2007 CBIS

Atmospheric Chemistry of Toxic Industrial Chemicals

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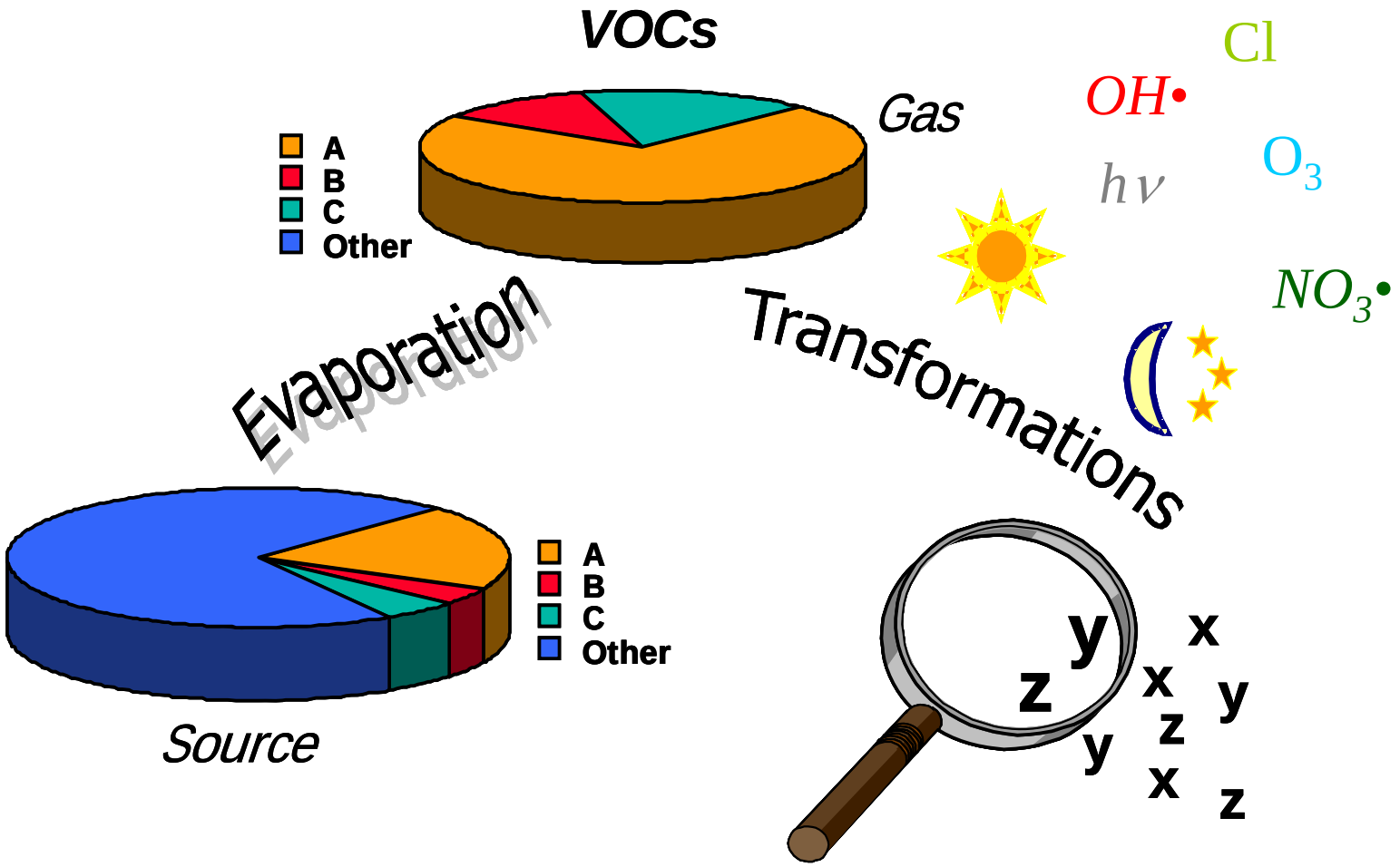
Overview

- Introduction to Atmospheric Chemistry
- Importance to Dispersion Modeling
- TIC Kinetics
- Past, Present, Future

Atmospheric Chemistry of Volatile Organic Compounds



Tropospheric Oxidant Formation

Ozone

$$NO_2 + h\nu \longrightarrow NO + O(^3P)$$

$$O(^3P) + O_2 \xrightarrow{M} O_3$$

OH Radical

$$O_3 + h\nu \longrightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \longrightarrow 2\ OH\bullet$$

NO_3 Radical

$$NO_2 + O_3 \longrightarrow NO_3\bullet + O_2$$

$$NO_2 + NO_3\bullet \rightleftharpoons N_2O_5$$

Tropospheric Transformations

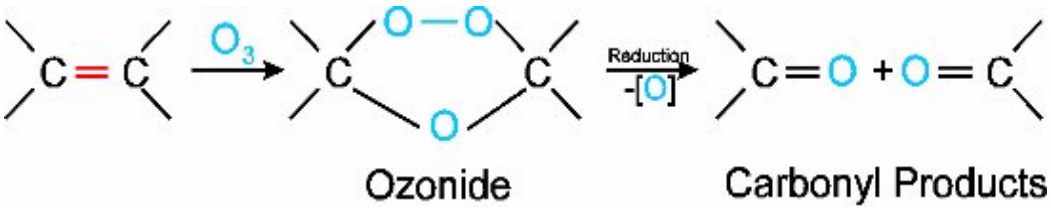
Photolysis

$$NO_2 + h\nu \xrightarrow{\lambda < 420nm} NO + O(^3P)$$

$$O_3 + h\nu \xrightarrow{\lambda < 325nm} O(^1D) + O_2$$

$$Cl_2 + h\nu \longrightarrow 2\ Cl$$

Ozonolysis



Typical $[O_3]$ = 2.5×10^{12} molecules/cm^3
100 ppb @STP

Important Radical Reactions

$$RH + OH \rightarrow R\cdot + H_2O$$
$$R\cdot + O_2 \rightarrow RO_2$$
$$RO_2 + NO \rightarrow NO_2 + RO$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

$$RH + OH + 2O_2 \rightarrow RO + H_2O + O_3$$

Typical [OH] =
1×10^6 molecules/cm^3
3.72×10^{-2} ppt @STP

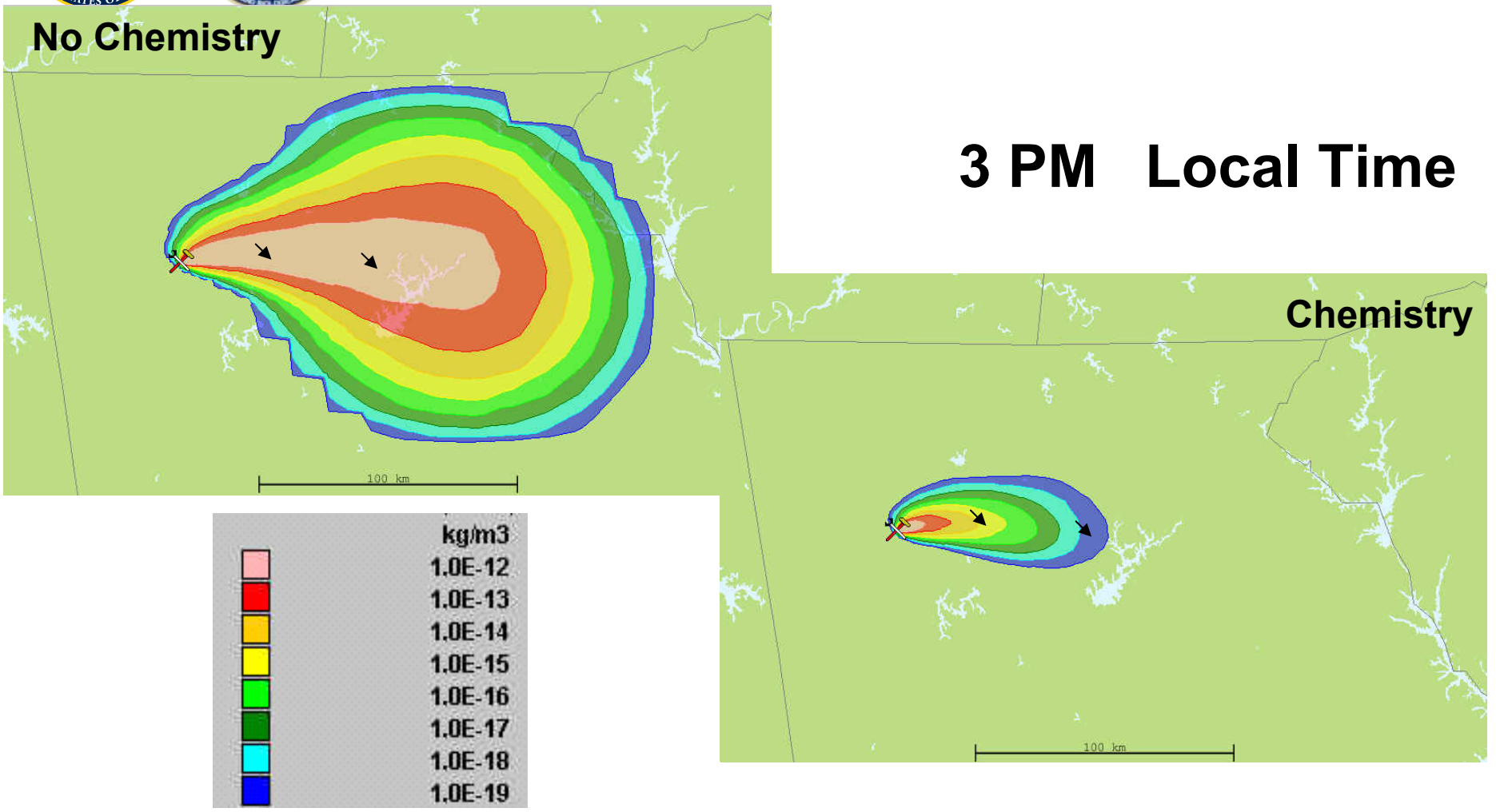
$$RH + NO_3\cdot \rightarrow R\cdot + HNO_3$$
$$R\cdot + O_2 \rightarrow RO_2$$
$$RO_2 + NO_3\cdot \rightarrow NO_2 + RO + O_2$$
$$NO_2 + O_3 \rightarrow NO_3\cdot + O_2$$

$$RH + NO_3\cdot + O_3 \rightarrow RO + HNO_3 + O_2$$

Typical [NO_3] =
2.5×10^8
molecules/cm^3
9.3 ppt @STP

Example: Methylpropene

8 hr continuous release starting at 8 am local time



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Reaction Kinetics

- Photolysis:

$$TIC \xrightarrow{h\nu} Products$$

$$-d[TIC]/dt = k_p[TIC],\ k_p \text{ in } sec^{-1}$$

- Bimolecular reaction:

$$TIC + OH/NO_3/O_3/Cl \longrightarrow Products$$

$$-d[TIC]/dt = k_{OH}\ [TIC][OH],$$
$$k_{OH} \text{ in } cm^3 \text{ molecules}^{-1} \text{ sec}^{-1}$$

Example of TIC Kinetic Data

Name	CAS #	Reaction with OH Radicals	Reaction with Ozone	Reaction with NO3 Radicals
		Reaction Rate, cm3 mol-1 s-1	Reaction Rate, cm3 mol-1 s-1	Reaction Rate, cm3 mol-1 s-1
1,1-dichloroethylene	75-35-4	8.1 x 10-12	3.7 x 10-21	1.23 x 10-15
1,1-difluoroethylene	75-38-7	4.0 x 10-12	1.4 x 10-19	
2-methylpropene	115-11-7	5.14 x 10-11	1.13 x 10-17	3.32 x 10-13
acetaldehyde	75-07-0	1.5 x 10-11	<6 x 10-21	2.7 x 10-15
acetylene	74-86-2	7.80 x 10-13	1 x 10-20	<1 x 10-16
carbon monoxide	630-08-0	2.08 x 10-13		<4 x 10-19
chloroethylene	75-01-4	2.36 x 10-12		2.93 x 10-16
chloromethane	74-87-3	4.2 x 10-14		
diethyl ether	60-29-7	1.3 x 10-11		
dimethyl ether	115-10-6	2.8 x 10-12		<3 x 10-15
dimethyl sulphide	75-18-3	4.80 x 10-12	<1.0 x 10-18	1.1 x 10-12
dimethylamine	124-40-3	6.54 x 10-11	2.61 x 10-18	
ethanethiol	75-08-1	4.64 x 10-11		9.87 x 10-13
ethyl vinyl ether	109-92-2	4.04 x 10-11	1.54 x 10-16	
ethylamine	75-04-7	2.77 x 10-11	2.76 x 10-20	
ethylene oxide	75-21-8	8 x 10-14		
hydrogen cyanide	74-90-8	3.0 x 10-14		
hydrogen sulfide	7783-06-4	4.7 x 10-12		<1 x 10-15
isoprene	78-79-5	1.0 x 10-10	1.27 x 10-17	7.0 x 10-13

Atmospheric Lifetime

- Bimolecular reaction:

$$TIC + OH/NO_3/O_3/Cl \longrightarrow Products$$

$$-d[TIC]/dt = k_{OH} [TIC][OH],$$

k_{OH} in cm^3 $molecules^{-1}$ sec^{-1}

- Lifetime (τ) Calculation
  - Time for the TIC to decrease to 1/e of its initial value
  - Oxidant [OH] assumed to be constant @ 1×10^6 molecules cm^{-3}
  - $\tau = 1/(k_{OH} * [OH])$
  - Example where kOH = 10×10^{-12} cm^3 $molecules^{-1}$ sec^{-1}

    $\tau = 1/(10 \times 10^{-12} * [1 \times 10^6])$

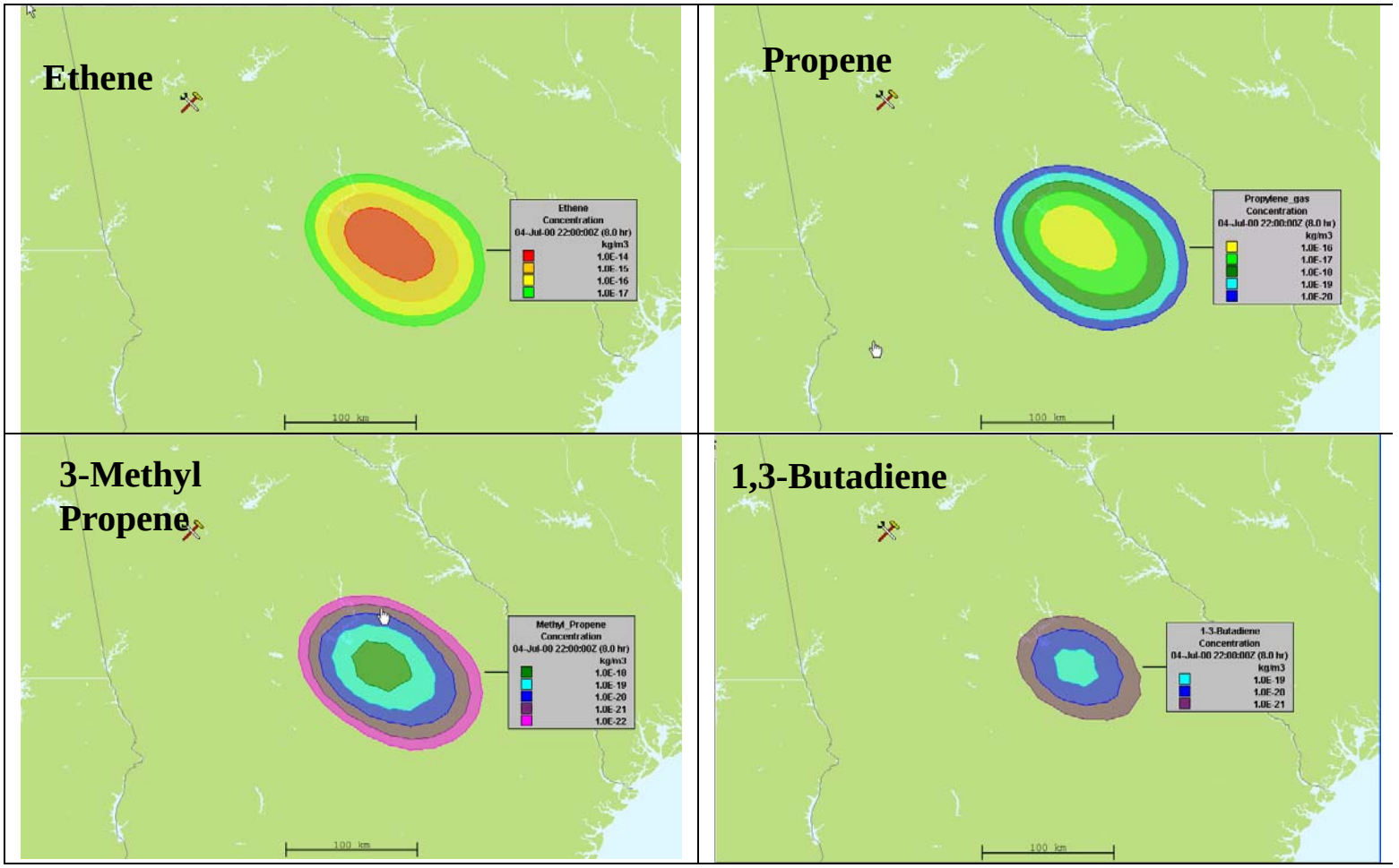
    $\tau = 1 \times 10^5$ sec ÷ 86,400 sec/day ~ 1.2 days

Estimated Atmospheric Lifetimes

Organic	OH [1 x 10^6 cm^{-3}], 0.038ppt	O_3 [2.5 x 10^{12} cm^{-3}], 100ppb	NO_3 [1.3 x 10^9 cm^{-3}], 50ppt	Cl [1 x 10^4 cm^{-3}], 0.00038ppt
n-Butane	5 days	≥ 1300 yr	205 days	5 days
trans-2-Butene	4.3 hours	36 min	35 min	~4 days
Acetylene	14 days	≥ 400 days	≥ 188 days	~22 days
Toluene	2 days	≥ 400 days	138 days	20 days
Formaldehyde	1.2 days	≥ 463 days	16 days	16 days
Hydrogen sulfide	2.5 days	-	≥ 213 days	-

Table derived from Finlayson-Pitts & Pitts, 2000

Calculated Plume is TIC Dependent



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Past, Present & Future

- Atmospheric chemistry plays significant role in dispersion of many TICs
- Kinetic data necessary to model reactivity
- Degrade algorithm developed for SCIPUFF
- Model optimization and sensitivity studies underway
- Chamber experiments for degrade algorithm validation being designed
- Heterogeneous aerosol interactions need addressing

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