Supplementary Information

Adjoint inversion of Chinese non-methane volatile organic compound emissions using space-based observations of formaldehyde and glyoxal

Hansen Cao[1], Tzung-May Fu[1, *], Lin Zhang[1], Daven K. Henze[2], Christopher Chan Miller[3], Christophe Lerot[4], Gonzalo González Abad[3], Isabelle De Smedt[4], Qiang Zhang[5], Michel van Roozendael[4], Kelly Chance[3], Jie Li[6], Junyu Zheng[7], Yuanhong Zhao[1]

[1]Department of Atmospheric and Oceanic Sciences and Laboratory for Climate and Ocean-Atmosphere Studies, School of Physics, Peking University, Beijing, China,100871
[2]Department of Mechanical Engineering, University of Colorado, Boulder, USA
[3]Atomic and Molecular Physics Division, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, USA
[4]Belgian Institute for Space Aeronomy (BIRA-IASB), Brussels, Belgium
[5]Center for Earth System Science, Tsinghua University, Beijing, China
[6]Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China
[7]College of Environmental Science and Engineering, South China University of Technology, Guangzhou, China

Correspondence to: Tzung-May Fu (tmfu@pku.edu.cn)

Table S1. Ground-based MAX-DOAS measurements of formaldehyde and glyoxal vertical column densities over China

Reference	Location	Time		Vertical column densities	
				9-10 LT	13-14 LT
Formaldehyde [10^{16} molecules cm^{-2}]					
Wang et al. (2017)	Wuxi (31.57°N,120.31°E)	2011 - 2014	JF	0.7 [a]	0.8 [a]
			MA	0.9±0.15 [a]	1.1±0.26 [a]
			MJ	1.5±0.12 [a]	1.9±0.15 [a]
			JA	1.7±0.10 [a]	2.2±0.26 [a]
			SO	1.2±0.12 [a]	1.7±0.12 [a]
			ND	0.8±0.30 [a]	1.4±0.32 [a]
Lee et al. (2015)	Beijing (39.59°N, 116.18°E)	August 16 to September 11, 2006			1.79
De Smedt et al., (2015)	Beijing (39.98°N,116.38° E)	2008 - 2013	DJF	0.9±0.2 [b]	0.8±0.2 [b]
			MAM	1.3±0.3 [b]	1.2±0.2 [b]
			JJA	2.0±0.6 [b]	2.5±0.5 [b]
			SON	1.3±0.3 [b]	1.6±0.3 [b]
Li et al. (2013)	Back Garden, Guangdong (23.50°N, 113.03°E)	July 2006		1.3±1.0 [c]	1.3±0.7 [c]
Glyoxal [10^{14} molecules cm^{-2}]					
Li et al. (2013)	Back Garden, Guangdong (23.50°N, 113.03°E)	July 2006		6.8±5.2 [d]	11.4±6.8 [d]

[a] Bimonthly mean computed from Figure 12 of Wang et al. (2017)

[b] From hourly data in Figure 10 of De Smedt et al. (2015)

[c] From Figure 4 of Li et al. (2013)

[d] From Figure 5 of Li et al. (2013)

30 **Table S2. Ground-based and ozonesonde measurements of surface ozone concentrations over China.**

Reference	Location	Platform	Time	Mixing ratio (ppb)
Wang et al. (2012)	Beijing (39.8^oN, 116.47^oE)	Ozonesonde	14:00 LT, June 2002-2010	100-120
			14:00 LT, December 2002-2010	<30
Sun et al. (2016)	Mt. Tai (36.25^oN, 117.10^oE, 1533m a.s.l.)	Ground-based	Maximum daily 8h-average, June 2006-2015	108
Li et al. (2007)	Mt. Tai (36.25^oN, 117.10^oE, 1533m a.s.l.)	Ground-based	13-17 LT, December 2004	46
Li et al. (2007)	Mt. Hua (110.09^oE, 34.49^oN, 2064m a.s.l.)	Ground-based	13-17 LT, June 2004	76
			13-17 LT, December 2004	38
Xu et al. (2008)	Lin'an (30^o3N, 119^o7E)	Ground-based	13-17 LT, June 2005-2006	62
			13-17 LT, December 2005-2006	27
Xu et al. (2016)	Waliguan (36.28^oN, 100.9^oE, 3816m a.s.l.)	Ground-based	11-16 LT, June 1994-2013	61
			11-16 LT, December 1994-2013	41
Zheng et al. (2010)	Huizhou (114.4^oE,23.09^oN)	Ground-based	13-17 LT, June 2007	34
			13-17 LT, December 2007	66
J.M. Zhang et al. (2009)	Lanzhou (36.13^oN, 103.69^oE, 1631m a.s.l.)	Ground-based	13-17 LT, June 2006	74
Li et al. (2015)	Changchun (43.9^oN, 125.2^oE)	Ozonesonde	14 LT, June 13, 2013	62
Wang et al. (2015)	Akedala (47.1^oN, 87.5^oE, 502m a.s.l.)	Ground-based	13-17 LT, July 2013	53
			13-17 LT, November 2013	21

31

32

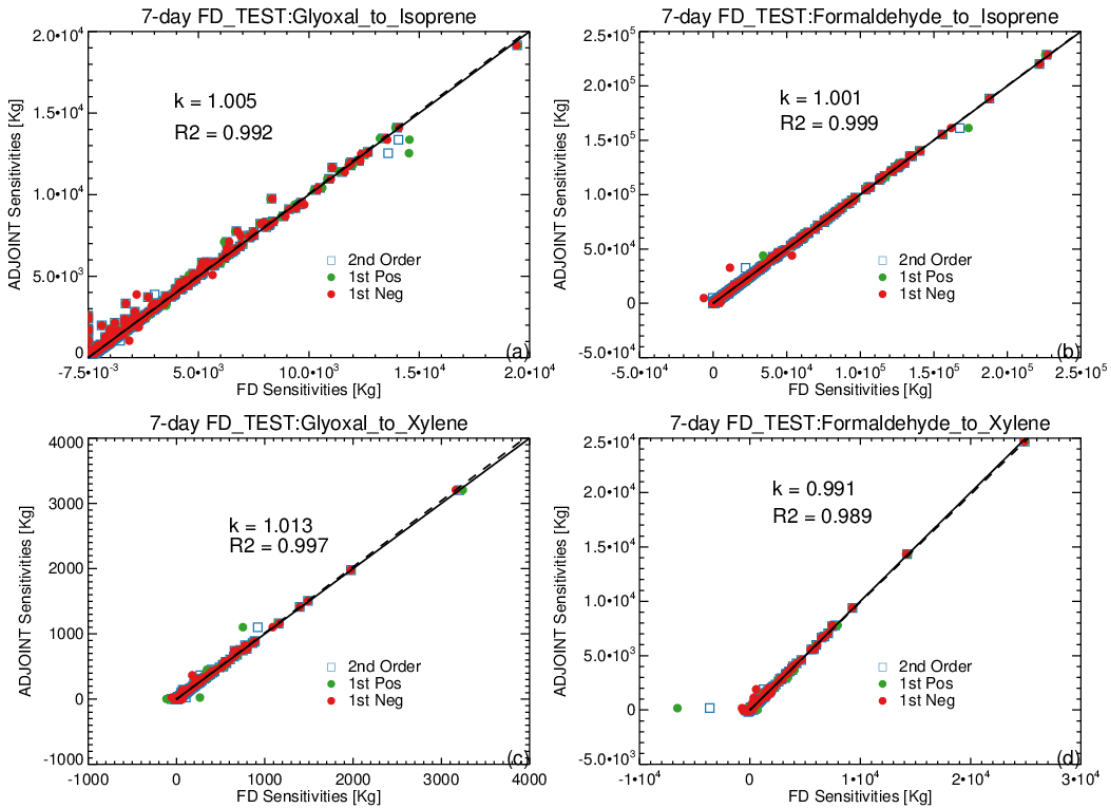

Figure S1. Finite difference test (July 1th to 7th, 2007) for adjoint model. (a): sensitivities of global glyoxal burden to biogenic isoprene emission scale factor; (b): sensitivities of global formaldehyde burden to biogenic isoprene emission scale factor; (c) sensitivities of global glyoxal burden to anthropogenic xylene emission scale factor; (d): sensitivities of global formaldehyde burden to anthropogenic xylene emission scale factor. ADJOINT sensitivities and FD sensitivities were calculated by adjoint model and forward model, respectively. 'k' and 'R2' represent regression slope and square of correlation coefficient, respectively. '2nd Order', '1st Pos' and '1st Nes' represent sensitivities calculated by central, forward, backward finite difference methods, respectively.

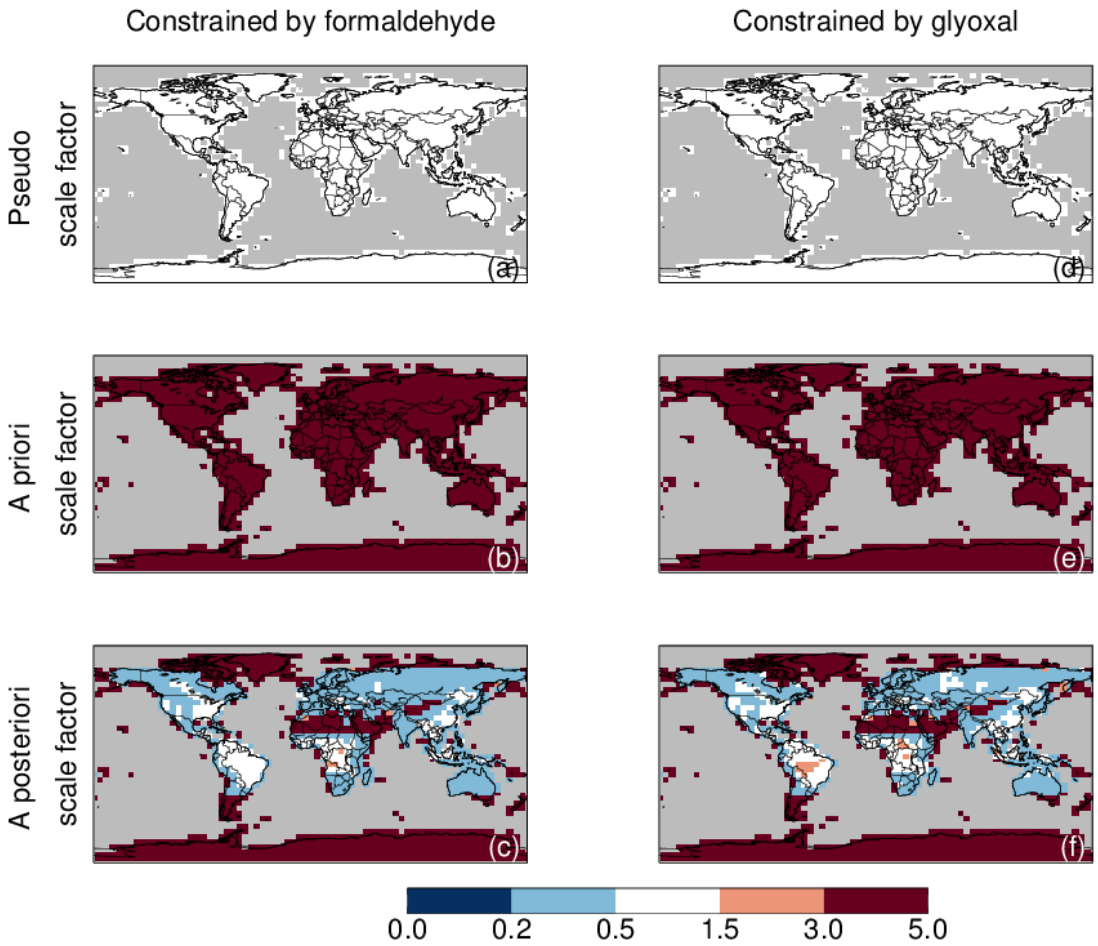

Figure S2. Pseudo isoprene emission scale factor ((a) and (d), uniformly set to 1.0 to generate pseudo observations), the *a priori* isoprene emission scale factor ((b) and (e), uniformly set to 5.0), and the *a posteriori* isoprene emission scale factor ((c) and (f)) in inversion tests (July 1th to 7th, 2007) constrained by pseudo observations of formaldehyde and glyoxal, respectively.

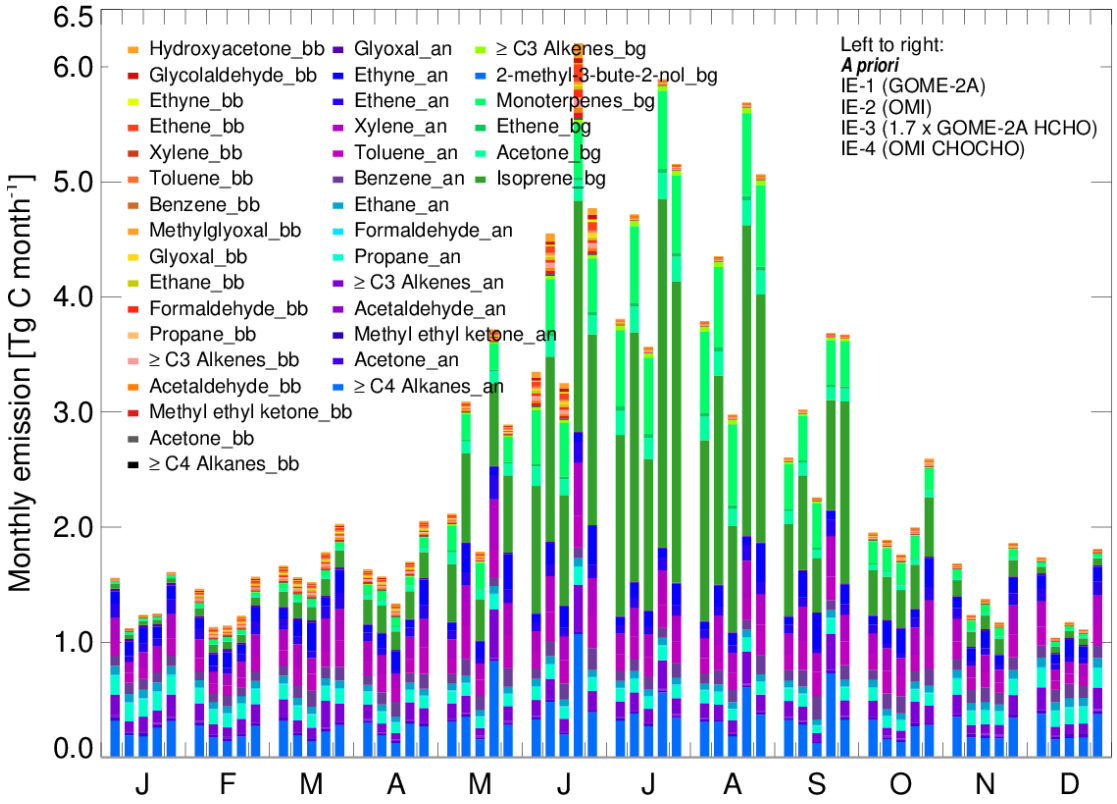

Figure S3. Comparison of the *a priori* and *a posteriori* monthly Chinese NMVOC emission estimates for the year 2007. The bars from left to right for each month represent the *a priori* emission estimates and the *a posteriori* emission estimates from IE-1, IE-2, IE-3, and IE-4, respectively. Color keys for the NMVOC species are shown inset; the suffixes 'an', 'bb', and 'bg' indicate anthropogenic source, biomass burning source, and biogenic source, respectively.

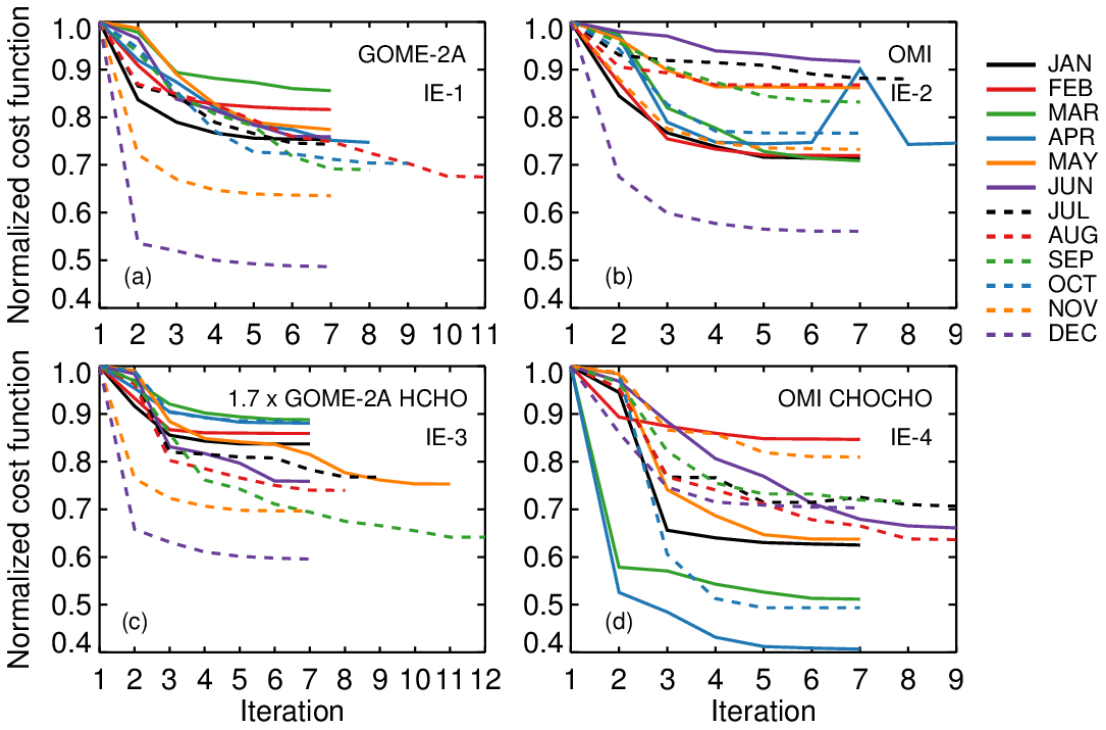

Figure S4. Change in the normalized cost function ($J(x)_i$ / $J(x)_{i=1}$) over China in the four inversion experiments: (a) IE-1, (b) IE-2, (c) IE-3, and (d) IE-4.

Reference

De Smedt, I., Stavrakou, T., Hendrick, F., Danckaert, T., Vlemmix, T., Pinardi, G., Theys, N., Lerot, C., Gielen, C., Vigouroux, C., Hermans, C., Fayt, C., Veefkind, P., Müller, J. F., and Van Roozendael, M.: Diurnal, seasonal and long-term variations of global formaldehyde columns inferred from combined OMI and GOME-2 observations, Atmos. Chem. Phys., 15, 12519-12545, doi: 10.5194/acp-15-12519-2015, 2015.

Lee, H., Ryu, J., Irie, H., Jang, S.-H., Park, J., Choi, W., and Hong, H.: Investigations of the Diurnal Variation of Vertical HCHO Profiles Based on MAX-DOAS Measurements in Beijing: Comparisons with OMI Vertical Column Data, Atmosphere, 6, 1816-1832, doi: 10.3390/atmos6111816, 2015.

Li, D., and Bian, J. C.: Observation of a Summer Tropopause Fold by Ozonesonde at Changchun, China: Comparison with Reanalysis and Model Simulation, Adv. Atmos. Sci., 32, 1354-1364, doi: 10.1007/s00376-015-5022-x, 2015.

Li, J., Wang, Z. F., Akimoto, H., Gao, C., Pochanart, P., and Wang, X. Q.: Modeling study of ozone seasonal cycle in lower troposphere over east Asia, J. Geophys. Res. Atmos., 112, doi: 10.1029/2006JD008209, 2007.

Li, X., Brauers, T., Hofzumahaus, A., Lu, K., Li, Y. P., Shao, M., Wagner, T., and Wahner, A.: MAX-DOAS measurements of NO2, HCHO and CHOCHO at a rural site in Southern China, Atmos. Chem. Phys., 13, 2133-2151, doi: 10.5194/acp-13-2133-2013, 2013.

Sun, L., Xue, L. K., Wang, T., Gao, J., Ding, A. J., Cooper, O. R., Lin, M. Y., Xu, P. J., Wang, Z., Wang, X. F., Wen, L., Zhu, Y. H., Chen, T. S., Yang, L. X., Wang, Y., Chen, J. M., and Wang, W. X.: Significant increase of summertime ozone at Mount Tai in Central Eastern China, Atmos. Chem. Phys., 16, 10637-10650, doi: 10.5194/acp-16-10637-2016, 2016.

Wang, H. Q., Ma, J. M., Shen, Y. J., and Wang, Y. A.: Assessment of Ozone Variations and Meteorological Influences at a Rural Site in Northern Xinjiang, Bull. Environ. Contam. Tox., 94, 240-246, doi: 10.1007/s00128-014-1451-y, 2015.

Wang, Y., Beirle, S., Lampel, J., Koukouli, M., De Smedt, I., Theys, N., Li, A., Wu, D. X., Xie, P. H., Liu, C., Van Roozendael, M., Stavrakou, T., Muller, J. F., and Wagner, T.: Validation of OMI, GOME-2A and GOME-2B tropospheric NO2, SO2 and HCHO products using MAX-DOAS observations from 2011 to 2014 in Wuxi, China: investigation of the effects of priori profiles and aerosols on the satellite products, Atmos. Chem. Phys., 17, 5007-5033, doi: 10.5194/acp-17-5007-2017, 2017.

Wang, Y., Konopka, P., Liu, Y., Chen, H., Muller, R., Ploger, F., Riese, M., Cai, Z., and Lu, D.: Tropospheric ozone trend over Beijing from 2002-2010: ozonesonde measurements and modeling analysis, Atmos. Chem. Phys., 12, 8389-8399, doi: 10.5194/acp-12-8389-2012, 2012.

Xu, W. Y., Lin, W. L., Xu, X. B., Tang, J., Huang, J. Q., Wu, H., and Zhang, X. C.: Long-term trends of surface ozone and its influencing factors at the Mt Waliguan GAW station, China - Part 1: Overall trends and characteristics, Atmos. Chem. and Phys., 16, 6191-6205, doi: 10.5194/acp-16-6191-2016, 2016.

Xu, X., Lin, W., Wang, T., Yan, P., Tang, J., Meng, Z., and Wang, Y.: Long-term trend of surface ozone at a regional background station in eastern China 1991-2006: enhanced variability, Atmos. Chem. Phys., 8, 2595-2607, doi: 10.5194/acp-8-2595-2008, 2008.

Zhang, J. M., Wang, T., Ding, A. J., Zhou, X. H., Xue, L. K., Poon, C. N., Wu, W. S., Gao, J., Zuo, H. C., Chen, J. M., Zhang, X. C., and Fan, S. J.: Continuous measurement of peroxyacetyl nitrate (PAN) in suburban and remote areas of western China, Atmos. Environ., 43, 228-237, doi: 10.1016/j.atmosenv.2008.09.070, 2009.

Zheng, J. Y., Zhong, L. J., Wang, T., Louie, P. K. K., and Li, Z. C.: Ground-level ozone in the Pearl River Delta region: Analysis of data from a recently established regional air quality monitoring network, Atmos. Environ., 44, 814-823, doi: 10.1016/j.atmosenv.2009.11.032, 2010.