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

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Science and Technology for Chem-Bio Information Systems (S&T CBIS)

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Atmospheric Chemistry Module for Toxic Industrial Chemicals

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DTRA / TDOC Alexandria, VA
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 H₂S)
    • 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

\[ k_A = \max\left(k_A^{\text{max}} \sin(\phi), k_A^{\text{min}}\right) \]

\[ k_A = k_{\text{eff}} = f(\phi, \text{[amb]}, T, cc, \text{humidity, etc.}) \]
Method: Create Degrade Dynamic Link Library

Details in the Software Development Plan

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

DEGRADE DLL

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Methodology: Chemistry of 1-butene

Determine ID Rxn’s, $E_A$, $k(T)$ (w/ OH, NO$_3$, H$_2$O, O$_3$, etc.)

Implement in Detailed Mechanism

Run PBM as $f$(met parm’s)

Obtain $c_{\text{TIC}}(t)$ as $f$(met parm’s)

Derive Empirical $k_{\text{eff}}$ (met parm’s)

Populate SCIPUFF data tables w/ $k_{\text{eff}}$ for TICs
Methodology: Chemistry of 1-butene

\[
\text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{OH} \rightarrow 0.94 \text{C}_2\text{H}_5\text{CHO} + \text{Other products}
\]

\[
\text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{NO}_3 \rightarrow 0.12 \text{C}_2\text{H}_5\text{CHO} + 0.6 \text{C}_3\text{H}_5\text{O-CH-O-NO}_2 + \text{Other products}
\]

\[
\text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{O}_3 \rightarrow 0.35 \text{C}_2\text{H}_5\text{CHO} + 0.41 \text{OH} + \text{Other products}
\]

\[
\text{Rate} = -(k_{\text{OH}}[\text{OH}] + k_{\text{NO}_3}[\text{NO}_3] + k_{\text{O}_3}[\text{O}_3]) [\text{1-butene}]
\]

\[
\text{Rate} = -k_{\text{eff}} [\text{1-butene}]
\]
Methodology: Chemistry of 1-butene

- Determine ID Rxn’s, $E_A$, $k(T)$ (w/ OH, NO$_3$, H$_2$O, 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.
  - Used to model the ambient conditions.
  - \([\text{OH}], [\text{NO}_3], [\text{O}_3], \text{NO}_x, \text{VOCs}, \text{etc.}\)

- **Append chemistry for TIC**
  - Data provided for 9 alkenes and \(\text{H}_2\text{S}\)
Methodology: Run Detailed Chemistry

Implement in Detailed Mechanism

Run PBM as \( f(\text{met parm's}) \)

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

Derive Empirical \( k_{\text{eff}} \) (met parm’s)

Populate SCIPUFF data tables w/ \( k_{\text{eff}} \) for TICs

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

\[ ZA = f(\text{Lat}, \text{Lon}, \text{DOY}, \text{Time of day}) \]

Temperature

Location (lat,long)
## Methodology: Parameter Space

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>SCIPUFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar Zenith Angle</td>
<td>0 – 90 Deg</td>
<td>X</td>
</tr>
<tr>
<td>Location (\text{lat}, \text{lon})</td>
<td>0 – 70 Deg</td>
<td>X</td>
</tr>
<tr>
<td>Time of Day</td>
<td>1440 min</td>
<td>X</td>
</tr>
<tr>
<td>Day of Year</td>
<td>3/21, 6/20, 12/20</td>
<td>X</td>
</tr>
<tr>
<td>Photochemistry (\text{Cloud Cover})</td>
<td>0 – 8 Eighths</td>
<td>X</td>
</tr>
<tr>
<td>Temperature</td>
<td>230 – 310 K</td>
<td>X</td>
</tr>
<tr>
<td>Water Concentration</td>
<td>100 – 40000 PPM</td>
<td></td>
</tr>
<tr>
<td>Moisture Mixing ratio</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Air Quality</td>
<td>[\text{NO}_x], \text{VOC}, \text{O}_3, \ldots</td>
<td></td>
</tr>
<tr>
<td>Land Use</td>
<td>Urban, ocean, forest, \ldots</td>
<td>X</td>
</tr>
</tbody>
</table>
# Methodology: Surrogate for Air Quality

- **Land Use**

<table>
<thead>
<tr>
<th>Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Developed</td>
</tr>
<tr>
<td>2</td>
<td>Dry Cropland &amp; pasture</td>
</tr>
<tr>
<td>3</td>
<td>Irrigated Cropland</td>
</tr>
<tr>
<td>4</td>
<td>Cropland/Grassland</td>
</tr>
<tr>
<td>5</td>
<td>Cropland/Woodland</td>
</tr>
<tr>
<td>6</td>
<td>Grassland</td>
</tr>
<tr>
<td>7</td>
<td>Woodland</td>
</tr>
<tr>
<td>8</td>
<td>Shrubland</td>
</tr>
<tr>
<td>9</td>
<td>Shrubland/Grassland</td>
</tr>
<tr>
<td>10</td>
<td>Savanna</td>
</tr>
<tr>
<td>11</td>
<td>Deciduous Broadleaf</td>
</tr>
<tr>
<td>12</td>
<td>Deciduous Needleleaf</td>
</tr>
<tr>
<td>13</td>
<td>Evergreen Broadleaf</td>
</tr>
<tr>
<td>14</td>
<td>Evergreen Needleleaf</td>
</tr>
<tr>
<td>15</td>
<td>Mixed Forest</td>
</tr>
<tr>
<td>16</td>
<td>Water</td>
</tr>
<tr>
<td>17</td>
<td>Herbaceous Wetland</td>
</tr>
<tr>
<td>18</td>
<td>Wooded Wetland</td>
</tr>
<tr>
<td>19</td>
<td>Barren</td>
</tr>
<tr>
<td>20</td>
<td>Herbaceous Tundra</td>
</tr>
<tr>
<td>21</td>
<td>Wooded Tundra</td>
</tr>
<tr>
<td>22</td>
<td>Mixed Tundra</td>
</tr>
<tr>
<td>23</td>
<td>Bare Tundra</td>
</tr>
<tr>
<td>24</td>
<td>Snow or Ice</td>
</tr>
<tr>
<td>25</td>
<td>Partly Developed</td>
</tr>
</tbody>
</table>

- **Superclasses**

<table>
<thead>
<tr>
<th>Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1001</td>
<td>Urban Superclass</td>
</tr>
<tr>
<td>1002</td>
<td>Grassland Superclass</td>
</tr>
<tr>
<td>1003</td>
<td>Forest Superclass</td>
</tr>
<tr>
<td>1004</td>
<td>Desert Superclass</td>
</tr>
<tr>
<td>1005</td>
<td>Water Superclass</td>
</tr>
</tbody>
</table>

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*Innovation Starts Here*

Engineering • Science • Technology
Methodology: Surrogate for Air Quality

NOx vs VOC (vary by Latitude)
(Mar, Jun, Dec, 2000, T = 280K, CC = 0, Lat 0-60)
Methodology: Refined Parameter Space (T, H₂O)

- Global 0.5 km LU Data Set

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Temperature (K)</th>
<th>[H₂O] (x10³) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>0</td>
<td>288</td>
<td>310</td>
</tr>
<tr>
<td>10</td>
<td>288</td>
<td>310</td>
</tr>
<tr>
<td>20</td>
<td>288</td>
<td>310</td>
</tr>
<tr>
<td>30</td>
<td>274</td>
<td>310</td>
</tr>
<tr>
<td>40</td>
<td>265</td>
<td>304</td>
</tr>
<tr>
<td>50</td>
<td>257</td>
<td>299</td>
</tr>
<tr>
<td>60</td>
<td>245</td>
<td>294</td>
</tr>
<tr>
<td>70</td>
<td>231</td>
<td>291</td>
</tr>
</tbody>
</table>

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).
Methodology: Run Detailed Chemistry

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

- Implement in Detailed Mechanism
- Run PBM as \( f(\text{met parm's}) \)
- Obtain \( c_{\text{TIC}}(t) \) as \( f(\text{met parm's}) \)
- Derive Empirical \( k_{\text{eff}} \) (met parm’s)
- Populate SCIPUFF data tables with \( k_{\text{eff}} \) for TICs
Methodology: Obtain $C_{\text{TIC}}$ as $f(t)$

\[ k_{\text{eff}} = \frac{-dc}{dt} \left[ \frac{1}{c} \right] \]

Implement in Detailed Mechanism

Run PBM as $f(\text{met parm’s})$

Obtain $c_{\text{TIC}}(t)$ as $f(\text{met parm’s})$

Derive Empirical $k_{\text{eff}} (\text{met parm’s})$

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

$T = 290 \, \text{K}, \, \text{Land Use} = \text{Urban}$

Latitude = 20 – 50º N

[Butene] as $f(\text{time})$

Butene [PPM]

Time of Day (min from midnight)
**Methodology:** Obtain $k_{\text{eff}}$ as $f(\text{met parms})$

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

**T = 291 K, Land Use = Urban**

### Steps:

1. **Implement in Detailed Mechanism**
2. **Run PBM as $f(\text{met parm’s})$**
3. **Obtain $c_{\text{TIC}}(t)$ as $f(\text{met parm’s})$**
4. **Derive Empirical $k_{\text{eff}}$ (met parm’s)**
5. **Populate SCIPUFF data tables w/ $k_{\text{eff}}$ for TICs**

---

**Graph:**

- **$k_{\text{eff}}$ as $f(\text{time})$**
- **Time of Day (min from midnight)**
- **$T = 291$ K, Land Use = Urban**
- **Temperatures:**
  - 25º
  - 30º
  - 35º
  - 40º
  - 45º
  - 50º

---

**Graph Details:**

- **$k_{\text{eff}}$ in $\text{min}^{-1}$**
- **Legend:**
  - Red: 25º
  - Orange: 30º
  - Green: 35º
  - Blue: 40º
  - Cyan: 45º
  - Black: 50º
Methodology: Derive Empirical $k_{\text{eff}}$

- Generate $k_{\text{eff}}$ 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 $k_{\text{eff}} = f(SE, T, \text{lat}, \text{tod}, \text{CC}, [H_2O])$
- Compare the $k_{\text{eff}}$ (empirical model) with the PBM derived $k_{\text{eff}}$.

Obtain $c_{\text{TIC}(t)}$ as $f(\text{met parm’s})$

Derive Empirical $k_{\text{eff}}$ (met parm’s)

Populate SCIPUFF data tables w/ $k_{\text{eff}}$ for TICs
Results: $k_{\text{eff}}$ (polynomial) vs $k_{\text{eff}}$ (PBM) for butene

Land Use = Urban

Model: 7 Parameters

$r^2 = 0.95$

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

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

> 500,000 points
Results: $k_{\text{eff}}$ (polynomial) vs $k_{\text{eff}}$ (PBM) for butene

Land Use = Grass

Lat 0°, Temp 300 K, Cloud Cover 0/8, [H$_2$O] = 20000 ppm,

![Graph showing $k_{\text{eff}}$ vs time from solar noon for polynomial and PBM methods. The polynomial method is represented by a black line with a peak at $1.50 \times 10^{-3}$ min$^{-1}$, and the PBM method is represented by a red line with a peak at $1.43 \times 10^{-3}$ min$^{-1}$.]
Results: $k_{\text{eff}}$ (polynomial) vs $k_{\text{eff}}$ (PBM) for butene

Land Use = Water

Lat 0°, Temp 300 K, Cloud Cover 0/8, $[\text{H}_2\text{O}] = 20000$ ppm,

- $9.3 \times 10^{-4}$ min$^{-1}$
- $9.2 \times 10^{-4}$ min$^{-1}$
Methodology: Obtain $X_{\text{eff}}$

$$\text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{OH} \rightarrow 0.94 \text{C}_2\text{H}_5\text{CHO} + \text{Other products}$$

$$\text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{NO}_3 \rightarrow 0.12 \text{C}_2\text{H}_5\text{CHO} + 0.6 \text{C}_3\text{H}_5\text{O-CH-O-NO}_2 + \text{Other products}$$

$$\text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{O}_3 \rightarrow 0.35 \text{C}_2\text{H}_5\text{CHO} + 0.41 \text{OH} + \text{Other products}$$

$$\text{Rate} = -\left( k_{\text{OH}}[\text{OH}] + k_{\text{NO}_3}[\text{NO}_3] + k_{\text{O}_3}[\text{O}_3] \right) [1\text{-butene}]$$

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

$$\text{Rate} = +\left( 0.94 k_{\text{OH}}[\text{OH}] + 0.12 k_{\text{NO}_3}[\text{NO}_3] + 0.35 k_{\text{O}_3}[\text{O}_3] \right) [\text{butene}]$$

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

$T = 295$ K, Land Use = Water

Stoichiometry for Propanal Formation

![Graph showing stoichiometric coefficients over time for OH, O$_3$, and NO$_3$.](Image)
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

SCIPUFF

Tracer

1-Butene
Results: Methylpropene
8 hr continuous release starting at 8 am local time
Results: Calculated Plume is TIC Dependent

Ethene

Propene

3-Methyl Propene

1,3-Butadiene
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”

- $k_{\text{min}} / k_{\text{max}}$
- $k_{\text{eff}}$ (met parms)

Diffusion
Summary & Future Work

- Developed Chemistry Model for 10 TICs
  - 9 Alkenes + H₂S
- No slow down in SCIPUFF
- Ability to model product formation

Future Work
- Site specific $k_{\text{eff}}$’s
- $k_{\text{eff}}$’s for other TICs
  - Complementary lab / theory development of fundamental $k_{\text{OH}}$, $k_{\text{O}_3}$, $k_{\text{H}_2\text{O}}$, etc.
- Chamber Studies (Chemistry Validation)
- Field Studies (Model Validation)
End of slides
Example: Crop Dusting Scenario – Bottom line

03 July 06:00 (Local) 13:00 Z
03 July 07:00 (Local) 14:00 Z
03 July 08:00 (Local) 15:00 Z
03 July 09:00 (Local) 16:00 Z
03 July 10:00 (Local) 17:00 Z
03 July 11:00 (Local) 18:00 Z
03 July 12:00 (Local) 19:00 Z
03 July 13:00 (Local) 20:00 Z
03 July 14:00 (Local) 21:00 Z
03 July 15:00 (Local) 22:00 Z
03 July 16:00 (Local) 23:00 Z
03 July 17:00 (Local) 00:00 Z
03 July 18:00 (Local) 01:00 Z
03 July 19:00 (Local) 02:00 Z
03 July 20:00 (Local) 03:00 Z
03 July 21:00 (Local) 04:00 Z
03 July 22:00 (Local) 05:00 Z

Chemistry vs T&D

Degrade Generation

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