

Chemical equation set and complete figures set

**A.Pozzer^{1,2}, J. Pollmann¹, D. Taraborrelli¹,
D. Helmig³, P. Jöckel^{2,4},
P.Tans⁵, J.Hueber³, J.Lelieveld^{1,2}**

1 EEWRC, The Cyprus Institute, 20 Kavafi Street, 1645 Nicosia, Cyprus

2 Air Chemistry Department, Max-Planck Institute of Chemistry, PO Box 3060,
55020 Mainz, Germany

3 Institute of Arctic and Alpine Research (INSTAAR), University of Colorado,
UCB 450, CO 80309, USA

4 now at: Deutsches Zentrum fuer Luft- und Raumfahrt, Oberpfaffenhofen,
Wessling, Germany

5 NOAA/ESRL CMDL, R/E/CG1, 325 Broadway, Boulder, CO 80303, USA

`pozzer@cyi.ac.cy`

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Table 1: Reaction added to the MECCA submodel in EMAC.

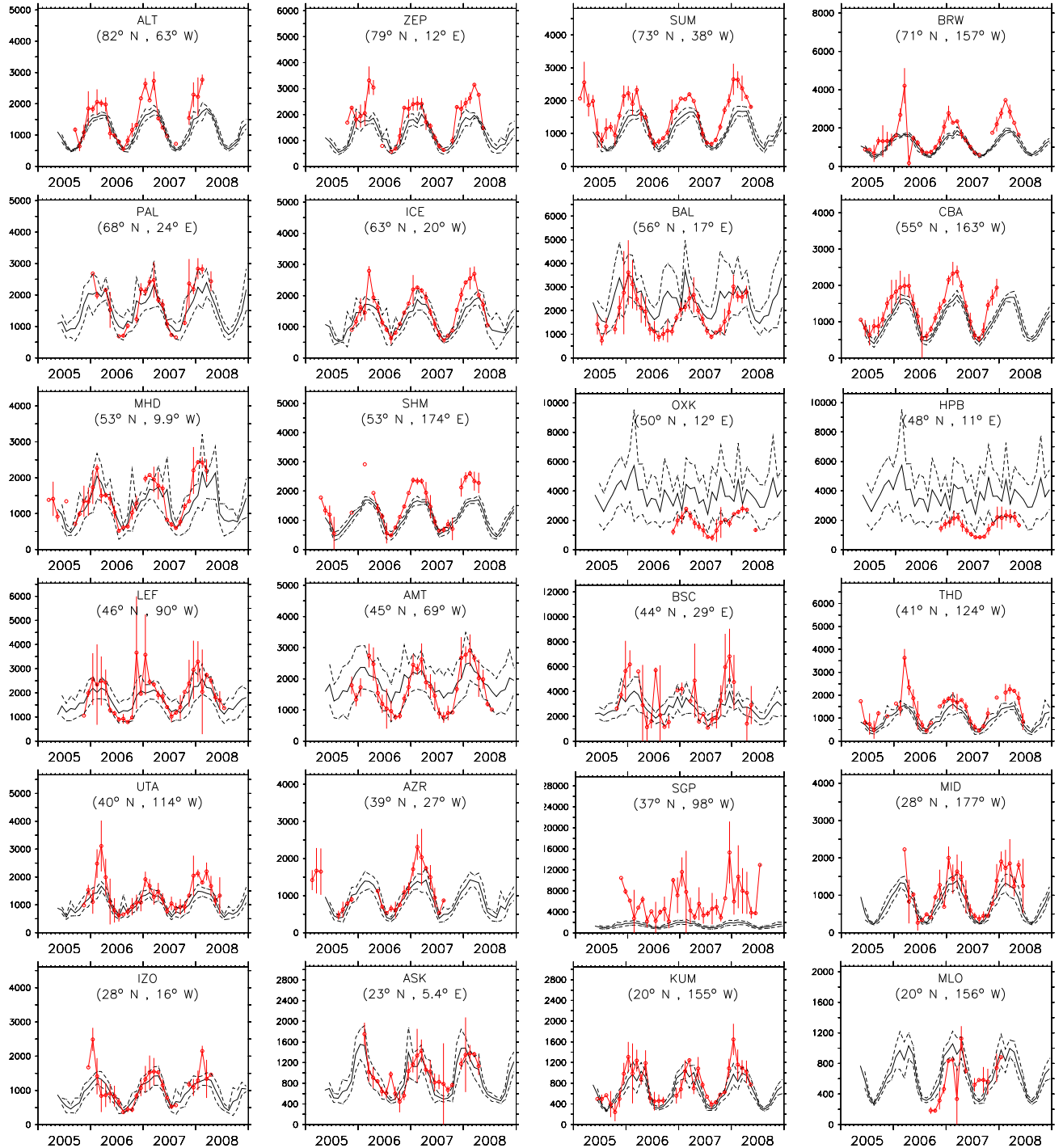
reaction	rate coefficient	reference/notes
$\text{OH} + \text{C}_4\text{H}_{10} \rightarrow \text{HCHO} + 0.4365 \text{ CH}_3\text{CHO} + 0.4365 \text{ PA} + 4.254 \text{ PINKO}_2$	$1.69 \times 10^{-17} * T^2 * e^{(145/T)}$	a, b
$\text{CL} + \text{C}_4\text{H}_{10} \rightarrow \text{HCHO} + 0.3575 \text{ CH}_3\text{CHO} + 0.3575 \text{ PA} + 4.57 \text{ PINKO}_2$	2.18×10^{-10}	a, b
$\text{NO}_3 + \text{C}_4\text{H}_{10} \rightarrow \text{HCHO} + 0.4365 \text{ CH}_3\text{CHO} + 0.4365 \text{ PA} + 4.2524 \text{ PINKO}_2$	$2.76 \times 10^{-12} * e^{(-3279/T)}$	c
$\text{OH} + \text{IC}_4\text{H}_{10} \rightarrow .206 \text{ P}\cdot\text{O}_2 + .794 \text{ CH}_3\text{COCH}_3 + .794 \text{ CH}_3\text{O}_2 + 1.206 \text{ PINKO}_2$	$1.16 \times 10^{-17} * T^2 * e^{(225/T)}$	a, b
$\text{CL} + \text{IC}_4\text{H}_{10} \rightarrow 0.564 \text{ P}\cdot\text{O}_2 + 0.436 \text{ CH}_3\text{COCH}_3 + 0.436 \text{ CH}_3\text{O}_2 + 1.564 \text{ PINKO}_2$	1.43×10^{-10}	a, b
$\text{NO}_3 + \text{IC}_4\text{H}_{10} \rightarrow 0.206 \text{ P}\cdot\text{O}_2 + 0.794 \text{ CH}_3\text{COCH}_3 + 0.794 \text{ CH}_3\text{O}_2 + 1.206 \text{ PINKO}_2$	1.06×10^{-16}	c
$\text{OH} + \text{C}_5\text{H}_{12} \rightarrow 1.4765 \text{ HCHO} + 0.349 \text{ CH}_3\text{CHO} + 0.1745 \text{ EtO}_2 + 6.302 \text{ PINKO}_2$	$2.44 \times 10^{-17} * T^2 * e^{(183/T)}$	a, b
$\text{CL} + \text{C}_5\text{H}_{12} \rightarrow 1.67 \text{ HCHO} + 0.220 \text{ CH}_3\text{CHO} + 0.11 \text{ EtO}_2 + 6.56 \text{ PINKO}_2$	2.80×10^{-10}	a, b
$\text{NO}_3 + \text{C}_5\text{H}_{12} \rightarrow 1.4765 \text{ HCHO} + 0.349 \text{ CH}_3\text{CHO} + 0.1745 \text{ EtO}_2 + 6.302 \text{ PINKO}_2$	8.7×10^{-17}	c
$\text{OH} + \text{IC}_5\text{H}_{12} \rightarrow 0.087 \text{ HCHO} + 0.384 \text{ CH}_3\text{CHO} + 0.297 \text{ P}\cdot\text{O}_2 + 0.616 \text{ CH}_3\text{COCH}_3 + 0.616 \text{ EtO}_2 + 1.435 \text{ PINKO}_2$	3.70×10^{-12}	a, b
$\text{CL} + \text{IC}_5\text{H}_{12} \rightarrow 0.408 \text{ HCHO} + 0.780 \text{ CH}_3\text{CHO} + 0.342 \text{ P}\cdot\text{O}_2 + 0.250 \text{ EtO}_2 + 3.04 \text{ PINKO}_2$	2.20×10^{-10}	a, b
$\text{NO}_3 + \text{IC}_5\text{H}_{12} \rightarrow 0.087 \text{ HCHO} + 0.384 \text{ CH}_3\text{CHO} + 0.297 \text{ P}\cdot\text{O}_2 + 0.616 \text{ CH}_3\text{COCH}_3 + 0.616 \text{ EtO}_2 + 1.435 \text{ PINKO}_2$	1.62×10^{-16}	c
$\text{PINKO}_2 + \text{NO} \rightarrow 0.95 \text{ NO}_2 + 0.475 \text{ HO}_2 + 0.475 \text{ PINK} + 0.05 \text{ PINKNO}_3$	$\left(2.54 * e^{(360./T)} + 8.10 * e^{(270./T)} \right) \times 10^{-12} / 2$	h
$\text{PINKO}_2 + \text{CH}_3\text{O}_2 \rightarrow 0.5 \text{ HO}_2 + 0.335 \text{ CH}_3\text{OH} + 0.665 \text{ HCHO} + 0.335 \text{ HO}_2$	$2. \times 10^{-12}$	h
$\text{PINKO}_2 + \text{HO}_2 \rightarrow \text{PINKOOH}$	$\left(4.30 * e^{(1040./T)} + 2.91 * e^{(1300./T)} \right) \times 10^{-13} / 2$	h
$\text{PINK} + \text{OH} \rightarrow \text{CO}_2$	2×10^{-11}	d
$\text{PINK} + \text{h}\nu \rightarrow \text{HO}_2$	$\text{J-CH}_3\text{CHO}$	d
$\text{PINKNO}_3 + \text{OH} \rightarrow \text{NO}_2$	$5. \times 10^{-12}$	d
$\text{PINKNO}_3 + \text{h}\nu \rightarrow \text{NO}_2$	3.7^*J-PAN	e
$\text{PINKOOH} + \text{h}\nu \rightarrow \text{OH} + 0.5 \text{ HO}_2$	$\text{J-CH}_3\text{OOH}$	f
$\text{PINKOOH} + \text{OH} \rightarrow \text{PINKO}_2$	$1.90 \times 10^{-12} * e^{(190./T)}$	f
$\text{PINKOOH} + \text{OH} \rightarrow \text{OH}$	$2. \times 10^{-11}$	a, b

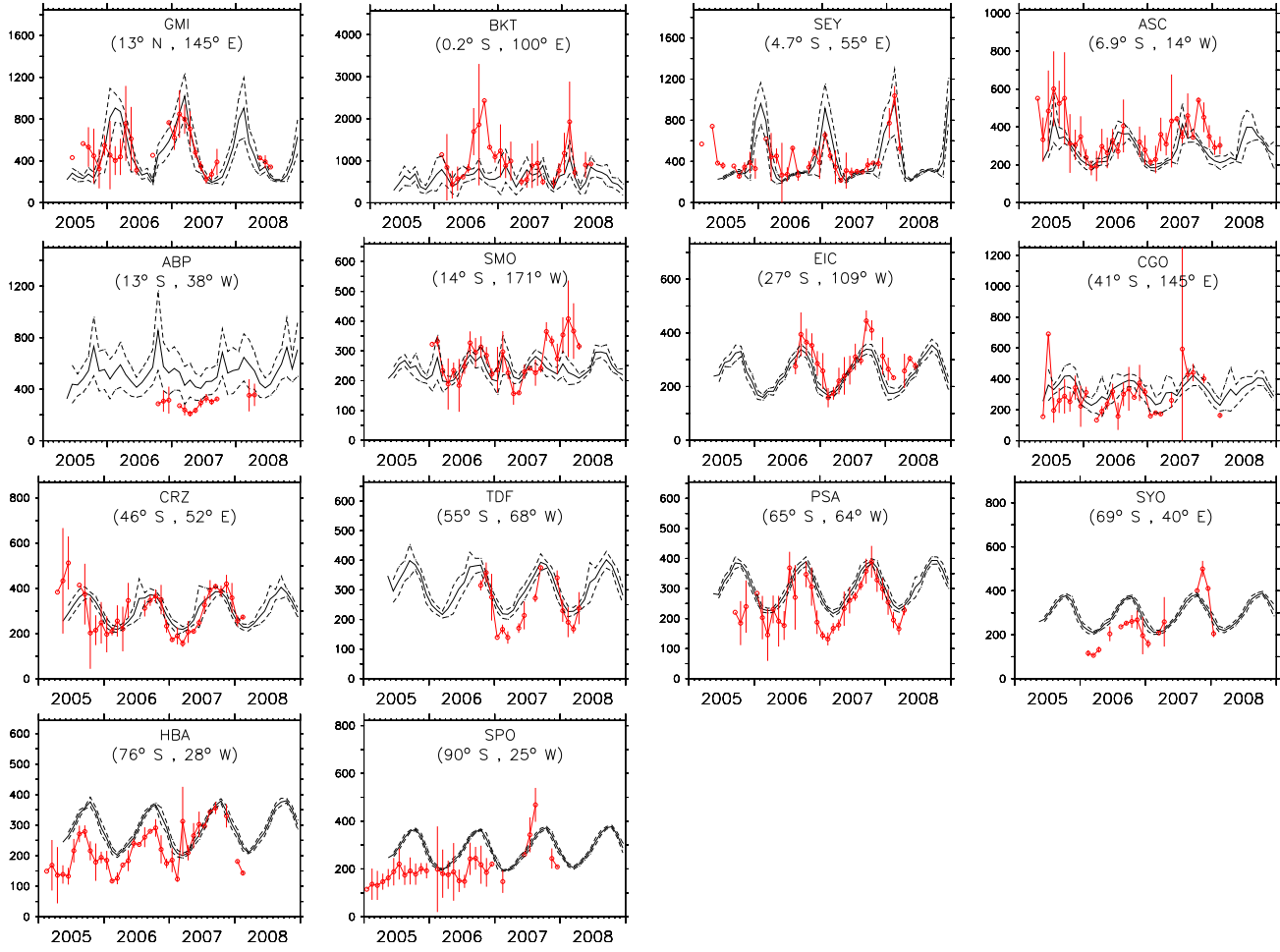
^aSaunders et al. (1997a)^bSaunders et al. (1997b)^cAtkinson and Arey (2003), branching ratio like the OH reaction^das general aldehyde^ephotolysis scale with PAN photolysis rate^fphotolysis scale with CH₃OOH photolysis rate^grepresentative for the H-abstraction of these peroxides^haverage between the reactions of the two different peroxides isomers

Model-observation comparison

Ethane (C_2H_6)

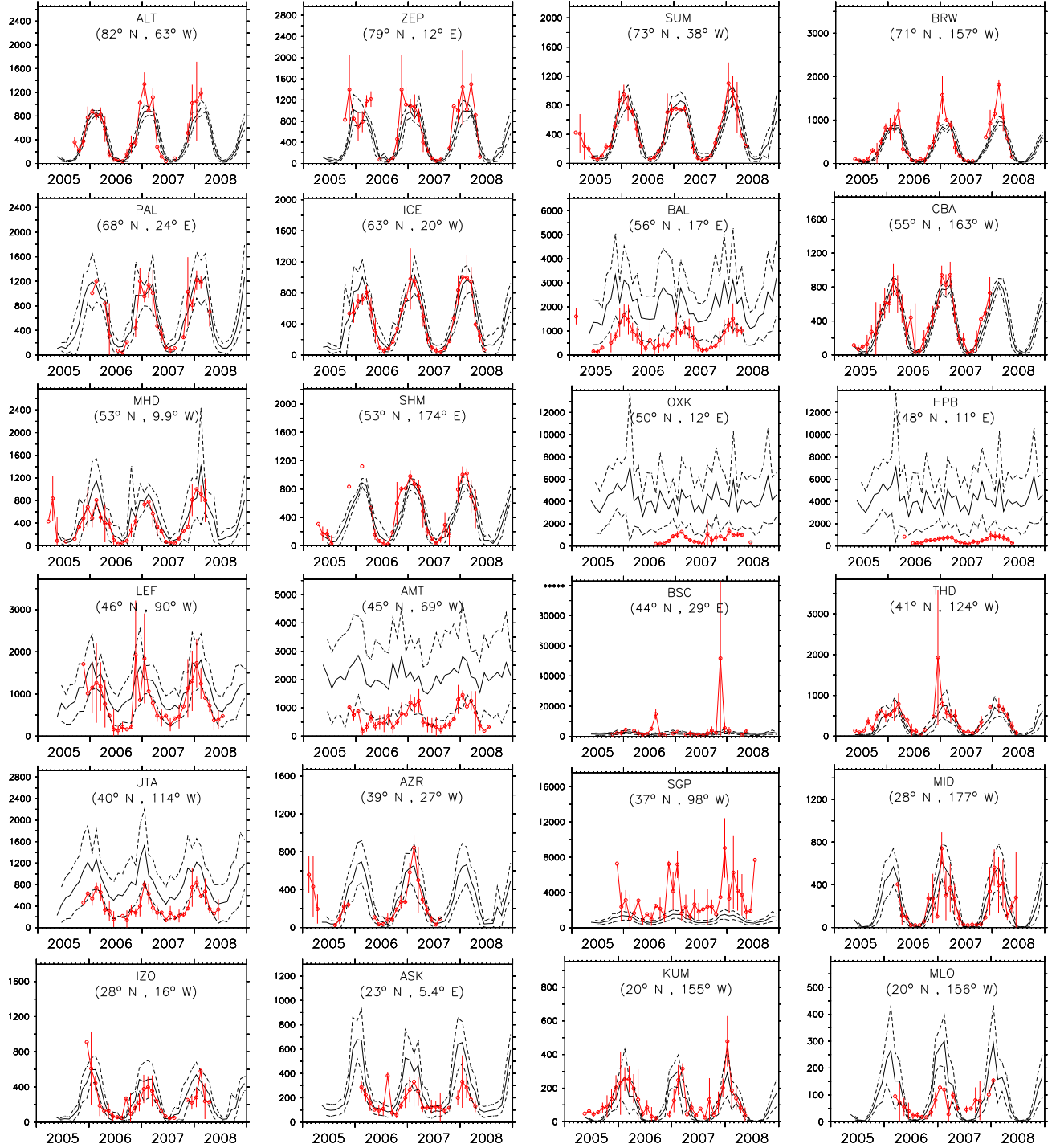
Comparison of simulated and observed C_2H_6 mixing ratios in pmol/mol for all the available locations (ordered by latitude). The red line and the bars represent the monthly average and the standard deviation (w.r.t. time) of the measurements in the region. No instrumental error has been included in this standard deviation. The simulated monthly average is indicated in the black line and the corresponding simulated standard deviation (w.r.t. time) by the dashed line.

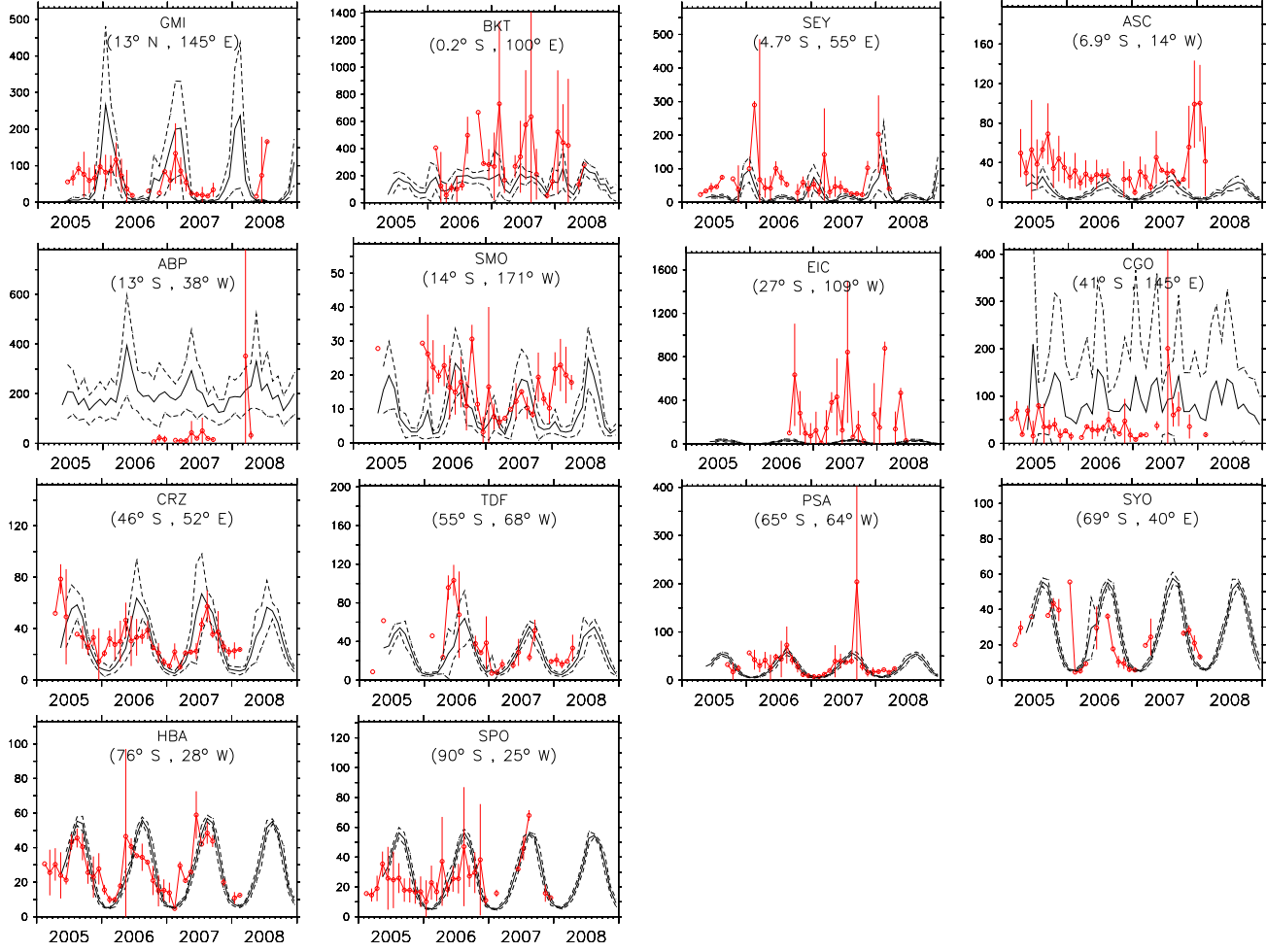




Propane (C_3H_8)

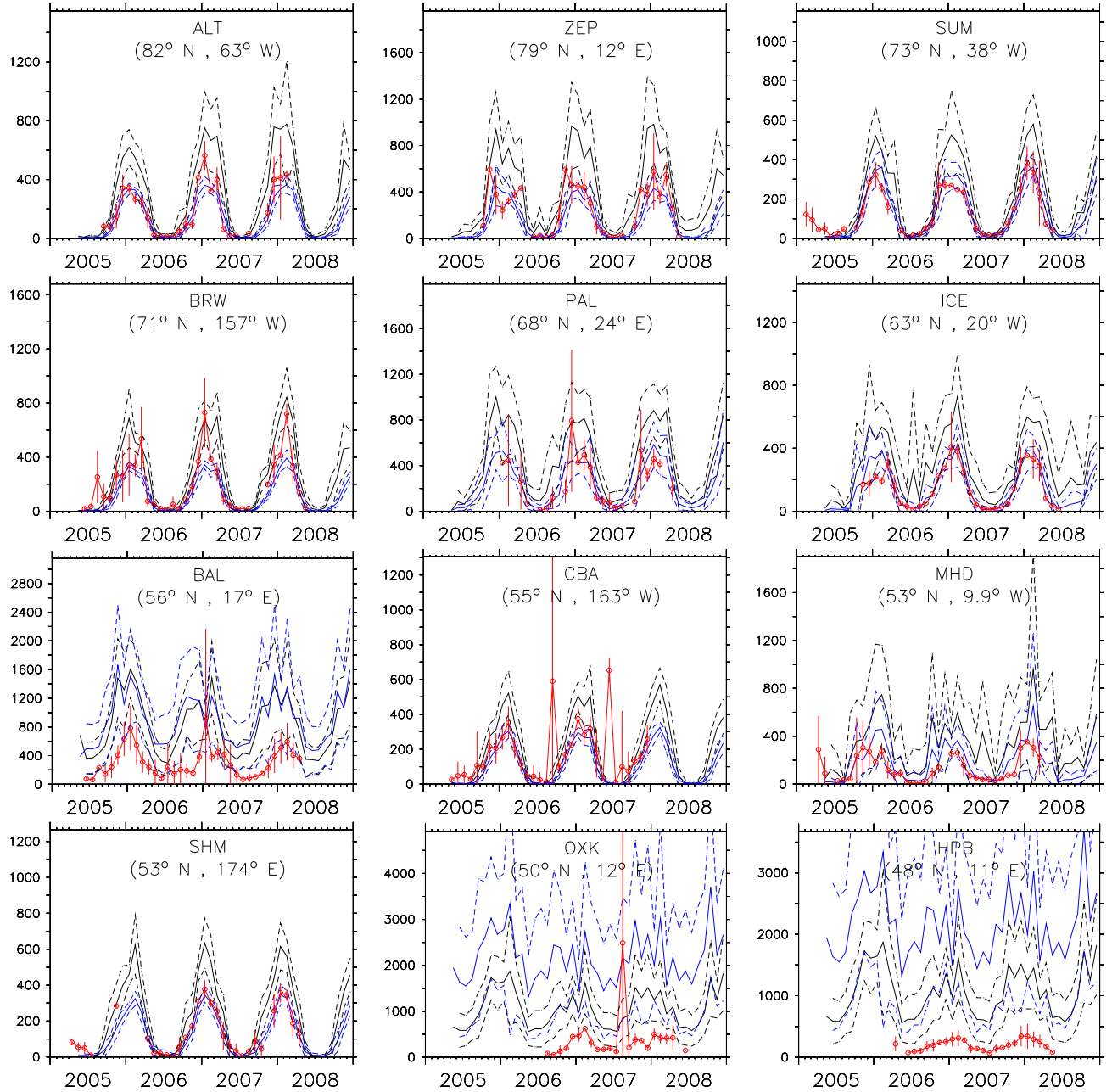
Comparison of simulated and observed C_3H_8 mixing ratios in pmol/mol for all the available locations (ordered by latitude). The red line and the bars represent the monthly average and the standard deviation (w.r.t. time) of the measurements in the region. No instrumental error has been included in this standard deviation. The simulated monthly average is indicated in the black line and the corresponding simulated standard deviation (w.r.t. time) by the dashed line.

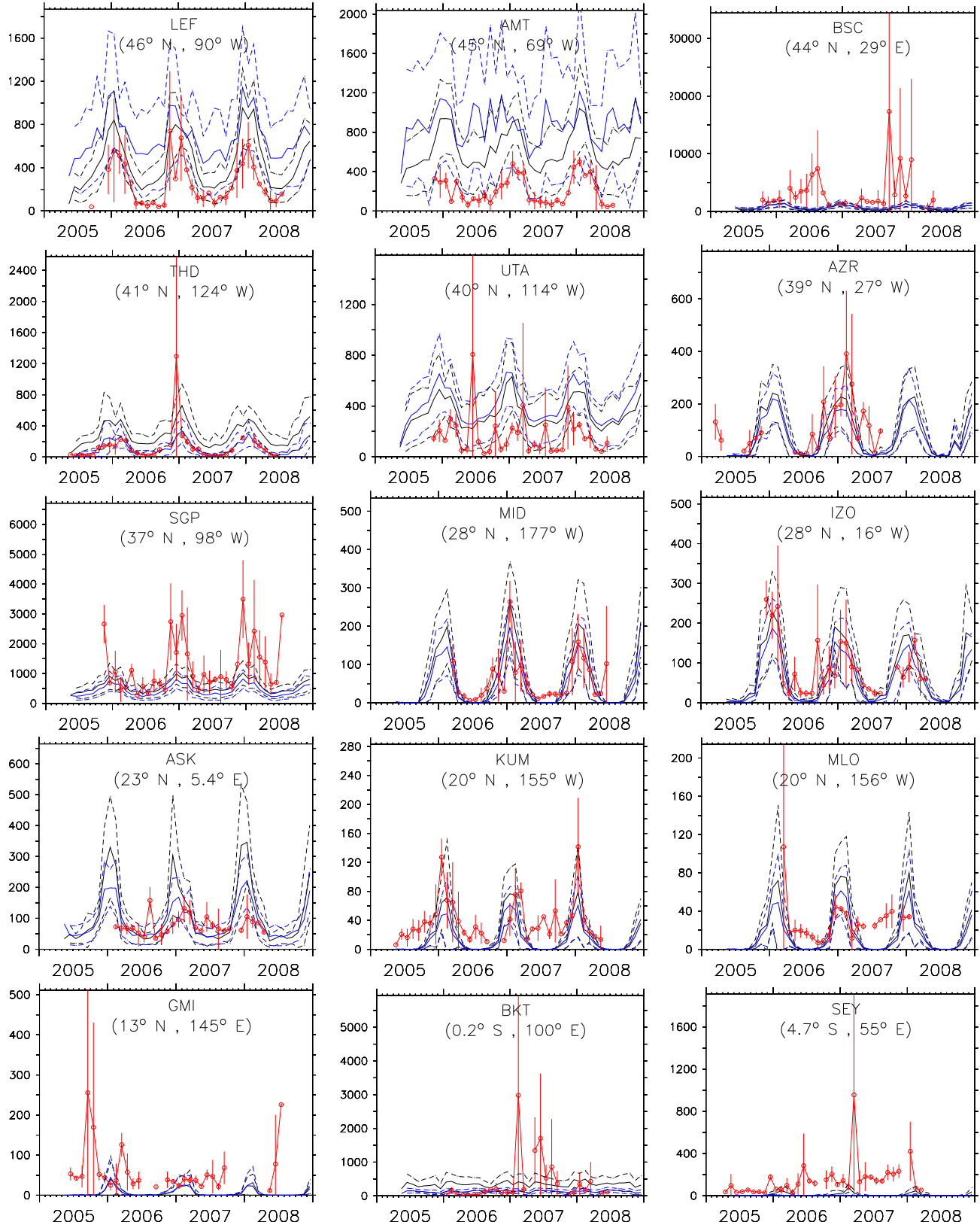


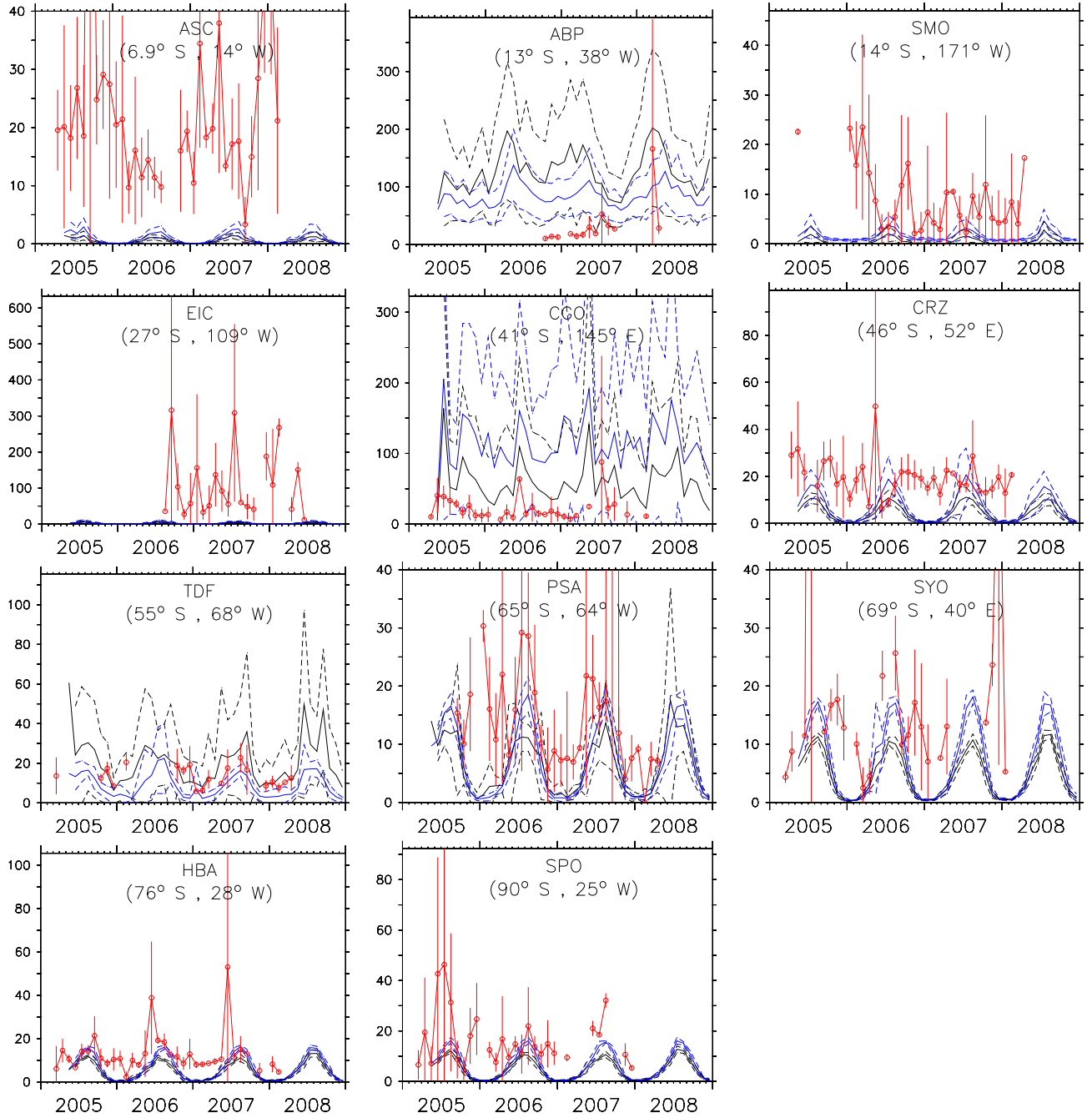


Butane (C_4H_{10})

Comparison of simulated and observed C_4H_{10} mixing ratios in pmol/mol for all the available locations (ordered by latitude). The red line and the bars represent the monthly average and the standard deviation (w.r.t. time) of the measurements in the region. No instrumental error has been included in this standard deviation. The simulated monthly average is indicated in the solid line and the corresponding simulated standard deviation (with respect to time) by the dashed line. The black and blue colors denote results from simulation *E1* and *E2*, respectively.

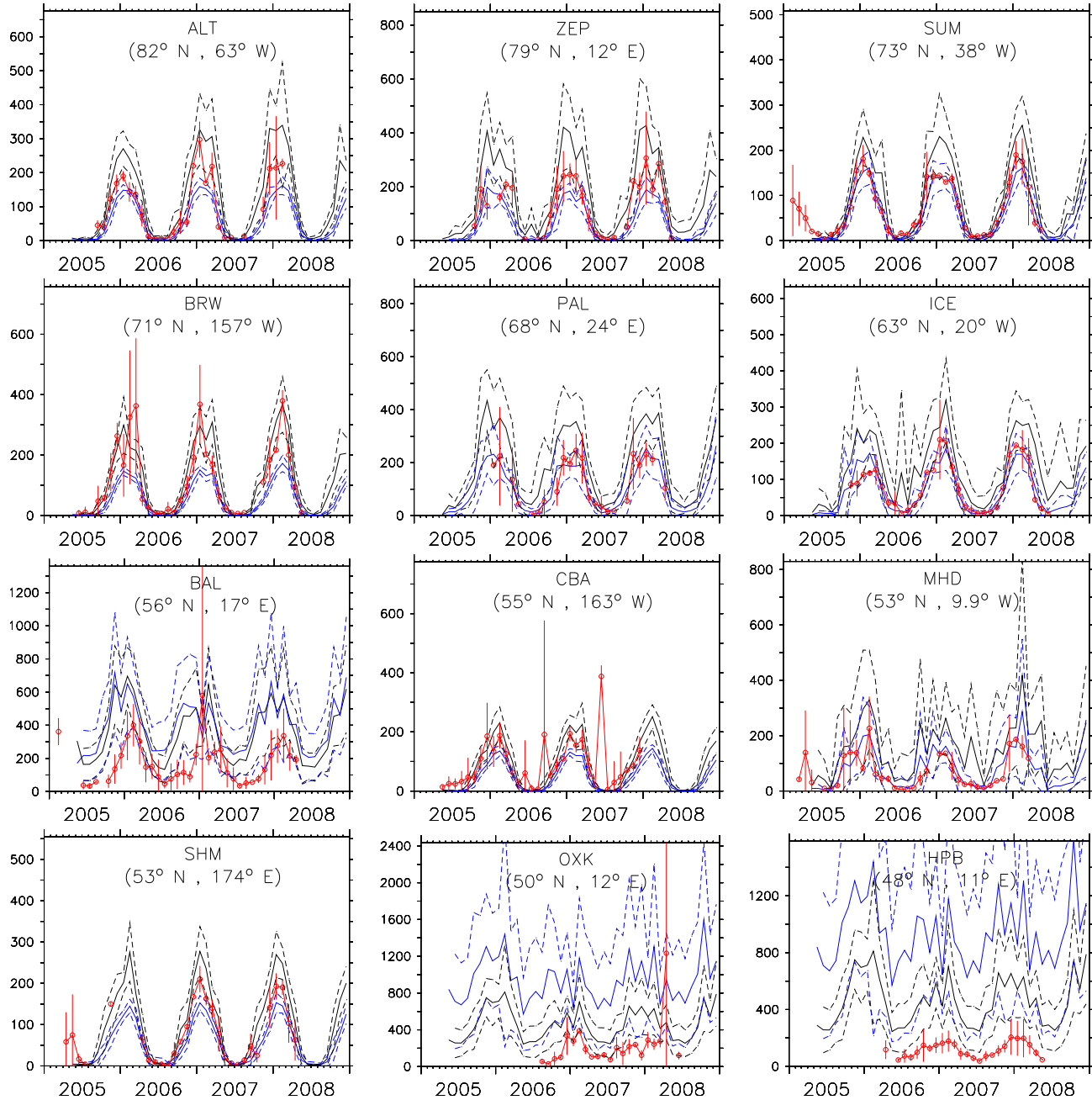


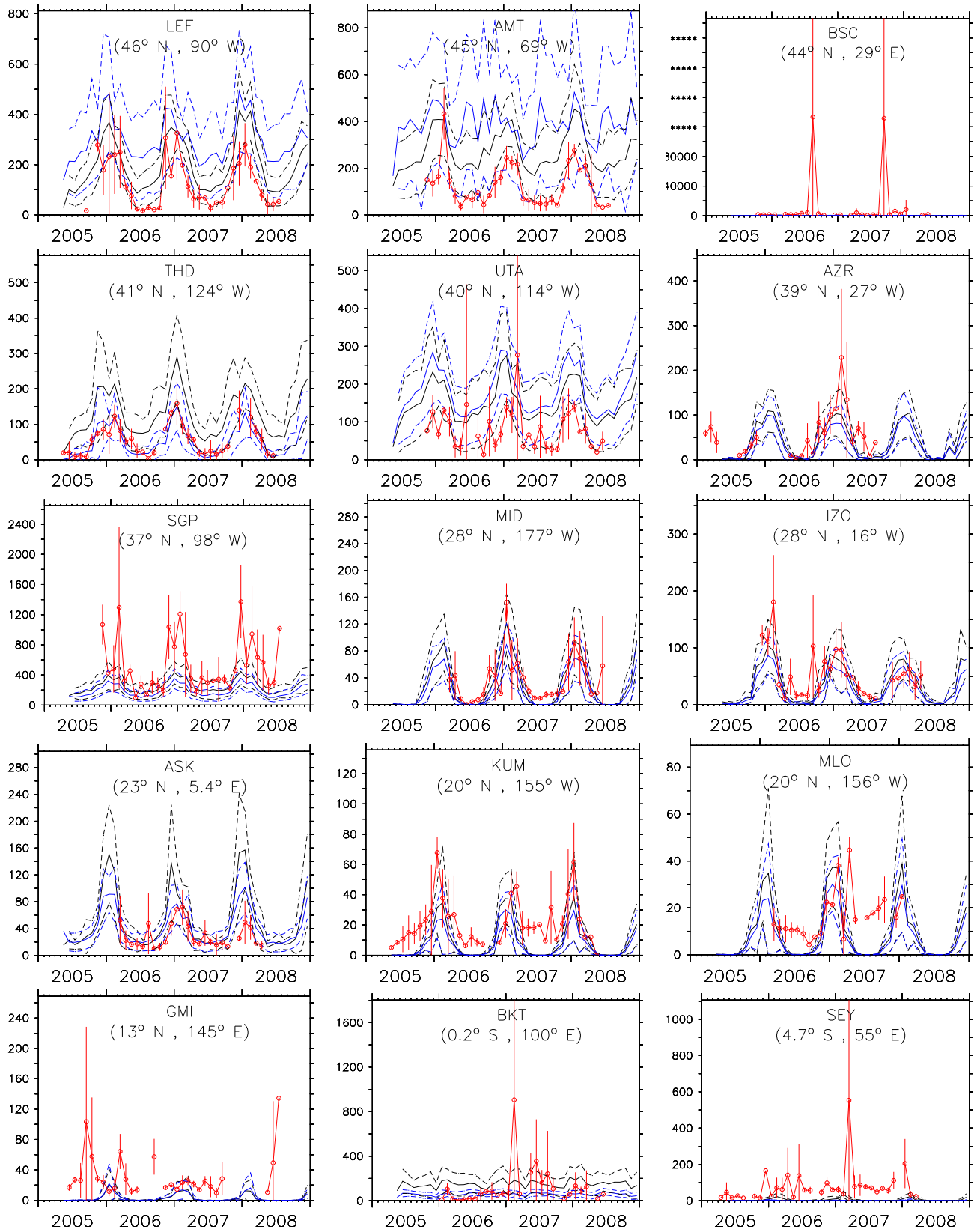


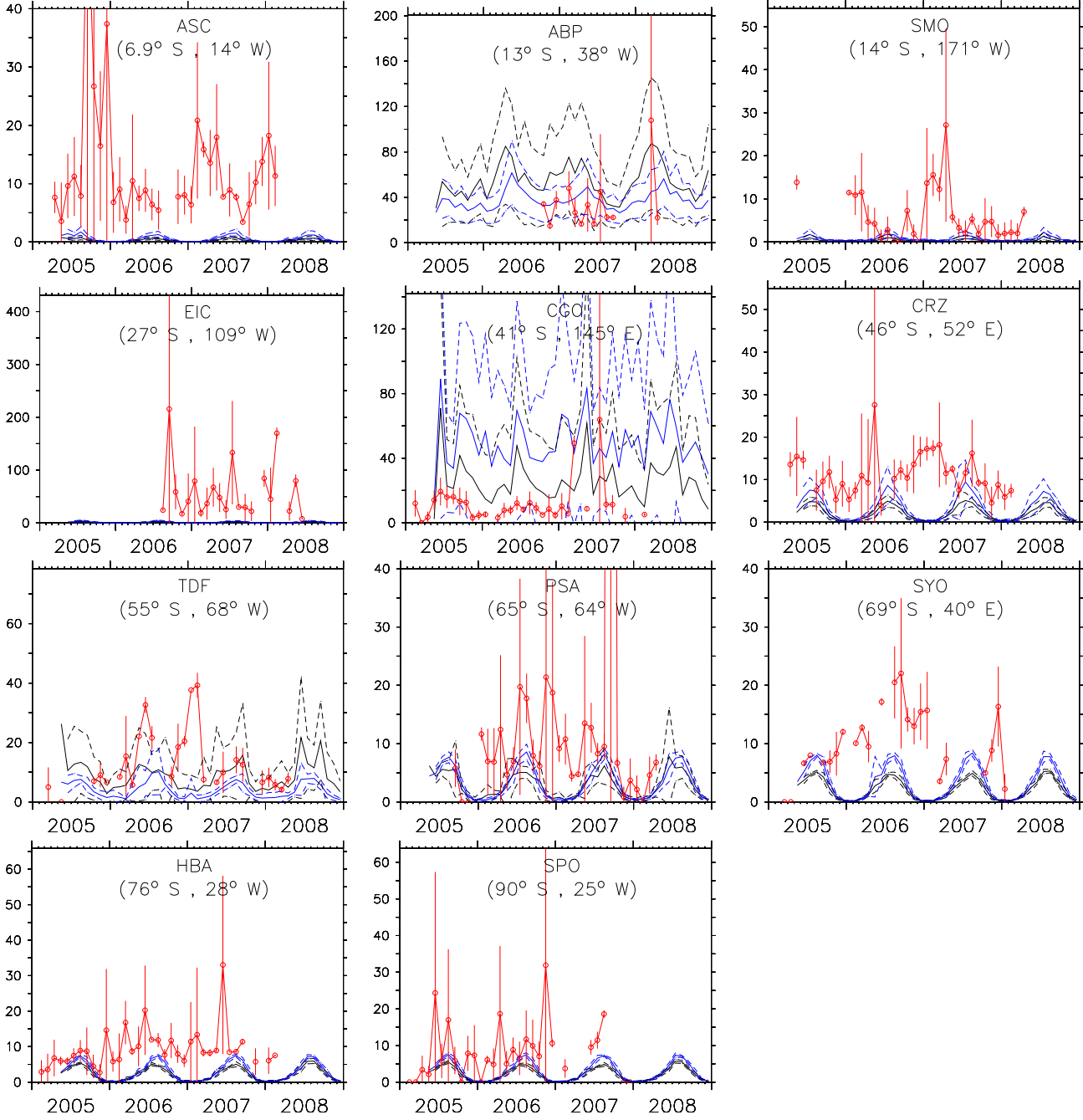


Isobutane (I-C₄H₁₀)

Comparison of simulated and observed I-C₄H₁₀ mixing ratios in pmol/mol for all the available locations (ordered by latitude). The red line and the bars represent the monthly average and the standard deviation (w.r.t. time) of the measurements in the region. No instrumental error has been included in this standard deviation. The simulated monthly average is indicated in the solid line and the corresponding simulated standard deviation (with respect to time) by the dashed line. The black and blue colors denote results from simulation *E1* and *E2*, respectively.

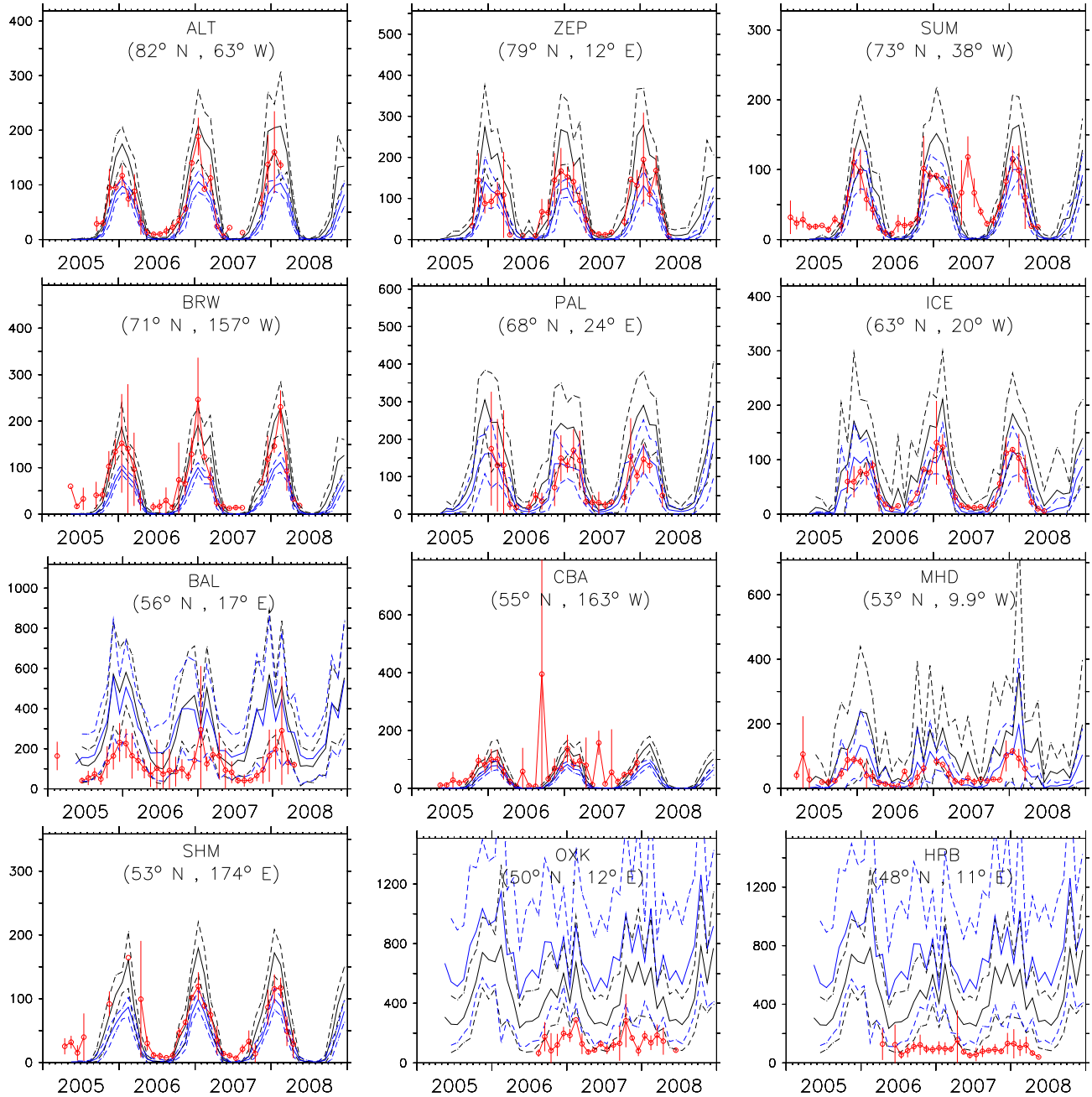


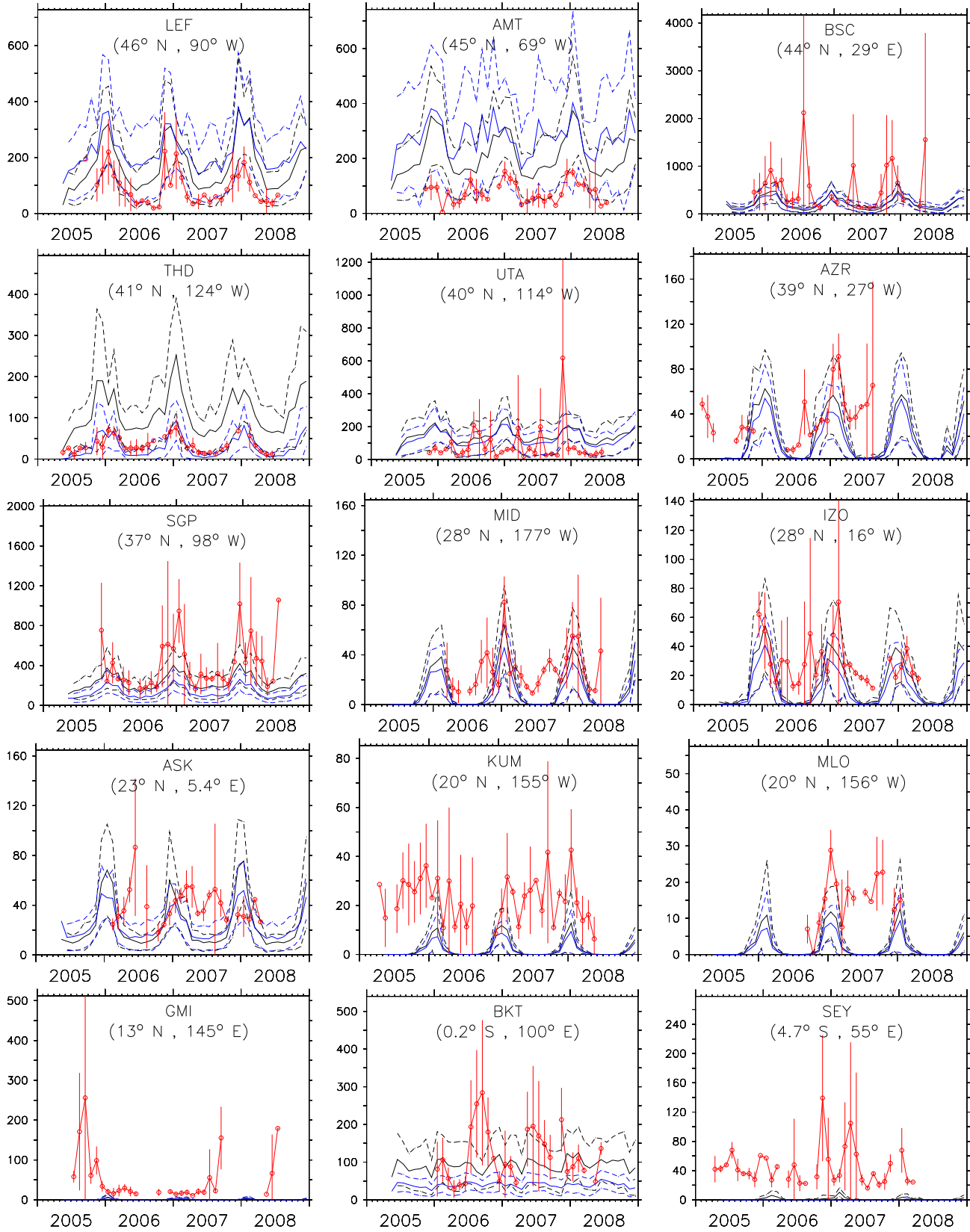


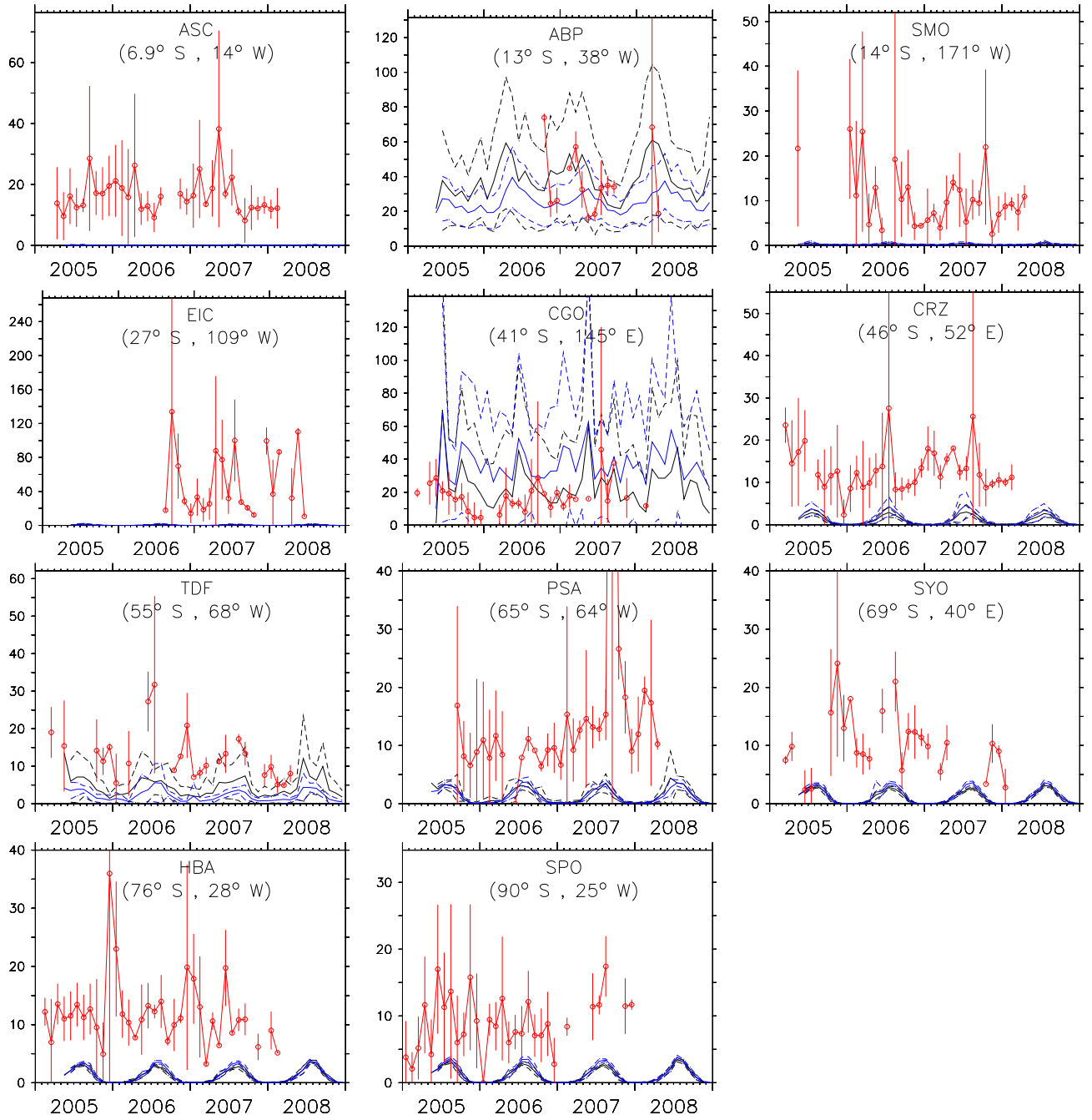


Pentane (C_5H_{12})

Comparison of simulated and observed C_5H_{12} mixing ratios in pmol/mol for all the available locations (ordered by latitude). The red line and the bars represent the monthly average and the standard deviation (w.r.t. time) of the measurements in the region. No instrumental error has been included in this standard deviation. The simulated monthly average is indicated in the solid line and the corresponding simulated standard deviation (with respect to time) by the dashed line. The black and blue colors denote results from simulation *E1* and *E2*, respectively.

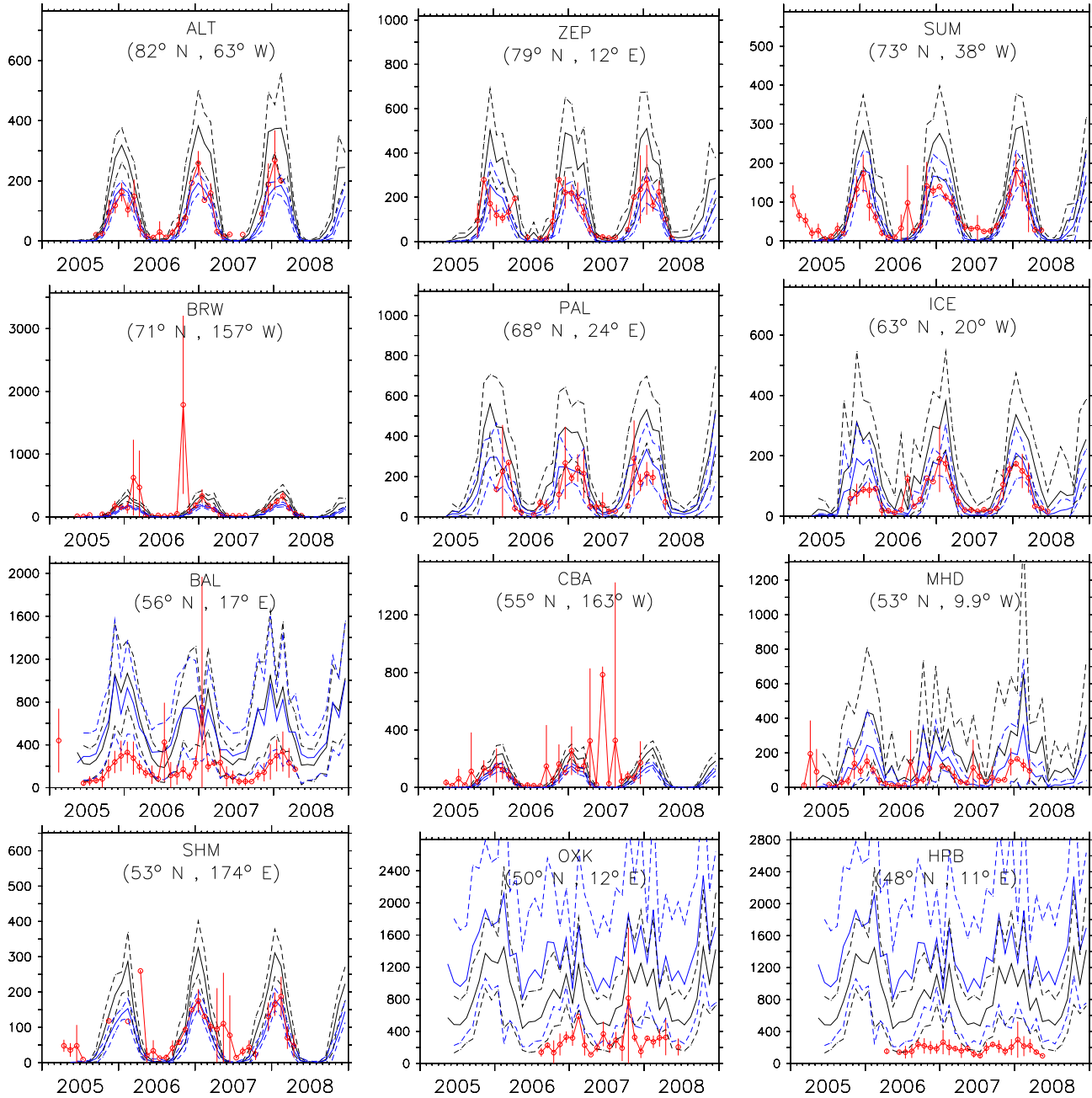


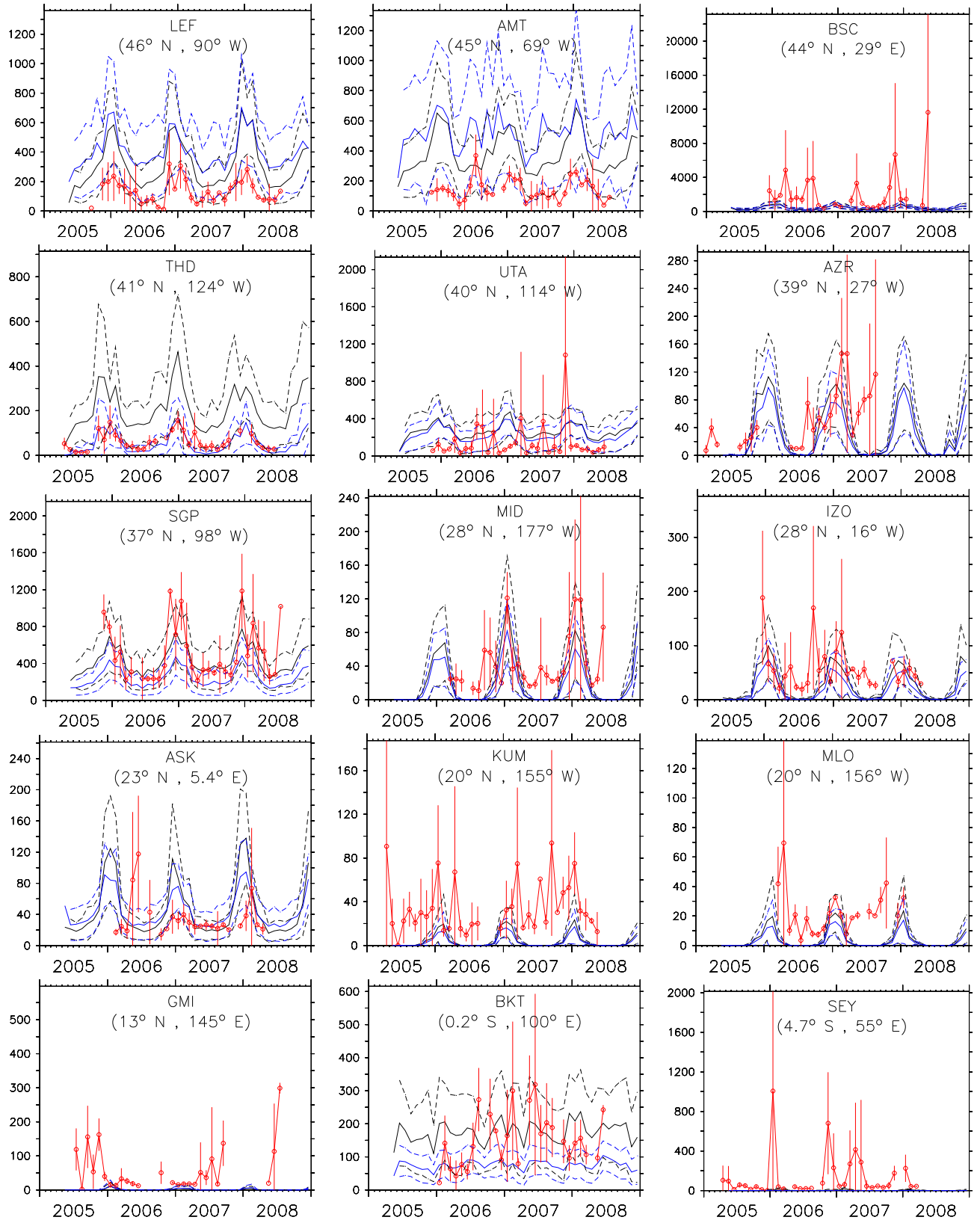


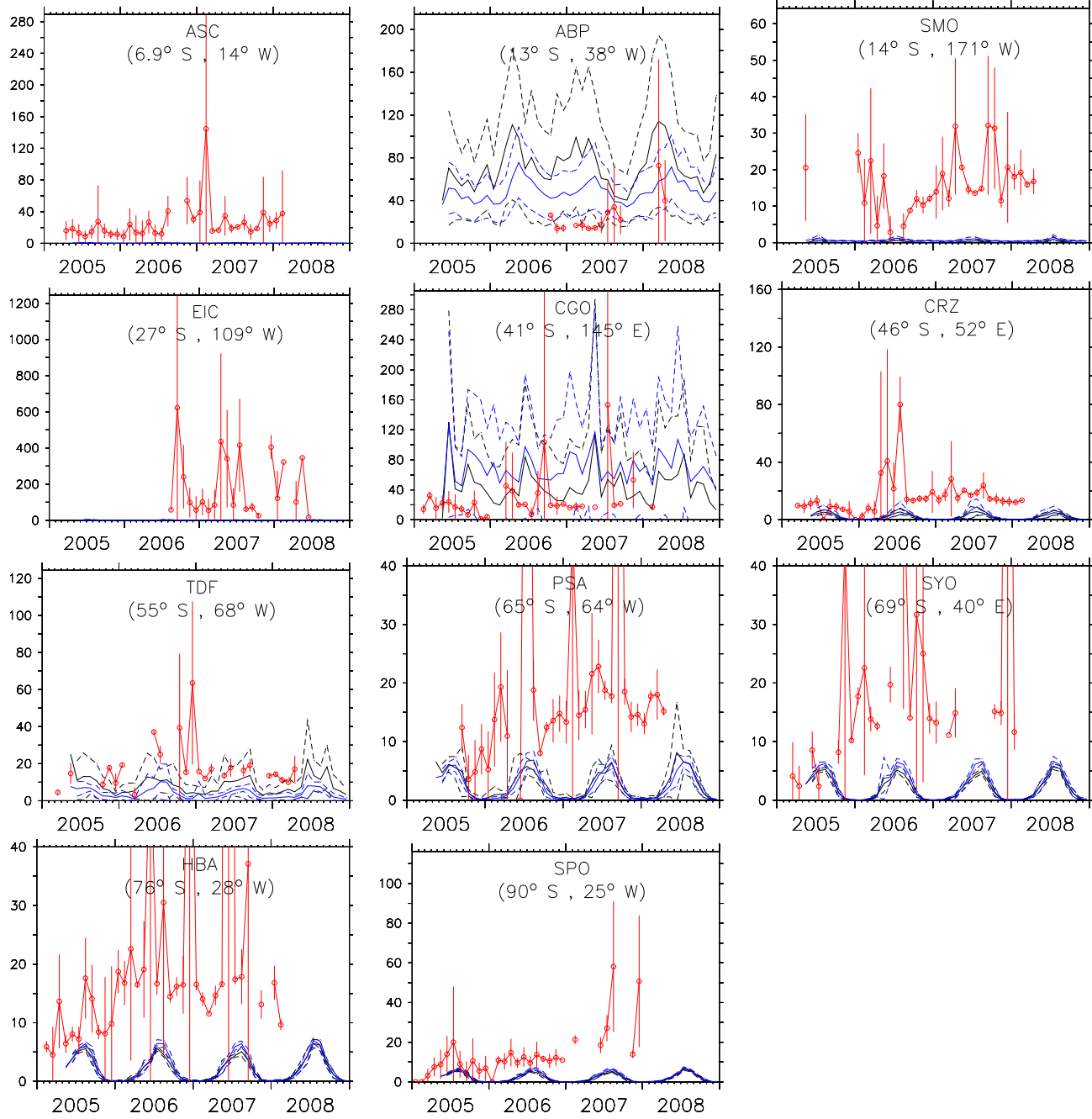


Isopentane (I-C₅H₁₂)

Comparison of simulated and observed I-C₅H₁₂ mixing ratios in pmol/mol for all the available locations (ordered by latitude). The red line and the bars represent the monthly average and the standard deviation (w.r.t. time) of the measurements in the region. No instrumental error has been included in this standard deviation. The simulated monthly average is indicated in the solid line and the corresponding simulated standard deviation (with respect to time) by the dashed line. The black and blue colors denote results from simulation *E1* and *E2*, respectively.

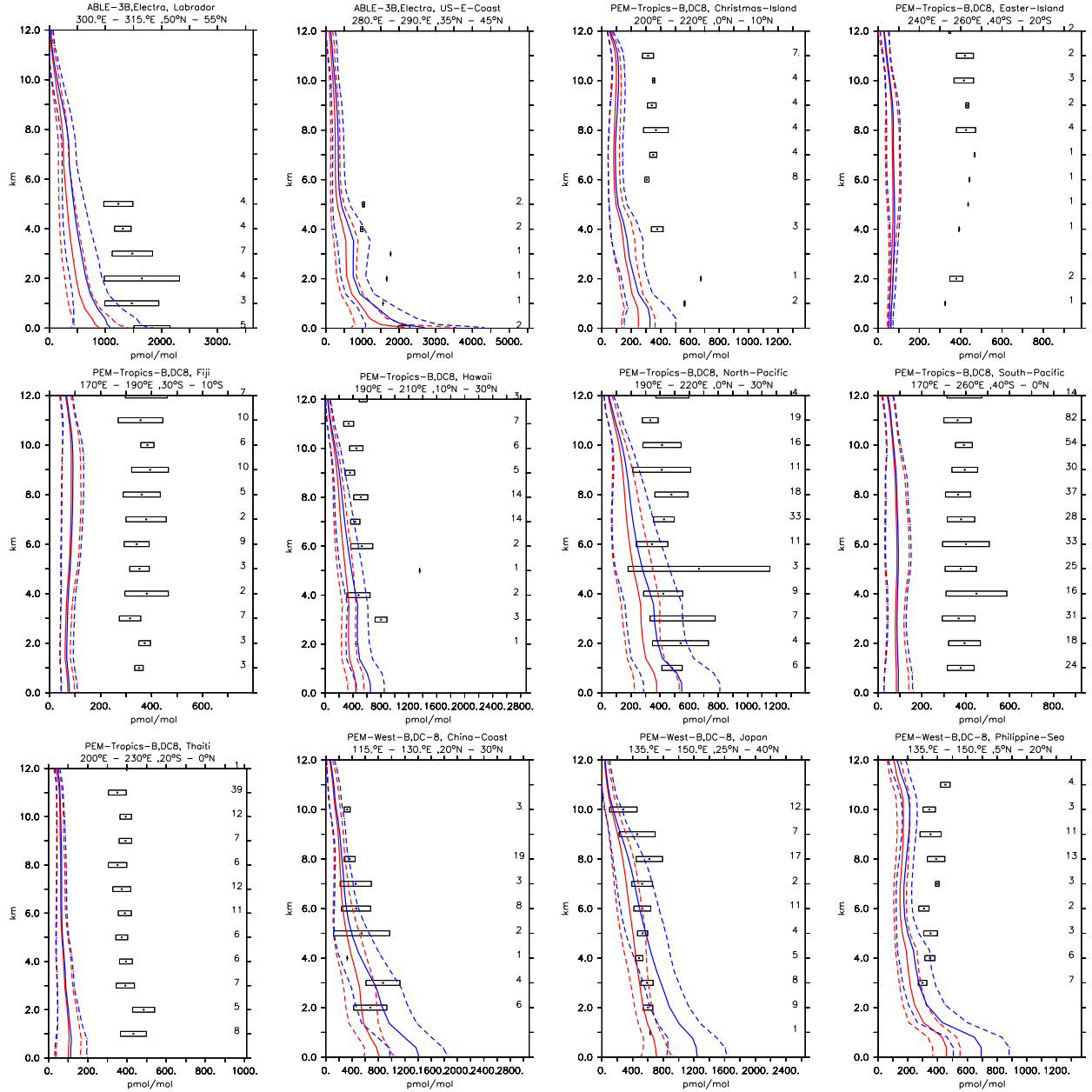


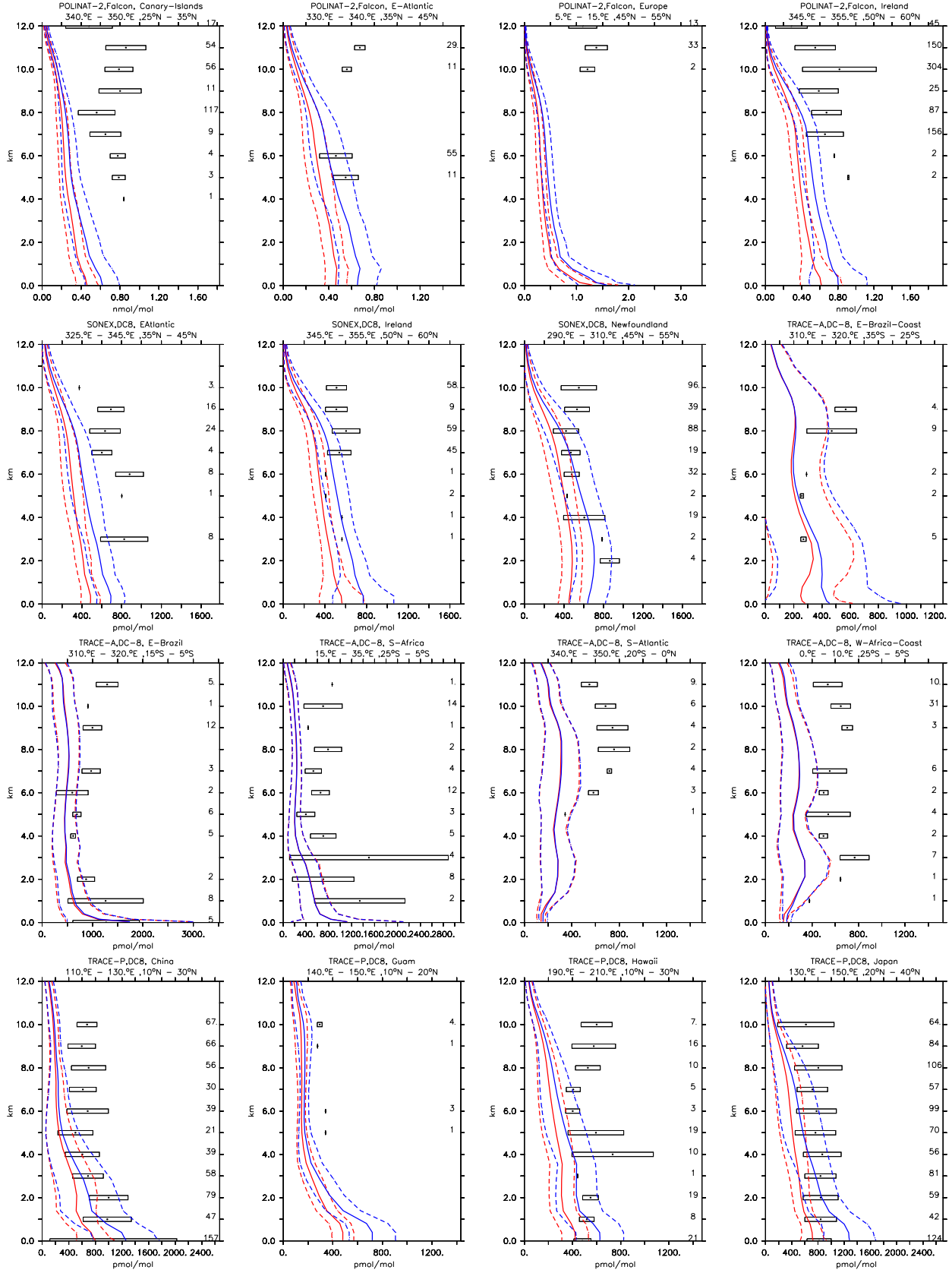




Acetone formation

Vertical profiles of CH_3COCH_3 (in pmol/mol) for all the available campaigns from Emmons et al. (2000). Asterisks and boxes represent the average and the standard deviation (with respect to space and time) of the measurements in the region, respectively. The simulated average is indicated by the solid line and the corresponding simulated standard deviation with respect to time and space by the dashed lines. On the right axis the numbers of measurements are listed. The red lines represent the simulation S1, the blue lines the simulation E2.





References

- Atkinson, R. and Arey, J.: Gas-Phase tropospheric chemistry of biogenic volatile compounds: a review, *Atmos. Environ.*, 37, 197–297, 2003.
- Emmons, L. K., Hauglustaine, D. A., Müller, J.-F., Carroll, M. A., Brasseur, G. P., Brunner, D., Staehelin, J., Thouret, V., and Marenco, A.: Data composites of airborne observations of tropospheric ozone and its precursors, *J. Geophys. Res.*, 105, 20 497–20 538, 2000.
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