

Application of the Direct Decoupled Method (DDM) for the TCOPS field study period

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The Tri-Cities Ozone Precursor Study

- Consistent high levels of ozone was identified by AIRPACT in the Tri-Cities in warm sunny days.
- Model results were verified by monitoring ozone in summer 2014 and 2015.
- The Ecology-LAR field study team monitored 3 fixed sites for ozone precursors for three weeks during summer 2016.

Objective

- What are the main sources for ozone precursors over Tri-Cities?
 - Are the precursors local or they've been transported to the region?
 - Is the region VOC-sensitive or NO_x-sensitive?
-
- ✓ Adding a new tool to AIRPACT-5 air quality system to calculate ozone sensitivities to its precursors.
 - ✓ CMAQ DDM-3D model calculates the changes in pollutant concentrations in response to 1% change in emissions.

Decoupled Direct Method (DDM)

atmospheric diffusion equation:

$$\frac{\partial C_i}{\partial t} = -\nabla(\mathbf{u}C_i) + \nabla(\mathbf{K}\nabla C_i) + R_i + E_i$$

First-order sensitivity coefficients calculated by differentiating the atmospheric governing equations with respect to the parameters of interest:

$$\mathbf{S}_j^{(1)} = \frac{\partial \mathbf{C}}{\partial \epsilon_j}, \quad \frac{\partial S_{ij}^{(1)}}{\partial t} = -\nabla(\mathbf{u}S_{ij}^{(1)}) + \nabla(\mathbf{K}\nabla S_{ij}^{(1)}) + E_i + \mathbf{J}_i \mathbf{S}_j^{(1)}$$

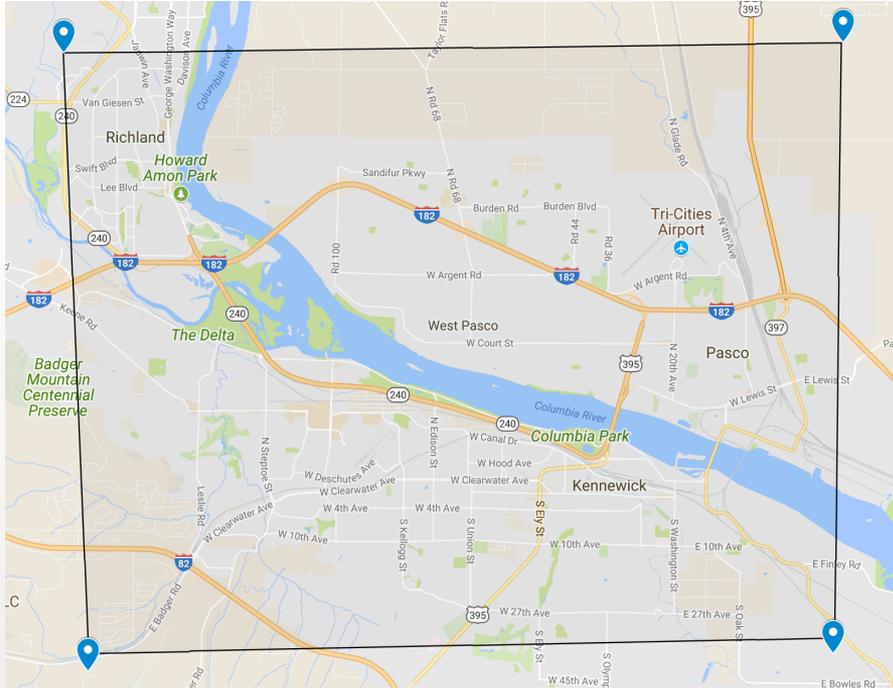
second-order sensitivity coefficients calculated by differentiating the governing equations of the first order sensitivities with respect to the parameters of interest:

$$\mathbf{S}_{j,k}^{(2)} = \frac{\partial^2 \mathbf{C}}{\partial \epsilon_j \partial \epsilon_k}, \quad \frac{\partial S_{ij}^{(2)}}{\partial t} = -\nabla(\mathbf{u}S_{ij}^{(2)}) + \nabla(\mathbf{K}\nabla S_{ij}^{(2)}) + \mathbf{J}_i \mathbf{S}_j^{(2)} + \mathbf{J}_{S^{(1)}}^* \mathbf{S}_j^{(1)}$$

Taylor expansion is used to project from a base case scenario:

$$C_{\epsilon_j, \epsilon_k} \approx C_{base} + \epsilon_j S_j^{(1)} + \frac{1}{2} \epsilon_j^2 S_j^{(2)} + \epsilon_k S_k^{(1)} + \frac{1}{2} \epsilon_k^2 S_k^{(2)} + \epsilon_j \epsilon_k S_{j,k}^{(2)}$$

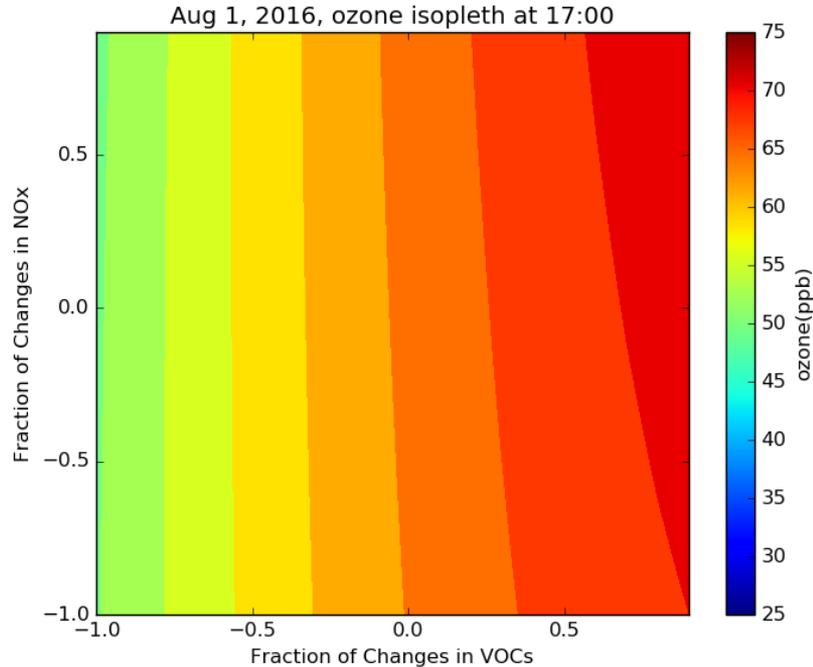
Tri-Cities DDM Emissions Area



- CMAQ5.0.2 DDM-3D was run for this box of 20 grid cells
- perturbed NO_x and VOCs emissions
- Calculated 1st and 2nd order sensitivities

DDM results from last meeting

$$C_{\varepsilon_j, \varepsilon_k} \approx C_{base} + \varepsilon_j S_j^{(1)} + \frac{1}{2} \varepsilon_j^2 S_j^{(2)} + \varepsilon_k S_k^{(1)} + \frac{1}{2} \varepsilon_k^2 S_k^{(2)} + \varepsilon_j \varepsilon_k S_{j,k}^{(2)}$$



$$-1 < \varepsilon_j < 1$$

$$-1 < \varepsilon_k < 1$$

$\varepsilon_j = \varepsilon_k = 0$ base case
 $\varepsilon_j = 1$ double VOCs
 $\varepsilon_k = 1$ double Nox
 $\varepsilon_j = -1$ no VOCs
 $\varepsilon_k = -1$ no NOx

ozone isopleths at the location of the peak
ozone at 17:00, 1 August 2016

CMAQ DDM Update

ISSUE:

CMAQ5.0.2 DDM-3D ->

- **NAN** values show up in initial condition files after a few days of run

PROPOSED SOLUTION:

- Upgrading CMAQ5.0.2 DDM-3D to CMAQ5.2 DDM-3D

STATUS:

- Upgrading libraries on AEOLUS

Evaluating the O₃ production sensitivity using the Kleinman Method

Radical Production Rate = Radical Loss Rate

It is found that a crossover from NO_x to VOC sensitive condition happens when $\frac{1}{2}$ of radicals are removed by R + NO_x.

Indicator Factor: The fraction of radical loss due to NO_x

Evaluating the O₃ production sensitivity using the ratio of LN/Q

LN : The radical loss via the reactions with NO_x

Q : The total primary radical production

- $LN/Q < 0.5$ -> atmosphere is in a NO_x-sensitive regime
- $LN/Q > 0.5$ -> atmosphere is in a VOC-sensitive regime

Kleinman et al., 2001;
Kleinman, 2005

Radical production and loss

Radical Production Rate (Q):

- $\text{O1D} + \text{H2O} = 2\text{OH}$
- $\text{FORM} = 2\text{HO2} + \text{CO}$
- $\text{H2O2} = 2\text{OH}$
- $\text{ROOH} = \text{OH} + \text{HO2} + 0.5\text{ALD2} + 0.5\text{ALDX}$
- $\text{MEPX} = \text{OH} + \text{HO2} + \text{FORM}$
- $\text{ALD2} = \text{MEO2} + \text{CO} + \text{HO2}$
- $\text{MGLY} = \text{C2O3} + \text{HO2} + \text{CO}$
- $\text{HONO} = \text{NO} + \text{OH}$

NOx Loss Rate (LN):

- $\text{NO2} + \text{OH} = \text{HNO3}$
- $\text{XO2N} + \text{NO} = \text{NTR}$
- $\text{C2O3} + \text{NO2} = \text{PAN}$

NOx Loss Constant Rates

$$K_0(T) = K_0^{300}(T/300)^{-n}$$

$$K_\infty(T) = K_\infty^{300}(T/300)^{-m}$$

$$k = \left[\frac{k^q[M]}{1 + k^o[M]/k^{\infty}} \right] F^G$$

where

$$G = \left[1 + \left(\frac{\log(k^o[M]/k^{\infty})}{n} \right)^{-2} \right]^{-1}$$

M = air density

| | | K_0^{300} | K_∞^{300} | n | m | F |
|-----|------------------|-------------|------------------|-----|-----|-----|
| R28 | NO2 + OH = HNO3 | 2.0E-30 | 2.5E-11 | 3 | 0 | 0.6 |
| R88 | C2O3 + NO2 = PAN | 2.7E-28 | 1.2E-11 | 7.1 | 0.9 | 0.3 |

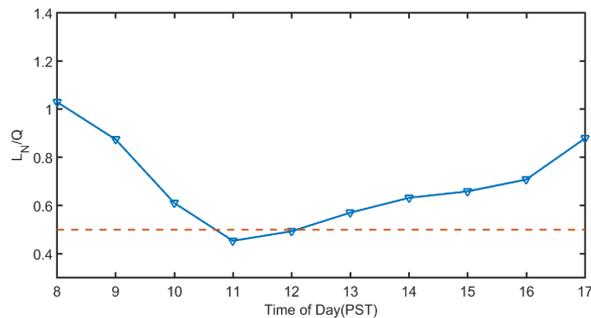
$$k = A \times \exp(-E/T)$$

| | | A | E |
|-----|-----------------|---------|------|
| R55 | XO2N + NO = NTR | 2.6E-12 | -365 |

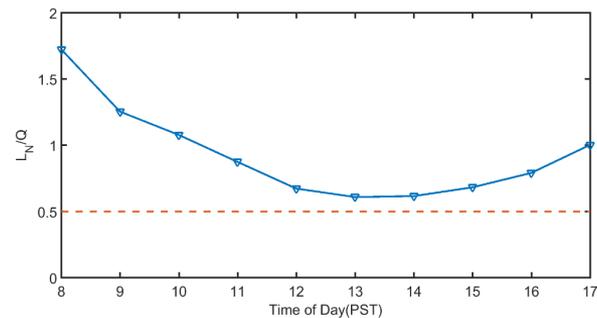
VOC and NOx-sensitive days identified by Kleinman method

VOC-Sensitive

8, Aug, 2016

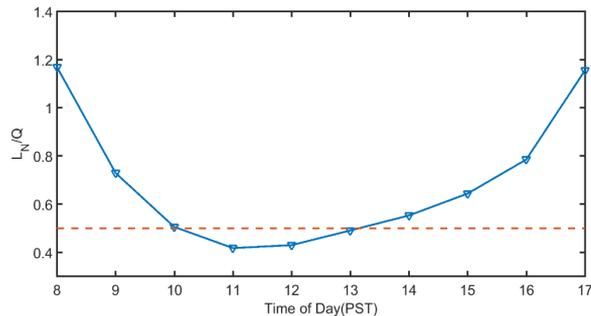


10, Aug, 2016

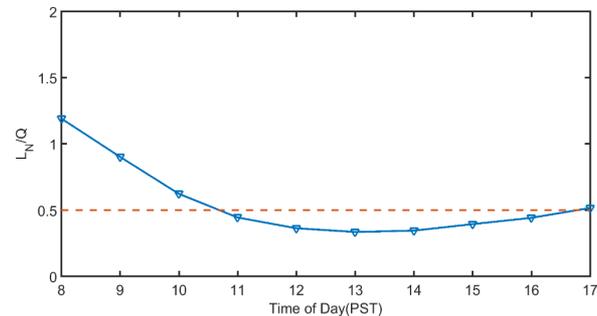


NOx-Sensitive

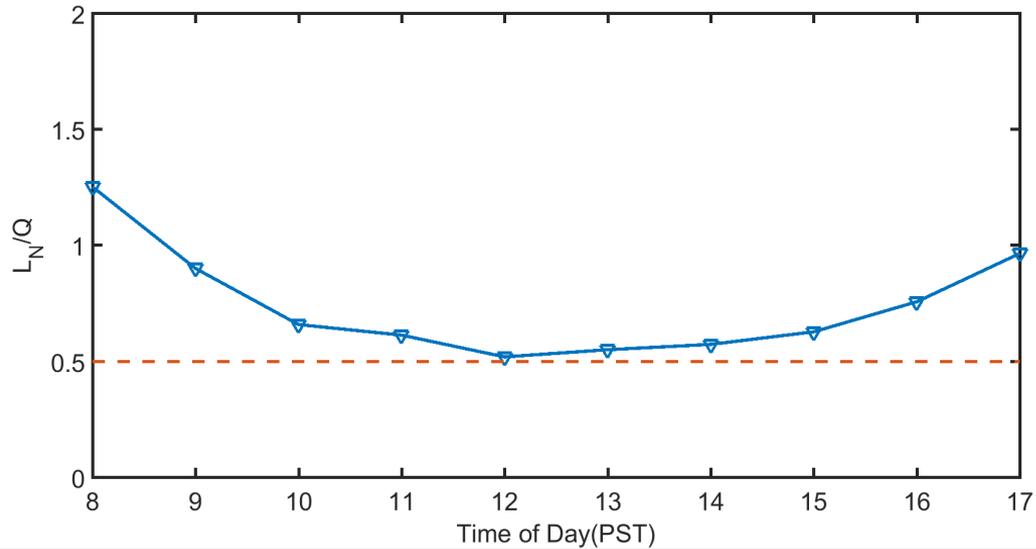
3, Aug, 2016



7, Aug, 2016



Ten-Day average result



The average is showing a VOC-sensitive regime.

Summary

- The Kleinman method agrees with DDM output in sense of identifying the Tri-Cities regime as VOC-sensitive.

Discussion?