

## **The Chemistry of Atmosphere-Forest Exchange (CAFE) Model,**

### **Part II: Application to BEARPEX-2007 Observations**

#### *Supplementary Online Material*

G. M. Wolfe, J. A. Thornton, N. C. Bouvier-Brown, A. H. Goldstein, J.-H. Park, M. McKay, D. M. Matross, J. Mao, W. H. Brune, B. W. LaFranchi, E. C. Browne, K.-E. Min, P. J. Wooldridge, R. C. Cohen, J. D. Crouse, I. C. Faloona, J. B. Gilman, W. C. Kuster, J. A. de Gouw, A. Huisman, and F. N. Keutsch

#### *Contents*

Table S1: BEARPEX-2007 chemical observations

Table S2: Model-measurement inter-comparison for selected observations

**Table S1.** BEARPEX-2007 chemical observations. Statistics are calculated from a merged, 30-minute averaged dataset for noontime (11:30 – 12:30 PST) data collected during the hot (28 August – 3 September) and cool (Averages from 13 – 18 September) periods as defined in the main paper. Comma-separated heights denote different measuring heights for hot and cold periods. Mean concentrations ( $\bar{C}$ ) and standard deviations ( $\sigma_C$ ) are in ppbv unless otherwise specified.  $N$  represents the number of points included in the average.

Species	Height m	Hot Period			Cool Period			Ref. <sup>a</sup>
		$\bar{C}$	$\sigma_C$	N	$\bar{C}$	$\sigma_C$	N	
OH ( $10^6$ molec cm <sup>-3</sup> )	9.4	6.8	0.5	4	4.0	1.2	7	i
	15	8.0	2.7	8	-	-	-	
HO <sub>2</sub>	9.4	0.029	0.003	4	0.021	0.004	7	i
	15	0.033	0.005	8	-	-	-	
CO	12.5	97	14	21	116	10	18	ii
O <sub>3</sub>	1.2	49.6	11.0	7	44.0	6.6	6	iii
	4.9	51.3	11.4	7	45.5	6.6	6	
	8.75	51.6	11.3	7	45.3	6.0	6	
	12.5	50.8	11.6	7	45.5	5.5	6	
$\tau_{OH}^{-1}$ (s <sup>-1</sup> )	9.9	12.4	2.0	17	6.8	1.2	12	iv
<u>NO<sub>y</sub></u> NO <sub>2</sub>	4.9	0.273	0.135	3	0.314	0.074	11	v
	9	0.139	0.065	4	0.368	0.115	12	
	12.7	0.050	0.022	3	0.346	0.091	13	
$\Sigma$ PN <sup>b</sup>	4.9	-	-	-	0.458	0.101	9	v
	9	0.185	0.104	3	0.430	0.099	11	
	12.7	0.295	0.177	3	0.413	0.097	12	
$\Sigma$ AN <sup>c</sup>	4.9	0.142	0.035	2	0.130	0.072	11	v
	9	0.147	0.146	2	0.119	0.066	11	
	12.7	-	-	-	0.096	0.074	10	
PAN	1.5	0.130	0.078	14	0.458	0.171	12	vi
	5	0.152	0.070	14	0.471	0.154	12	
	17.8	0.159	0.079	7	0.449	0.129	6	

**Table S1.** Continued.

PPN	1.5	0.006	0.004	14	0.039	0.014	12	vi
	5	0.009	0.005	14	0.041	0.014	12	
	17.8	0.009	0.005	7	0.039	0.011	6	
MPAN	1.5	0.031	0.012	14	0.029	0.009	12	vi
	5	0.031	0.013	14	0.034	0.014	12	
	17.8	0.020	0.011	7	0.030	0.011	6	
HNO <sub>3</sub>	16.8	0.555	0.190	16	0.273	0.004	3	vii
HONO	16.8	0.022	0.014	9	0.046	0.007	2	vii
<b><u>Alkenes</u></b>								
isoprene	6.4	1.645	0.676	20	0.211	0.071	15	viii
<b><u>Organic Acids</u></b>								
CH <sub>3</sub> CO <sub>2</sub> H	16.8	4.494	2.398	16	2.078	0.149	3	vii
HCOOH	16.8	4.099	2.530	13	2.396	0.028	3	vii
CH <sub>3</sub> CO <sub>3</sub> H	16.8	0.289	0.087	12	0.138	0.012	3	vii
<b><u>Alcohols</u></b>								
MBO	6.4	3.182	1.092	20	0.623	0.261	15	viii
CH <sub>3</sub> OH	6.4	5.637	1.683	20	4.644	1.083	15	viii
C <sub>2</sub> H <sub>5</sub> OH	6.4	1.560	0.519	20	1.400	0.389	15	viii
IPOPOL	6.4	0.080	0.035	20	0.074	0.016	15	viii
<b><u>Aldehydes</u></b>								
MACR	6.4	0.404	0.189	20	0.120	0.036	15	viii
CH <sub>3</sub> CHO	6.4	0.549	0.185	20	0.426	0.100	15	viii
C <sub>2</sub> H <sub>5</sub> CHO	6.4	0.066	0.015	20	0.061	0.014	15	viii
GLYOX	3, 12	0.077	0.022	21	0.037	0.002	9	ix
HCHO	11.8	-	-	-	12.5	4.0	9	xi
<b><u>Ketones</u></b>								
MVK	6.4	1.448	0.664	20	0.140	0.065	15	viii
CH <sub>3</sub> COCH <sub>3</sub>	6.4	2.446	0.843	20	1.948	0.371	15	viii
ACETOL	16.8	0.243	0.130	12	0.165	0.025	15	vii
NOPINONE	1.5, 9.2	0.007	0.005	5	0.005	0.004	4	x
<b><u>Peroxides</u></b>								
H <sub>2</sub> O <sub>2</sub>	16.8	0.884	0.191	16	0.634	0.054	3	vii
ISOPOOH+IEPOX	16.8	0.247	0.147	12	0.055	0.010	3	vii

**Table S1.** Continued.

<b><i>Terpenoids</i></b>								
$\alpha$ -pinene	1.5, 9.2	0.079	0.008	5	0.024	0.003	3	x
	6.4	0.047	0.011	20	0.013	0.003	15	viii
$\beta$ -pinene	1.5, 9.2	0.232	0.005	5	0.074	0.007	4	x
	6.4	0.152	0.042	20	0.044	0.012	15	viii
limonene	1.5, 9.2	0.061	0.006	5	0.012	0.008	4	x
	6.4	0.011	0.003	20	0.003	0.001	15	viii
3-carene	1.5, 9.2	0.148	0.021	5	0.040	0.004	3	x
myrcene	1.5, 9.2	0.009	0.001	5	0.003	0.000	4	x
camphene	1.5, 9.2	0.004	0.002	5	bdl	bdl	4	x
terpinolene	1.5, 9.2	0.004	0.002	5	bdl	bdl	4	x
$\alpha$ -terpinene	1.5, 9.2	bdl <sup>j</sup>	bdl	5	bdl	bdl	4	x
$\gamma$ -terpinene	1.5, 9.2	0.001	0.001	5	bdl	bdl	4	x
methyl chavicol	1.5, 9.2	0.079	0.013	5	0.037	0.006	4	x
$\alpha$ -bergamotene	1.5, 9.2	0.034	0.002	5	0.003	0.001	4	x
unspeciated SQT	1.5, 9.2	0.022	0.007	5	0.003	0.001	4	x

<sup>a</sup>Measurement technique references: (1) Faloon et al. (2004). (2) Goldstein et al. (2000). (3) Bauer et al. (2000). (4) Mao et al. (2009). (5) Farmer et al. (2010). (6) Wolfe et al. (2009). (7) Crouse et al. (2006). (8) Goldan et al. (2004). (9) Huisman et al. (2008). (10) Bouvier-Brown et al. (2009). (11) Choi et al. (2010).

<sup>b</sup>Sum peroxy nitrates.

<sup>c</sup>Sum alkyl nitrates.

<sup>d</sup>Below detection limit.

**Table S2.** Model-measurement inter-comparison for selected observations. Comma-separated heights denote different measuring heights for hot and cold periods. Measurements are taken from Table S1. Concentrations are in ppbv unless otherwise specified.

Species	Height m	Hot Period			Cool Period		
		Model	Meas	% Diff. <sup>a</sup>	Model	Meas	% Diff.
O <sub>3</sub>	12.5	50.6	50.8	-0.3	45.6	45.5	0.3
CO	12.5	97	97	0.5	\$113	116	-2.9
OH (10 <sup>6</sup> molec cm <sup>-3</sup> )	9.4	3.08E-04	3.24E-04	-5.0	1.96E-04	1.87E-04	5.0
HO <sub>2</sub>	9.4	0.033	0.029	13.4	0.018	0.021	-14.9
<b><u>NO<sub>y</sub></u></b>							
NO <sub>2</sub>	9	0.142	0.139	1.9	0.385	0.368	4.6
PAN	17.8	0.207	0.159	29.9	0.438	0.449	-2.5
PPN	17.8	0.009	0.009	-4.2	0.042	0.039	8.5
MPAN	17.8	0.032	0.031	2.8	0.035	0.030	16.5
ΣPN	9	0.290	0.185	56.7	0.533	0.430	24.0
ΣAN	9	0.125	0.142	-12.3	0.093	0.119	-21.8
HNO <sub>3</sub>	16.8	0.562	0.555	1.3	0.285	0.273	4.2
HONO	16.8	0.001	0.022	-97.4	0.001	0.046	-92.2
<b><u>Alkenes</u></b>							
isoprene	6.4	1.627	1.645	-1.1	0.251	0.211	19.2
<b><u>Organic Acids</u></b>							
CH <sub>3</sub> CO <sub>2</sub> H	16.8	4.582	4.494	2.0	2.055	2.078	-1.1
HCOOH	16.8	4.085	4.099	-0.3	2.417	2.396	0.9
CH <sub>3</sub> CO <sub>3</sub> H	16.8	0.297	0.289	2.7	0.137	0.138	-0.4
<b><u>Alcohols</u></b>							
MBO	6.4	3.237	3.182	1.7	0.659	0.623	5.7
CH <sub>3</sub> OH	6.4	5.346	5.637	-5.2	4.297	4.644	-7.5
C <sub>2</sub> H <sub>5</sub> OH	6.4	1.577	1.56	1.1	1.363	1.400	-2.7
IPROPOL	6.4	0.077	0.08	-3.4	0.071	0.074	-3.4
<b><u>Aldehydes</u></b>							
MACR	6.4	0.395	0.404	-2.3	0.112	0.12	-6.9
CH <sub>3</sub> CHO	6.4	0.457	0.549	-16.7	0.402	0.426	-5.6
C <sub>2</sub> H <sub>5</sub> CHO	6.4	0.066	0.066	-0.2	0.057	0.061	-6.0
GLYOX	3, 12	0.071	0.077	-8.4	0.035	0.037	-4.1
HCHO	11.8	4.165	-	-	1.400	12.5	-89

**Table S2.** Continued.

<b><u>Ketones</u></b>							
MVK	6.4	1.432	1.448	-1.1	0.144	0.14	2.5
CH <sub>3</sub> COCH <sub>3</sub>	6.4	2.545	2.446	4.1	1.892	1.948	-2.9
ACETOL	16.8	0.238	0.243	-2.3	0.164	0.165	-0.7
NOPINONE	1.5, 9.2	0.010	0.007	44.0	0.005	0.005	7.7
<b><u>Peroxides</u></b>							
H <sub>2</sub> O <sub>2</sub>	16.8	0.856	0.884	-3.2	0.531	0.634	-16.3
ISOPOOH+IEPOX	16.8	0.495	0.247	100.4	0.027	0.055	-50.1
<b><u>Terpenoids</u></b>							
α-pinene	1.5, 9.2	0.086	0.079	8.6	0.020	0.024	-17.5
β-pinene	1.5, 9.2	0.156	0.232	-32.7	0.030	0.074	-59.7
limonene	1.5, 9.2	0.053	0.061	-13.6	0.015	0.012	21.1
3-carene	1.5, 9.2	0.081	0.148	-45.0	0.020	0.04	-51.0
myrcene	1.5, 9.2	0.037	0.009	311.0	0.009	0.003	185.2
camphene	1.5, 9.2	0.057	0.004	1316.8	0.016	bdl	-
terpinolene	1.5, 9.2	0.008	0.004	110.5	0.002	bdl	-
α-terpinene	1.5, 9.2	0.004	bdl <sup>b</sup>	-	0.001	bdl	-
γ-terpinene	1.5, 9.2	0.009	0.001	777.8	0.002	bdl	-
Methyl chavicol	1.5, 9.2	0.081	0.079	3.0	0.013	0.037	-64.0
α-bergamotene	1.5, 9.2	0.027	0.034	-19.6	0.008	0.003	173.0
unspeciated SQT	1.5, 9.2	0.008	0.022	-64.7	0.004	0.003	31.4

<sup>a</sup>Calculated as 100\*(Model - Meas)/Meas.

<sup>b</sup>Below detection limit.

**References**

- Bauer, M. R., Hultman, N. E., Panek, J. A., and Goldstein, A. H.: Ozone deposition to a ponderosa pine plantation in the Sierra Nevada Mountains (CA): A comparison of two different climatic years, *J. Geophys. Res.*, 105, 22123-22136, 2000.
- Bouvier-Brown, N. C., Goldstein, A. H., Gilman, J. B., Kuster, W. C., and de Gouw, J. A.: In-situ ambient quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds during BEARPEX 2007: implications for gas- and particle-phase chemistry, *Atmos. Chem. Phys.*, 9, 5505-5518, 2009.
- Choi, W., Faloon, I. C., Bouvier-Brown, N. C., McKay, M., Goldstein, A. H., Mao, J., Brune, W. H., LaFranchi, B. W., Cohen, R. C., Wolfe, G. M., Thornton, J. A., Sonnenfroh, D. M., and Millet, D. B.: Observations of elevated formaldehyde over a forest canopy suggest missing sources from rapid oxidation of arboreal hydrocarbons, *Atmos. Chem. Phys.*, 10, 8761-8781, 2010.
- Crounse, J. D., McKinney, K. A., Kwan, A. J., and Wennberg, P. O.: Measurement of gas-phase hydroperoxides by chemical ionization mass spectrometry, *Analytical Chemistry*, 78, 6726-6732, 2006.
- Faloon, I. C., Tan, D., Leshner, R. L., Hazen, N. L., Frame, C. L., Simpas, J. B., Harder, H., Martinez, M., Di Carlo, P., Ren, X. R., and Brune, W. H.: A laser-induced fluorescence instrument for detecting tropospheric OH and HO<sub>2</sub>: Characteristics and calibration, *J. Atmos. Chem.*, 47, 139-167, 2004.
- Farmer, D. K., Perring, A. E., Wooldridge, P. J., Blake, D. R., Baker, A., Meinardi, S., Huey, L. G., Tanner, D., O.Vargas, and Cohen, R. C.: Impact of organic nitrates on urban ozone production, *Atmos. Chem. Phys. Discuss.*, 10, 23423-23448, 2010.
- Goldan, P. D., Kuster, W. C., Williams, E., Murphy, P. C., Fehsenfeld, F. C., and Meagher, J.: Nonmethane hydrocarbon and oxy hydrocarbon measurements during the 2002 New England Air Quality Study, *Journal Of Geophysical Research-Atmospheres*, 109, D21309, 10.1029/2003JD004455, 2004.
- Goldstein, A. H., Hultman, N. E., Fracheboud, J. M., Bauer, M. R., Panek, J. A., Xu, M., Qi, Y., Guenther, A. B., and Baugh, W.: Effects of climate variability on the carbon dioxide, water, and sensible heat fluxes above a ponderosa pine plantation in the Sierra Nevada (CA), *Agr. Forest Meteorol.*, 101, 113 - 129, 2000.
- Huisman, A. J., Hottle, J. R., Coens, K. L., DiGangi, J. P., Galloway, M. M., Kammrath, A., and Keutsch, F. N.: Laser-induced phosphorescence for the in situ detection of glyoxal at part per trillion mixing ratios, *Analytical Chemistry*, 80, 5884-5891, 2008.
- Mao, J., Ren, X., Brune, W. H., Olson, J. R., Crawford, J. H., Fried, A., Huey, L. G., Cohen, R. C., Heikes, B., Singh, H. B., Blake, D. R., Sachse, G. W., Diskin, G. S., Hall, S. R., and Shetter, R. E.: Airborne measurement of OH reactivity during INTEX-B, *Atmos. Chem. Phys.*, 9, 163-173, 2009.
- Wolfe, G. M., Thornton, J. A., Yatavelli, R. L. N., McKay, M., Goldstein, A. H., LaFranchi, B., Min, K. E., and Cohen, R. C.: Eddy covariance fluxes of acyl peroxy nitrates (PAN, PPN and MPAN) above a Ponderosa pine forest, *Atmos. Chem. Phys.*, 9, 615-634, 2009.