An Atmospheric Chemistry Module for Modeling Toxic Industrial Chemicals (TICs) in SCIPUFF

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BAA TYN 03-001
Atmospheric Chemistry Module for Toxic Industrial Chemicals

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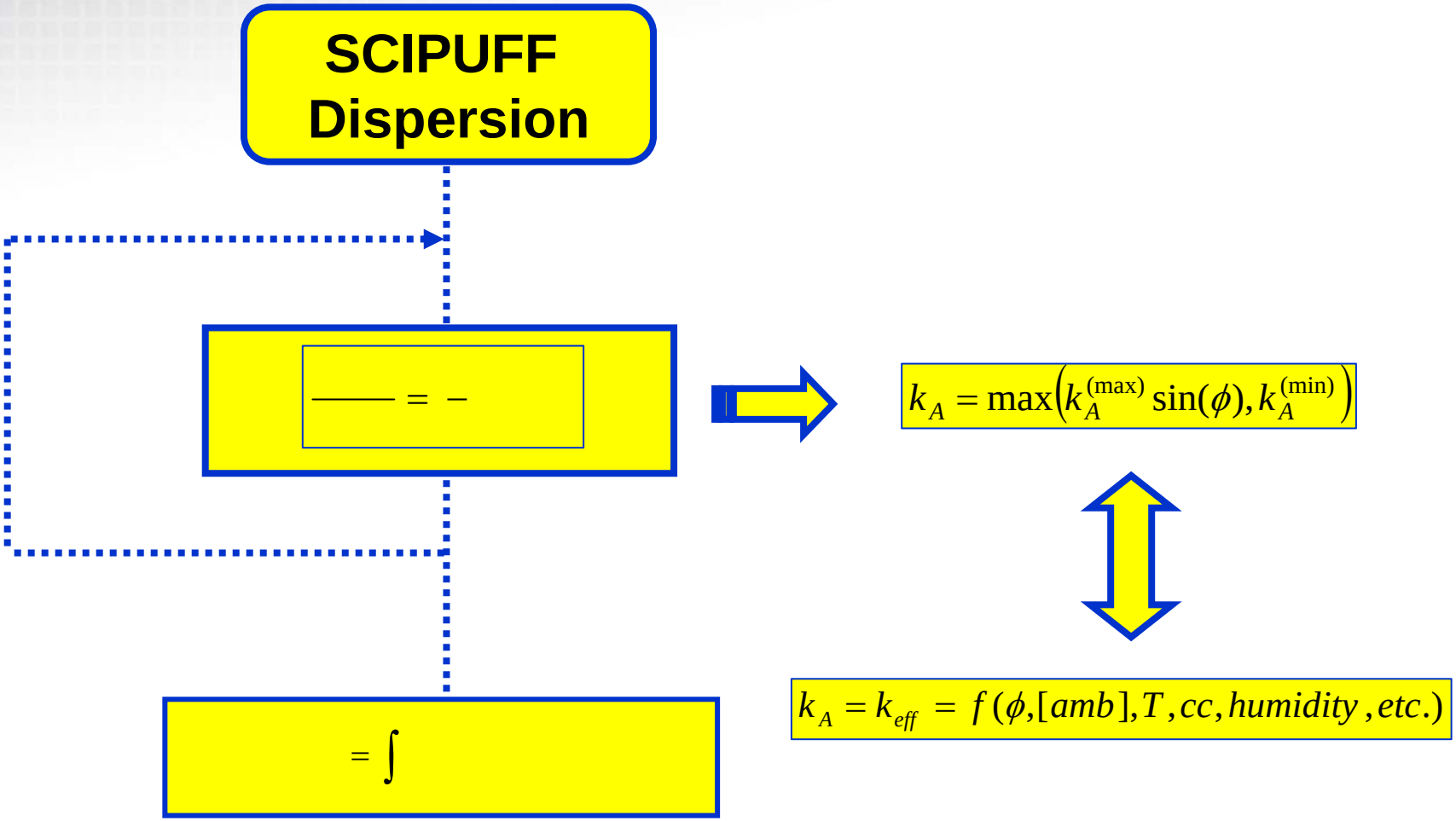
Outline

- **Project Goals**
- **Methodology**
  - Integration in SCIPUFF
  - Chemistry of 1-butene
  - Derivation of k_{eff}, X_{eff}
  - Parameter Space
- **Results**
  - Model output
    - Decay of TICs (1-Butene, Methylpropene)
    - Product Formation
- **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**

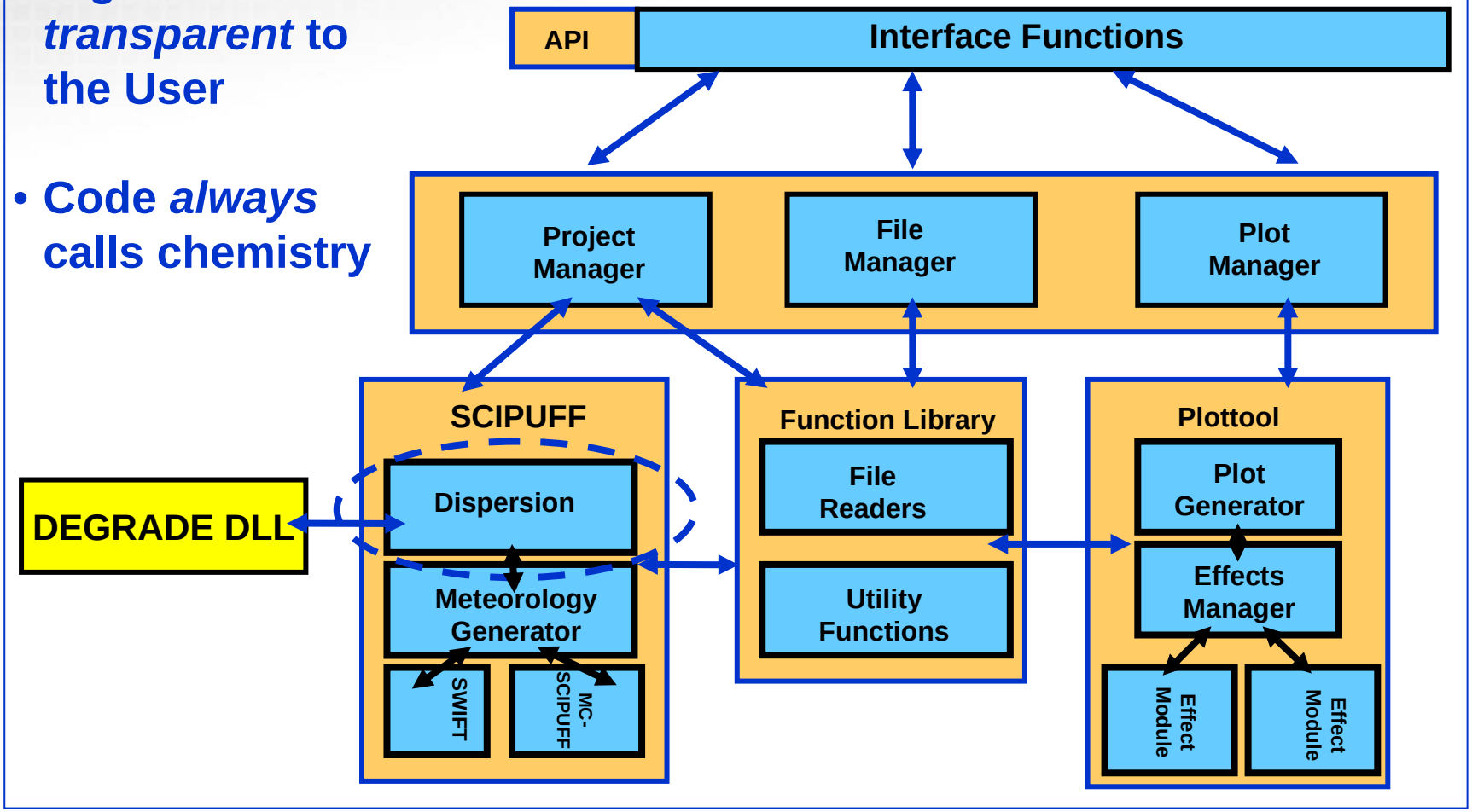
Methodology: Minor Modification to SCIPUFF



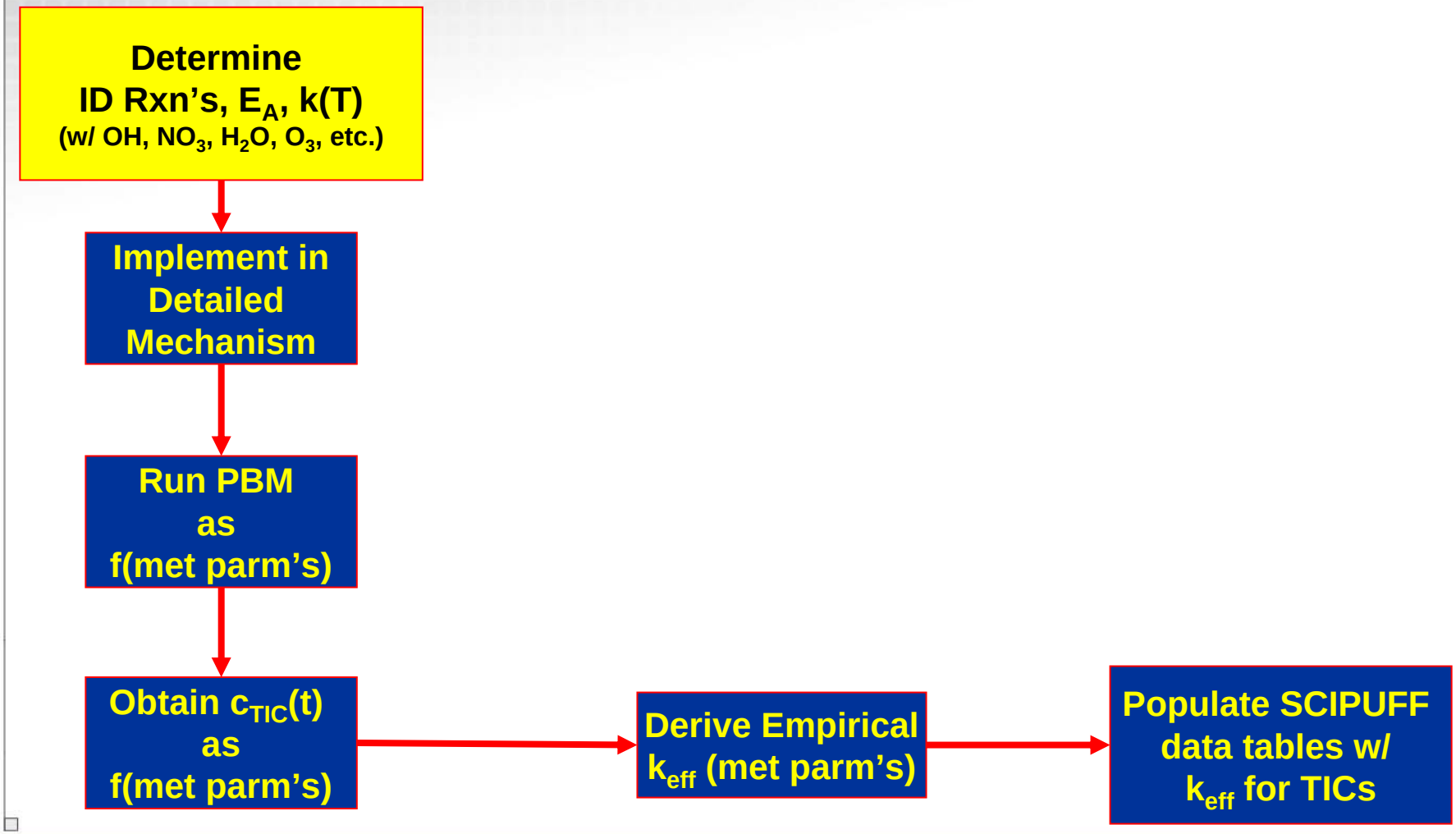
Method: Create Degrade Dynamic Link Library

Details in the Software Development Plan

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



Methodology: Chemistry of 1-butene



Methodology: Chemistry of 1-butene

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

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

$CH_2=CHCH_2CH_3 + O_3 \longrightarrow 0.35\ C_2H_5CHO$ + 0.41 OH + 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)

↓

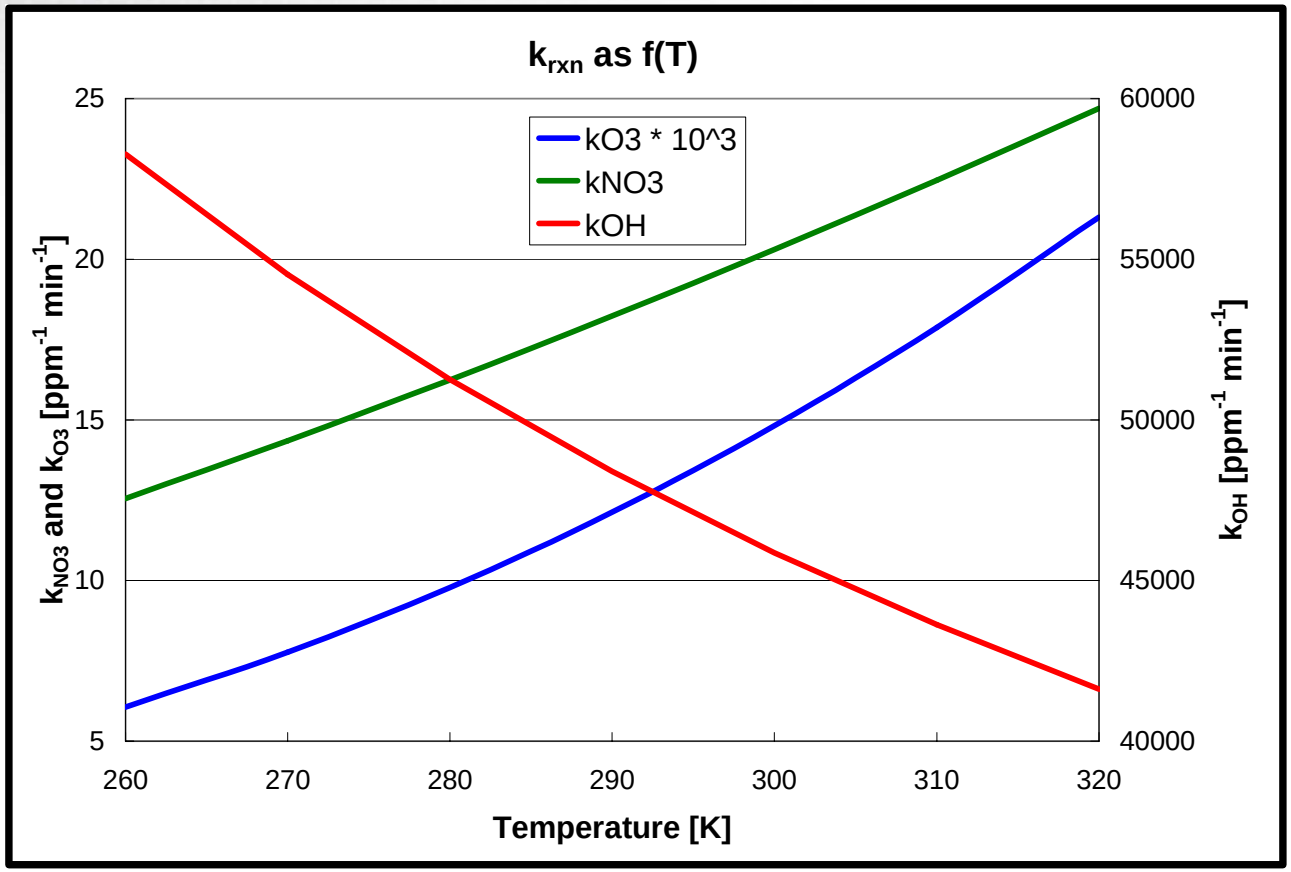
Obtain $c_{TIC}(t)$ as f(met parm's)

→

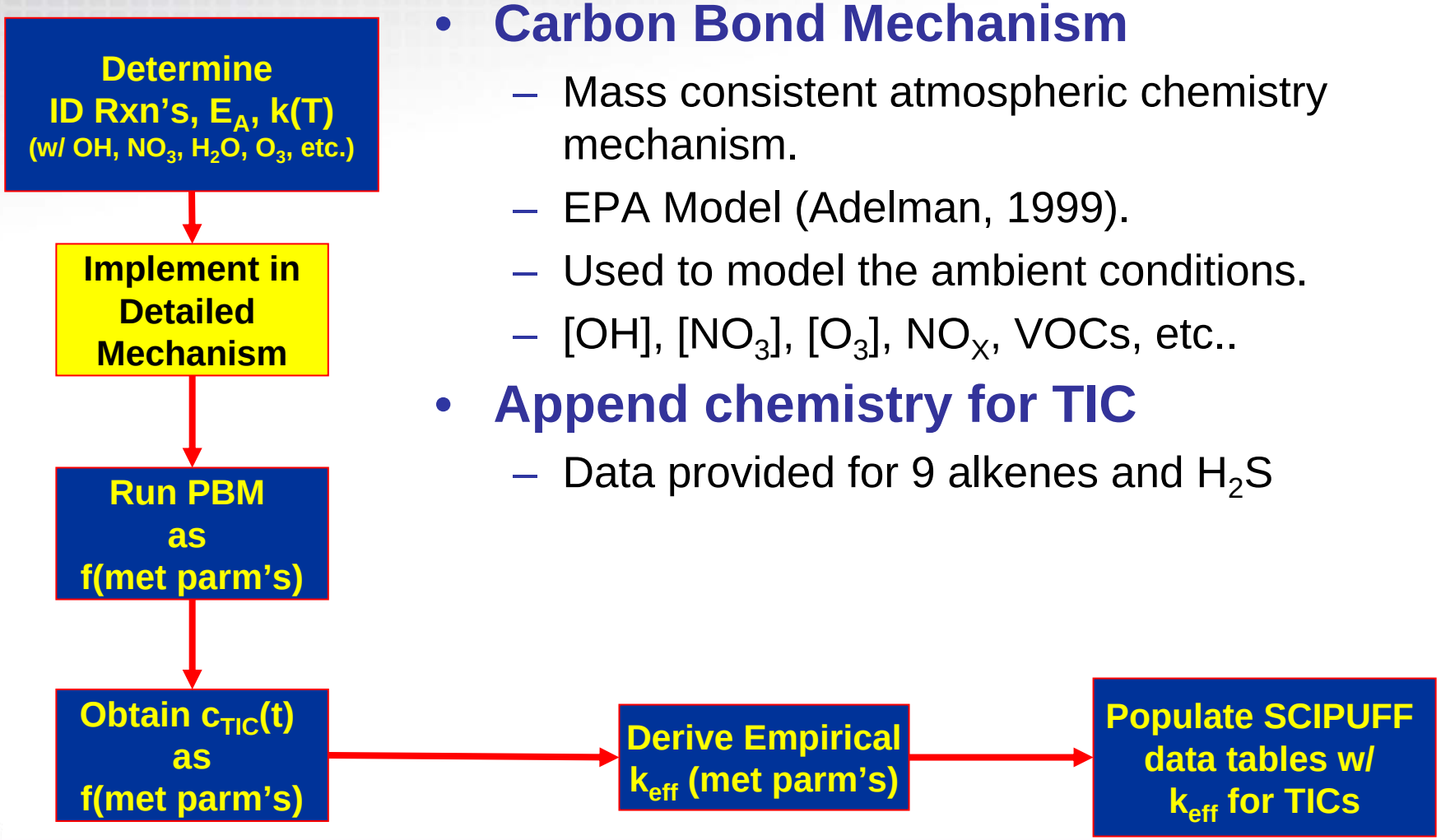
Derive Empirical k_{eff} (met parm's)

→

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

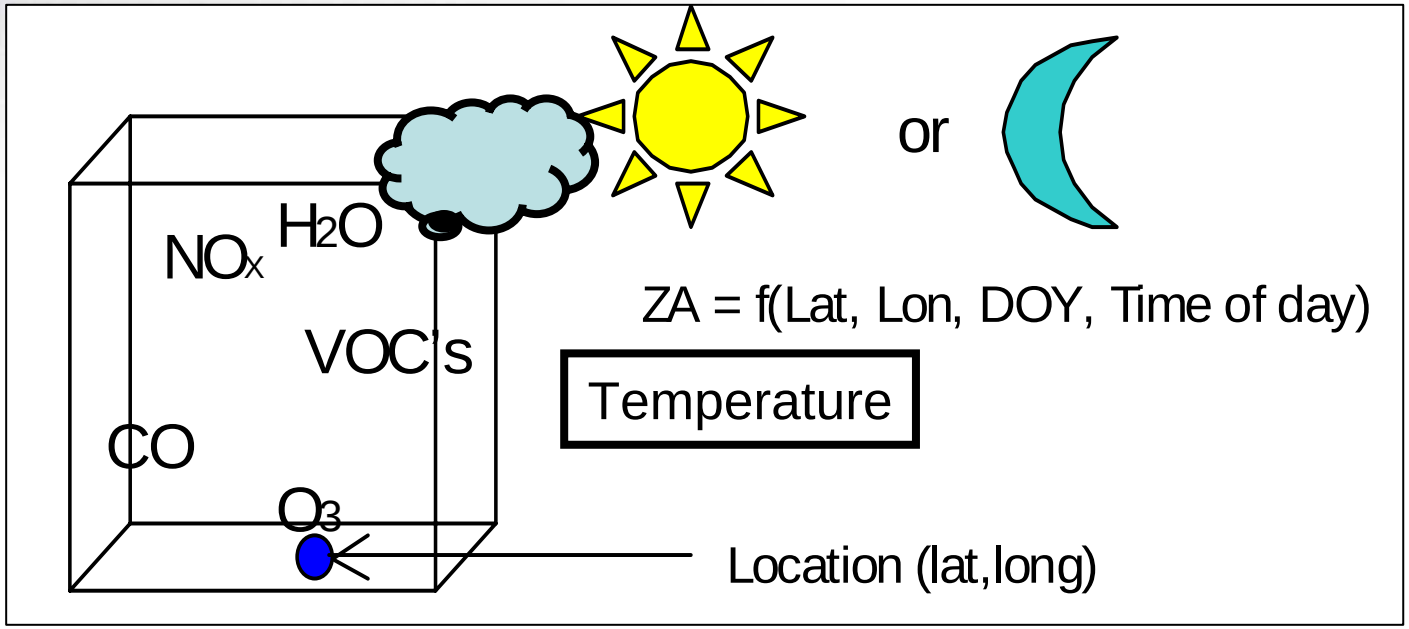


Methodology: Detailed Mechanism



- **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



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

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

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**

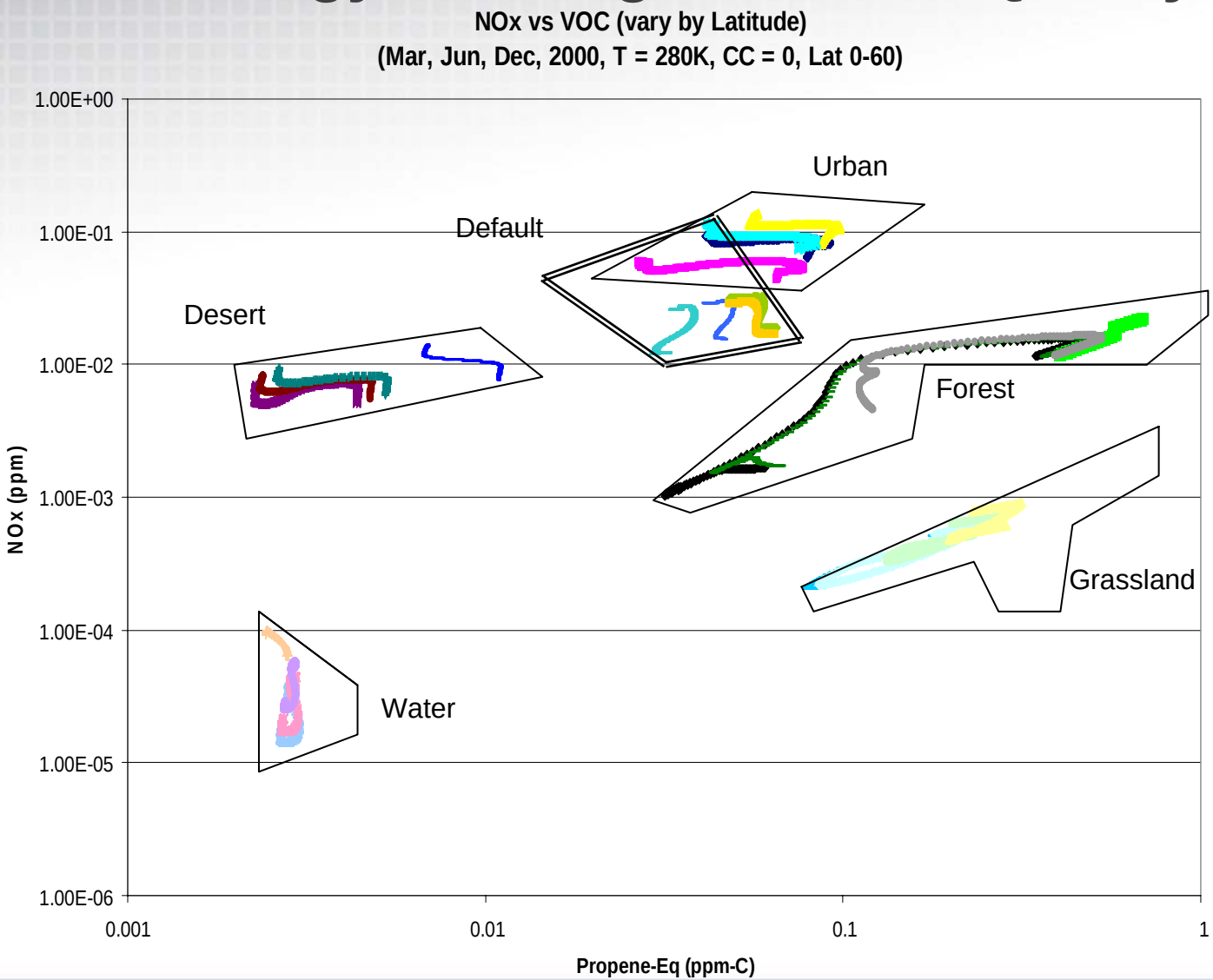
Methodology: Surrogate for Air Quality

- **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

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

Implement in Detailed Mechanism

Run PBM as f(met parm's)

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

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

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

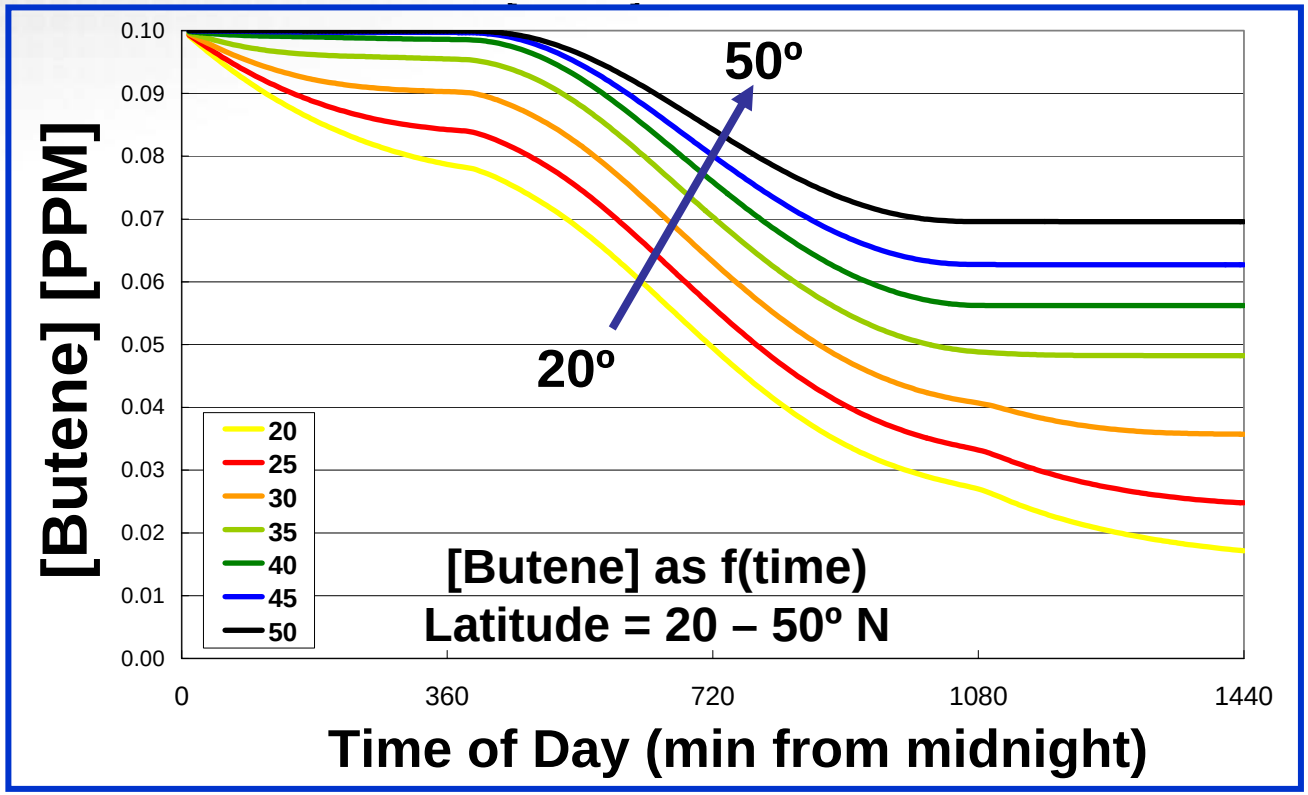
Derive Empirical k_{eff} (met parm's)

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)

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

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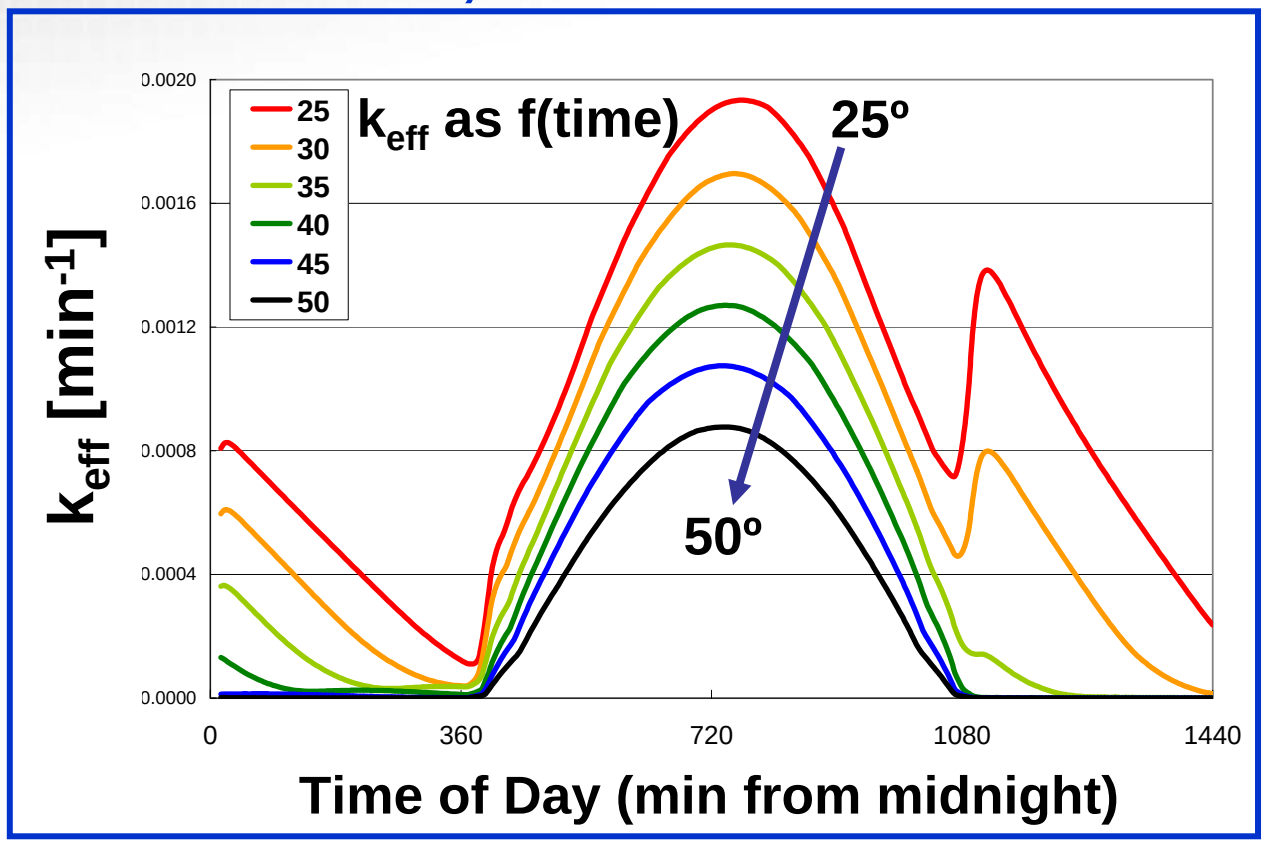


Implement in Detailed Mechanism

Run PBM as f(met parm's)

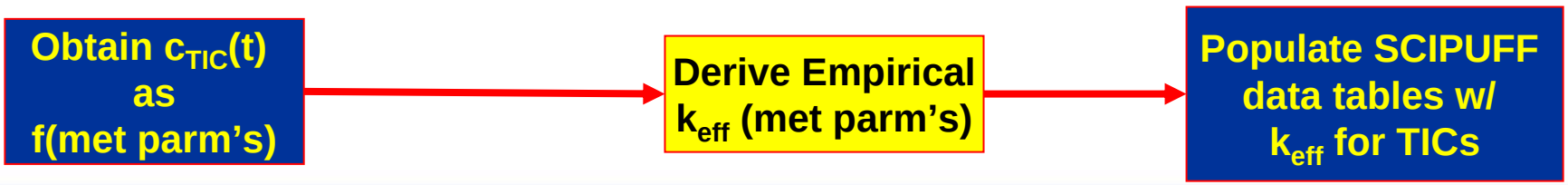
Obtain $c_{TIC}(t)$ as f(met parm's)

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

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

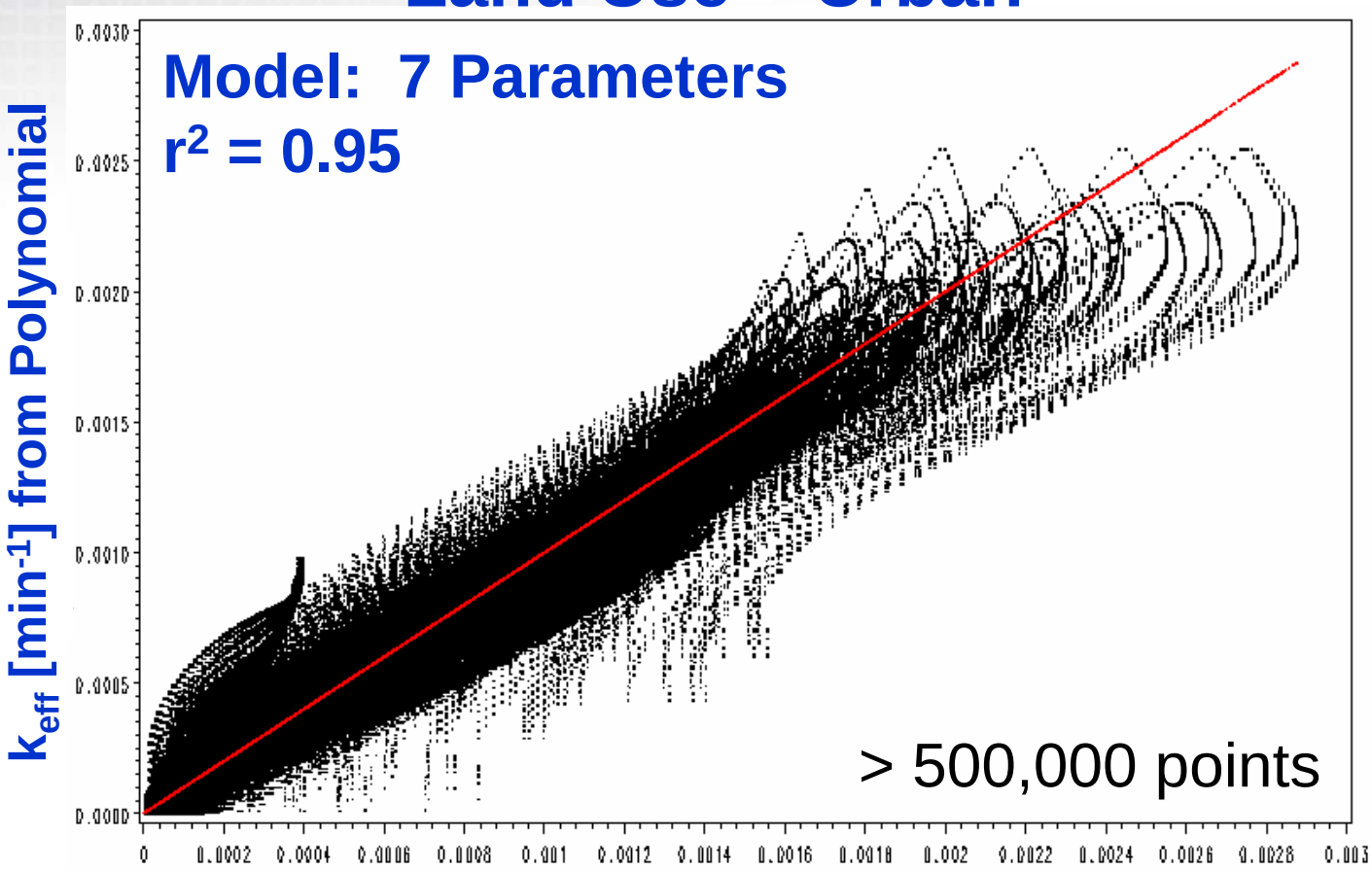
Methodology: Derive Empirical k_{eff}

- 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}.



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

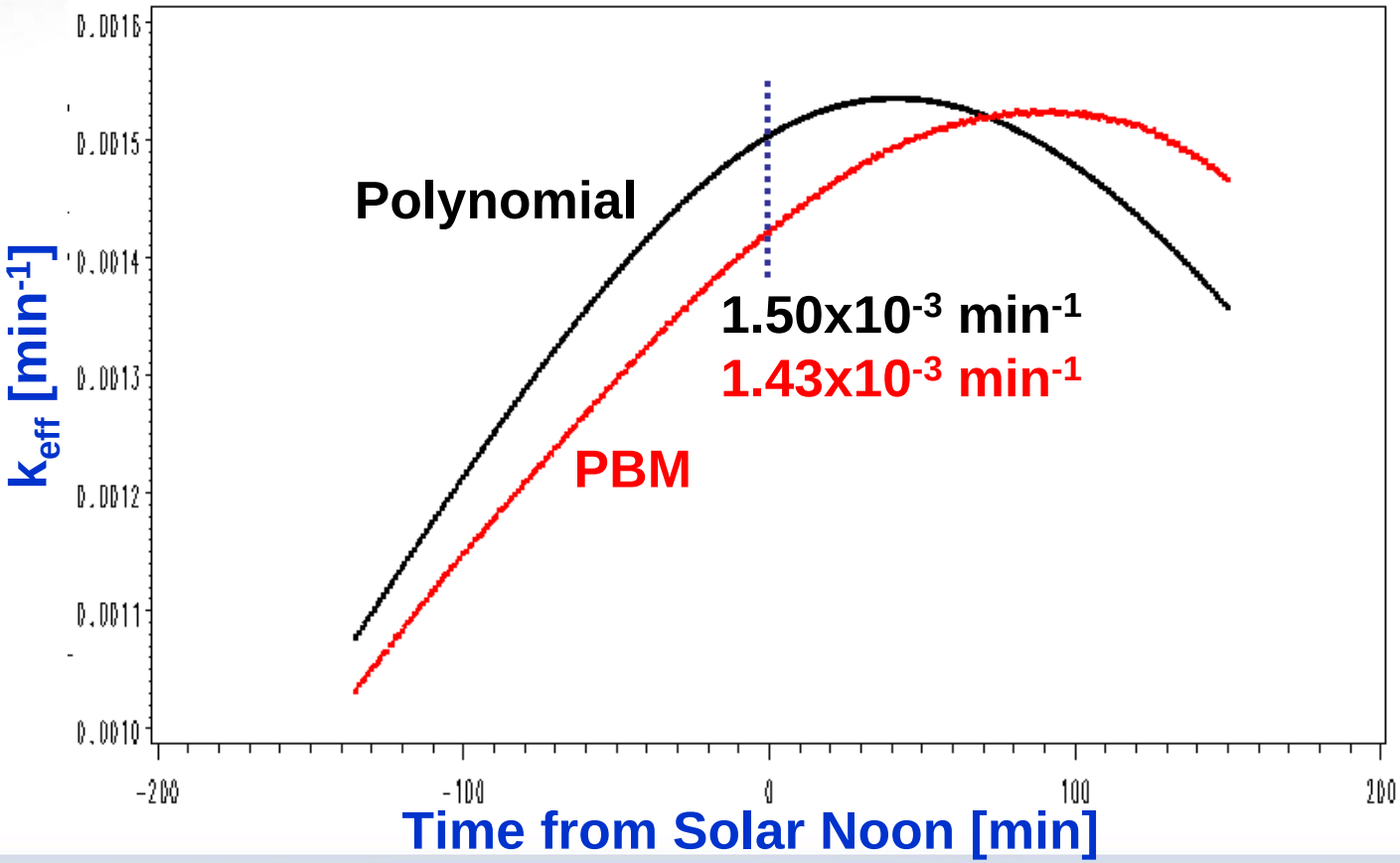
Land Use = Urban



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

Land Use = Grass

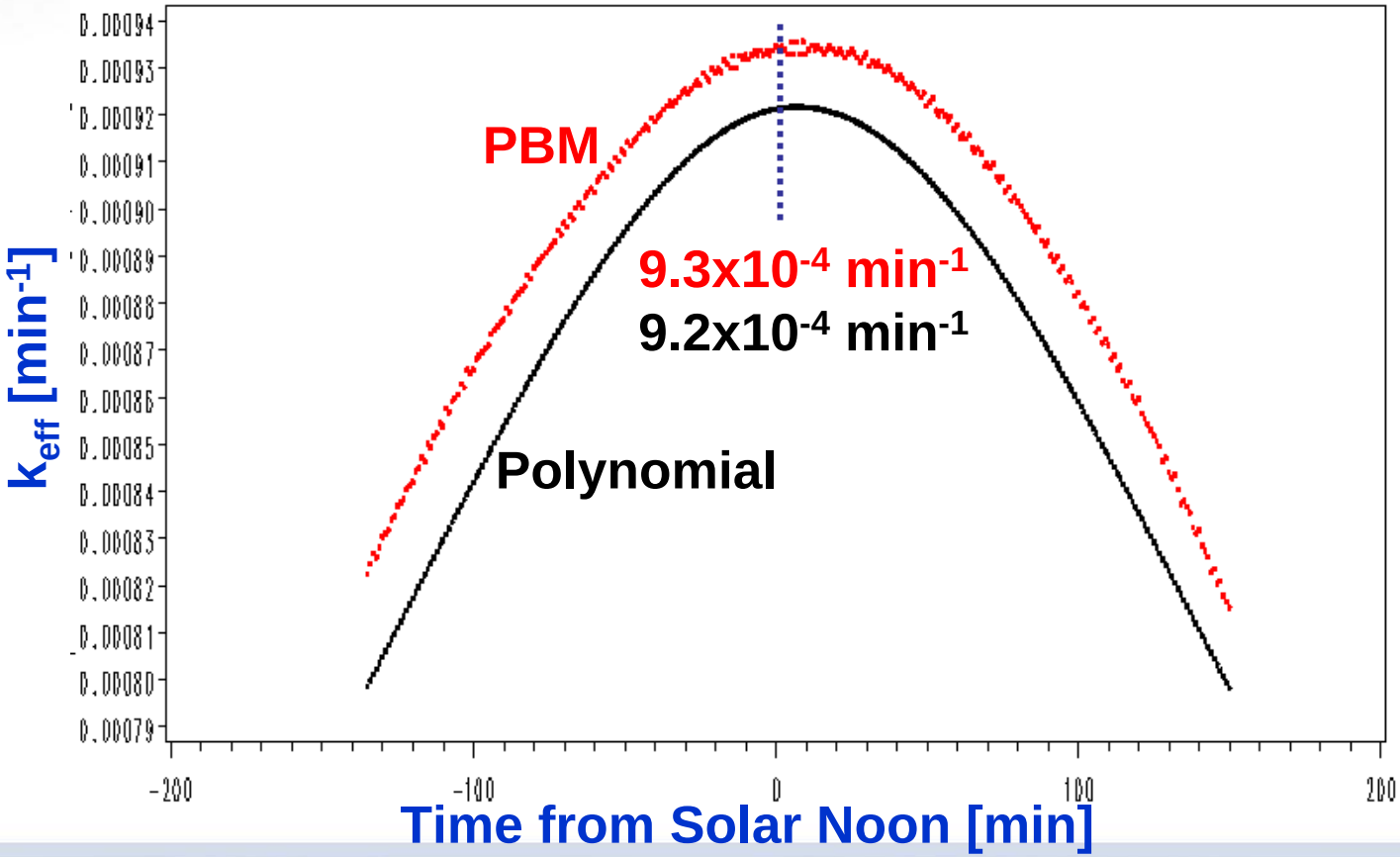
Lat 0°, Temp 300 K, Cloud Cover 0/8, [H_2O] = 20000 ppm,



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

Land Use = Water

Lat 0°, Temp 300 K, Cloud Cover 0/8, [H_2O] = 20000 ppm,



Methodology: Obtain X_{eff}

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

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

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

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

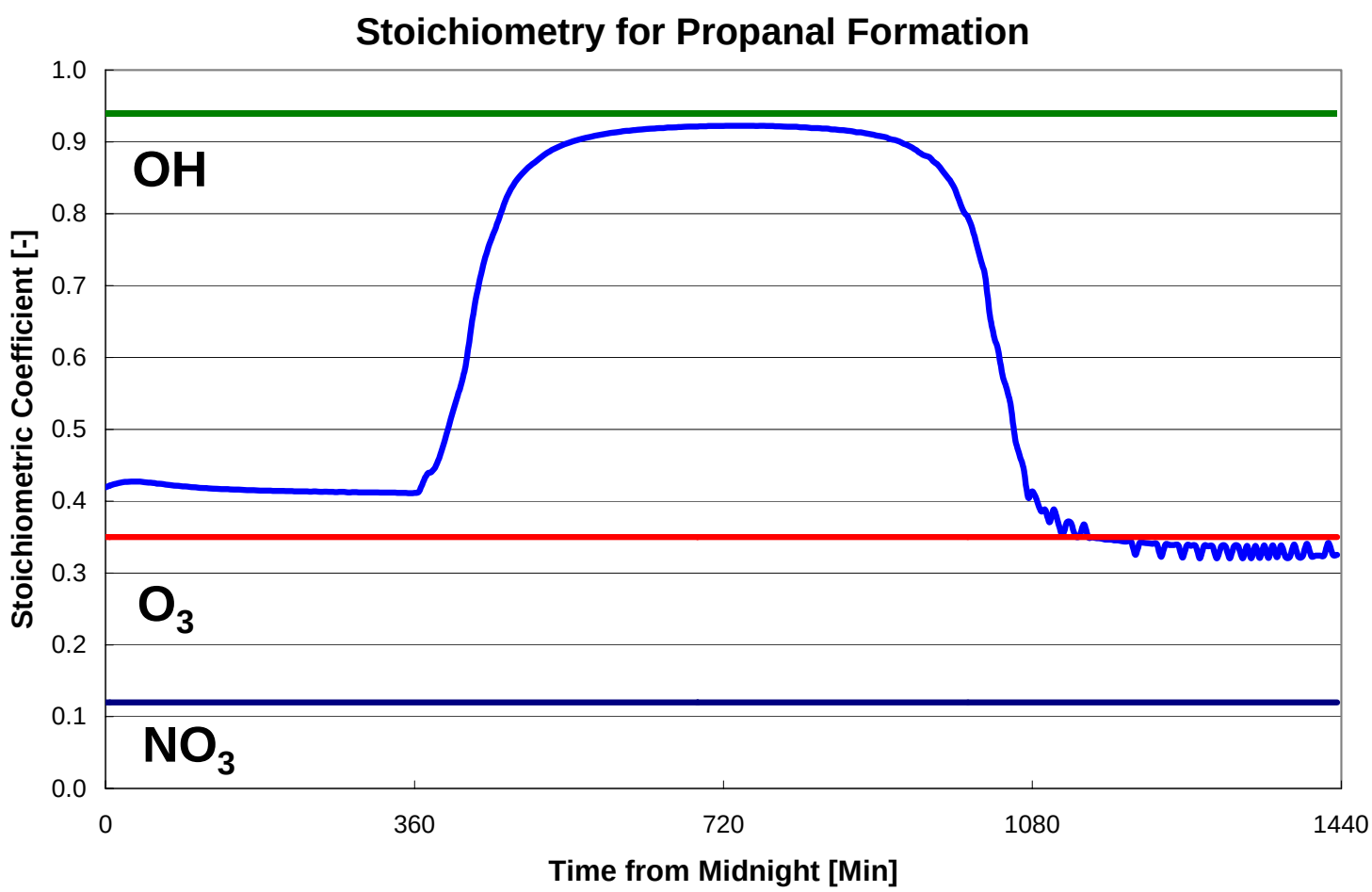
$$\text{Rate} = -k_{eff}\ [\text{1-butene}]$$

$$\text{Rate} = +\left(0.94\ k_{OH}[OH] + 0.12\ k_{NO_3}[NO_3] + 0.35\ k_{O_3}[O_3]\right)[\text{butene}]$$

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

Methodology: Obtain X_{eff}

T = 295 K, Land Use = Water



Results: Nine Alkenes

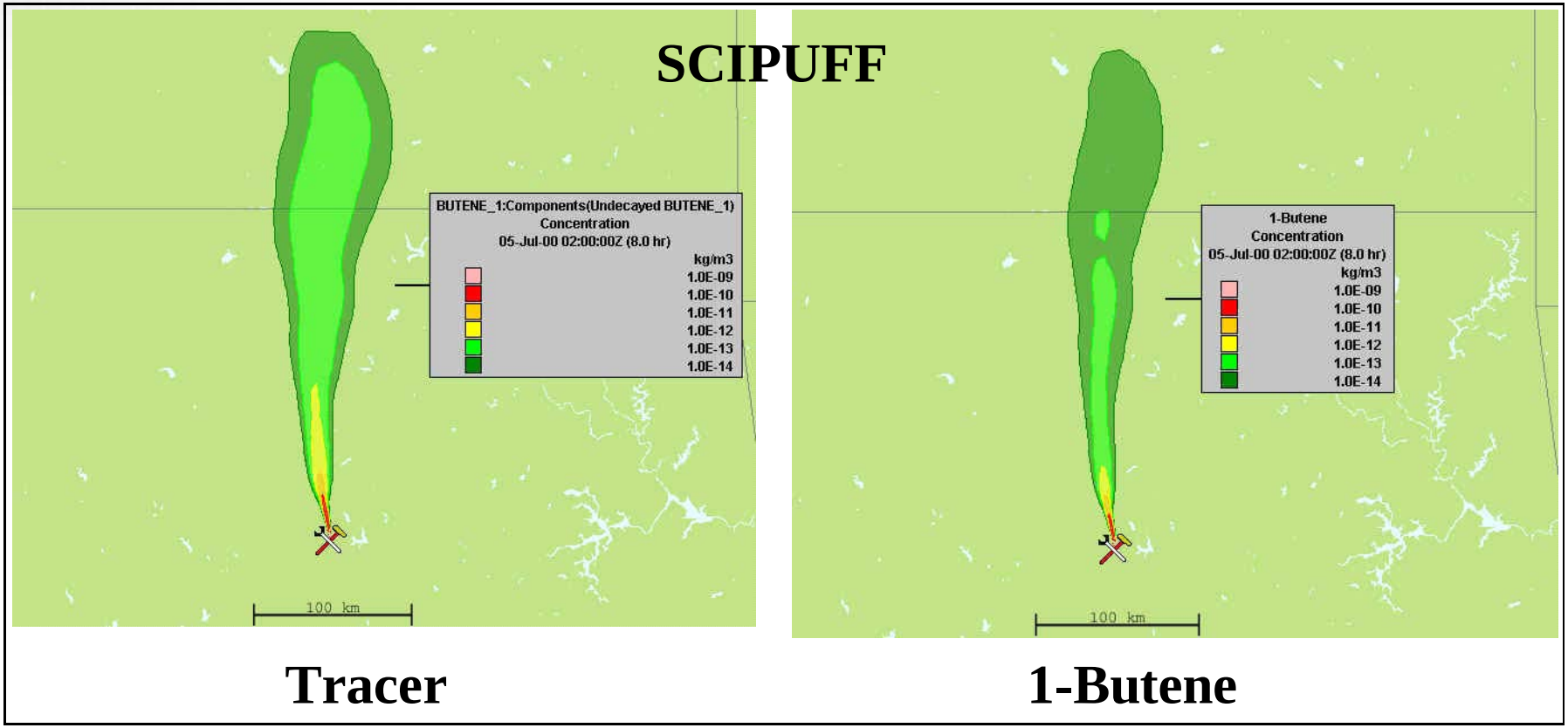
- **Priority I**
  - **1-Butene**
    - Products (**Propanal**, Nitroxybutanone).
  - Ethene
  - Propene
  - **Methylpropene**
  - 1,3-Butadiene
- **Priority II**
  - Styrene
- **Priority III**
  - cis-2-Butene
  - trans-2-Butene
  - Isoprene

Why Chemistry is Important in AT&D Modeling

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

T&D Only

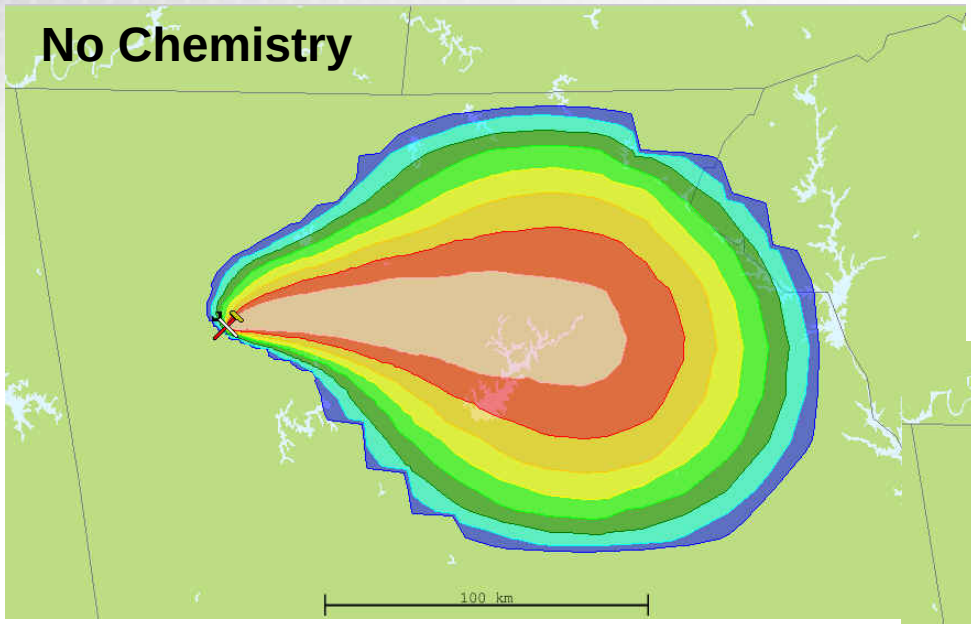
T&D + Chemistry

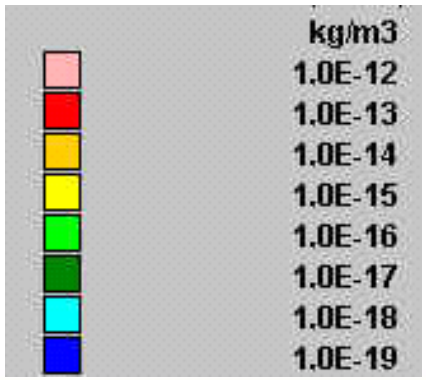


Tracer **1-Butene**

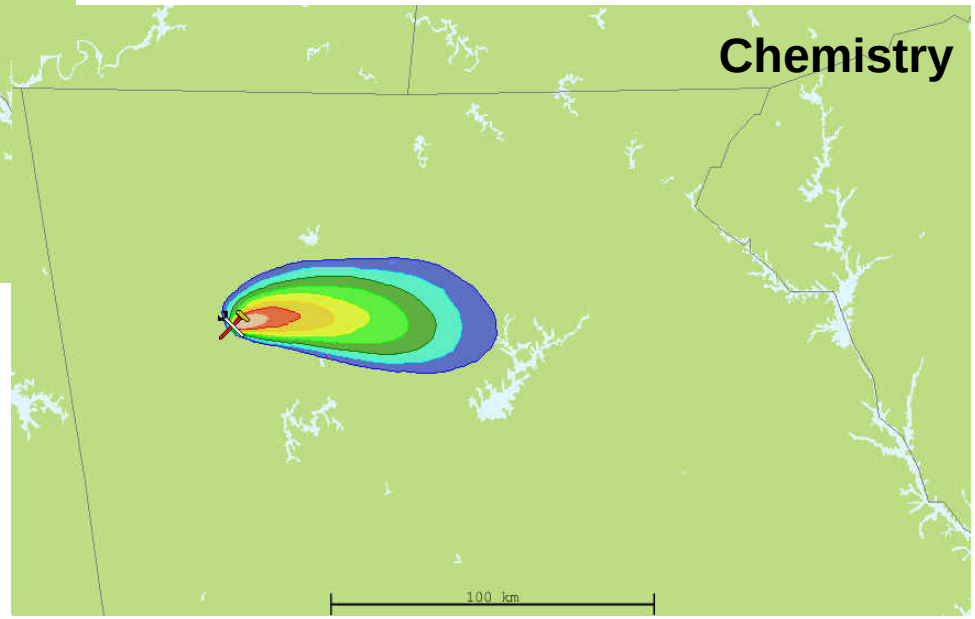
Results: Methylpropene

8 hr continuous release starting at 8 am local time

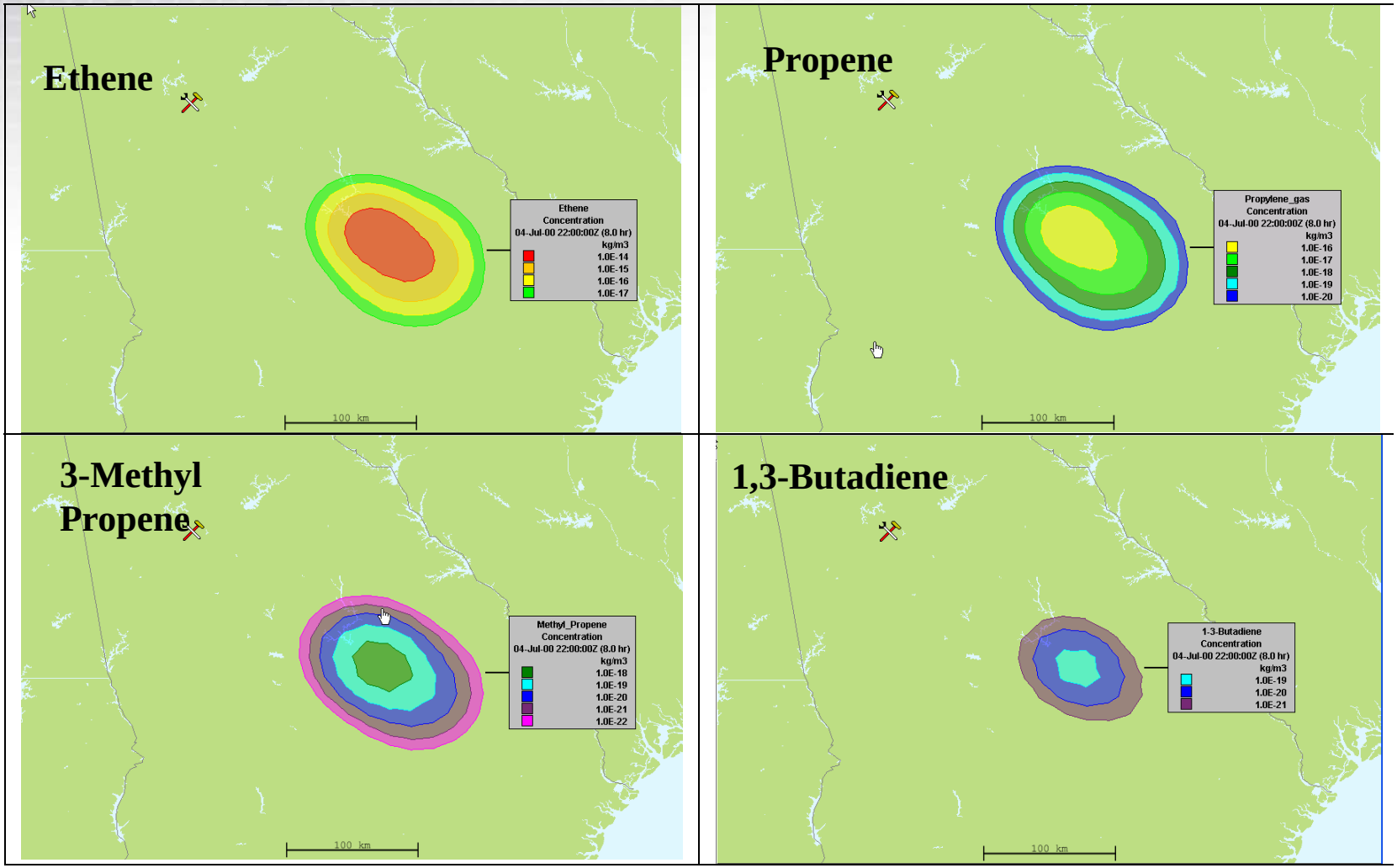




3 PM Local Time

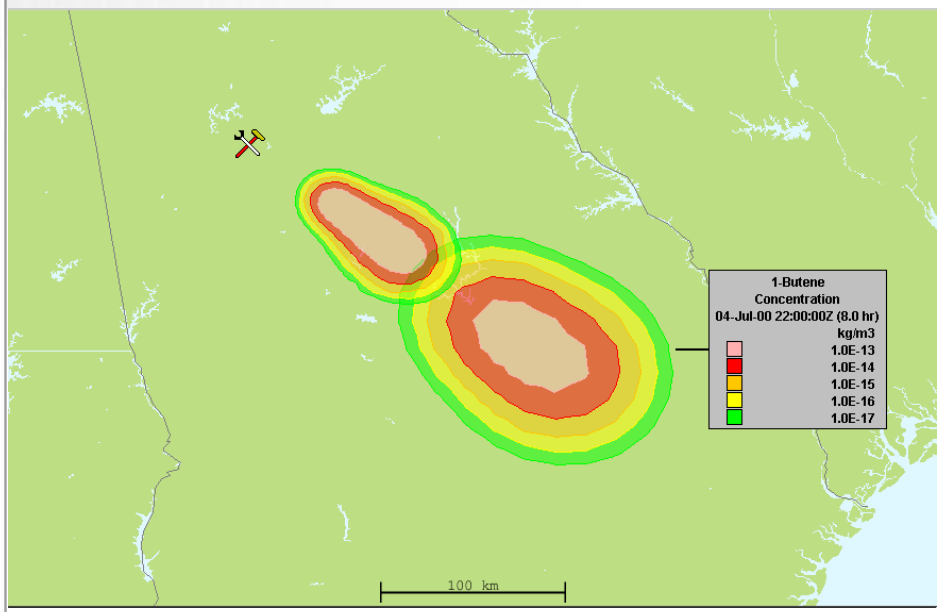


Results: Calculated Plume is TIC Dependent

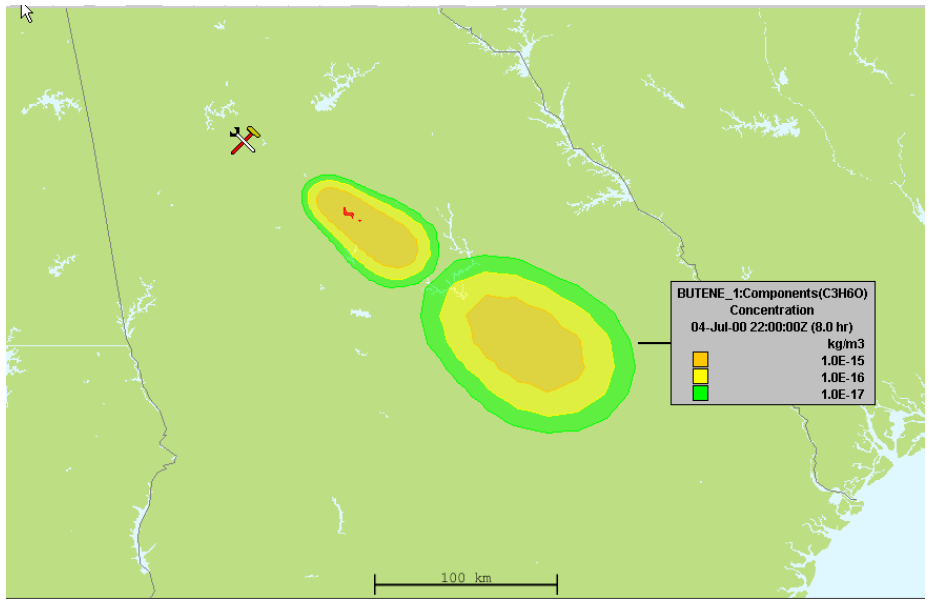


Results: TIC Decay and Product Formation

1-Butene



Propanal

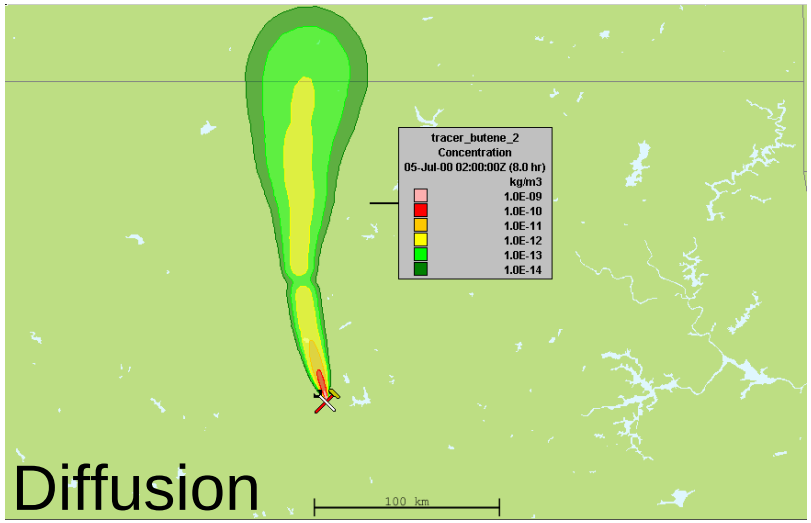


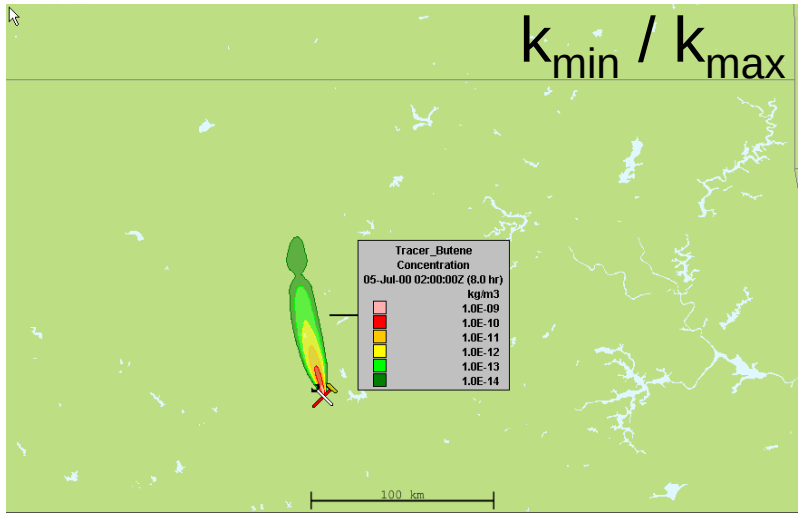
At 4 hrs and 8 hrs after release

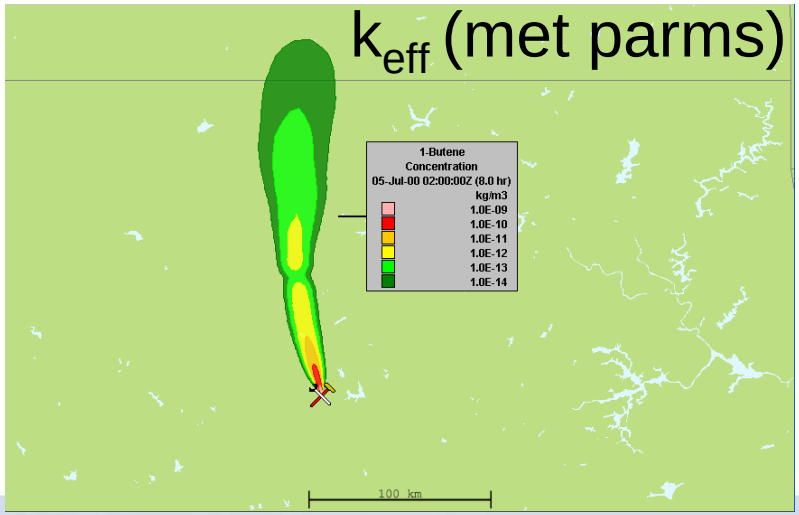
2 hr continuous release starting at noon local time

Results: Test and Evaluate (Output)

Comparison of Original SCIPUFF and “Degrade”





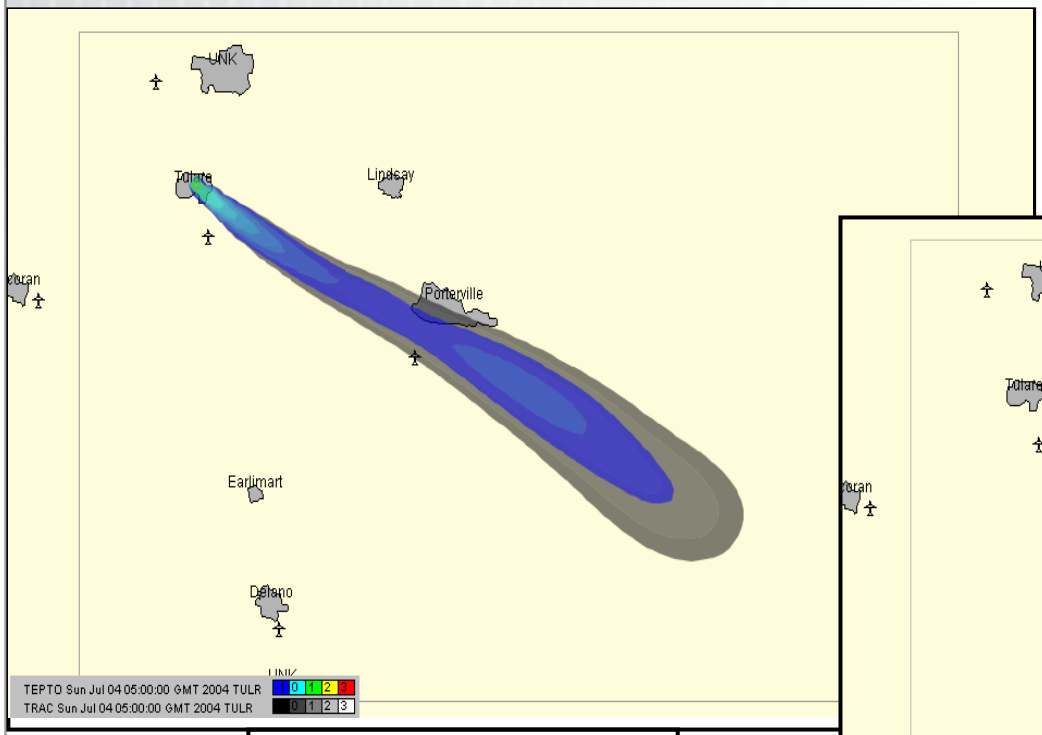


Summary & Future Work

- Developed Chemistry Model for 10 TICs
  - 9 Alkenes + H_2S
- No slow down in SCIPUFF
- Ability to model product formation
- Future Work
  - Site specific k_{eff}'s
  - k_{eff}'s for other TICs
    - Complementary lab / theory development of fundamental k_{OH}, k_{O3}, k_{H2O}, etc.
  - Chamber Studies (Chemistry Validation)
  - Field Studies (Model Validation)

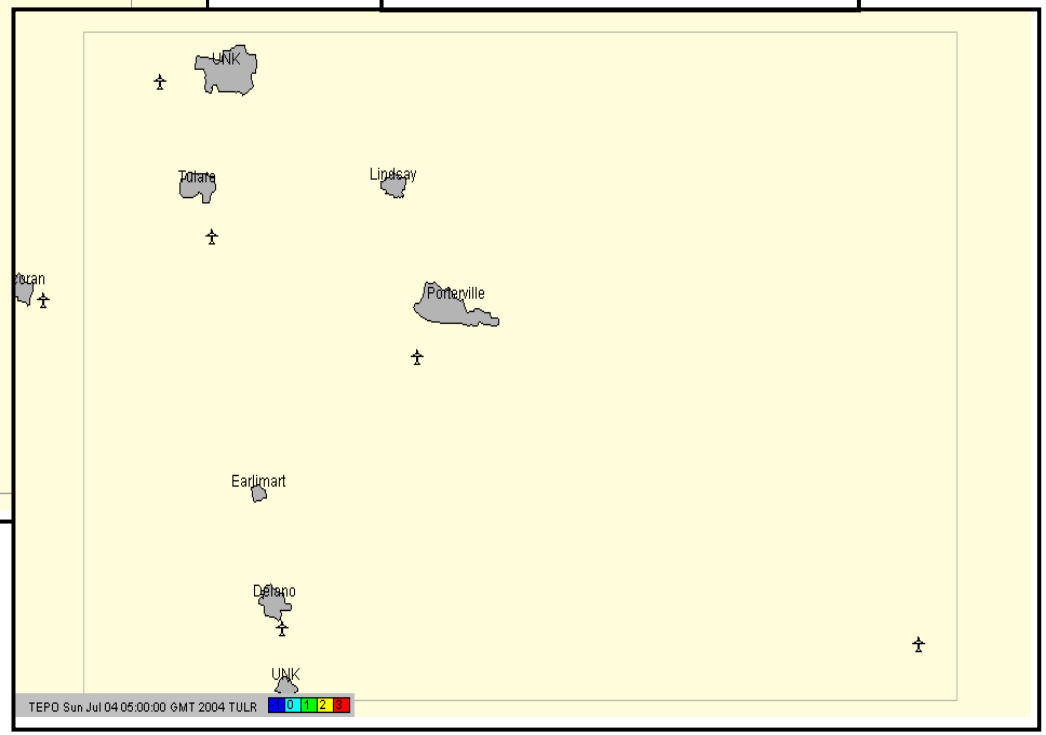
End of slides

Example: Crop Dusting Scenario – Bottom line



Chemistry vs T&D

Degrade Generation



03 July 22:00 (Local) 05:00 Z