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*Supplement of*

## **Path-integral method for the source apportionment of photochemical pollutants**

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## Special Case – Taylor Series Expansions

If there are two sources, the Taylor series expansions of the first-order sensitivities about the point  $\Lambda = 1$  (base case) through first order in  $\lambda_1, \lambda_2$  are:

$$\frac{\partial c_i}{\partial \lambda_1} = \left. \frac{\partial c_i}{\partial \lambda_1} \right|_{\Lambda=1} + \left. \frac{\partial^2 c_i}{\partial \lambda_1^2} \right|_{\Lambda=1} (\lambda_1 - 1) + \left. \frac{\partial^2 c_i}{\partial \lambda_1 \partial \lambda_2} \right|_{\Lambda=1} (\lambda_2 - 1) \quad (S1)$$

$$\frac{\partial c_i}{\partial \lambda_2} = \left. \frac{\partial c_i}{\partial \lambda_2} \right|_{\Lambda=1} + \left. \frac{\partial^2 c_i}{\partial \lambda_2^2} \right|_{\Lambda=1} (\lambda_2 - 1) + \left. \frac{\partial^2 c_i}{\partial \lambda_1 \partial \lambda_2} \right|_{\Lambda=1} (\lambda_1 - 1) \quad (S2)$$

Along the diagonal path,  $\lambda_1 = \lambda_2 = s$ . Substituting Eq. (S1) into Eq. (2) and integrating with respect to  $s$  yields

$$\begin{aligned} S_{i1}(diag) &= \left. \frac{\partial c_i}{\partial \lambda_1} \right|_{\Lambda=1} + \left. \frac{\partial^2 c_i}{\partial \lambda_1^2} \right|_{\Lambda=1} \left. \frac{(s-1)^2}{2} \right|_0^1 + \left. \frac{\partial^2 c_i}{\partial \lambda_1 \partial \lambda_2} \right|_{\Lambda=1} \left. \frac{(s-1)^2}{2} \right|_0^1 \\ &= \left. \frac{\partial c_i}{\partial \lambda_1} \right|_{\Lambda=1} - \frac{1}{2} \left( \left. \frac{\partial^2 c_i}{\partial \lambda_1^2} \right|_{\Lambda=1} + \left. \frac{\partial^2 c_i}{\partial \lambda_1 \partial \lambda_2} \right|_{\Lambda=1} \right) \end{aligned}$$

Similarly,

$$S_{i2}(diag) = \left. \frac{\partial c_i}{\partial \lambda_2} \right|_{\Lambda=1} - \frac{1}{2} \left( \left. \frac{\partial^2 c_i}{\partial \lambda_2^2} \right|_{\Lambda=1} + \left. \frac{\partial^2 c_i}{\partial \lambda_1 \partial \lambda_2} \right|_{\Lambda=1} \right)$$

For the path  $B-b1-b$  in Fig. 1,  $\lambda_2 = 0$  from  $b$  to  $b1$ , and  $d\lambda_1 = 0$  from  $b1$  to  $B$ . Using this information and integrating Eq. (S1) with respect to  $\lambda_1$  from  $b$  to  $b1$  gives

$$\begin{aligned} S_{i1}(B-b1-b) &= \left. \frac{\partial c_i}{\partial \lambda_1} \right|_{\Lambda=1} + \left. \frac{\partial^2 c_i}{\partial \lambda_1^2} \right|_{\Lambda=1} \left. \frac{(\lambda_1 - 1)^2}{2} \right|_0^1 - \left. \frac{\partial^2 c_i}{\partial \lambda_1 \partial \lambda_2} \right|_{\Lambda=1} \\ &= \left. \frac{\partial c_i}{\partial \lambda_1} \right|_{\Lambda=1} - \frac{1}{2} \left. \frac{\partial^2 c_i}{\partial \lambda_1^2} \right|_{\Lambda=1} - \left. \frac{\partial^2 c_i}{\partial \lambda_1 \partial \lambda_2} \right|_{\Lambda=1} \end{aligned}$$

Noting that  $d\lambda_2 = 0$  from  $b$  to  $b1$  and that  $\lambda_1 = 1$  from  $b1$  to  $B$  and integrating Eq. (S2) with respect to  $\lambda_2$  from  $b1$  to  $B$  gives

$$S_{i2}(B-b1-b) = \left. \frac{\partial c_i}{\partial \lambda_2} \right|_{\Lambda=1} - \frac{1}{2} \left. \frac{\partial^2 c_i}{\partial \lambda_2^2} \right|_{\Lambda=1}$$

By a procedure analogous to that for path  $B-b1-b$ , the results for path  $B-b2-b$  are:

$$\begin{aligned} S_{i1}(B-b2-b) &= \left. \frac{\partial c_i}{\partial \lambda_1} \right|_{\Lambda=1} - \frac{1}{2} \left. \frac{\partial^2 c_i}{\partial \lambda_1^2} \right|_{\Lambda=1} \\ S_{i2}(B-b2-b) &= \left. \frac{\partial c_i}{\partial \lambda_2} \right|_{\Lambda=1} - \frac{1}{2} \left. \frac{\partial^2 c_i}{\partial \lambda_2^2} \right|_{\Lambda=1} - \left. \frac{\partial^2 c_i}{\partial \lambda_1 \partial \lambda_2} \right|_{\Lambda=1} \end{aligned}$$

The expansion of the concentration in a Taylor series about  $\Lambda = 1$  through second order is:

$$c_i(\mathbf{\Lambda}) = c_i(\mathbf{\Lambda=1}) + \left. \frac{\partial c_i}{\partial \lambda_1} \right|_{\mathbf{\Lambda=1}} (\lambda_1 - 1) + \left. \frac{\partial c_i}{\partial \lambda_2} \right|_{\mathbf{\Lambda=1}} (\lambda_2 - 1) + \left. \frac{1}{2} \frac{\partial^2 c_i}{\partial \lambda_1^2} \right|_{\mathbf{\Lambda=1}} (\lambda_1 - 1)^2 \\ + \left. \frac{1}{2} \frac{\partial^2 c_i}{\partial \lambda_2^2} \right|_{\mathbf{\Lambda=1}} (\lambda_2 - 1)^2 + \left. \frac{\partial^2 c_i}{\partial \lambda_1 \partial \lambda_2} \right|_{\mathbf{\Lambda=1}} (\lambda_1 - 1)(\lambda_2 - 1)$$

With this expansion, the concentration difference  $\Delta c_i = c_i(\mathbf{\Lambda=1}) - c_i(\mathbf{\Lambda=0})$  is then

$$\Delta c_i = \left. \frac{\partial c_i}{\partial \lambda_1} \right|_{\mathbf{\Lambda=1}} + \left. \frac{\partial c_i}{\partial \lambda_2} \right|_{\mathbf{\Lambda=1}} - \left. \frac{1}{2} \frac{\partial^2 c_i}{\partial \lambda_1^2} \right|_{\mathbf{\Lambda=1}} - \left. \frac{1}{2} \frac{\partial^2 c_i}{\partial \lambda_2^2} \right|_{\mathbf{\Lambda=1}} - \left. \frac{\partial^2 c_i}{\partial \lambda_1 \partial \lambda_2} \right|_{\mathbf{\Lambda=1}}$$

For all three paths,  $\Delta c_i = S_{i1} + S_{i2}$ , and thus the source apportionments equal the concentration difference between the base and background cases through second-order in  $\lambda_1$  and  $\lambda_2$ .

Table S1. Input data for the CAMx simulations.

Latitude	N 34° (Los Angeles/Atlanta)	
Days	June 20-22	
Temperature (K), diurnally varying	Cell 1: 290 →305 → 290	Cell 2: 295 → 307 →295
Cell height (m), diurnally varying	Cell 1: 100 → 300 →100	Cell 2: 1400 →1200 →1400
Deposition	Wesely/Slinn algorithm <sup>a, b</sup>	
Chemistry	Carbon Bond 6	
Initial VOC (ppbC <sup>c</sup> )	8.0	
Initial VOC/NOx (ppbC/ppb)	16.	
Species	Description	Initial Concentration (ppb) <sup>d</sup>
O <sub>3</sub>		35.
NO		0.1
NO <sub>2</sub>		0.4
CO		120.
SO <sub>2</sub>		1.
ACET	acetone	0.0
ALD2	acetaldehyde	0.05
ALDX	C3 & higher aldehydes	0.01
BENZ	benzene	0.0
ETH	ethene	0.11
ETHA	ethane	0.02
ETHY	ethyne	0.0
ETOH	ethanol	0.11
FORM	formaldehyde	0.10
IOLE	internal olefin carbon	0.14
ISOP	isoprene	0.57
KET	ketone carbon	0.0
MEOH	methanol	0.33
OLE	terminal olefin carbon	0.21
PAR	paraffin carbon	1.25
PRPA	propane	0.0
TERP	mono-terpenes	0.16
TOL	mono-alkyl aromatics	0.0
XYL	poly-alkyl aromatics	0.0
NR	non-reactive carbon	0.27

<sup>a</sup> Wesely, M.L.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, *Atmos. Environ.*, 23, 1293-1304, 1989.

<sup>b</sup> Slinn, S.A., and Slinn, W.G.N.: Predictions for particle deposition on natural waters, *Atmos. Environ.*, 24, 1013-1016, 1980.

<sup>c</sup> Parts per billion of carbon

<sup>d</sup> Initial concentrations of the VOC species are in the same relative proportions as the daily biogenic emissions.

Table S2. All daily emission rates used in the base-case simulation.

Species	Emission Rate (mol day <sup>-1</sup> km <sup>-2</sup> )					
	Biogenic Sources <sup>a</sup>	Fuel Combustion	Industrial Sources	On-road Vehicles	Non-road Vehicles	Other Sources
NO	13.5	77.4	19.7	132.9	73.2	1.9
NO2	0.00	8.60	2.19	13.59	7.48	0.21
HONO	0.00	0.00	0.00	1.18	0.65	0.00
CO	35.9	51.8	58.2	1158.4	683.0	57.0
ACET	0.00	0.00	10.54	0.11	0.06	0.00
ALD2	2.39	0.00	0.03	0.69	0.71	0.00
ALDX	0.61	0.00	0.62	0.10	0.22	0.01
BENZ	0.00	0.14	0.10	1.47	1.66	0.04
ETH	5.38	0.00	0.03	6.72	4.85	0.00
ETHA	1.21	0.00	5.90	1.69	1.77	0.00
ETHY	0.00	0.00	0.00	1.19	2.87	0.00
ETOH	5.38	0.00	1.23	6.16	2.61	2.78
FORM	4.78	0.73	0.25	1.52	1.73	0.13
IOLE	7.07	0.00	0.06	1.12	0.66	0.38
ISOP	28.82	0.00	0.00	0.04	0.00	0.00
KET	0.00	0.00	1.00	0.00	0.03	0.00
MEOH	16.47	0.00	4.15	0.37	0.00	0.00
OLE	10.32	0.00	0.77	3.40	6.27	0.36
PAR	62.61	4.95	189.04	96.74	82.80	54.34
PRPA	0.00	0.25	13.63	0.17	0.21	0.01
TERP	8.17	0.00	0.38	0.00	0.00	0.00
TOL	0.00	0.06	5.91	4.48	4.21	0.43
XYL	0.00	0.00	3.15	2.69	3.45	0.13
NR	13.55	0.01	7.50	1.19	0.99	0.70

<sup>a</sup> Includes lightning

Table S3. Average error and bias for different numerical integration formulas. The sum of the source contributions calculated using the formula is compared to the anthropogenic increment of NO<sub>2</sub> or HNO<sub>3</sub>.

Path	Formula <sup>a</sup>	Mean Absolute Error <sup>b</sup> (ppb)	Mean Bias <sup>b</sup> (ppb)
NO <sub>2</sub> Increment			
Diag	TR2	2.74	2.66
Diag	GL2s	0.19	-0.15
Diag	GL2r	0.49	-0.45
Diag	GL3s	0.06	-0.05
Diag	GL3r	0.13	-0.08
Diag	GL4s	0.04	-0.03
Diag	GL4r	0.07	-0.01
NOxF	GL3s	0.20	0.00
NOxF	GL3r	1.12	-1.06
NOxF	GL4s	0.12	-0.04
VOCF	GL3s	1.49	1.46
VOCF	GL3r	3.06	-3.05
VOCF	GL4s	0.76	-0.73
HNO <sub>3</sub> Increment			
Diag	TR2	4.55	-4.55
Diag	GL2s	0.28	0.06
Diag	GL2r	0.53	-0.15
Diag	GL3s	0.20	-0.18
Diag	GL3r	0.24	-0.19
Diag	GL4s	0.28	-0.27
Diag	GL4r	0.28	-0.28
NOxF	GL3s	0.44	0.40
NOxF	GL3r	0.80	-0.35
NOxF	GL4s	0.57	-0.57
VOCF	GL3s	1.37	-1.32
VOCF	GL3r	1.99	1.97
VOCF	GL4s	0.54	0.47

<sup>a</sup> TR2 = trapezoidal rule, 2 points. GL<sub>n</sub>x = Gauss-Legendre formula using *n* points and *x* as the integration variable.

<sup>b</sup> Hourly average over the 3-day simulation.

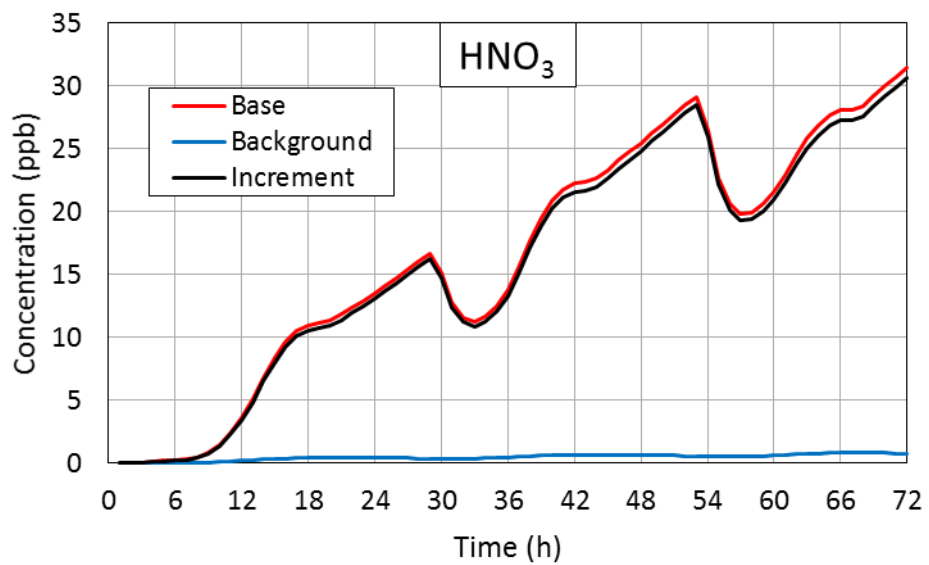
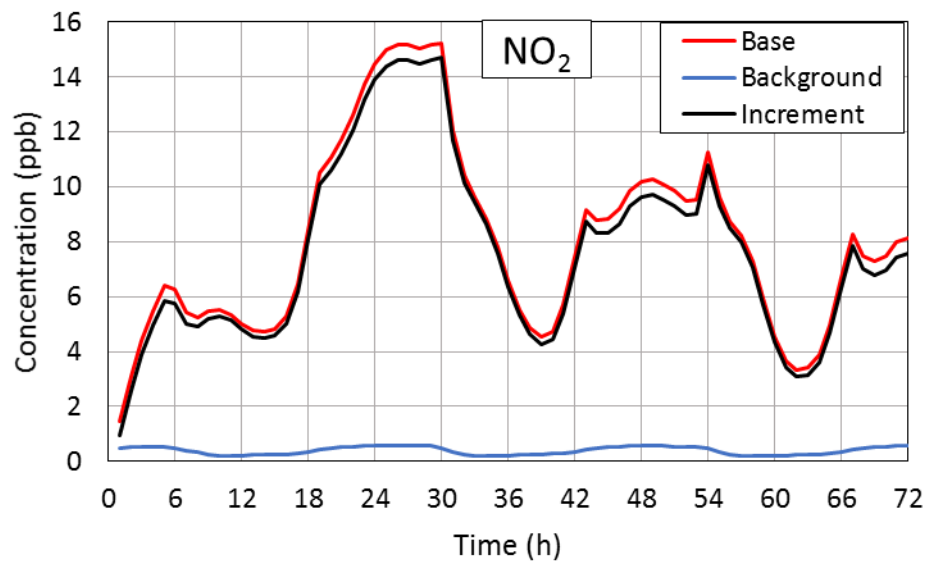


Figure S1. Concentrations of NO<sub>2</sub> and HNO<sub>3</sub> from the base case, the background case and the anthropogenic increment.

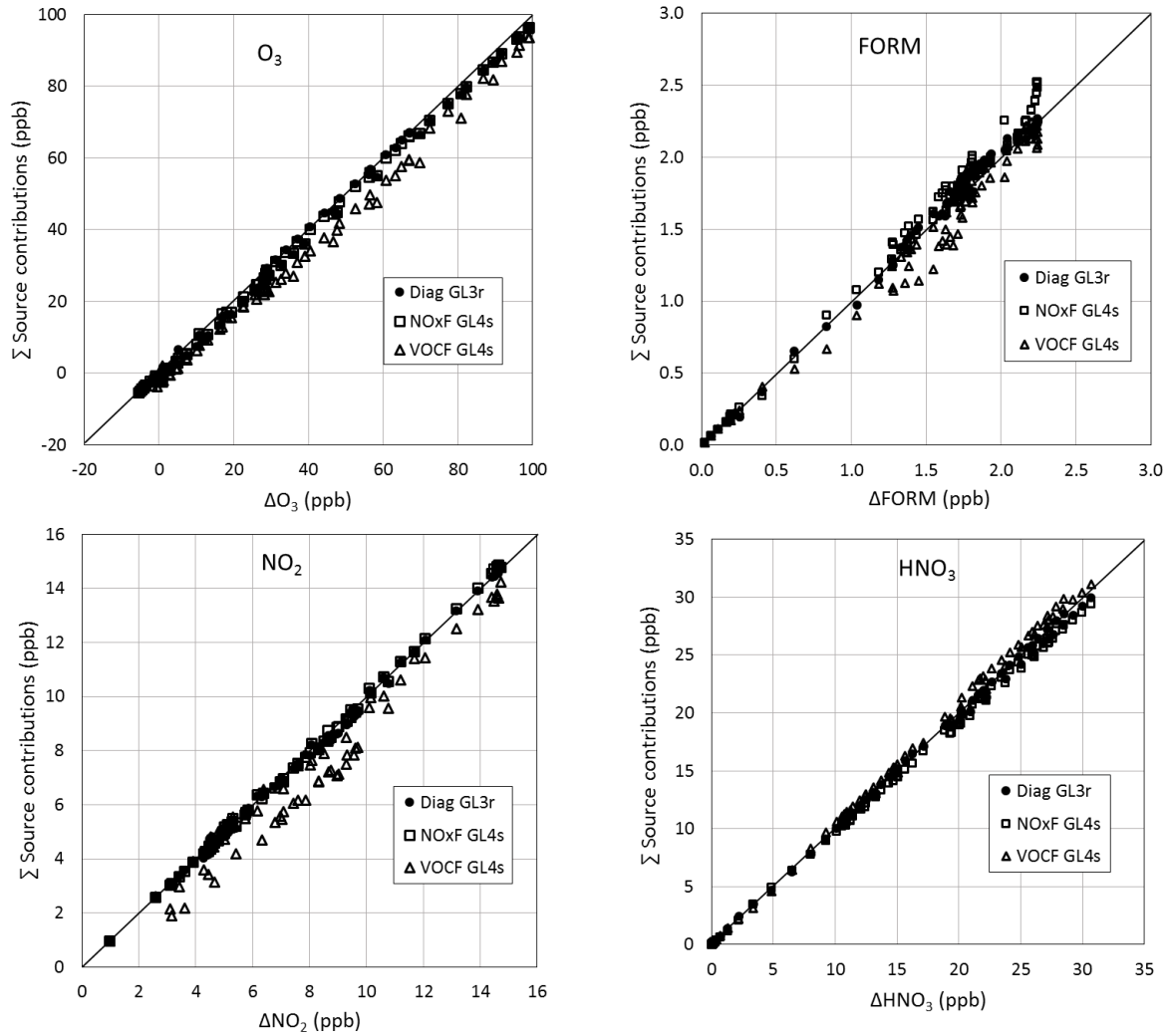


Figure S2. Comparison of the sum of the source contributions to the anthropogenic increment. Points are hourly values during the 3-day simulation. Also shown is a 1-to-1 correspondence line.



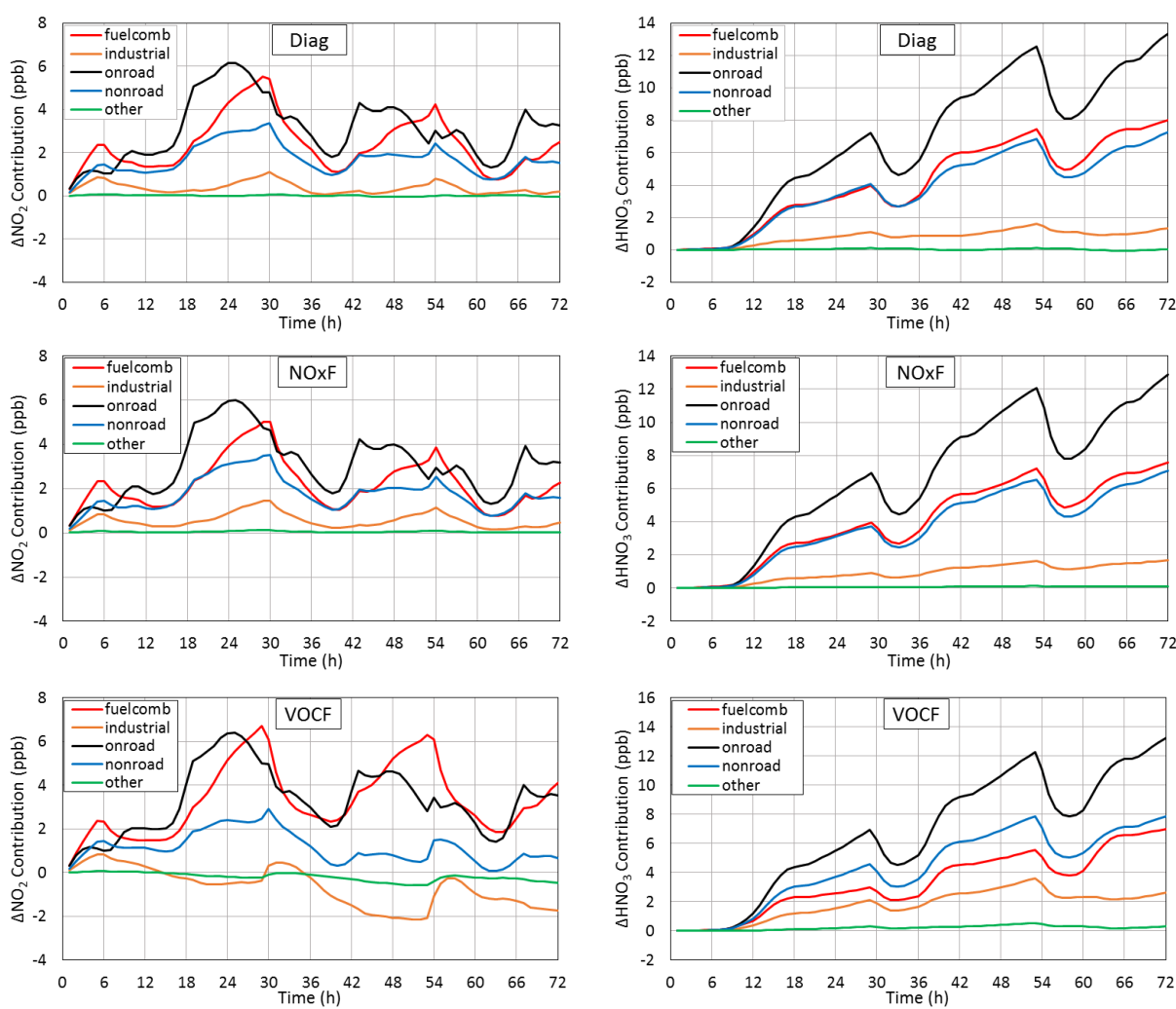


Figure S3. Apportionment of the anthropogenic  $\text{NO}_2$  increment (left) and  $\text{HNO}_3$  increment (right) to sources using the Diag, NOxF, and VOCF emission-control paths.