Chlorine Emissions from Activated Sea-Salt Aerosols and Their Potential Impact on Ozone

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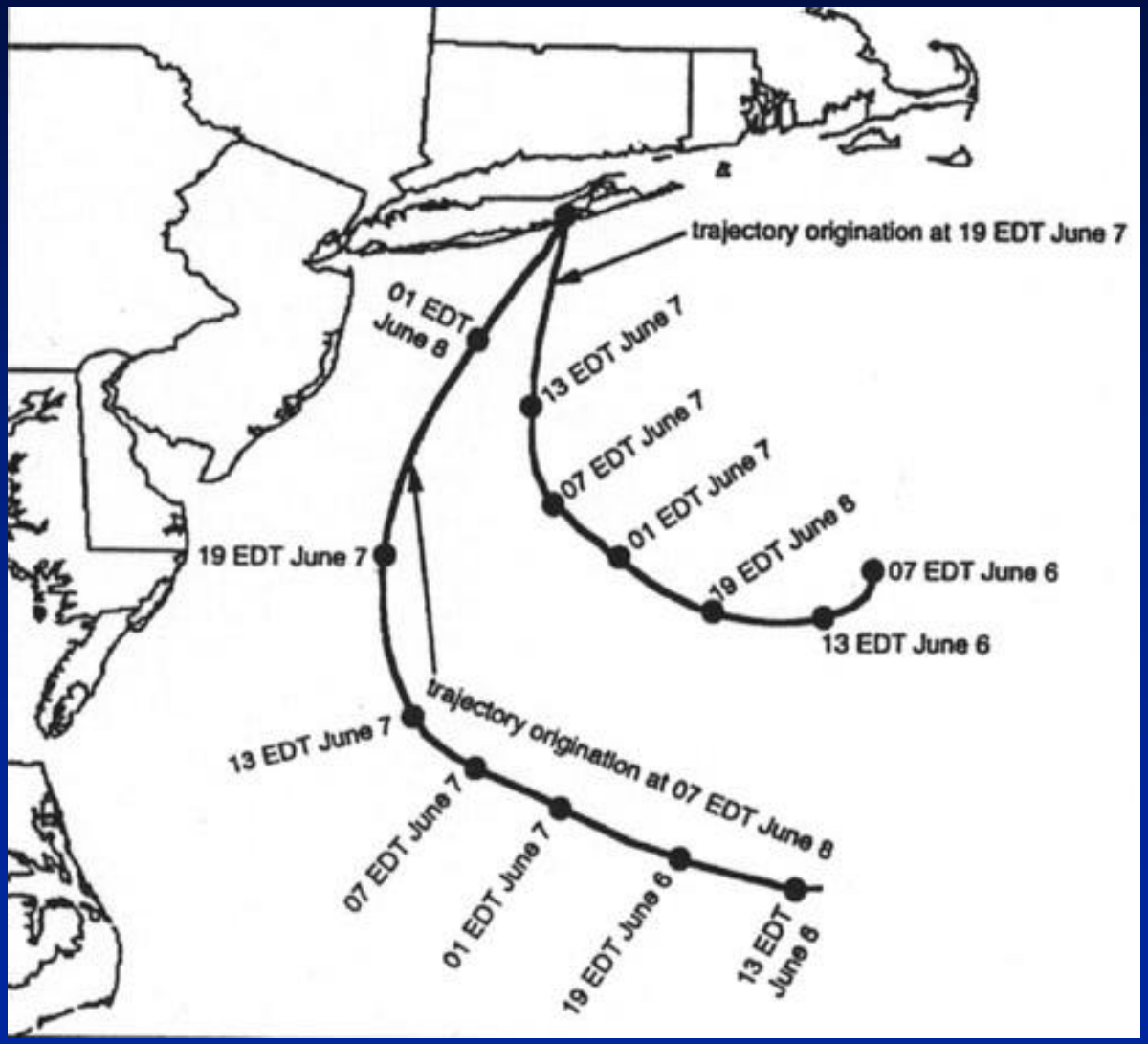
Chairman's Air Pollution Seminar

California Air Resources Board

July 22, 2002

The Measurements

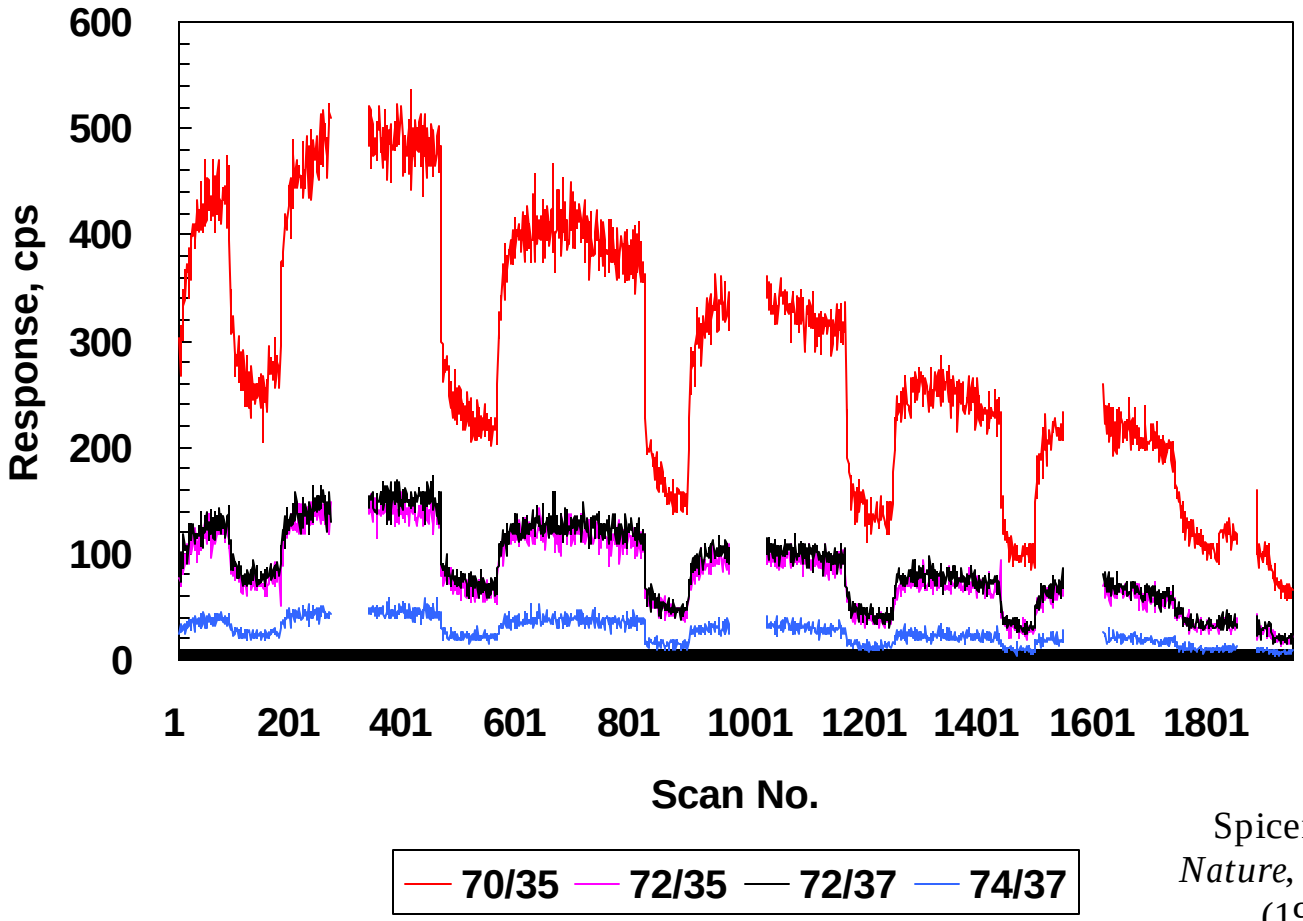


Unexpected high concentration of molecular chlorine in coastal air

Spicer *et al.*
Nature, 1998

Cl_2 Signals at a Coastal Site

Long Island, N.Y., June 7/8, 1996



Spicer *et al.*, *Nature*, **394**, 353 (1998)

Important Questions

- **Is there any evidence for chlorine and bromine atom sources in the lower atmosphere?**

- **If "yes", what is the chemistry forming these sources?**

  "The mechanism for Cl atom precursors from the sea salt aerosol is unclear"

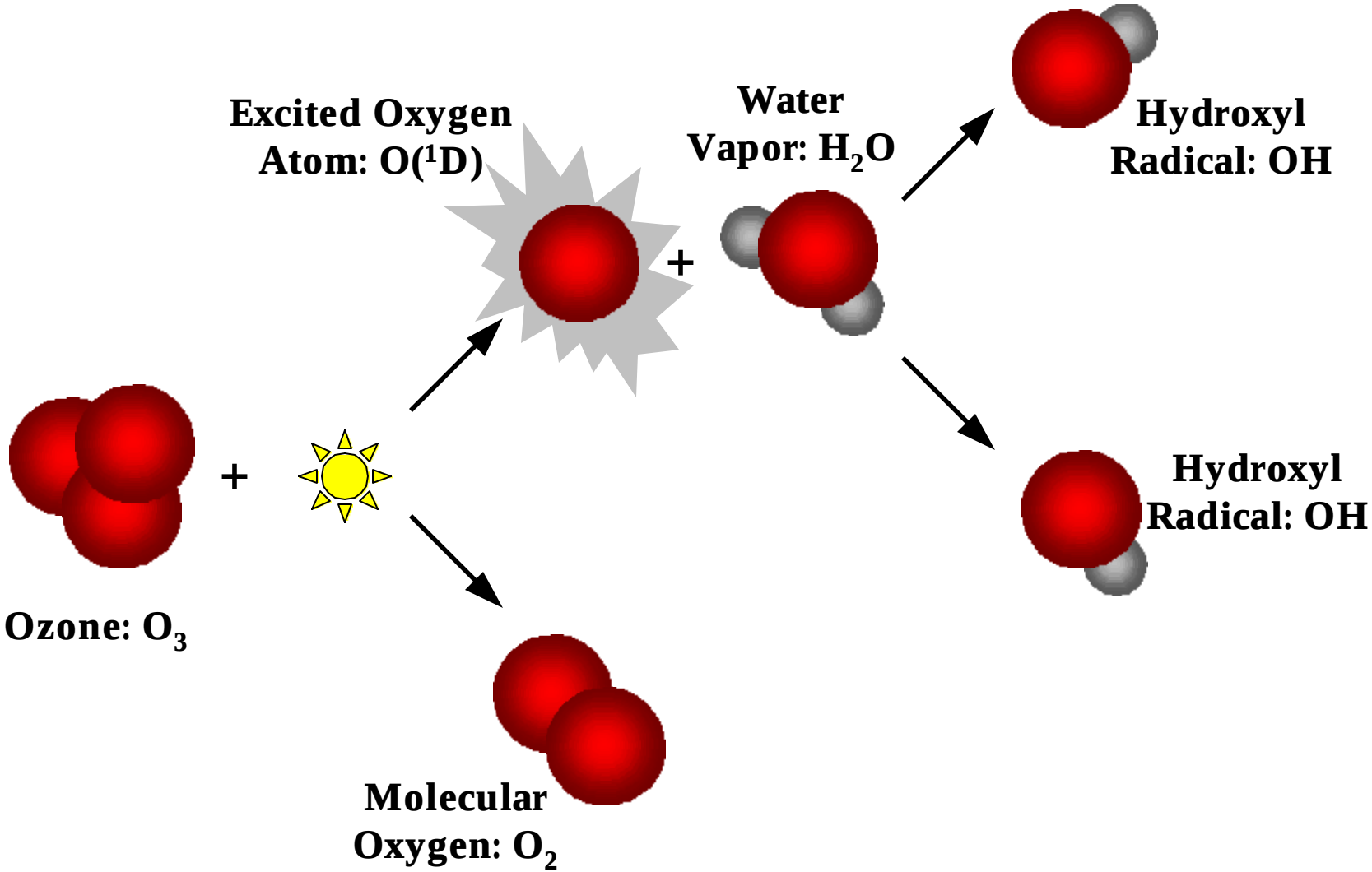
  (D. J. Jacob, Heterogeneous chemistry and tropospheric ozone, Atm Env 2000)

- **Is there some "new" chemistry? If so, how does it affect air quality in California?**

The Experiments

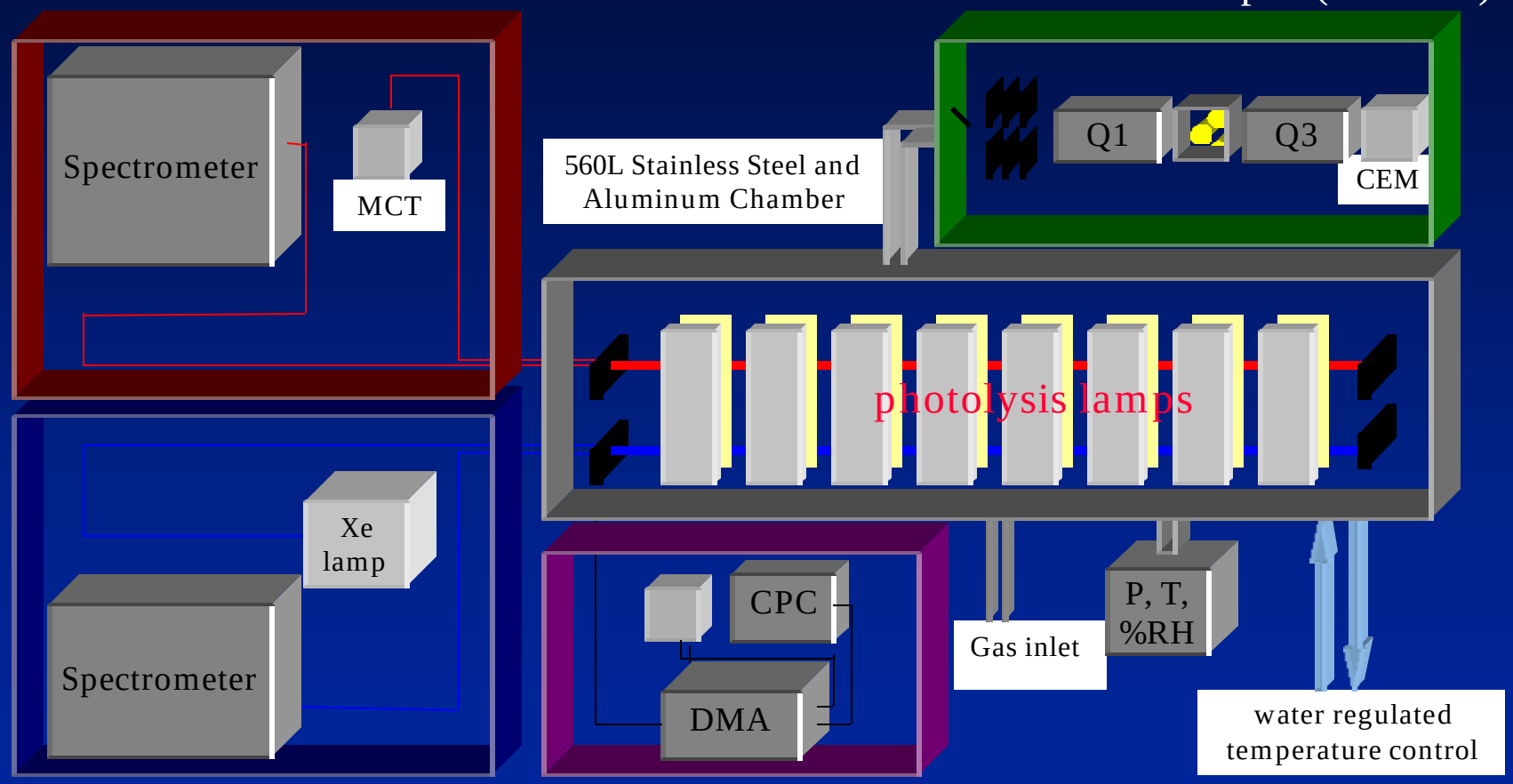
- Add NaCl particles to aerosol chamber
- Add humid air to a relative humidity above the deliquescence point
- Add ozone
- Photolyze at 254 nm (generate OH radicals)
- Measure gaseous reactants and products using FTIR, DOAS, and API-MS

Formation of Hydroxyl Radicals



Aerosol Chamber

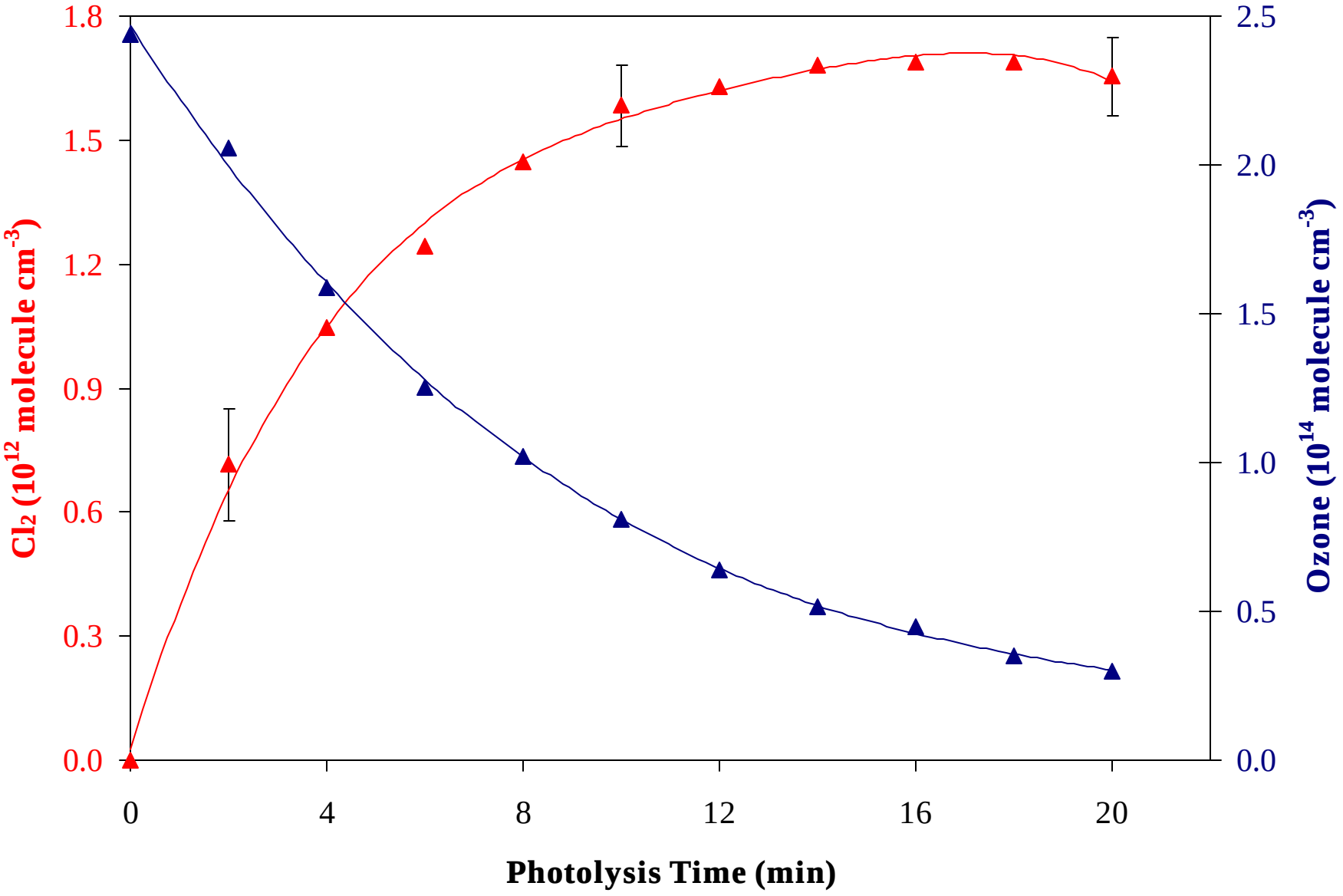
(Top View)



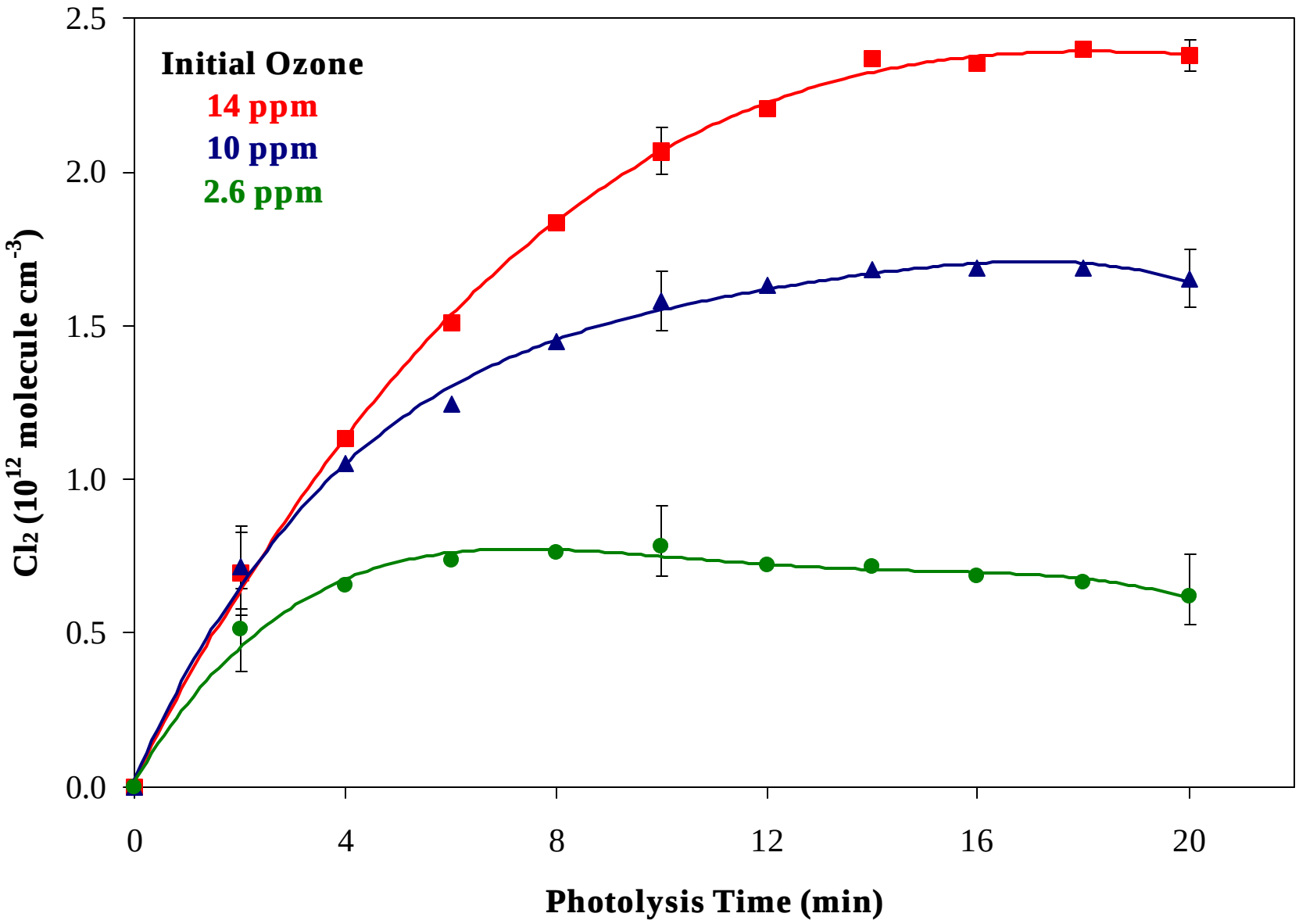
Differential Optical Absorption Spectroscopy (DOAS)

Aerosol Generation and Measurement

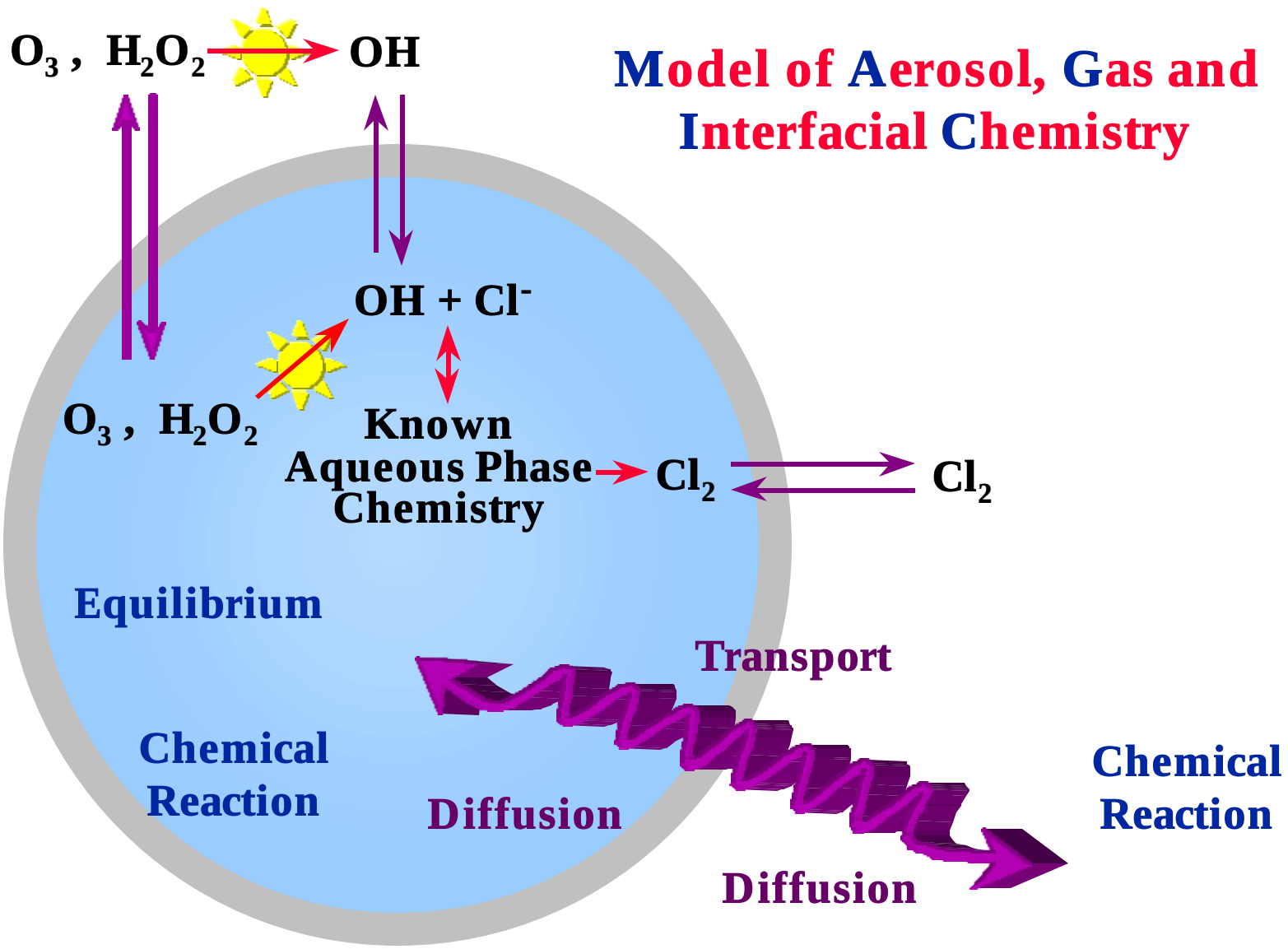
Typical Experiment: Cl_2 Production



Experiments Varying Initial O_3 Concentration



Physical and Chemical Processes of MAGIC



Schwartz 1986 Mass Transfer Method

Mass transfer coefficient: $$k_{mt} = \left[\frac{R_p^2}{3D_g} + \frac{4R_p}{3\bar{c}\,a} \right]^{-1}$$

$$Q = 3\left(\frac{\coth q_j}{q_j} - \frac{1}{q_j^{\,2}} \right)$$

Aqueous-phase diffusion: $$\langle C_j \rangle = QC_j^* + (1-Q)\frac{P_j}{k_{L,j}}$$

$$q_j = R_p \left(\frac{k_{L,j}}{D_{aq,j}} \right)^{1/2}$$

Activity coefficients: Pitzer ion-interaction approach

Kinetic salt effect: $$\log k = \log k^\circ + \frac{A\Delta z^2 \sqrt{I}}{1+\sqrt{I}}$$

Debye-Huckel-Bronsted equation

Governing Equations of Gas- and Aqueous-Phase Chemistry/Mass Transport Model

Gas Phase:

$$\frac{dC_g}{dt} = -k_{mt} w_L C_g + \frac{k_{mt}}{H_A RT} C_{aq} w_L + R_g + R_{int}$$

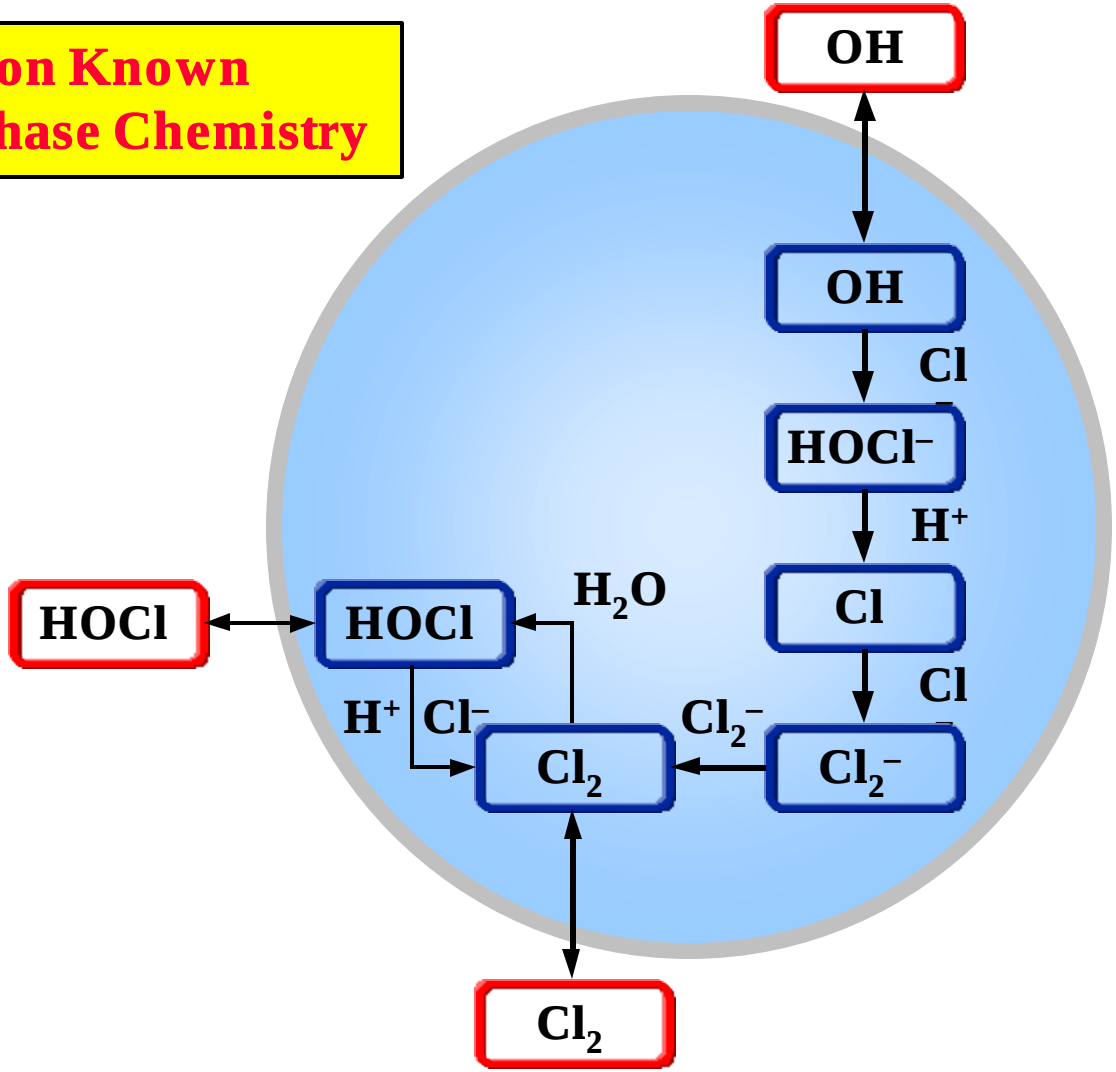
mass transfer into aerosol	mass transfer out of aerosol	chemical reaction	surface reaction

Aqueous Phase:

$$\frac{dC_{aq}}{dt} = k_{mt} C_g - \frac{k_{mt}}{H_A RT} C_{aq} + \langle R_{aq} \rangle + R_{int}$$

Potential Mechanism for Cl_2 Production

Based on Known Aqueous-Phase Chemistry



Eigen and Kustin, 1962; Jayson *et al.*, 1973; Nagaran and Fessedon, 1985; Neta *et al.*, 1988 and references therein

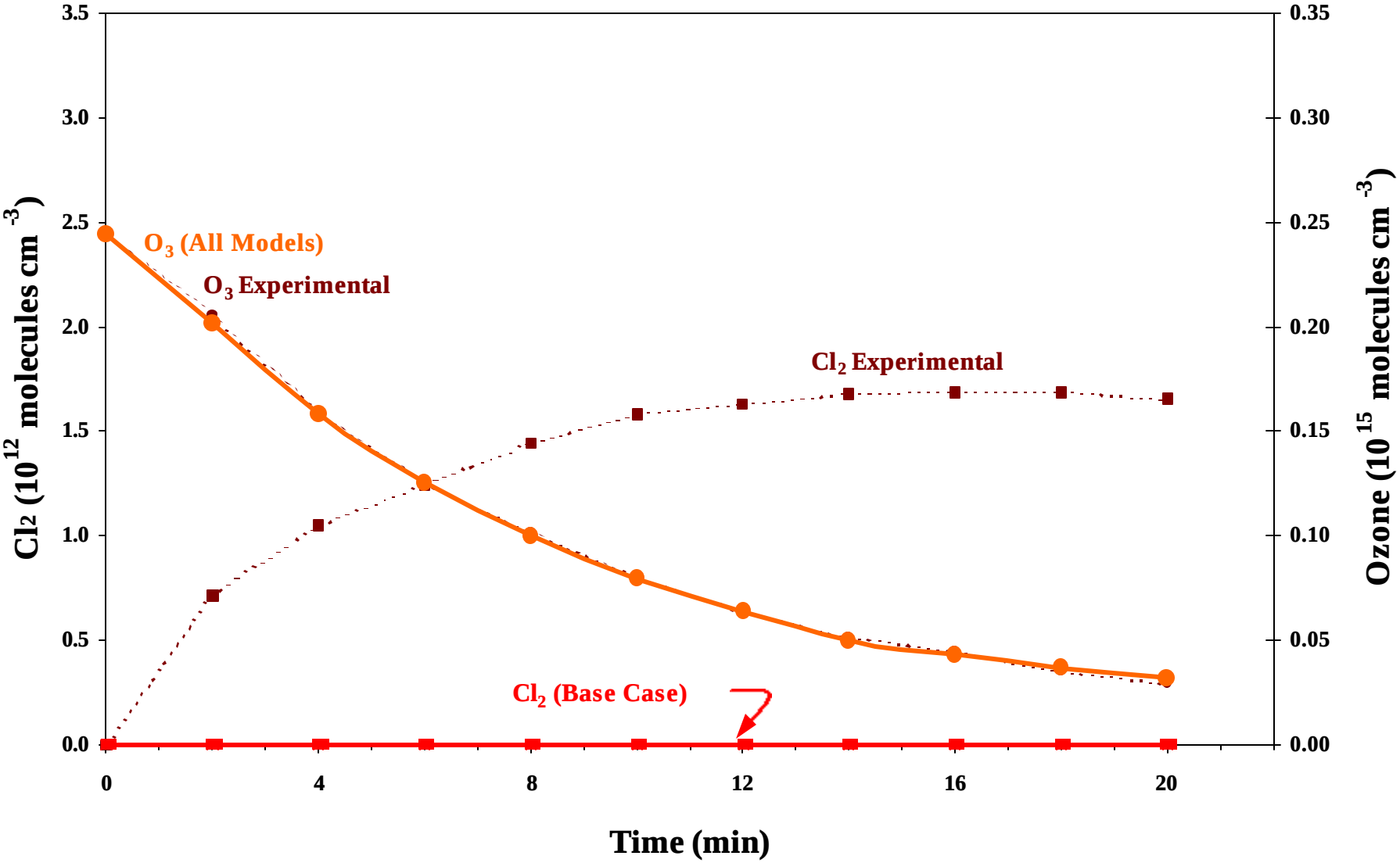
Description of Chamber Model Chemistry

- **Gas Phase:**
  - 15 Species
  - 52 Reactions
- **Aqueous Phase:**
  - 32 Species
  - 99 Reactions
    - » 48 - Chlorine chemistry
    - » 37 - Oxygen-Hydrogen chemistry
    - » 14 - Carbonate chemistry
  - 8 Aqueous acid / base equilibria
  - 10 Mass transfers between gas and aqueous phases
  - Aqueous phase diffusion treatment for transported species
  - Activity coefficient evaluation: Pitzer method

† Gas-phase and aqueous-phase organic, nitrogen and sulfur chemistry included during model evaluations of the marine boundary layer

Base Case and Constant pH Modeling Scenarios

Using Known Gas- and Aqueous-Phase Chemistry and Mass Transfer



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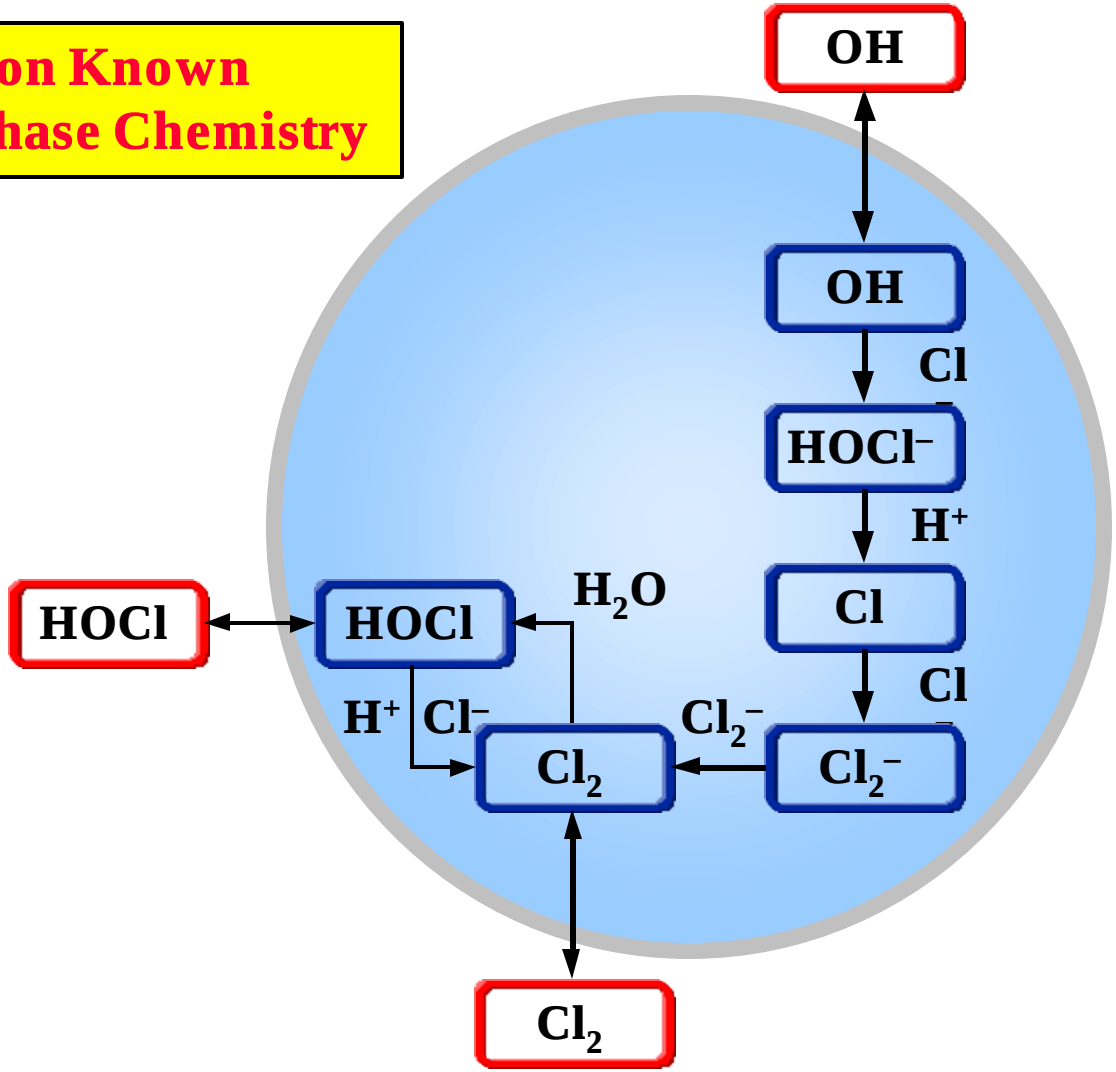

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Base Case and Constant pH Modeling Scenarios

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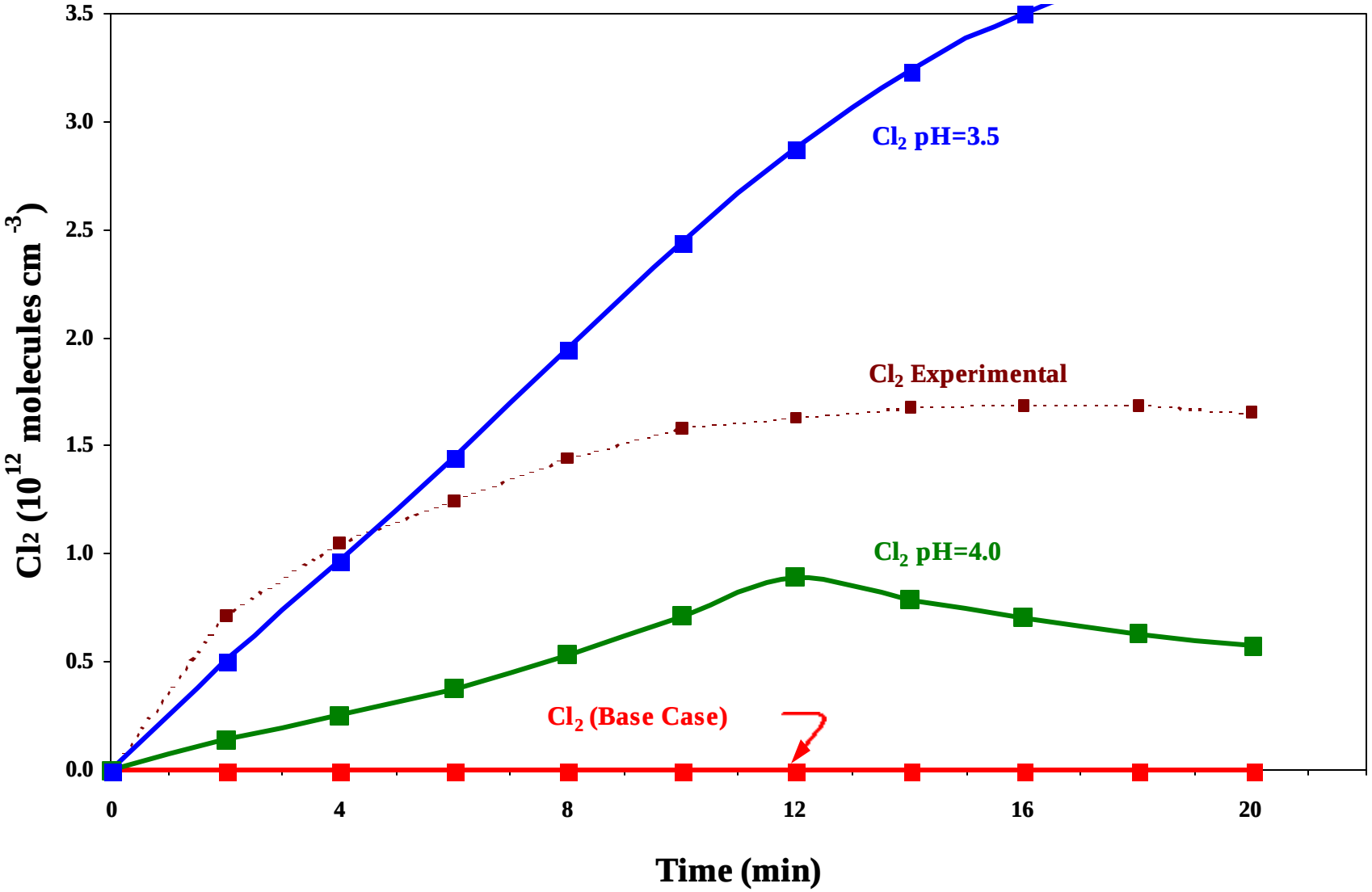
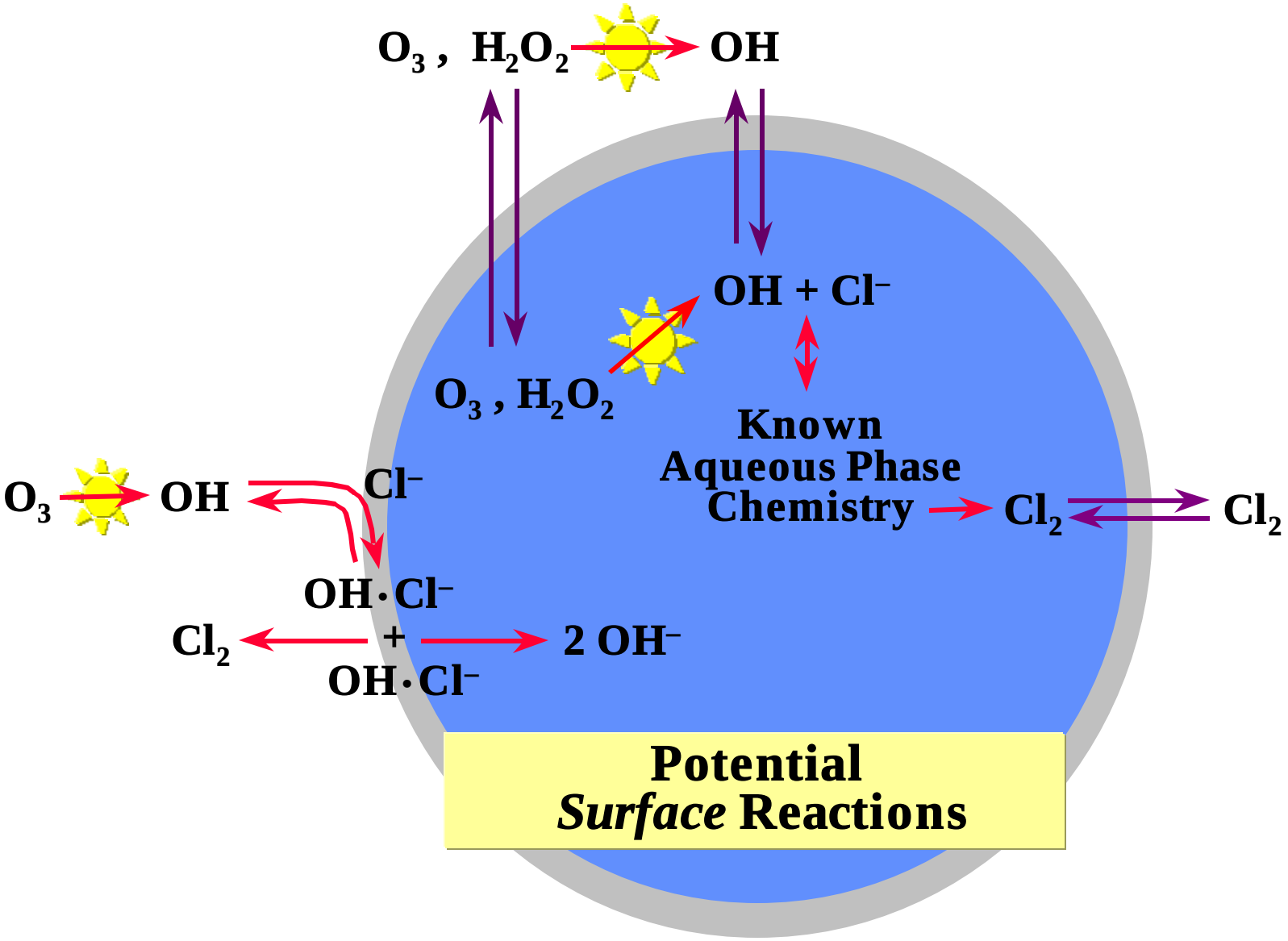
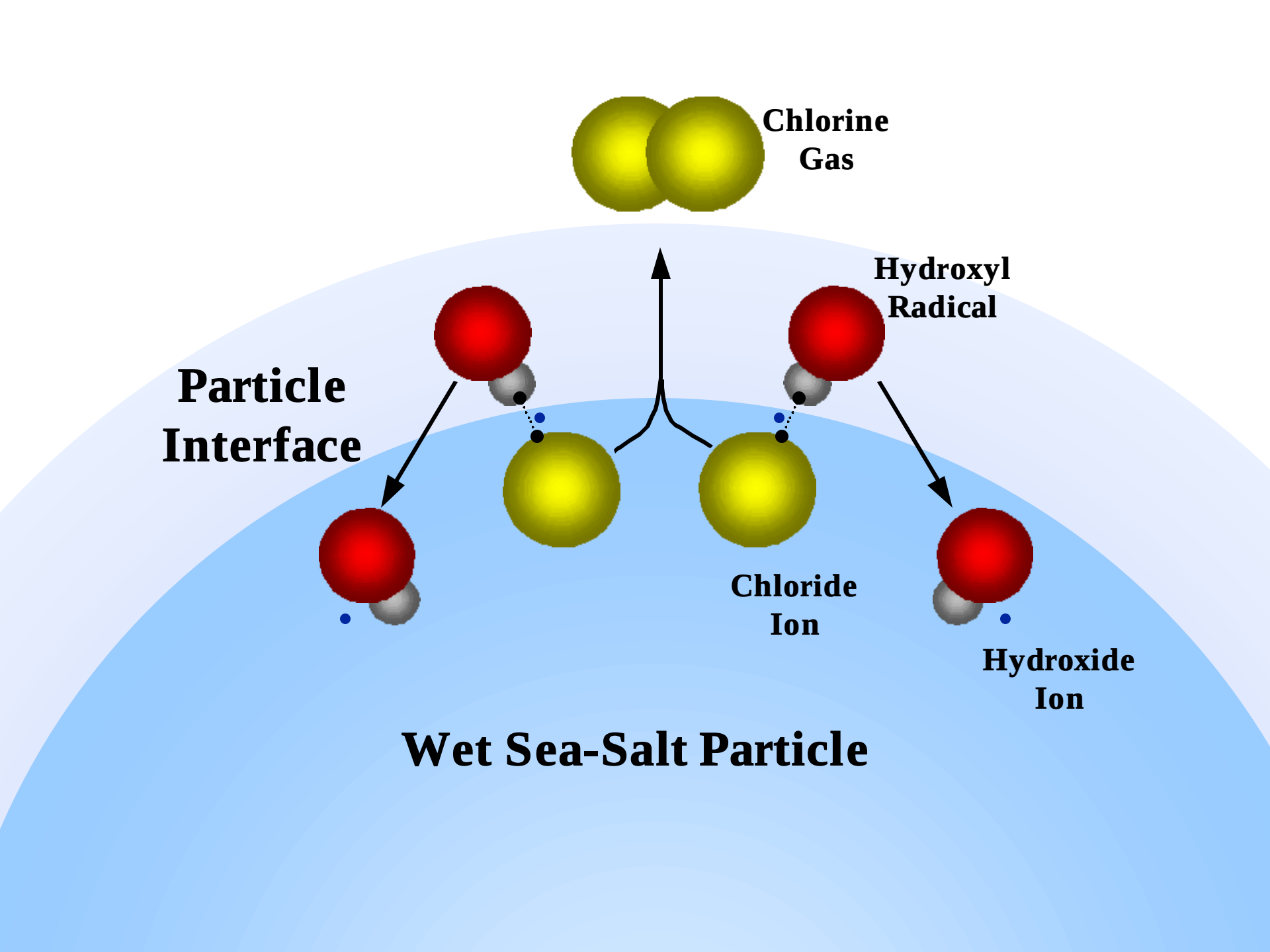
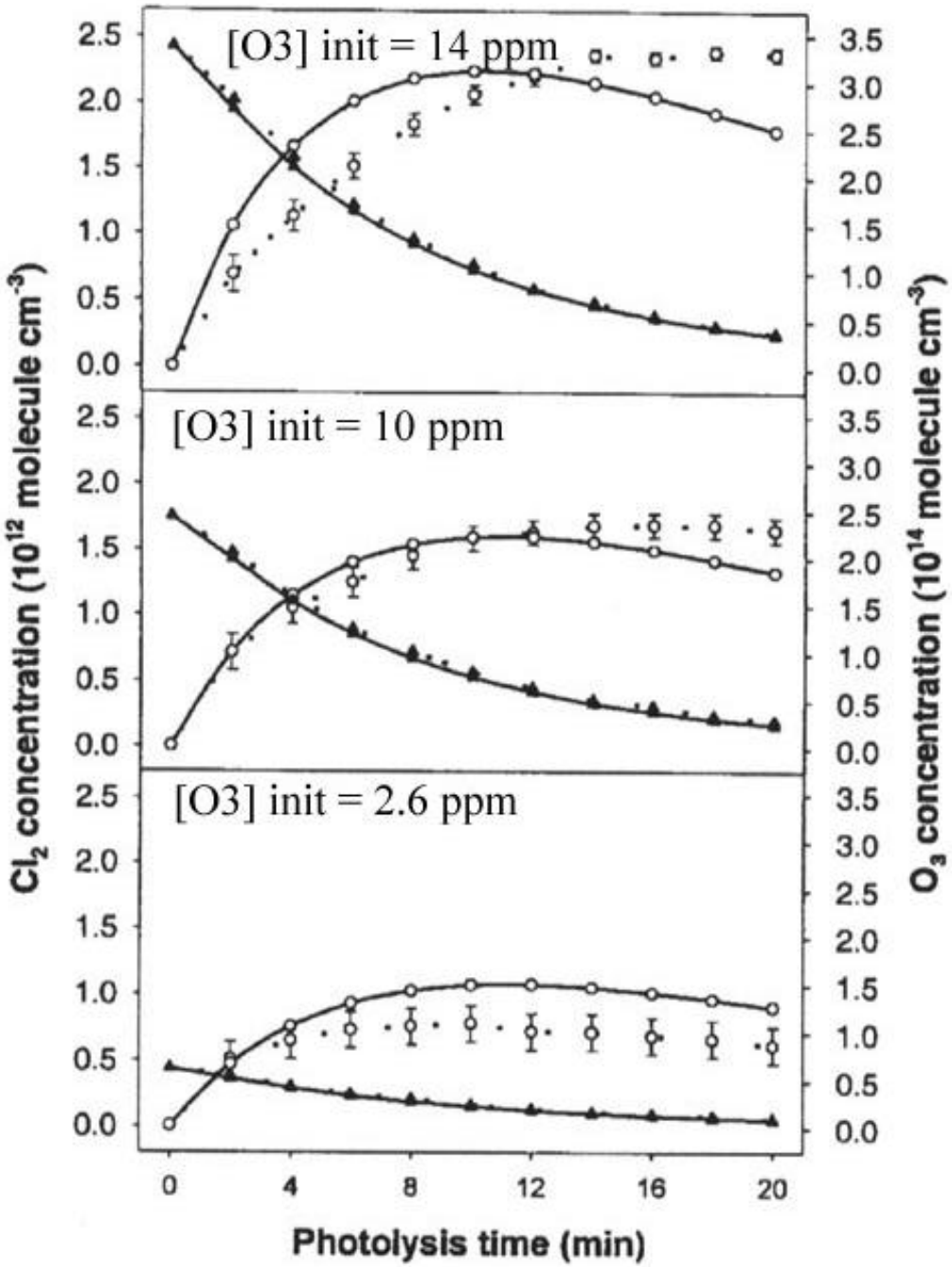


Proposed Mechanism for Cl_2 Production



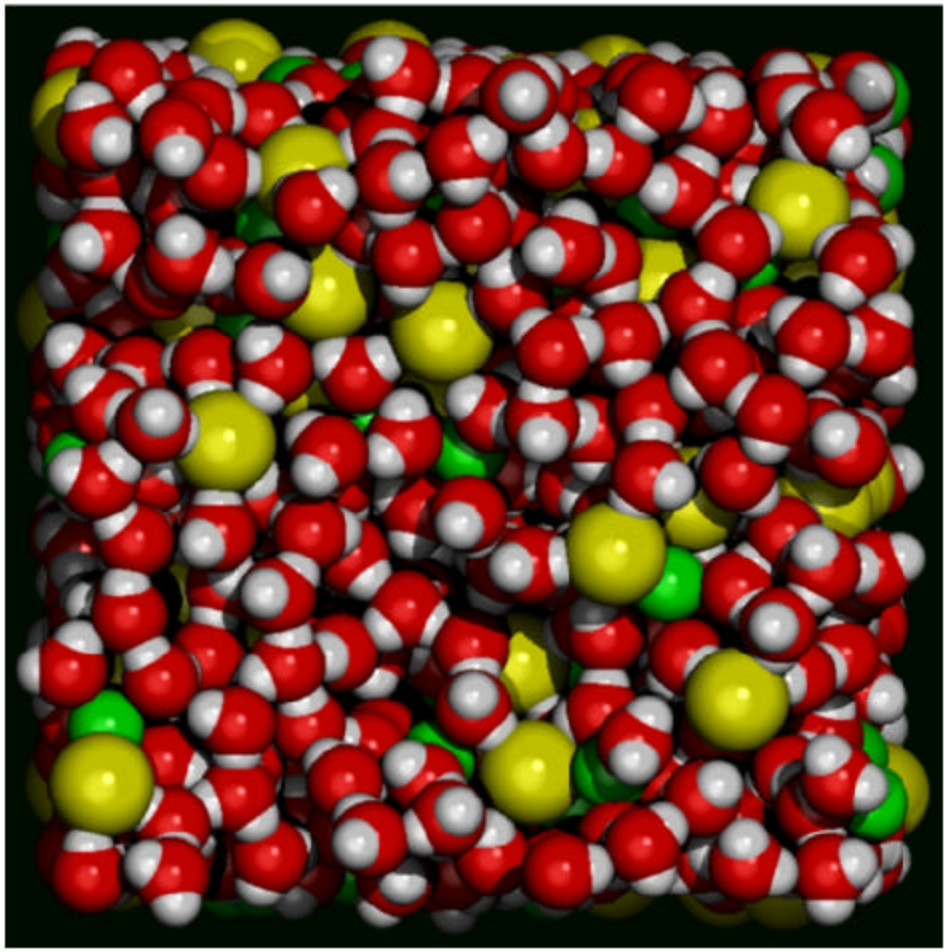

Chlorine
Gas
Hydroxyl
Radical
Particle
Interface
Chloride
Ion
Hydroxide
Ion
Wet Sea-Salt Particle


[O3] init = 14 ppm
[O3] init = 10 ppm
[O3] init = 2.6 ppm
Cl2 concentration (10^12 molecule cm^-3)
O3 concentration (10^14 molecule cm^-3)
Photolysis time (min)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0
4
8
12
16
20

Questions to be examined

- Are chloride ions available at the interface?
- If all is correct, what is the impact of Cl in the overall chemistry of the atmosphere?
- What is the role of other halogen compounds?

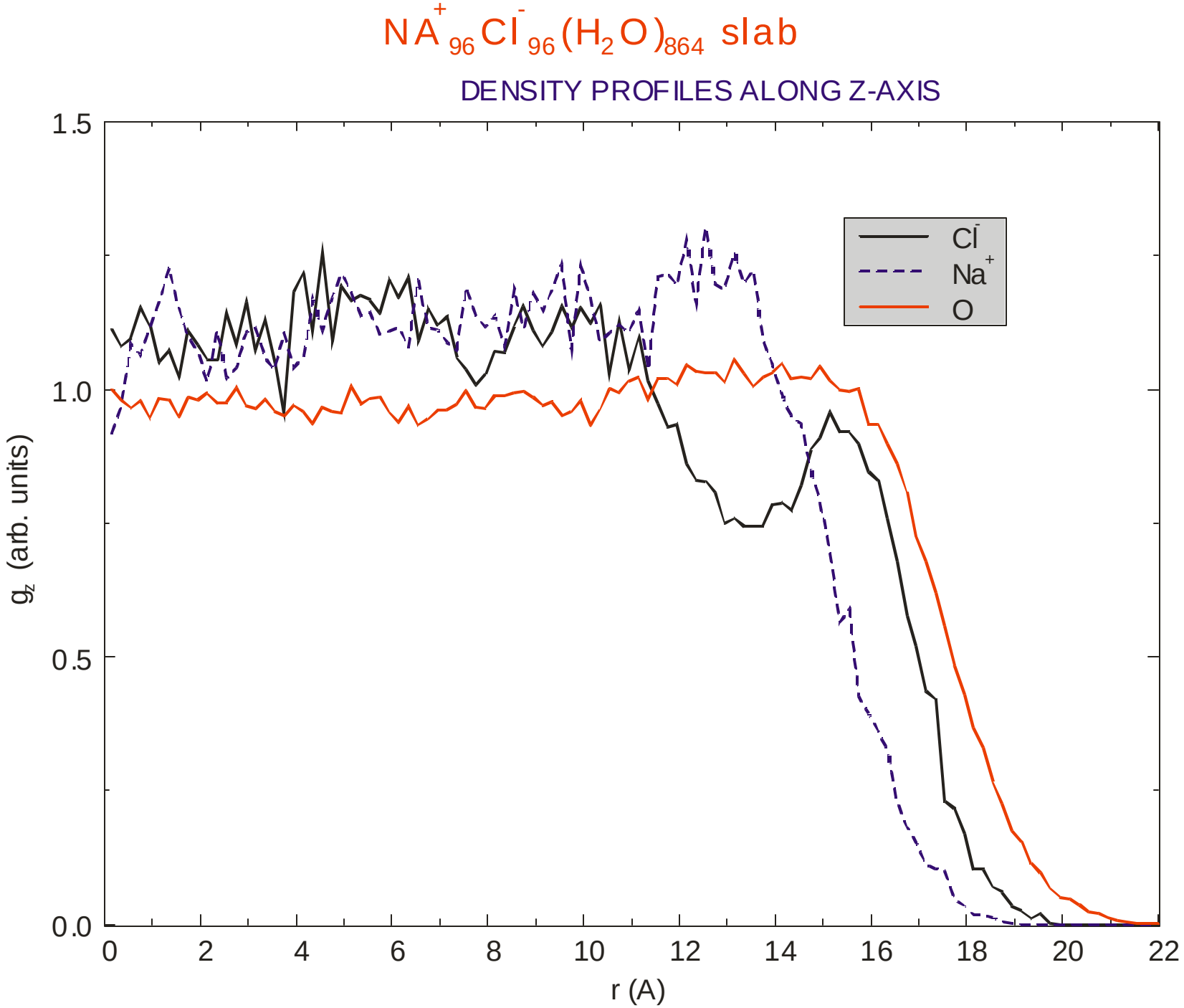
Molecular Dynamics Simulations of NaCl / H_2O



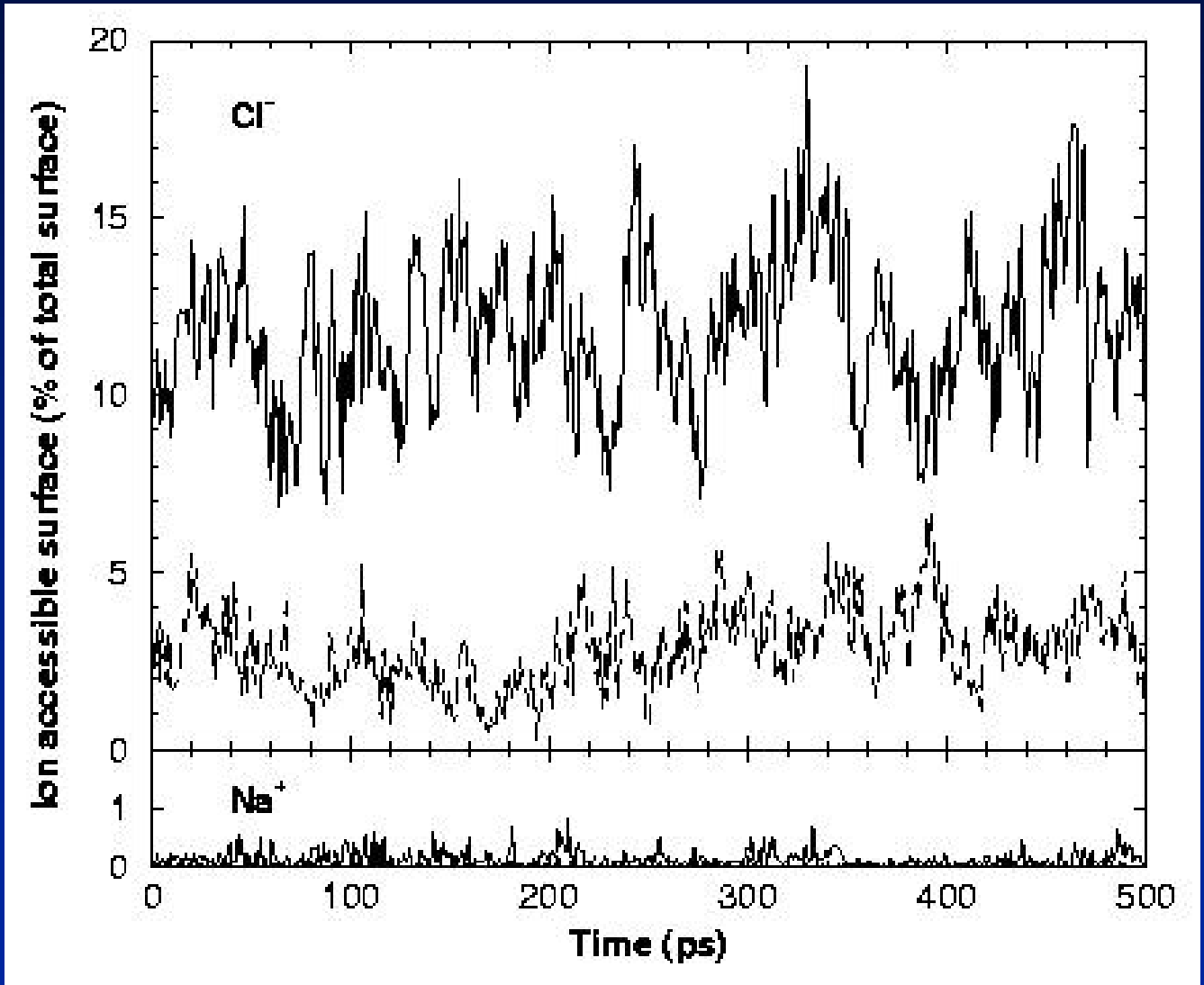
Snapshot of the open surface of an infinite "slab" consisting of 96 NaCl and 864 water molecules per unit cell.

Model predicted surface coverage:

- 11.9% Cl^-
- <0.2% Na^+


$NA^+_{96}Cl^-_{96}(H_2O)_{864}$ slab
DENSITY PROFILES ALONG Z-AXIS
Cl^-
Na^+
O
g_z (arb. units)
r (A)
1.5
1.0
0.5
0.0
0
2
4
6
8
10
12
14
16
18
20
22

Accessible Surface Exposure: Cl^- and Na^+



How Does Sea-Salt Aerosol Affect Coastal Urban Ozone?

How does chlorine affect the atmosphere?

Cl + O3 → Ozone destruction

Cl + organics → Ozone production

Oxides of Nitrogen

Ozone generation

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5$$

Alkyl radical and O_2 forms peroxy alkyl radical (RO_2)

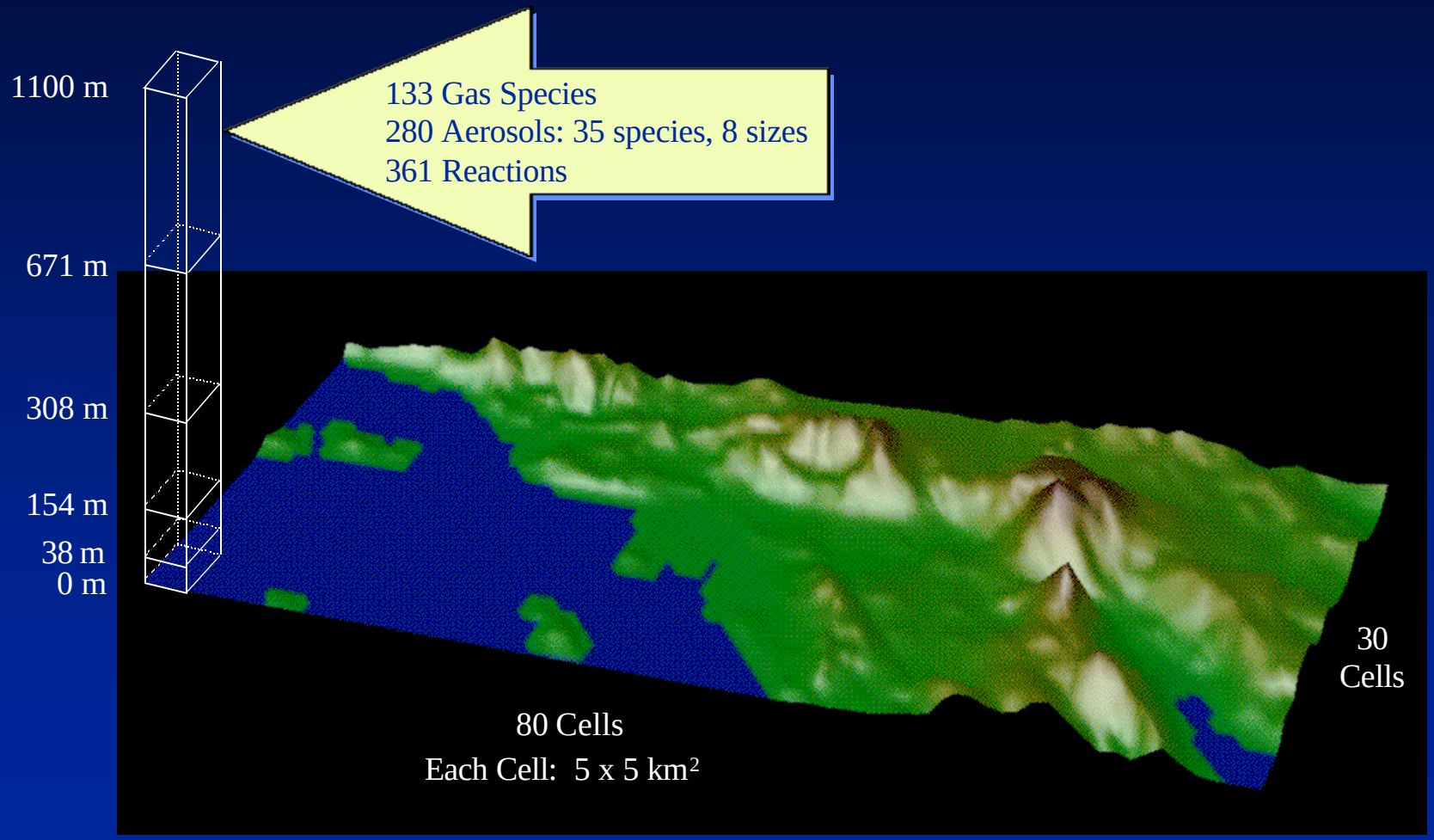
$$RO_2 + NO \rightarrow RO + NO_2$$

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

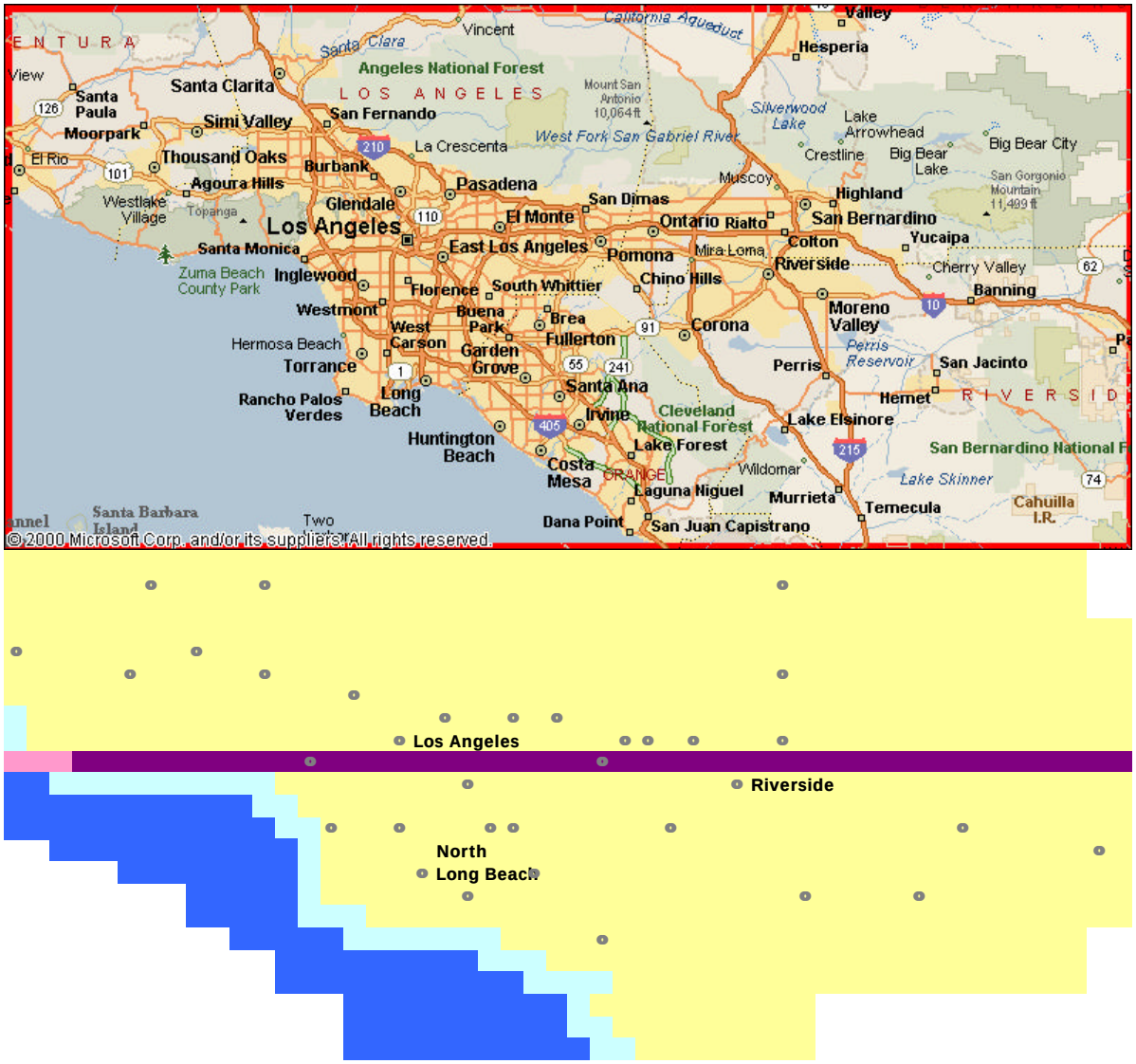
$$O(^3P) + O2 \rightarrow O_3$$

Photolysis of NO_2 generates ozone

The Modeling



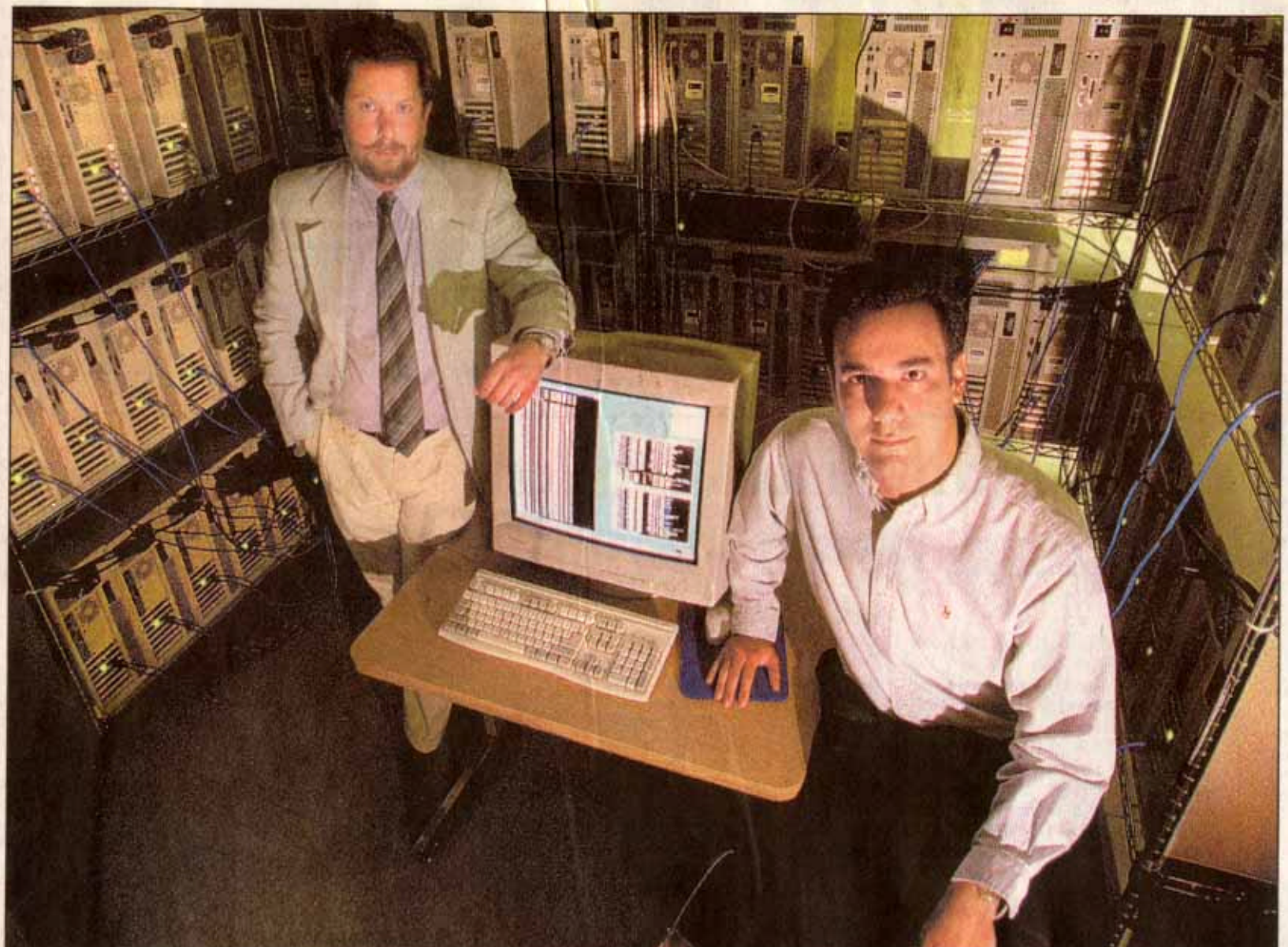
South Coast Air Basin Model Domain



Available Parallel Machines

	CRAY T3E SDSC	CRAY T3E UTexas	IBM SP SDSC	SUN HPC SDSC	IBM SP UMichigan	HP Exemplar Caltech
Number of Processors	272	88	128	64	64	256
Processor Type	DEC Alpha 21164	DEC Alpha 21164	IBM 160 Mhz Power2 Thin Nodes	UltraSparc II	IBM 160 Mhz Power2 Thin Nodes	PA–8000 180MHz
Memory per Processor	128 MB	128 MB	256 MB	64 GB (Total)	1 GB	256 MB
Peak Performance	154 Gflops	34 Gflops	82 Gflops	51 Gflops	31 Gflops	184 Gflops
Largest Available Filesystem	100 GB	34 GB	71 GB	140 GB	1.5 TB	64 GB
Operating System	Unicos/mk 2.0.3	Unicos/mk 2.0.4	AIX 4.2	Solaris 7.0	AIX 4.1/4.2.1	HP–UX 10.20

THE CUTTING EDGE



UC Irvine professors Herbert Hamber, left, and Donald Dabdub use the Linux operating system to link their computers to create a

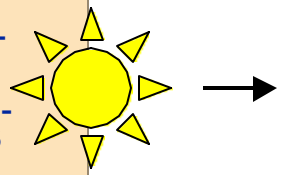
Blue Horizon

On February 2001, SDSC dedicated Blue Horizon, the newest addition to the NPACI complement of high-performance computers. Blue Horizon, a 1,152-processor IBM RS/6000 SP capable of 1.02 teraflops, is the most powerful computer available to the U.S. academic community and the world's tenth most powerful computer.

New Chlorine Chemistry

- **New Cl Chemistry:**
  - **12 additional gas-phase species**
  - **83 additional gas-phase reactions**
    - » **Includes oxidation of VOC's by $Cl^{\bullet}$**

  - **Heterogeneous reactions:**
    - » $OH^{\bullet} + Cl^{-}$? $\frac{1}{2} Cl_2 + OH^{-}$
    - » $N_2O_5 + Cl^{-}$? $ClNO_2 + NO_3^{-}$
    - » $ClONO_2 + Cl^{-}$? $Cl_2 + NO_3^{-}$
    - » $(NO_3^{\bullet} + Cl^{-}$? $\frac{1}{2} Cl_2 + NO_3^{-})$



$Cl^{\bullet}$ Radicals

  - JPL & IUPAC recommendations were considered. However, results from uptake studies on solid salts, salt powders and fresh synthetic sea-salt aerosol are not easily transferable to urban airshed models.

  - **New model for sea-salt aerosol emission at coastal surf zone**
    - » ***de Leeuw and coworkers***

Source Functions for Sea-Salt Aerosol

- **Monaham *et al.*, 1986 open ocean source function.**
  - **Used in global models, e.g. Gong *et al.*, 1997 and Erickson *et al.*, 1999.**

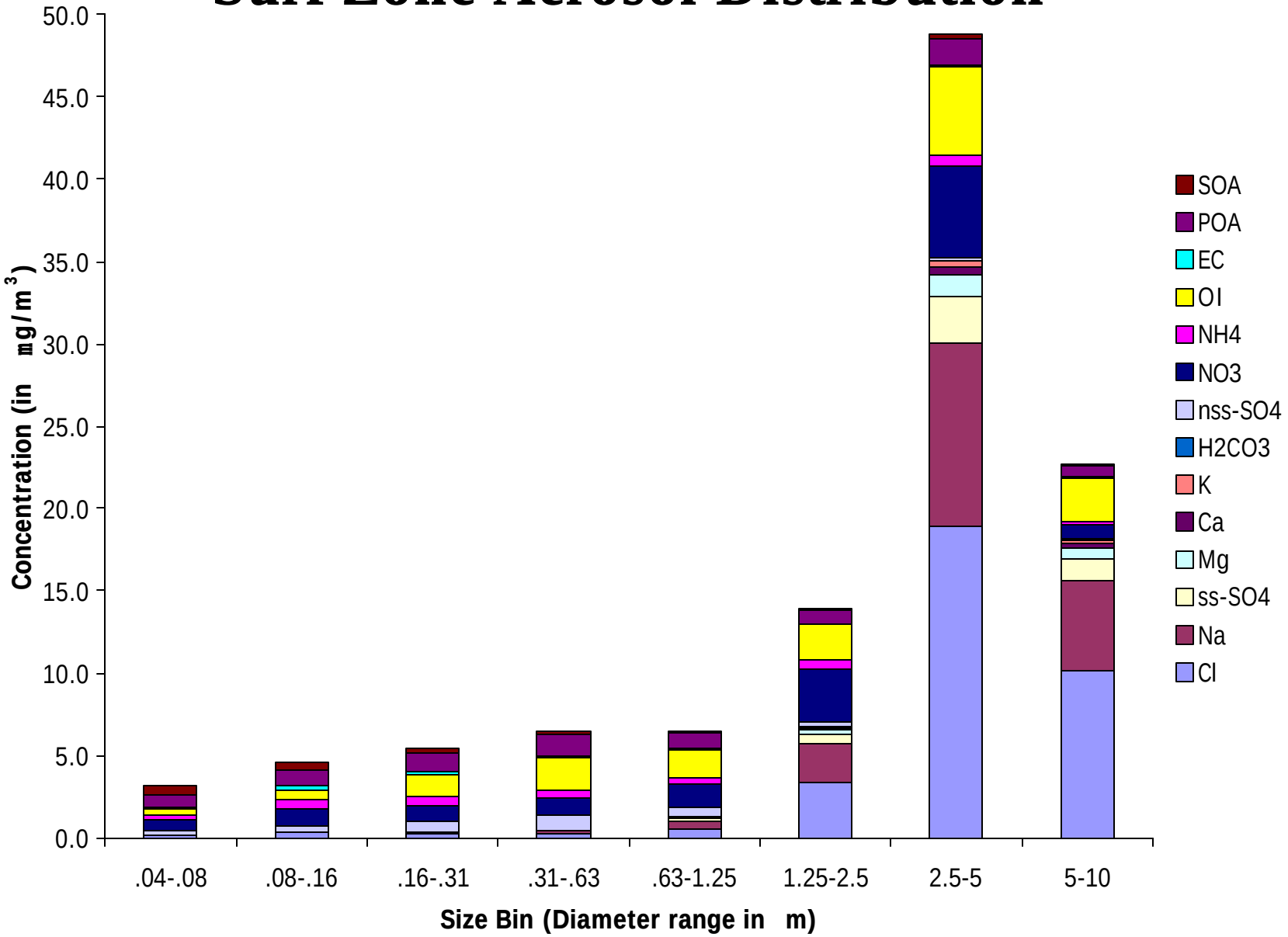
- **De Leeuw *et al.*, 2001 surf zone source function.**

$$\frac{dF_{N-Surf}}{dD_0} = 1.1\times10^7 \times e^{0.23\times U_{10}} \times D_0^{-1.65}$$

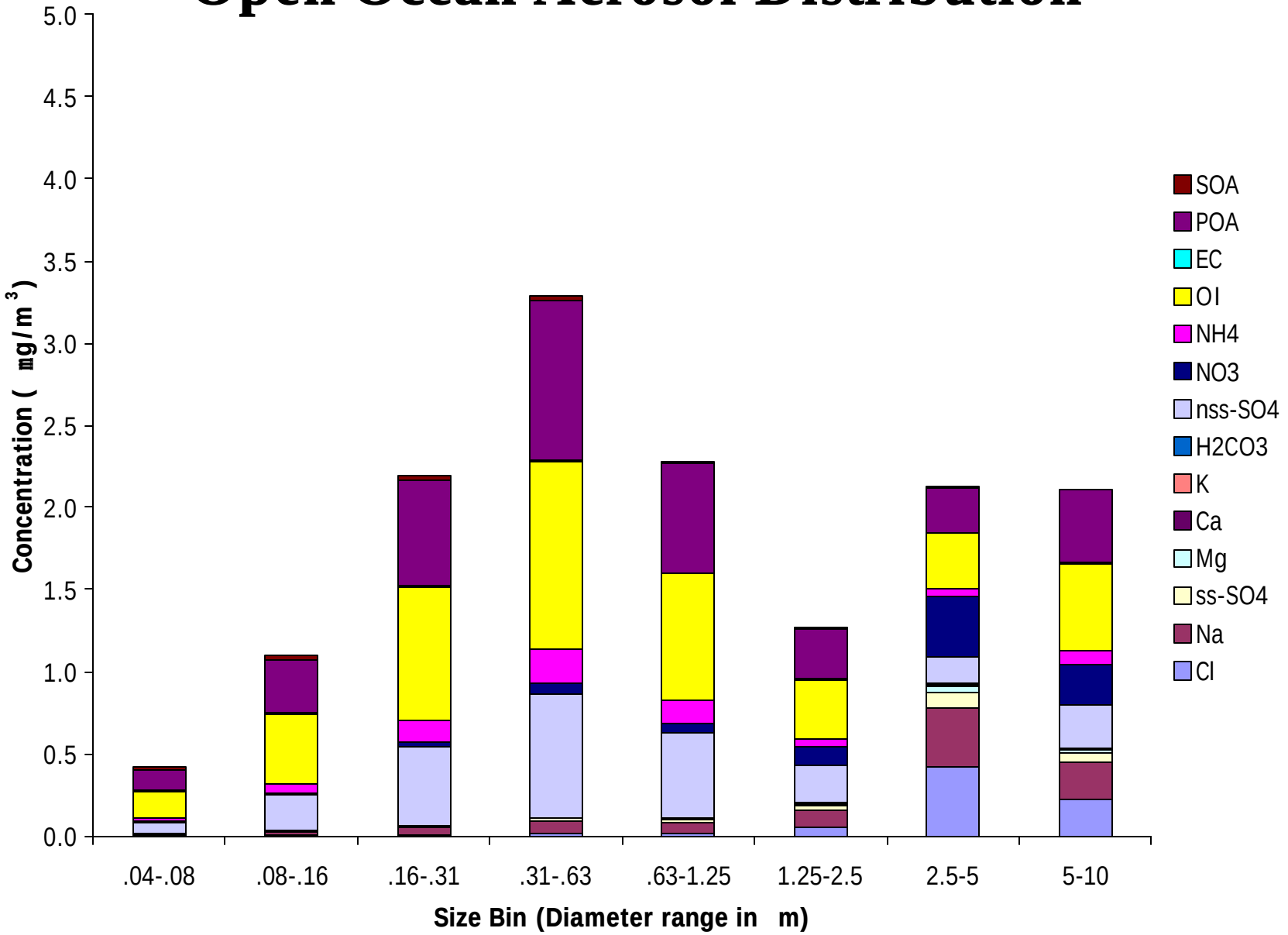
  - **Developed from measurements in La Jolla, CA and Monterey, CA.**
  - **Assuming 231 km of coast and 100m wide surf zone.**

- **Source function defined for particle diameter at formation.**
  - $D_0 = 2\ D_{80} = 4\ D_{dry}$
  - **A 10 micron particle will settle from the TOP of the lower model layer (12.98m) in ~ 1 hr .**

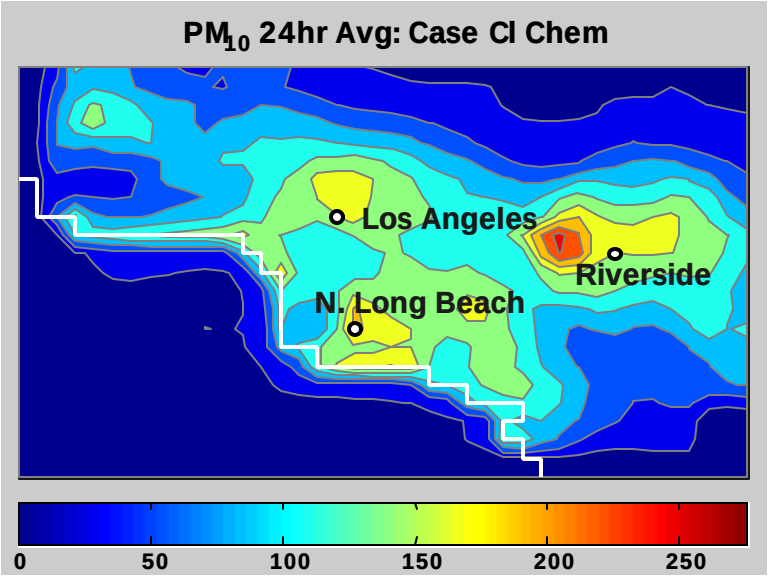
Surf Zone Aerosol Distribution

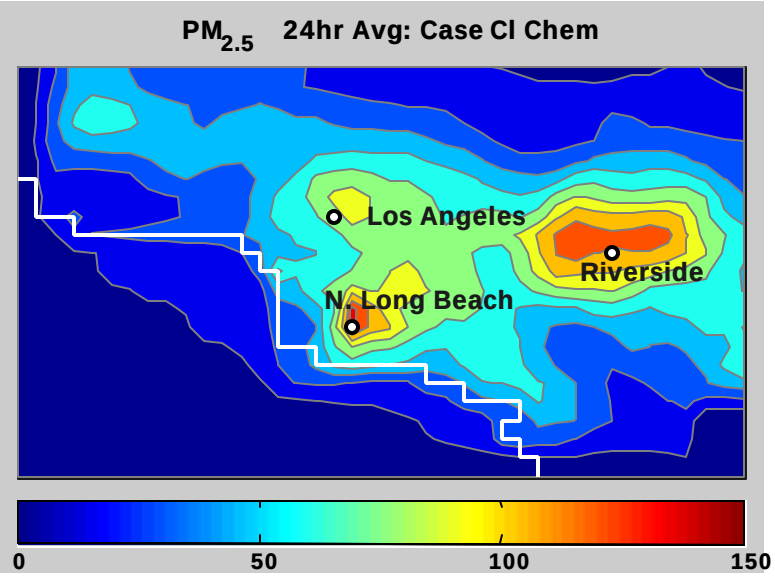


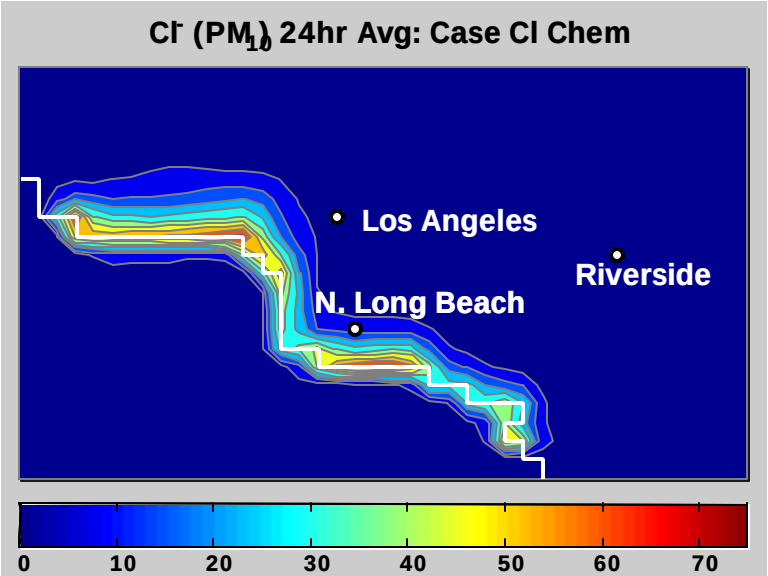
Open Ocean Aerosol Distribution

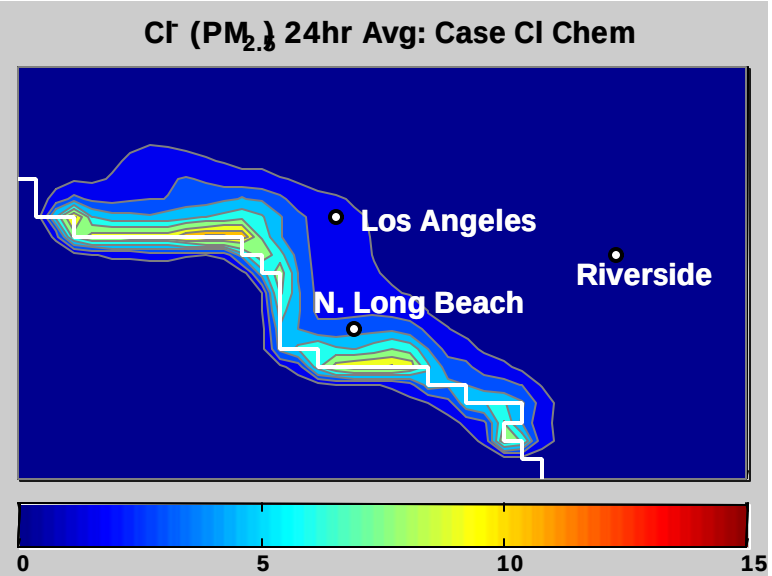


24-hr Average PM Contours: Friday, September 9, 1993



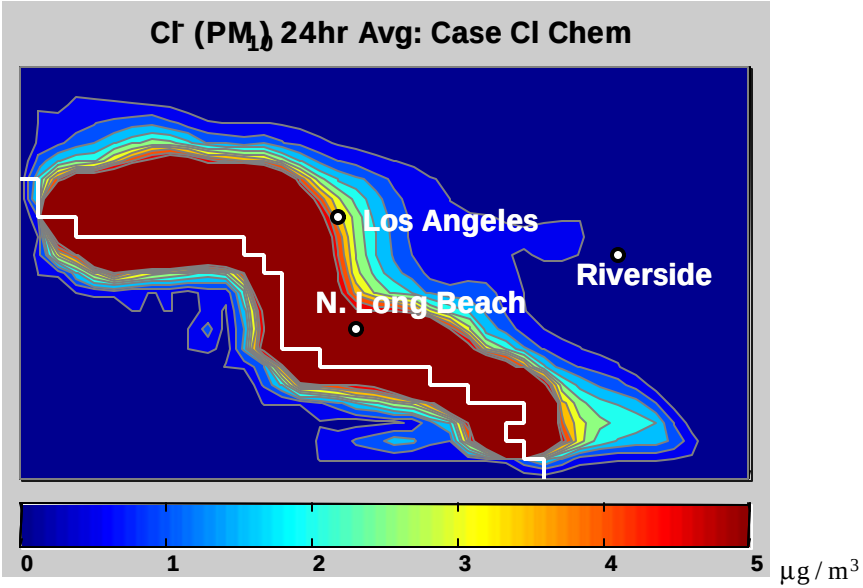


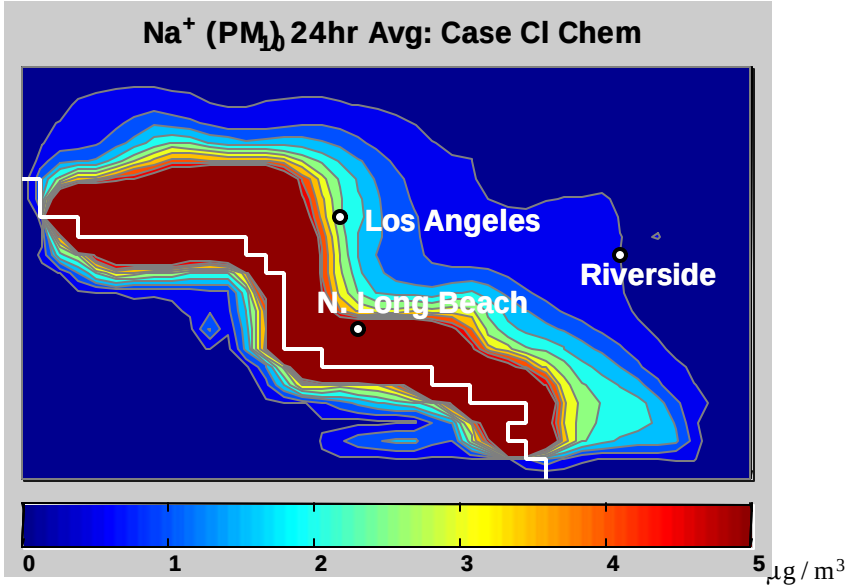




all units in $\mu g / m^3$

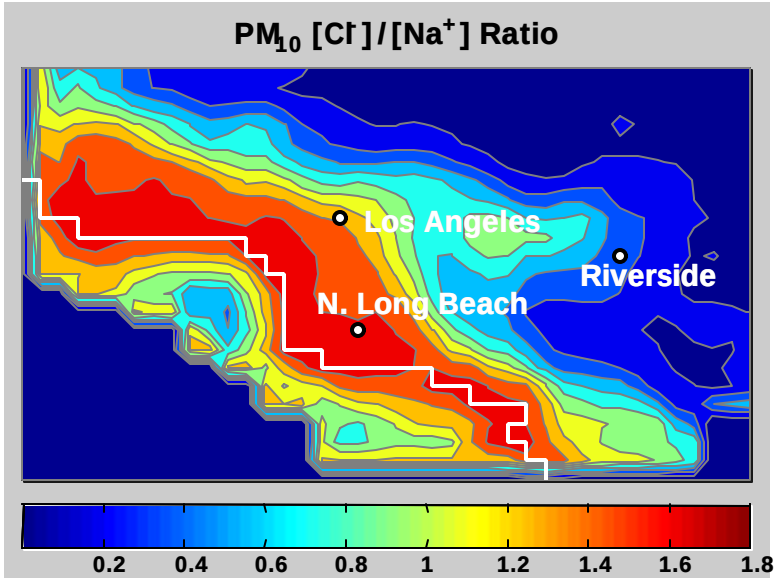
24-hr Average PM Contours: Friday, September 9, 1993





Chloride deficits are predicted due to hydrochloric acid displacement.

Most sea-salt particles settle quickly and do not reach inland regions.



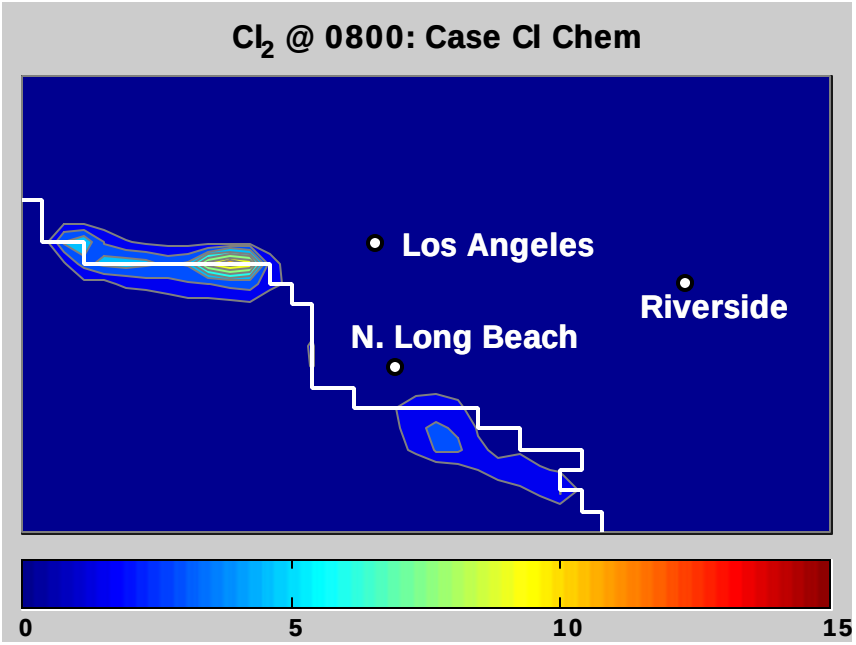
Comparison of 24-hr Average Sodium Concentrations

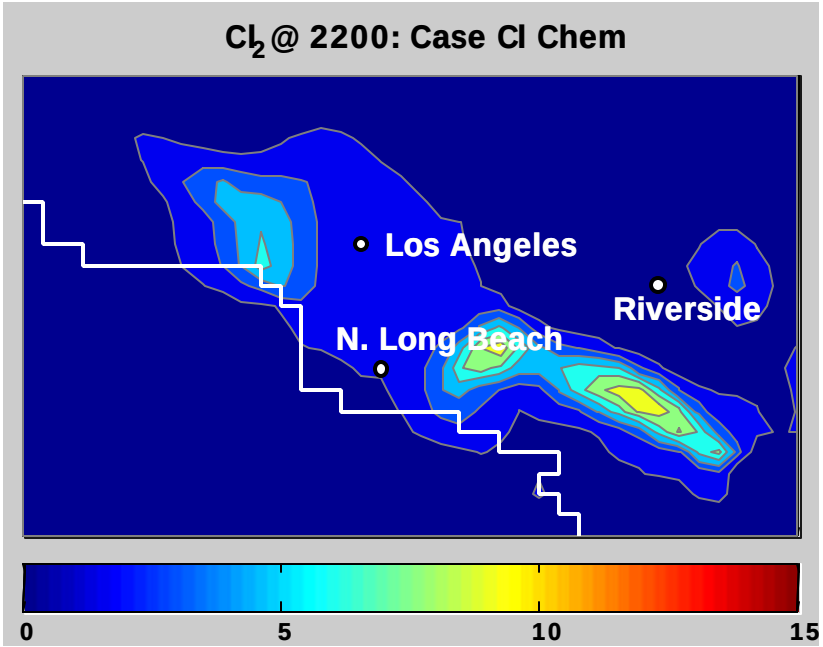
Friday, September 9, 1993

	Long Beach		Claremont	
	$PM_{2.5\text{-sodium}}$	$TSP_{\text{-sodium}}$	$PM_{2.5\text{-sodium}}$	$TSP_{\text{-sodium}}$
Observed	0.50	3.11	0.64	1.09
		$PM_{10\text{-sodium}}$		$PM_{10\text{-sodium}}$
Modeled	0.91	2.65	0.28	0.62

(all units in µg/m$^{3)}$

Cl_2 Contours: Friday September 9, 1993

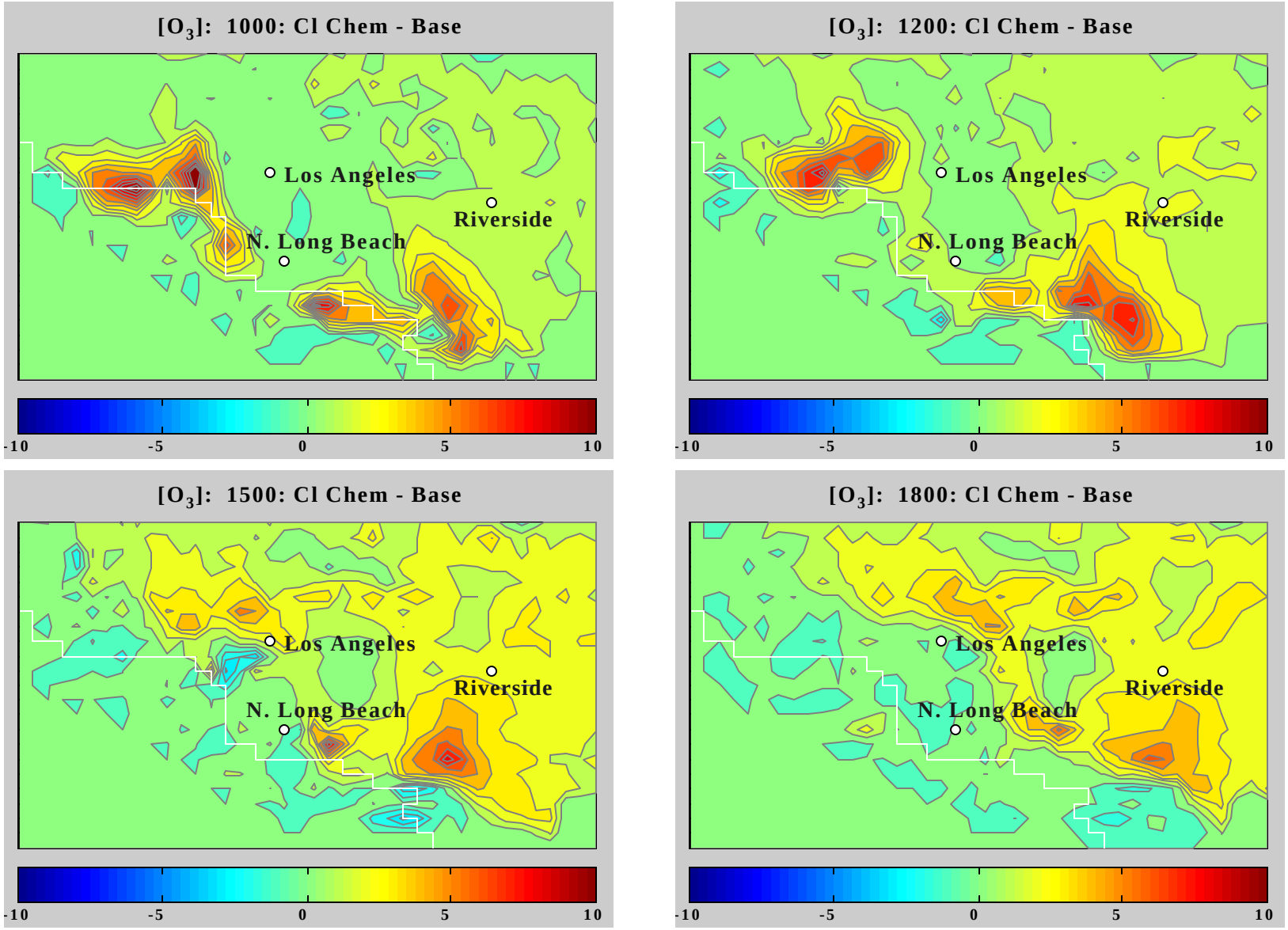




Cl_2 levels reach up to 12 ppt – a thirty fold improvement over the simulations of Spicer *et al.*, albeit an order of magnitude below observations.

all units in ppt

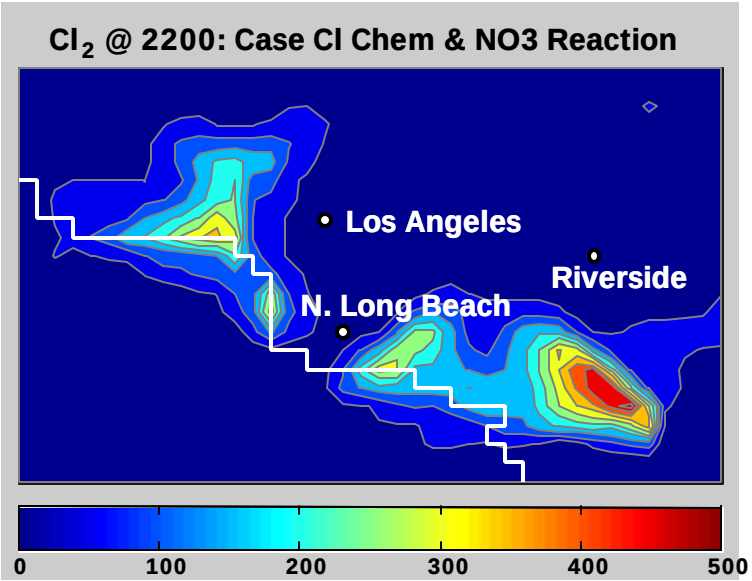
DO_3 Contours: Friday, September 9, 1993

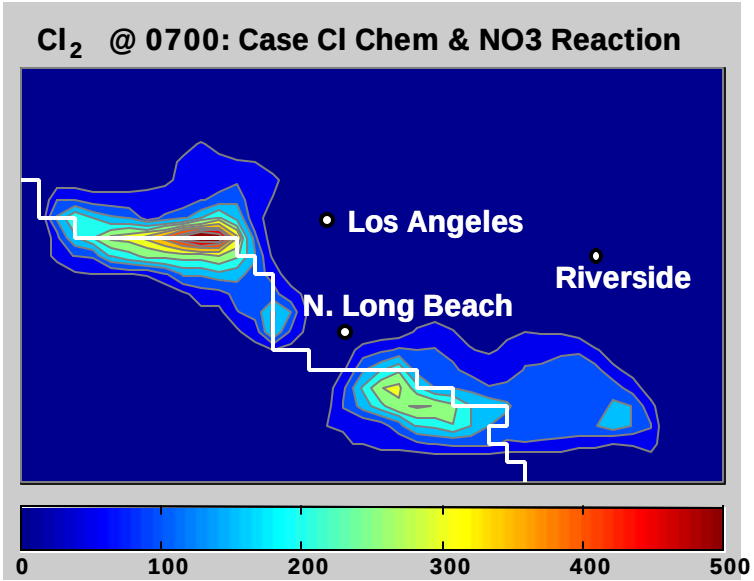


all units in ppb

Cl_2 Contours: Friday September 9, 1993

adding nighttime chlorine production



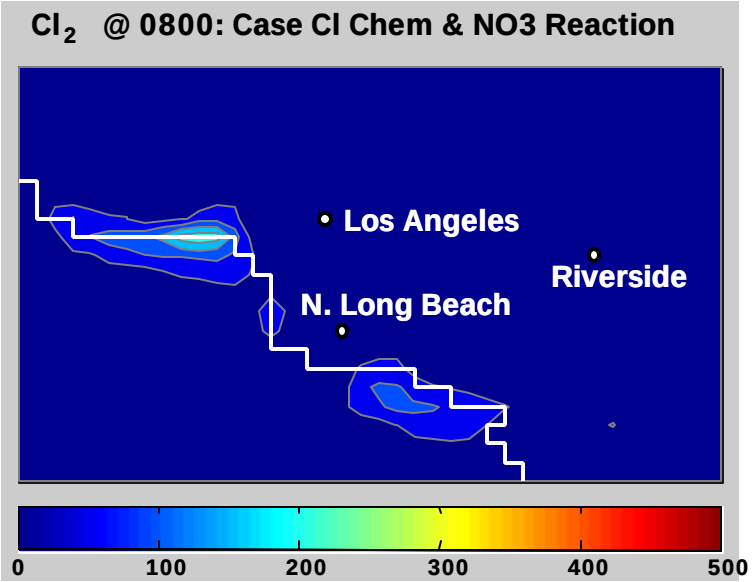


Cl_2 concentrations are on the order observed by Spicer *et al.* and Keene *et al.* …

all units in ppt

Cl_2 Contours: Friday September 9, 1993

adding nighttime chlorine production

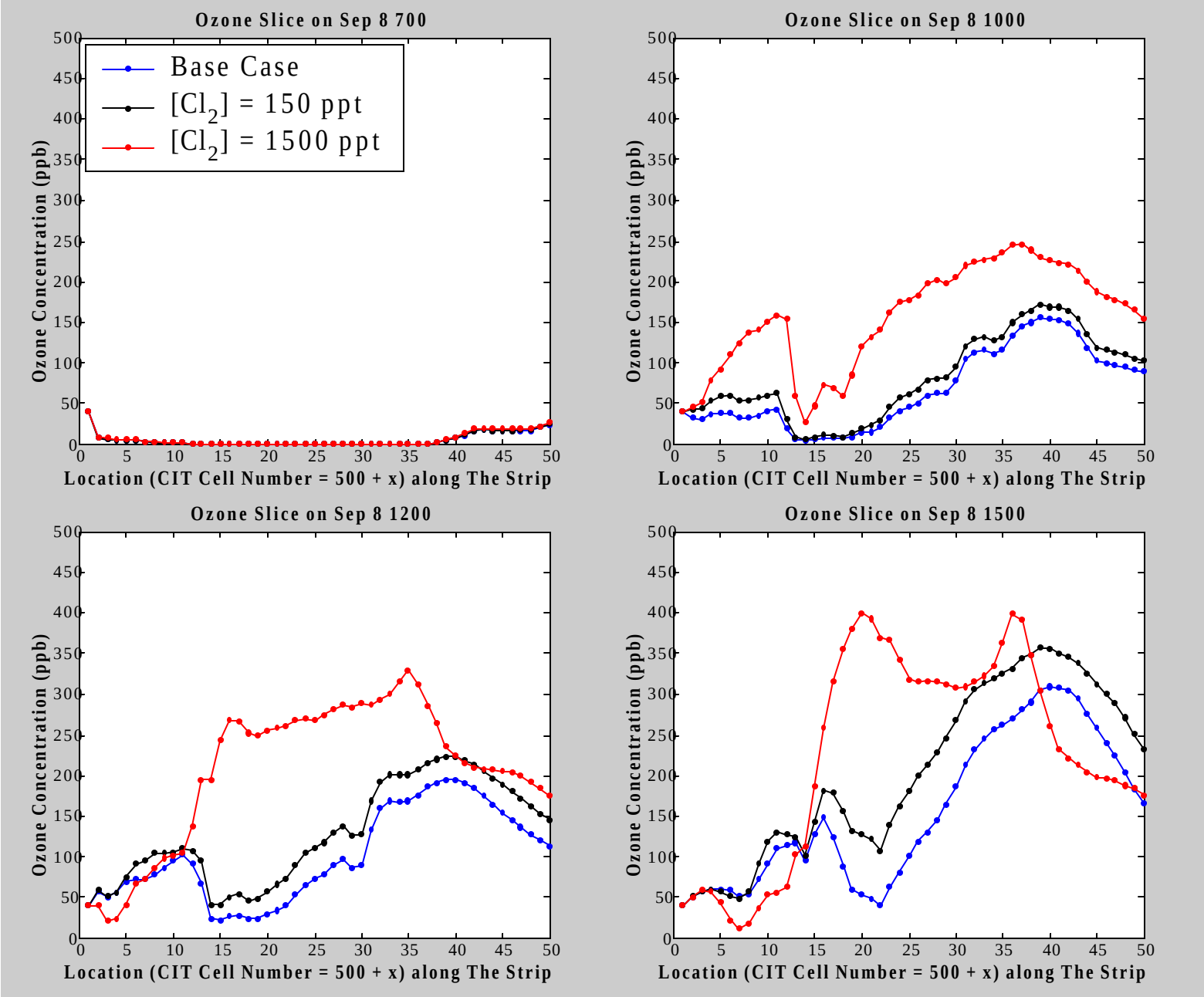


… however, photolysis of NO_3 and Cl_2 at dawn cause Cl_2 concentrations to drop rapidly.

Cl concentrations similar to the Case Cl Chem simulation are predicted and D[O_3] are only slightly different than in previous slides.

all units in ppt

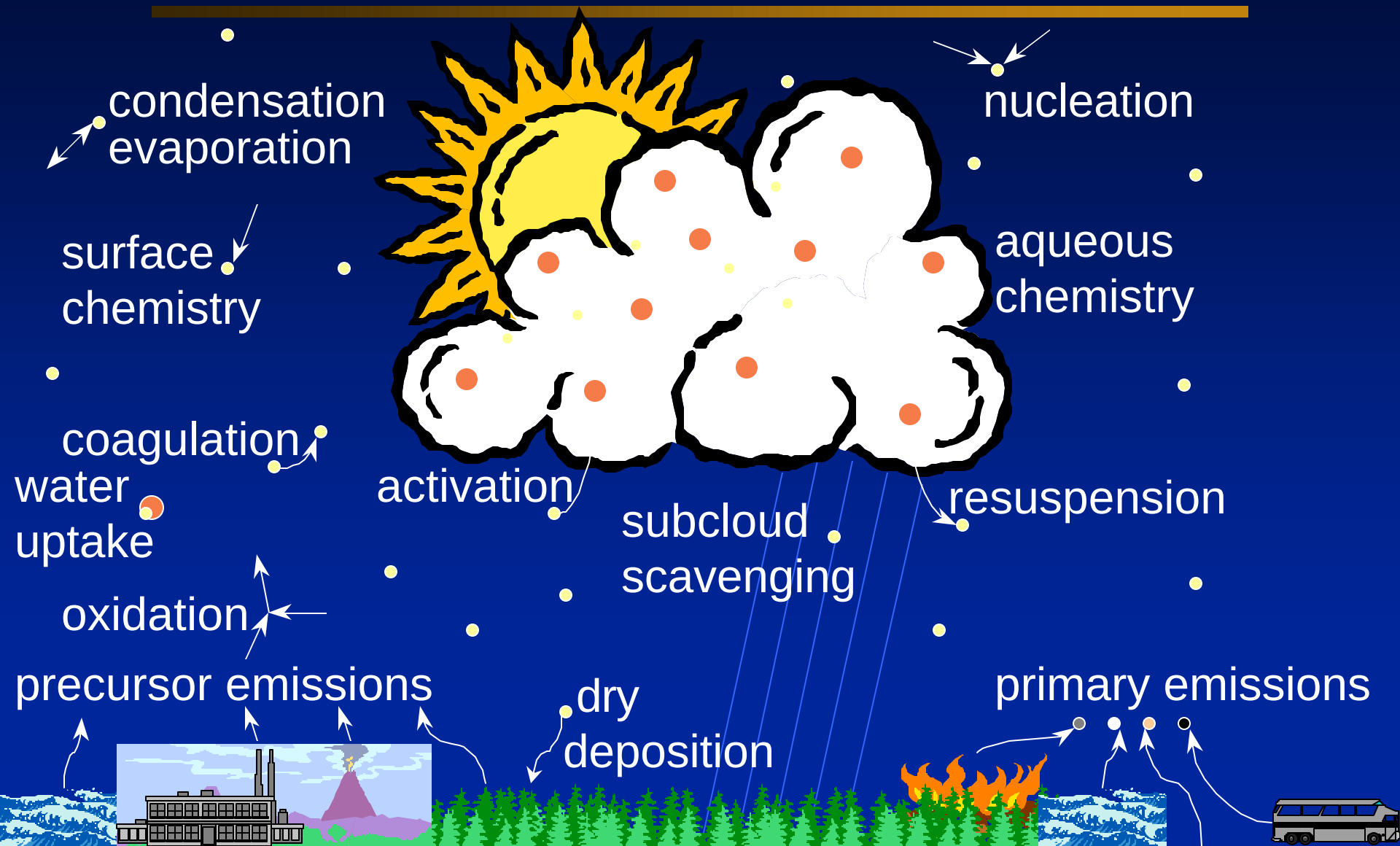
O_3 Contour Slices along "The Strip"



Conclusions

- Modeling results adequately reproduce regional sea-salt particle concentration
- Chlorine levels in the model are predicted an order of magnitude below observed values, albeit 30 times better than previous studies.
- Inclusion of sea-salt derived chlorine chemistry may increase:
  - morning ozone predictions by as much as ~12 ppb in coastal regions
  - peak domain ozone by ~ 4 ppb in the afternoon
- Most monitoring sites experience an increase:
  - in peak ozone concentration of 2-4 ppb
  - even higher ozone increases, up to 7 ppb, at times not coinciding with the peak
- These particular heterogeneous/multiphase chemical reactions do not affect the rate of hydrochloric acid displacement nor do they enhance aerosol nitrate formation

Aerosol Processes



Acknowledgements

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  Air Resources Board of California

  U.S. National Science Foundation

  U.S. Environmental Protection Agency

  Organization of American States

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