Improvement and Sensitivity Analysis of the Atmospheric Chemistry Module for Modeling TICs in SCIPUFF

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Background

- **Phase I**
  - 9/03 – 9/05
  - “*Atmospheric Chemistry Module for TICs*”
  - Mike Henley, AFRL/MLQ Tyndall AFB, FL
- **Phase II**
  - 9/06 – current
  - “*Modeling the Atmospheric Chemistry of Toxic Industrial Chemicals*”

Outline

- **Background**
  - Project Goals
  - Phase I Status
- **Methodology**
  - Integration in SCIPUFF
  - Derivation of k_{eff} (example: 1-butene)
  - Parameter Space
- **Results**
  - Improved regression on k_{eff}
  - Model output
- **Summary**

Project Goals

- **Develop initial atmospheric chemistry capability**
  - Develop Atmospheric Chemistry Algorithm
    - Algorithm MUST run rapidly.
    - Develop generic algorithm so that a detailed chemical kinetics approach is not required.
    - Algorithm must account for all (most) modeling scenarios (e.g., CC, T, ambient conditions).
    - Algorithm must be robust enough to account for diurnal changes to degradation rates.
    - Algorithm should account for the potential generation of intermediate toxic compounds.
  - Develop Chemical data for the Chemistry Algorithm
    - Review existing chemistry data for nine alkenes (and H_2S)
    - Develop mechanisms used to generate chemistry algorithm.
- **Couple Algorithm to SCIPUFF**
  - Work with Dr. Sykes to create interface with SCIPUFF
- **Launch Chemistry Module from HPAC**

Phase I Atmospheric Chemistry Modeling Capabilities

- Alpha code Delivered Feb 2005
  - Ability to model
    - reactant decomposition
    - product formation
  - Butene + Propanal (R and P)
- Beta code Delivered Sep 2005
  - 10 TICs (9 Alkene's + H_2S)
- No impact on wall-clock run time

Methodology: Minor Modification to SCIPUFF

SCIPUFF Dispersion

$$\text{———} = -$$

$$= \int$$

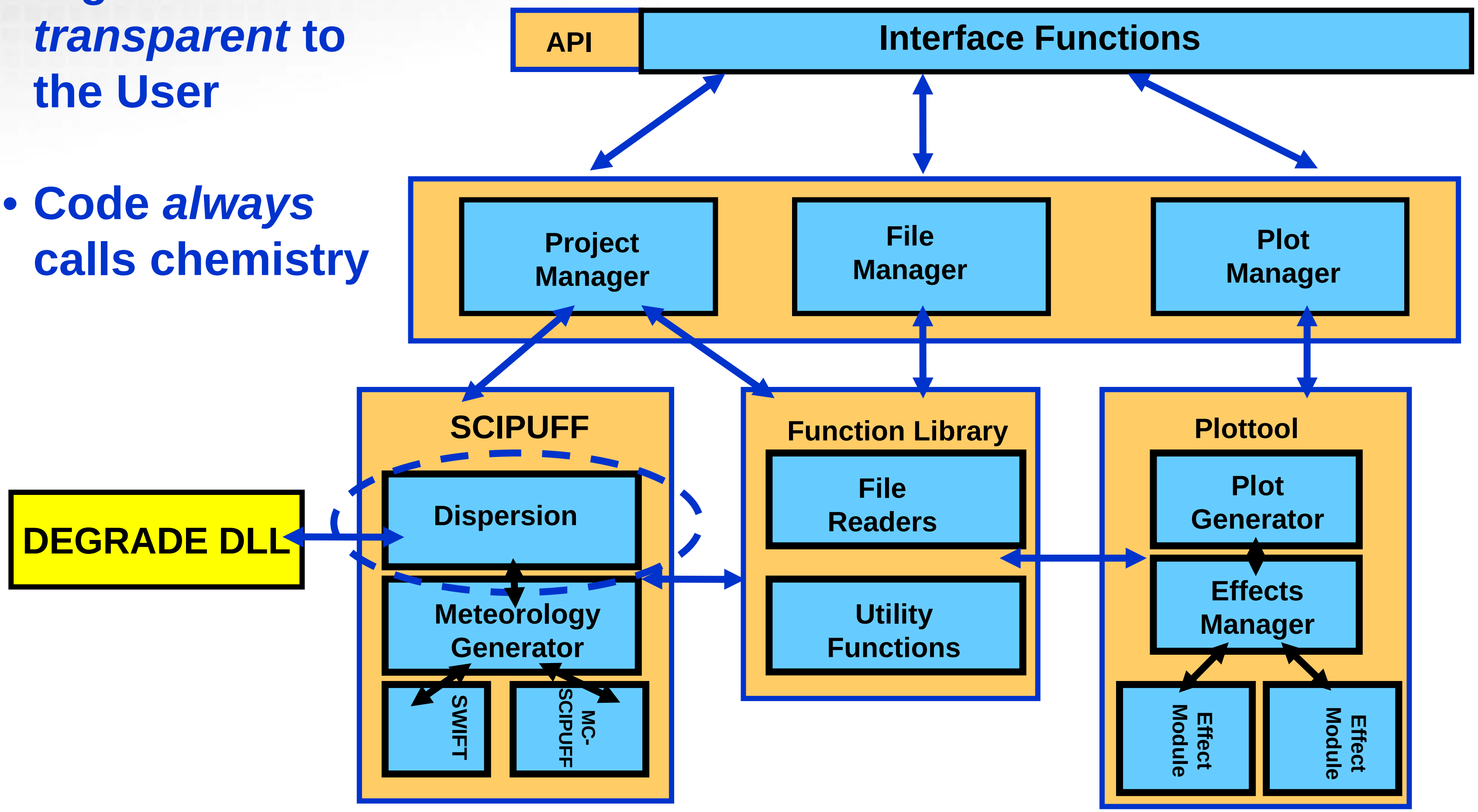
$$k_A = \max\left(k_A^{(\max)} \sin(\phi), k_A^{(\min)}\right)$$

$$k_A = k_{eff} = f(\phi, [amb], T, cc, humidity, etc.)$$

Method: Create Degrade Dynamic Link Library

Details in the Software Development Plan

- **Algorithm is *transparent* to the User**
- **Code *always* calls chemistry**



Methodology: Chemistry of 1-butene

$CH_2{=}CHCH_2CH_3 + OH \longrightarrow 0.94\ C_2H_5CHO + \text{Other products}$

$CH_2{=}CHCH_2CH_3 + NO_3 \longrightarrow 0.12\ C_2H_5CHO + 0.6\ C_3H_5O\text{-}CH\text{-}O\text{-}NO_2 + \text{Other products}$

$CH_2{=}CHCH_2CH_3 + O_3 \longrightarrow 0.35\ C_2H_5CHO + 0.41\ OH + \text{Other products}$

$$\text{Rate} = -\left(k_{OH}[OH] + k_{NO_3}[NO_3] + k_{O_3}[O_3]\right)[\text{1-butene}]$$

$$\text{Rate} = -k_{eff}\,[\text{1-butene}]$$

Methodology: Chemistry of 1-butene

Determine ID Rxn's, E_A, k(T)
(w/ OH, NO_3, H_2O, O_3, etc.)

↓

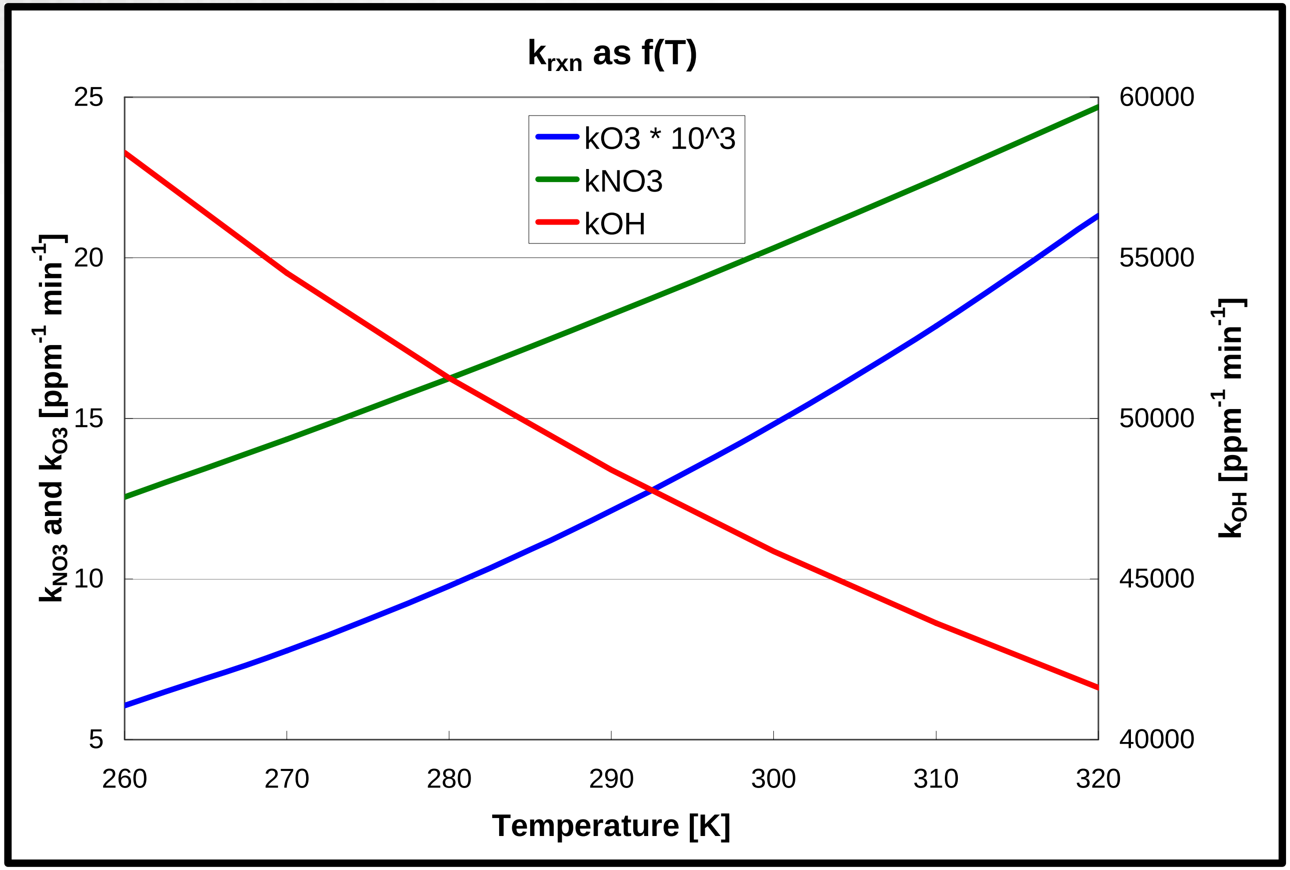
Implement in Detailed Mechanism

↓

Run PBM as f(met parm's)

↓

Obtain $c_{TIC}(t)$ as f(met parm's) → **Derive Empirical k_{eff} (met parm's)** → **Populate SCIPUFF data tables w/ k_{eff} for TICs**



Methodology: Detailed Mechanism

Determine ID Rxn's, E_A, k(T)
(w/ OH, NO_3, H_2O, O_3, etc.)

Implement in Detailed Mechanism

Run PBM as f(met parm's)

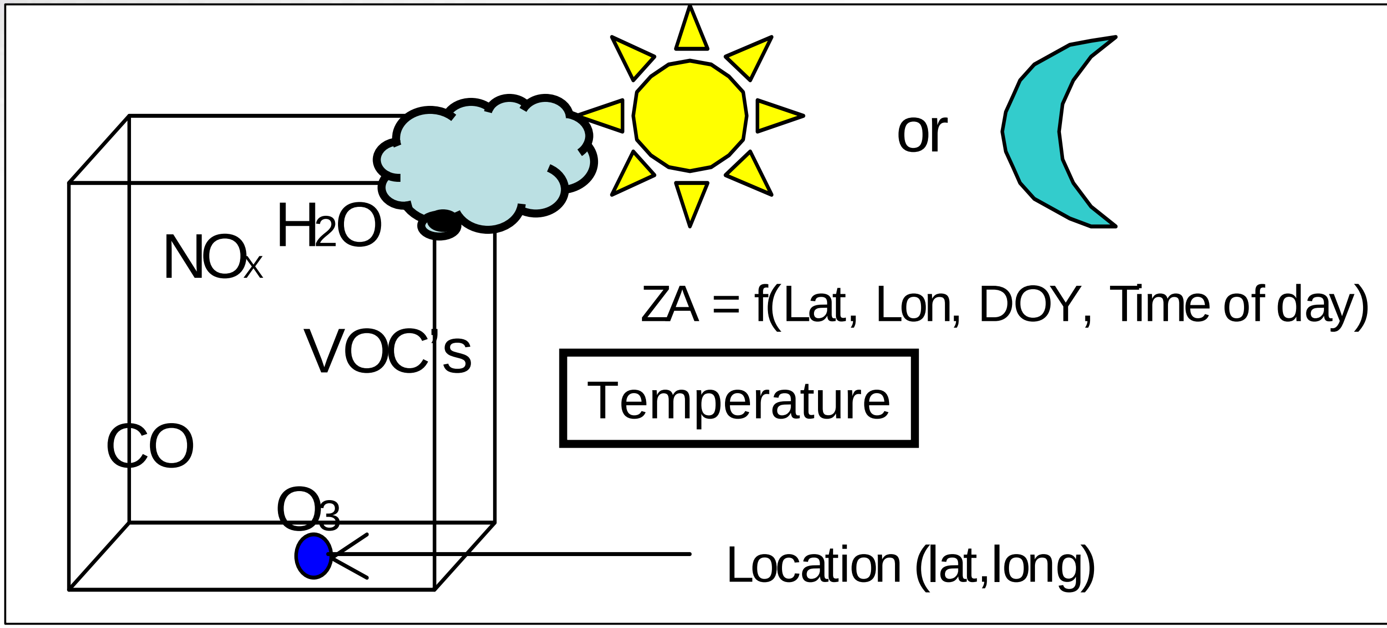
Obtain $c_{TIC}(t)$ as f(met parm's)

Derive Empirical k_{eff} (met parm's)

Populate SCIPUFF data tables w/ k_{eff} for TICs

- **Carbon Bond Mechanism**
  - Mass consistent atmospheric chemistry mechanism.
  - EPA Model (Adelman, 1999).
  - Used to model the ambient conditions.
  - [OH], [NO_3], [O_3], NO_X, VOCs, etc.
- **Append chemistry for TIC**
  - Data provided for 9 alkenes and H_2S

Methodology: Run Detailed Chemistry



k_{eff} is a function of solar elevation, cloud cover, air quality, temperature, humidity, etc

Implement in Detailed Mechanism → **Run PBM as f(met parm's)** → **Obtain $c_{TIC}(t)$ as f(met parm's)** → **Derive Empirical k_{eff} (met parm's)** → **Populate SCIPUFF data tables w/ k_{eff} for TICs**

Methodology: Parameter Space

Parameter	Units	SCIPUFF
Solar Zenith Angle	0 – 90 Deg	X
Location (**lat**, lon)	0 – 70 Deg	X
Time of Day	1440 min	X
Day of Year	3/21, 6/20, 12/20	X
Photochemistry (**Cloud Cover**)	0 – 8 Eighths	X
Temperature	**230 – 310 K**	X
Water Concentration	**100 – 40000 PPM**	
Moisture Mixing ratio		X
Air Quality	[NO_X], VOC, O_3, …	
Land Use	Urban, ocean, forest, …	X

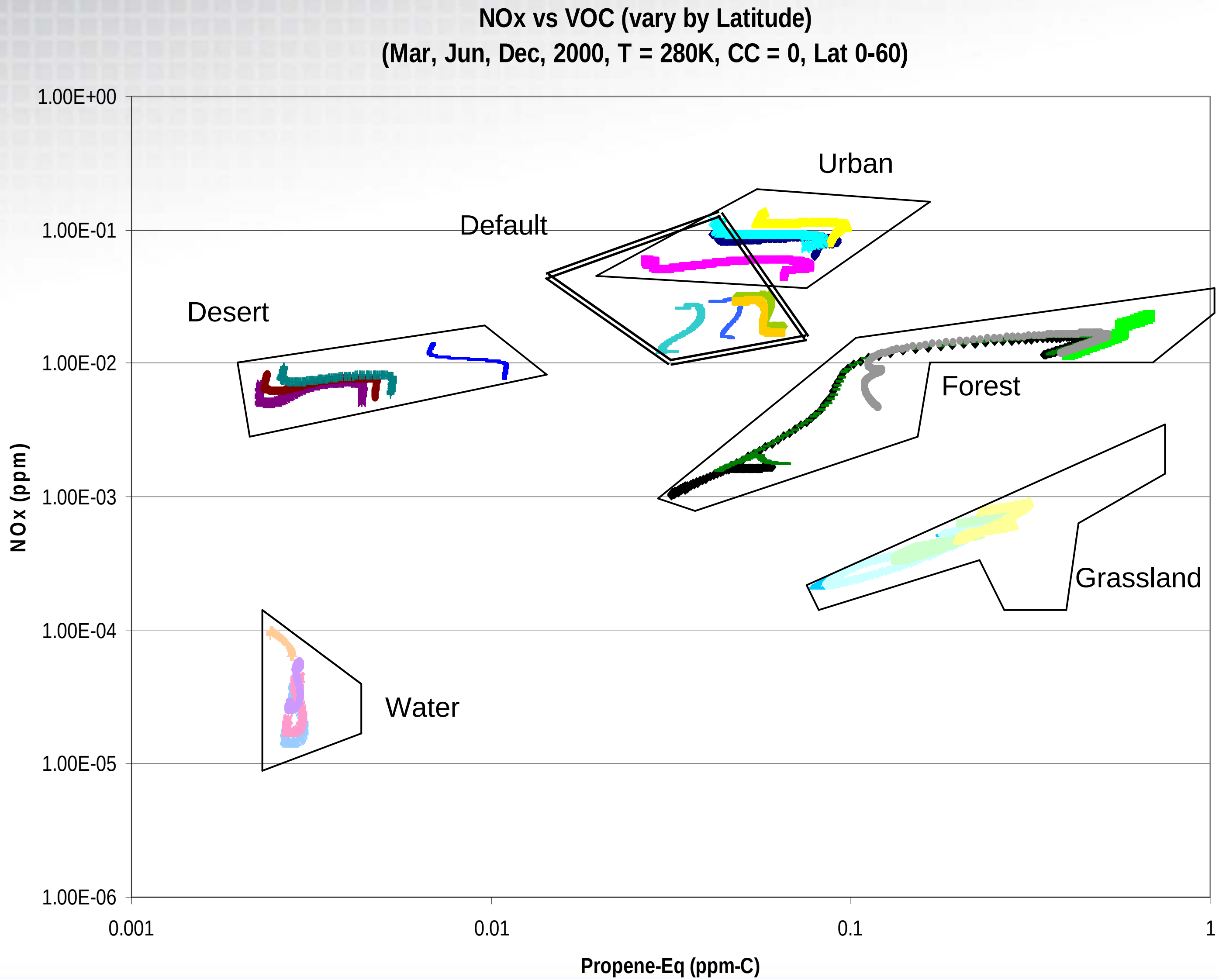
Methodology: Surrogate for Air Quality

- **Land Use**

1=Developed
2=Dry Cropland & pasture
3=Irrigated Cropland
5=Cropland/Grassland
6=Cropland/Woodland
7=Grassland
8=Shrubland
9=Shrubland/Grassland
10=Savanna
11=Deciduous Broadleaf
12=Deciduous Needleleaf
13=Evergreen Broadleaf
14=Evergreen Needleleaf
15=Mixed Forest
16=Water
17=Herbaceous Wetland
18=Wooded Wetland
19=Barren
20=Herbaceous Tundra
21=Wooded Tundra
22=Mixed Tundra
23=Bare Tundra
24=Snow or Ice
25=Partly Developed

1001=Urban Superclass
1002=Grassland Superclass
1003=Forest Superclass
1004=Desert Superclass
1005=Water Superclass

Methodology: Surrogate for Air Quality



Methodology: Refined Parameter Space (T, H_2O)

- **Surface Stations Nov 2003 – Sep 2004.**
- **Global 0.5 km LU Data Set**

1. Extracted data using 3 hr interval instead of 30 sec data. (both day and night)
2. Removed extreme data points (i.e., T<-60 °C or T<Dew point).
3. Matched weather station data with LU data before analysis (5 categories).

Latitude	Temperature (K)		$[H_2O]$ ($x10^3$) ppm)	
	Min	Max	Min	Max
0	288	310	12.4	37.1
10	288	310	7.05	37.4
20	288	310	4.55	37.1
30	274	310	3.81	34.9
40	265	304	1.54	28.5
50	257	299	1.02	19.8
60	245	294	0.400	14.2
70	231	291	0.113	11.6

Methodology: Run Detailed Chemistry

$$r_i = \left(-\frac{\partial c_i}{\partial t} \right)_{Chemistry} = -k_{OH}[OH][c_i] - k_{NO_3}[NO_3][c_i] - k_{O_3}[O_3][c_i] - k[c_i] - \ldots..$$

$$-\left(\frac{dc_i}{dt} \right)_{chemistry} = k_{eff}[c_i]$$

$$k_{eff} = \frac{-\frac{dc}{dt}}{[c]}$$

Implement in Detailed Mechanism

↓

Run PBM as f(met parm's)

↓

Obtain $c_{TIC}(t)$ as f(met parm's)

→

Derive Empirical k_{eff} (met parm's)

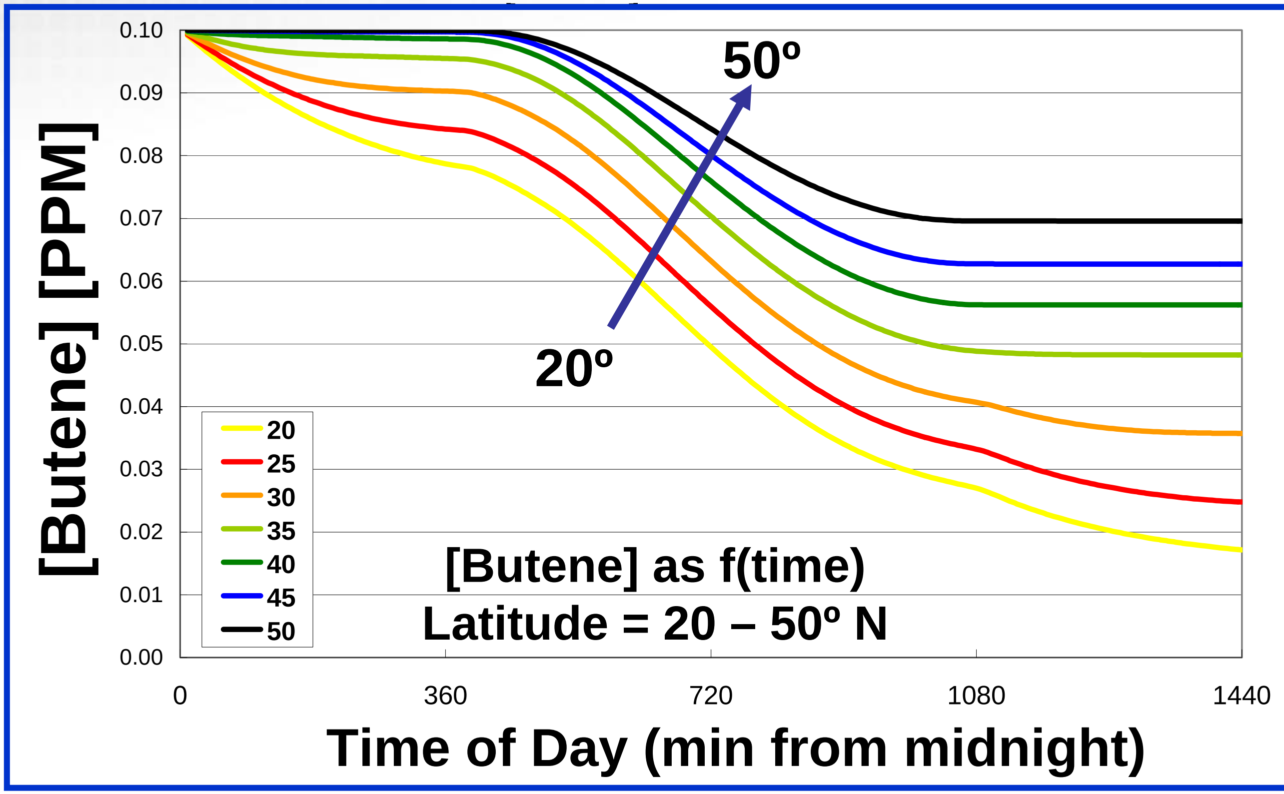
→

Populate SCIPUFF data tables w/ k_{eff} for TICs

Methodology: Obtain C_{TIC} as f(t)

$$k_{eff} = \frac{-\frac{dc}{dt}}{[c]}$$

T = 290 K, Land Use = Urban



Implement in Detailed Mechanism

↓

Run PBM as f(met parm's)

↓

Obtain c_{TIC}(t) as f(met parm's)

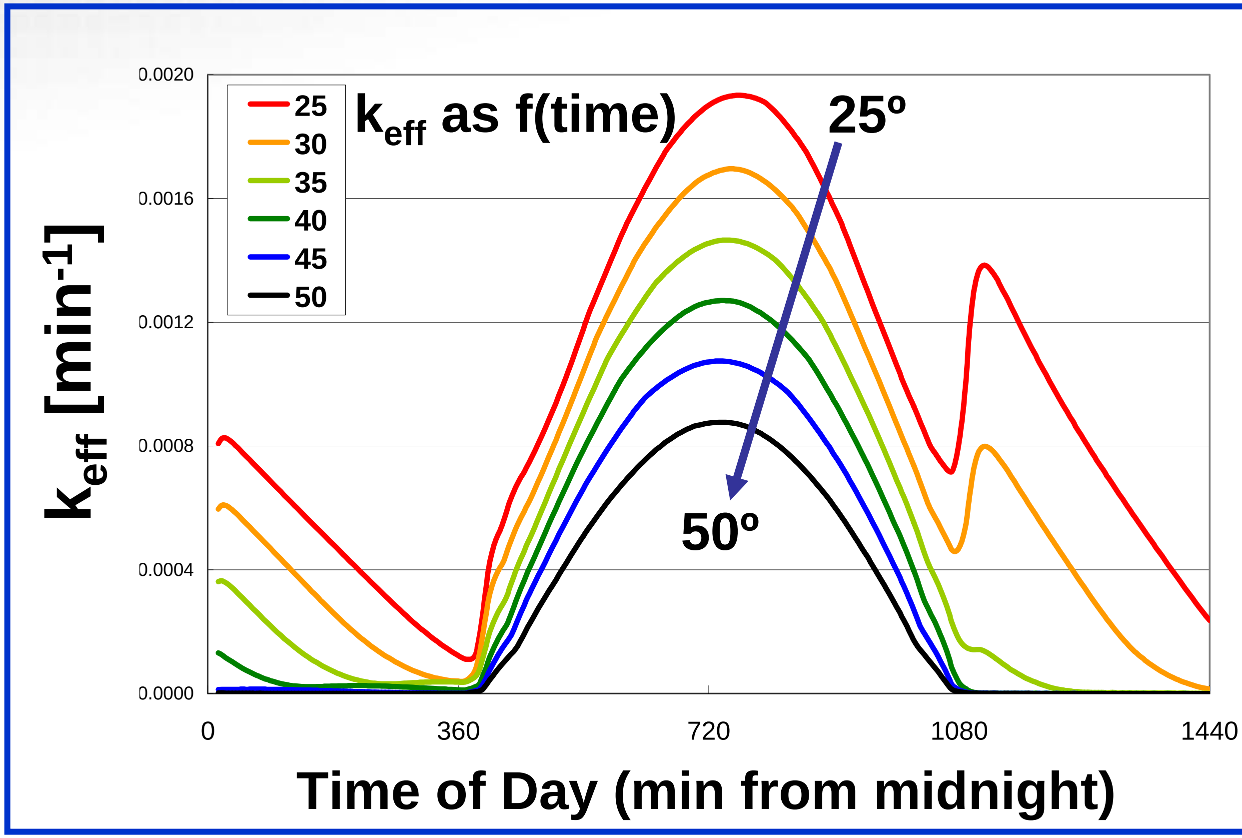
→ Derive Empirical k_{eff} (met parm's)

→ Populate SCIPUFF data tables w/ k_{eff} for TICs

Methodology: Obtain k_{eff} as f(met parms)

$$k_{eff} = \frac{-\frac{dc}{dt}}{[c]}$$

T = 290 K, Land Use = Urban



Implement in Detailed Mechanism

↓

Run PBM as f(met parm's)

↓

Obtain $c_{TIC}(t)$ as f(met parm's) → **Derive Empirical k_{eff} (met parm's)** → **Populate SCIPUFF data tables w/ k_{eff} for TICs**

Phase I Methodology: Derive Empirical k_{eff}

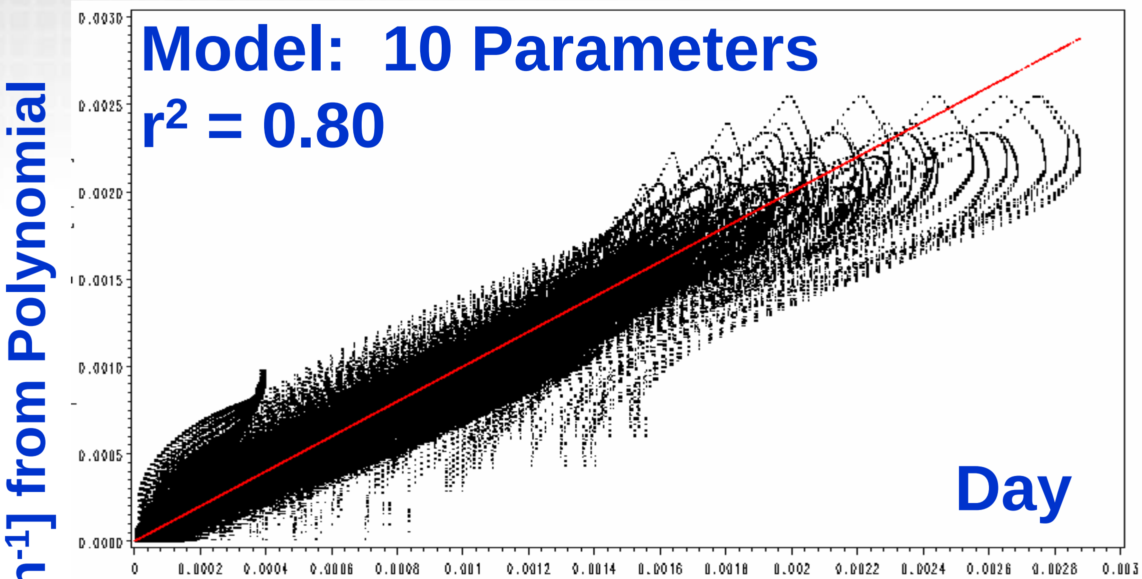
- Generate k_{eff} for various combinations of meteorological parameters for each land use
- Transform data to center on all parameters
- Perform statistical regression - correlation
  - Review Equation
  - Review Statistical Parameters (e.g., r^2)
  - Weigh fit vs number of parameters
- Derive an empirical k_{eff} = f(SE, T, lat, tod, CC, [H_2O])
- Compare the k_{eff} (empirical model) with the PBM derived k_{eff}.

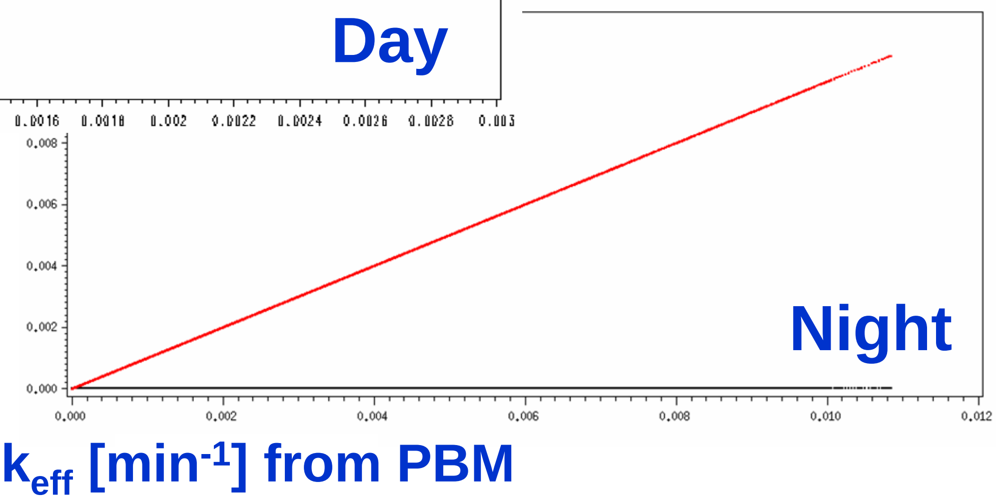
Obtain $c_{TIC}(t)$ as f(met parm's) → **Derive Empirical k_{eff} (met parm's)** → **Populate SCIPUFF data tables w/ k_{eff} for TICs**

Results: k_{eff} (polynomial) vs k_{eff} (PBM) for butene

Land Use = Urban

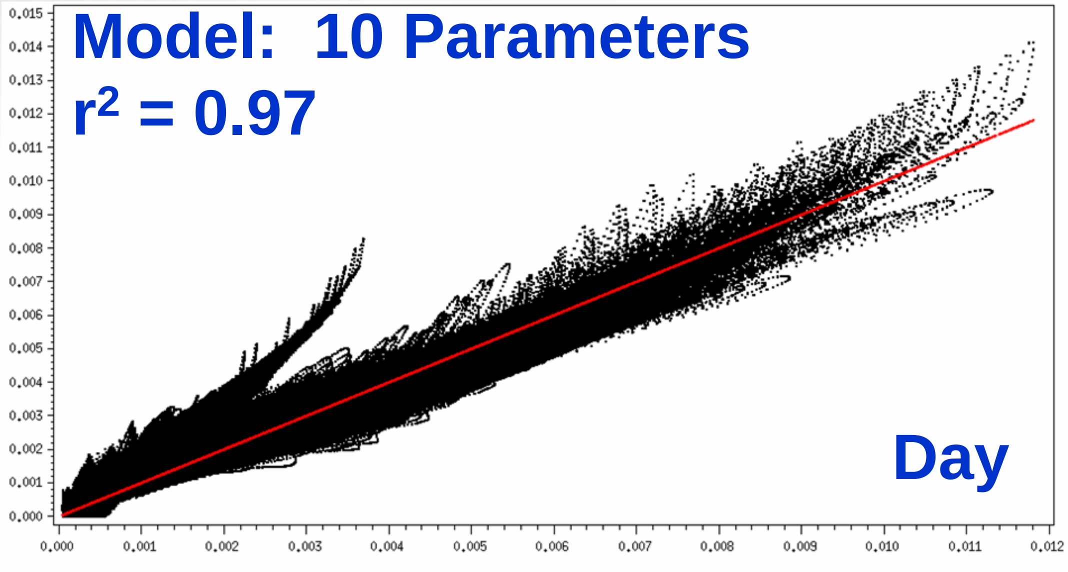
> 500,000 points



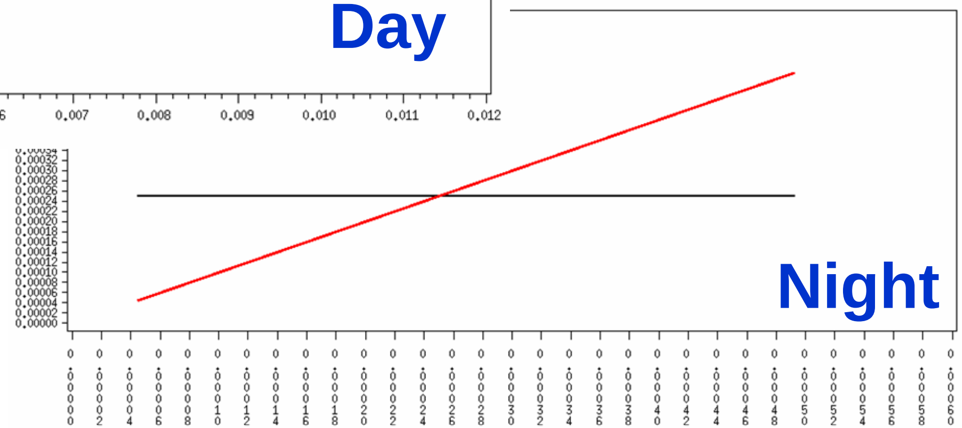


Results: k_{eff} (polynomial) vs k_{eff} (PBM) for butene

Land Use = Water



> 500,000 points



k_{eff} [min^{-1}] from Polynomial

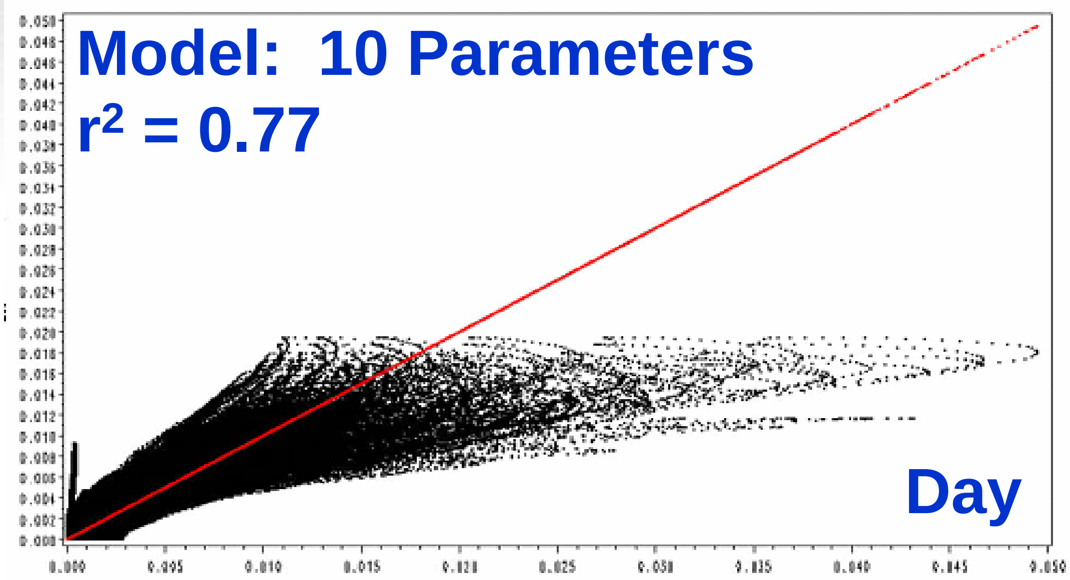
k_{eff} [min^{-1}] from PBM

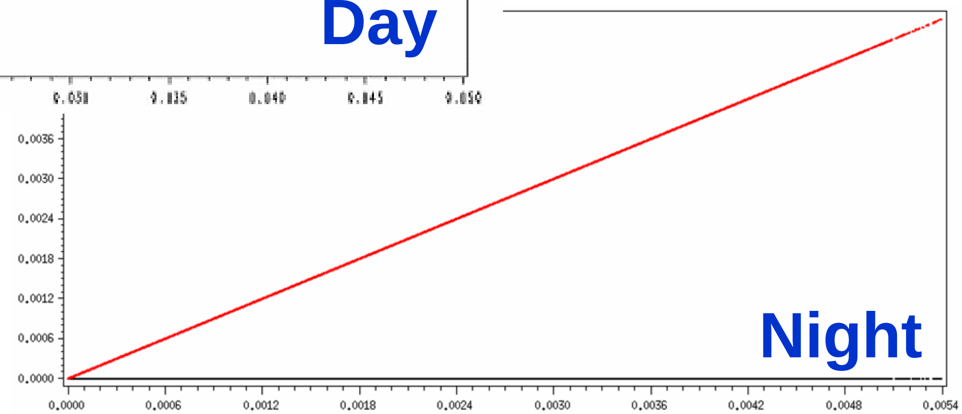
Results: k_{eff} (polynomial) vs k_{eff} (PBM) for butene

Land Use = Forest

> 500,000 points

k_{eff} [min^{-1}] from Polynomial





k_{eff} [min^{-1}] from PBM

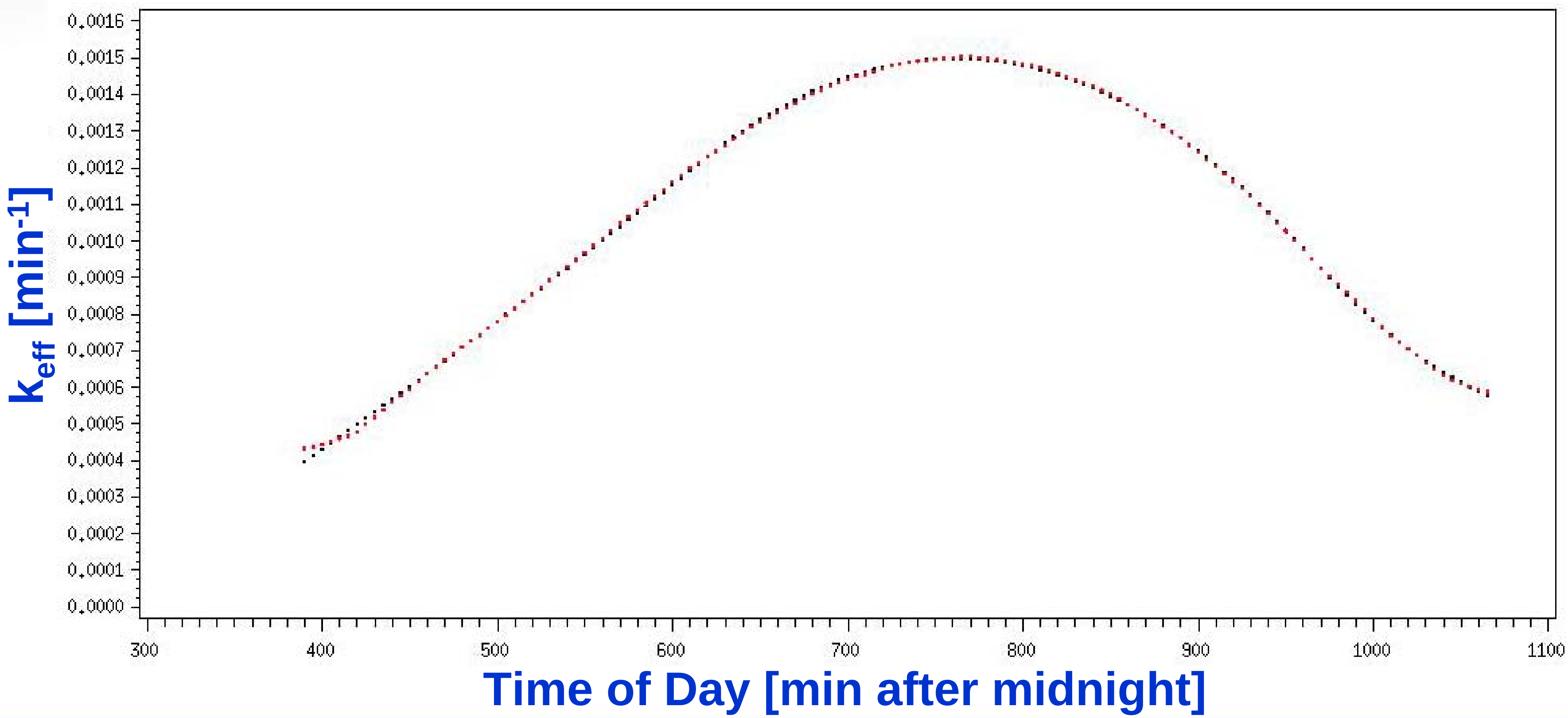
Current Effort – Improve Regression Analysis

- **Goal:**
  - Obtain better correlation with fewer fitting parameters for k_{eff}.
- **Method:**
  - Daytime (SE > 5°)
    - Fit polynomial spline for the 4104 unique combinations of latitude, temperature, cloud cover, and humidity
    - 7 parameter estimates for each combination used to estimate k_{eff} for a given time.
  - Nighttime (SE < 5°)
    - Data for each time span before sunrise and after sunset were divided into quartiles.
    - Average k_{eff} calculated for each of the eight quartile.
- F90 code written to ingest lat, T, CC, Humidity, and Time.
  - Interpolate k_{eff} values that lie between parameter values.
  - Will become the new degrade.dll code once completely tested.
  - Must verify run-time performance

Results: k_{eff} (spline) vs Time of Day for butene

Land Use = Urban

Lat 0°, Temp 311 K, Cloud Cover 0/8, $[H_2O]$ = 37000 ppm,

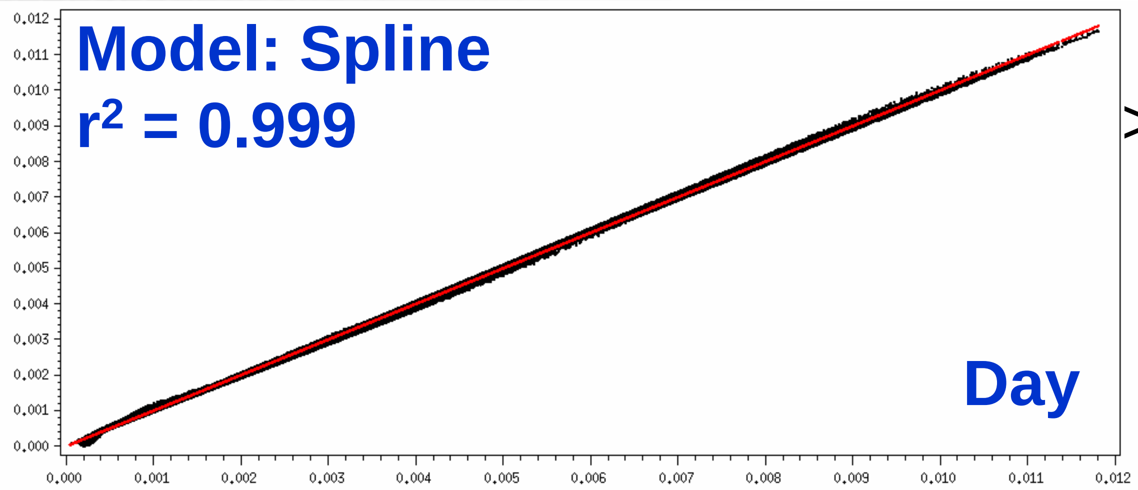


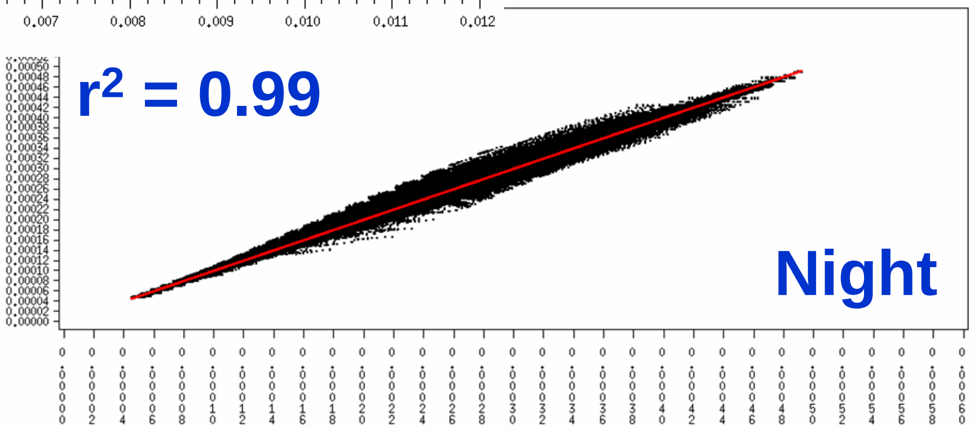
Results: k_{eff} (spline) vs k_{eff} (PBM) for butene

Land Use = Water

> 500,000 points

k_{eff} [min^{-1}] from Spline Fit



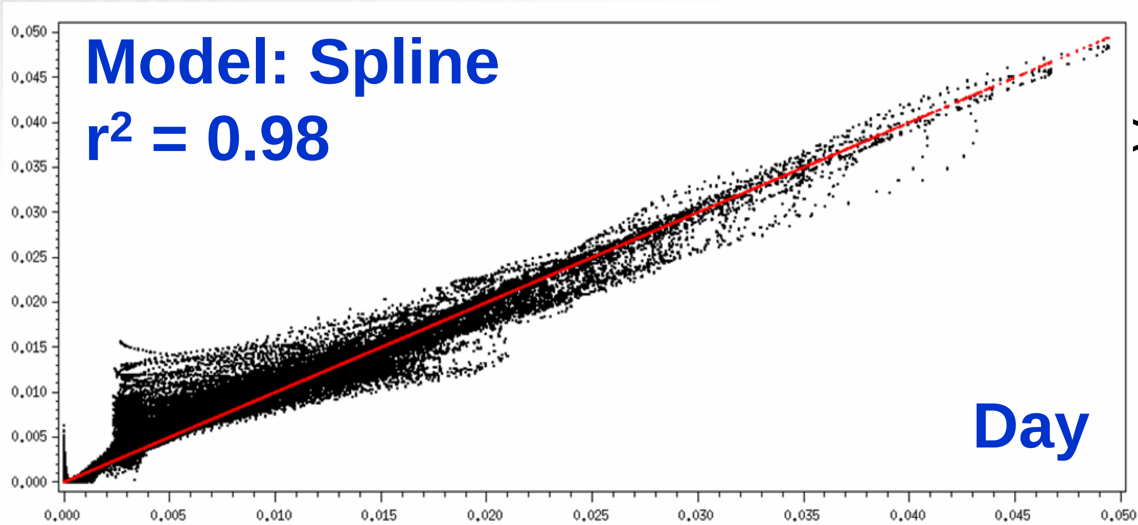


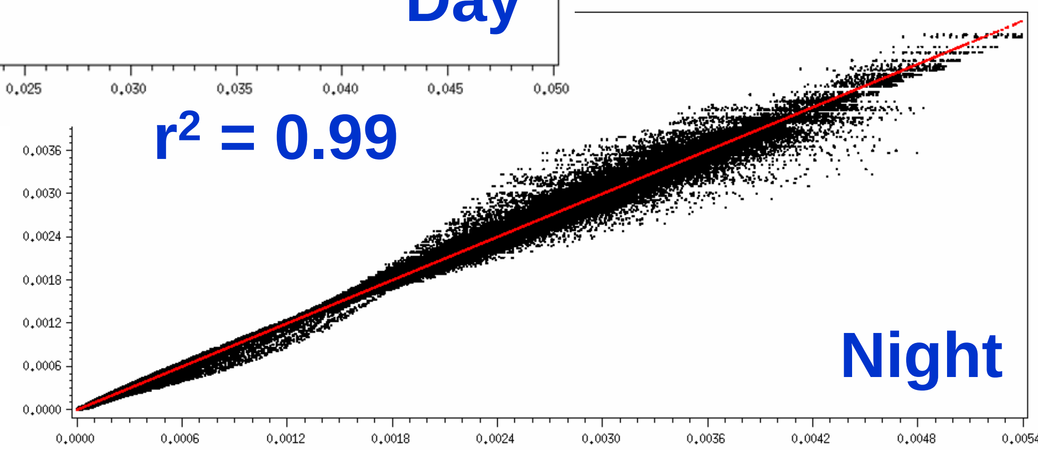
k_{eff} [min^{-1}] from PBM

Results: k_{eff} (spline) vs k_{eff} (PBM) for butene

Land Use = Forest

> 500,000 points





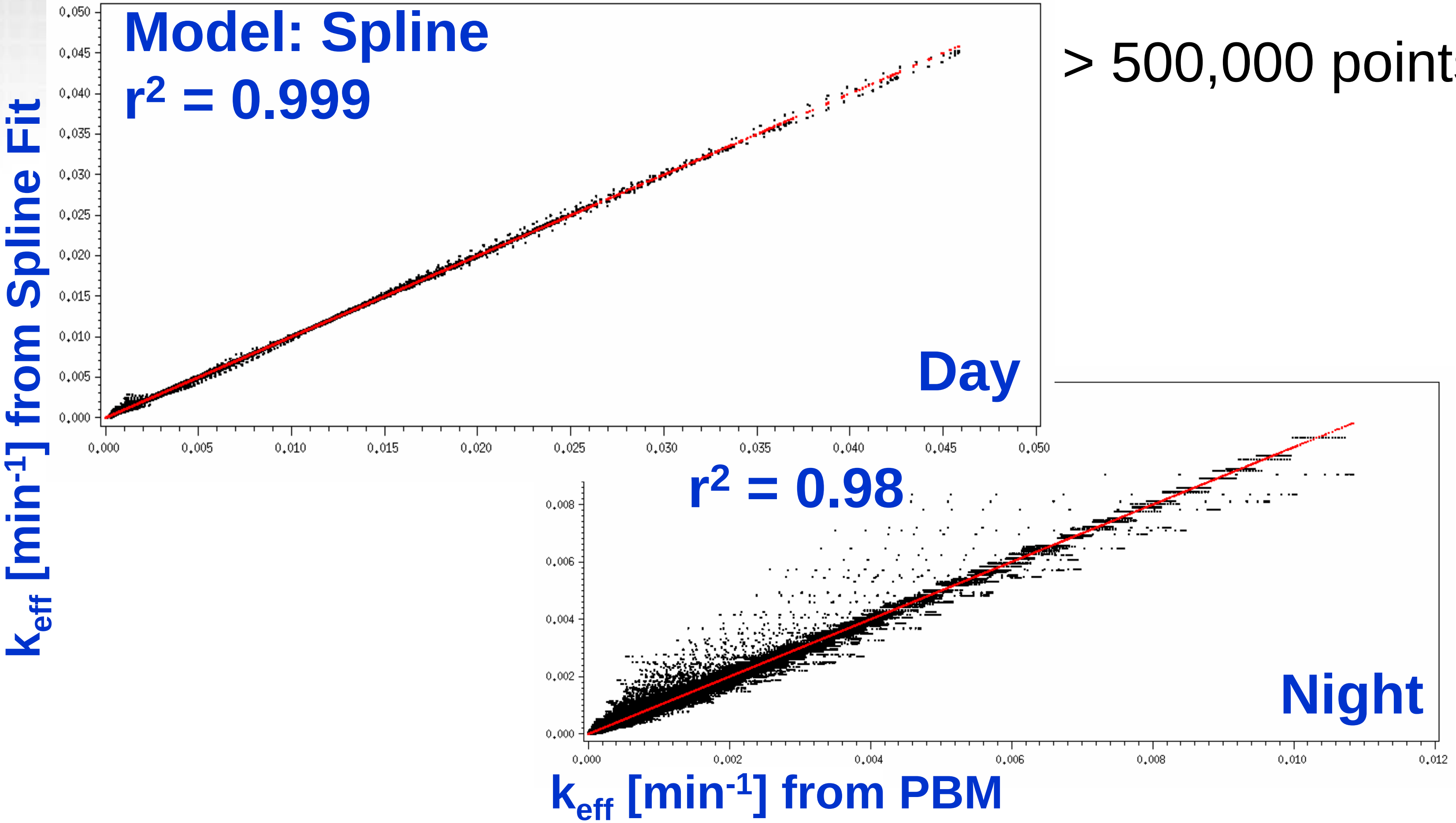
k_{eff} [min^{-1}] from Spline Fit

k_{eff} [min^{-1}] from PBM

Results: k_{eff} (spline) vs k_{eff} (PBM) for butene

Land Use = Urban

> 500,000 points



Summary: Improved Regression

- Phase I: 7 – 10 parameter polynomial
- Phase II: Spline Fit

Comparison & Summary of r^2 values

Land Use	Day (SE > °5)		Night (SE < °5)	
	Phase I	Phase II	Phase I	Phase II
Water	0.97	0.999	NA*	0.99
Urban	0.80	0.999	NA	0.98
Grass	0.98	0.999	NA	0.999
Forest	0.77	0.98	NA	0.99
Desert	0.83	0.99	NA	0.99
Default	0.68	0.99	NA	0.99

* Phase I k_{eff}(night) was set to a constant.

Results: Nine Alkenes

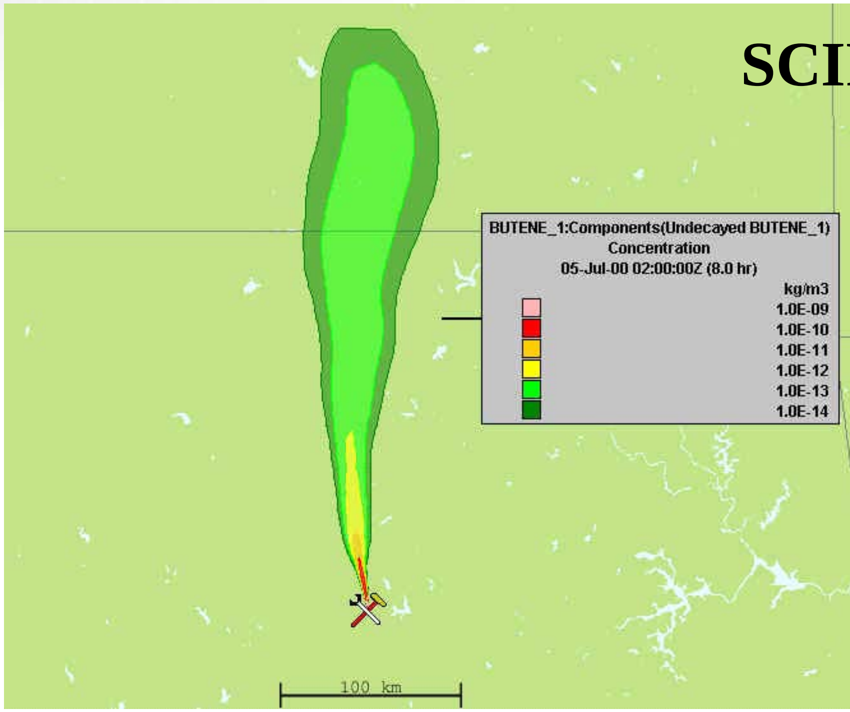
- Priority I
  - **1-Butene**
    - Products (**Propanal**, Nitroxybutanone).
  - Ethene
  - Propene
  - **Methylpropene**
  - 1,3-Butadiene
- Priority II
  - Styrene
- Priority III
  - cis-2-Butene
  - trans-2-Butene
  - Isoprene

Why Chemistry is Important in AT&D Modeling

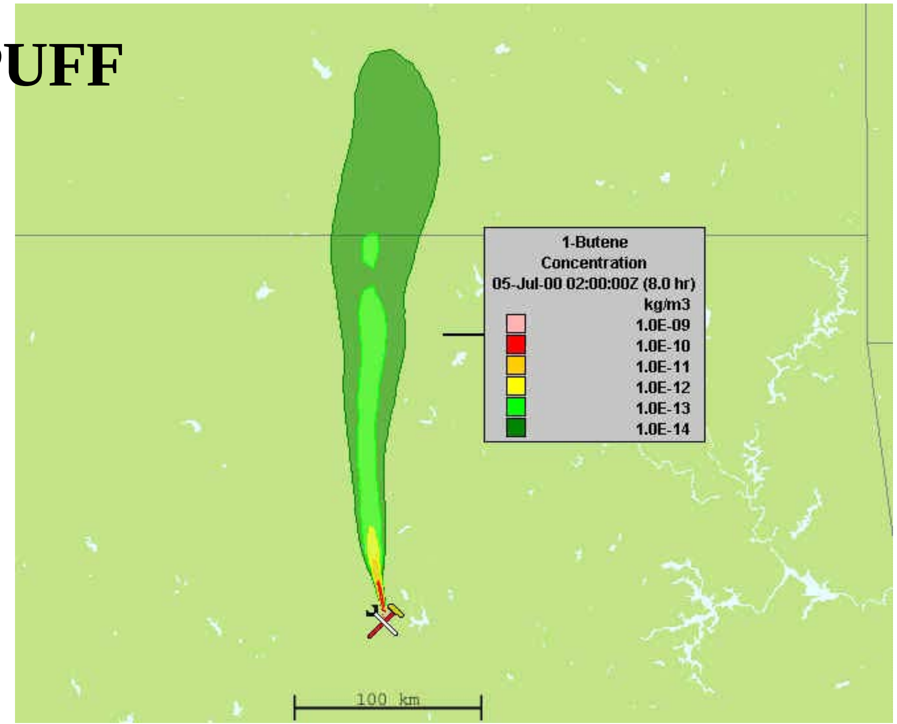
Results: T&D Compared to T&D + Chemistry (Butene)

SCIPUFF

T&D Only	T&D + Chemistry



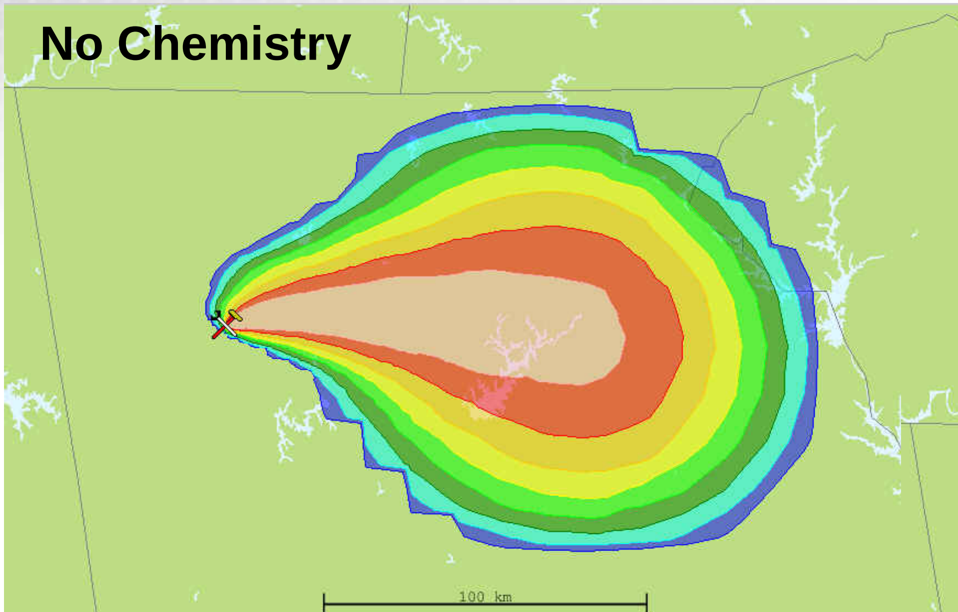
Tracer



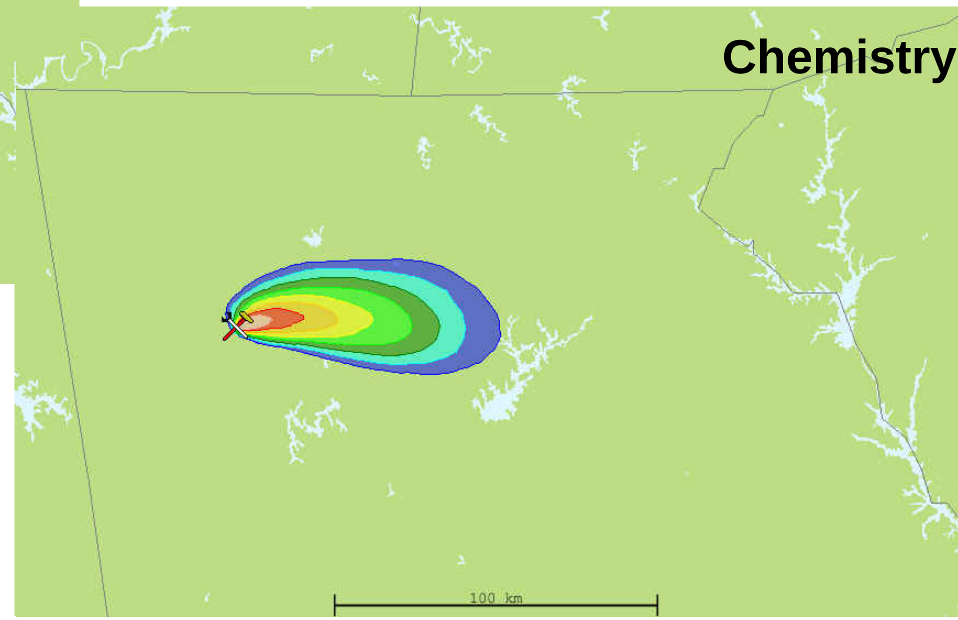
1-Butene

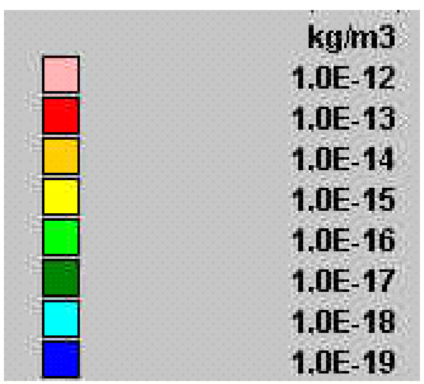
Results: Methylpropene

8 hr continuous release starting at 8 am local time

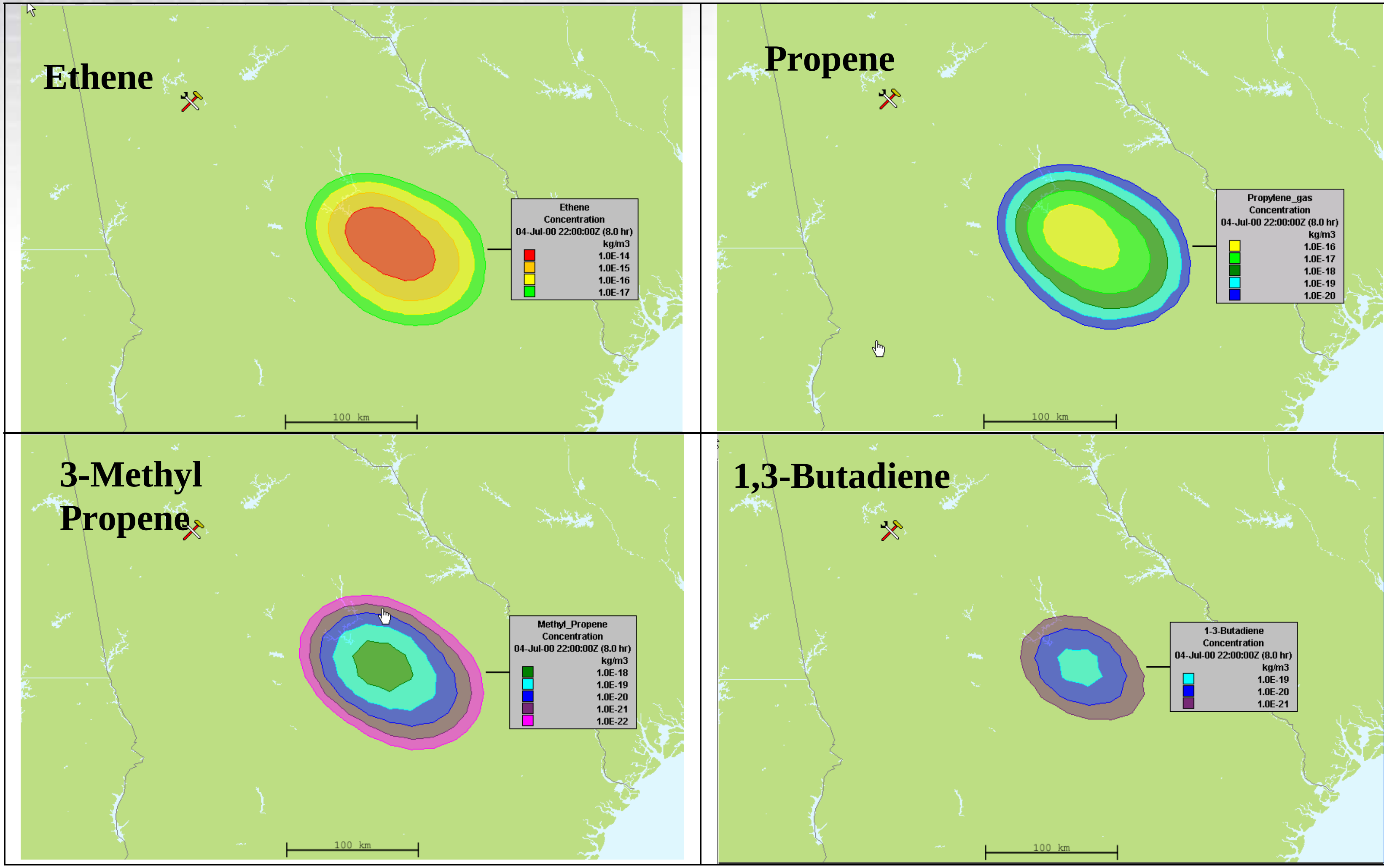


3 PM   Local Time



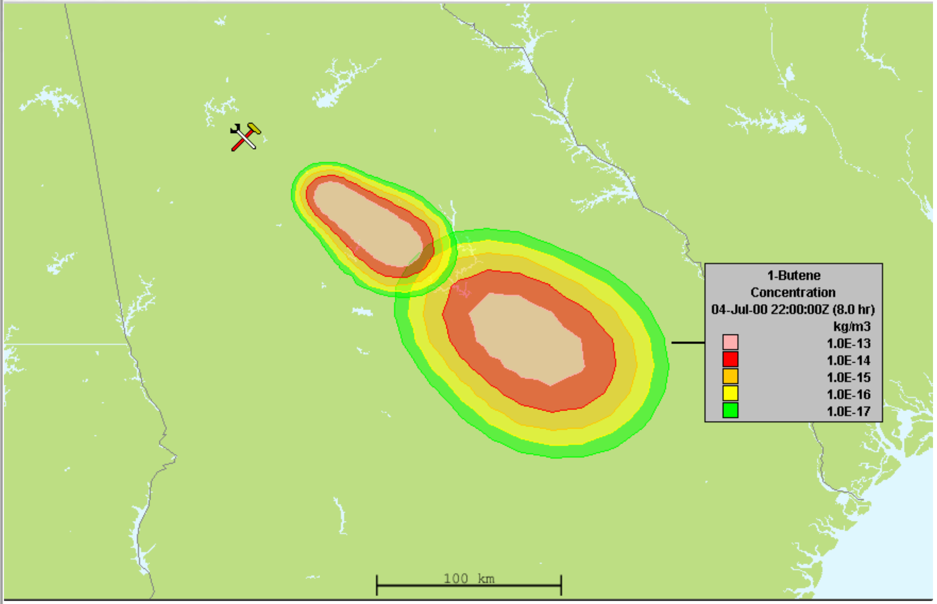


Results: Calculated Plume is TIC Dependent

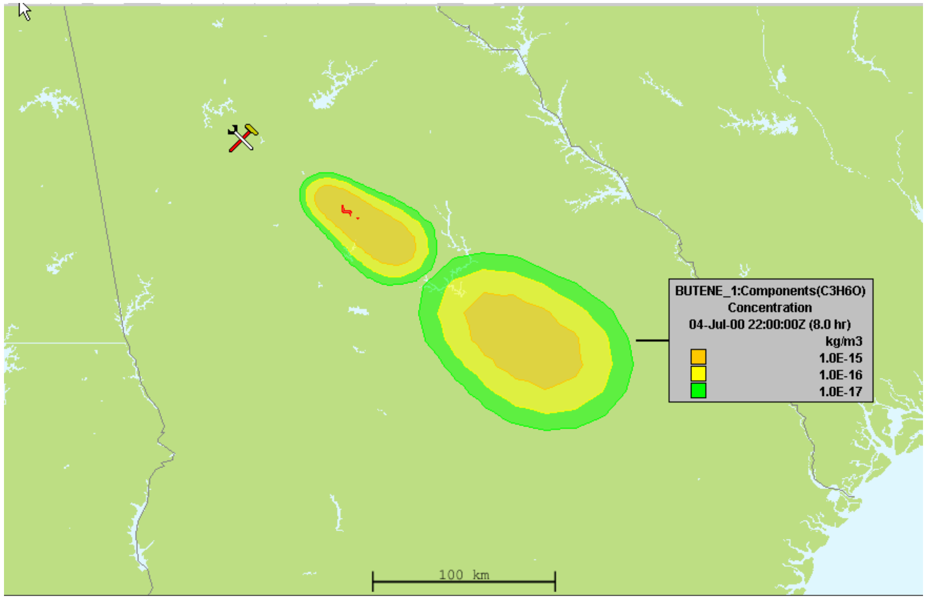


Results: TIC Decay and Product Formation

1-Butene



Propanal



At 4 hrs and 8 hrs after release

2 hr continuous release starting at noon local time

Summary & Future Work

- Phase I model
  - ***No slow down*** in SCIPUFF
  - Ability to model product formation
- Phase II Model Improved daytime k_{eff}
  - $R^2 \rightarrow$ 0.98 to 0.999 for the various land uses
- Phase II Model Significantly improved nighttime k_{eff}
  - No longer an assumed constant value
- Future Work
  - Complete testing of spline model in SCIPUFF / HPAC
    - Verify no slow down in SCIPUFF
    - Develop spline models for balance of TICs
  - Continue Sensitivity Analysis studies
  - Develop k_{eff}'s for other priority TICs
  - Chamber Expt's being Designed (Chemistry Validation)

End of slides