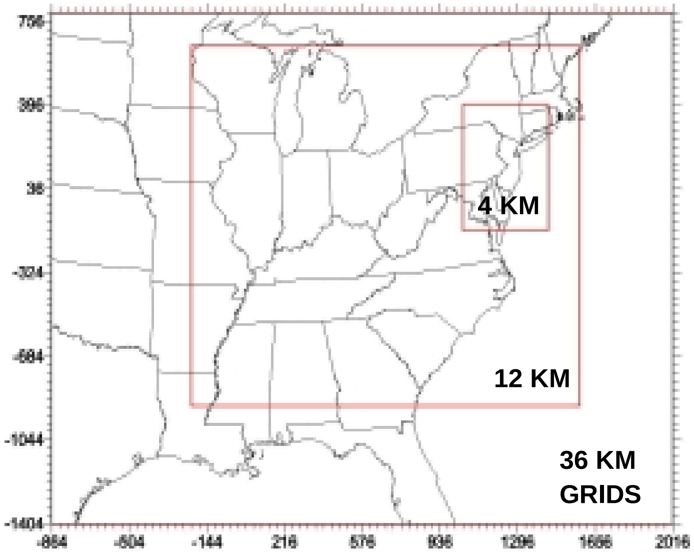
ASSESS VOC REACTIVITY EFFECTS USING AN EXISTING REGIONAL MODELING DATABASE REPRESENTING THE EASTERN U.S.

ASSESS RELATIVE INCREMENTAL OZONE IMPACTS OF VOC MODEL SPECIES WITH RESPECT TO:

- VARIATION WITHIN THE MODELING DOMAIN
- DERIVATION OF VARIOUS REACTIVITY METRICS
- COMPARISON WITH REACTIVITIES CALCULATED USING EKMA MODELS
- PREDICTIONS OF EFFECTS OF SELECTED LARGE SCALE SUBSTITUTIONS

ASSESS APPROACHES FOR DERIVING A GENERAL REACTIVITY SCALE REPRESENTING REGIONAL O_3 IMPACTS

CRC-NARSTO MODELING DATABASE



MODEL:	CAMx VERSION 3.01 WITH DDM
EPISODE DATES:	JULY 7-15, 1995 (DATA FOR 11th-14th USED IN ASSESSMENT)
EMISSIONS:	EPA NET96
MET DATA:	MM5
MECHANISM:	UPDATED CB4 (ETHANE ADDED)

(Analysis of fine grid data still underway. Current analysis uses 4 and 12 km data averaged into the 36 KM grids.)

CARBON BOND 4 MECHANISM

ADVANTAGES

- LEAST EXPENSIVE TO USE FOR INITIAL STUDY
- WIDELY USED
- REPRESENTS MOST OF THE IMPORTANT CLASSES OF REACTIVE VOCs

DISADVANTAGES

- OUT-OF-DATE (DEVELOPED IN1989)
- HIGHLY CONDENSED. CANNOT BE USED TO ASSESS MOST INDIVIDUAL VOCs
- INAPPROPRIATE OR NO REPRESENTATION OF SOME IMPORTANT TYPES OF VOCs:
  - INTERNAL ALKENES (only products represented; effects of initial OH and O_3 reaction ignored)
  - TOLUENE (reactivity characteristics significantly different than predicted using current mechanisms)
  - RADICAL INHIBITING VOCs (not represented)
- MAY BE MORE SENSITIVE TO RADICAL EFFECTS THAN CURRENT MECHANISM

NEVERTHELESS, CB4 PROBABLY SUITABLE FOR INITIAL QUALITATIVE ASSESSMENT OF VARIABILITY OF REACTIVITY WITH MODELING DOMAIN

PHASE1: DDM CALCULATIONS

DECOUPLED DIRECT METHOD (DDM) USED TO CALCULATE SENSITIVITIES OF SURFACE O_3 CONCENTRATIONS TO CHANGES IN EMISSIONS

SENSITIVITIES CALCULATED AS FUNCTION OF TIME AND SPACE AND OUTPUT AS HOURLY AVERAGES FOR ALL GROUND LEVEL CELLS.

FIRST DDM CALCULATION:

- SENSITIVITY TO TOTAL VOC AND NO_x EMISSIONS
- RESULTS GIVE PPM O_3 CHANGE RESULTING FROM 100% CHANGE IN EMISSIONS (IF LINEAR)

SECOND DDM CALCULATION:

- SENSITIVITY TO SURFACE EMISSIONS OF CO AND 9 VOC MODEL SPECIES VARIED.
- SAME TIME AND SPACE DISTRIBUTION AS TOTAL ANTHROPOGENIC VOC
- RESULTS GIVE PPM O_3 CHANGE FROM 100% CHANGE IN ANTHROPOGENIC VOC CARBON EMISSIONS AS THE SPECIES (IF LINEAR)

THE SENSITIVITIES OF O_3 TO MODEL SPECIES EMISSIONS ARE THE SAME AS THE **INCREMENTAL REACTIVITIES** OF THESE MODEL SPECIES

CARBON BOND 4 MODEL SPECIES WHOSE OZONE SENSITIVITIES WERE DETERMINED

SPECIES	APPROXIMATELY REPRESENTATIVE OF
PAR	C_4 - C_6 ALKANES
ETH	ETHENE (EXPLICIT)
OLE	PROPENE (PRIMARILY)
TOL	NO SPECIFIC COMPOUND. MAY BE INDICATIVE OF COMPOUNDS WITH VERY NO_x SENSITIVE REACTIVITIES (E.G., PHENOLS, STYRENES)
XYL	XYLENES
FORM	FORMALDEHYDE (EXPLICIT)
ALD2	ACETALDEHYDE (EXPLICIT)
ETOH	ETHANOL (EXPLICIT)
ETHA	ETHANE (ADDED FOR THIS STUDY)
CO	CARBON MONOXIDE (EXPLICIT)

OZONE IMPACT METRICS USED

IMPACTS BASED ON EFFECTS OF SPECIES ON DAILY MAXIMUM 1-HOUR AND 8-HOUR AVERAGE O_3

REACTIVITIES DERIVED RELATIVE TO REACTIVITIES OF TOTAL ANTHROPOGENIC VOC EMISSIONS MIXTURE (BASE ROG)

- GIVES BENEFITS OF REDUCING A SINGLE VOC COMPARED TO REDUCING ALL VOCs EQUALLY
- BASE ROG SENSITIVITIES DERIVED FROM SENSITIVITIES OF COMPONENT SPECIES
- BASE ROG COMPOSITION DERIVED FROM EPA REGIONAL EMISSIONS DATABASE
- TOTAL VOC SENSITIVITIES COULD NOT BE USED BECAUSE THEY INCLUDED BIOGENIC VOCs

4 GLOBAL RELATIVE REACTIVITY METRICS DERIVED

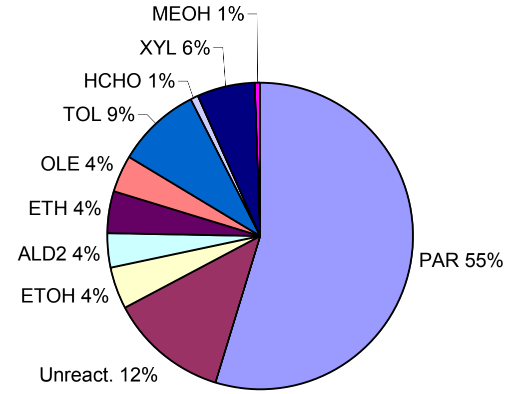
- MINIMUM SUBSTITUTION ERROR
- REGIONAL MIR
- REGIONAL MAXIMUM O_3
- REGIONAL AVERAGE O_3

EXCLUDING LOW O_3 OR ZERO EMISSIONS CELLS FOUND NOT TO SIGNIFICANTLY AFFECT RESULTS

COMPOSITION OF BASE ROG MIXTURE USED TO DERIVE RELATIVE REACTIVITIES

CB4 MODEL SPECIES:

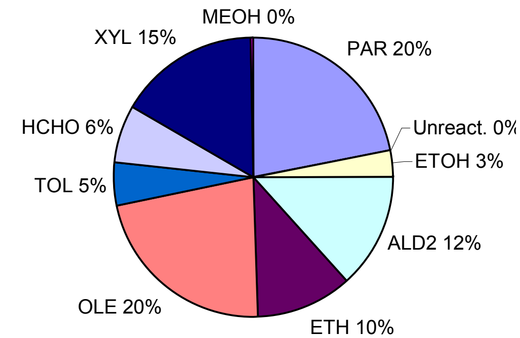
CARBON BASIS



CB4 MODEL SPECIES:

REACTIVITY BASIS

(EKMA MIR SCALE)



(BASED ON NEW EMISSIONS ASSIGNMENTS 5/02)

GLOBAL RELATIVE REACTIVITY METRIC #1

MINIMUM SUBSTITUTION ERROR: BASE ROG FOR SPECIES

DEFINITION

RELATIVE REACTIVITY TO MINIMIZE SUBSTITUTION ERROR FROM REACTIVITY-BASED SUBSTITUTION OF THE BASE ROG FOR THE MODEL SPECIES

SUBSTITUTION ERROR =

$$\Sigma_{cells}\ [RR(Species) \cdot IR_{cell}(Base\ ROG) - IR_{cell}(Species)]^2$$

ADVANTAGES

- WEIGHS CELLS THAT ARE SENSITIVE TO VOCs MORE HIGHLY WHILE TAKING THE MANY CELLS WITH LOWER SENSITIVITIES INTO ACCOUNT
- REPRESENTATIVE OF STRATEGIES INVOLVING REPLACING HIGHLY REACTIVE VOCs WITH VOCs OF AVERAGE REACTIVITY
- REACTIVITIES OF MIXTURES ARE LINEAR SUMS OF REACTIVITIES OF COMPONENTS

DISADVANTAGES

- MAY NOT OPTIMALLY WEIGH CONTRIBUTIONS OF DIFFERENT TYPES OF REGIONS
- NOT A PARTICULARLY REALISTIC SUBSTITUTION FOR EXEMPTION ISSUES

GLOBAL RELATIVE REACTIVITY METRIC #2

REGIONAL MAXIMUM INCREMENTAL REACTIVITY

DEFINITION

USE REACTIVITIES AT THE LOCATION WHERE THE INCREMENTAL REACTIVITY OF THE BASE ROG AT THE TIME OF THE O_3 MAXIMUM IS THE HIGHEST

ADVANTAGES

- COMPARABLE TO THE WIDELY-USED CARTER (1994) MIR SCALE
- REPRESENTATIVE OF IMPACTS IN REGIONS MOST SENSITIVE TO ANTHROPOGENIC VOC CONTROLS

DISADVANTAGES

- NOT A TRUE GLOBAL METRIC. DERIVED FROM IMPACTS IN ONLY ONE TYPE OF REGION
- REPRESENTS ONLY A SMALL FRACTION CELLS IN MODELING DOMAIN
- DOES NOT REPRESENT IMPACTS IN CELLS WITH THE HIGHEST O_3
- DOES NOT REPRESENT IMPACTS IN THE MANY NO_x-LIMITED CELLS

GLOBAL RELATIVE REACTIVITY METRIC #3

REGIONAL MAXIMUM OZONE REACTIVITY

DEFINITION

USE REACTIVITIES AT THE TIME AND LOCATION OF THE DOMAIN-WIDE O_3 MAXIMUM

ADVANTAGES

- ADDRESSES NEEDS TO REDUCE PEAK O_3, WHICH IS OF REGULATORY INTEREST
- SIMPLEST METRIC TO IMPLEMENT

PROBLEMS

- NOT A TRUE GLOBAL METRIC. DERIVED FROM IMPACTS IN ONLY ONE LOCATION
- NOT NECESSARILY REPRESENTATIVE OF "MOIR" CONDITIONS AS DEFINED BY CARTER (1994)
- REACTIVITY CHARACTERISTICS OF THE HIGHEST O_3 CELL CAN VARY SIGNIFICANTLY DEPENDING ON THE EPISODE
- THE DOMAIN-WIDE MAXIMUM O_3 MAY BE INSENSITIVE TO ANTHROPOGENIC VOCs

GLOBAL RELATIVE REACTIVITY METRIC #4

REGIONAL AVERAGE OZONE REACTIVITY

DEFINITION

USE AVERAGE OF REACTIVITIES THROUGHOUT THE ENTIRE DOMAIN, I.E., EFFECT OF VOC ON DOMAIN-WIDE AVERAGE.

ADVANTAGES

- REFLECTS THE EFFECT OF THE VOC ON TOTAL AMOUNT OF GROUND-LEVEL O_3 FORMED
- WEIGHS VOC SENSITIVE CELLS MORE HIGHLY (THOUGH NOT AS MUCH AS MIN. SUB. ERROR)
- SIMPLEST GLOBAL METRIC TO UNDERSTAND
- SIMILAR METRIC OBTAINED IF LOW O_3 CELLS EXCLUDED FROM AVERAGE

PROBLEMS

- WEIGHTS IMPACTS ON CELLS WHERE O_3 IS NOT IMPORTANT EQUALLY WITH O_3 PROBLEM AREAS
- RELATIVELY SMALL NUMBER OF URBAN CELLS MAKES THIS INSENSITIVE TO URBAN O_3 IMPACTS

EKMA REACTIVITY SCALES FOR COMPARISON WITH REGIONAL MODEL REACTIVITIES

SAME EKMA SCENARIOS AND CALCULATION METHODS AS USED TO DERIVE "CARTER" REACTIVITY SCALES (CARTER, 1994; CARTER, 2000)

SAME VERSION OF CB4 AS USED IN THE CAMx REGIONAL MODEL CALCULATIONS

RELATIVE REACTIVITIES USE SAME BASE ROG MIXTURE AS USED FOR REGIONAL METRICS

MIR SCALE

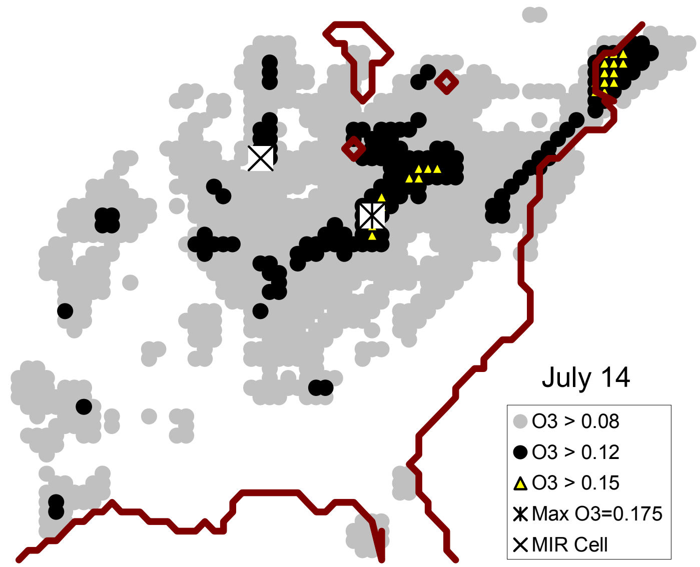
- AVERAGES OF INCREMENTAL REACTIVITIES IN THE SCENARIOS WITH NO_x ADJUSTED TO YIELD MAXIMUM BASE ROG REACTIVITY
- ANALOGOUS TO REGIONAL MIR METRIC

BASE CASE SCALE MINIMUM SUBSTITUTION ERROR SCALE

- RELATIVE REACTIVITIES DERIVED TO MINIMIZE SUBSTITUTION ERRORS IN THE BASE CASE (UNADJUSTED NO_x) SCENARIOS
- ANALOGOUS TO MINIMUM SUBSTITUTION ERROR METRIC FOR 1-HOUR AVG.

GEOGRAPHICAL DISTRIBUTION OF REGIONS WITH HIGH DAILY MAXIMUM 1-HOUR AVERAGE O_3

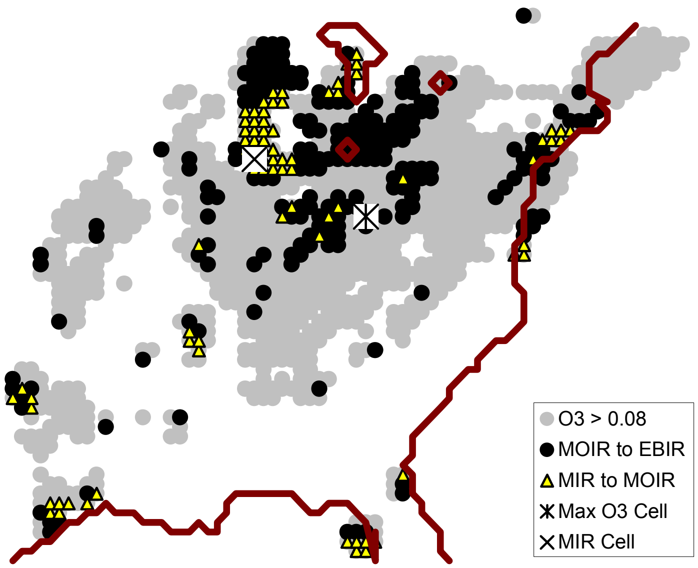
JULY 14, 36K DOMAIN



GEOGRAPHICAL DISTRIBUTION OF VOC-SENSITIVE REGIONS WITH HIGH O_3

JULY 14, 36K DOMAIN

BASED ON SENSITIVITIES OF MAXIMUM 1-HOUR AVERAGE O_3 TO TOTAL VOC AND NO_x

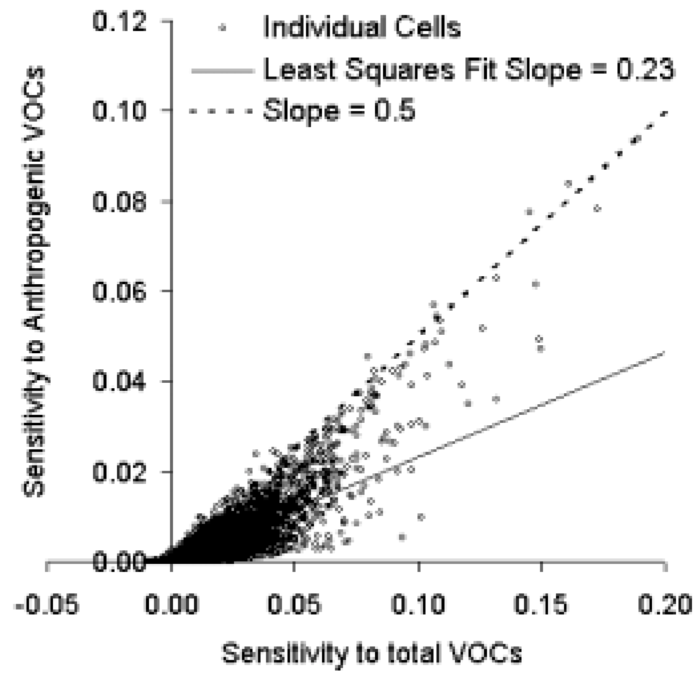


VOC SENSITIVE REGIONS WHERE THE MAXIMUM 1-HOUR AVERAGE O_3 IS LESS THAN 0.08 PPM ARE NOT SHOWN

ANTHROPOGENIC VOC <u>VS</u>. TOTAL VOC SENSITIVITIES

JULY 12-15, 36K DOMAIN

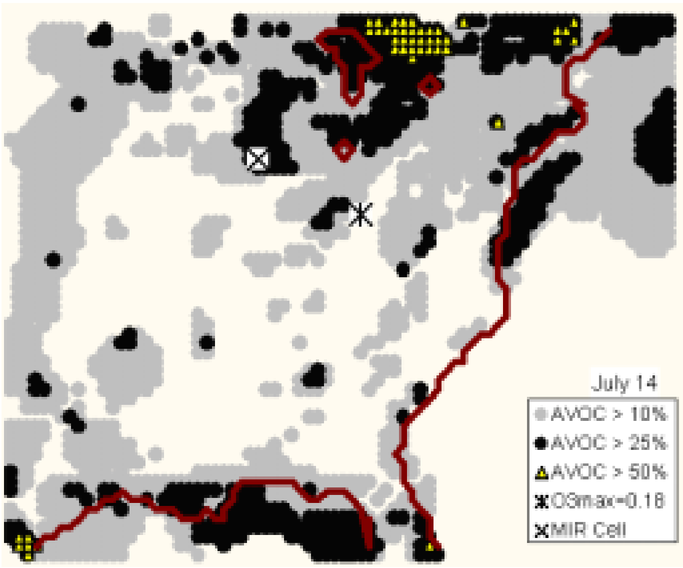
EFFECTS ON DAILY MAXIMUM 1-HOUR O_3 (PPM ΔO_3 PER 100% CHANGE IN VOC EMISSIONS)



REGIONS OF HIGHEST SENSITIVITY TO ANTHROPOGENIC VOCs

JULY 14, 36K DOMAIN

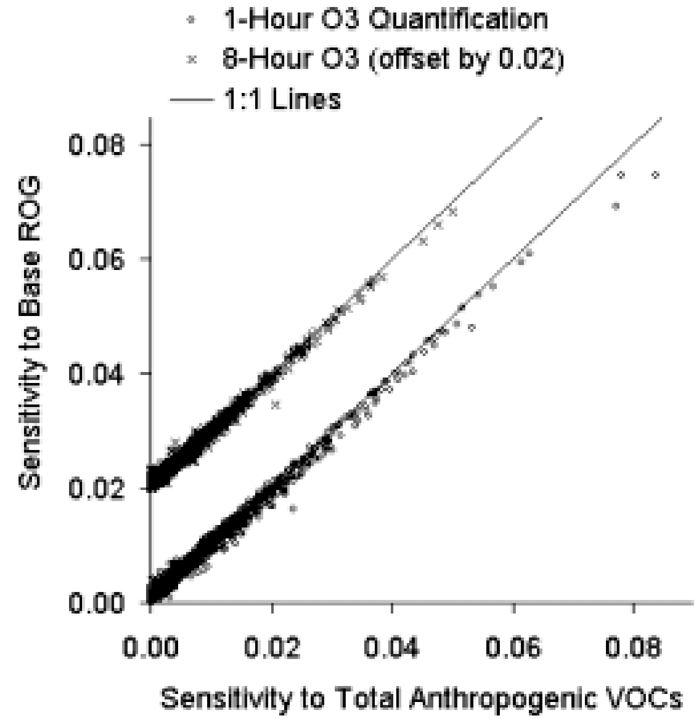
BASED ON RATIOS OF SENSITIVITIES OF MAXIMUM 1-HOUR AVERAGE OF TOTAL AVOCs / TOTAL VOCs



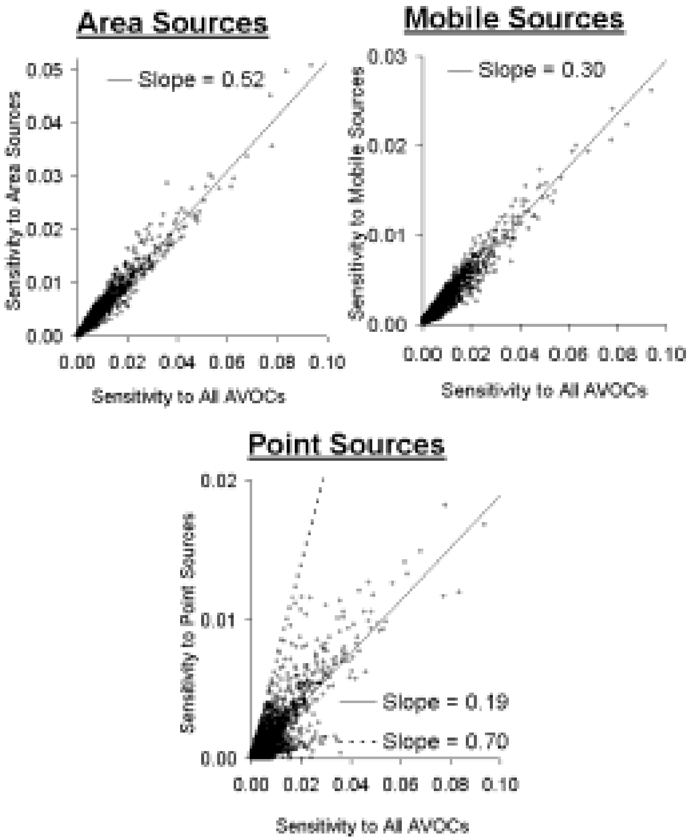
BASE ROG MIXTURE VS. TOTAL ANTHROPOGENIC VOC SENSITIVITIES

JULY 12-15, 36K DOMAIN

(PPM ΔO_3 PER 100% CHANGE IN VOC EMISSIONS)



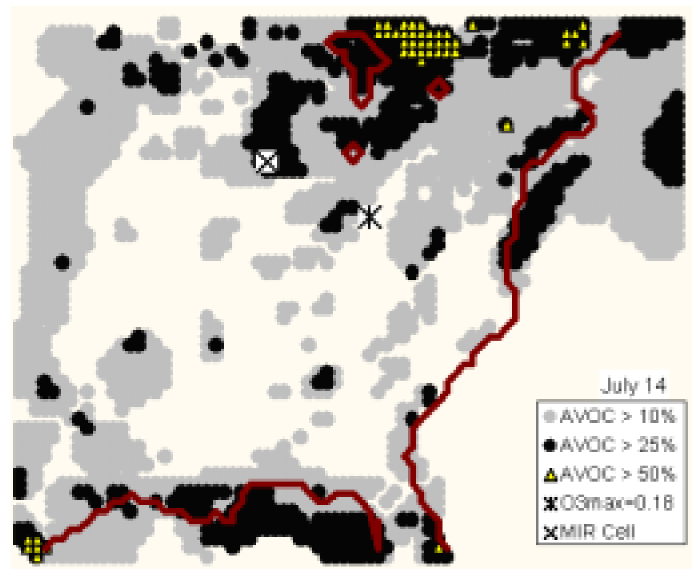
O_3 SENSITIVITIES FOR VARIOUS ANTHROPOGENIC VOC SOURCE TYPES



REGIONS OF HIGHEST SENSITIVITY TO ANTHROPOGENIC VOCs

JULY 14, 36K DOMAIN

BASED ON RATIOS OF SENSITIVITIES OF MAXIMUM 1-HOUR AVERAGE OF TOTAL AVOCs / TOTAL VOCs



REACTIVITY CHARACTERISTICS OF EPISODE DAYS

MAXIMUM 1-HOUR AVERAGE O_3 QUANTIFICATION

EPISODE DAY	7/12	7/13	7/14	7/15
DOMAIN-WIDE OZONE MAXIMUM (ppb)				
36K DOMAIN	162	187	175	170
4K DOMAIN	126	140	173	177
CELLS WITH MAXIMUM O_3 >80 PPB				
36K DOMAIN	22%	25%	25%	19%
4K DOMAIN	27%	37%	72%	76%
CELLS WITH MAXIMUM O_3 >120 PPB				
36K DOMAIN	1%	2%	4%	2%
4K DOMAIN	0%	2%	12%	15%
CELLS MORE SENSITIVE TO VOCs THAN NO_x				
36K DOMAIN	23%	27%	25%	22%
4K DOMAIN	68%	52%	28%	28%

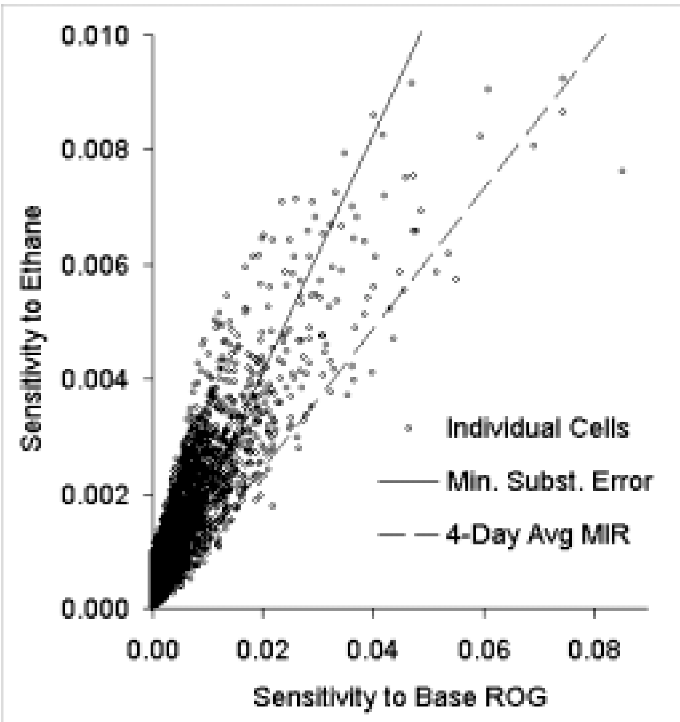
REACTIVITY CHARACTERISTICS OF EPISODE DAYS

MAXIMUM 8-HOUR AVERAGE O_3 QUANTIFICATION

EPISODE DAY	7/12	7/13	7/14	7/15
DOMAIN-WIDE OZONE MAXIMUM (ppb)				
36K DOMAIN	127	139	147	-
4K DOMAIN	99	100	135	-
CELLS WITH MAXIMUM O_3 >60 PPB				
36K DOMAIN	37%	38%	37%	-
4K DOMAIN	54%	54%	86%	-
CELLS WITH MAXIMUM O_3 >80 PPB				
36K DOMAIN	7%	10%	12%	-
4K DOMAIN	2%	14%	39%	-
CELLS MORE SENSITIVE TO VOCs THAN NO_x				
36K DOMAIN	17%	23%	20%	-
4K DOMAIN	41%	37%	20%	-

ETHANE VS BASE ROG SENSITIVITIES IN 36K DOMAIN

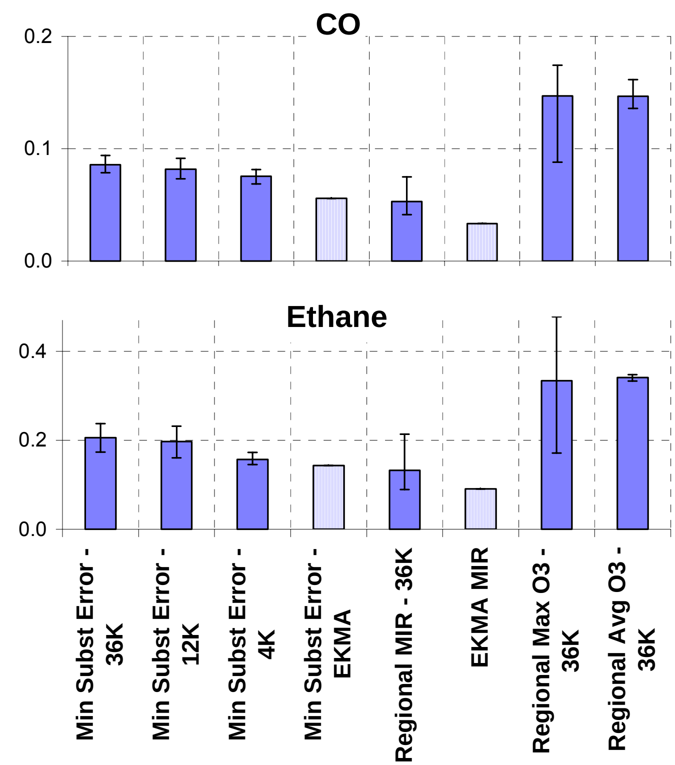
MAXIMUM 1-HOUR AVERAGE O_3 QUANTIFICATION 7/12 – 7/15 EPISODE DAYS (36K DOMAIN)



SLOPE OF LINE FORCED THROUGH ZERO IS MINIMUM SUBSTITUTION ERROR REACTIVITY

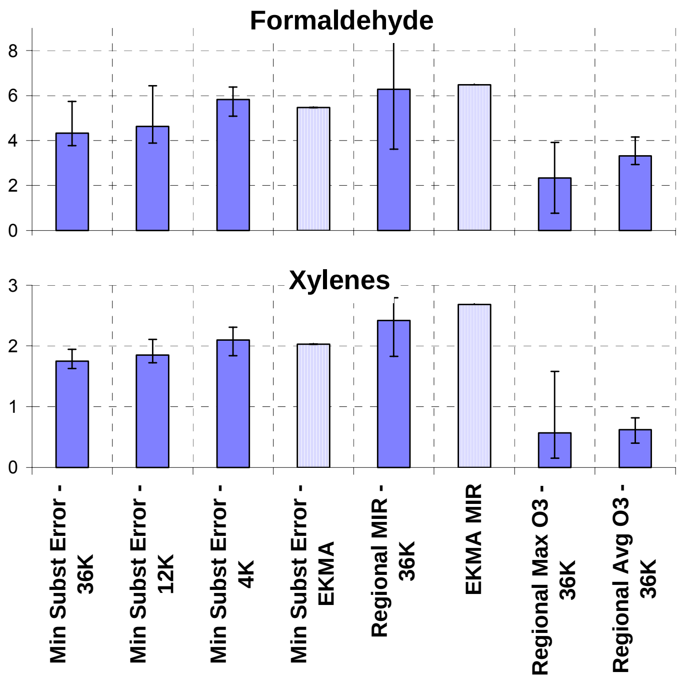
COMPARISON OF RELATIVE REACTIVITIES FOR SLOWLY REACTING SPECIES

MAXIMUM 1-HOUR AVERAGE O_3 QUANTIFICATION (CARBON BASIS)



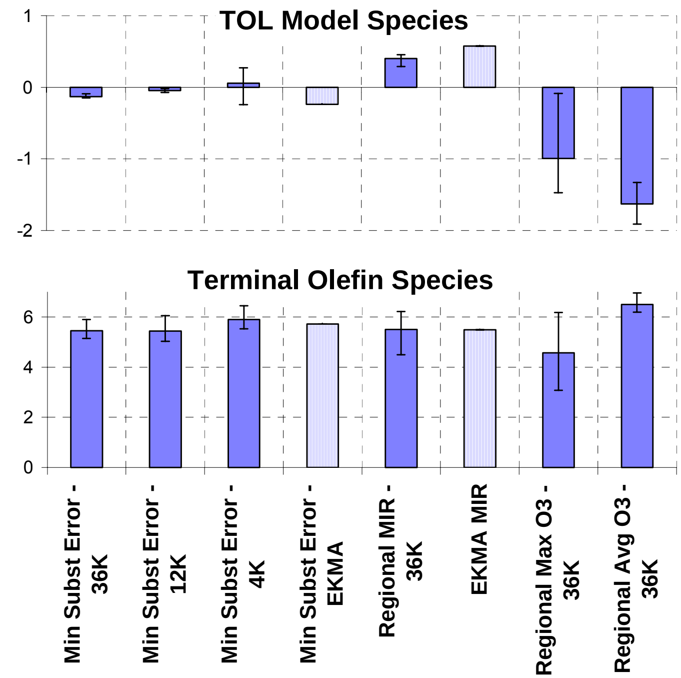
COMPARISON OF RELATIVE REACTIVITIES FOR RADICAL INITIATING SPECIES

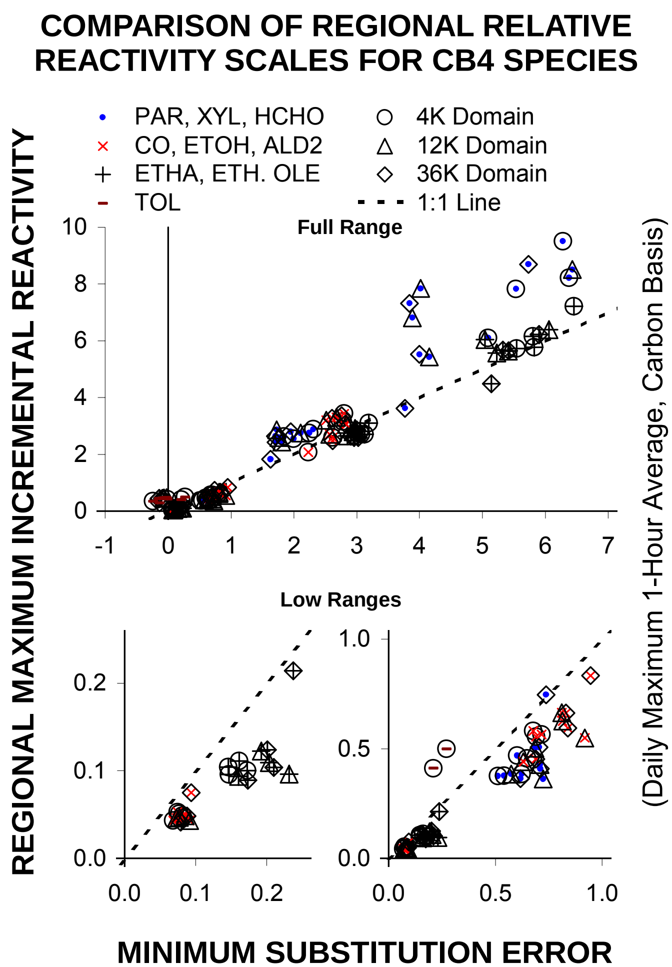
MAXIMUM 1-HOUR AVERAGE O_3 QUANTIFICATION (CARBON BASIS)

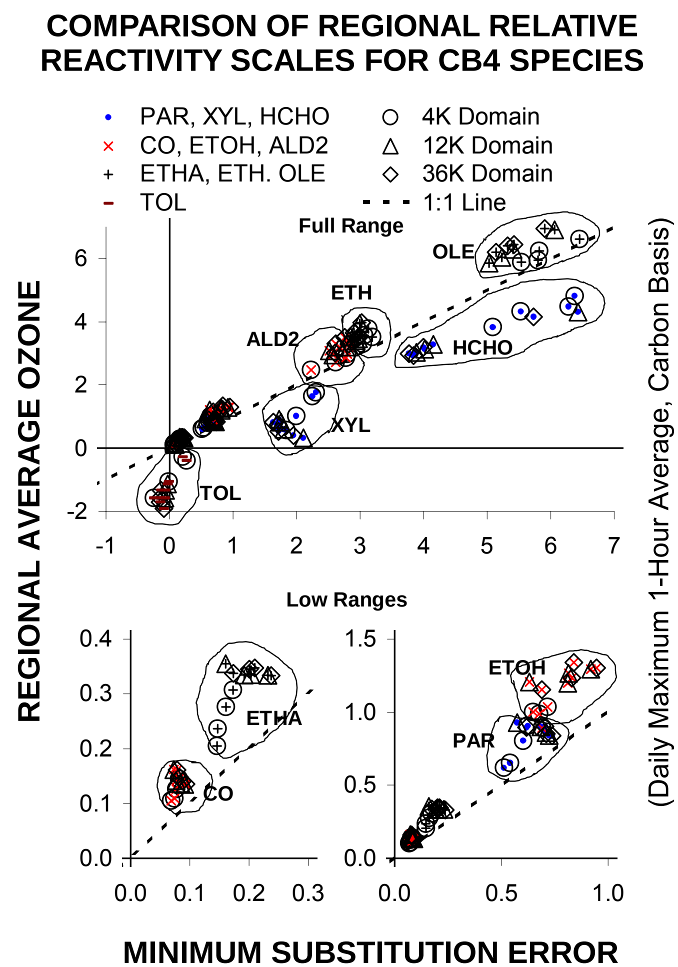


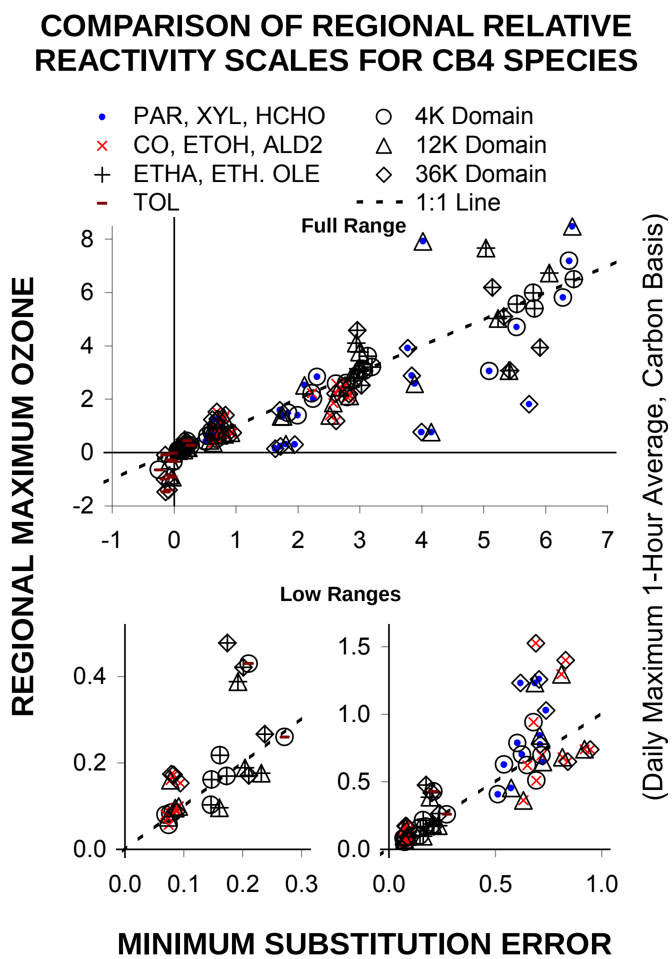
COMPARISON OF RELATIVE REACTIVITIES FOR MOST AND LEAST VARIABLE SPECIES

MAXIMUM 1-HOUR AVERAGE O_3 QUANTIFICATION (CARBON BASIS)

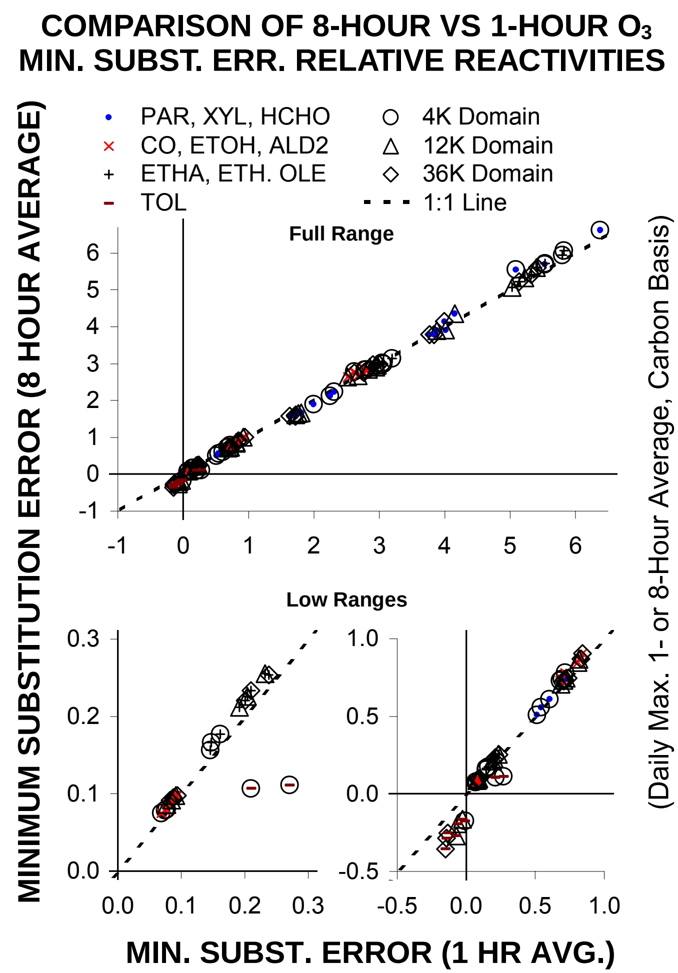



COMPARISON OF REGIONAL RELATIVE REACTIVITY SCALES FOR CB4 SPECIES
PAR, XYL, HCHO
CO, ETOH, ALD2
ETHA, ETH. OLE
TOL
4K Domain
12K Domain
36K Domain
1:1 Line
Full Range
Low Ranges
REGIONAL MAXIMUM INCREMENTAL REACTIVITY
(Daily Maximum 1-Hour Average, Carbon Basis)
MINIMUM SUBSTITUTION ERROR

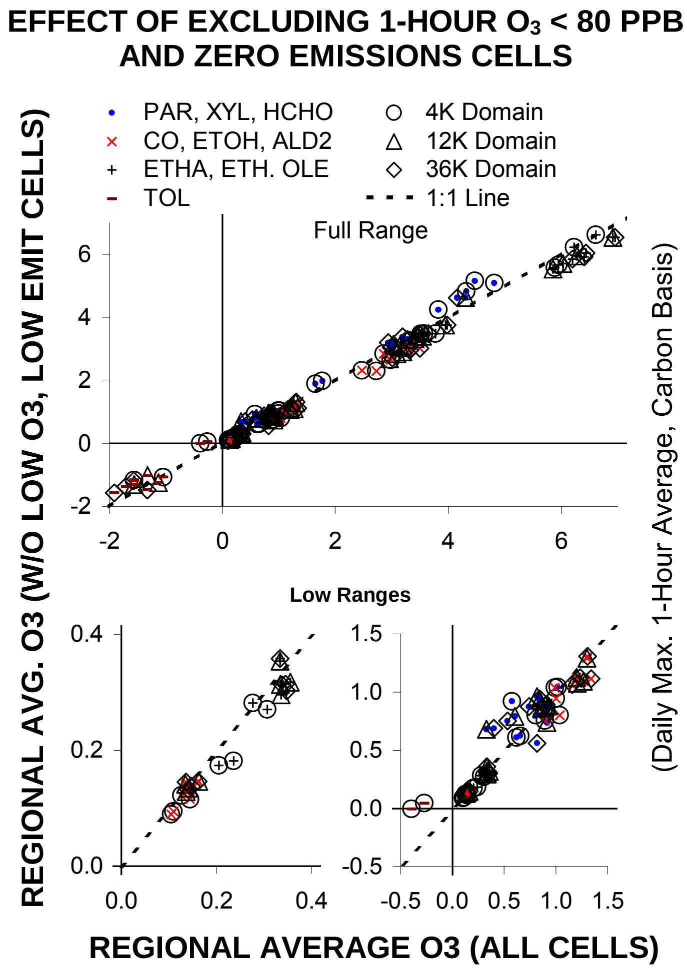

COMPARISON OF REGIONAL RELATIVE REACTIVITY SCALES FOR CB4 SPECIES
PAR, XYL, HCHO
CO, ETOH, ALD2
ETHA, ETH. OLE
TOL
4K Domain
12K Domain
36K Domain
1:1 Line
Full Range
OLE
ETH
ALD2
HCHO
XYL
TOL
Low Ranges
ETHA
CO
ETOH
PAR
REGIONAL AVERAGE OZONE
(Daily Maximum 1-Hour Average, Carbon Basis)
MINIMUM SUBSTITUTION ERROR



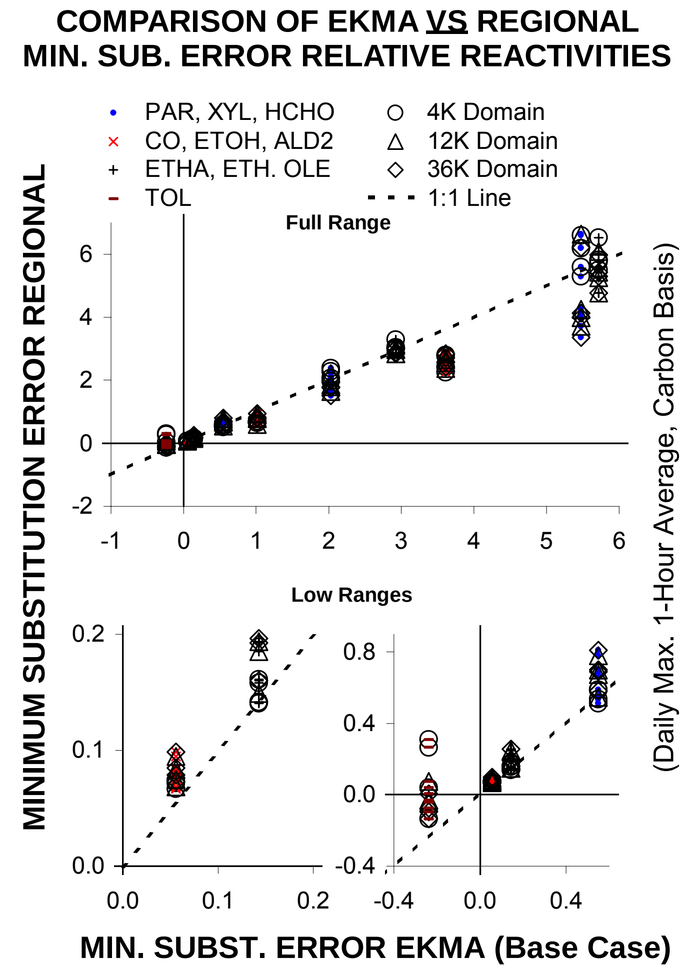
COMPARISON OF REGIONAL RELATIVE
REACTIVITY SCALES FOR CB4 SPECIES
PAR, XYL, HCHO
CO, ETOH, ALD2
ETHA, ETH. OLE
TOL
4K Domain
12K Domain
36K Domain
1:1 Line
Full Range
Low Ranges
REGIONAL MAXIMUM OZONE
(Daily Maximum 1-Hour Average, Carbon Basis)
MINIMUM SUBSTITUTION ERROR



COMPARISON OF 8-HOUR VS 1-HOUR O3
MIN. SUBST. ERR. RELATIVE REACTIVITIES
PAR, XYL, HCHO
CO, ETOH, ALD2
ETHA, ETH. OLE
TOL
4K Domain
12K Domain
36K Domain
1:1 Line
Full Range
Low Ranges
MINIMUM SUBSTITUTION ERROR (8 HOUR AVERAGE)
(Daily Max. 1- or 8-Hour Average, Carbon Basis)
MIN. SUBST. ERROR (1 HR AVG.)

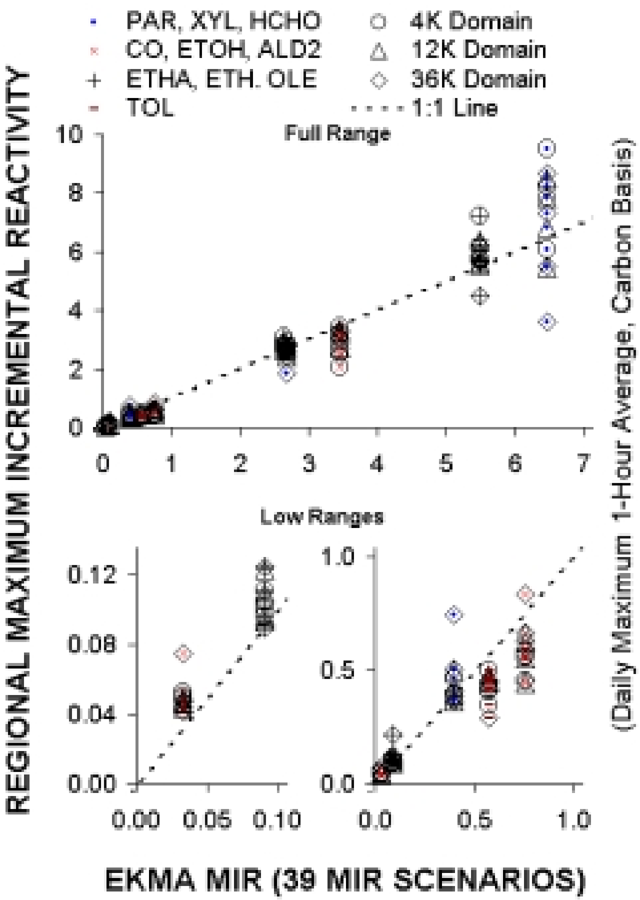


EFFECT OF EXCLUDING 1-HOUR O3 < 80 PPB
AND ZERO EMISSIONS CELLS
PAR, XYL, HCHO
CO, ETOH, ALD2
ETHA, ETH. OLE
TOL
4K Domain
12K Domain
36K Domain
1:1 Line
Full Range
Low Ranges
REGIONAL AVG. O3 (W/O LOW O3, LOW EMIT CELLS)
REGIONAL AVERAGE O3 (ALL CELLS)
(Daily Max. 1-Hour Average, Carbon Basis)



COMPARISON OF EKMA VS REGIONAL
MIN. SUB. ERROR RELATIVE REACTIVITIES
PAR, XYL, HCHO
CO, ETOH, ALD2
ETHA, ETH. OLE
TOL
4K Domain
12K Domain
36K Domain
1:1 Line
Full Range
Low Ranges
MINIMUM SUBSTITUTION ERROR REGIONAL
MIN. SUBST. ERROR EKMA (Base Case)
(Daily Max. 1-Hour Average, Carbon Basis)

COMPARISON OF EKMA VS REGIONAL MIR RELATIVE REACTIVITIES



LARGE SCALE SUBSTITUTION CALCULATIONS

CALCULATION	ETHANE CARBON SUBST. FACTOR	12K DOMAIN 7/12 – 7/15 AVG. MAX 1-Hr O_3 (PPB)	12K DOMAIN 7/12 – 7/15 CELLS OVER 8-Hr STD.
BASE CASE	-	193	18%
NO AVOCs	0	178	13%
ETHANE SUBSTITUTIONS TO REPLACE AVOCs			
100% ETHANE BY MOLE	0.5	180	13%
100% ETHANE BY "MASS"	1	182	14%
100% ETHANE BY REACTIVITY (NULL TEST)	5.1 [a]	193 [b]	21%
50% ETHANE BY REACTIVITY (NULL TEST)	5.1 [a]	193 [c]	19%

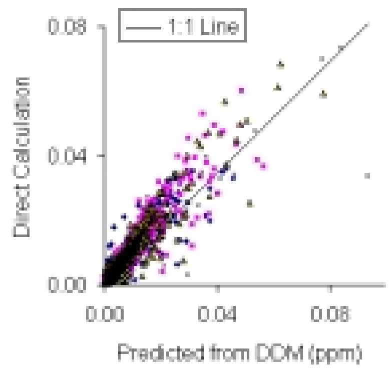
[a] NULL TEST SUBSTITUTION FACTOR BASED ON AVERAGE OF MINIMUM SUBSTITUTION ERROR RELATIVE REACTIVITIES FOR THE 12K DOMAIN

[b] INCREASES BY 0.8 PPB

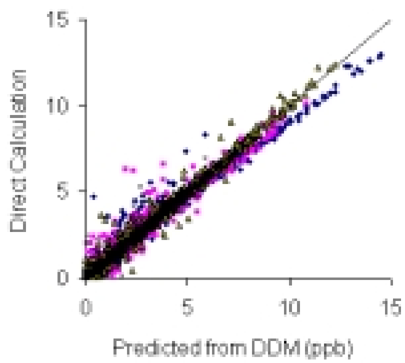
[c] INCREASES BY 0.3 PPB

ABILITY OF LINEAR APPROXIMATION TO PREDICT O_3 CHANGES IN THE CELLS IN THE 100% SUBSTITUTION CALCULATIONS

AVOC REMOVAL (36K DOMAIN)



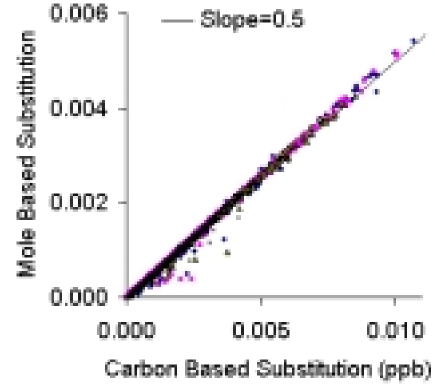
ETHANE NULL TEST (36K DOMAIN)



LINEARITY OF ETHANE ADDITIONS

36K DOMAIN, 1-HOUR AVERAGE QUANTIFICATION

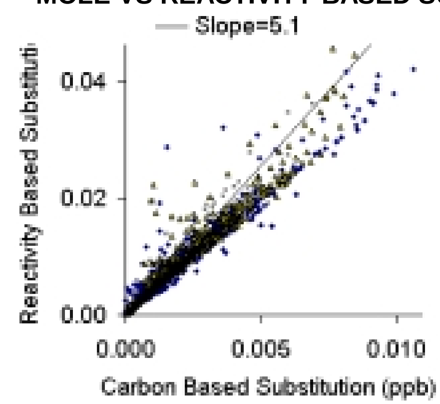
MOLE VS CARBON-BASED SUBSTITUTION



0.5 CARBON
VS 1 CARBON
ETHANE FOR
AVOC
SUBSTITUTION

36K DOMAIN
1-Hr Avg.
Quantification

MOLE VS REACTIVITY-BASED SUBSTITUTION

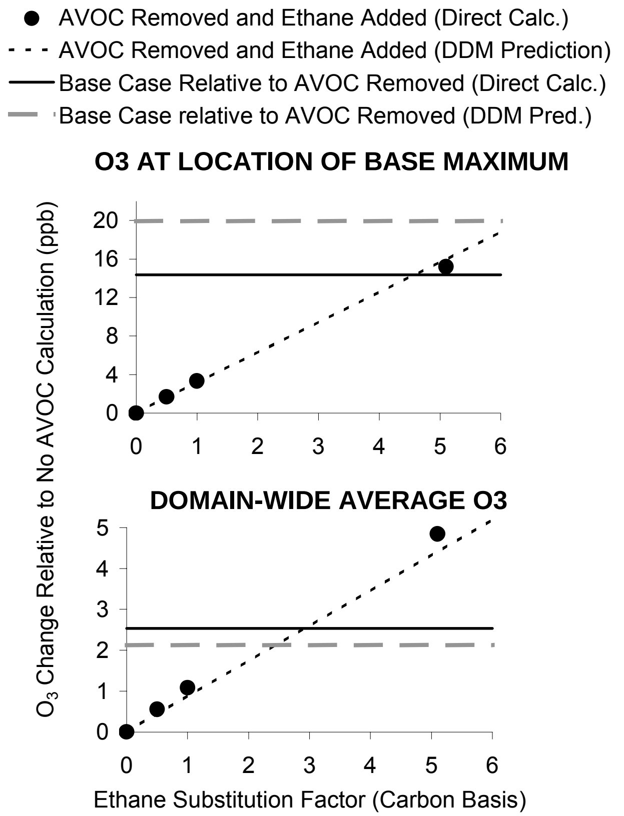


5.1 CARBON
VS 1 CARBON
ETHANE FOR
AVOC
SUBSTITUTION

36K DOMAIN
1-Hr Avg.
Quantification

O_3 CHANGES RELATIVE TO NO AVOC CALCULATION

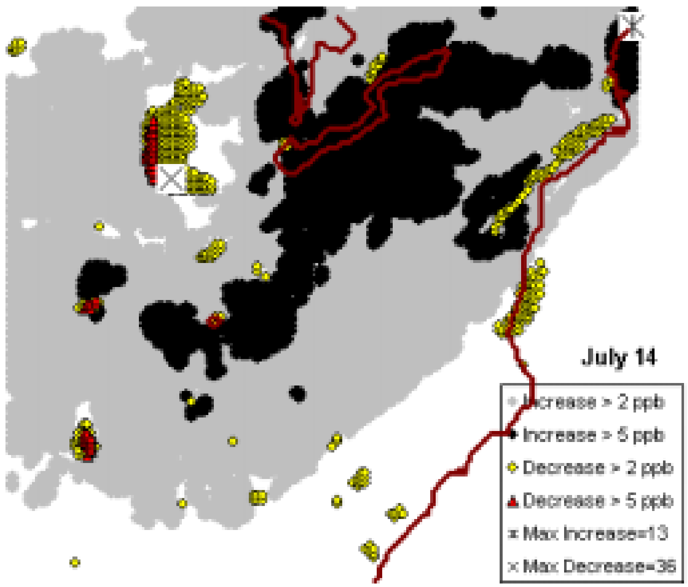
AVERAGE OF DATA IN 12K DOMAIN MAXIMUM 1-HOUR AVERAGE O_3 QUANTIFICATION



EFFECT OF NULL TEST ETHANE SUBSTITUTION

CHANGE IN 1-HOUR AVERAGE O_3 RESULTING FROM SUBSTITUTING ALL AVOCs FOR 5.1 MOLES CARBON OF ETHANE

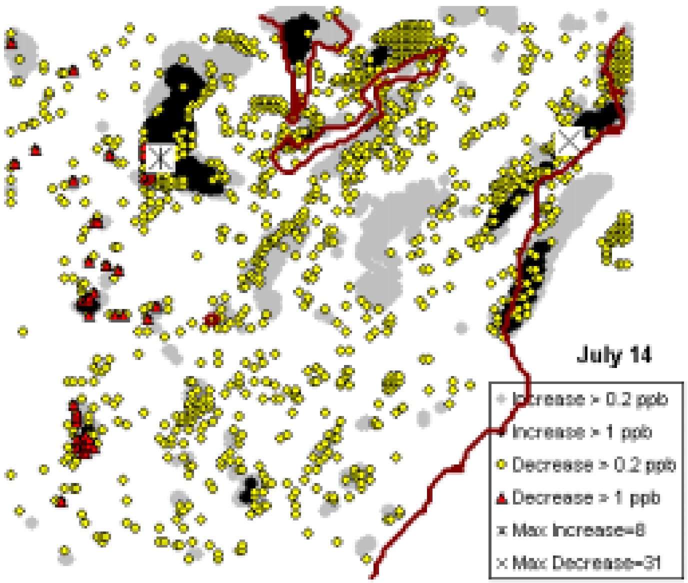
SUBSTITUTION FACTOR BASED ON MINIMUM SUBSTITUTION ERROR RELATIVE REACTIVITY IN 12K DOMAIN



12K DOMAIN

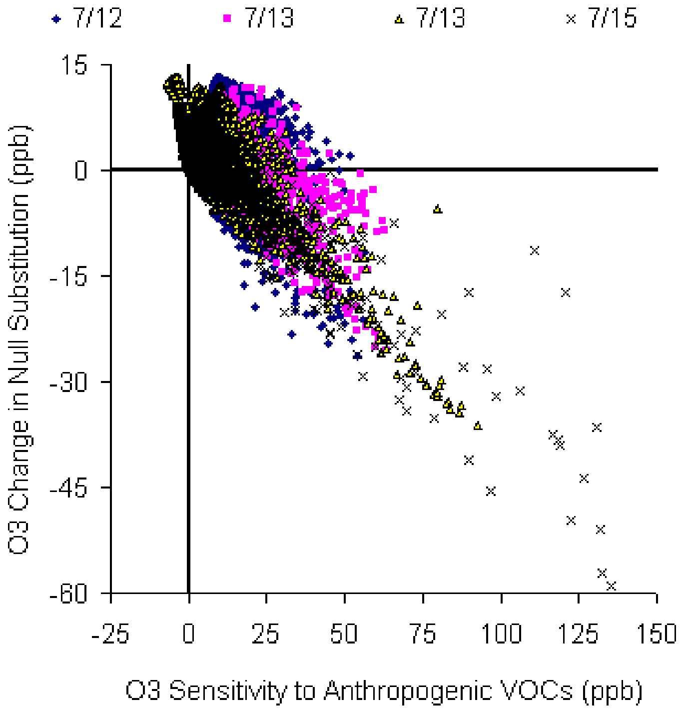
MAP OF LINEAR ASSUMPTION PREDICTION ERROR FOR 100% ETHANE NULL TEST SUBSTITUTION CALCULATION

JULY 14, 12K DOMAIN
1-HOUR AVERAGE O_3 QUANTIFICATION



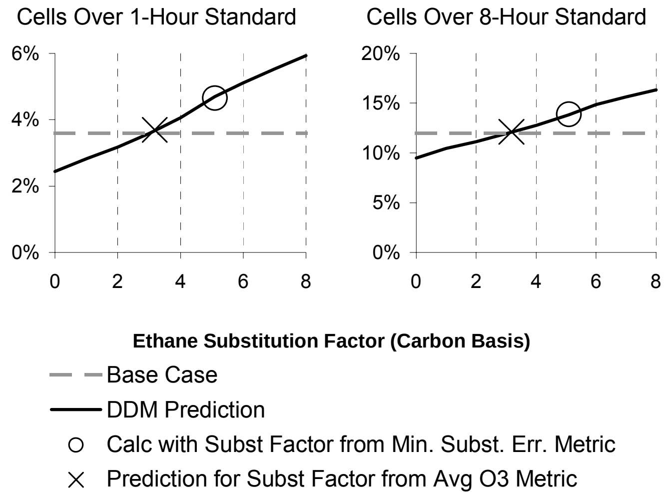
O_3 CHANGE IN 100% ETHANE NULL SUBSTITUTION VS. BASE ROG SENSITIVITY

12K DOMAIN
1-HOUR AVERAGE O_3 QUANTIFICATION



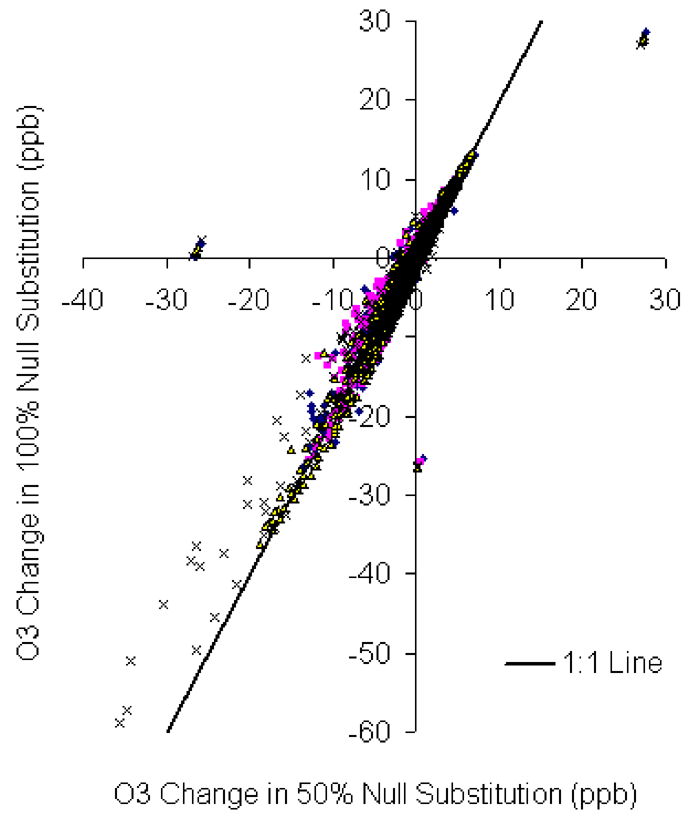
CELLS ABOVE THE O_3 STANDARDS IN ETHANE SUBSTITUTION CALCULATIONS

CALCULATIONS FOR JUNE 14 IN 23K DOMAIN



A NULL TEST USING A SUBSTITUTION FACTOR FROM THE AVERAGE O_3 METRIC BEST PREDICTION OF FRACTIONS OF CELLS OVER STANDARDS

COMPARISON OF ΔO_3 IN 50% AND 100% NULL SUBSTITUTION CALCULATIONS



CONCLUSIONS

GENERAL

NO_x CONTROL IS MORE EFFECTIVE THAN VOC CONTROL IN MOST OF THIS MODELING DOMAIN

BIOGENIC VOCs DOMINATE OVER ANTHROPOGENICS IN MOST IN MOST OF THIS MODELING DOMAIN

ANTHROPOGENIC VOC SOURCE TYPE REACTIVITY CONTRIBUTIONS ARE: AREA: ~50%; MOBILE: ~30%; POINT: ~20%

RELATIVE REACTIVITIES VARY WITH LOCATION AND FROM DAY-TO-DAY, BUT VARIABILITY IS LESS IN THE MORE VOC-SENSITIVE CELLS

COMPARABLE REACTIVITY RESULTS ARE OBTAINED IN THE DIFFERENT GRID SIZE DOMAINS

BASE ROG SENSITIVITIES ARE GOOD APPROXIMATIONS OF SENSITIVITIES TO TOTAL ANTHROPOGENIC VOCs

CONCLUSIONS (CONTINUED)

REGIONAL METRICS

THE MINIMUM SUBSTITUTION ERROR AND REGIONAL AVERAGE O_3 METRICS REPRESENT TWO TYPES OF APPROACHES TO DERIVE TRUE GLOBAL METRICS

- BOTH TAKE IMPACTS ON ALL CELLS INTO ACCOUNT, BUT MIN. SUBST. ERROR GIVES GREATER WEIGHT VOC-SENSITIVE AREAS
- NEITHER METRICS AFFECTED SIGNIFICANTLY BY EXCLUDING LOW O_3 OR OVER-WATER CELLS
- BOTH METHODS GIVE ALMOST SAME RESULTS FOR 8-HOUR AS 1-HOUR O_3 QUANTIFICATION
- CONSISTENT DIFFERENCES BETWEEN THE TWO METHODS FOR SOME SPECIES. AVERAGE O_3 RELATIVE REACTIVITIES ARE:
  - HIGHER FOR SLOWLY REACTING SPECIES
  - LOWER FOR RADICAL INITIATING SPECIES

THE REGIONAL MIR METRICS GIVES COMPARABLE RESULTS TO MINIMUM SUBST. ERROR EXCEPT

- MIR SOMEWHAT LOWER FOR SLOWER REACTING COMPOUNDS
- MIR USUALLY HIGHER FOR FORMALDEHYDE

THE REGIONAL AVERAGE O_3 METRIC GIVES THE MOST VARIABLE RESULTS BECAUSE OF VARYING CONDITIONS WHERE PEAK O_3 OCCUR

CONCLUSIONS (CONTINUED)

EKMA vs REGIONAL MODELS

EKMA-BASED REACTIVITY SCALES ARE VERY SIMILAR TO REGIONAL SCALES DERIVED USING A COMPARABLE METRIC.

- EKMA REACTIVITIES OF SLOWLY REACTING COMPOUNDS TEND TO BE SOMEWHAT LOWER
- EKMA REACTIVITIES OF OTHER COMPOUNDS IN RANGE OF REGIONAL VARIABILITY

LARGE SCALE SUBSTITUTIONS

INCREMENTAL REACTIVITY ANALYSIS CAN GIVE FAIR ESTIMATES OF VERY LARGE SCALE SUBSTITUTIONS

REMOVING AVOCs BUT NOT NO_x GIVES RELATIVELY SMALL REGIONAL O_3 REDUCTIONS.

O_3 INCREASES APPROXIMATELY LINEARLY AS AMOUNT OF ETHANE REPLACING AVOCs INCREASES

- MOLE-BASED ETHANE SUBST. GIVES HALF THE O_3 CHANGE AS MASS-BASED BECAUSE ETHANE HAS ABOUT HALF THE AVERAGE AVOC MWt.

ETHANE NULL-TEST SUBSTITUTIONS BASED ON MSE GIVE HIGHER O_3 IN MOST OF THE DOMAIN, BUT LOWER O_3 IN AVOC-SENSITIVE AREAS

AVERAGE O_3 METRIC PERFORMS BETTER IN NULL-TEST PREDICTIONS OF NUMBERS OF CELLS OVER THE 1-HOUR AND 8-HOUR STANDARDS

IMPLICATIONS

REGIONAL AND EKMA MODELS GIVE DIRECTIONALLY CONSISTENT REACTIVITY RANKINGS FOR MOST MAJOR TYPES OF REACTIVE VOCs

THE LEAST VARIABLE REACTIVITY METRICS ARE THOSE BASED ON IMPACTS IN THE ENTIRE DOMAIN

AVERAGING TIME FOR THE O_3 STANDARDS SHOULD NOT SIGNIFICANTLY AFFECT REACTIVITY SCALES

ALTHOUGH RANKINGS ARE USUALLY PRESERVED, NUMERICAL METRICS DEPEND ON HOW IMPACTS IN DIFFERENT TYPES OF AREAS ARE WEIGHED

RECOMMENDATIONS

MORE QUALITATIVE RESEARCH ON WHETHER REACTIVITY "WORKS" IS PROBABLY NOT NEEDED.

POLICY MAKERS NEED TO DECIDE SOON ON WHAT TYPE OF METRIC IS BEST FOR REGULATORY USE

RESEARCH SHOULD FOCUS ON HOW BEST TO CALCULATE REACTIVITY SCALES WITH THIS METRIC

- USE STATE-OF-SCIENCE DETAILED AND *EXPERIMENTALLY-EVALUATED* MECHANISMS
- REPRESENT THE FULL RANGE OF CONDITIONS THAT AFFECT THE CHOSEN METRIC
- NEED TO DEVELOP APPROPRIATE MODELING APPROACH TO CALCULATE A *COMPLETE* SCALE