TX AQRP Project 10-008:

Factors influencing ozone-precursor response in Texas attainment modeling

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SE Texas Photochemical Modeling Technical Committee
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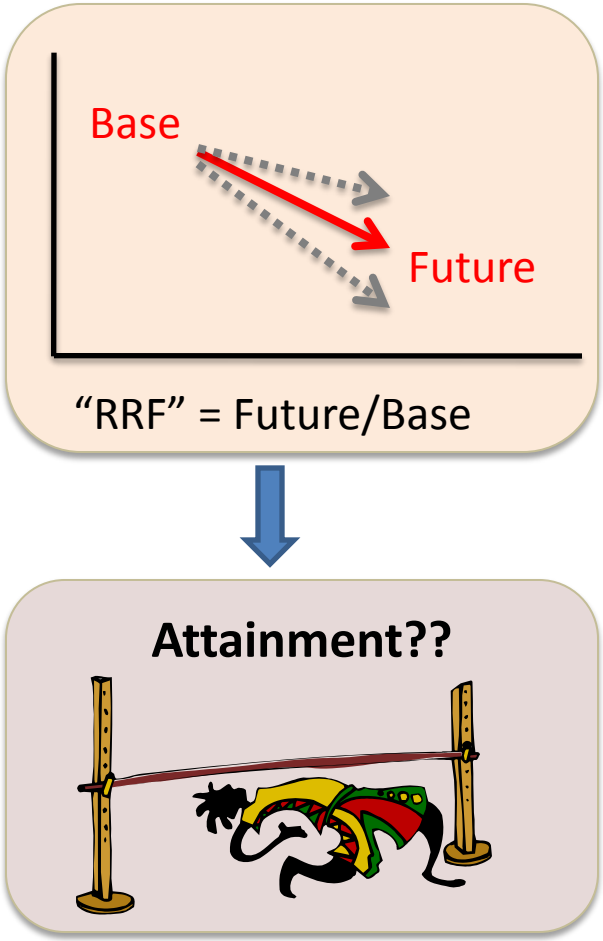
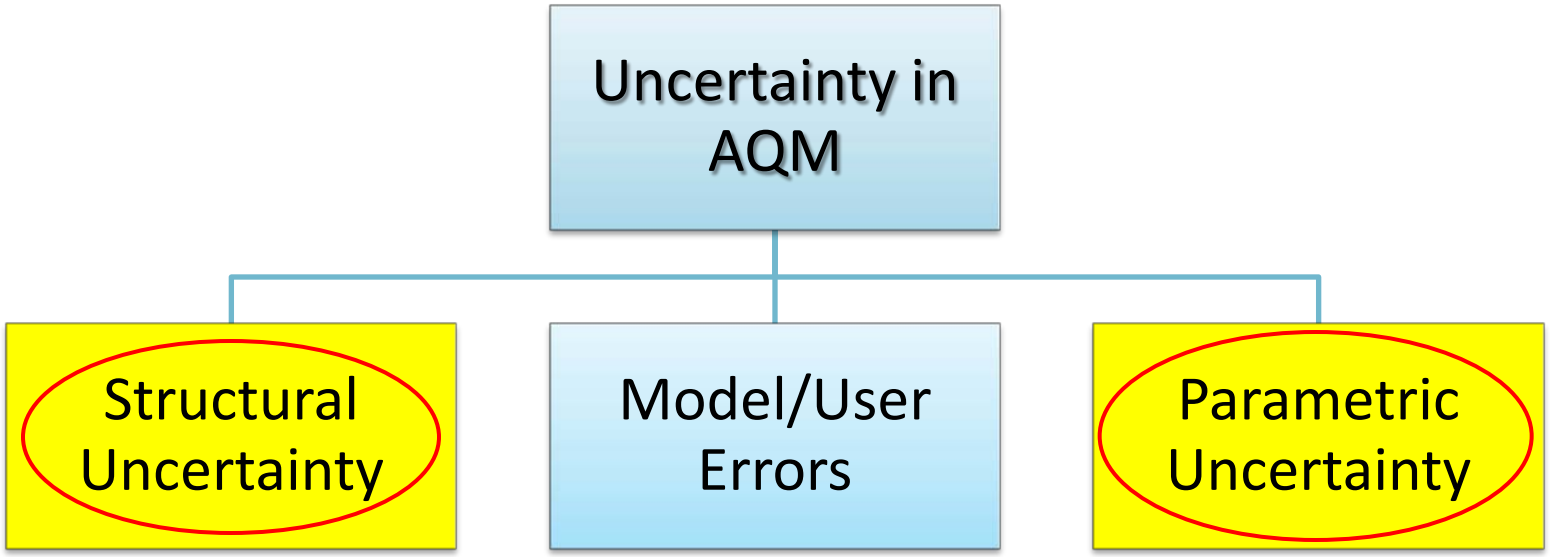
Motivation: Characterize uncertainty in attainment modeling

- SIPs rely upon models for attainment demonstrations & strategy selection
- Models known to be uncertain, but applied deterministically
- **<u>Goal</u>**: Characterize probabilistic responsiveness of ozone to controls
  - Identify inputs that most influence uncertainty
  - Efficient Monte Carlo simulations of concentrations & sensitivities
  - Use observations to weight cases



Causes of Uncertainty in AQMs



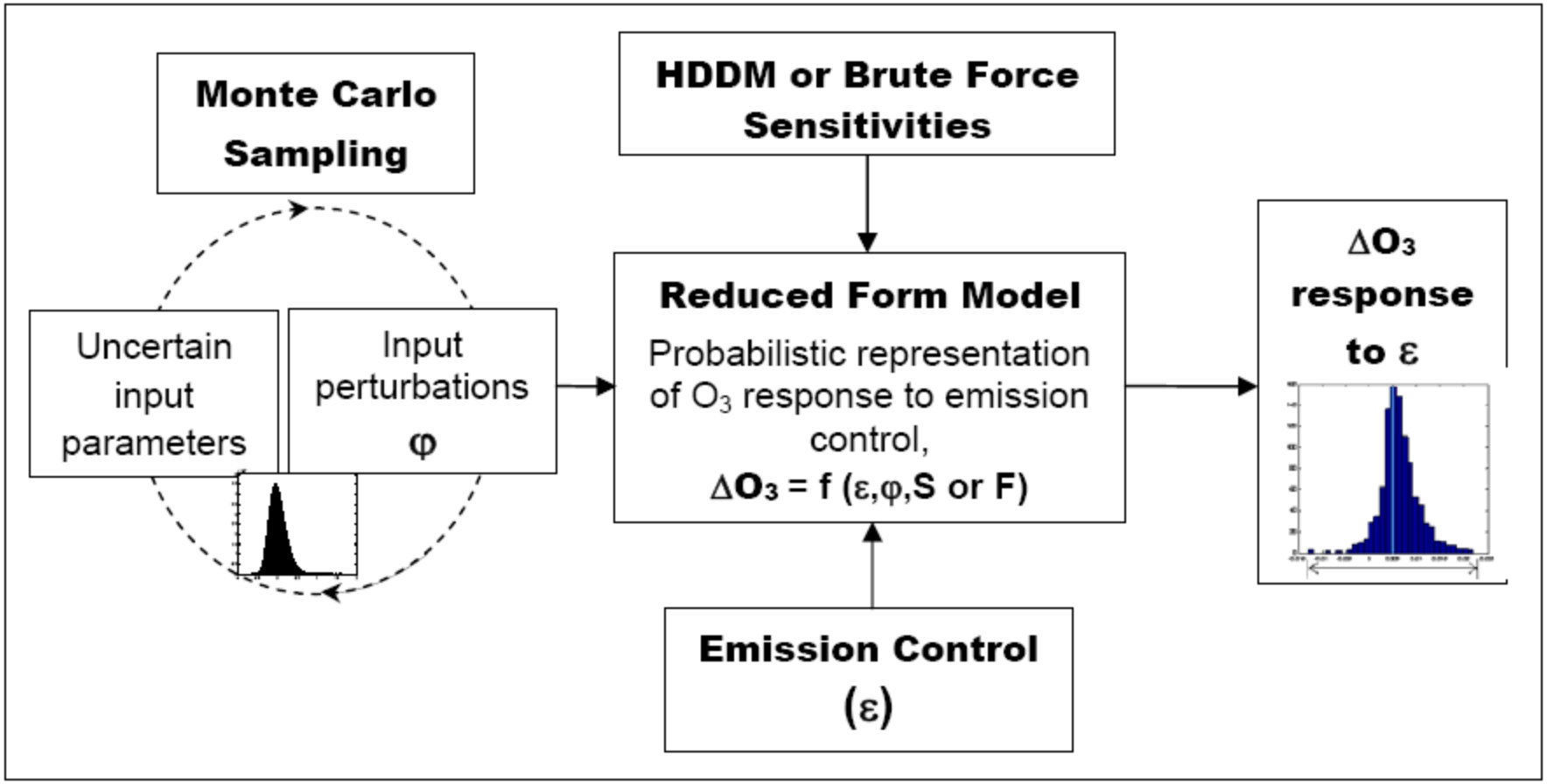
Imperfections in numerical representations of atmospheric processes:

- ✓ Chemical mechanism
- ✓ Deposition scheme
- ✓ Vertical mixing scheme
- ✓ Grid resolution
- ✓ Input models (emissions, boundary conditions, meteorology)

Error in model input parameters:

- ✓ Emission rates
- ✓ Reaction rate constants
- ✓ Boundary conditions
- ✓ Deposition velocities
- ✓ Meteorology parameters

Prior Work: Reduced Form Model to parametric uncertainty characterization



How can we use observations to weight or screen the cases??

Digar et al., ES&T 2011

Prior work: Probabilistic evaluation of control strategies in Georgia

TABLE 3. Reduction in 8-h Ozone at Atlanta Confederate Avenue Monitor Due to Each Emission Control Package

control strategy[a]	description	deterministic O_3 reduction[b] (ppb)	day-to-day variation (σ) of deterministic O_3 reduction[c] (ppb)	O_3 reduction under parametric uncertainty, mean (5th, 95th percentiles)[d] (ppb)	likelihood to achieve T_{fixed}[e]	likelihood to achieve $T_{flexible}$[f]
C1	ATL(6)	1.1	0.4	1.0 (−0.7, 2.1)	19.6%	37.5%
C2	EGUs (B, S)	1.2	1.1	1.2 (0.7, 1.7)	4.4%	41.1%
C3	ATL(6) + MAC + REST	1.4	0.4	1.2 (−0.4, 2.5)	37.1%	44.9%
C4	ATL(6) + EGU(M)	1.7	0.8	1.5 (−0.6, 3.2)	57.8%	52.5%
C5	EGUs (B, S, H)	1.7	1.7	1.7 (1.2, 2.3)	77.9%	56.1%
C6	ATL(6) + EGUs (B, S)	2.2	1.3	2.1 (0.1, 3.6)	78.4%	63.5%
C7	ATL(12)	2.3	0.8	2.0 (−1.2, 4.5)	71.7%	62.6%
C8	EGUs (M, B, H, S)	2.3	1.1	2.4 (1.5, 3.3)	94.4%	70.6%
C9	ATL(12) + MAC + REST	2.6	0.8	2.3 (−0.9, 5.0)	78.0%	67.8%
C10	ATL(12) + EGU(M)	2.8	1.2	2.7 (−1.1, 5.6)	79.9%	71.9%
C11	EGUs (M, B, H, S, Y)	2.9	2.8	2.9 (1.2, 7.6)	99.9%	81.7%
C12	ATL(12) + EGUs (B, S)	3.4	1.6	3.2 (−0.3, 6.0)	86.6%	79.0%
C13	ATL(12) + EGUs (B, H, S)	4.0	2.1	3.7 (0.3, 6.4)	90.3%	84.5%
C14	ATL(12) + EGUs (M, B, H, S, Y)	5.1	3.2	5.0 (1.1, 8.1)	94.0%	91.5%

[a] In ascending order based on deterministic O_3 reduction. [b] Mean of the impacts among the high ozone days in episode; underlining indicates O_3 reduction ≥1.5 ppb. [c] Standard deviation of the daily impacts within the high O_3 days of the episode. [d] 90% confidence intervals. [e] *Fixed* reduction target of 1.5 ppb. [f] *Flexible* reduction target of 1.5 ppb with 3 ppb uncertainty.

Example of ranking reversal

Digar et al., ES&T 2011

Motivation: Large Δ(Sens O_3_Emis) for modest Δ(inputs) in Texas

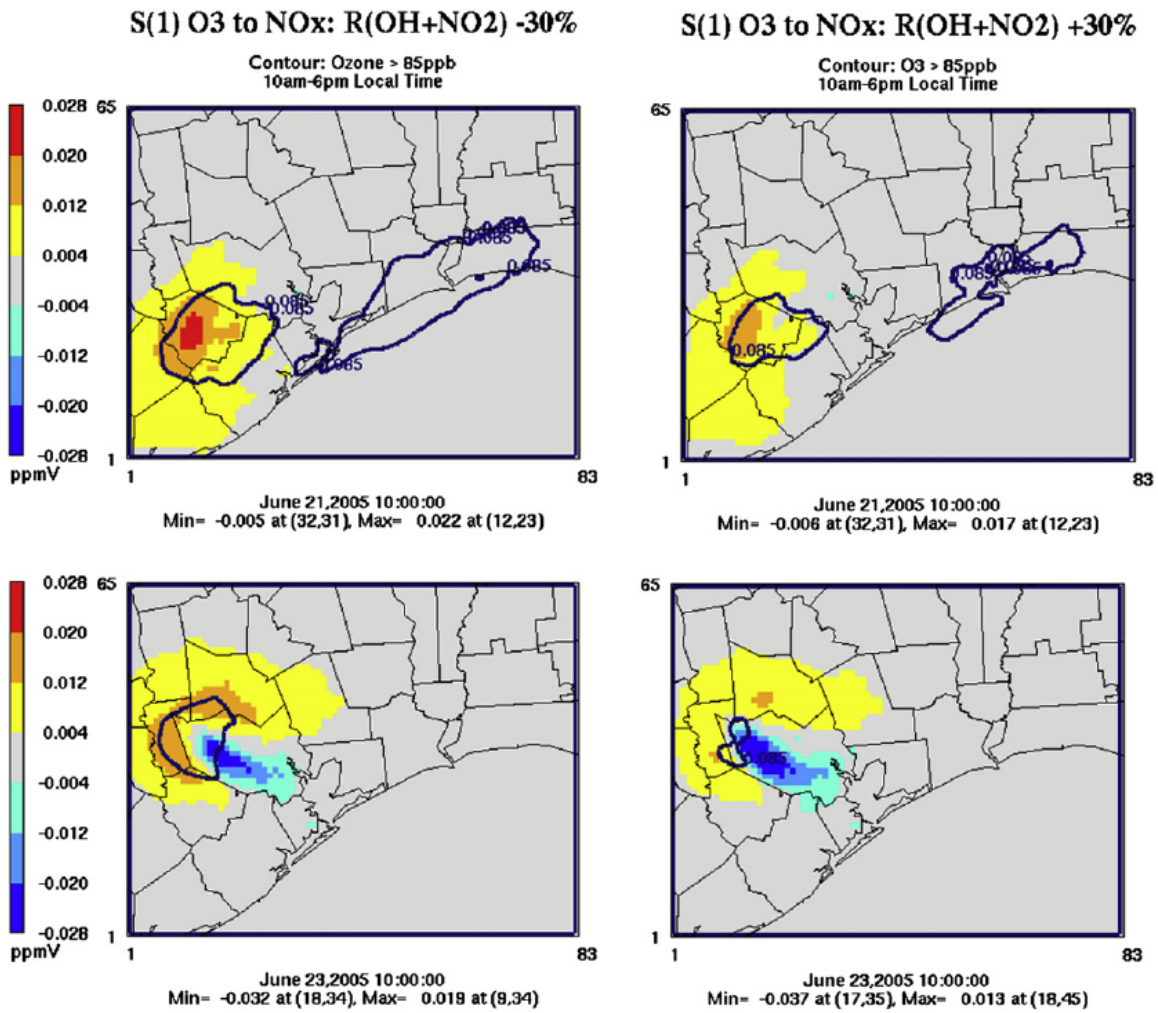
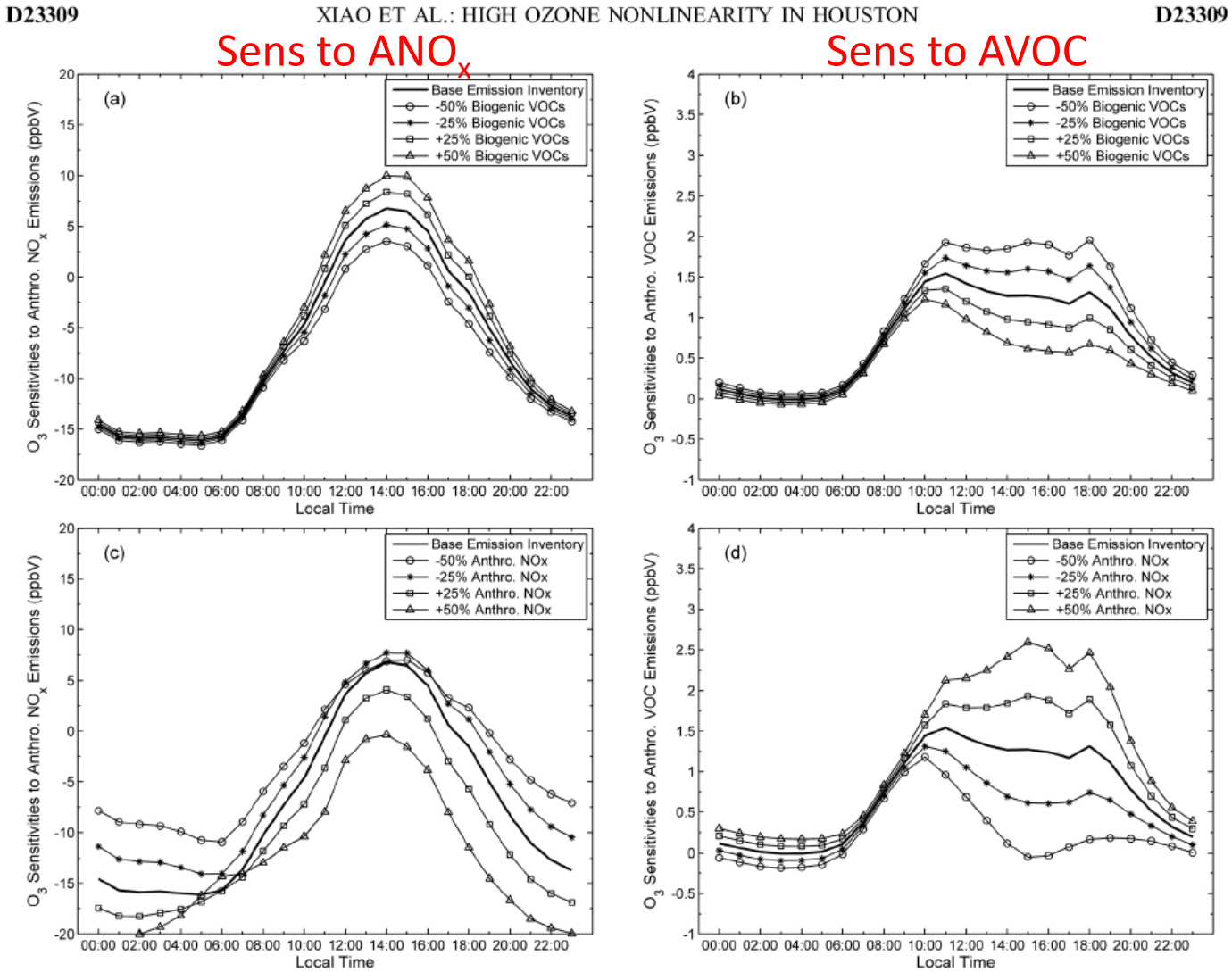


Fig. 3. Sensitivity of ozone to Houston anthropogenic NO_x emissions, if k_{NO_2+OH} is 30% smaller (L) or larger (R) than in base case, for June 21 (top) and June 23 (bottom). Contours show $O_3 > 85$ ppb in each case.

Cohan et al., Atmos. Environ. (2010), 3101-3109

Motivation: Large Δ(Sens O_3_Emis) for modest Δ(inputs) in Texas



Uncertain BVOC

Uncertain ANO_x

Xiao et al., JGR, 2010

STUDY GOALS

- Improved understanding of how **structural** and **parametric** uncertainties influence ozone SIP modeling in Texas non-attainment regions

- **Prioritize** model inputs whose improvement is most critical to reliable predictions of ozone concentration and sensitivity

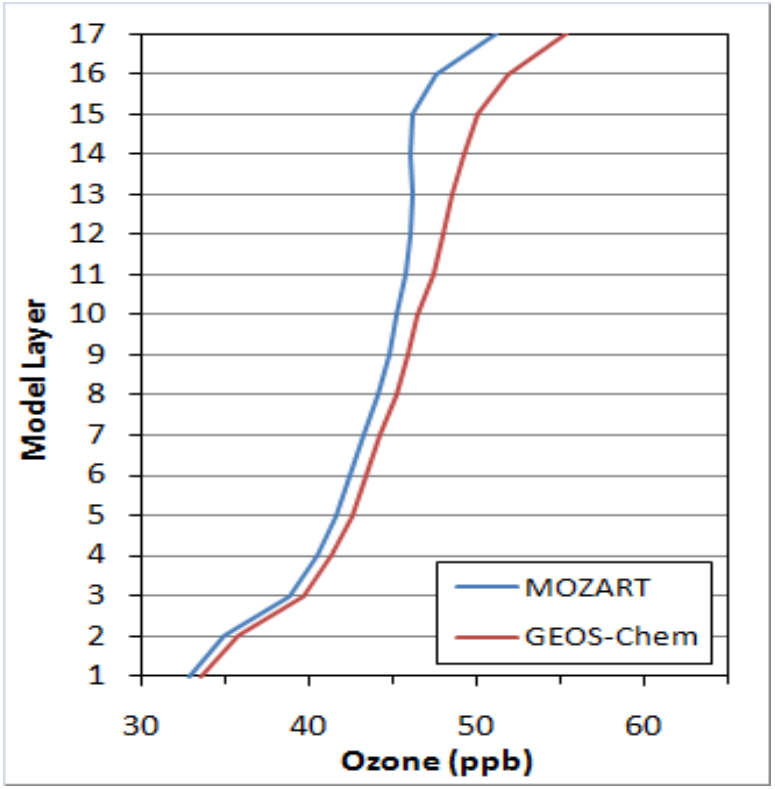
- Use observations to evaluate which model cases best represent ozone-precursor response in Texas

Alternate inputs for Texas 2006 Ozone SIP modeling in DFW & Houston

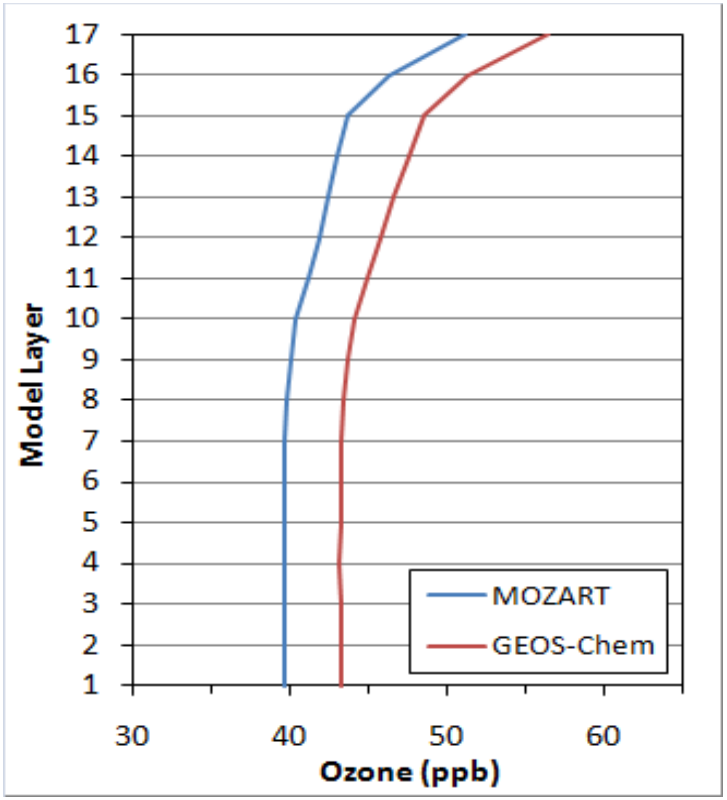
- GloBEIS vs MEGAN biogenic emissions model
- MOZART vs GEOSChem boundary conditions
- Default vs Zhang deposition scheme
- CB-05 vs CB-6 (and modCB-6) chemical mechanism
- Satellite-based photolysis rates (2-weeks only)

GEOS-Chem: higher O3 at boundaries

West Boundary



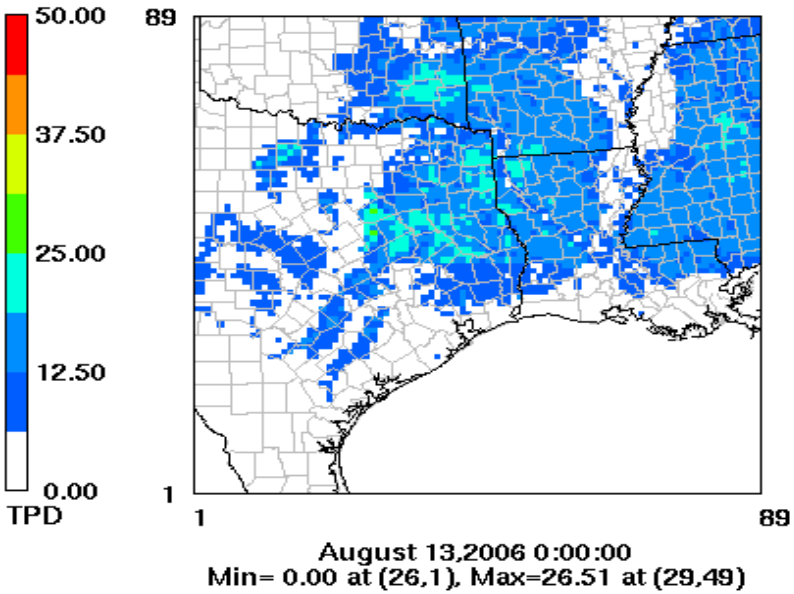
East Boundary



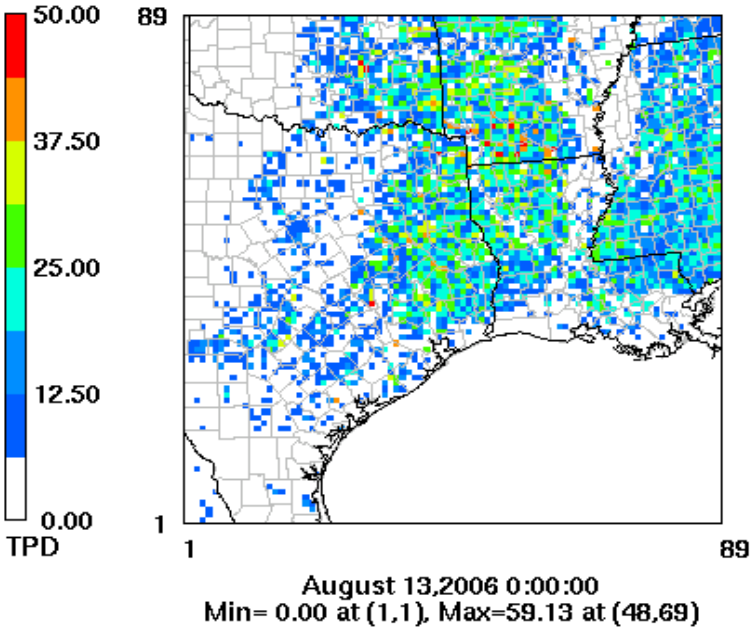
Aug-Sept 2006 episode

MEGAN: Higher biogenic NMVOC, lower biogenic NO_x

GloBEIS (default)



MEGAN



Species	36-km Domain		12-km Domain	
	GloBEIS	MEGAN	GloBEIS	MEGAN
NOx	6,932	2,168	1,123	590
NMVOC	159,943	185,059	48,176	59,527
CO	16,622	19,684	4,457	5,723

Aug-Sept 2006 episode

Screening for Structural Factors: Chemical mechanism & biogenic model most influence O_3 sensitivities to emissions

Root Mean Square Error ,

$$RMS = \sqrt{\frac{\sum_{j=1}^{N}(Y_j - O_j)^2}{N}}$$

Mean Bias ,

$$BIAS = \frac{1}{N}\sum_{j=1}^{N}(Y_j - O_j)$$

Normalized Mean Bias ,

$$NMB = \frac{\sum_{j=1}^{N}(Y_j - O_j)}{\sum_{j=1}^{N}O_j} \cdot 100\%$$

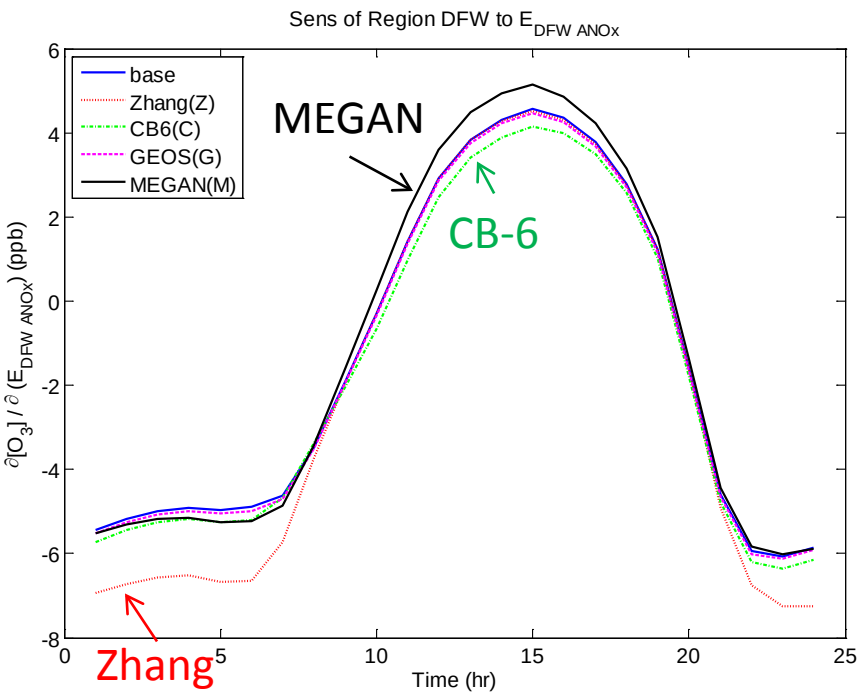
Normalized Mean Error ,

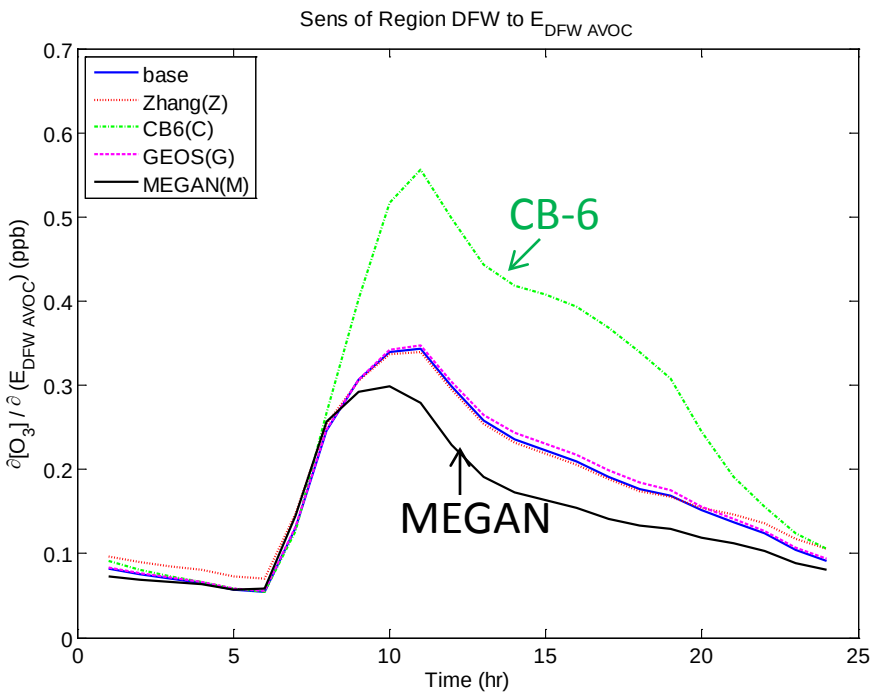
$$NME = \frac{\sum_{j=1}^{N}|Y_j - O_j|}{\sum_{j=1}^{N}O_j} \cdot 100\%$$

	STRUCTURAL CASES				
	Base	**CHEM**	**BIO**	**DEP**	**BC**
Comparison of each structural case against the observations for 8-hour O_3 concentration in DFW					
RMS (ppb)	13.01	**13.21**	**13.63**	12.95	13.01
BIAS (ppb)	-0.61	**4.59**	**-1.06**	1.88	0.02
NMB (%)	-1.04	**7.83**	**-1.82**	3.22	0.04
NME (%)	17.79	**16.88**	**18.85**	17.08	17.76
Comparison of each alternate case against the Base case for DFW 8-hour O_3 sensitivity to DFW ANO_X					
RMS (ppb)	-	**0.79**	**1.37**	0.12	0.16
BIAS (ppb)	-	**-0.40**	**0.75**	-0.01	-0.09
NMB (%)	-	**-12.07**	**22.81**	-0.25	-2.81
NME (%)	-	**15.35**	**26.08**	2.13	2.83
Comparison of each alternate case against the Base case for DFW 8-hour O_3 sensitivity to DFW AVOC					
RMS (ppb)	-	**0.44**	**0.17**	0.02	0.02
BIAS (ppb)	-	**0.26**	**-0.08**	-0.00	0.01
NMB (%)	-	**63.35**	**-19.33**	-0.80	1.88
NME (%)	-	**63.45**	**21.90**	2.04	2.14

DFW sensitivities under each structural case

- All show predominately NOx-limited
- CB-6 favors VOC sensitivity
- MEGAN favors NOx sensitivity
- Boundary conditions do not affect sensitivities
- Zhang deposition affects sensitivities only at night
- Similar trends for Houston sensitivities (Aug-Sept episode)





Reduced Form Model to consider parametric uncertainties

- Apply Reduced Form Model to estimate C and $S^{(1)}$ under alternate settings of input parameters

$$C^{*}_{j+k} = C_0 + \sum_j \varphi_j S_j^{(1)} + \sum_k \varphi_k S_k^{(1)} + \frac{1}{2}\sum_j \varphi_j^2 S_{j,j}^{(2)} + \frac{1}{2}\sum_k \varphi_k^2 S_{k,k}^{(2)} + \sum_{j,k} \varphi_j \varphi_k S_{j,k}^{(2)}$$

$$S_j^{(1)*} = \left(1 + \varphi_j\right)\left(S_j^{(1)} + \varphi_j S_j^{(2)} + \sum_k \varphi_k S_{j,k}^{(2)}\right)$$

- Accuracy of Reduced Form Model demonstrated by Digar and Cohan (2010)
- Here: Monte Carlo sampling of 1000 input parameter settings (1000 parametric * 4 structural = 4000 cases)

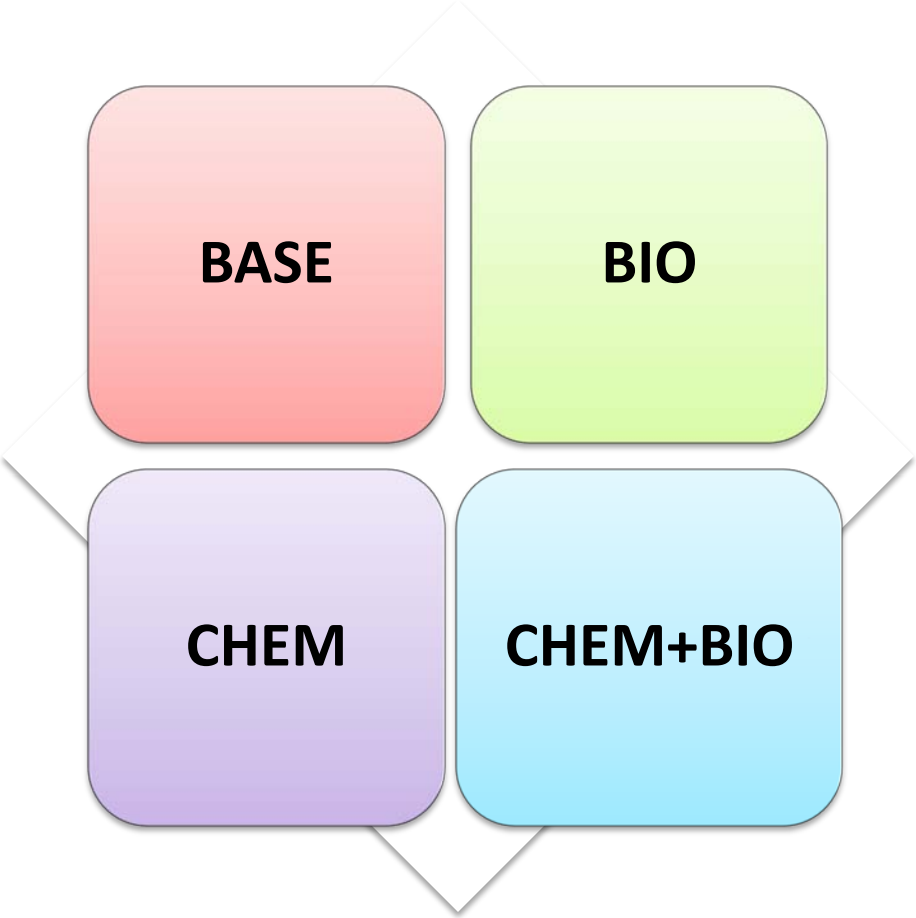
Screening for Parametric Uncertainty

Parameter[1]	Uncertainty[2] (1σ) L-N	Reference	Impact[3] on O_3 concentration	Impact[3] on O_3 sensitivity to ANO_X	Impact[3] on O_3 sensitivity to AVOC
Emission Rates:					
Domain-wide NO_X	0.336	Deguillaume, 2007	**0.105**	**-0.463**	**0.496**
Domain-wide biogenic VOC	0.405		**0.026**	**0.216**	**-0.319**
Domain-wide anthropogenic VOC	0.336		0.006	**0.073**	**-0.150**
Reaction Rate Constants:					
All photolysis frequencies	0.347	Hanna, 2001	**0.091**	**0.401**	**0.091**
$R(OH+NO_2)$	0.131	Sander, 2006	**-0.017**	**-0.057**	**0.029**
$R(NO+O_3)$	0.095	Hanna, 2001	**-0.023**	**-0.058**	**-0.024**
R(All VOCs+OH)	0.095	Deguillaume, 2007	0.003	**0.021**	**0.014**
Boundary Conditions:					
BC (O_3)	0.203	Deguillaume, 2007	**0.036**	0.006	**-0.042**
BC (NO_X)	0.549		0.002	-0.001	-0.001
BC (HNO_3)	0.549		0.001	-0.000	-0.000
BC (PAN)	0.549		0.008	-0.003	-0.002
BC (HONO)	0.549		0.000	-0.000	-0.000
BC (N_2O_5)	0.549		0.000	-0.000	0.000

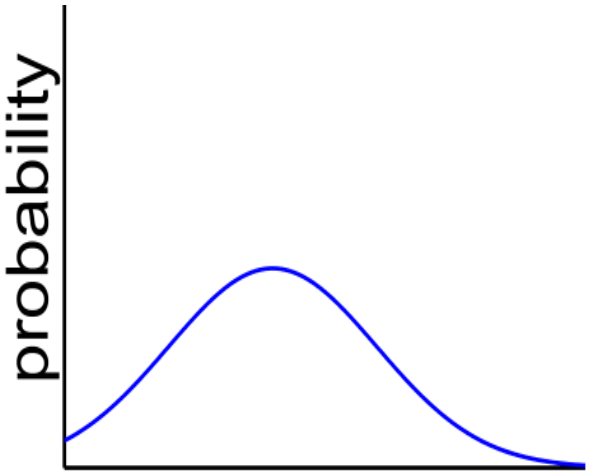
Impact factor for the influence of a parameter 'j' on concentration 'C' $= \varphi_j S_j^{(1)} / C$

Impact factor for the influence of a parameter 'k' on sensitivity $S_j^{(1)} = \varphi_k S_{j,k}^{(2)} / S_j^{(1)}$

Final Ensemble



4 Structural Members

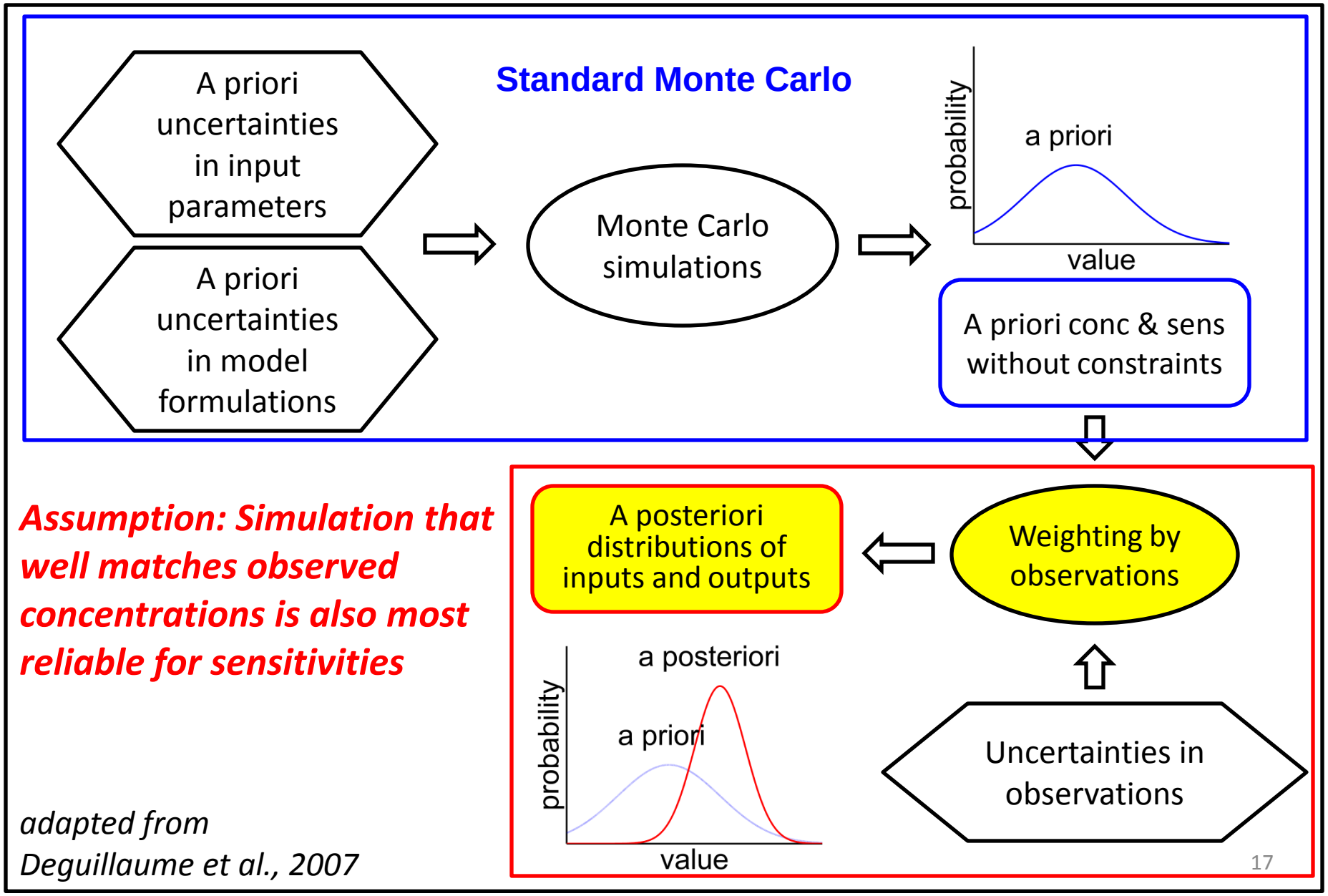


O_3 conc. or sens.

1000 Parametric Values

4000 Scenarios

Observation-Constrained Monte Carlo



Assumption: Simulation that well matches observed concentrations is also most reliable for sensitivities

adapted from Deguillaume et al., 2007

Bayesian Inference to "weight" relative likelihoods of Monte Carlo cases

- Use observational evidence to update the estimated likelihood of probabilistic predictions
- Initially assume each prediction is equally likely
- Apply Bayes Theorem to assign relative likelihood to each model case X_i, given observation O

$$P(X_i|O) = \frac{P(O|X_i)P(X_i)}{\sum_j [P(O|X_j)P(X_j)]}$$

- Assign standard error (σ) to each observation, but not to the model results

Metrics for Bayesian Analysis in AQRP Report

- **Metric 1**: 8-hr ozone at each target monitor (Denton, Eagle Mt. Lake and Keller) on each day, considering only monitor-days > 70 ppb
  - Truncated likelihood function (N=48)
- **Metric 2**: 8-hr ozone averaged across all DFW monitors on each day
  - Normal likelihood function (N=30)
- Note: If each O_k is assumed independent, function essentially multiplies together likelihoods
  - Results in huge range in weights

$$L(Y_j \mid O) = \frac{1}{(\sqrt{2\pi})^N \prod_{k=1}^{N} \sigma_k} \exp\left\{ -\frac{1}{2} \sum_{k=1}^{N} \left[\frac{(O_k - Y_{j,k})^2}{\sigma_k^2} \right] \right\}$$

Bayesian Likelihood Functions

Approach of most past studies:

Normal Likelihood Function of ozone prediction ($Y_{j,k}$) given observations (O_k):

$$L(Y_j \mid O) = \frac{1}{(\sqrt{2\pi})^N \prod_{k=1}^{N} \sigma_k} \exp\left\{ -\frac{1}{2} \sum_{k=1}^{N} \left[\frac{(O_k - Y_{j,k})^2}{\sigma_k^2} \right] \right\}$$

Bergin and Milford, ES&T, 2000

If threshold is applied to observations, need an alternate approach:

Truncated Normal Likelihood Function of ozone prediction ($Y_{j,k}$) given that observation (O_k) exceeds a threshold concentration (*a*) :

$$L(Y_j \mid O) = \frac{\dfrac{1}{(\sqrt{2\pi})^N \prod_{k=1}^{N} \sigma_k} \exp\left\{ -\dfrac{1}{2} \sum_{k=1}^{N} \left[\dfrac{(O_k - Y_{j,k})^2}{\sigma_k^2} \right] \right\}}{\sum_{k-1}^{N} \left[\dfrac{1}{2} \left\{ 1 - erf\left(\dfrac{a - Y_{j,k}}{\sqrt{2\sigma_k^2}} \right) \right\} \right]}$$

σ_k is the observation standard error

Non-Bayesian Metric 3 in AQRP report

Mean Normalized Bias (MNB)

$$\mathbf{MNB} = \frac{1}{n}\sum_{i=1}^{n}\frac{y_i - o_i}{o_i}$$

Mean Normalized Gross Error (MNGE)

$$\mathbf{MNGE} = \frac{1}{n}\sum_{i=1}^{n}\frac{\left|y_i - o_i\right|}{o_i}$$

Unpaired Peak Accuracy (UPA)

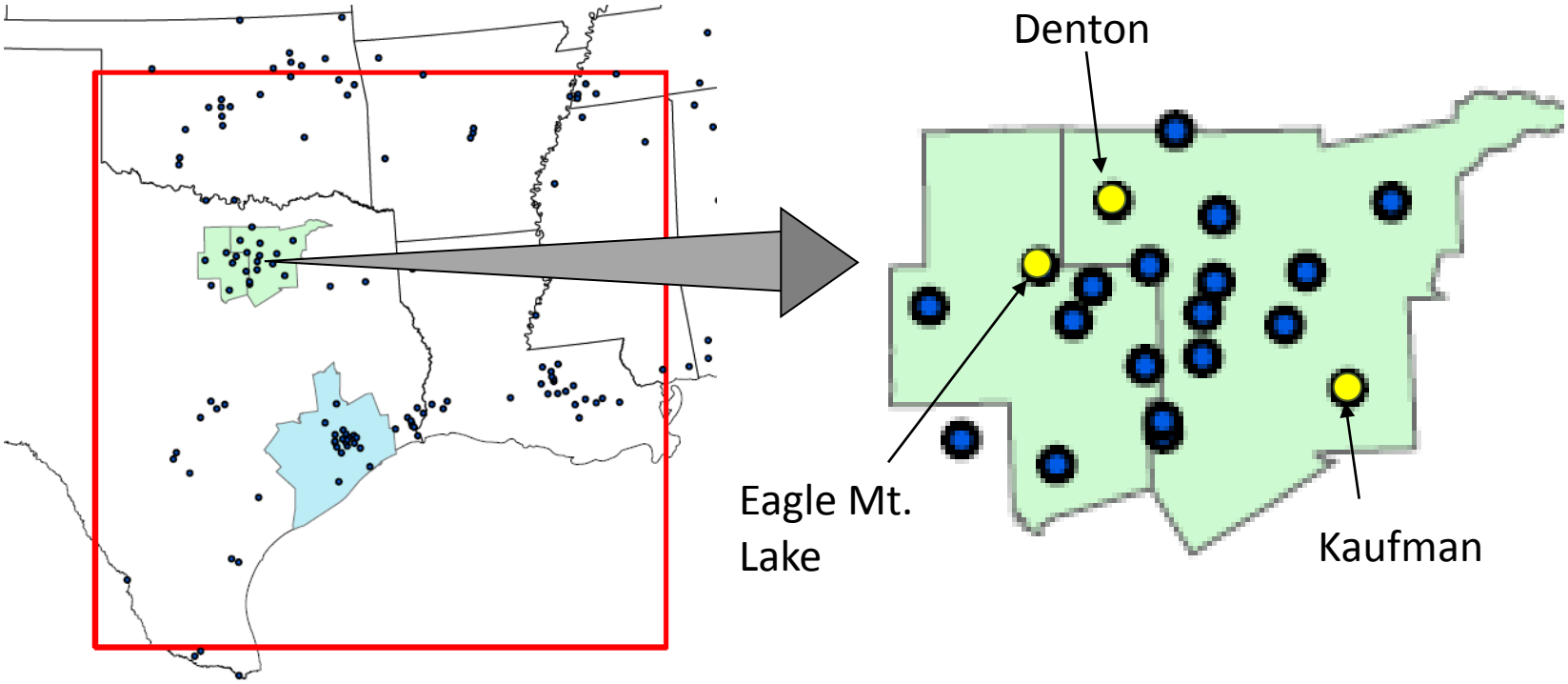
$$\mathbf{UPA} = \frac{y_{max} - o_{max}}{o_{max}}$$

METRIC 3

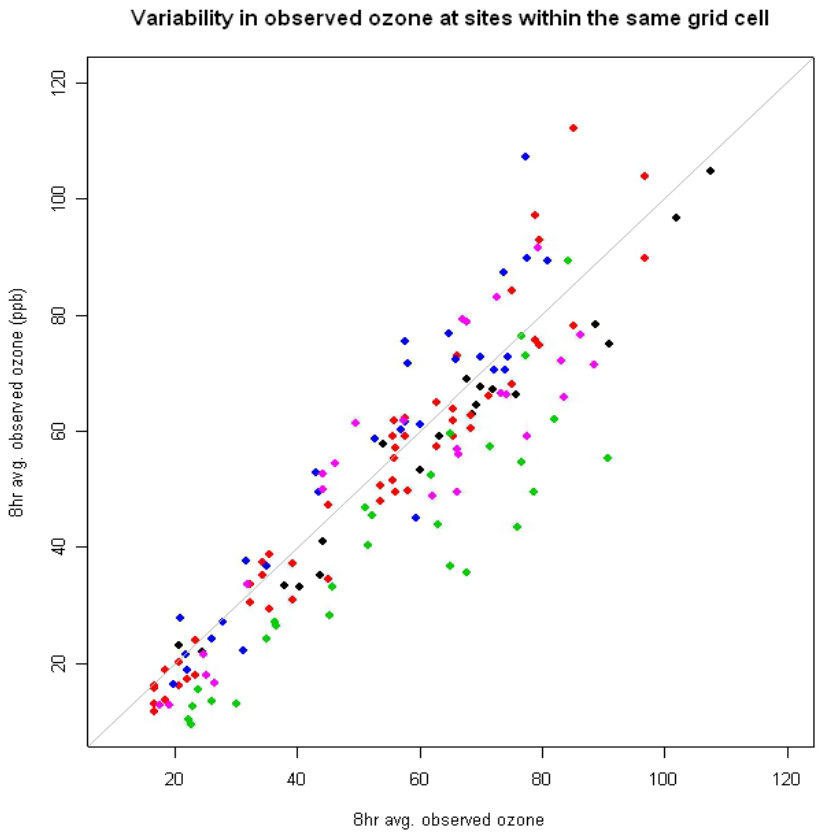
Non-Bayesian Weight

$$= \frac{1}{\left|\mathbf{MNB}\right| + \mathbf{MNGE} + \left|\mathbf{UPA}\right|}$$

Ozone monitors considered in metrics



Estimate observation standard error based on grid cells with multiple monitors



Standard deviation between observed 8hr ozone values at these same-grid-cell sites ranges from 3.0 to 10.5ppb

Figure courtesy: K. Foley, US EPA

Thus, we chose **σ = 8 ppb for Metric 1** to be near the midpoint of this range. **Metric 2** should have less uncertainty due to its averaging across sites, and thus **σ = 5 ppb** was chosen for this metric.

Results in AQRP Report: Weighting of structural cases

- Weightings differed widely by metric, and if parametric uncertainty was included
- Metrics 1 & 2 placed most weight on handful of cases (unrealistic??)
- Metric 3 had flatter distribution

		***a posteriori* probabilities**			
		BASE	**CB6 (C)**	**MEGAN (M)**	**C+M**
Metric 1 (N = 48)	structural only	0.00%	16.34%	0.00%	83.66%
	w/ parametric	14.91%	5.26%	65.01%	14.82%
Metric 2 (N = 30)	structural only	0.19%	80.06%	0.16%	19.58%
	w/ parametric	0.00%	25.32%	0.00%	74.68%
Metric 3 (non-Bayesian, N=356)	w/ parametric	21.63%	29.57%	21.42%	27.39%

Results: Scaling of input parameters in weighted ensembles

- Weightings differ across metrics
- Metric 1 sought to overcome low bias for $[O_3]$
- Metric 3 assigned flat distribution of weights

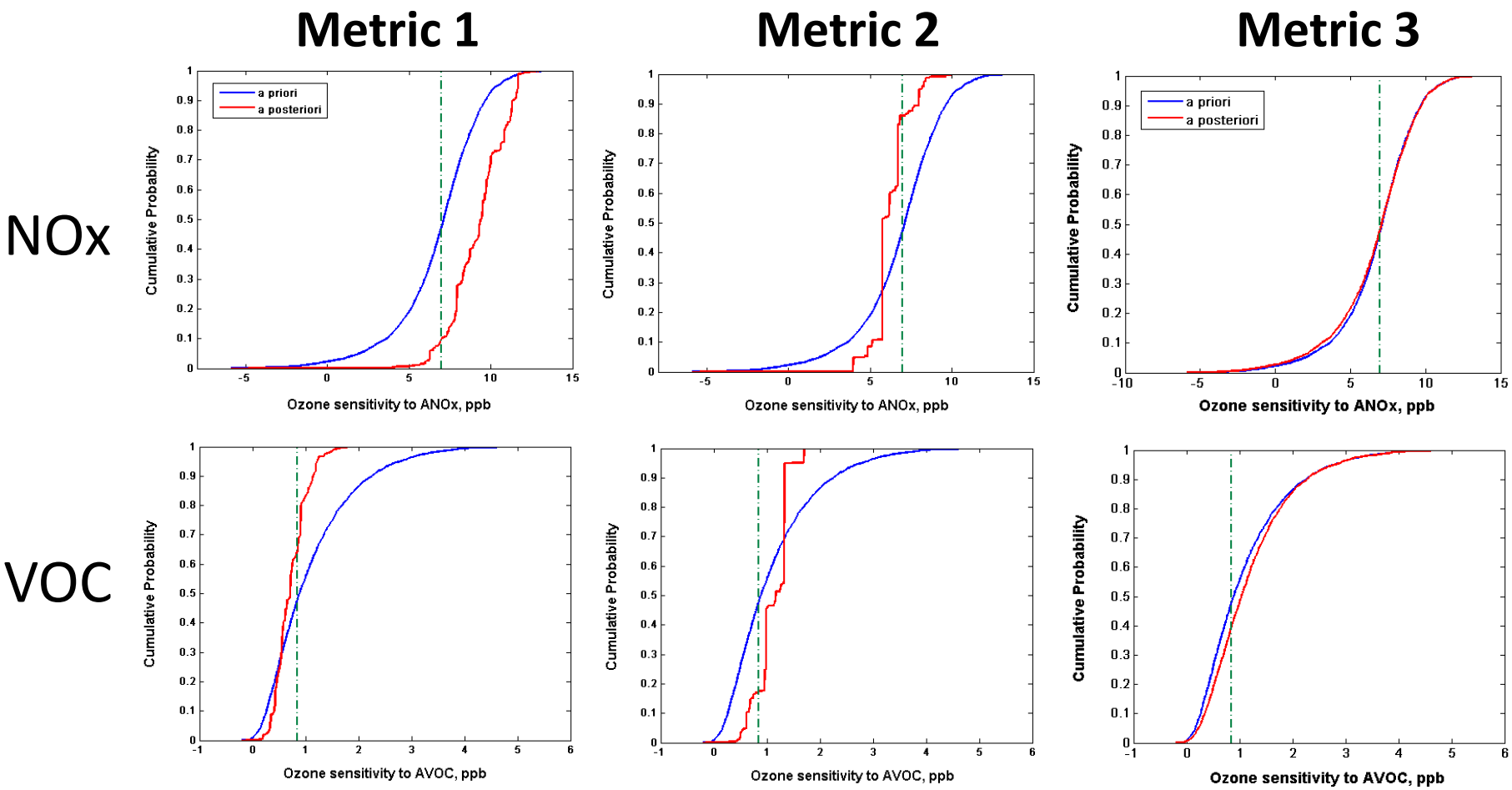
Weighted mean scaling factor for each input parameter

Input Parameters	***a posteriori* mean ± 1σ**		
	Metric 1	**Metric 2**	**Metric 3**
ENO_X	1.05 ± 0.16	0.90 ± 0.07 ↓	1.06 ± 0.25
EBVOC	1.07 ± 0.27	0.85 ± 0.14	1.03 ± 0.25
R(photolysis)	1.06 ± 0.07 ↑	1.11 ± 0.07 ↑	1.01 ± 0.08
R(NO_2+OH)	0.89 ± 0.24	1.45 ± 0.16 ↑	1.03 ± 0.27
R(NO+O_3)	0.97 ± 0.06	1.04 ± 0.08	1.00 ± 0.08
BC(O_3)	1.23 ± 0.13 ↑	1.30 ± 0.05 ↑	1.02 ± 0.16

Results: Predicted sensitivities to DFW NOx and VOC

		S_{ANOx} (ppb)		S_{AVOC} (ppb)	
		a priori **mean ± 1σ**	***a posteriori*** **mean ± 1σ**	***a priori*** **mean ± 1σ**	***a posteriori*** **mean ± 1σ**
Denton	Metric 1	6.79 ± 2.59	9.23 ± 1.64 ↑	1.10 ± 0.82	0.73 ± 0.29 ↓
	Metric 2		6.21 ± 1.01 ↓		1.12 ± 0.30 ↑
Eagle Mt. Lake	Metric 1	6.79 ± 2.46	9.17 ± 1.58 ↑	0.95 ± 0.76	0.60 ± 0.28 ↓
	Metric 2		6.28 ± 0.94 ↓		0.98 ± 0.27 ↑
Kaufman	Metric 1	3.39 ± 0.57	3.92 ± 0.34 ↑	0.05 ± 0.06	0.01 ± 0.02 ↓
	Metric 2		3.22 ± 0.17 ↓		0.06 ± 0.02 ↑

Results: Weighted and unweighted ensemble predictions of ozone sensitivity at Denton



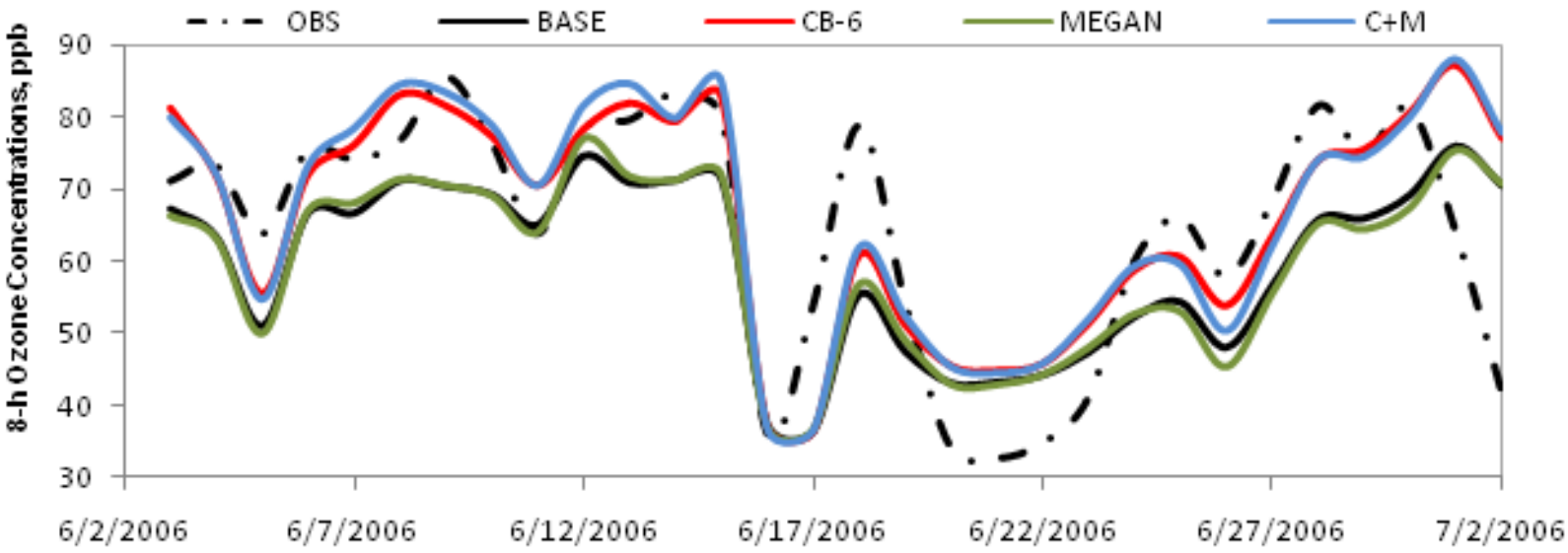
Performance of Ensembles vs. DFW 8-hour Ozone Observations

- Base model already performed well
- Equal-weight ensemble corrected bias by including CB-6 cases with higher [O_3]
- Weightings achieved low bias but did not substantially improve error or correlation

Statistics	Base Case (deterministic)	Equal weighted full ensemble	Bayesian (Metric-1)	Bayesian (Metric-2)	Non-Bayesian (Metric-3)
RMS (ppb)	12.62	11.50	11.58	10.23	11.45
NMB (%)	-7.81	-2.44	3.21	-0.31	-0.46
Correlation	0.759	0.770	0.769	0.819	0.770

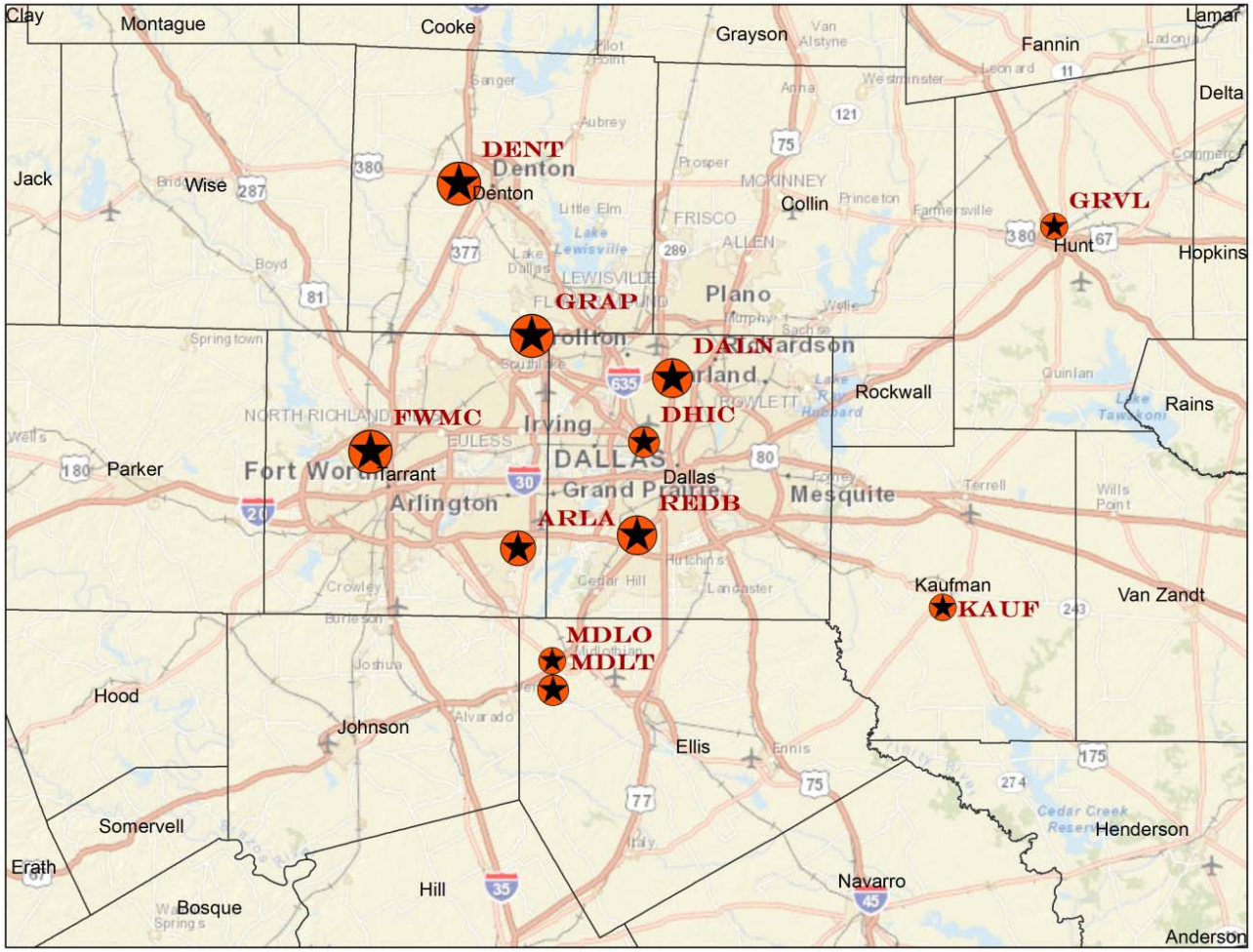
Structural ensemble was "underdispersive": Ensemble range did not capture some observations

Daily 8-hour ozone averaged over DFW monitors



WORK SINCE AQRP: PUBLICATION IN PREPARATION FOR JGR

Observations (8-h O_3 & 24-h NO_X)



Note: NO_X concentrations were bias-corrected for interference with other nitrogen species based on the work of Lamsal et al., JGR, 2008.

JGR paper Metric 1 (Bayesian)

- Episode-average 8-hr O_3 and 24-hr NO_x at 11 sites (N = 11)
- Set σ = 7.2 ppb (8-hr O_3) and 8.2 ppb (24-hr NO_x), based on data from monitors in same grid cells
- Applied Bayesian likelihood function

$$L(C_m^* \mid O) = \frac{1}{\left(\sigma\sqrt{2\pi}\right)^N} \exp\left\{-\frac{1}{2}\sum_{n=1}^{N}\left[\frac{(O_n - C_{m,n}^*)^2}{\sigma^2}\right]\right\}$$

A posteriori probability for C (applying Bayes' Theorem),

$$p'(C_m^* \mid O) = \frac{L(C_m^* \mid O)\, p(C_m^*)}{\sum_{m=1}^{M} L(C_m^* \mid O)\, p(C_m^*)}$$

Prior probability,

$$p(C_m^*) = \frac{1}{M}$$

JGR paper Metric 2 (EPA-based screening)

Screening cases that pass all of the following test criteria for 8-hr Ozone,

Mean Normalized Gross Error

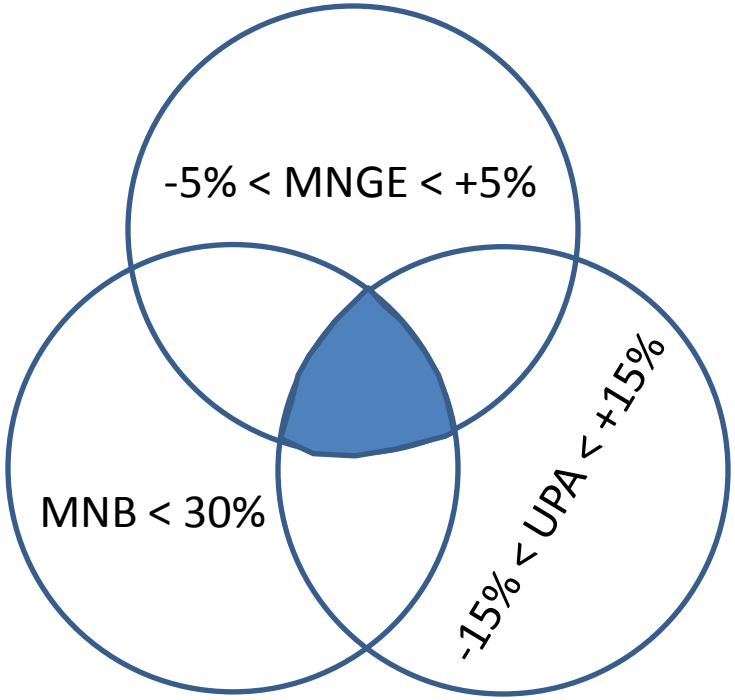
$$\mathrm{MNGE} = \frac{1}{N}\sum_{1}^{N}\left(\frac{|\mathrm{Model} - \mathrm{Obs}|}{\mathrm{Obs}}\right) \times 100\%$$

Mean Normalized Bias

$$\mathrm{MNB} = \frac{1}{N}\sum_{1}^{N}\left(\frac{\mathrm{Model} - \mathrm{Obs}}{\mathrm{Obs}}\right) \times 100\%$$

Unpaired Peak Accuracy

$$\mathrm{UPA} = \frac{\mathrm{Model}_{max} - \mathrm{Obs}_{max}}{\mathrm{Obs}_{max}} \times 100\%$$



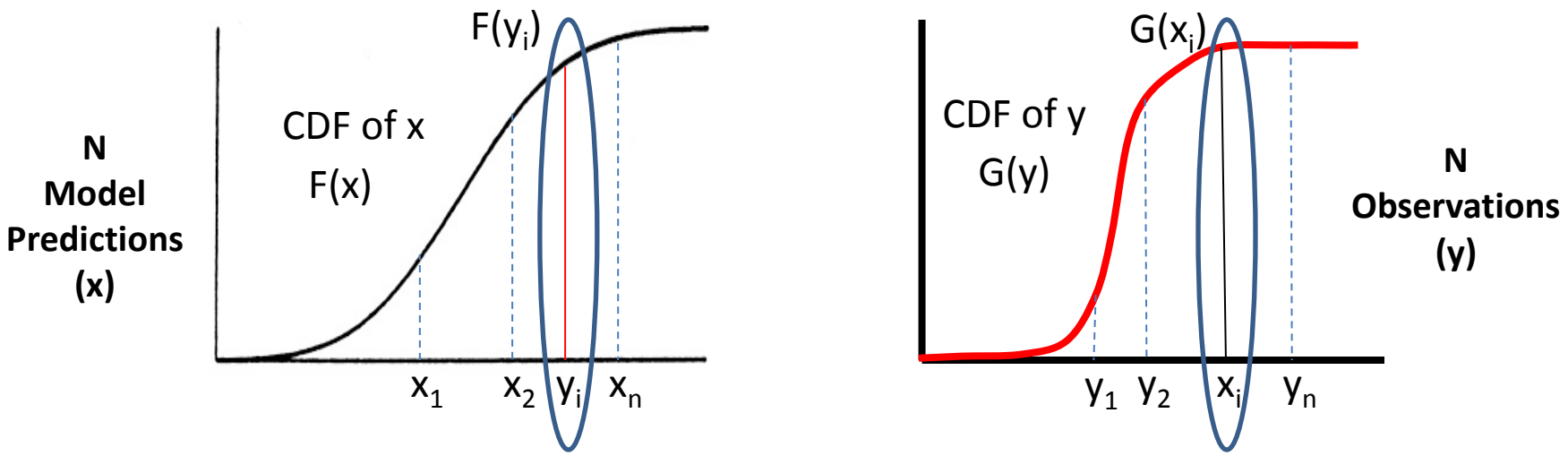
8-hr O_3 at all sites and days

N = 289

Note: MNB and MNGE were computed for model results (Model) when O_3 observations (Obs) were greater than the recommended threshold of 60 ppb [*USEPA*, 2007]

JGR paper Metric 3 (CvM screening)

The Cramér-von Mises (CvM) criterion [*Anderson,* 1962] provides a non-parametric test of the null hypothesis (H_0) that two samples are drawn from the same (unspecified) distribution



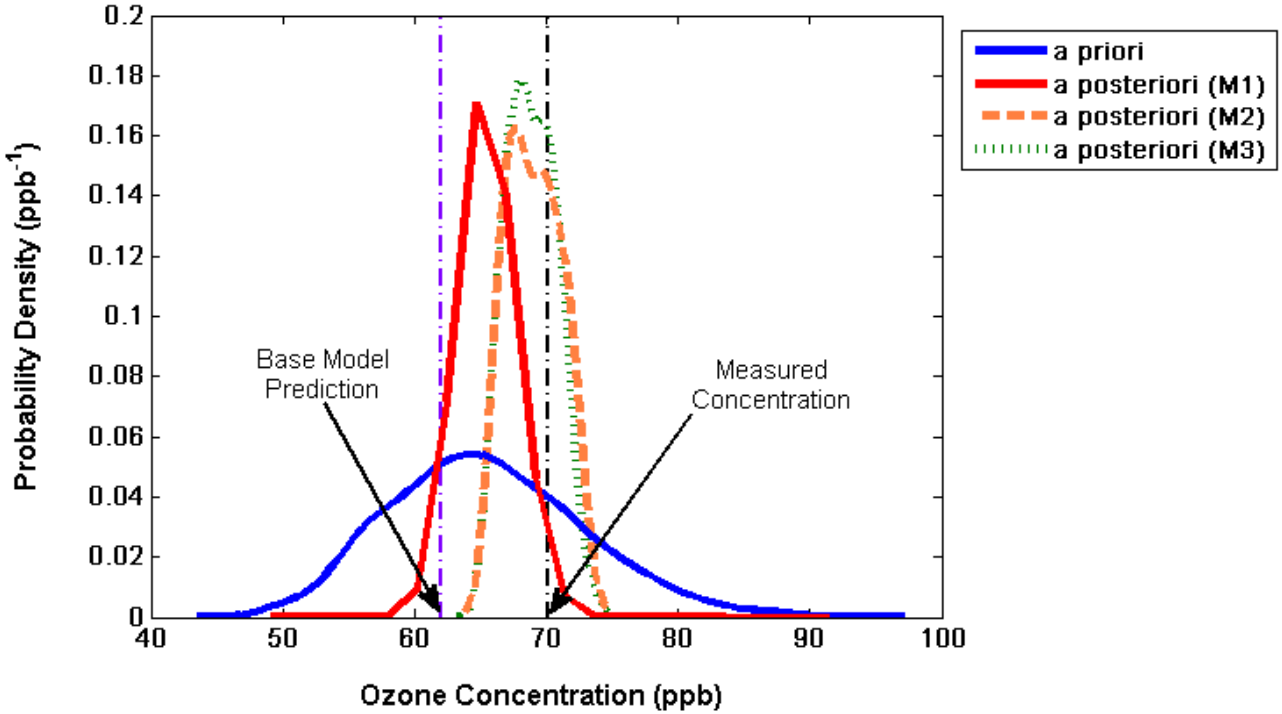
For each mth simulation, $$T = \frac{1}{4}\left\{\sum_{i=1}^{N}\left[F_A(x_i) - G_B(x_i)\right]^2 + \sum_{j=1}^{N}\left[F_A(y_j) - G_B(y_j)\right]^2\right\}$$

One rejects the null hypothesis that F(x)≡G(y) if T is too large

We select only those cases that yields p-values > 0.1, for both of the observational constraints (O_3 and NO_X)

8-hr O_3 (N = 289) and 24-hr NOx (N = 303) at all sites and days

Episode-Average 8-hr Ozone Prediction at Denton



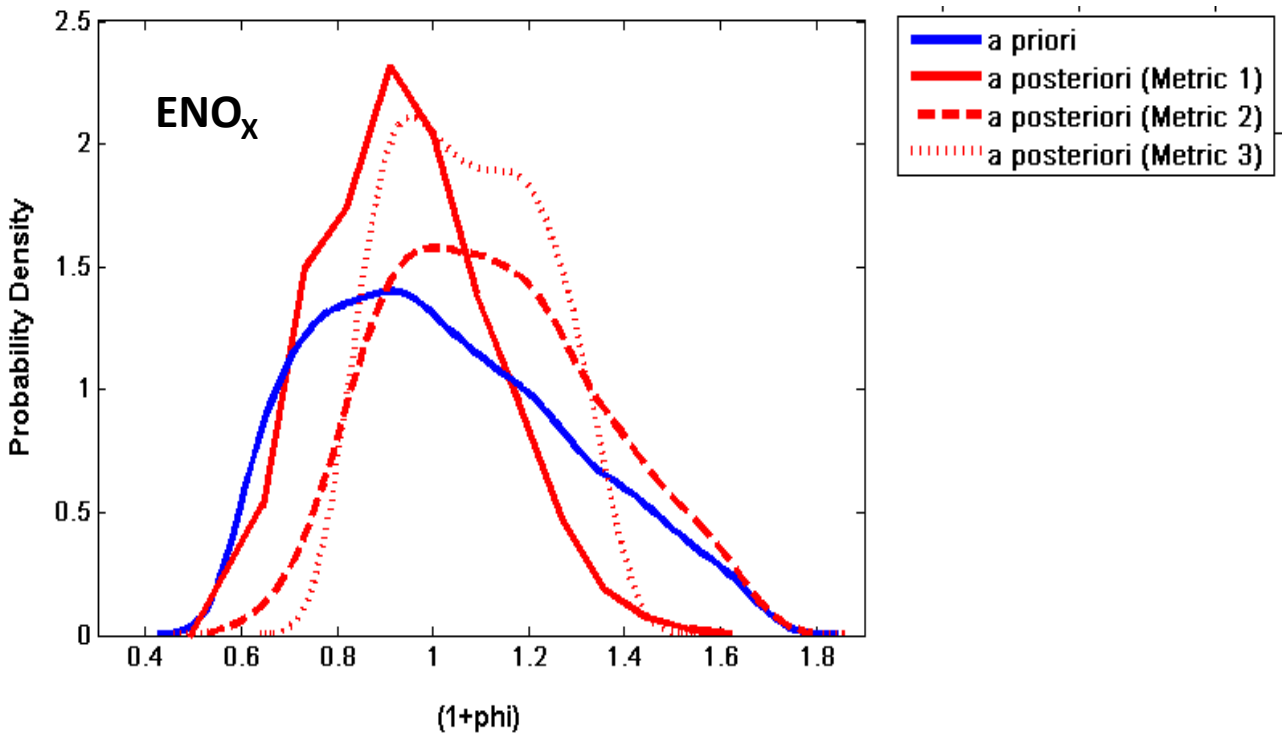
Metric	O_3 Concentration (ppb) Obs = 70.11 ppb	
	a priori ($\mu \pm \sigma$)	*a posteriori* ($\mu \pm \sigma$)
Metric 1	65.51 ± 7.33	65.53 ± 2.16
Metric 2		69.04 ± 2.03
Metric 3		68.85 ± 1.87

Distribution of Posterior Weights across Structural Cases

Metrics	Method	Constrained by Measurements of	Base	CHEM	BIO	CHEM+BIO
Metric 1	Bayesian	O_3 and NO_X	19.37%	35.37%	16.14%	29.12%
Metric 2	EPA Performance	O_3	16.14%	33.69%	17.99%	32.19%
Metric 3	CvM Test	O_3 and NO_X	12.92%	37.08%	16.97%	33.03%

All metrics gave more weight to simulations using CB-6 chemical mechanism

Posterior distribution of NOx Emission Scaling Factors

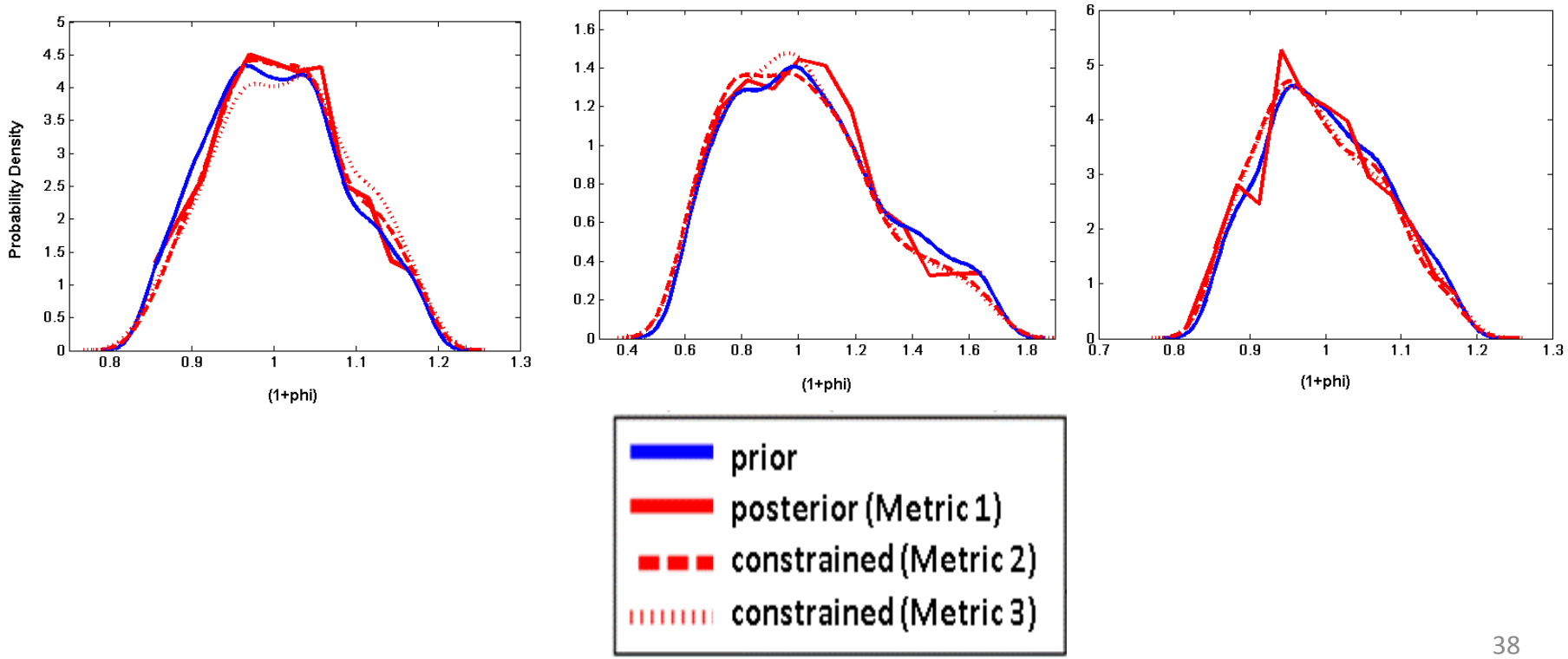


Metrics 2 and 3 favored cases with scaled-up ENO$_x$

Metric 1 favored cases with ENO$_x$ near base inventory

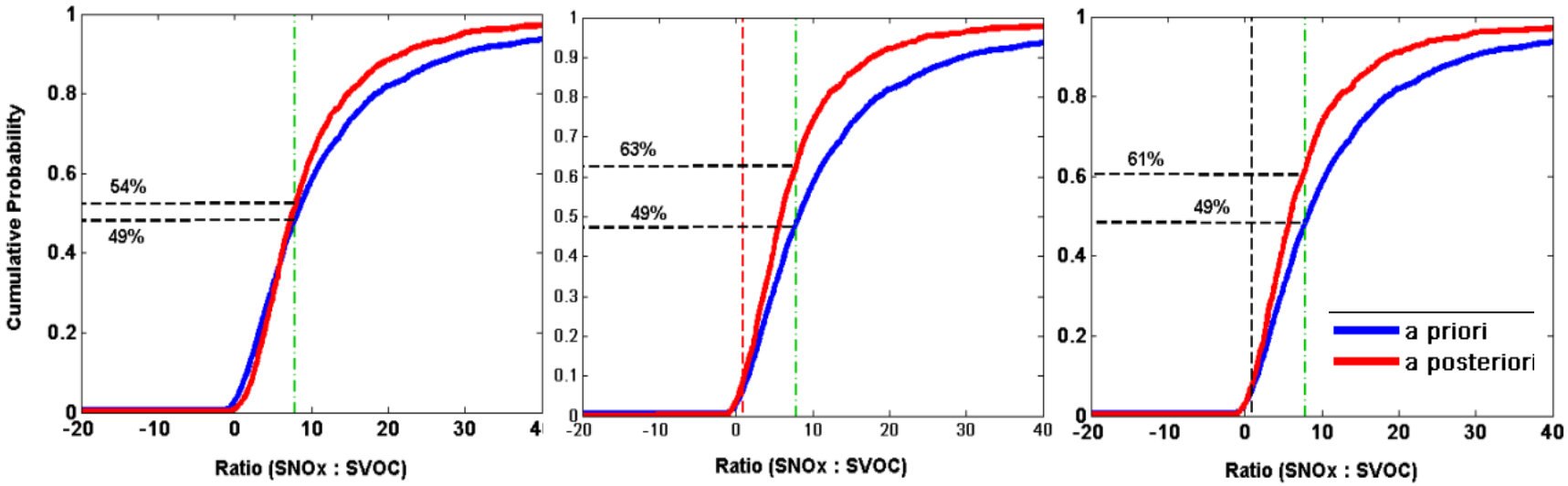
Obs-based constraints did not significantly change reaction rate distributions

R(photolysis) R(NO_2 + OH) R(NO + O_3)



A posteriori result for SNOx : SVOC

Cumulative Distribution Functions for Ratio (SNOx : SVOC)



Negative shift in the posterior CDFs (particularly for Metric 2 and 3) indicate slight preference towards SVOC, although the region is predominantly NOx-limited (i.e. SNOx : SVOC > 1.0)

SNOx:SVOC decreases because..

- All metrics gave more weight to simulations using CB-6 chem,
- CB-6 favors VOC controls
- Higher NOx emissions were needed to better match with observations
- Slight preference for VOC controls → higher SVOC compared to SNOx, hence lower SNOx:SVOC

CONCLUSIONS

- Demonstrated Bayesian and non-Bayesian approaches for observation-constrained Monte Carlo probabilities
- Developed probability distributions for response of DFW ozone to local NO_x and VOC emissions
- Identified structural and parametric choices that most influence concentrations and sensitivities
- Choice of observational metric is crucial to results
- Future work could consider additional uncertainties (e.g., meteorology; ensemble of models) and metrics (e.g., using data from satellites or aircraft)

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