

# Chemical equation set and complete figures set

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

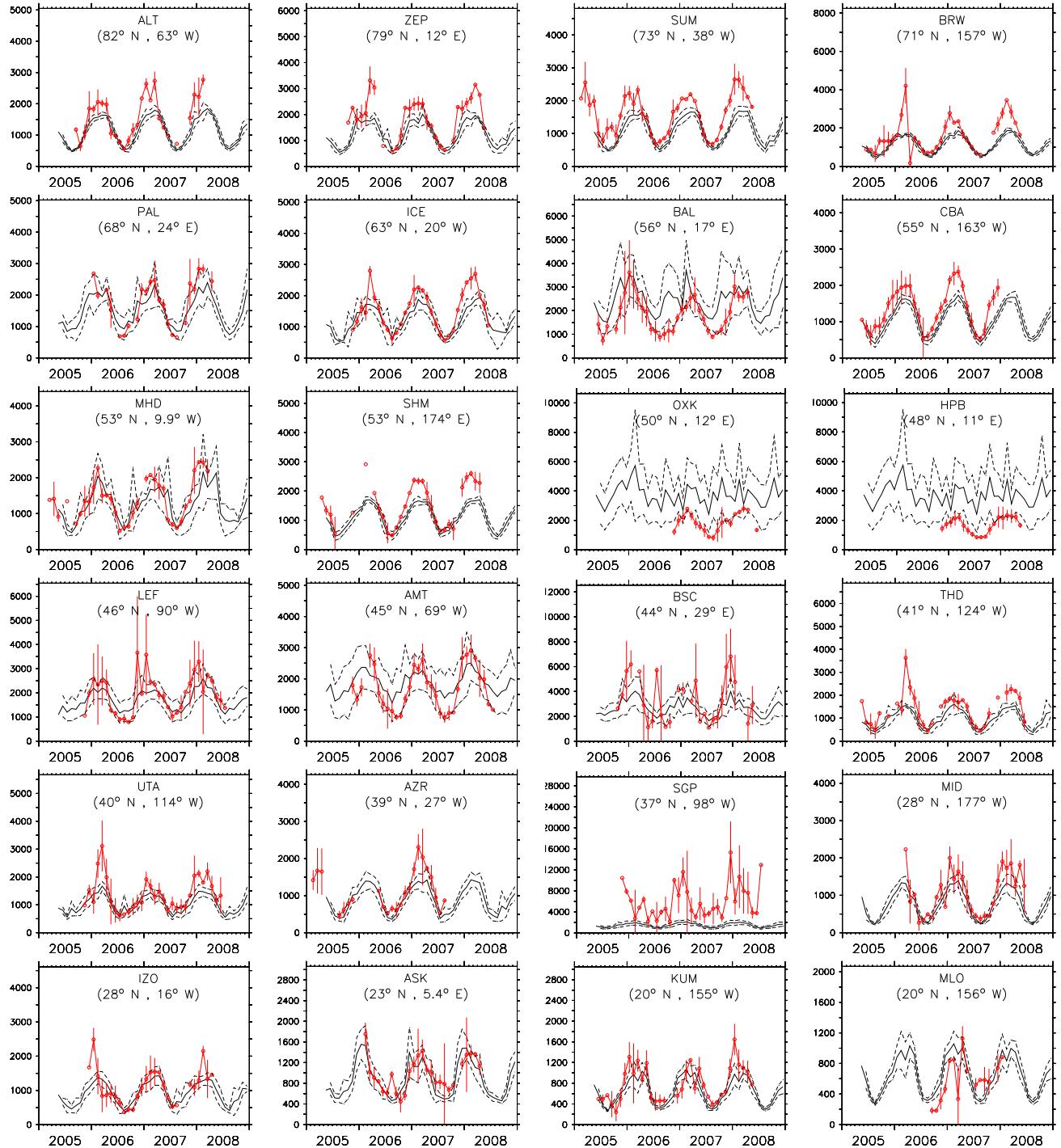
reaction	rate coefficient	reference/notes
$\text{OH} + \text{C}_4\text{H}_{10} \rightarrow \text{HCHO} + 0.4365 \text{CH}_3\text{CHO} + 0.4365 \text{PA} + 4.254 \text{PINKO}_2$	$1.69 \times 10^{-17} * T^2 * e^{(145/T)}$	a, b
$\text{CL} + \text{C}_4\text{H}_{10} \rightarrow \text{HCHO} + 0.3575 \text{CH}_3\text{CHO} + 0.3575 \text{PA} + 4.57 \text{PINKO}_2$	$2.18 \times 10^{-10}$	a, b
$\text{NO}_3 + \text{C}_4\text{H}_{10} \rightarrow \text{HCHO} + 0.4365 \text{CH}_3\text{CHO} + 0.4365 \text{PA} + 4.254 \text{PINKO}_2$	$2.76 \times 10^{-12} * e^{(-3279/T)}$	c
$\text{OH} + \text{IC}_4\text{H}_{10} \rightarrow 2.06 \text{PrO}_2 + .794 \text{CH}_3\text{COC}_3 + .794 \text{CH}_3\text{O}_2 + 1.206 \text{PINKO}_2$	$1.16 \times 10^{-17} * T^2 * e^{(225/T)}$	a, b
$\text{CL} + \text{IC}_4\text{H}_{10} \rightarrow 0.564 \text{PrO}_2 + 0.436 \text{CH}_3\text{COC}_3 + 0.436 \text{CH}_3\text{O}_2 + 1.564 \text{PINKO}_2$	$1.43 \times 10^{-10}$	a, b
$\text{NO}_3 + \text{IC}_4\text{H}_{10} \rightarrow 2.06 \text{PrO}_2 + 0.794 \text{CH}_3\text{COC}_3 + 0.794 \text{CH}_3\text{O}_2 + 1.206 \text{PINKO}_2$	$1.06 \times 10^{-16}$	c
$\text{OH} + \text{C}_5\text{H}_{12} \rightarrow 1.4765 \text{HCHO} + 0.340 \text{CH}_3\text{CHO} + 0.1745 \text{EtO}_2 + 6.302 \text{PINKO}_2$	$2.44 \times 10^{-17} * T^2 * e^{(183/T)}$	a, b
$\text{CL} + \text{C}_5\text{H}_{12} \rightarrow 1.67 \text{HCHO} + 0.220 \text{CH}_3\text{CHO} + 0.11 \text{EtO}_2 + 6.56 \text{PINKO}_2$	$2.80 \times 10^{-10}$	a, b
$\text{NO}_3 + \text{C}_5\text{H}_{12} \rightarrow 1.4765 \text{HCHO} + 0.349 \text{CH}_3\text{CHO} + 0.1745 \text{EtO}_2 + 6.302 \text{PINKO}_2$	$8.77 \times 10^{-17}$	c
$\text{OH} + \text{IC}_5\text{H}_{12} \rightarrow 0.087 \text{HCHO} + 0.384 \text{CH}_3\text{CHO} + 0.297 \text{PrO}_2 + 0.616 \text{CH}_3\text{COC}_3 + 0.616 \text{EtO}_2 + 1.435 \text{PINKO}_2$	$3.70 \times 10^{-12}$	a, b
$\text{CL} + \text{IC}_5\text{H}_{12} \rightarrow 0.408 \text{HCHO} + 0.750 \text{CH}_3\text{CHO} + 0.342 \text{PrO}_2 + 0.250 \text{CH}_3\text{COC}_3 + 0.250 \text{EtO}_2 + 3.04 \text{PINKO}_2$	$2.20 \times 10^{-10}$	a, b
$\text{NO}_3 + \text{IC}_5\text{H}_{12} \rightarrow 0.087 \text{HCHO} + 0.384 \text{CH}_3\text{CHO} + 0.297 \text{PrO}_2 + 0.616 \text{CH}_3\text{COC}_3 + 0.616 \text{EtO}_2 + 1.435 \text{PINKO}_2$	$1.62 \times 10^{-16}$	c
$\text{PINKO}_2 + \text{NO} \rightarrow 0.95 \text{NO}_2 + 0.475 \text{HO}_2 + 0.475 \text{PINK} + 0.05 \text{PINKNO}_3$	$(2.54 * e^{(360./T)} + 8.10 * e^{(270./T)}) \times 10^{-12}/2$	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
$\text{PINKO}_2 + \text{HO}_2 \rightarrow \text{PINKO}_2$	$(4.30 * e^{(1040./T)} + 2.91 * e^{(1300./T)}) \times 10^{-13}/2$	h
$\text{PINK} + \text{OH} \rightarrow \text{CO}_2$	$2 \times 10^{-11}$	d
$\text{PINK} + \text{hv} \rightarrow \text{HO}_2$	$\text{J-CH}_3\text{CHO}$	d
$\text{PINKNO}_3 + \text{OH} \rightarrow \text{NO}_2$	$5 \times 10^{-12}$	d
$\text{PINKNO}_3 + \text{hv} \rightarrow \text{NO}_2$	$3.7^{*}\text{J-PAN}$	e
$\text{PINKO}_2 + \text{hv} \rightarrow \text{OH} + 0.5 \text{HO}_2$	$\text{J-CH}_3\text{OOH}$	f
$\text{PINKO}_2 + \text{OH} \rightarrow \text{PINKO}_2$	$1.90 \times 10^{-12} * e^{(190./T)}$	a, b
$\text{PINKO}_2 + \text{OH} \rightarrow \text{OH}$	$2. \times 10^{-11}$	g

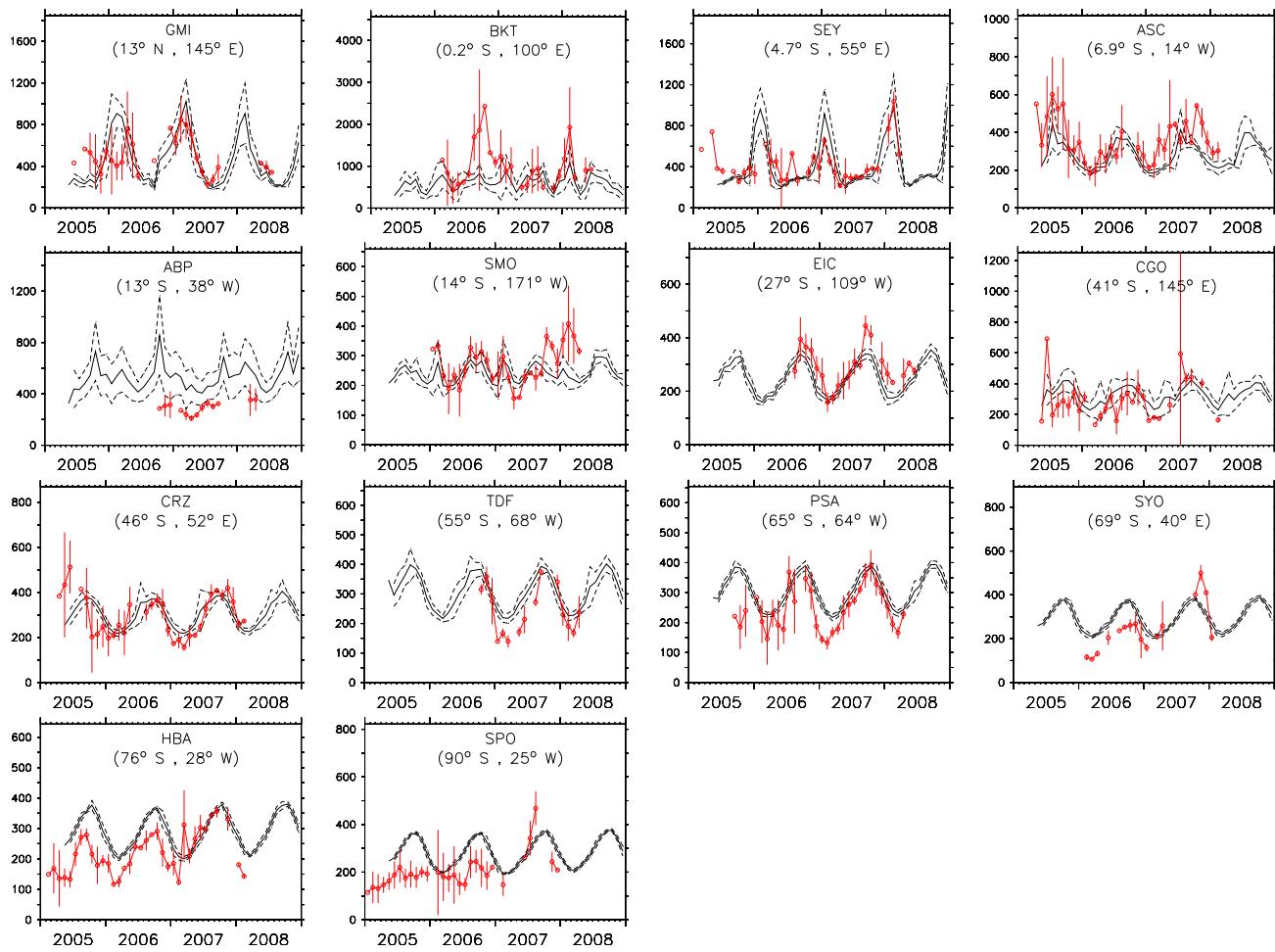
<sup>a</sup>Saunders et al. (1997a)<sup>b</sup>Saunders et al. (1997b)<sup>c</sup>Atkinson and Arey (2003), branching ratio like the OH reaction<sup>d</sup>as general aldehyde<sup>e</sup>photolysis scale with PAN photolysis rate<sup>f</sup>photolysis scale with  $\text{CH}_3\text{OOH}$  photolysis rate<sup>g</sup>representative for the H-abstraction of these peroxides<sup>h</sup>average between the reactions of the two different peroxides isomers

## Model-observation comparison

Ethane ( $C_2H_6$ )

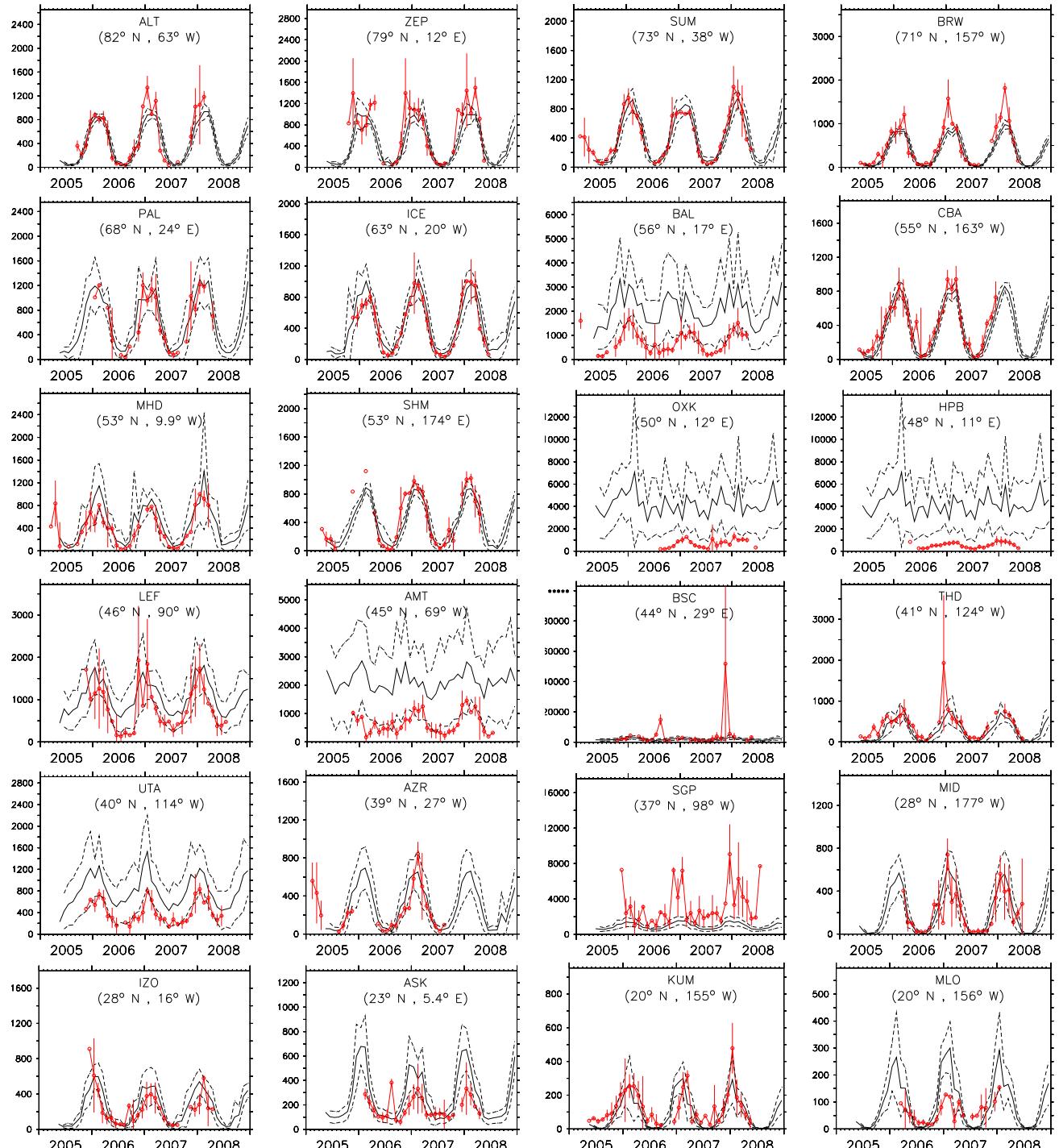
Comparison of simulated and observed  $C_2H_6$  mixing ratios in pmol/mol for all the available locations (ordered by latitude). The red line and the bars represent the monthly average and the standard deviation (w.r.t. time) of the measurements in the region. No instrumental error has been included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

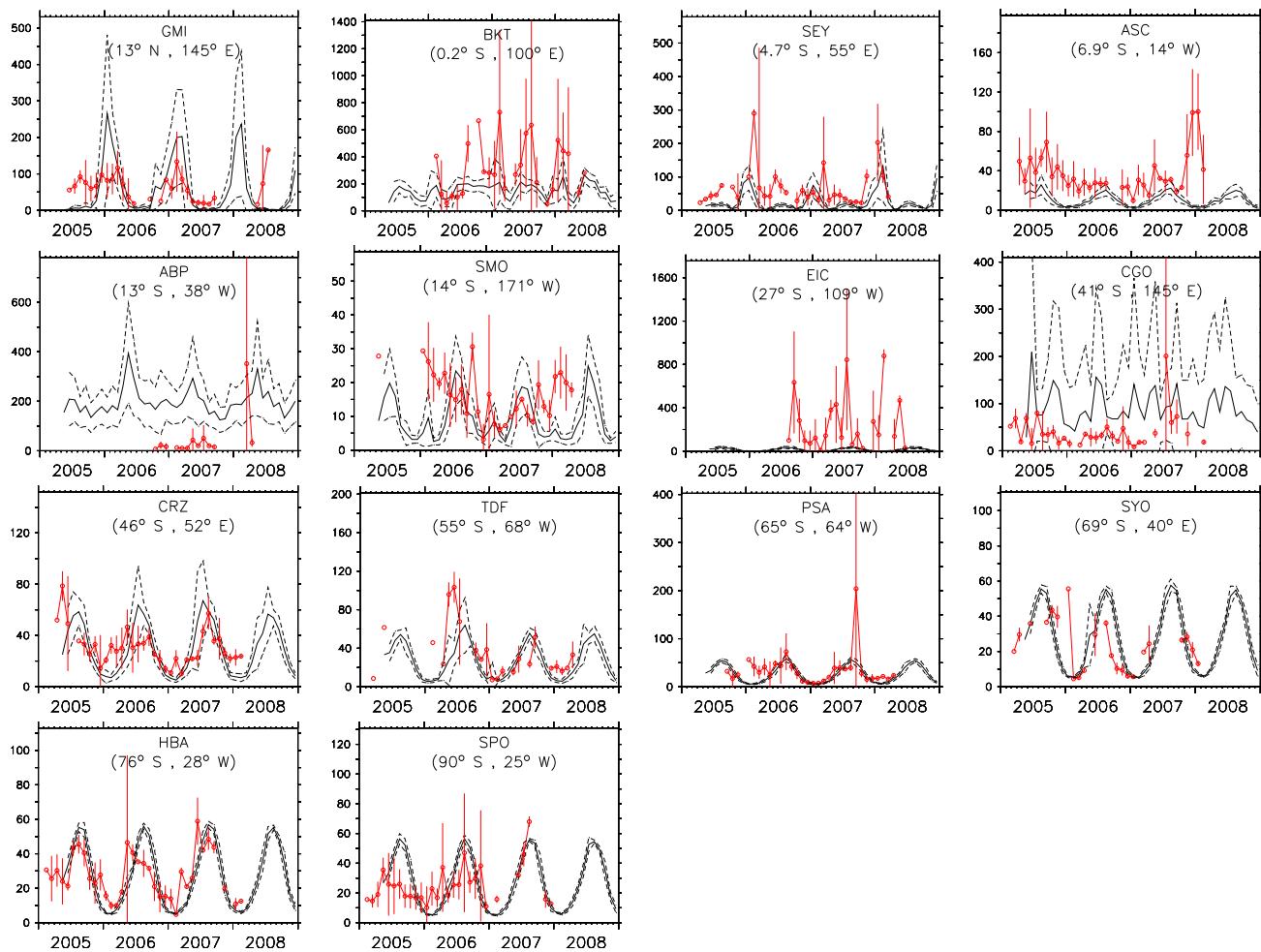




## Propane ( $C_3H_8$ )

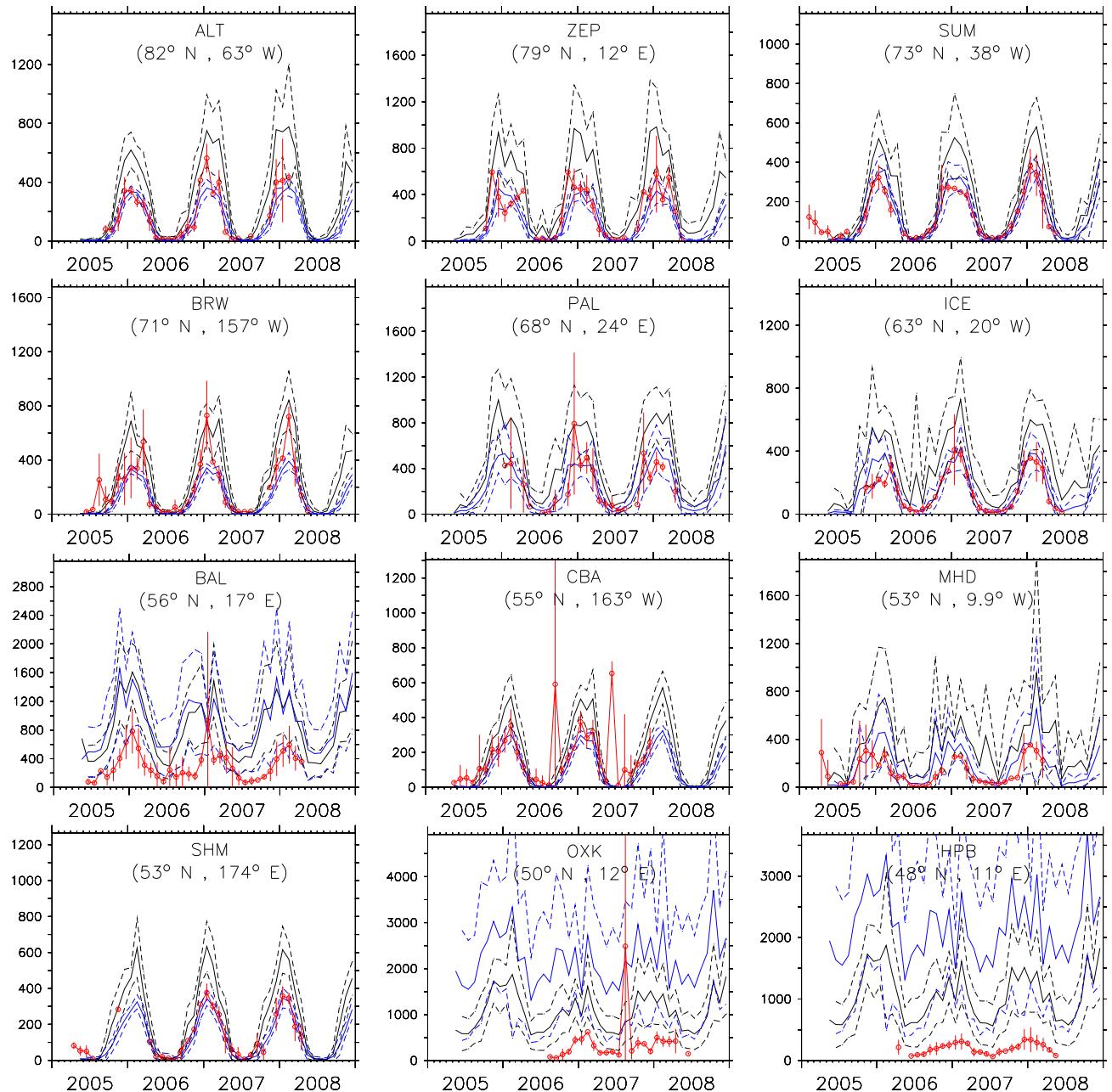
Comparison of simulated and observed  $C_3H_8$  mixing ratios in pmol/mol for all the available locations (ordered by latitude). The red line and the bars represent the monthly average and the standard deviation (w.r.t. time) of the measurements in the region. No instrumental error has been included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

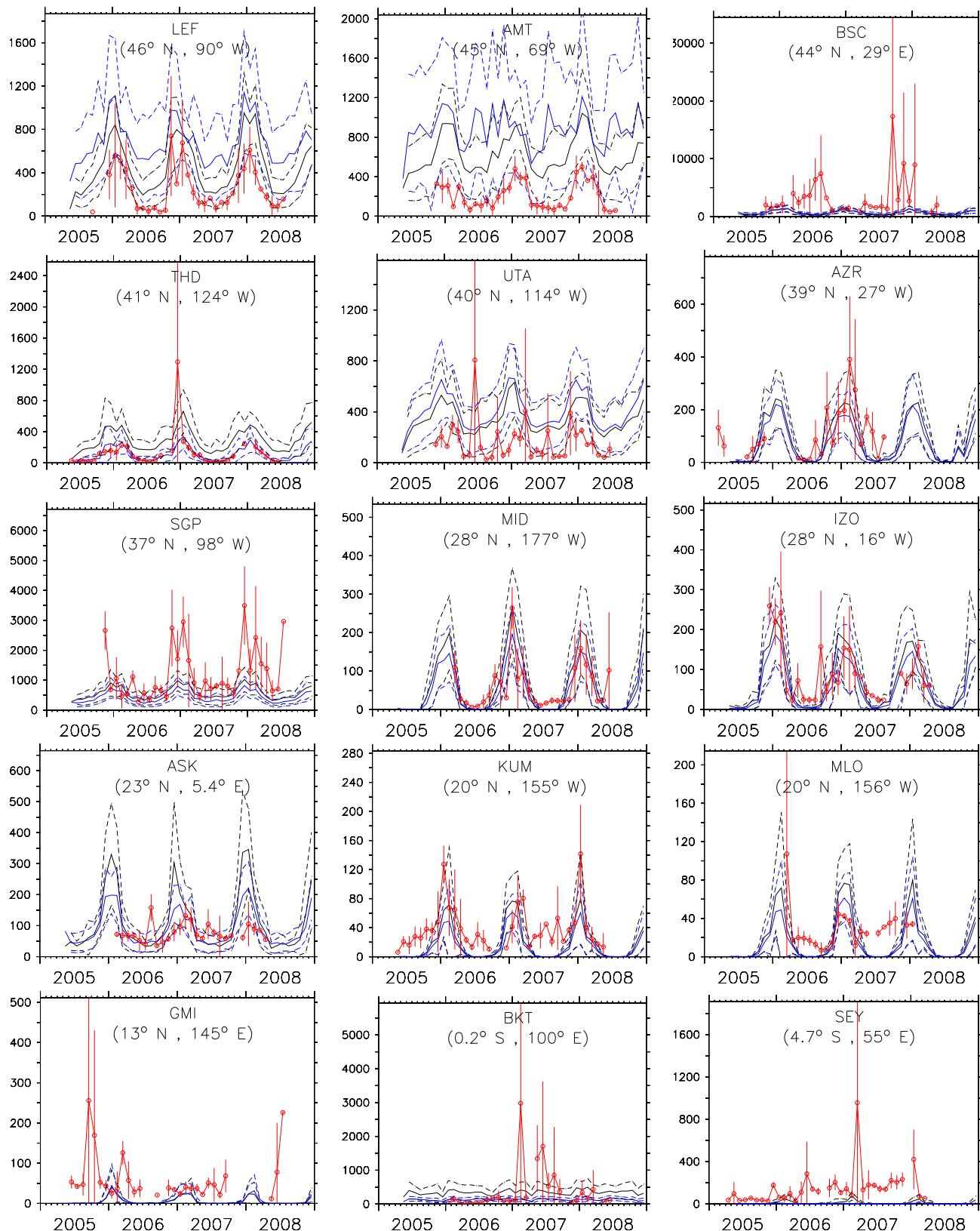


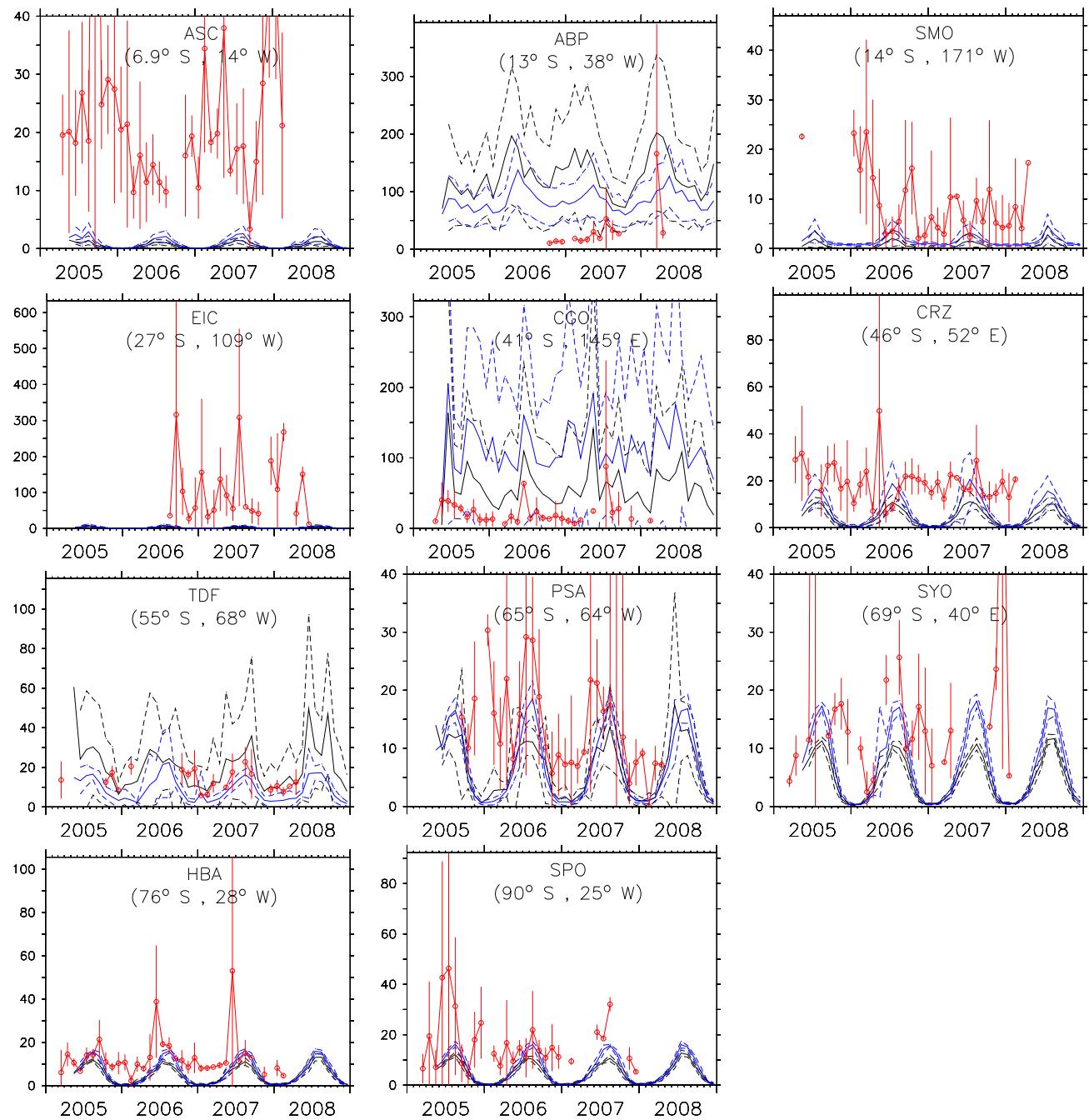


## Butane ( $C_4H_{10}$ )

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.

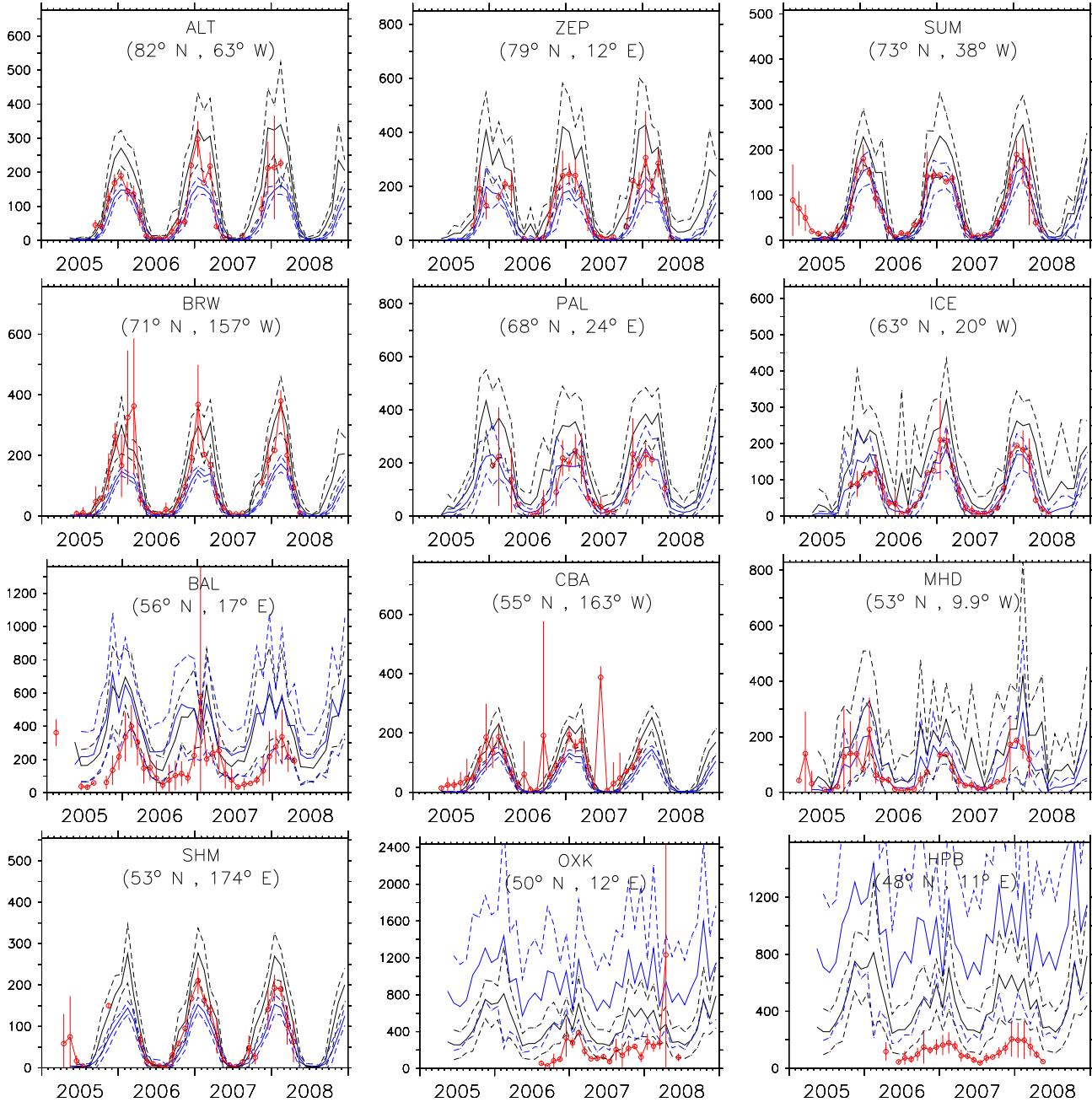


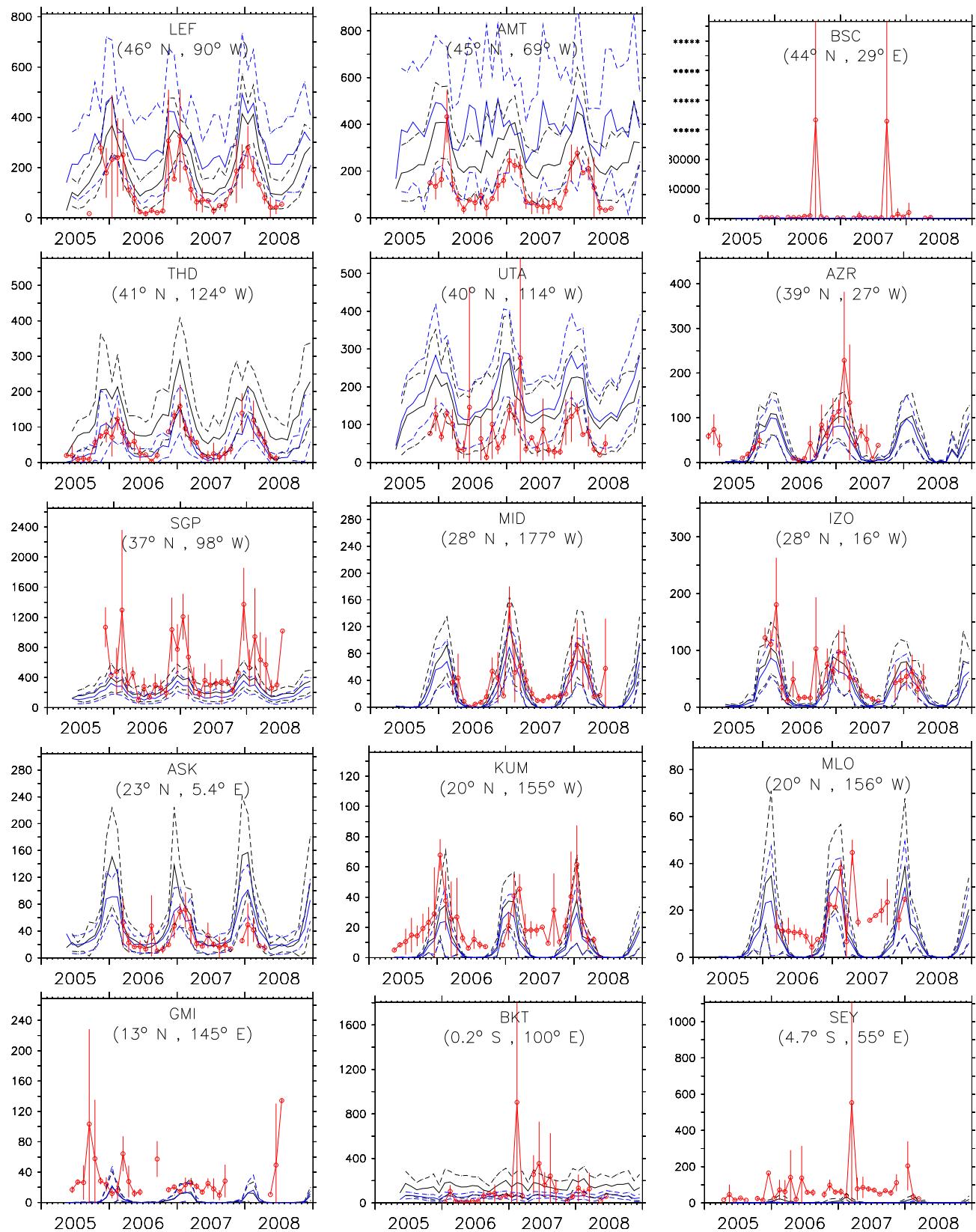


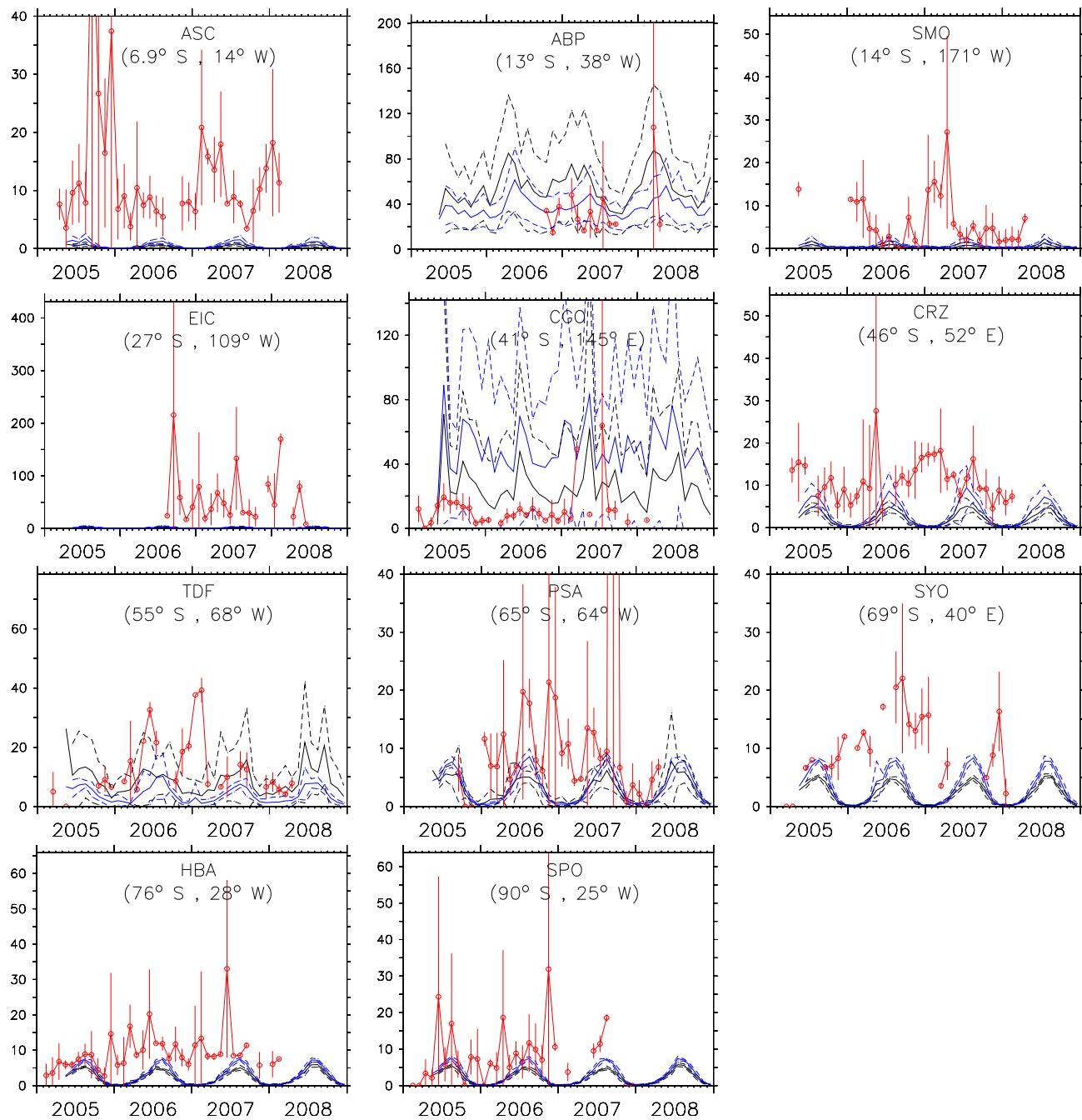


## Isobutane ( $\text{I-C}_4\text{H}_{10}$ )

Comparison of simulated and observed  $\text{I-C}_4\text{H}_{10}$  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.

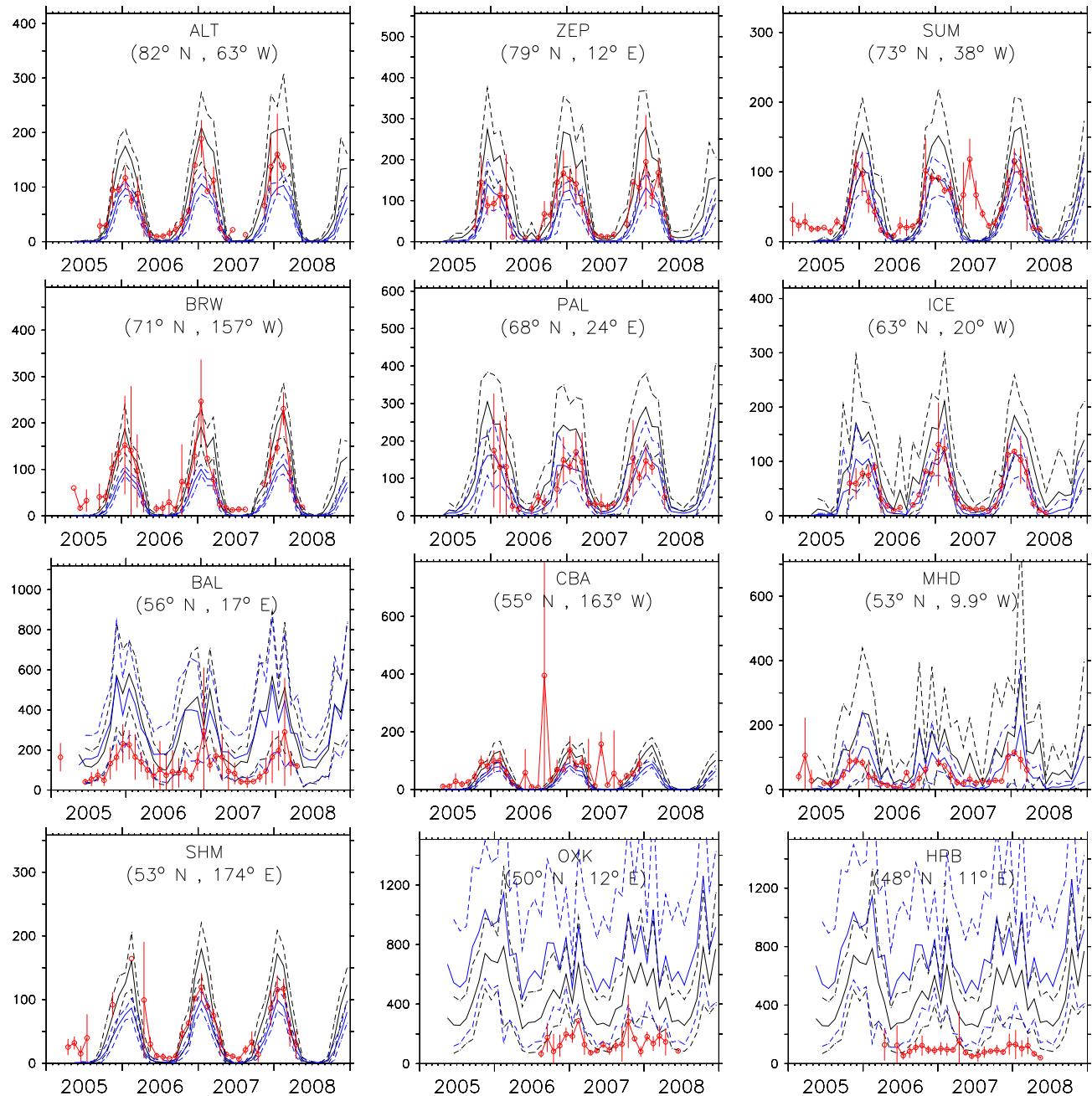


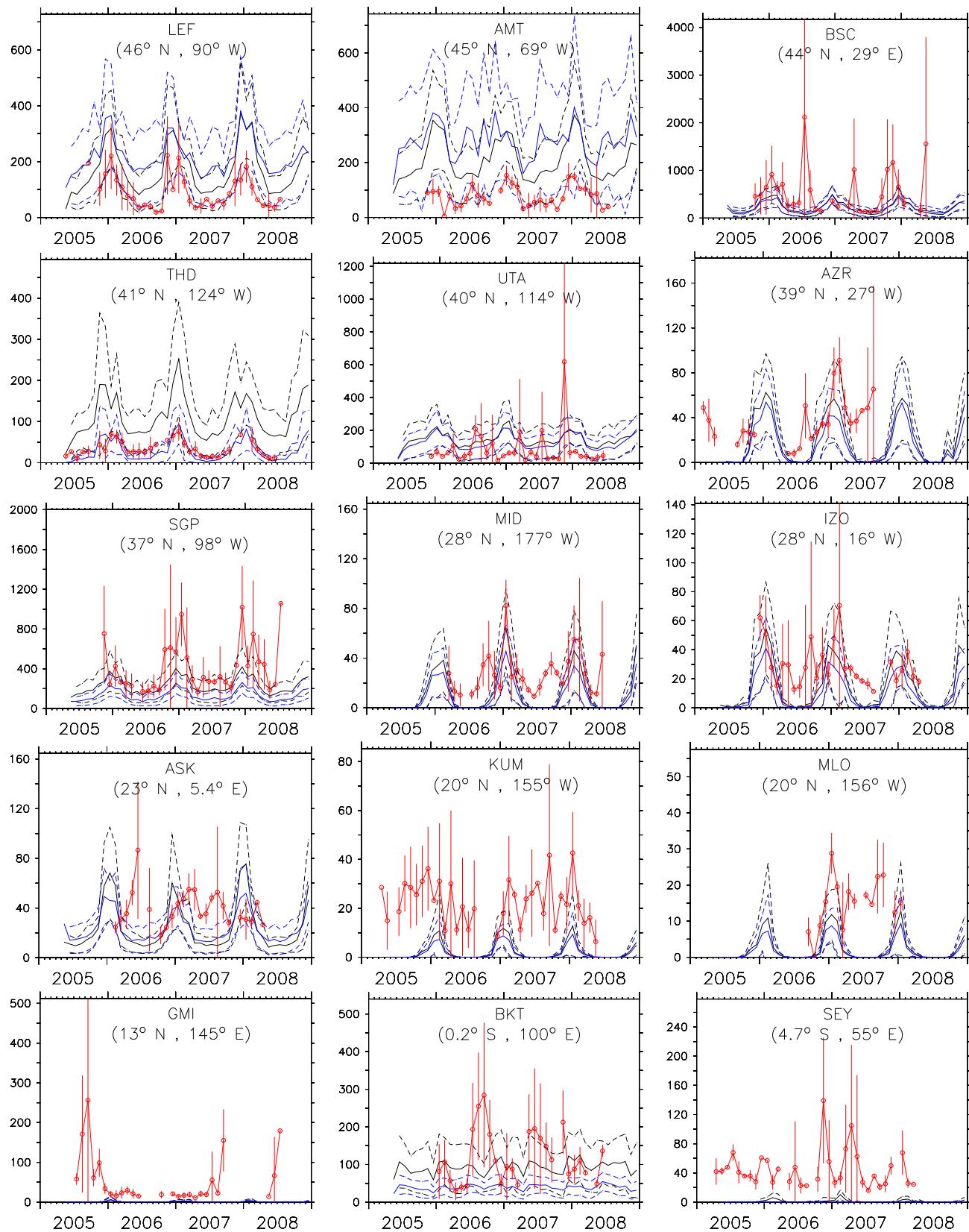


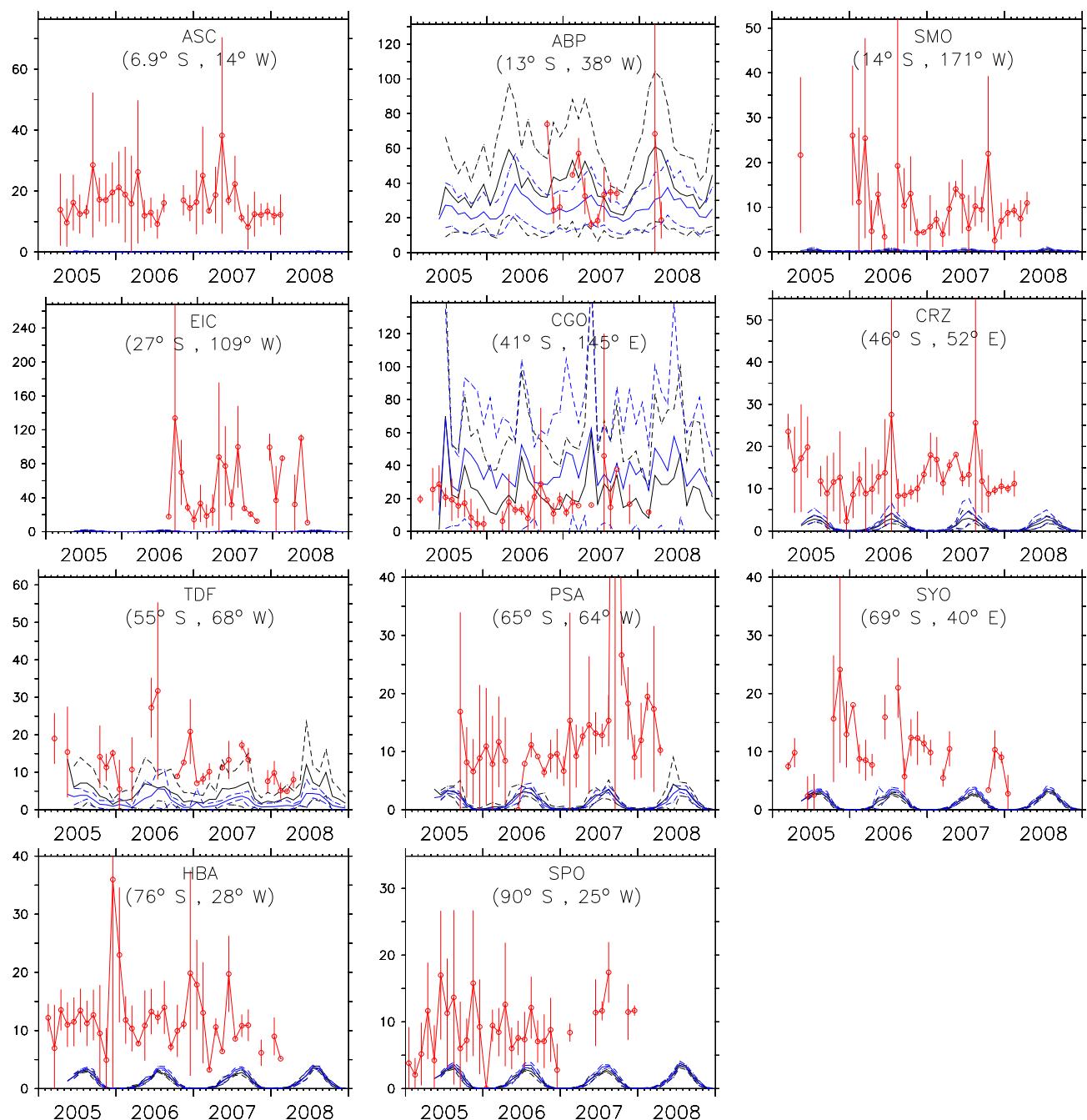


## Pentane ( $C_5H_{12}$ )

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.

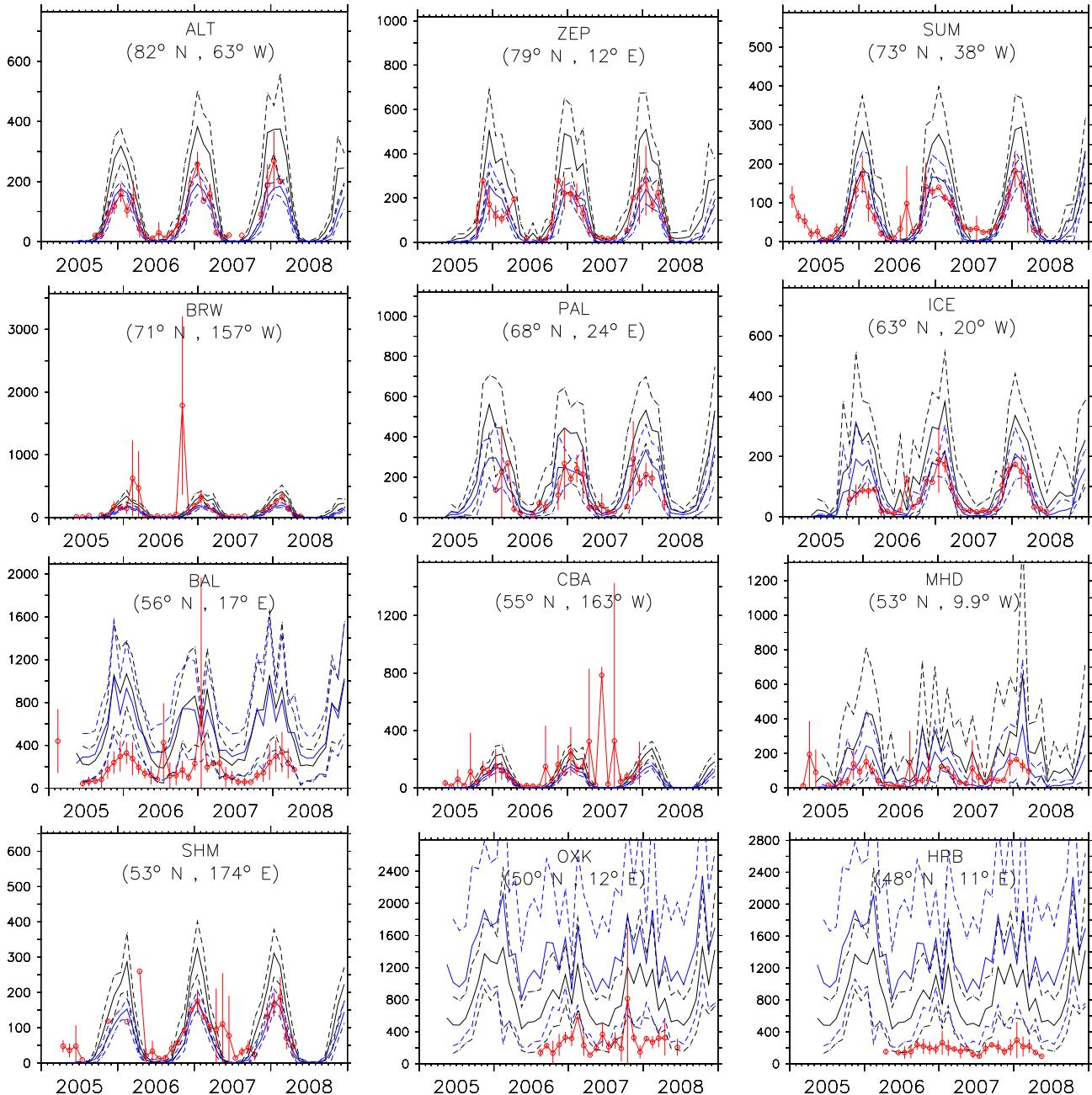


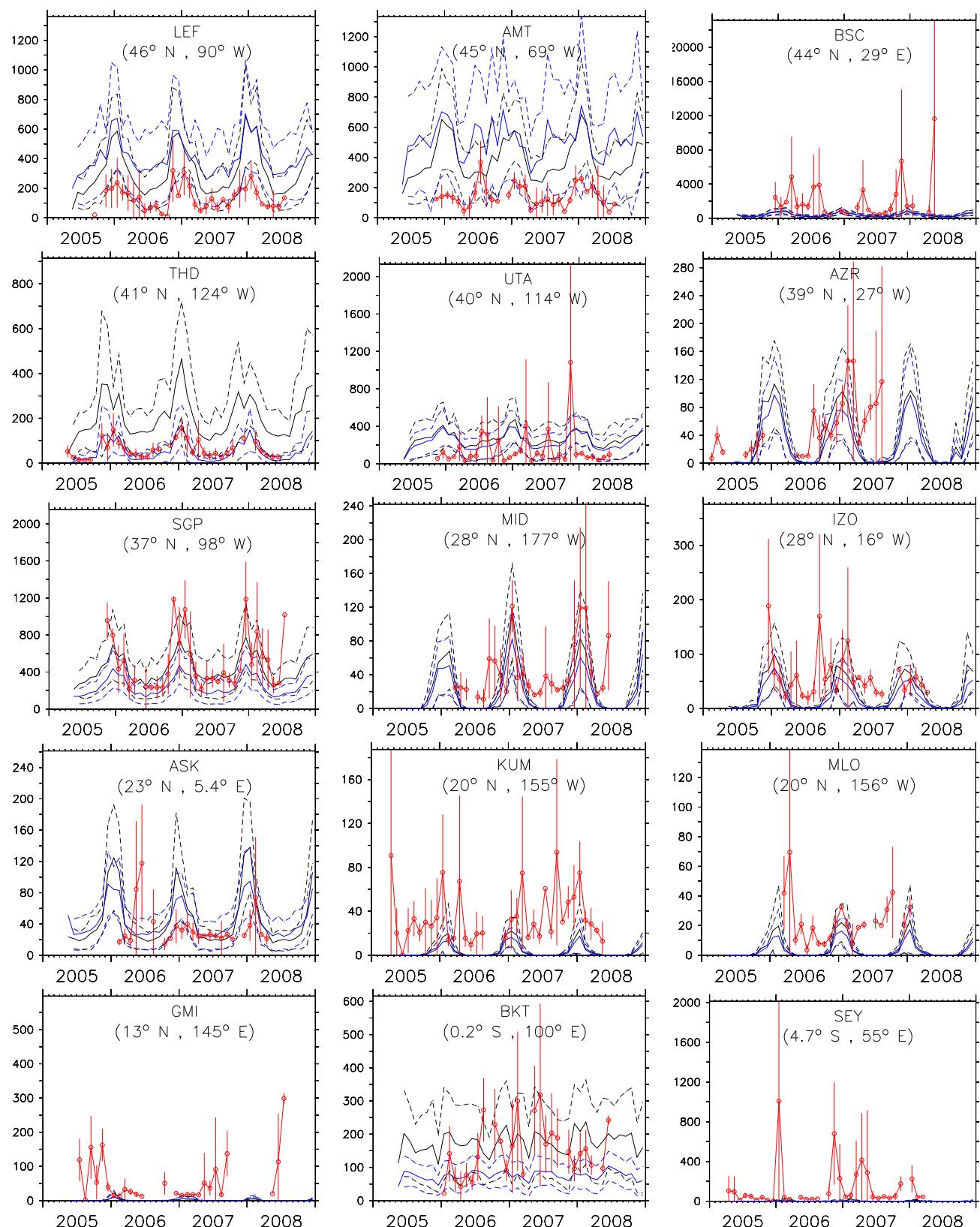


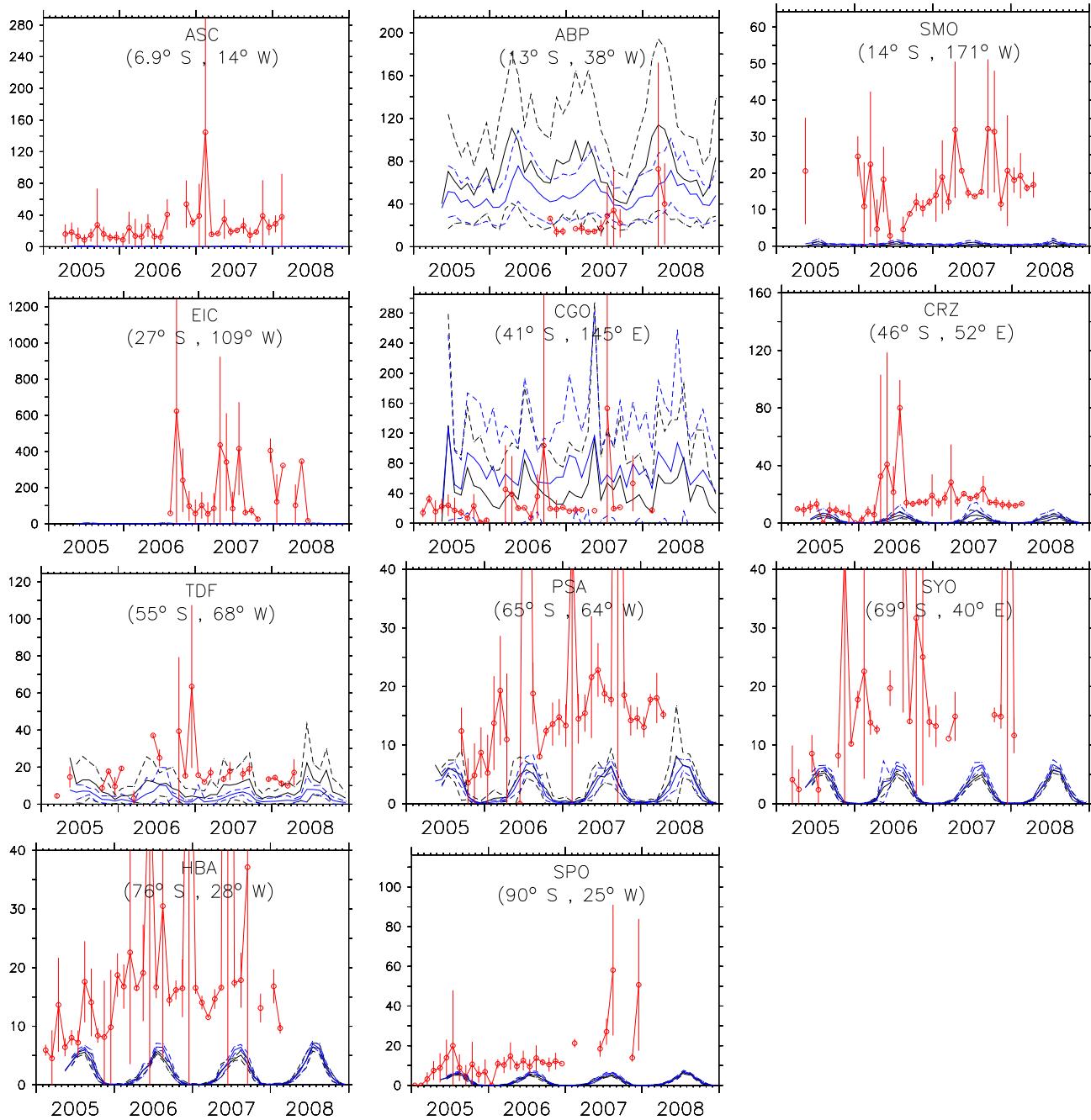


## Isopentane ( $\text{I-C}_5\text{H}_{12}$ )

Comparison of simulated and observed  $\text{I-C}_5\text{H}_{12}$  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.

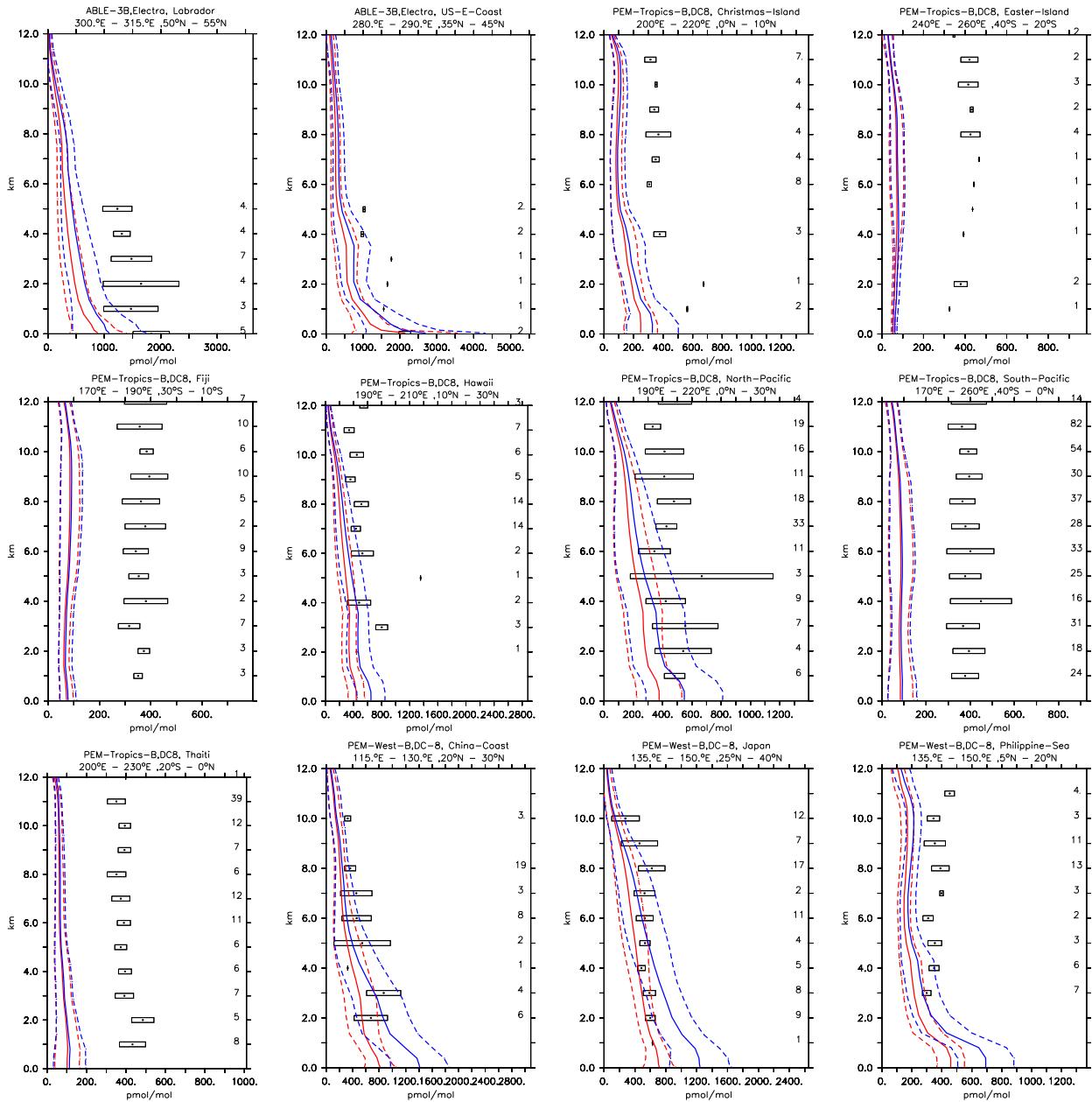


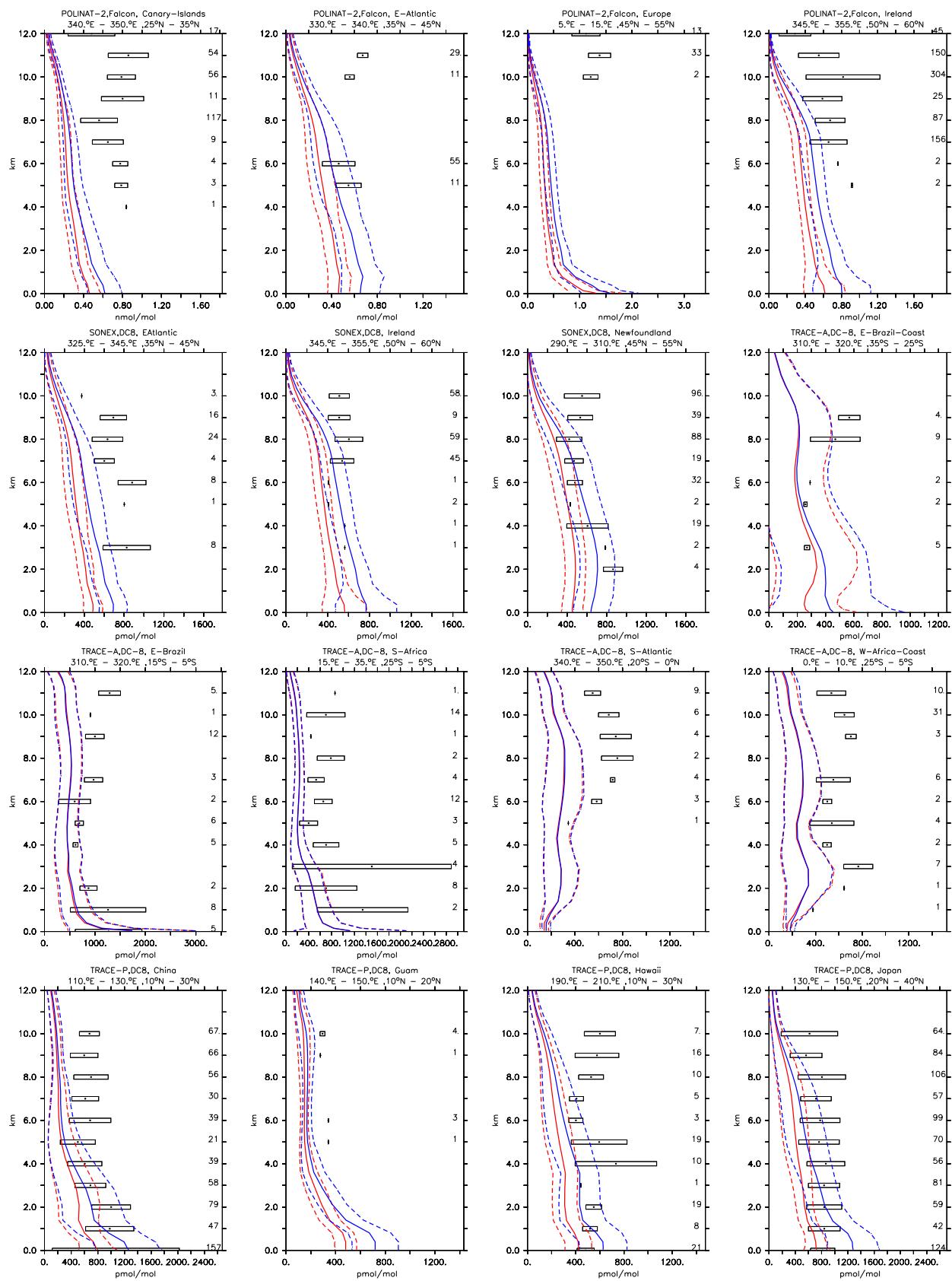




## Acetone formation

Vertical profiles of  $\text{CH}_3\text{COCH}_3$  (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.

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Development of a Master Chemical Mechanism for Use in Tropospheric Chemistry Models, *EUROTRAC Newsletter* 18, 1997a.

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