Study of the Sensitivity of Air Masses to Emission Controls Using The IER- REACTIVE MODEL

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CCOS CORROBORATIVE ANALYSIS WORKSHOP

By

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Commonwealth Scientific and Industrial Research Organisation (CSIRO) - Division of Energy Technology Australia

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WHO WE ARE and WHAT WE DO

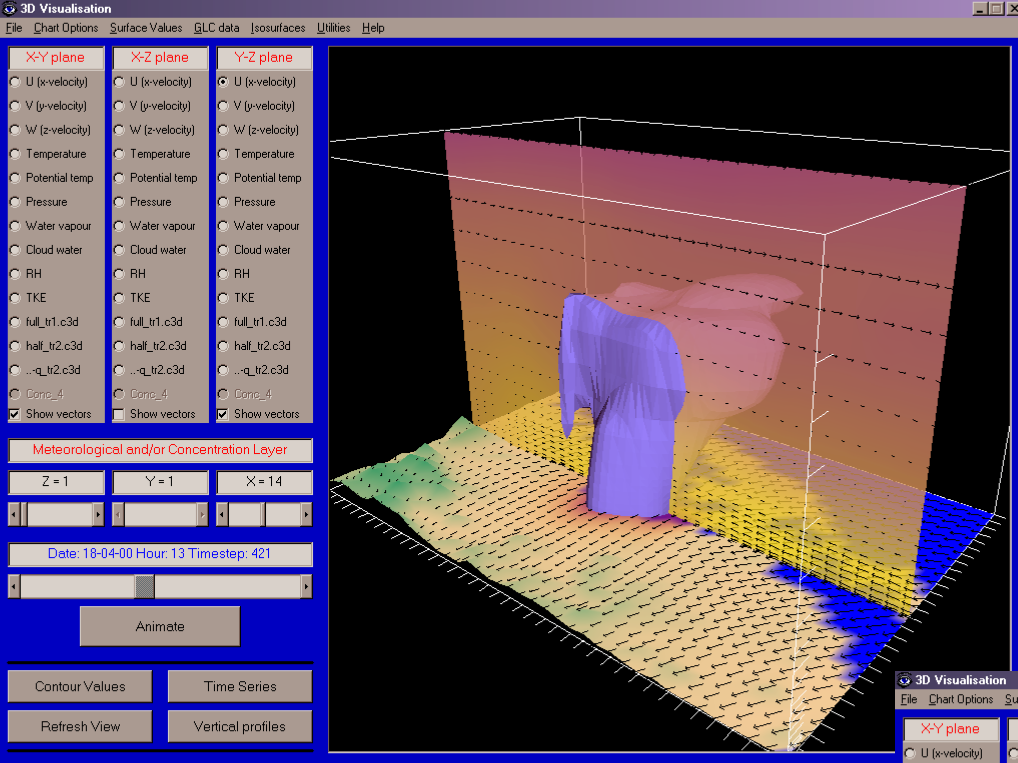
- Provide Science underpinnings for Environmental Issues from Energy Sources
- Development and application of new tools and technologies for the assessment and management of contaminants from the energy, minerals and other urban and industrial activities

‘Clean air’ skills

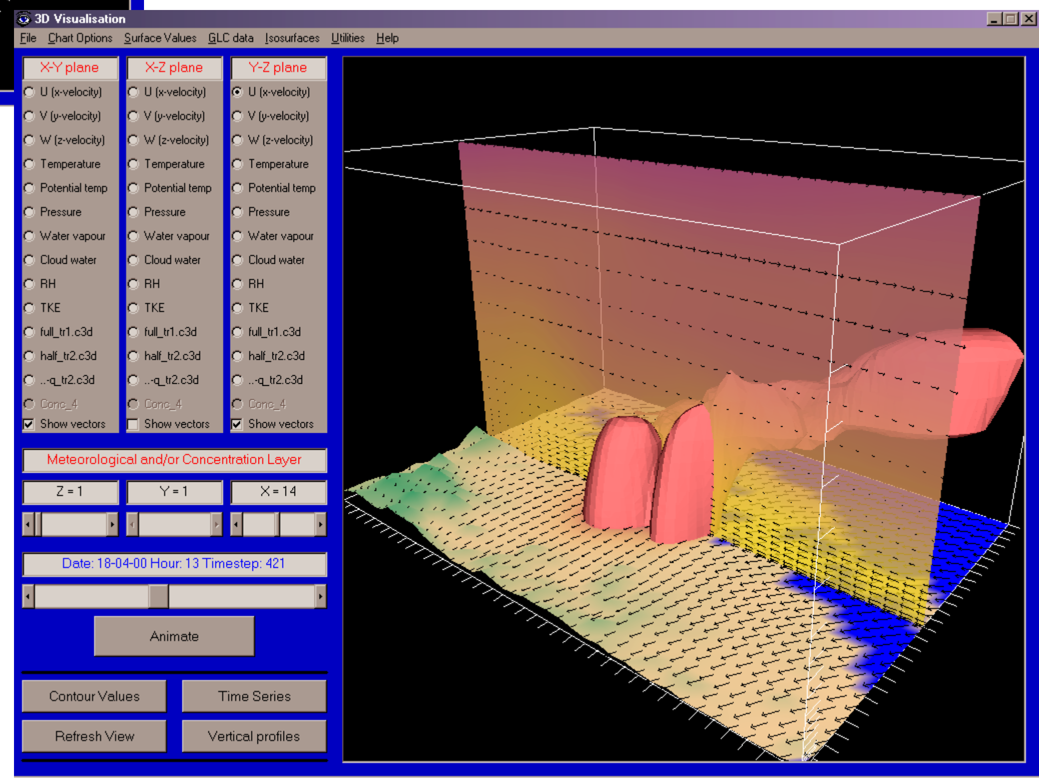
- Air process studies
- Fine particle characterisation
- Air toxics analysis, including organics and inorganic (e.g. mercury)
- Air quality modelling
- Greenhouse gas emissions - from coal mining and other sources
- Gas cleaning research- improved fabric filtration, electrostatic precipitation
- Trace element analyses

Plume Impact: Hour_13

Eraring



Vales Pt

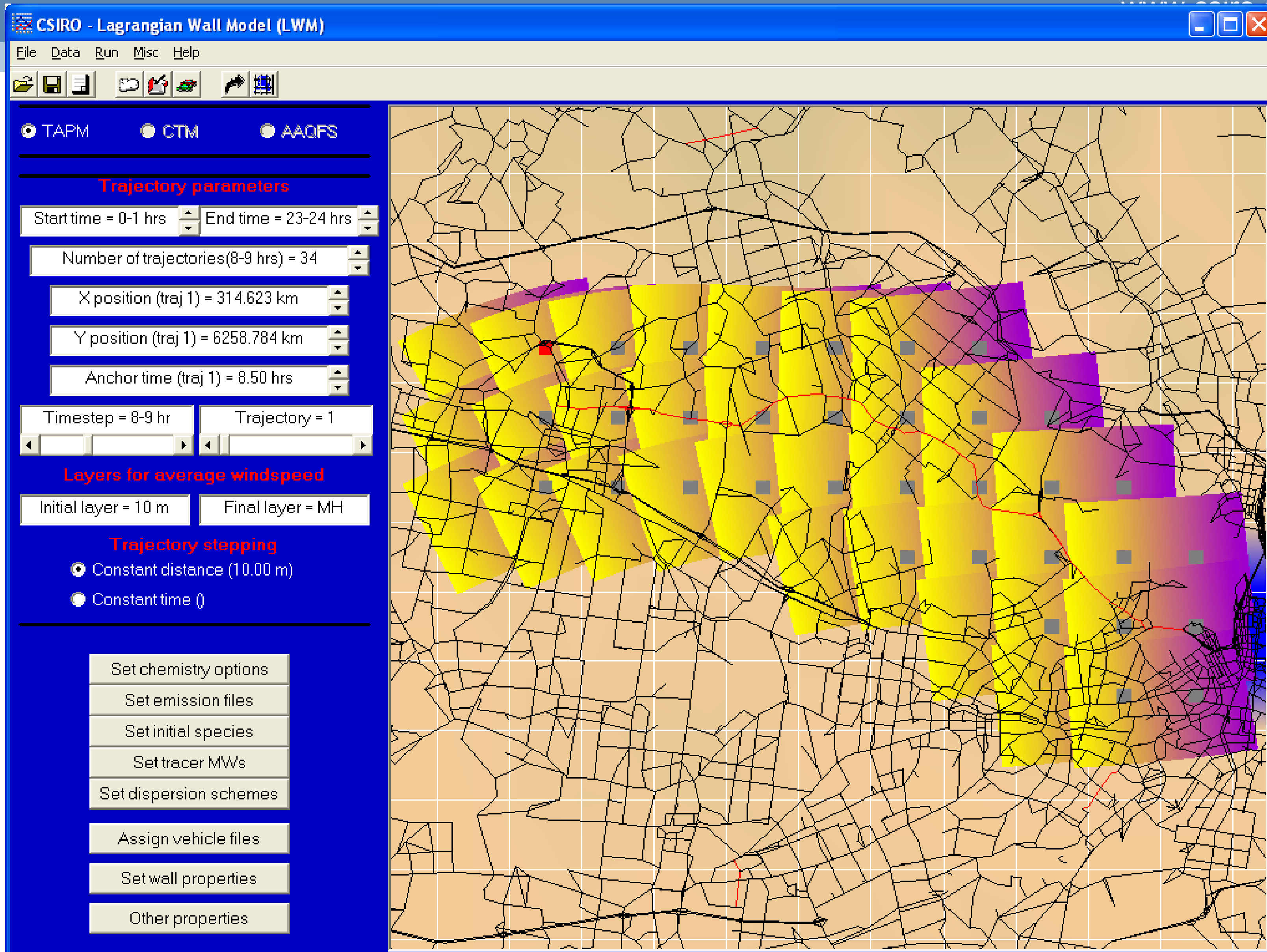


Lagrangian Wall Model

Very high resolution impacts and source reconciliation over short or extended periods.

Custom definable tracer and complex chemistry modes

Multi overlapping walls for exposure modelling



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Impact of VOC/NOx Chemistry

- Sensitivity to emission reduction
  - VOC sensitive, NOx sensitive, or both
- VOC reactivity
  - depends upon chemical nature: reaction rate, radical yields, products
- NOx suppression or inhibition
  - if ozone is highly VOC sensitive, NOx reduction may incur disbenefits
  - two mechanisms operative
    - (1) direct titration (or scavenging) of ozone by fresh NO emissions
    - (2) scavenging of radicals by NO_2 inhibits ozone production

Related Issues

- What is the fate of HC oxidation products and their contribution to the regional scale OH, HO_2 and RO_2 budgets
  - How does VOC reactivity change with downwind urban plume
  - Is there a unique chemical species that can be used to assess photochemical progress within a given plume
  - How much potential for O3 production remains in a given air parcel, and does it compare with the initial O3 production

Gas Phase Issues

- Can we identify a specific chemical signature for different urban plumes?
  - Can observed data be used to track a selected plume
  - Is there a unique chemical species that can be used to assess photochemical progress within a given plume
- Can we explain the rapid formation of ozone formation events?
  - Inventory, chemical reactions or both?

Environmental chamber studies

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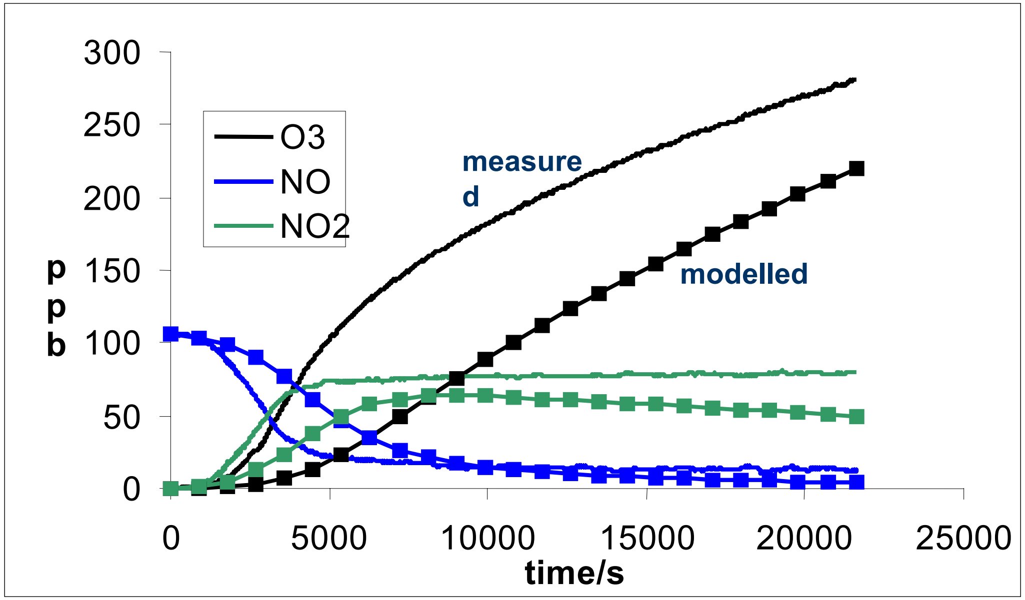
Photodecomposition of unleaded petrol-ethanol headspace vapour + NO



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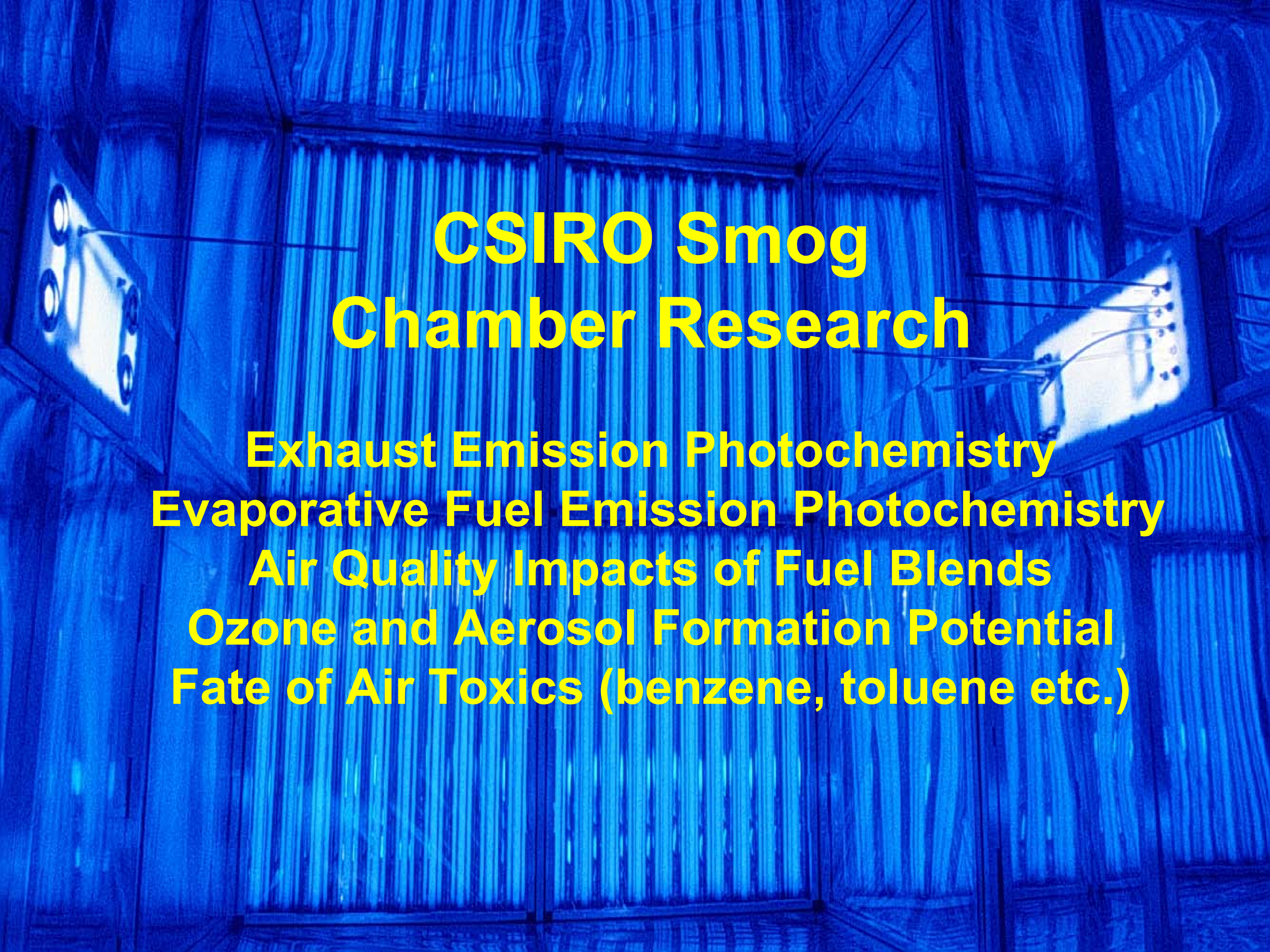


CSIRO Smog Chamber Research

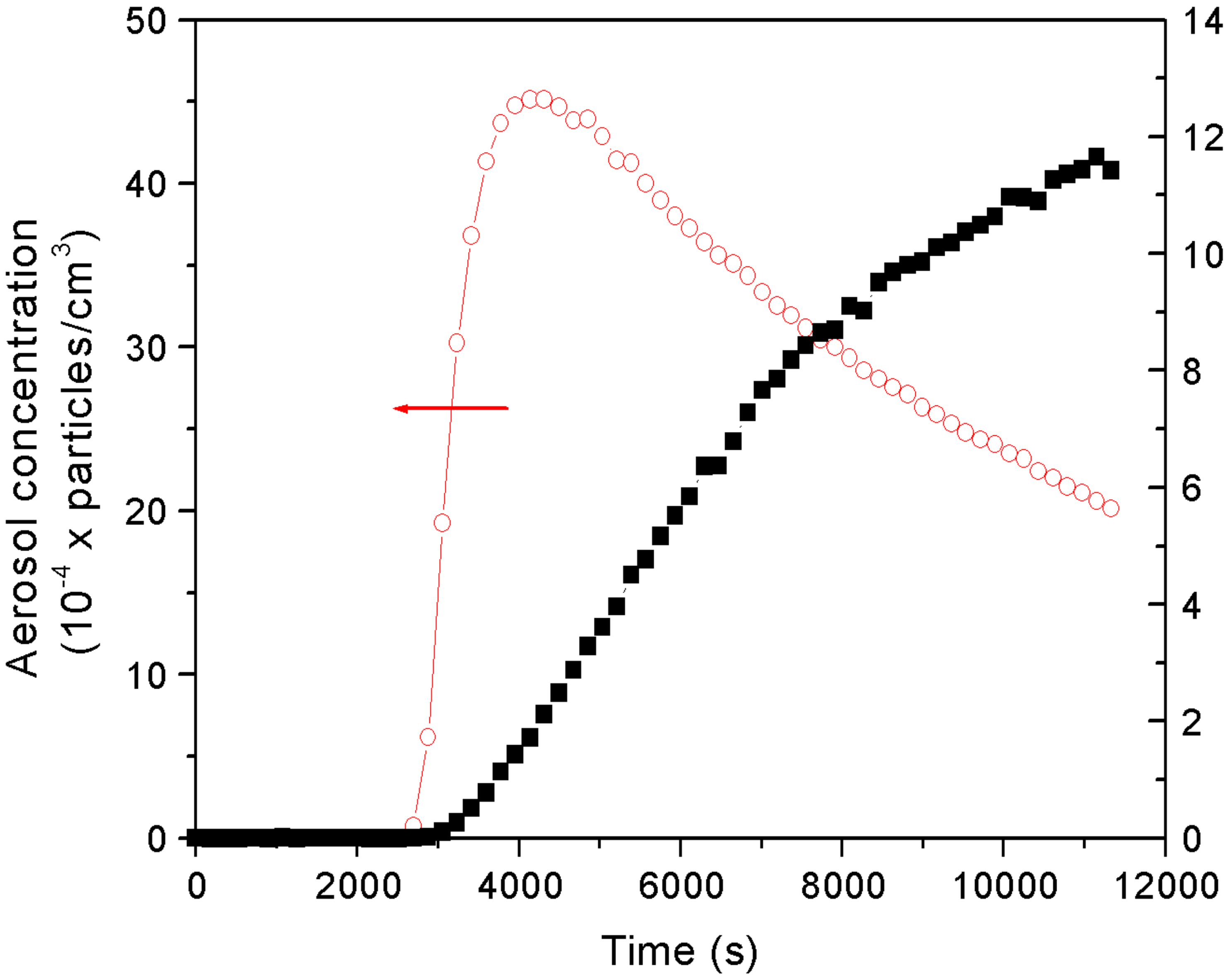
- Exhaust Emission Photochemistry
- Evaporative Fuel Emission Photochemistry
- Air Quality Impacts of Fuel Blends
- Ozone and Aerosol Formation Potential
- Fate of Air Toxics (benzene, toluene etc.)

Smog Chamber Facility

- Study of the chemical basis for O3, NO2 and aerosol formation.
- Provide necessary data to develop and test chemical mechanisms for different range of ambient conditions
- Evaluation of atmospheric impacts of using different types of fuels on ozone formation
- Identification of the appropriate chemical reaction paths for ozone and SOA formation

SOA formation in the 1,3-butadiene system (E52)

$[C_4H_6]$ = 1000 ppb, $[NO_x]$ = 1100 ppb, J_{NO_2} = 0.83 min^{-1}



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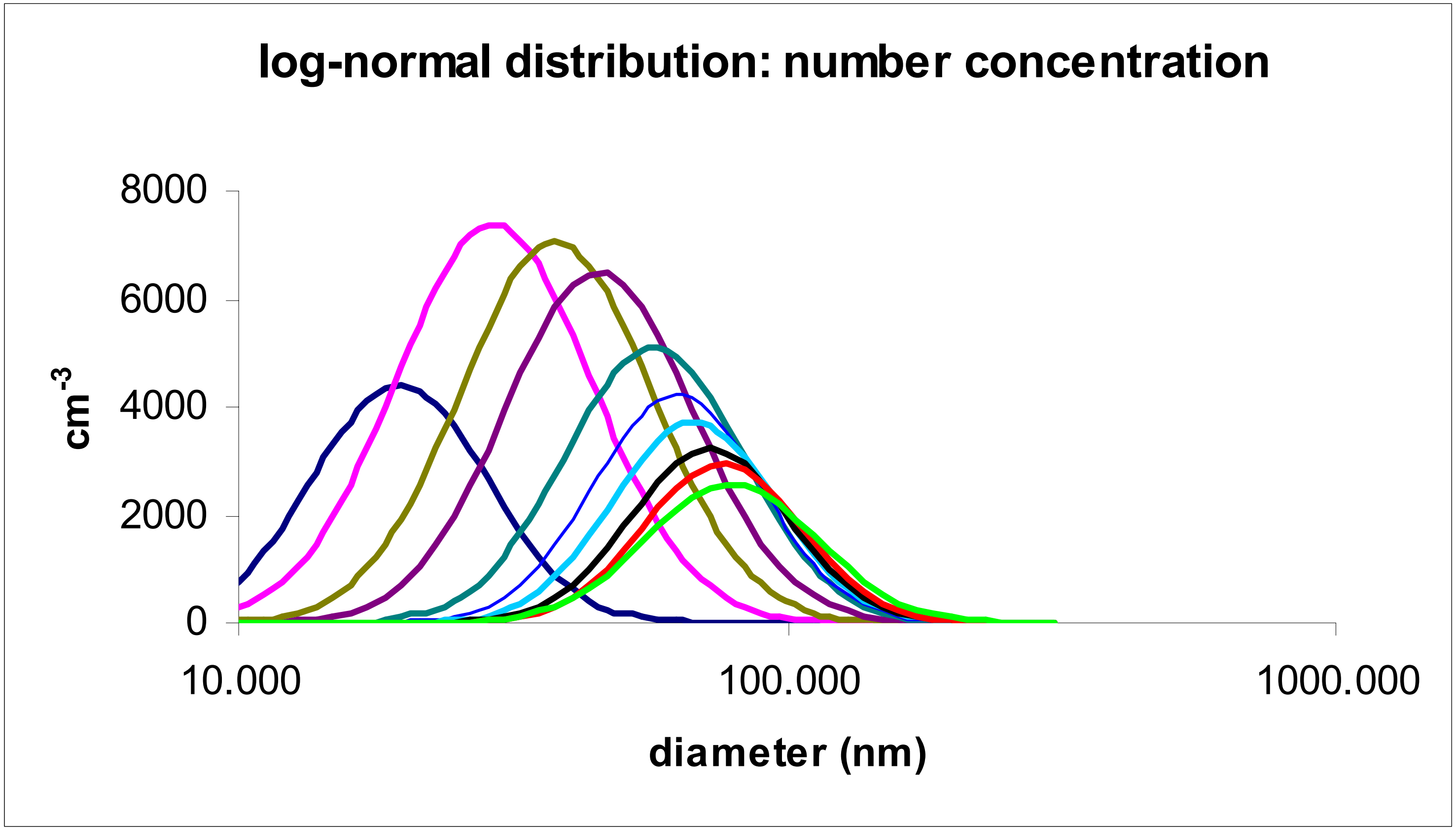
Aerosol Size Distribution



Future Emissions Control Scenarios

Possible “variables” include

- species/emissions type (e.g., VOC, NO_x, CO)
- amount of emissions reduction (depend on the type of selected industry)
- general category (e.g., low-level, elevated, anthropogenic)
- source category (area, motor-vehicle, non-road, elevated or low-level point)
- geographical area (e.g., domain, region, states, counties, grid cells)
- time period (e.g., weekday only, weekend only, daytime, nighttime)

Future Emissions Control Scenarios

Emission-sensitivity simulations provide information about

- sensitivity of the model/episode to different levels and types of emission reductions
- amount, type, source, and geographical distribution of reductions that reduce ozone, NO_2 and aerosols

Emission-sensitivity simulations used to guide the development of "real-world" control strategies

GRS1=7 reactions, GRS2=22 reactions, CBIV=89 reactions

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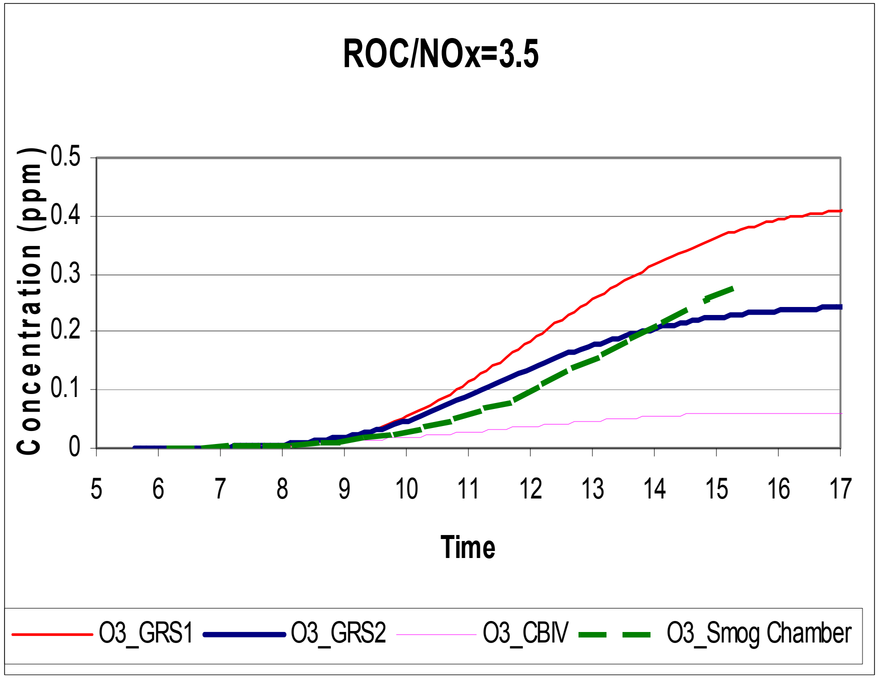

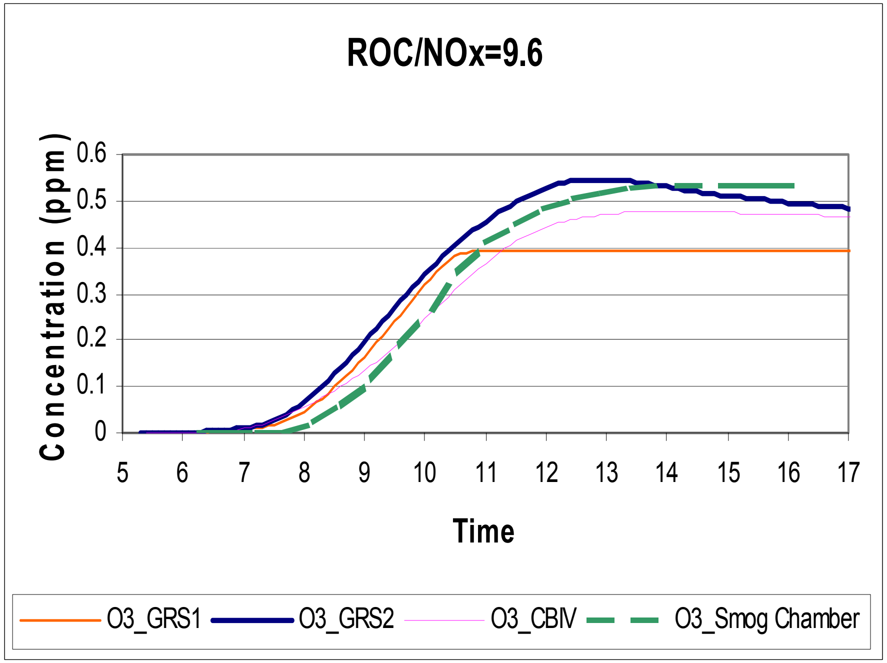

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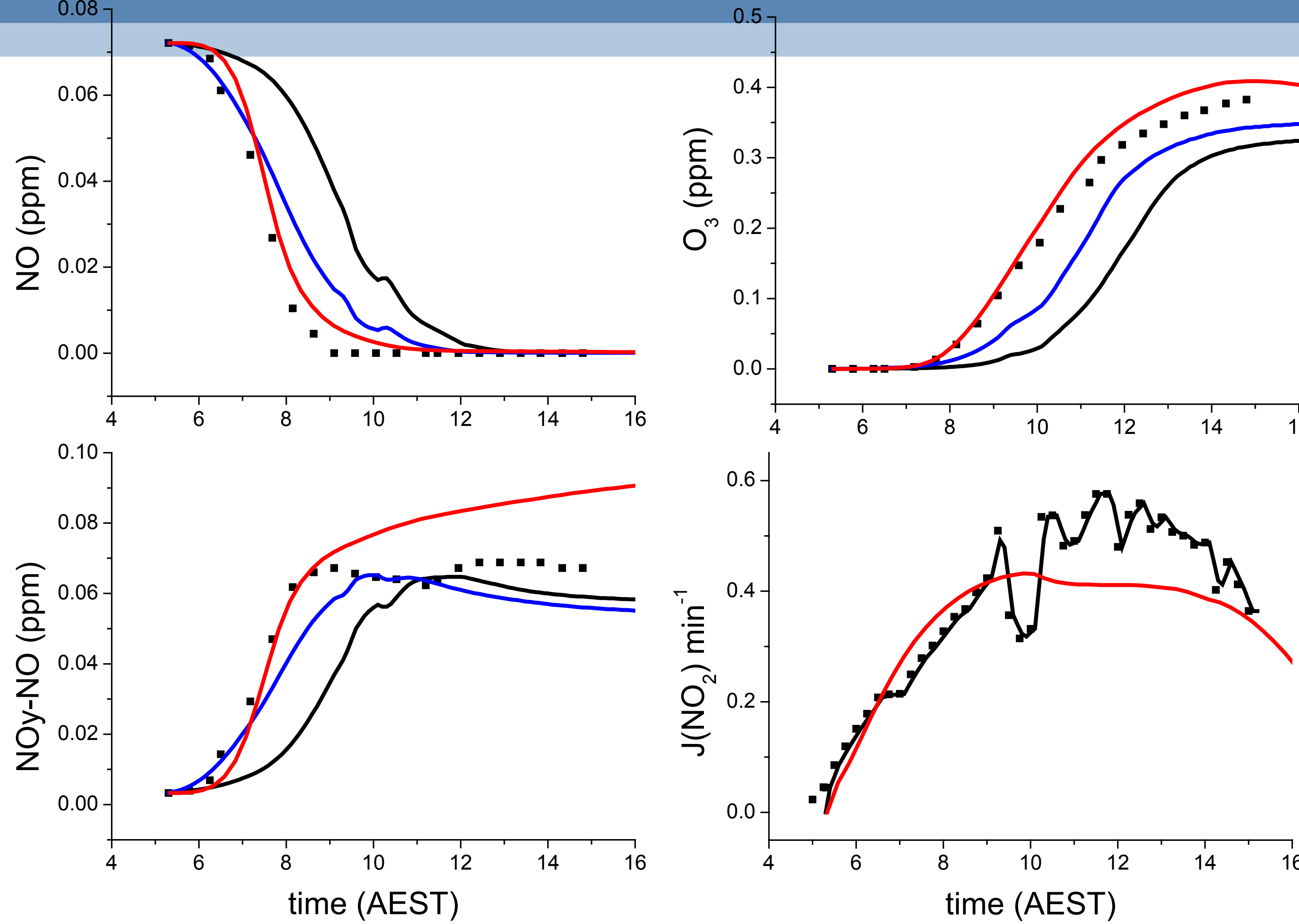
Test 1: VOC/NOx = 15



■ : experiments; ▬ CBIV with initial HONO = 2 ppb ; ▬ CBIV with initial HONO = 2 ppb + 2 ppb/hour emission ; ▬ SAPRC-99 predictions

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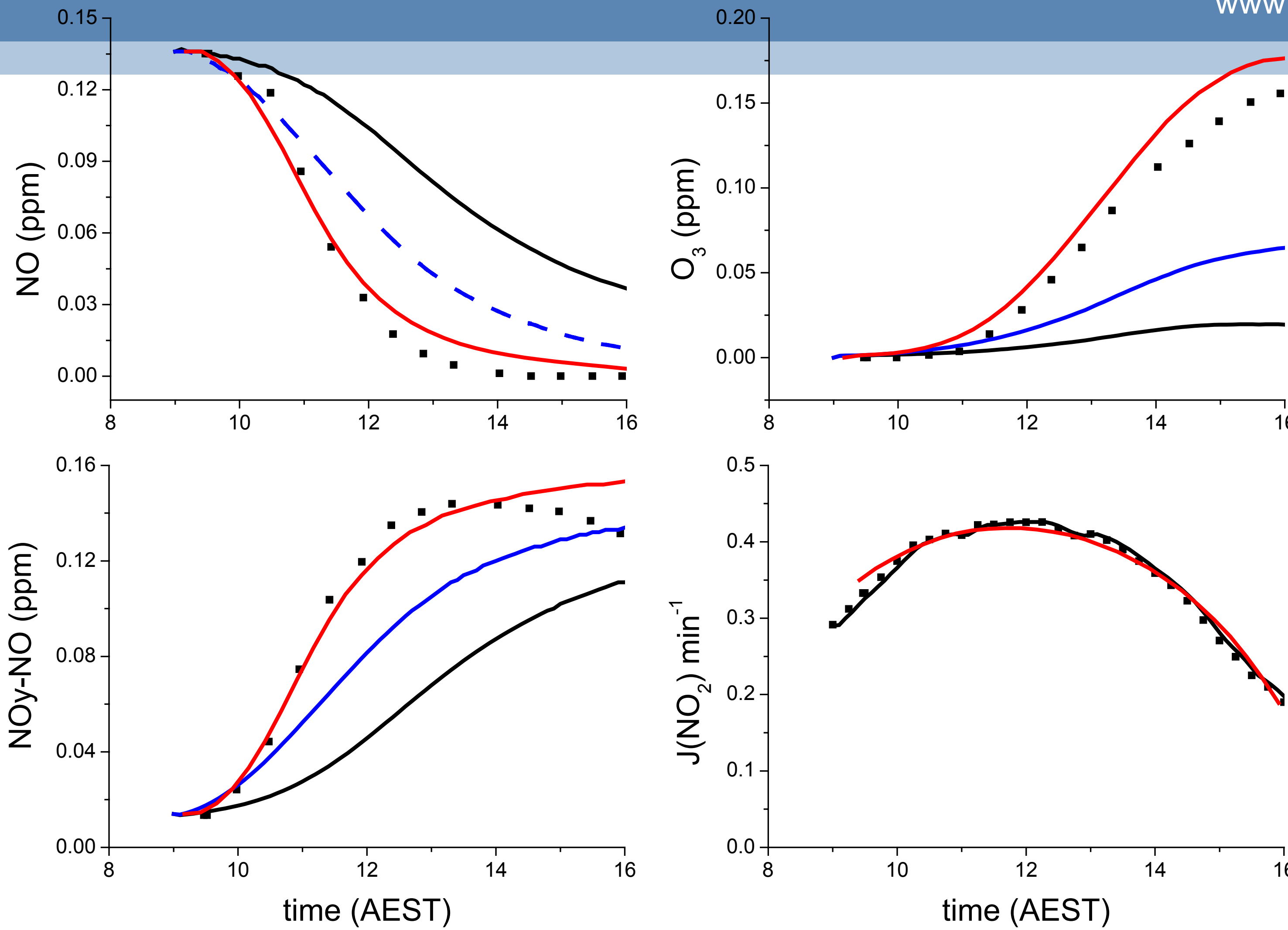
Test 2: VOC/NOx = 8



■ : experiments; ▬ CBIV with initial HONO = 2 ppb ; ▬ CBIV with initial HONO = 2 ppb + 2 ppb/hour emission ; ▬ SAPRC-99 predictions

Test 3: VOC/NOx = 3.5

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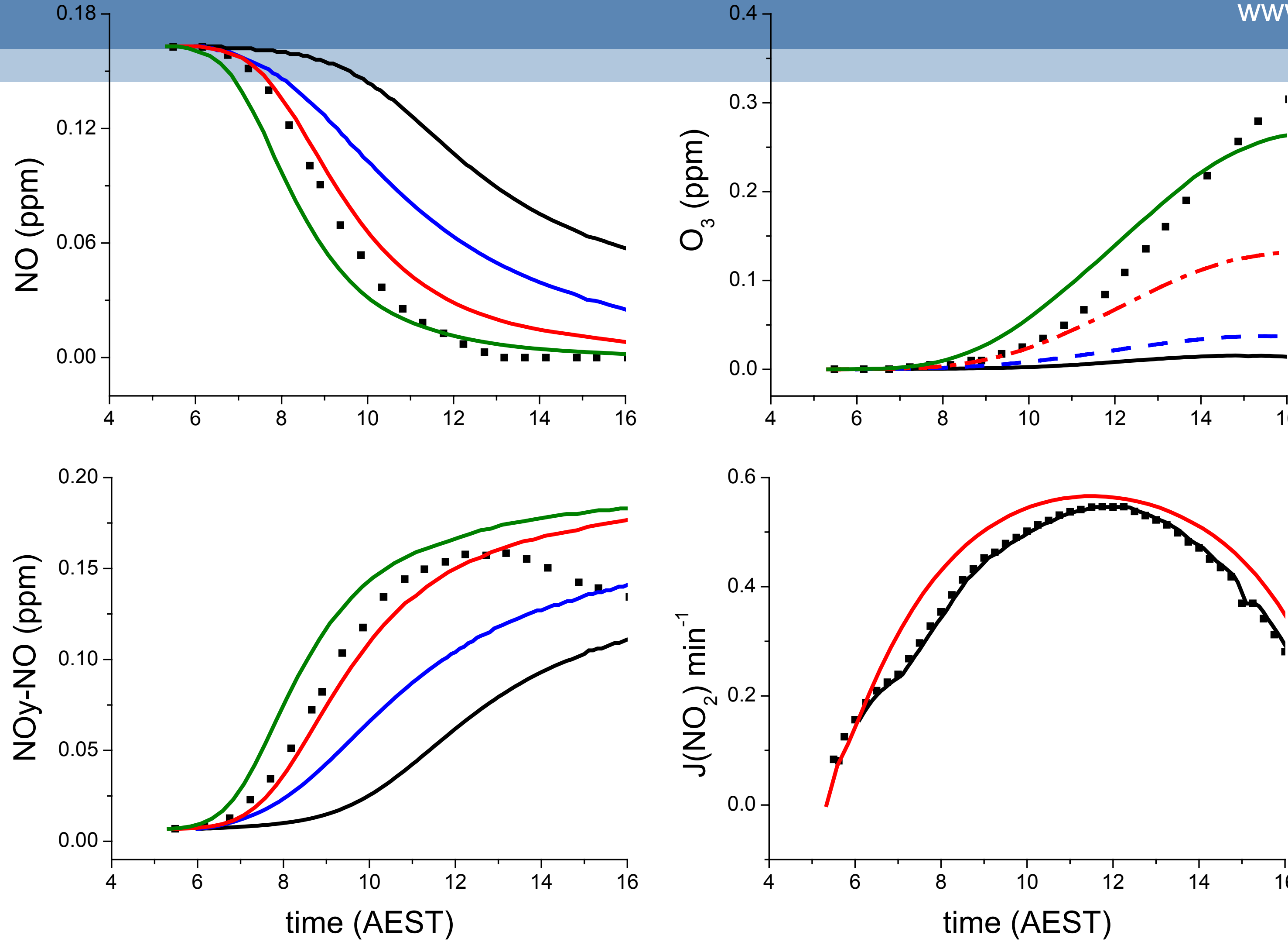

■ : experiments; ▬▬ CBIV with initial HONO = 2 ppb ; ▬▬ CBIV with initial HONO = 2 ppb + 2 ppb/hour emission ; ▬▬ SAPRC-99 predictions
▬▬ SAPRC-99 with large light + wall → OH rate.

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- For each chemical mechanism we need to know :

  - The distribution of the percentage of error associated with each ROC/NOX ratios .

  - These errors should be taken into account when calculating the final results.

IER Model " SP Model"

Using the CSIRO Smog Chamber

- Three regimes of Photochemical smog production
  - Hydrocarbon Regime (SP proportional to VOC reactivities)
  - Transition regime
  - NOx-limited regime (SP proportional to initial NOx)

When NOx or VOC's are injected into a given air parcel the secondary oxidants production would depend on the Extent of smog formation

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A given airshed would have different Extent.

When calculating smog oxidants at each grid cell of a given domain, we need to take into account the initial SP of the grid cell and allow for the new VOC and NOX injected into the selected grid cell to interact for the current SP.

$$SP_{total} = SP_{current} + SP_{new}$$

INTEGRATED EMPIRICAL RATES (IER) EQUATIONS

Initial IER Equations Have Been Corrected to Account for Ambient and Background Conditions.

SMOG PRODUCED is defined as:

$$[SP]^t = [O3]^t + [NO]^0 - [NO]^t$$

- During the light-limited regime the rate of SP increase is proportional to the photolytic rate coefficient defined as Rsmog , which is calculated by

$$[SP]^t = [R_{smog}]^{t} * \int J_{NO2} * f(T)\, dt$$

- During the light-limited regime

$$[SP]^{max} = \beta\, [NOx]^0$$

$$SP = SP_{anthrop} + SP_{pristine}$$

$$= [NO]^{0}_{amb} - [NO]^{t}_{amb} + [O_3]^{t}_{amb} - [O_3]^{0}_{amb}$$

$$[SP]^{t}_{anthrop} = \frac{[O_3]^{t}_{amb} - [O_3]^{t}_{pristine} - [NO]^{t}_{amb} + F[NO_y]^{t}_{amb}}{1 - FP}$$

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- The IER model can be used:
  - to classify a given airshed in terms of smog production (ozone and NO_2)
  - to identify best options for future control startegies
  - To validate a given emission inventory

MANAGEMENT OF ADDITIONAL NO_x EMISSIONS IN THE SYDNEY REGION

Photochemical Wall Model

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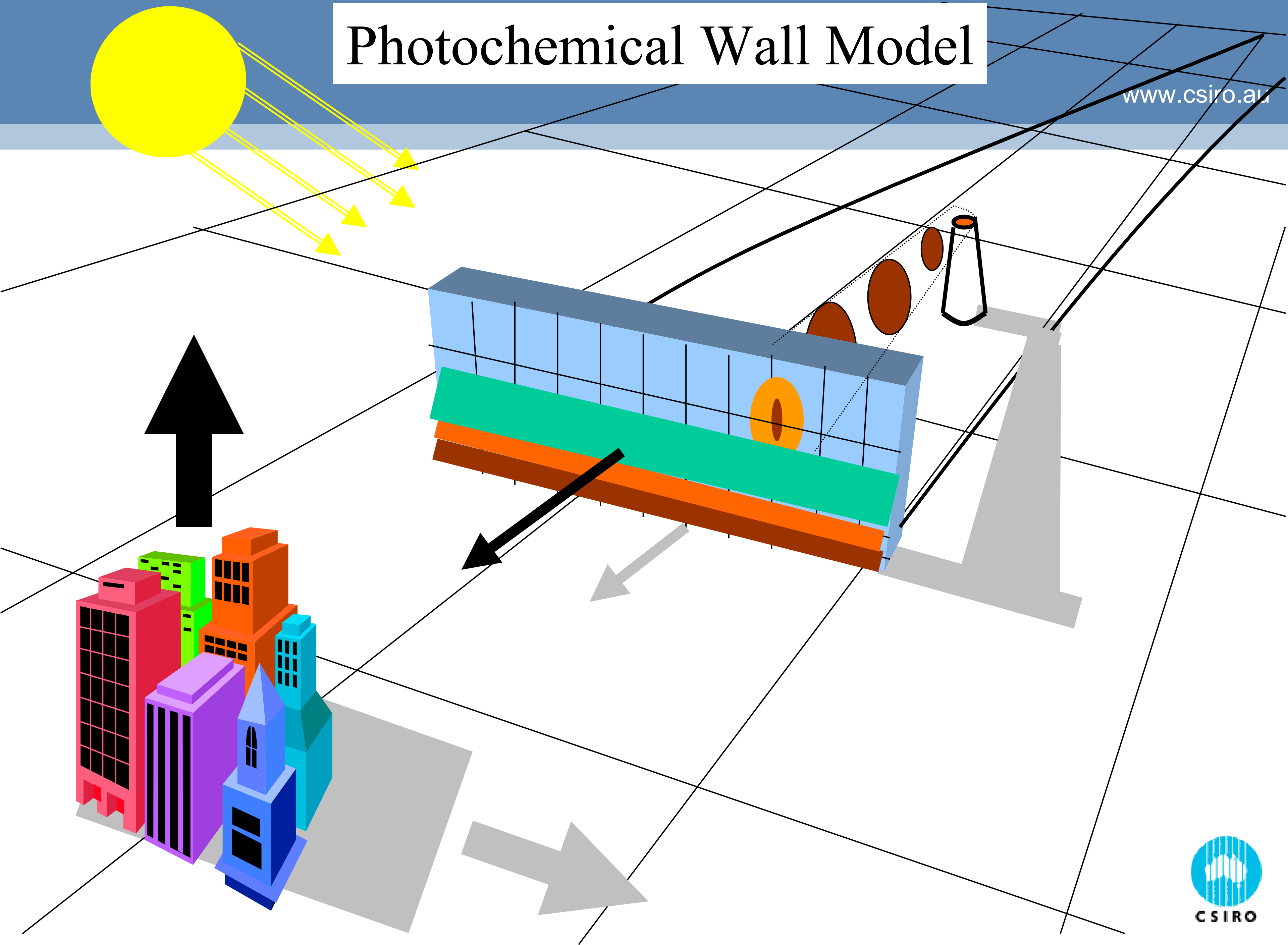

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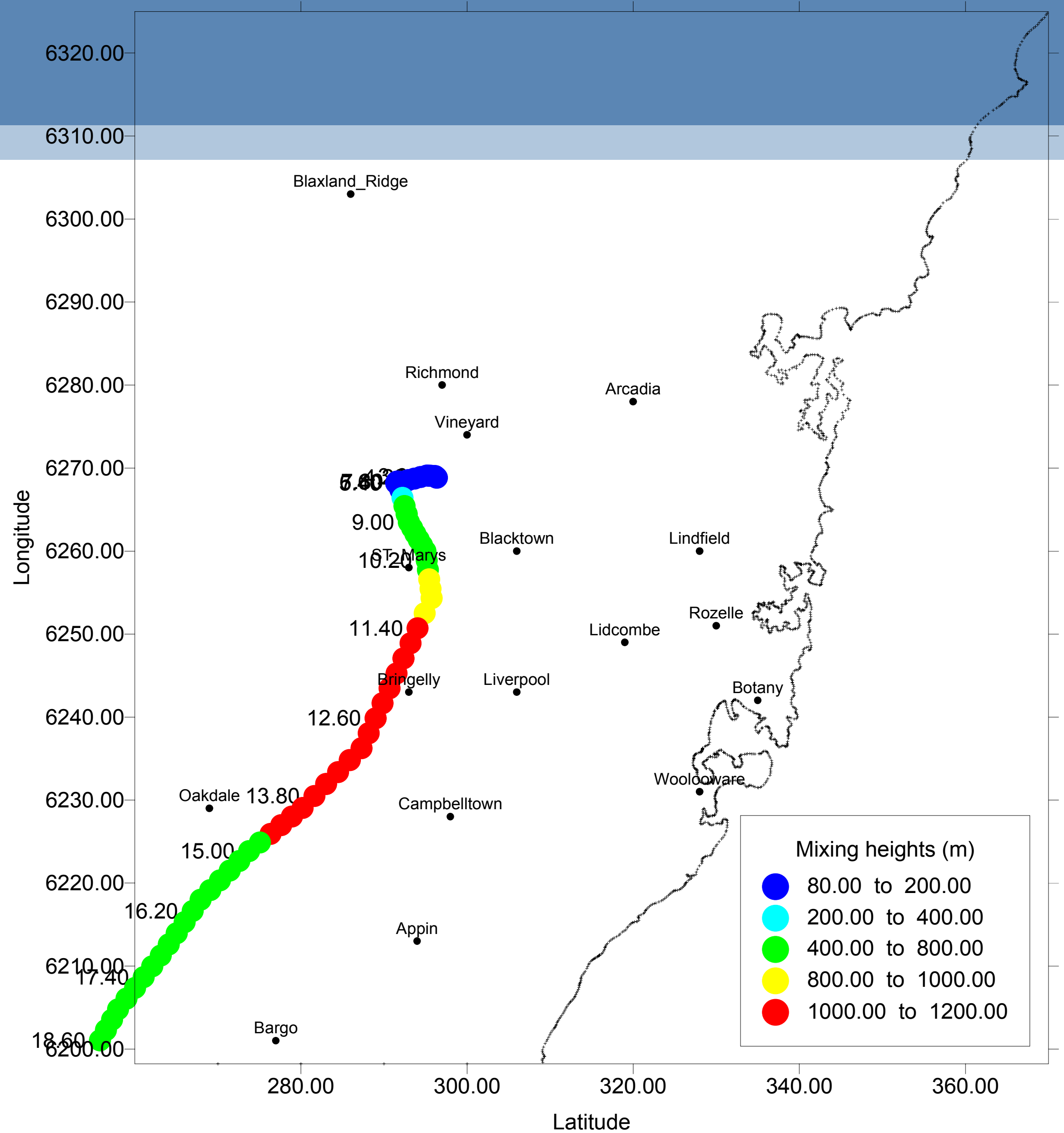

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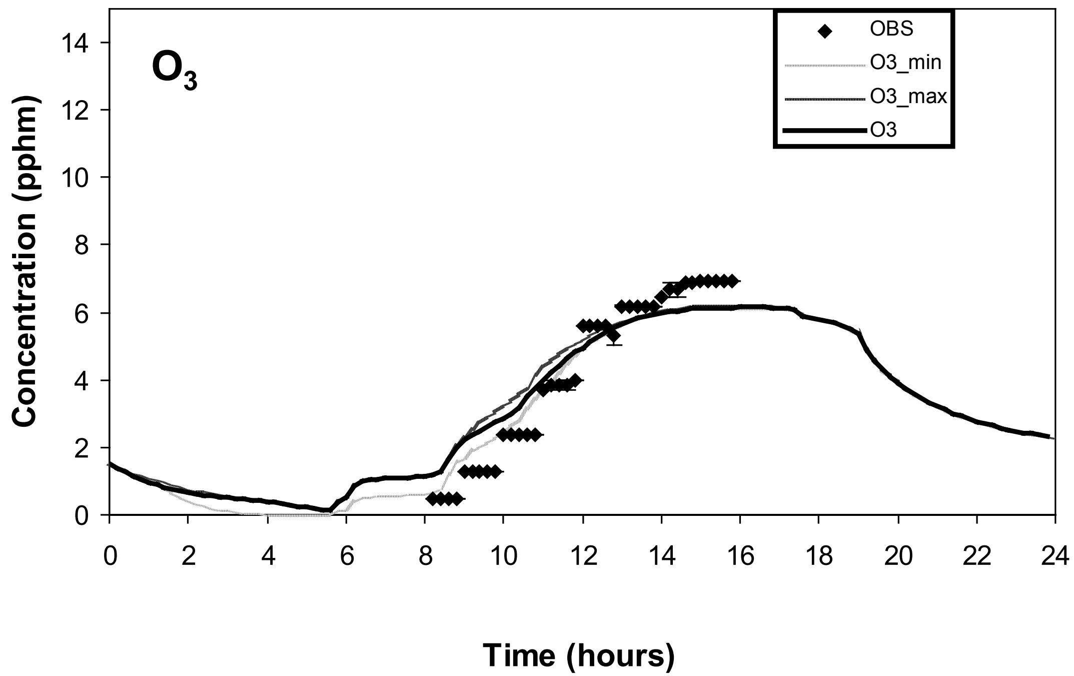

Predicted and observed ozone concentrations along a trajectory passing near the St Marys area at 1000 hours

Cross-Wind Integrated Concentration difference

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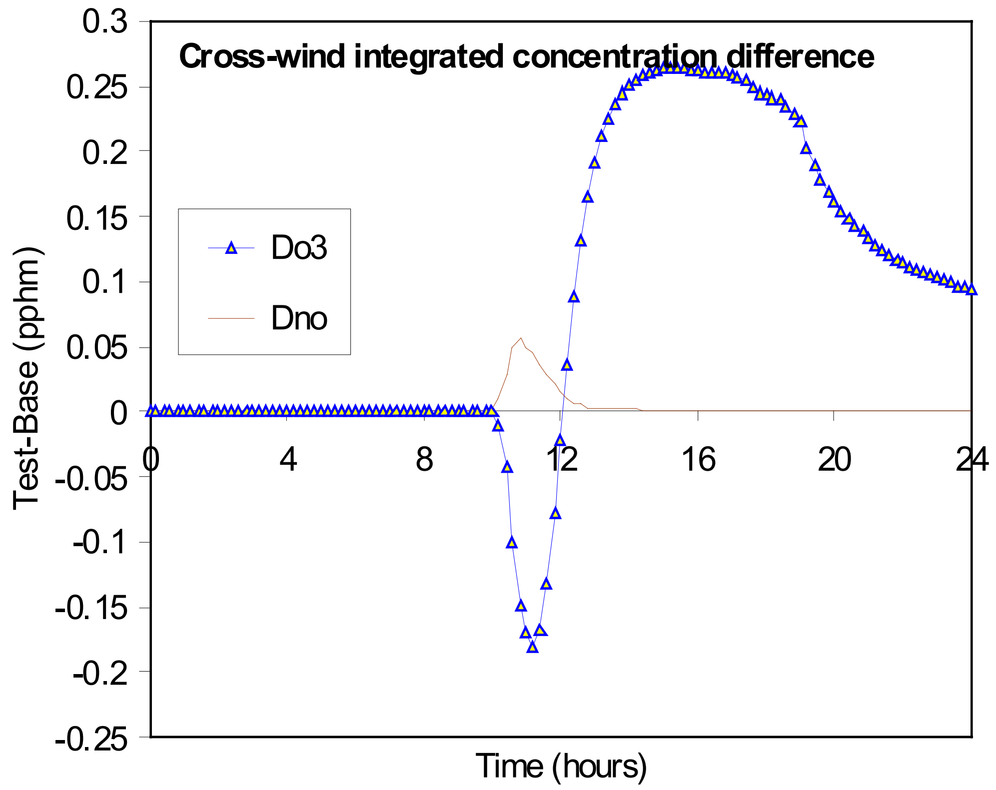

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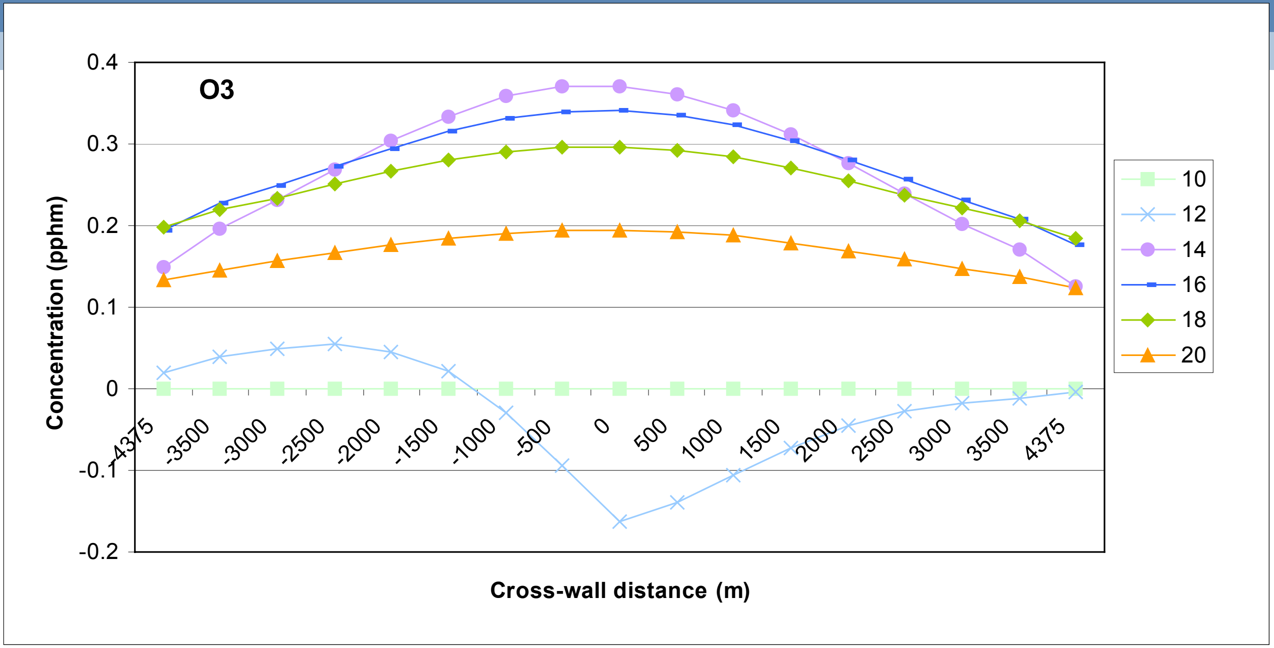

Crosswind differences between the base case (No additional NO_x) and test case (with 10 hours additional NO_x from nearby of St Marys) ground level concentrations of ozone using the CBIV chemistry.

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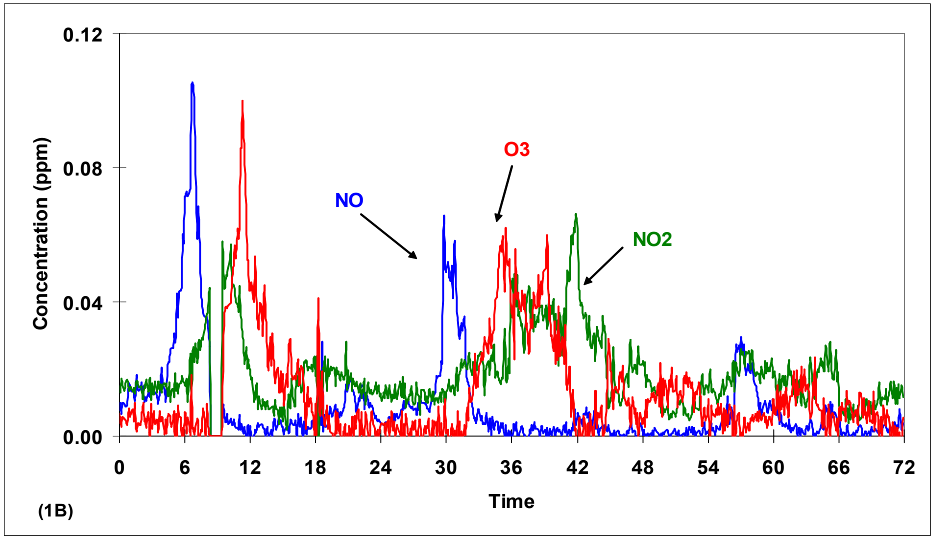
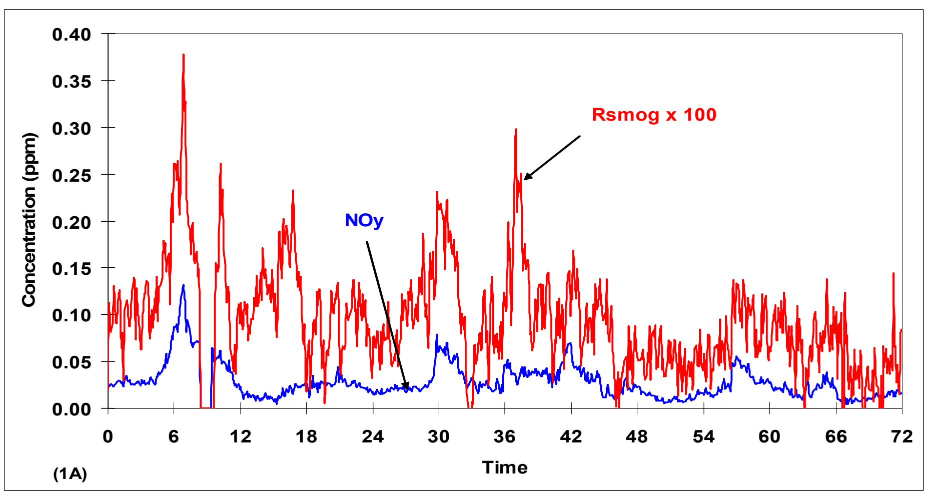
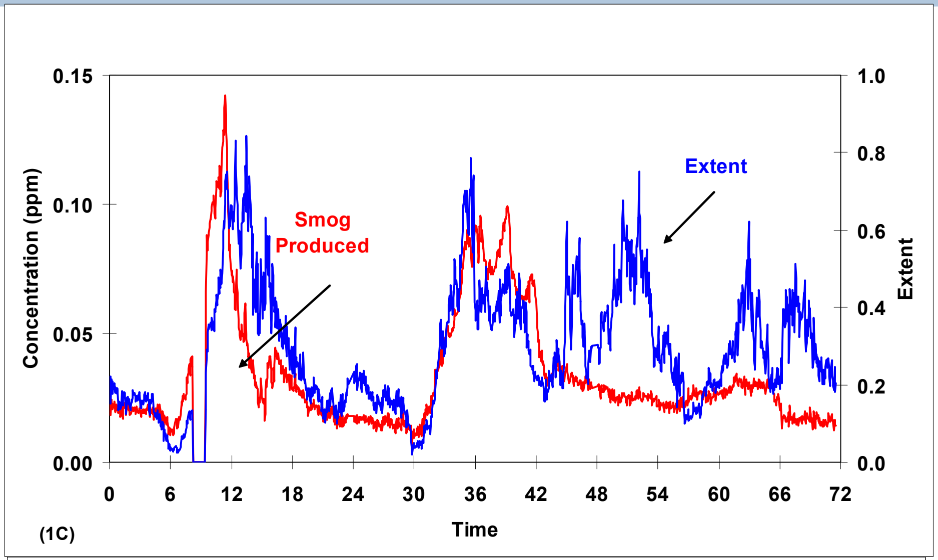
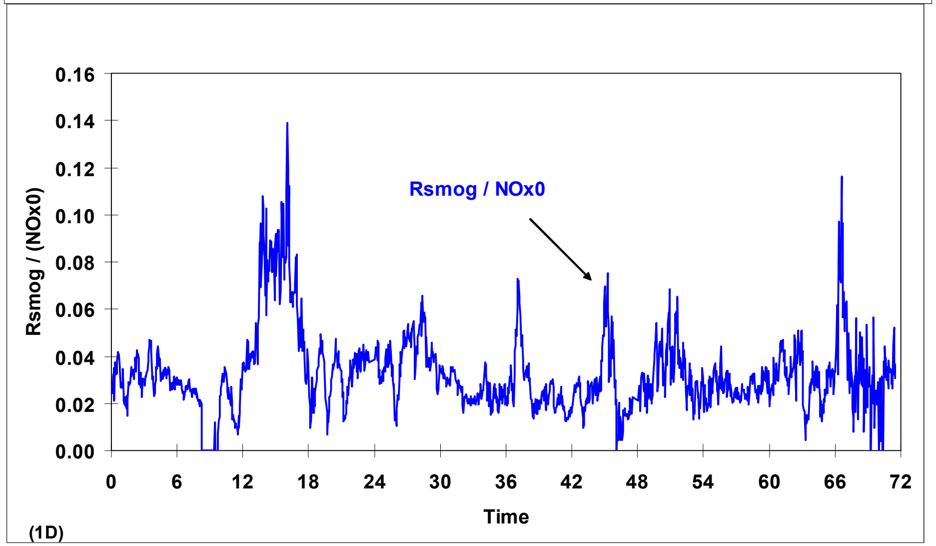
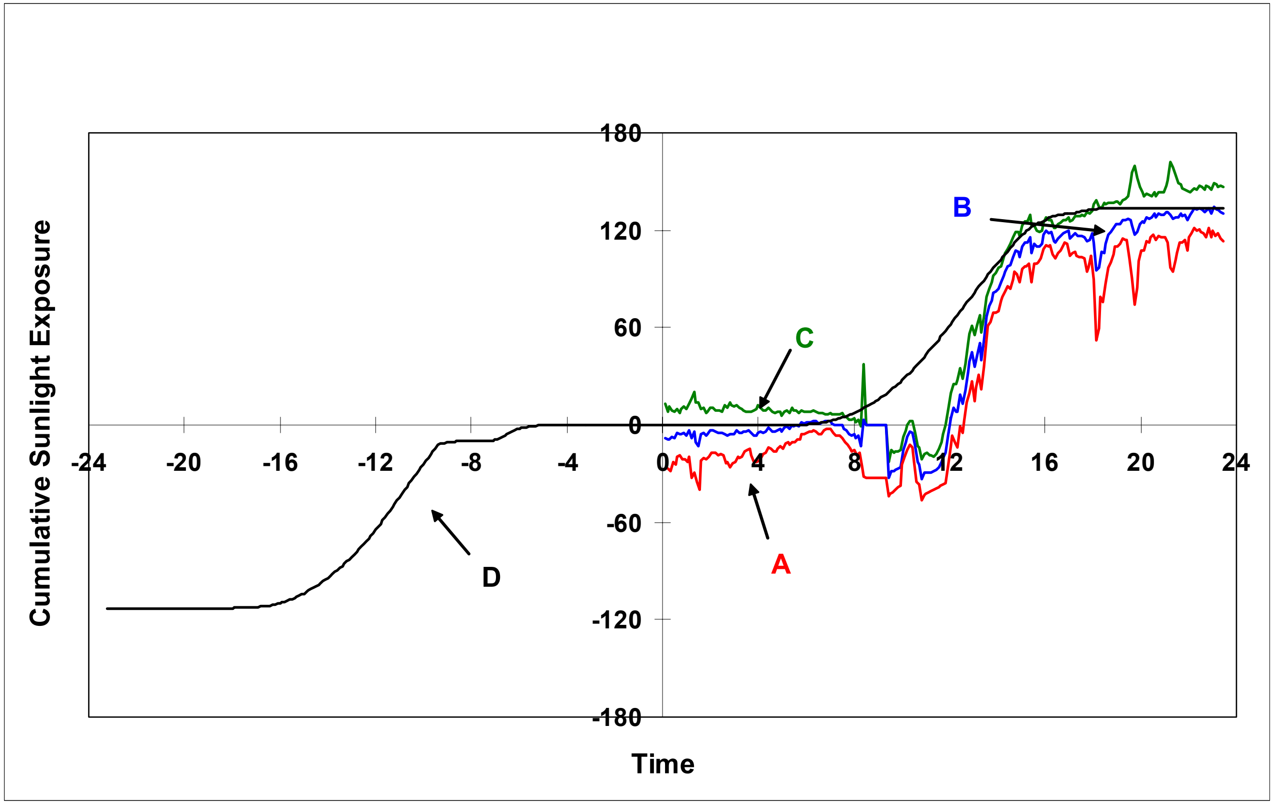
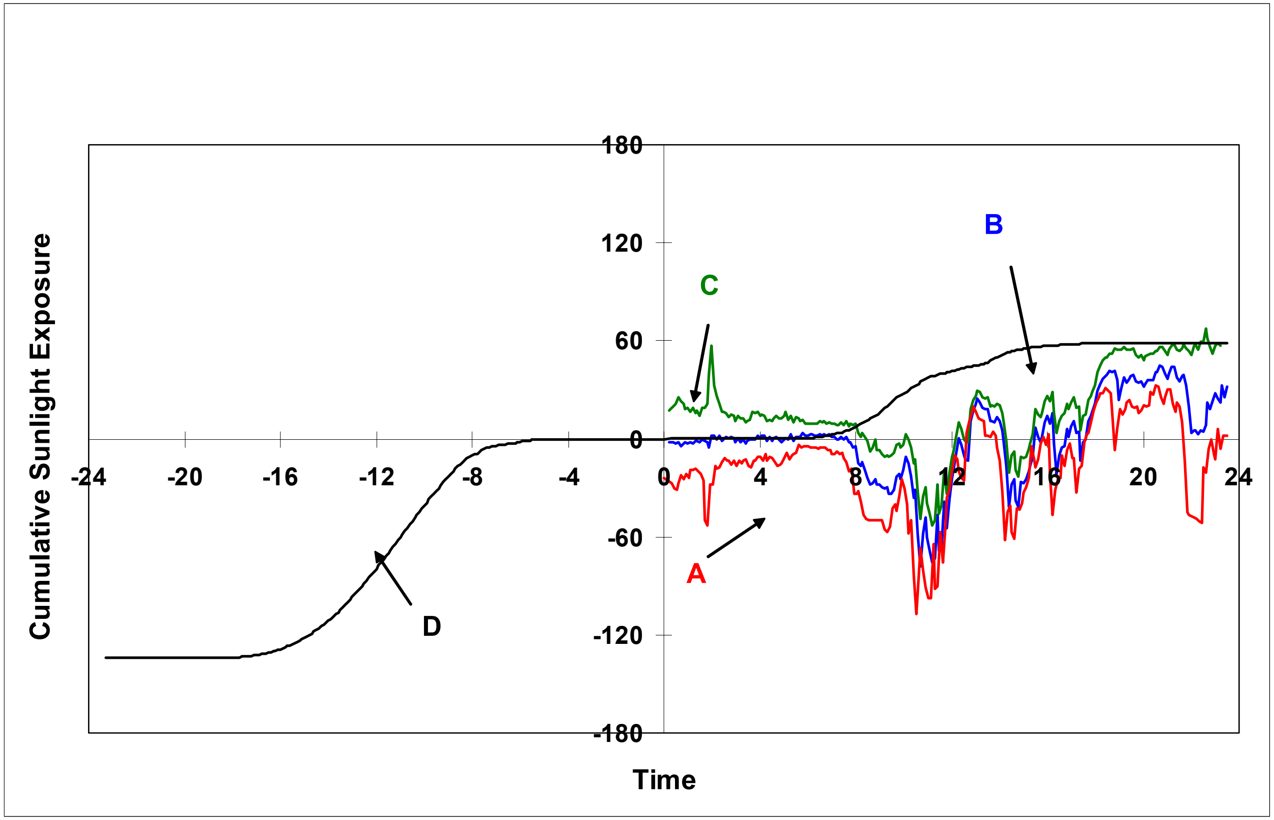

0.12
0.08
0.04
0.00
Concentration (ppm)
NO
O3
NO2
0
6
12
18
24
30
36
42
48
54
60
66
72
Time
(1B)


0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Concentration (ppm)
Rsmog x 100
NOy
0
6
12
18
24
30
36
42
48
54
60
66
72
Time
(1A)


0.15
0.10
0.05
0.00
1.0
0.8
0.6
0.4
0.2
0.0
Concentration (ppm)
Extent
Smog
Produced
Extent
0
6
12
18
24
30
36
42
48
54
60
66
72
Time
(1C)


0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Rsmog / (NOx0)
Rsmog / NOx0
0
6
12
18
24
30
36
42
48
54
60
66
72
Time
(1D)


Cumulative Sunlight Exposure
Time
180
120
60
0
-60
-120
-180
-24
-20
-16
-12
-8
-4
0
4
8
12
16
20
24
A
B
C
D



Cumulative Sunlight Exposure
180
120
60
0
-60
-120
-180
-24
-20
-16
-12
-8
-4
0
4
8
12
16
20
24
Time
A
B
C
D

FINE PARTICLES

Fine Particles

- What are the chemical and physical processes responsible for the composition and evolution of aerosols? Is there any difference between daytime and nighttime processes?
- How does the ratio of secondary and primary organics change as a function of size and age?
- What is the impact of aerosols on radiation and how this would influence the photochemistry?

Case Study 3 – Ambient Air Particulates

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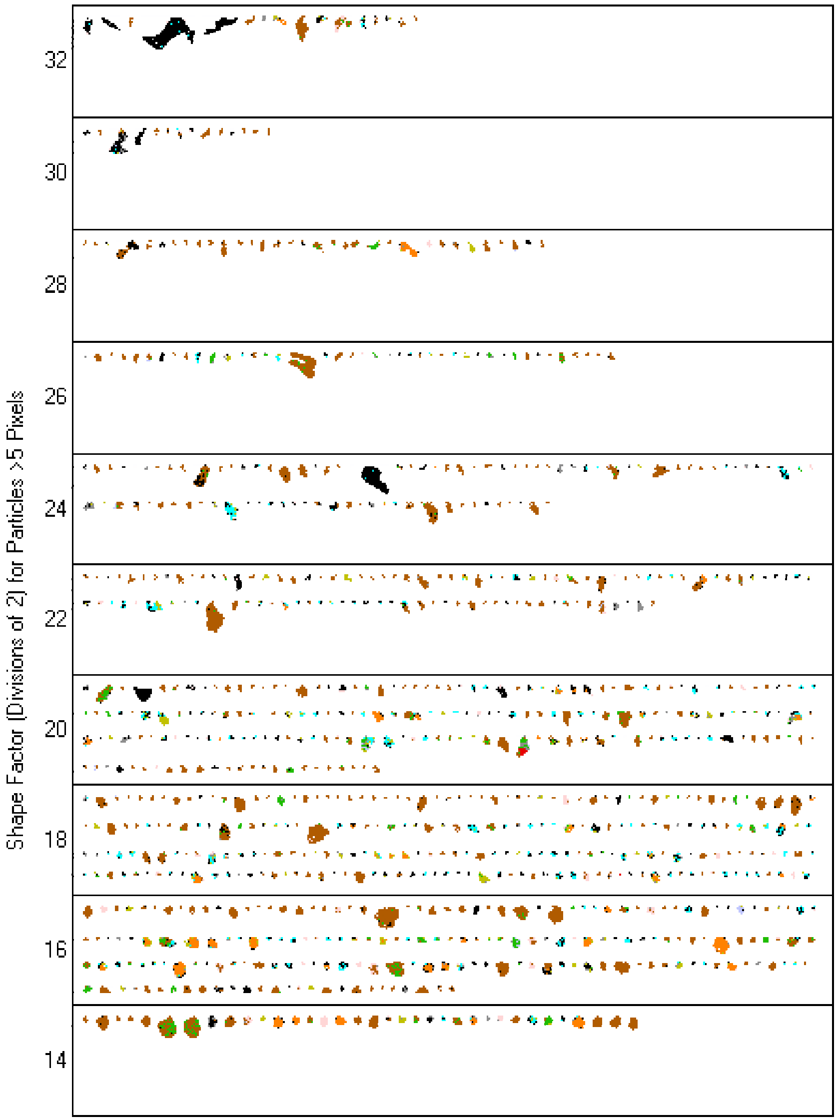

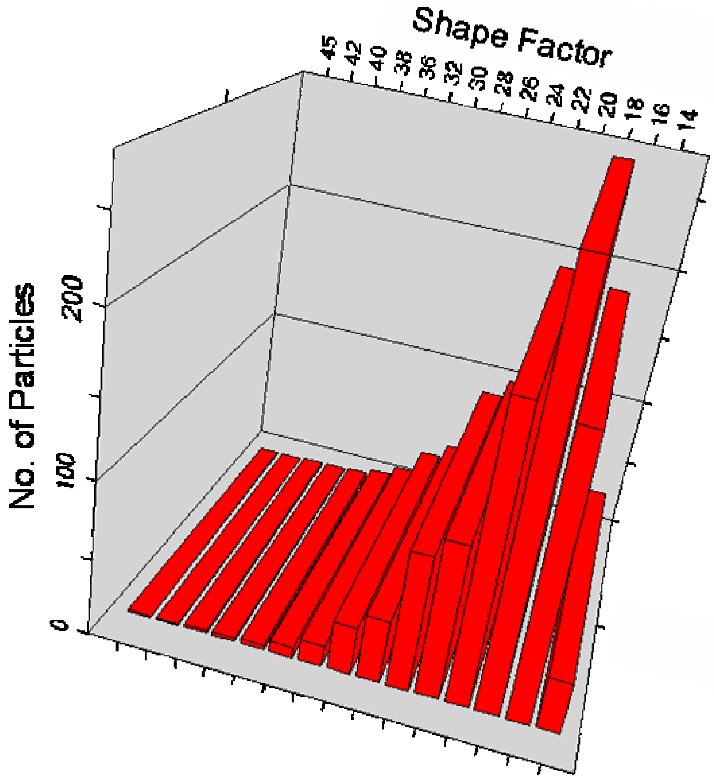

Shape

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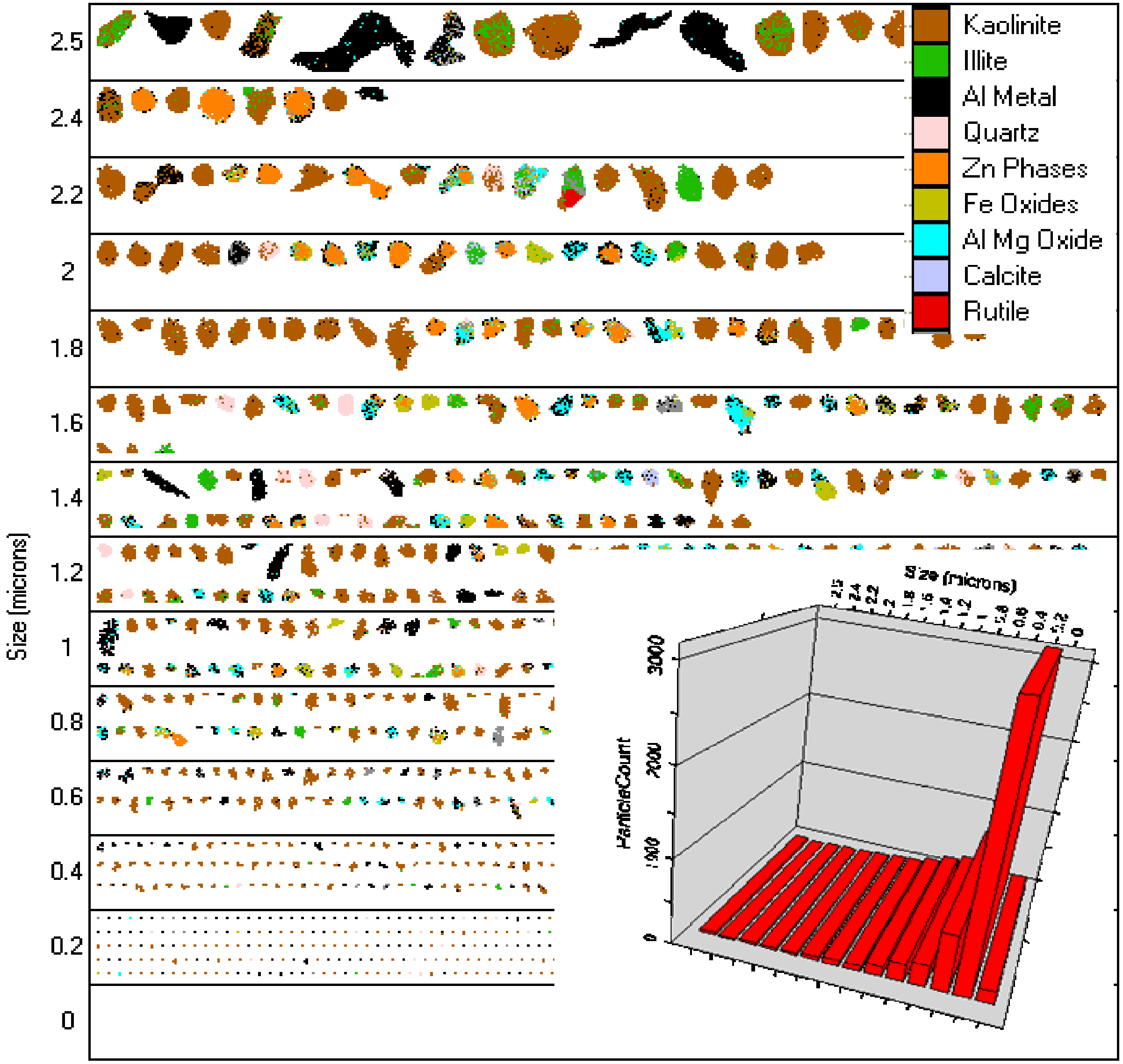
Case Study 3 – Ambient Air Particulates



Size

Case Study 4: Motorway Tunnel

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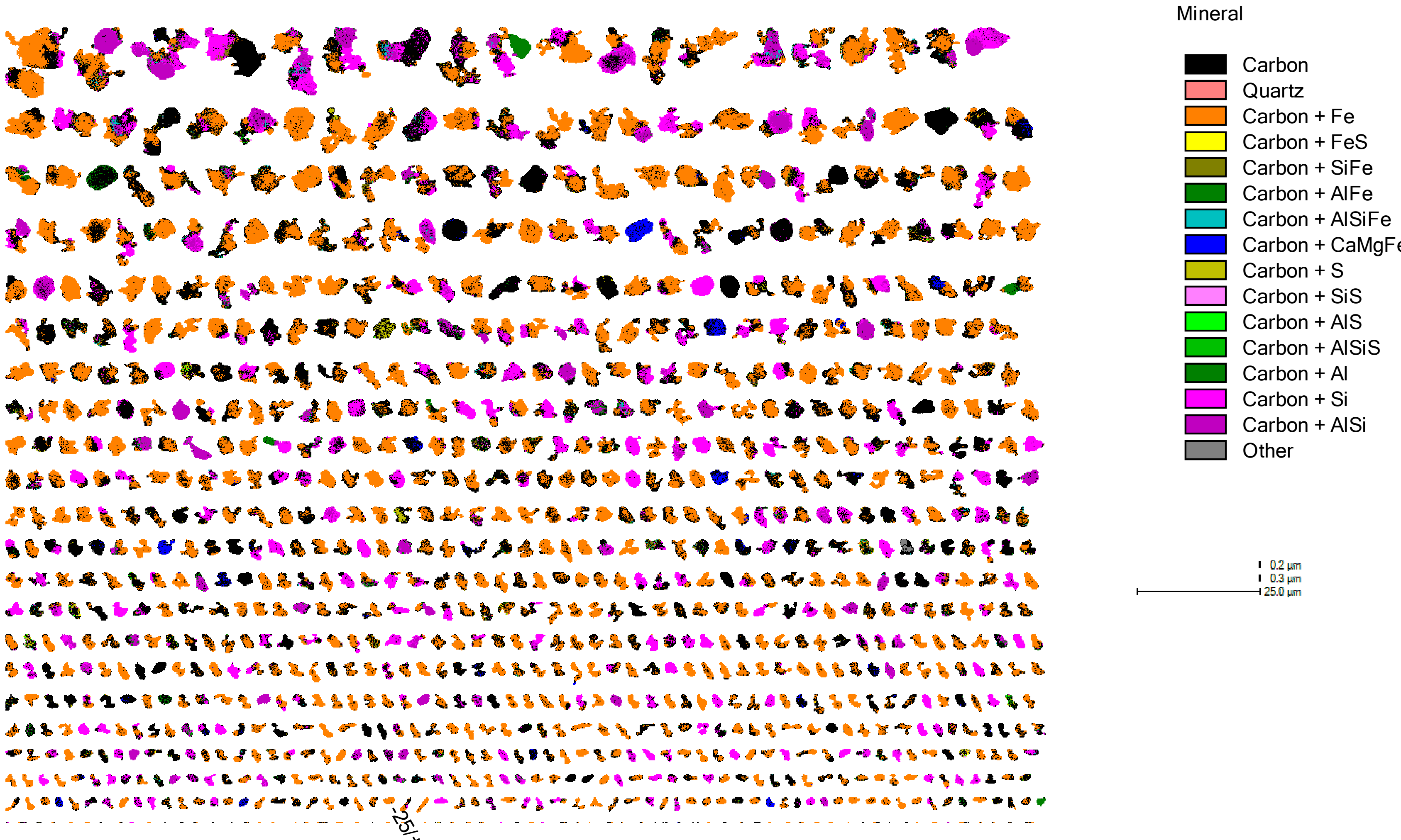
- Dust sample collected from a motorway tunnel using a kapton filter in a cascade impactor



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