



*Supplement of*

**Description and evaluation of a detailed gas-phase chemistry scheme in the TM5-MP global chemistry transport model (r112)**

**Stelios Myriokefalitakis et al.**

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Supplementary Tables

Table S1: Selection of effective Henry law coefficients ( $H^*$ ) used in TM5-MP for the MOGUNTIA chemical scheme.

| Trace gas  | $H^*$ (M atm <sup>-1</sup> ) | $\Delta H R^{-1}$ (K) | Reference |
|--|------------------------------|-----------------------|-----------|
| CH <sub>3</sub> OOH, <i>n</i> -C <sub>3</sub> H <sub>7</sub> OOH, <i>i</i> -C <sub>3</sub> H <sub>7</sub> OOH, CH <sub>3</sub> COCH <sub>2</sub> OH, C <sub>4</sub> H <sub>9</sub> OOH, MEKOOH, ISOPOOH, MVKOOH, MACROOH | 2.9 x 10 <sup>2</sup>        | 5200                  | 1         |
| CH <sub>3</sub> ONO <sub>2</sub>   | 2.0                          | 4700                  | 1         |
| CH <sub>3</sub> OONO <sub>2</sub>  | 2.0                          | 4700                  | 1         |
| HCHO   | 3.2 x 10 <sup>3</sup>        | 6800                  | 1         |
| CH <sub>3</sub> OH   | 2.0 x 10 <sup>2</sup>        | 5600                  | 1         |
| HCOOH  | 8.8 x 10 <sup>3</sup>        | 6100                  | 1         |
| CH <sub>3</sub> CH <sub>2</sub> OOH  | 3.3                          | 6000                  | 1         |
| CH <sub>3</sub> CH <sub>2</sub> ONO <sub>2</sub>   | 1.6                          | 5400                  | 1         |
| HOCH <sub>2</sub> CH <sub>2</sub> OOH  | 1.7 x 10 <sup>6</sup>        | 9700                  | 1         |
| HOCH <sub>2</sub> CH <sub>2</sub> ONO <sub>2</sub>   | 3.9 x 10 <sup>4</sup>        |                       | 1         |
| CH <sub>3</sub> CHO  | 13                           | 5900                  | 1         |
| CH <sub>3</sub> COOH   | 8.3 x 10 <sup>2</sup>        | 5300                  | 1         |
| HOCH <sub>2</sub> CHO  | 4.1 x 10 <sup>4</sup>        | 4600                  | 1         |
| CHOCHO   | 4.19 x 10 <sup>5</sup>       | 7500                  | 1         |
| CH <sub>3</sub> CH <sub>2</sub> OH   | 190                          | 6400                  | 1         |
| CH <sub>3</sub> COOH   | 4.0 x 10 <sup>3</sup>        | 6200                  | 1         |
| <i>n</i> -C <sub>3</sub> H <sub>7</sub> ONO <sub>2</sub>   | 1.1                          | 5500                  | 1         |
| <i>i</i> -C <sub>3</sub> H <sub>7</sub> ONO <sub>2</sub>   | 0.78                         | 5400                  | 1         |
| HOC <sub>3</sub> H <sub>6</sub> OOH  | 1.7 x 10 <sup>6</sup>        | 9700                  | 1         |
| CH <sub>3</sub> COCH <sub>3</sub>  | 27                           | 5500                  | 1         |
| CH <sub>3</sub> CH <sub>2</sub> CHO  | 9.9                          | 4300                  | 1         |
| CH <sub>3</sub> COCHO  | 3.2 x 10 <sup>3</sup>        | 7500                  | 1         |
| CH <sub>3</sub> C(O)COOH   | 3.1 x 10 <sup>5</sup>        | 5100                  | 1         |
| C <sub>4</sub> H <sub>9</sub> ONO <sub>2</sub>   | 1                            | 5800                  | 1         |
| MEK  | 18                           | 5700                  | 1         |
| MEKONO <sub>2</sub>  | 0.7                          | 5200                  | 1         |
| CH <sub>3</sub> COCOCH <sub>3</sub>  | 73                           | 5700                  | 1         |
| ISOPONO <sub>2</sub> , MACRONO <sub>2</sub> , MVKONO <sub>2</sub>  | 1.7 x 10 <sup>4</sup>        | 9200                  | 2         |
| IEPOX  | 9.1 x 10 <sup>4</sup>        | 6600                  | 3         |
| HPALD  | 2.3                          |                       | 1         |
| MVK  | 26                           | 4800                  | 1         |
| MACR   | 4.8                          | 4300                  | 1         |

<sup>1</sup> Sander (2015) and references therein  
<sup>2</sup> Ito et al. (2007) for all biogenic hydroxy nitrates  
<sup>3</sup> Browne et al. (2014), as for H<sub>2</sub>O<sub>2</sub>



**Table S2: Soil, water, snow/ice and mesophyl resistances ( $s\ m^{-1}$ ) used in TM5-MP for the CB05 and MOGUNTIA chemical schemes.**

| Trace gas   | $r_{soil}$      | $r_{wat}$       | $r_{snow/ice}$  | $r_{mes}$ | $r_{ent}$       |
|---|-----------------|-----------------|-----------------|-----------|-----------------|
| O <sub>3</sub>  | 400             | 2000            | 2000            | 1         | 10 <sup>5</sup> |
| CO  | 5000            | 10 <sup>5</sup> | 10 <sup>5</sup> | 5000      | 10 <sup>5</sup> |
| NO  | 10 <sup>5</sup> | 10 <sup>5</sup> | 10 <sup>5</sup> | 500       | 10 <sup>5</sup> |
| NO <sub>2</sub> /NO <sub>3</sub>  | 600             | 3000            | 3000            | 1         | 10 <sup>5</sup> |
| HNO <sub>3</sub> /N <sub>2</sub> O <sub>5</sub>   | 1               | 1               | 1               | 1         | 1               |
| H <sub>2</sub> O <sub>2</sub> , IEPOX   | 80              | 72              | 80              | 1         | 10 <sup>5</sup> |
| SO <sub>2</sub>   | 100             | 1               | 1               | 1         | 10 <sup>5</sup> |
| CH <sub>3</sub> ONO <sub>2</sub> , CH <sub>3</sub> OONO <sub>2</sub> , CH <sub>3</sub> C(O)OONO <sub>2</sub> , <i>n</i> -C <sub>3</sub> H <sub>7</sub> ONO <sub>2</sub> ,<br><i>i</i> -C <sub>3</sub> H <sub>7</sub> ONO <sub>2</sub> , C <sub>4</sub> H <sub>9</sub> ONO <sub>2</sub> , MEKONO <sub>2</sub> , ISOPONO <sub>2</sub>   | 3994            | 295             | 3394            | 1         | 10 <sup>5</sup> |
| CH <sub>3</sub> CHO, C <sub>2</sub> H <sub>5</sub> CHO, CH <sub>3</sub> C(O)CH <sub>3</sub> , CH <sub>3</sub> C(O)C(O)CH <sub>3</sub> ,<br>HOCH <sub>2</sub> C(O)CH <sub>3</sub> , MEK, MVK, MACR, HPALD  | 10 <sup>5</sup> | 300             | 10 <sup>5</sup> | 200       | 10 <sup>5</sup> |
| HCHO, CH <sub>3</sub> COCHO, CHOCHO, HOCH <sub>2</sub> CHO,   | 1666            | 254             | 1666            | 1         | 10 <sup>5</sup> |
| CH <sub>3</sub> OOH, CH <sub>3</sub> OH, HCOOH, CH <sub>3</sub> CH <sub>2</sub> OOH, CH <sub>3</sub> CH <sub>2</sub> OH, CH <sub>3</sub> COOH, <i>n</i> -<br>C <sub>3</sub> H <sub>7</sub> OOH, <i>i</i> -C <sub>3</sub> H <sub>7</sub> OOH, CH <sub>3</sub> C(O)CH <sub>2</sub> OOH,<br><i>n</i> -C <sub>3</sub> H <sub>7</sub> OOH, <i>i</i> -C <sub>3</sub> H <sub>7</sub> OOH, HOC <sub>3</sub> H <sub>6</sub> OOH, CH <sub>3</sub> C(O)COOH, C <sub>4</sub> H <sub>9</sub> OOH,<br>MEKOOH, MVKOOH, MACROOH, CH <sub>3</sub> C(O)OOH, ISOPOOH | 3650            | 293             | 3650            | 1         | 10 <sup>5</sup> |
| NH <sub>3</sub>   | 100             | 1               | 10 <sup>5</sup> | 1         | 10 <sup>5</sup> |

5 Table S3: TM5-MP performance calculations of the mCB05(EBI), mCB05(KPP) and MOGUNTIA configurations for the different components, i.e., the transport (advection in the x-, y- and z-directions along with the vertical transport), the chemistry as well as all other procedures contribution, the simulated years per day (SYPD), and the core-hours per simulated years (CHPSY) using a) 360 cores, and b) 450 cores. Timings are in seconds and changes are in %. In parentheses, the runtime and the SYPD without the meteorology reading are also presented. All simulations have been performed in the ECMWF CRAY XC40 high-performance computer facility.

a)

| Configuration              | Transport        |                  |                  |          |       | Chemistry | Other | Runtime       | SYPD        | CHPSY |
|----------------------------|------------------|------------------|------------------|----------|-------|-----------|-------|---------------|-------------|-------|
|                            | Adv <sub>x</sub> | Adv <sub>y</sub> | Adv <sub>z</sub> | Vertical | Total |           |       |               |             |       |
| CB05(EBI)                  | 1322             | 948              | 165              | 364      | 2799  | 3338      | 3925  | 10062 (6723)  | 0.73 (1.10) | 12000 |
| CB05(KPP)                  | 1312             | 934              | 165              | 362      | 2773  | 5301      | 4222  | 12296 (9105)  | 0.60 (0.81) | 14000 |
| MOGUNTIA                   | 1892             | 1303             | 233              | 527      | 3955  | 8230      | 4680  | 16865 (13556) | 0.44 (0.54) | 20000 |
| % solver changes           | -1%              | -1%              | 0%               | -1%      | -1%   | -1%       | 59%   | 8% (35%)      | -18% (-26%) | 17%   |
| % chemistry scheme changes | 44%              | 40%              | 41%              | 46%      | 43%   | 43%       | 55%   | 11% (49%)     | -27% (-33%) | 43%   |

10 b)

| Configuration              | Transport        |                  |                  |          |       | Chemistry | Other | Runtime       | SYPD        | CHPSY |
|----------------------------|------------------|------------------|------------------|----------|-------|-----------|-------|---------------|-------------|-------|
|                            | Adv <sub>x</sub> | Adv <sub>y</sub> | Adv <sub>z</sub> | Vertical | Total |           |       |               |             |       |
| CB05(EBI)                  | 1268             | 860              | 138              | 292      | 2558  | 2639      | 3687  | 8884 (5696)   | 0.83 (1.30) | 13000 |
| CB05(KPP)                  | 1292             | 853              | 133              | 300      | 2578  | 4320      | 4079  | 10977 (7733)  | 0.67 (0.95) | 16000 |
| MOGUNTIA                   | 1806             | 1126             | 193              | 423      | 3548  | 6526      | 4376  | 14450 (11211) | 0.51 (0.65) | 21000 |
| % solver changes           | 2%               | -1%              | -4%              | 3%       | 1%    | 64%       | 11%   | 24% (36%)     | -19% (-27%) | 23%   |
| % chemistry scheme changes | 40%              | 32%              | 45%              | 41%      | 38%   | 51%       | 7%    | 32% (45%)     | -24% (-32%) | 31%   |

Table S4: Tropospheric chemical budget of ORGNTR\* for the year 2006 in Tg(N) yr<sup>-1</sup>, using the 150 ppb O<sub>3</sub> mixing ratio to define tropopause level. Tropospheric burdens in Gg(N) yr<sup>-1</sup>.

| Production terms                       | mCB05 (EBI) | mCB05 (KPP) | MOGUNTIA | Loss terms  | mCB05 (EBI) | mCB05 (KPP) | MOGUNTIA |
|--|-------------|-------------|----------|-------------|-------------|-------------|----------|
| XO <sub>2</sub> N/RO <sub>2</sub> + NO | 8.6         | 8.1         | 7.0      | ORGNTR + hv | 4.1         | 4.0         | 2.6      |
| RH + NO <sub>3</sub>                   | 4.3         | 4.2         | 6.7      | ORGNTR + OH | 1.3         | 1.4         | 5.8      |
| Tropospheric Burden                    | 159.6       | 159.8       | 63.0     | Deposition  | 7.4         | 7.6         | 5.1      |

15 \*For the MOGUNTIA configuration ORGNTR represents the sum of CH<sub>3</sub>ONO<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>ONO<sub>2</sub>, OHCH<sub>2</sub>CH<sub>2</sub>ONO<sub>2</sub>, CH<sub>3</sub>CH<sub>3</sub>CH<sub>2</sub>ONO<sub>2</sub>, CH<sub>3</sub>CH(ONO<sub>2</sub>)CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>CH(ONO<sub>2</sub>)CH<sub>3</sub>, nitrates from isoprene (ISOPNO<sub>3</sub>), nitrates from methyl-ethyl ketone (MEKNO<sub>3</sub>), nitrates from methyl vinyl ketone (MVKNO<sub>3</sub>) and nitrates from methacrolein (MACRNO<sub>3</sub>)

## Supplementary Equations

5 **Statistics Formulas:** Correlation coefficient (R; Eq. S1), mean normalized bias (MNB; Eq. S2), root mean square error (RMSE; Eq. S3), mean normalized error (MNE; Eq. S4) and standard error (STD; Eq. S5) values have been calculated to compare the model calculations, where  $O_i$  and  $P_i$  stand for observations and predictions respectively and N is the number of pairs (observations, predictions) that are compared.

$$R = \left[ \frac{\frac{1}{N} \sum_{i=1}^N (O_i - \bar{O})(P_i - \bar{P})}{\sigma_O \sigma_P} \right] \quad (\text{Eq. S1})$$

$$NMB = \frac{\sum_{i=1}^N (M_i - O_i)}{\sum_{i=1}^N O_i} \times 100 \quad (\text{Eq. S2})$$

$$10 \quad RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (P_i - O_i)^2} \quad (\text{Eq. S3})$$

$$NME = \frac{\sum_{i=1}^N |M_i - O_i|}{\sum_{i=1}^N O_i} \times 100 \quad (\text{Eq. S4})$$

$$STD = \frac{\sqrt{\frac{1}{N} \sum_{i=1}^N (O_i - \bar{O})^2}}{\sqrt{N}} \quad (\text{Eq. S5})$$

Supplementary Figures

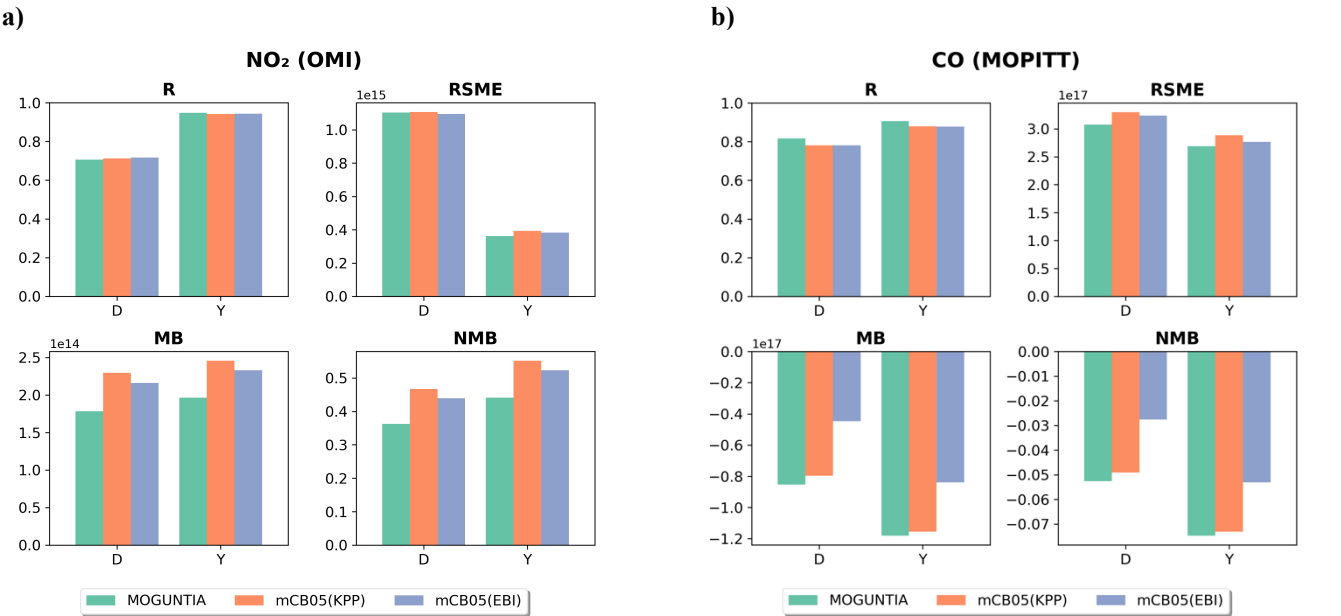
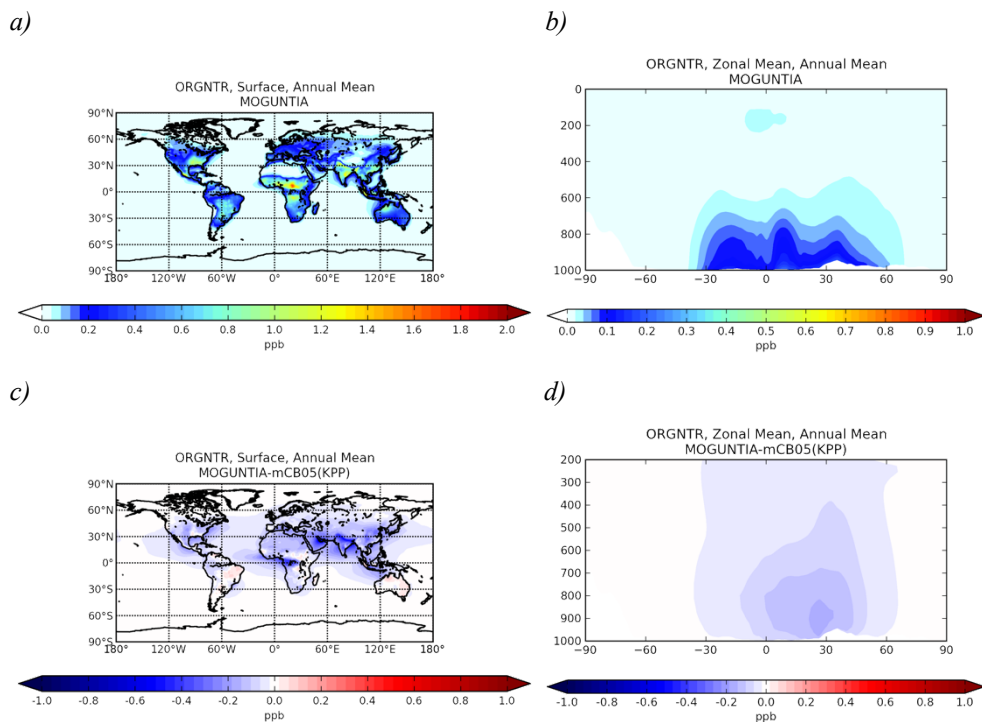


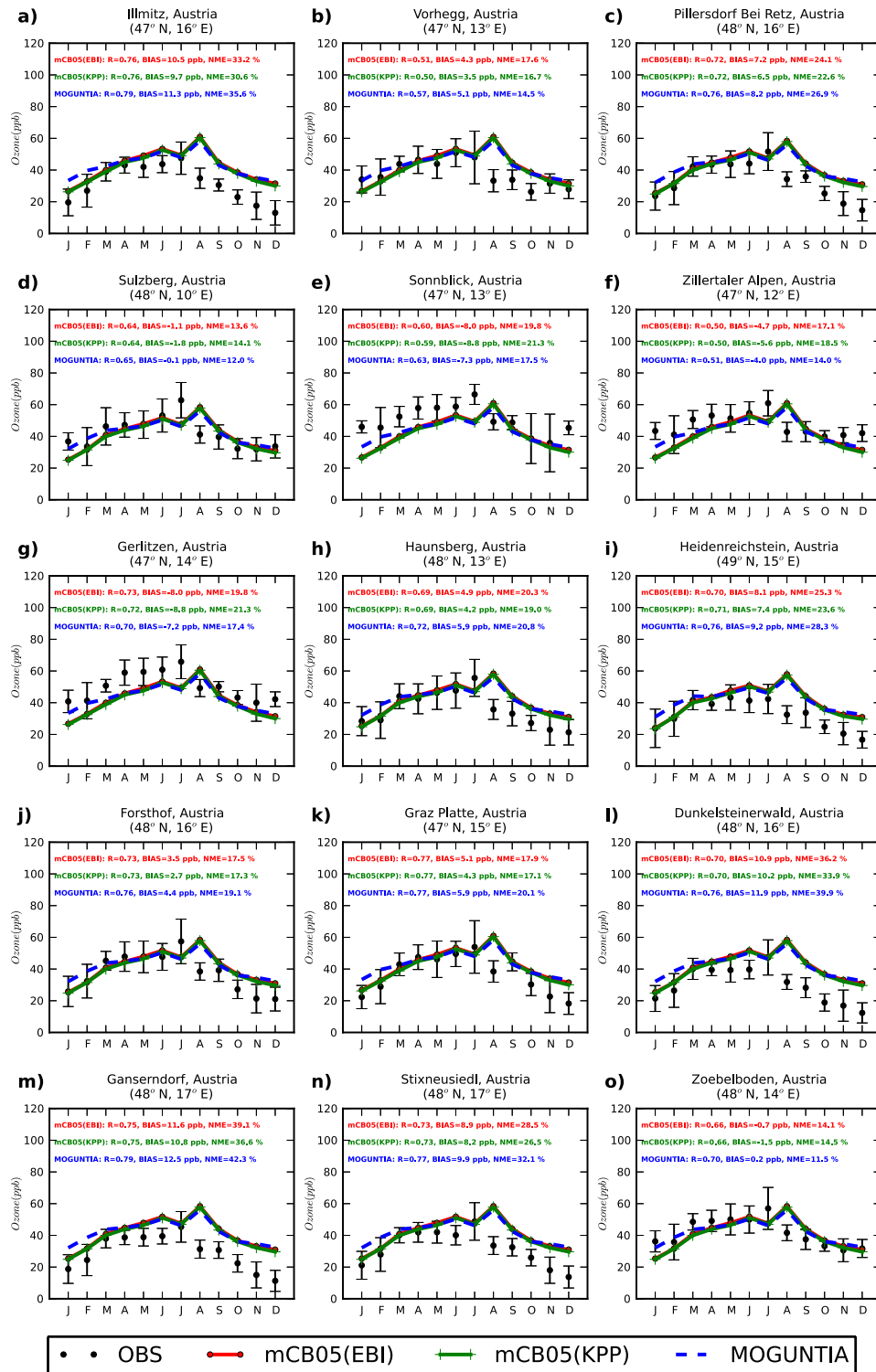
Figure S1: Comparison of simulated a) tropospheric NO<sub>2</sub> columns with OMI retrievals from the QA4ECV dataset and b) simulated total CO columns with MOPITT retrievals (vers. MOP02J\_V008) for the year 2006. Green, orange, and blue bars show the comparison of OMI with the MOGUNTIA, mCB05(KPP), and mCB05(EBI) chemistry mechanisms, respectively: Pearson correlation coefficient (top left), root mean square error (top right), mean bias (measurement minus model, bottom left), and normalized mean bias (measurement minus model, bottom right) are given for both daily (D) and yearly (Y) averages per model grid cell.

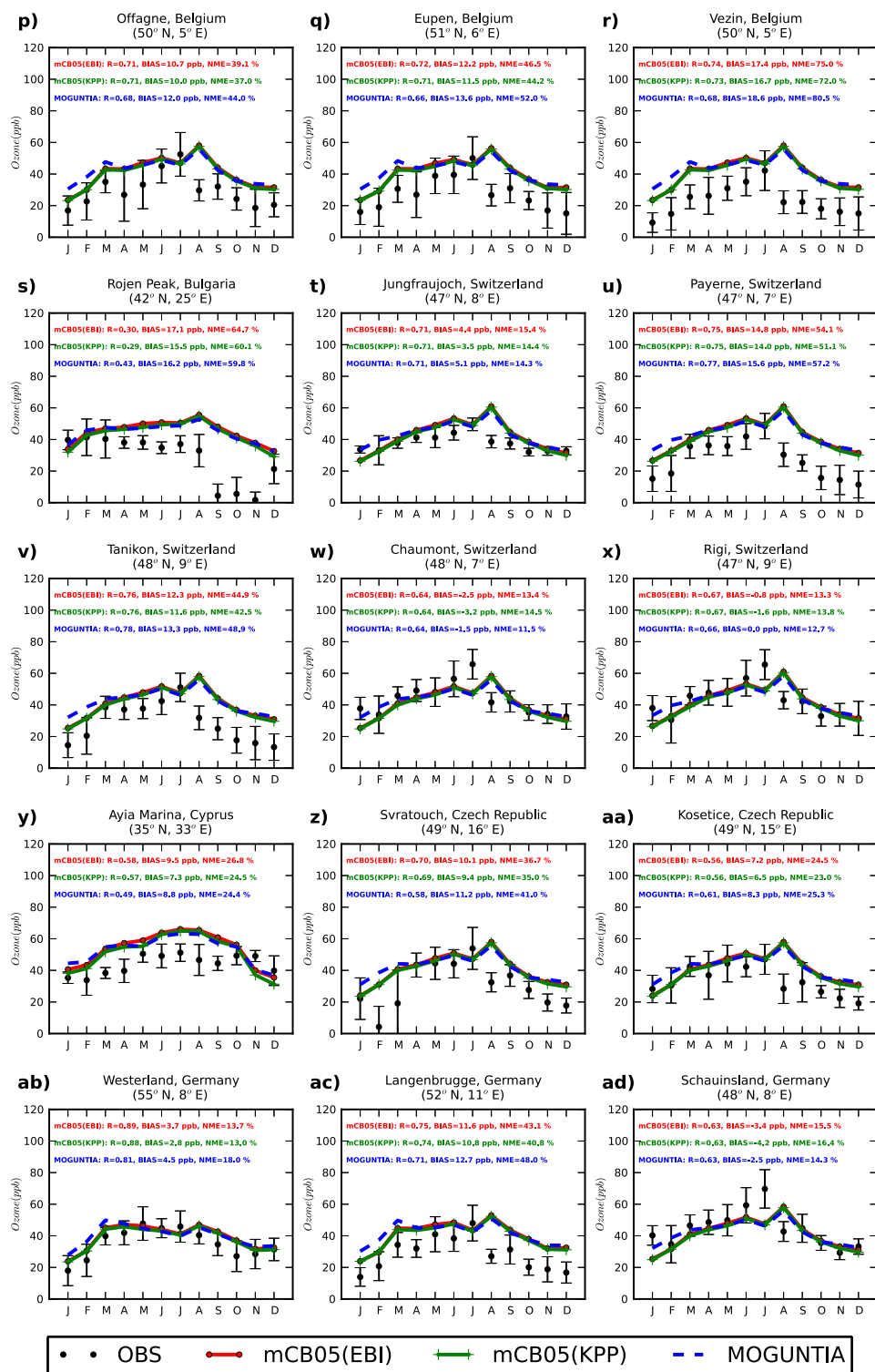


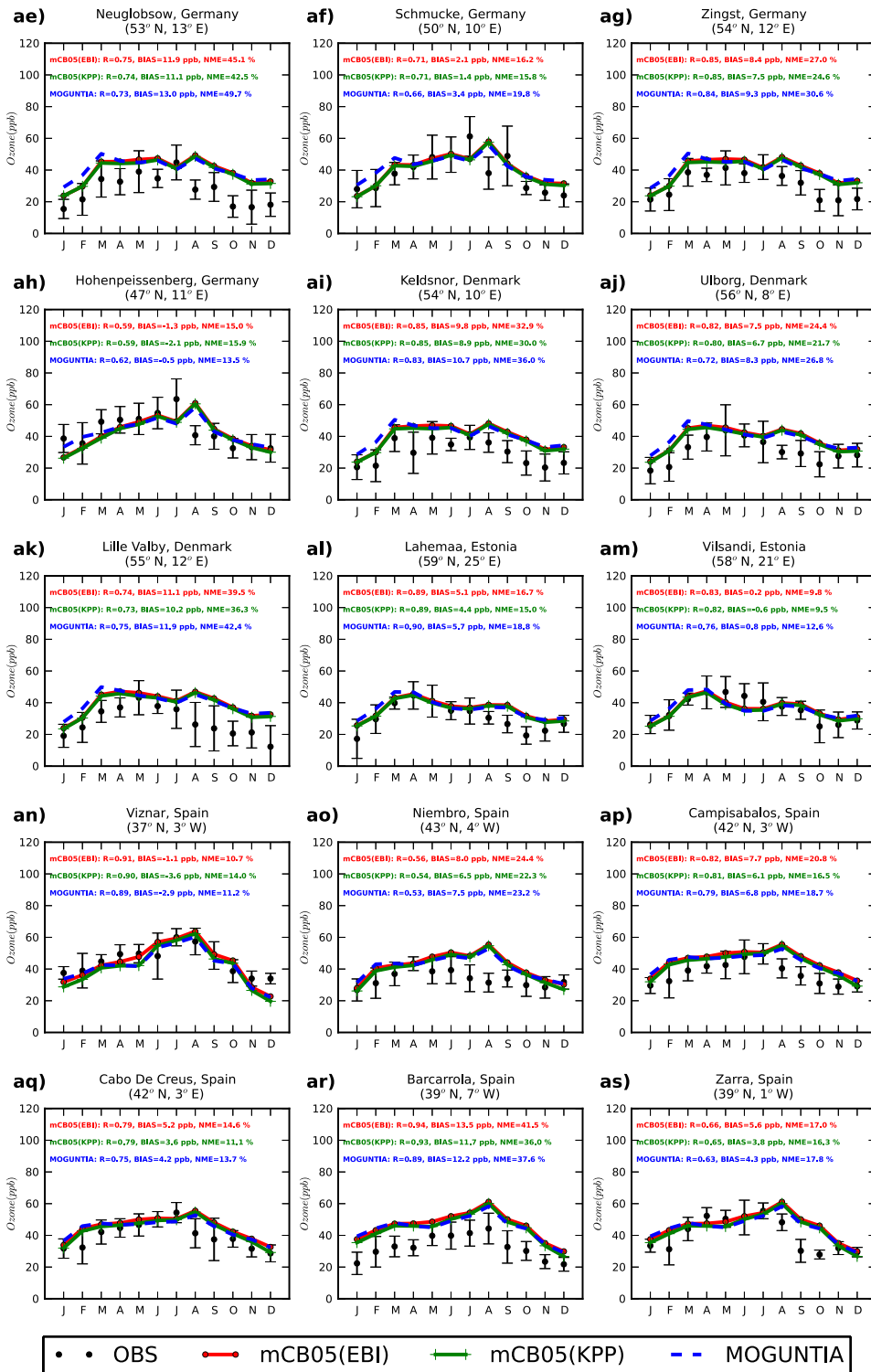
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**Figure S2: Simulated annual mean surface (left columns) and zonal mean (right columns) mixing ratios (ppb) of organic nitrates (ORGNTR) for the MOGUNTIA chemistry scheme for the year 2006 (a,b), and the respective differences compared to mCB05(KPP) (c,d). For the MOGUNTIA configuration, ORGNTR represents the sum of  $\text{CH}_3\text{ONO}_2$ ,  $\text{C}_2\text{H}_5\text{ONO}_2$ ,  $\text{OHCH}_2\text{CH}_2\text{ONO}_2$ ,  $\text{CH}_3\text{CH}_3\text{CH}_2\text{ONO}_2$ ,  $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_3$ , nitrates from isoprene ( $\text{ISOPNO}_3$ ), nitrates from methyl-ethyl ketone ( $\text{MEKNO}_3$ ), nitrates from methyl vinyl ketone ( $\text{MVKNO}_3$ ) and nitrates from methacrolein ( $\text{MACRNO}_3$ ).**

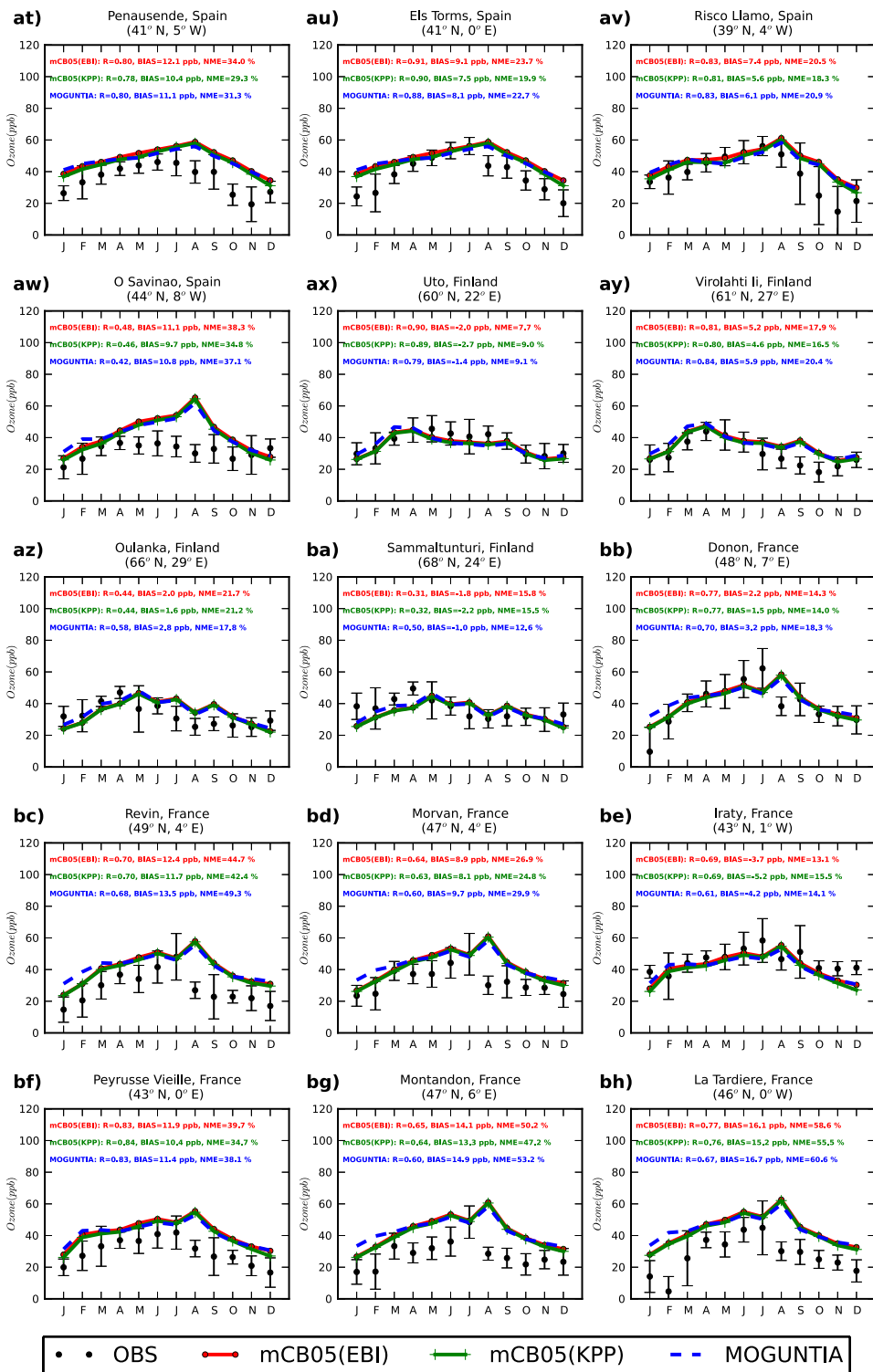
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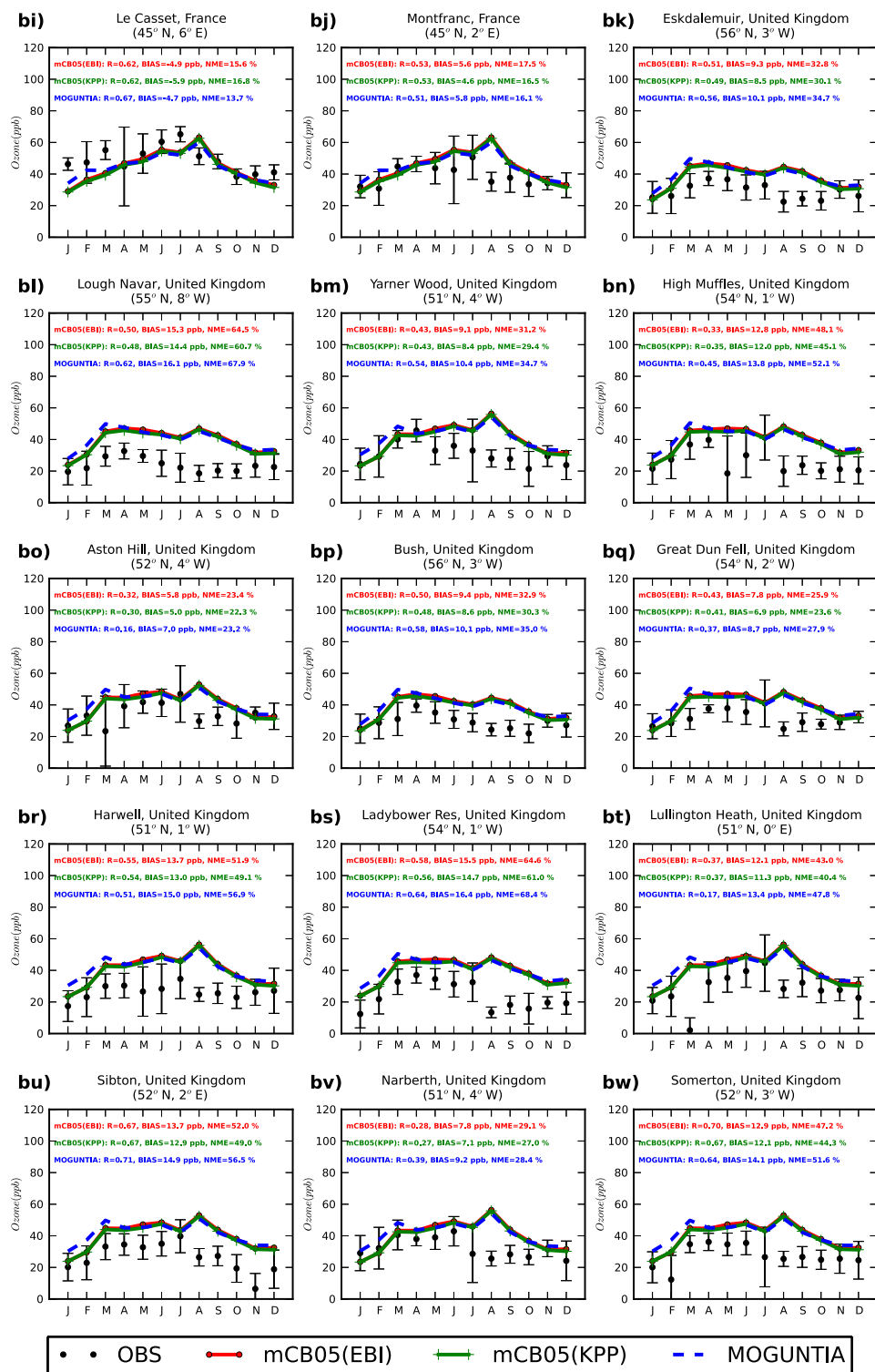


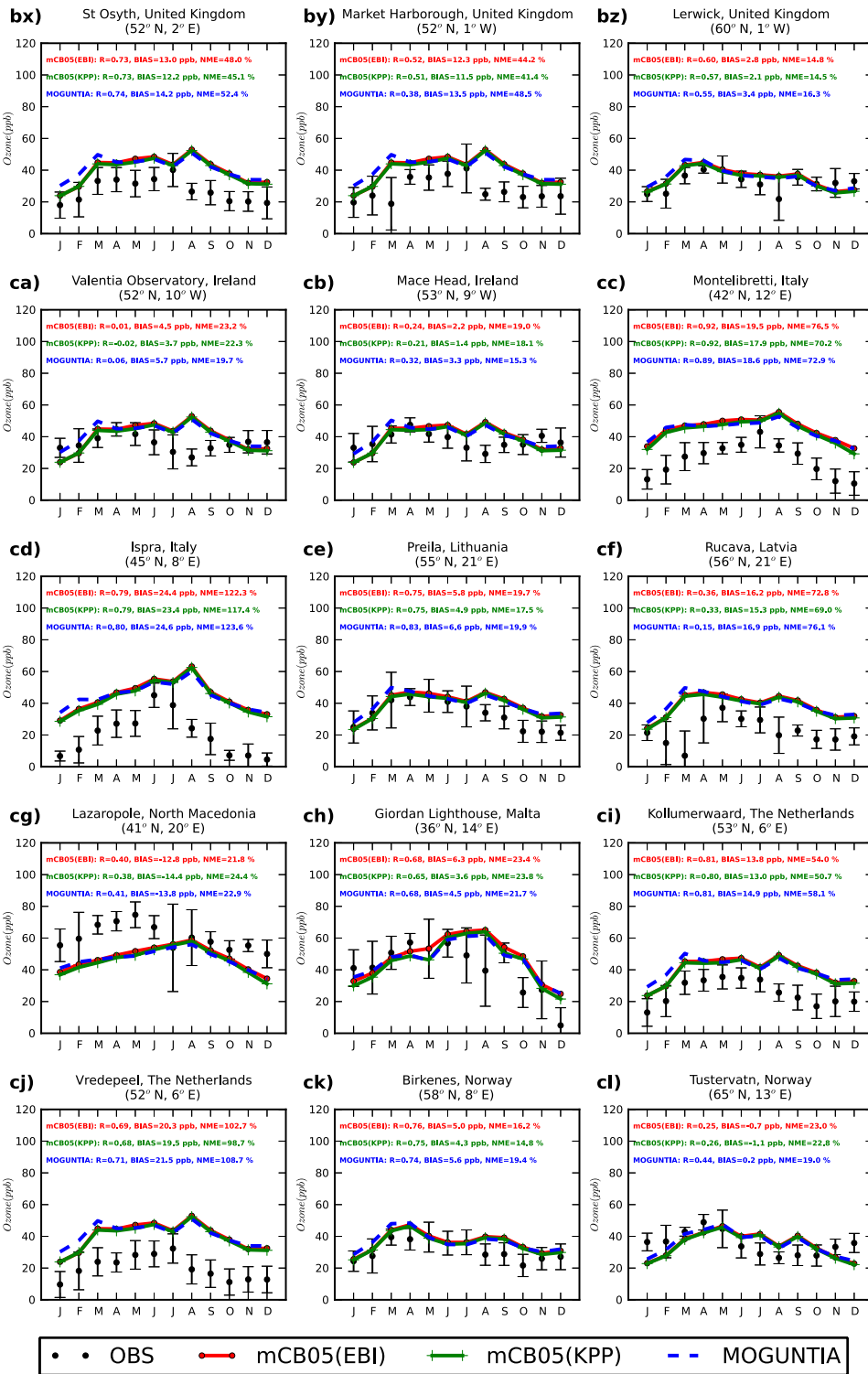


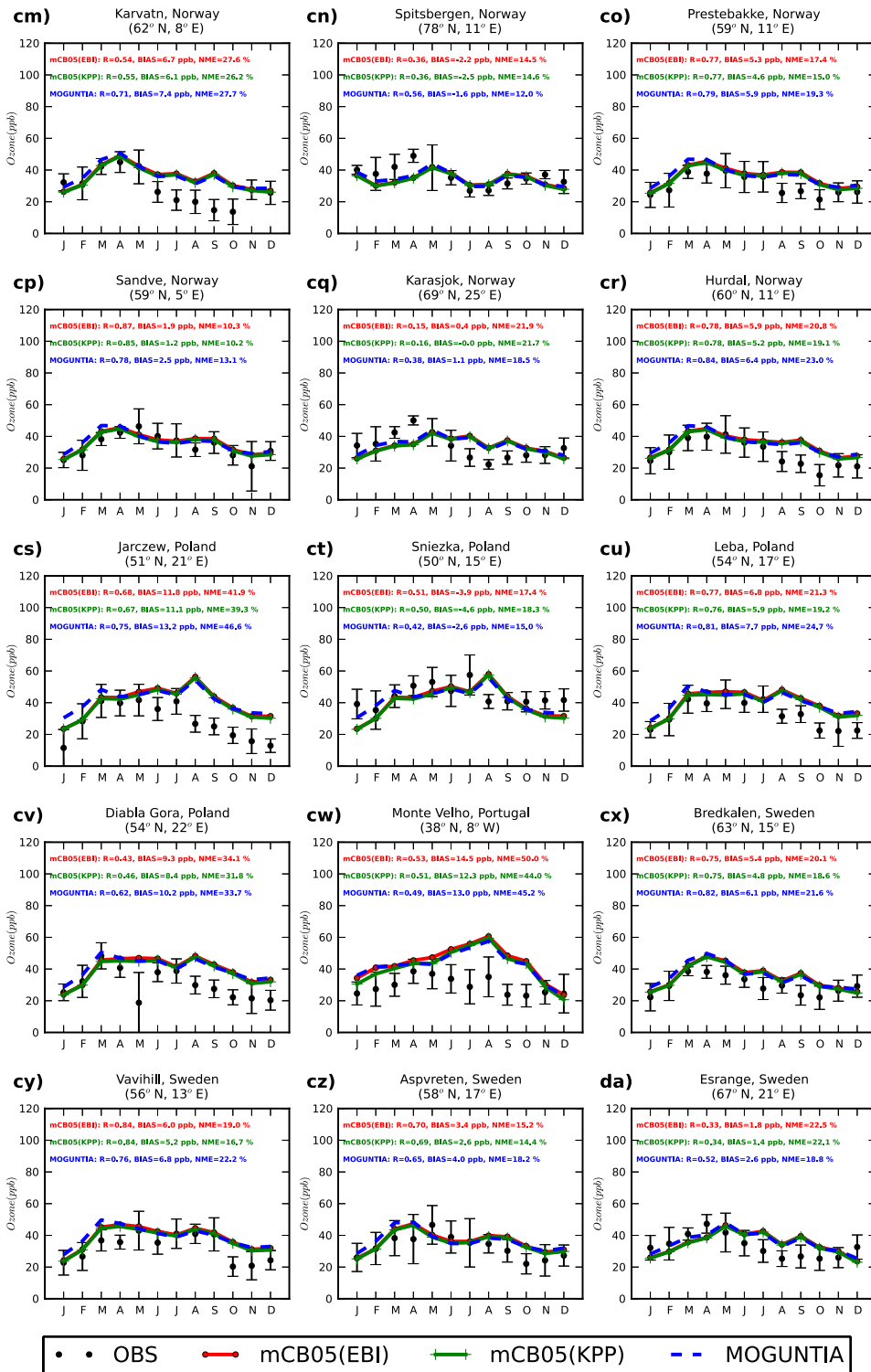


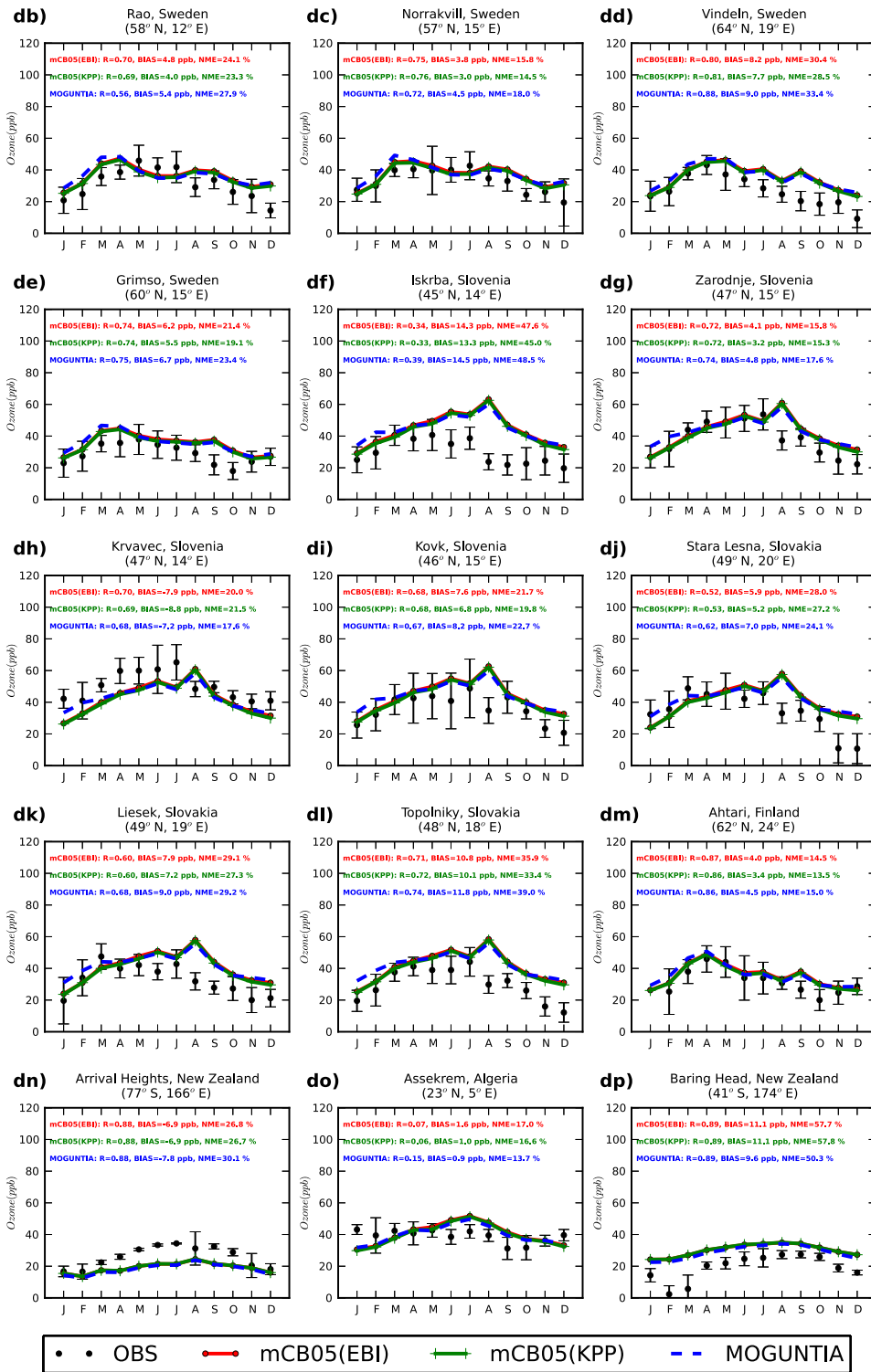


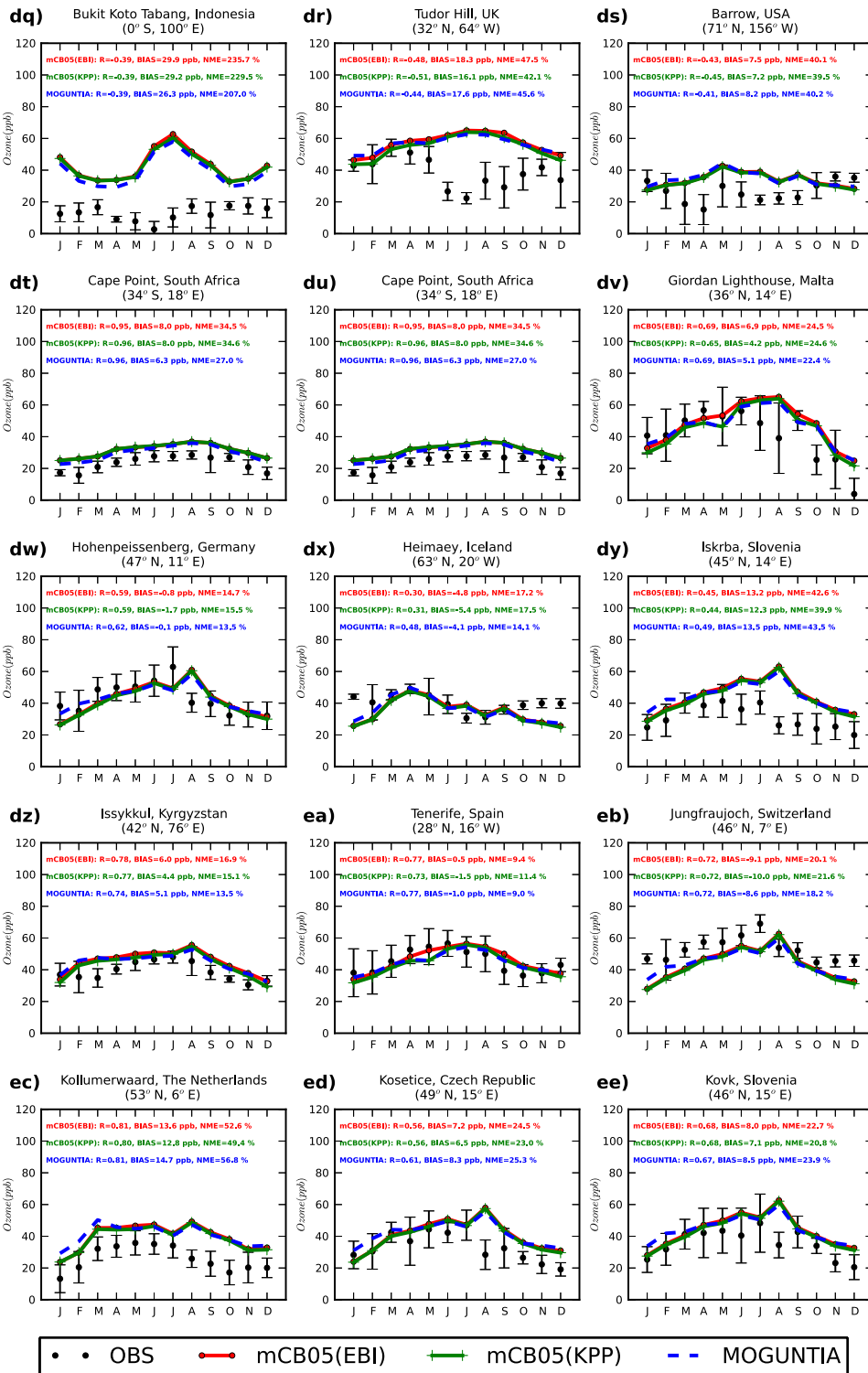


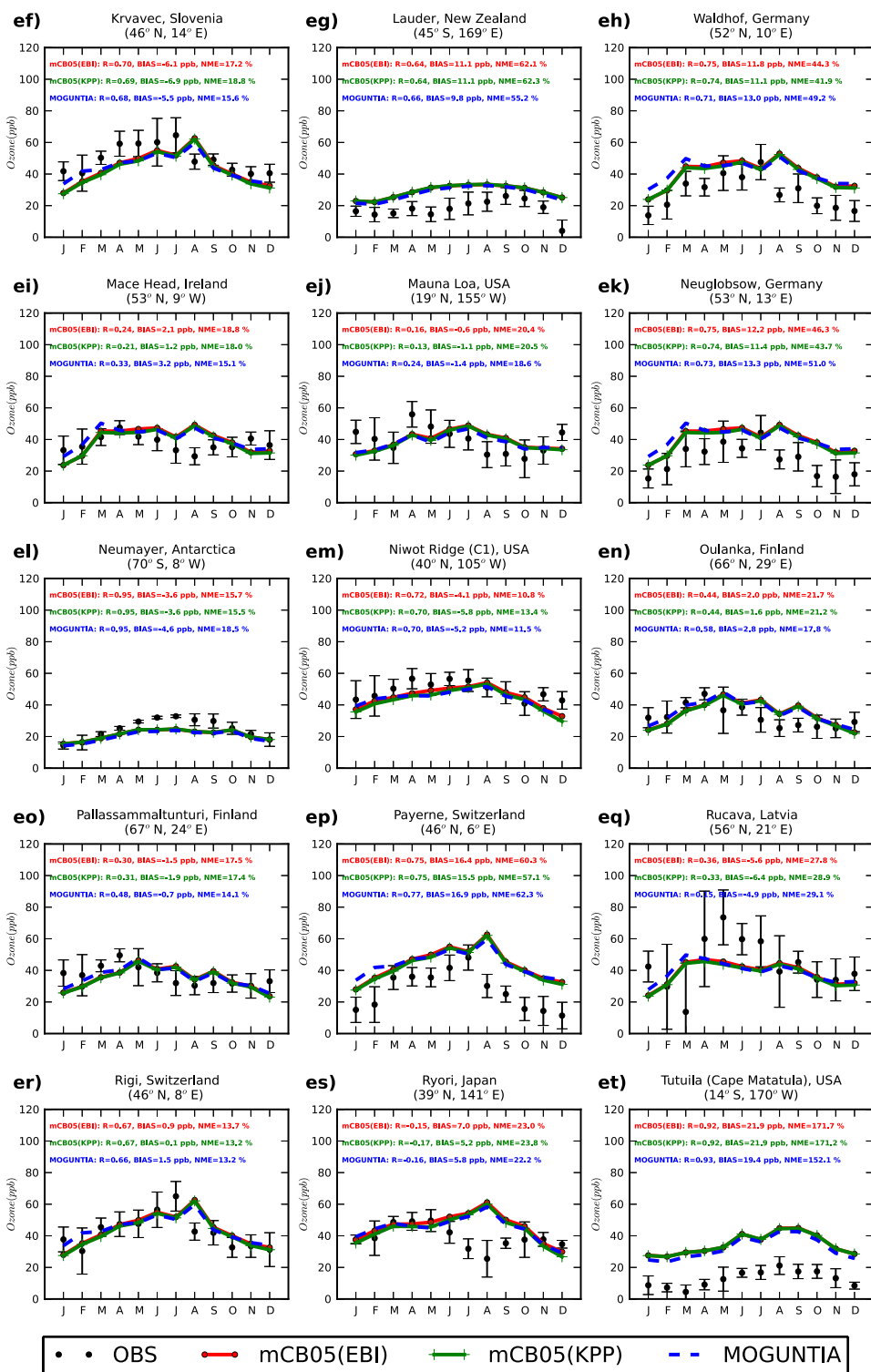


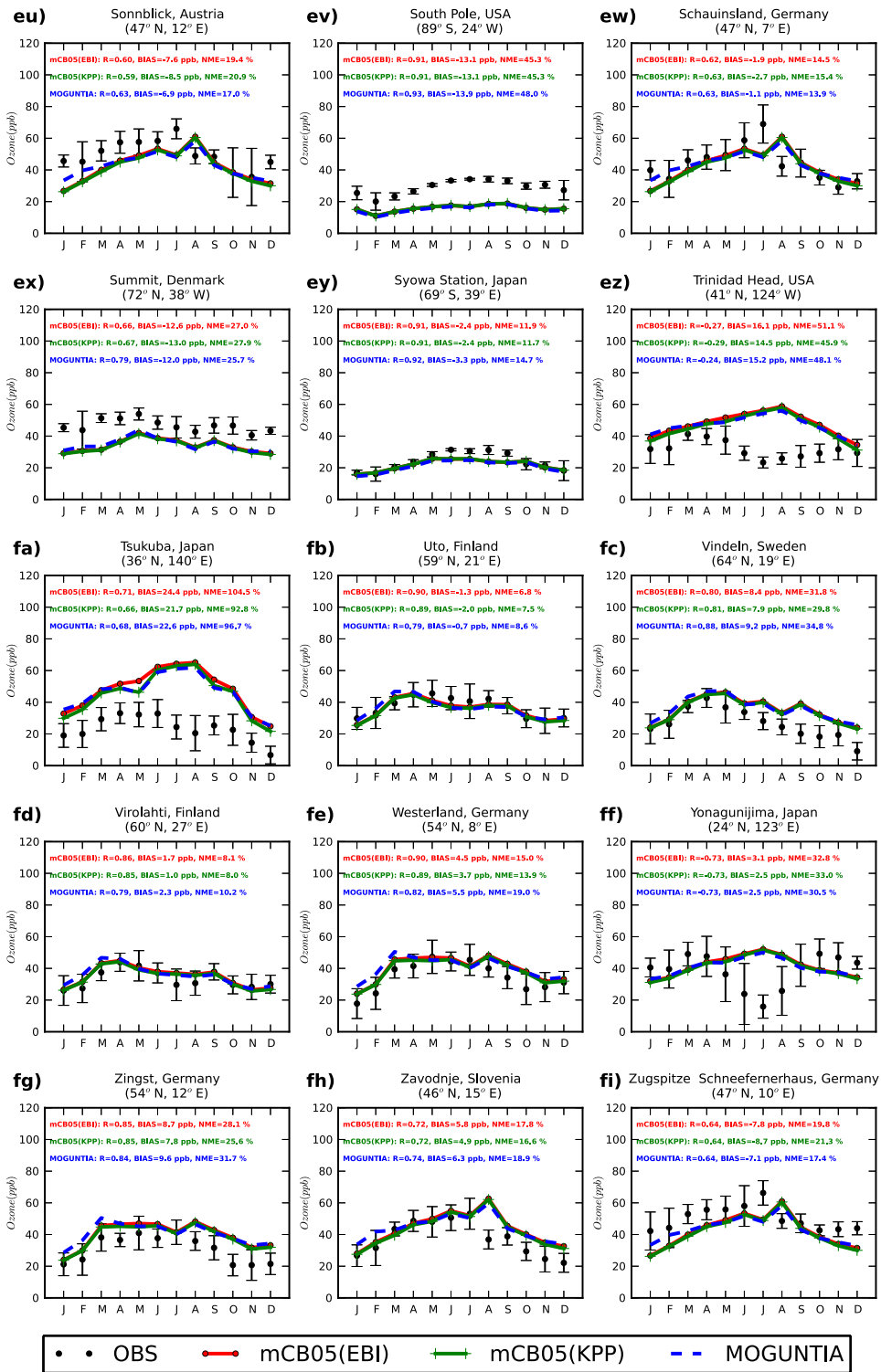














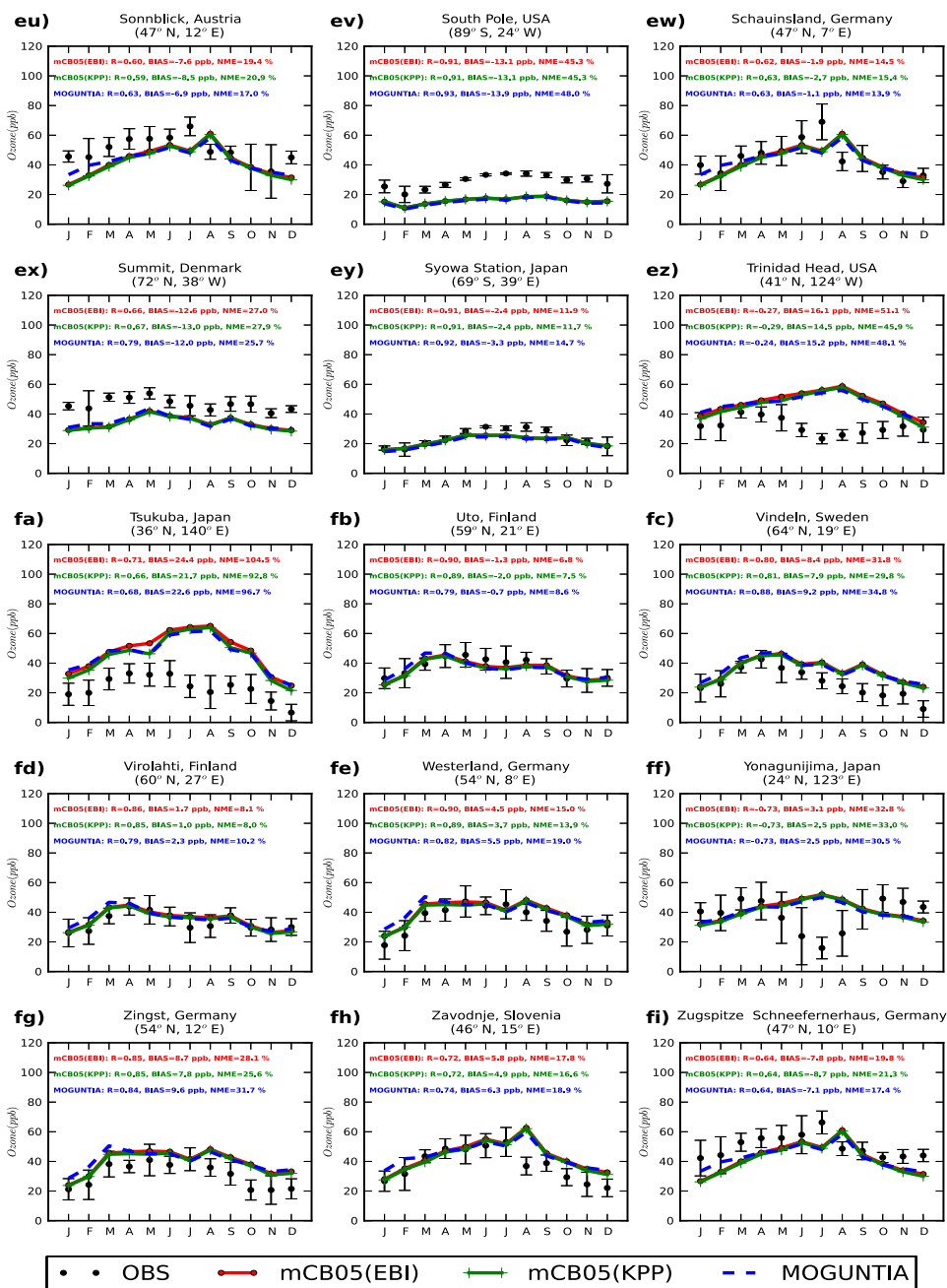
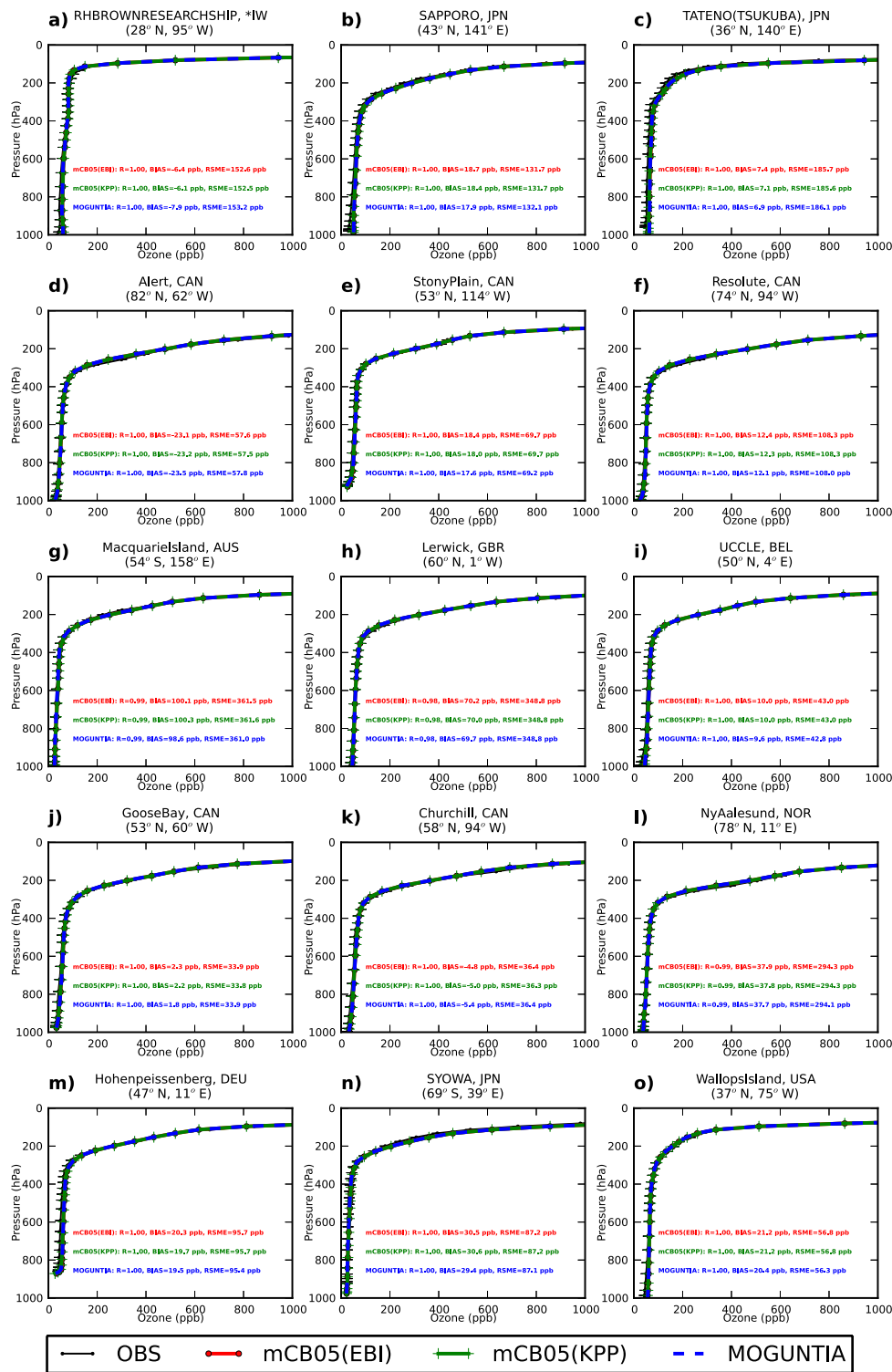
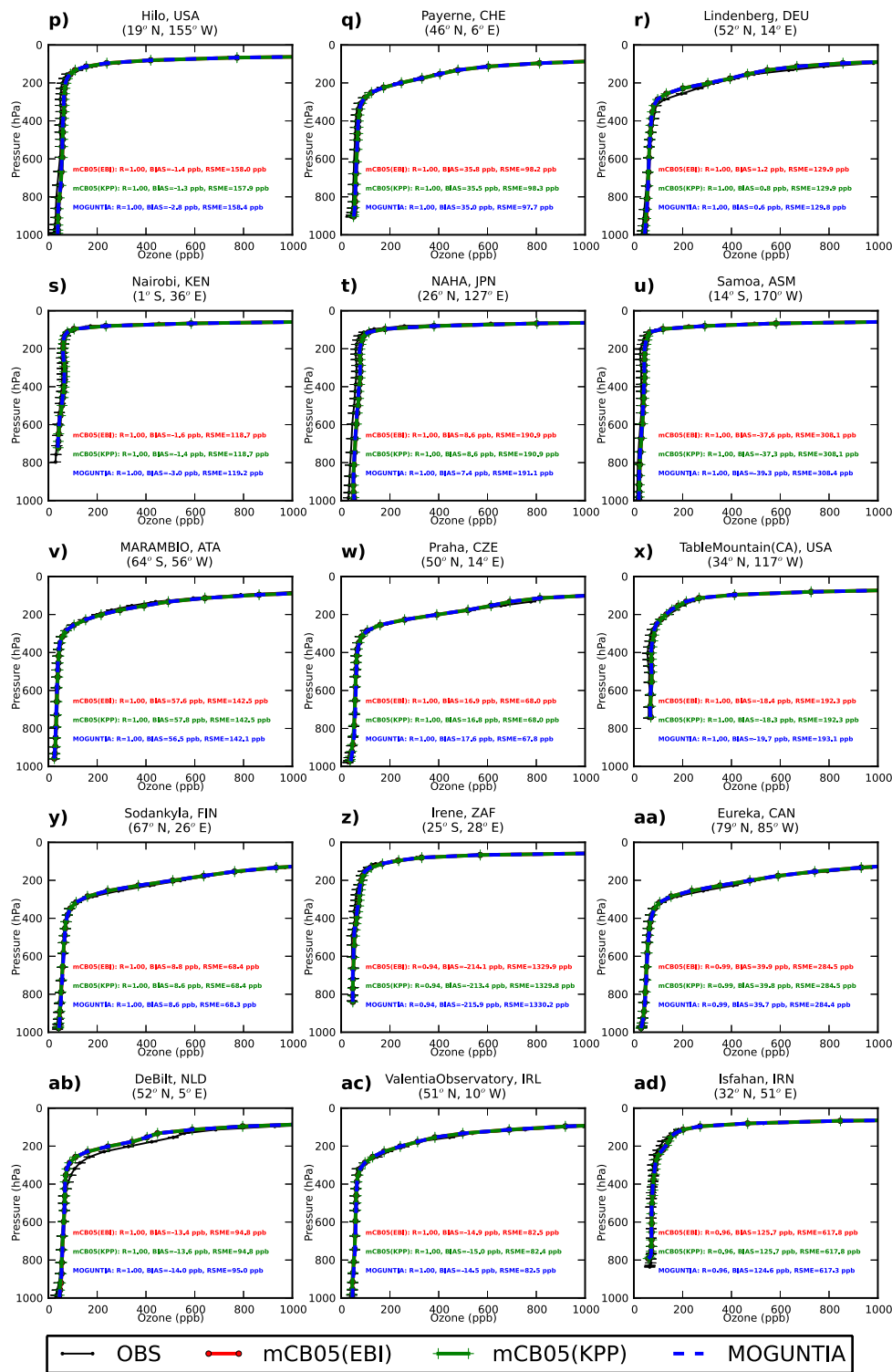
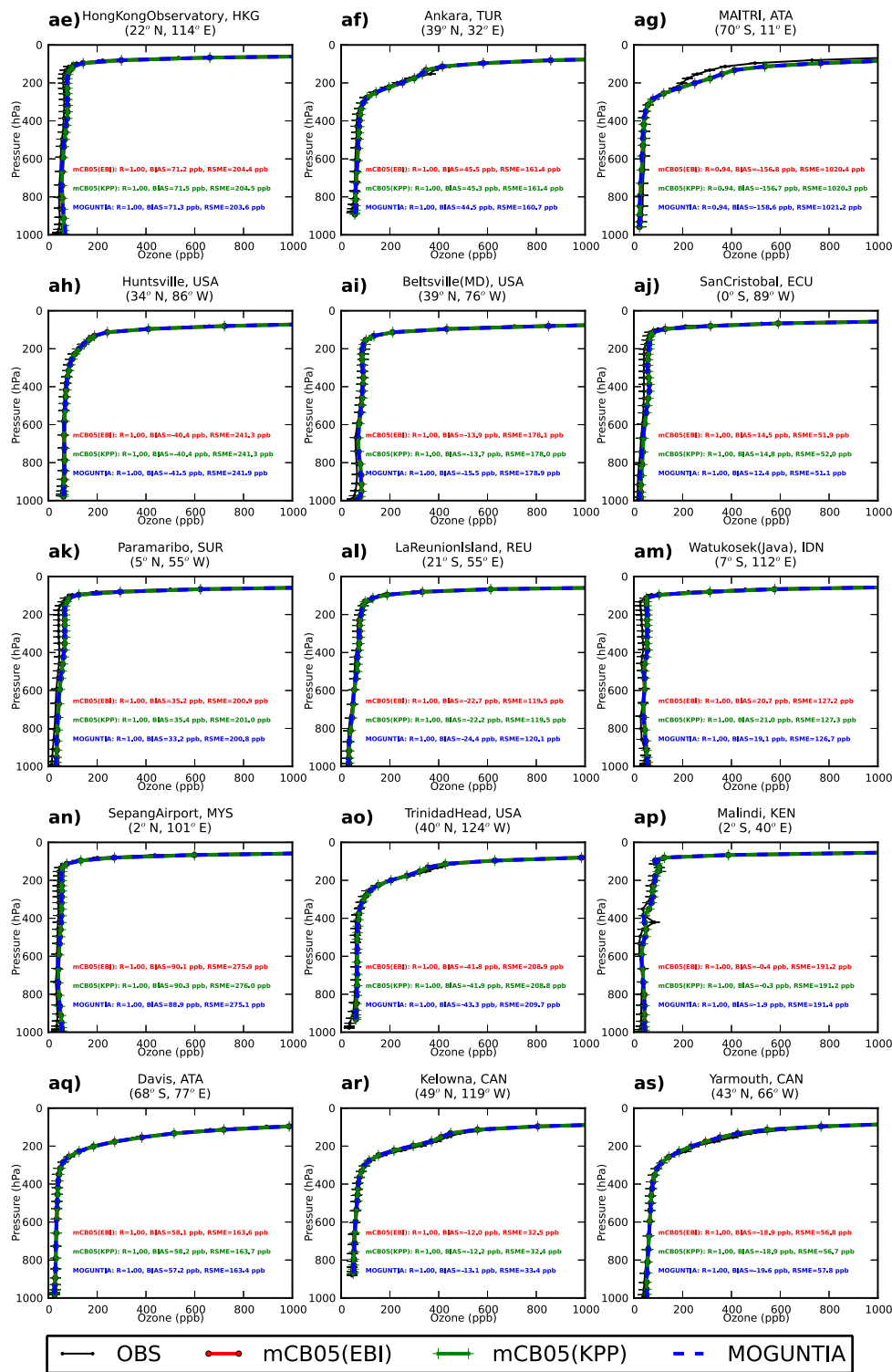


Figure S3: Comparison of monthly mean surface  $O_3$  observations (black dots) in ppb with model results (red-line for mCB05(EBI), green-line for mCB05(KPP) and blue-line for MOGUNTIA) at various stations around the globe, as obtained from the European Monitoring and Evaluation Programme (EMEP; <http://www.emep.int>) and the World Data Centre for Greenhouse Gases (WDCGG; <http://ds.data.jma.go.jp/gmd/wdcgg/introduction.html>), for the year 2006.







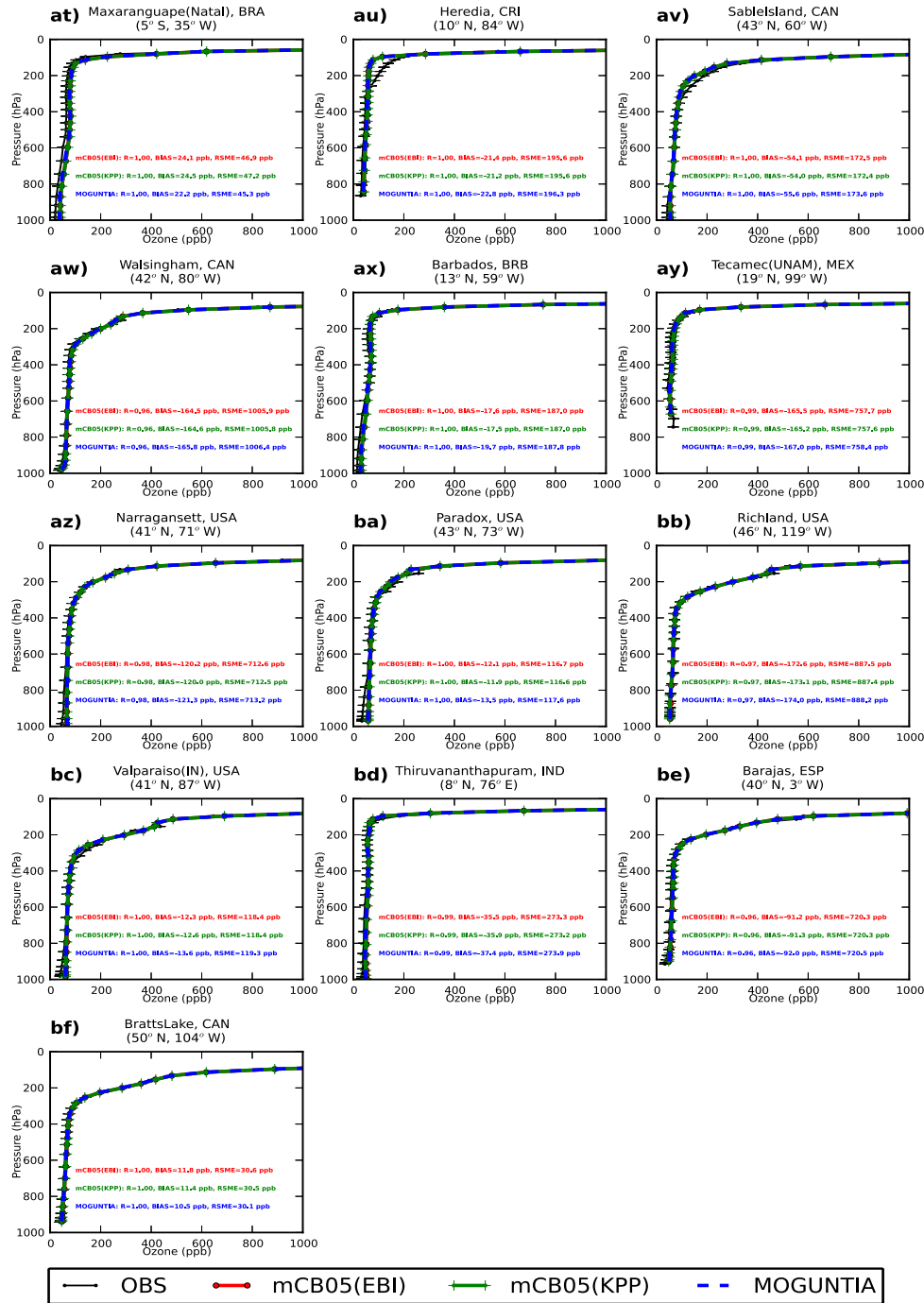
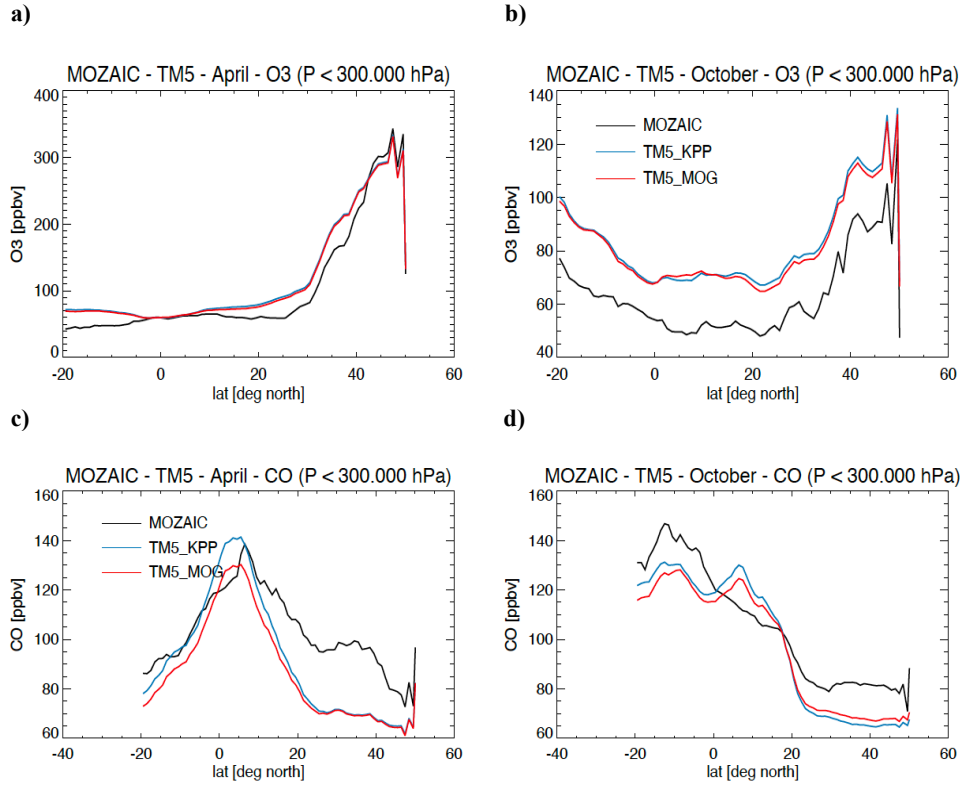
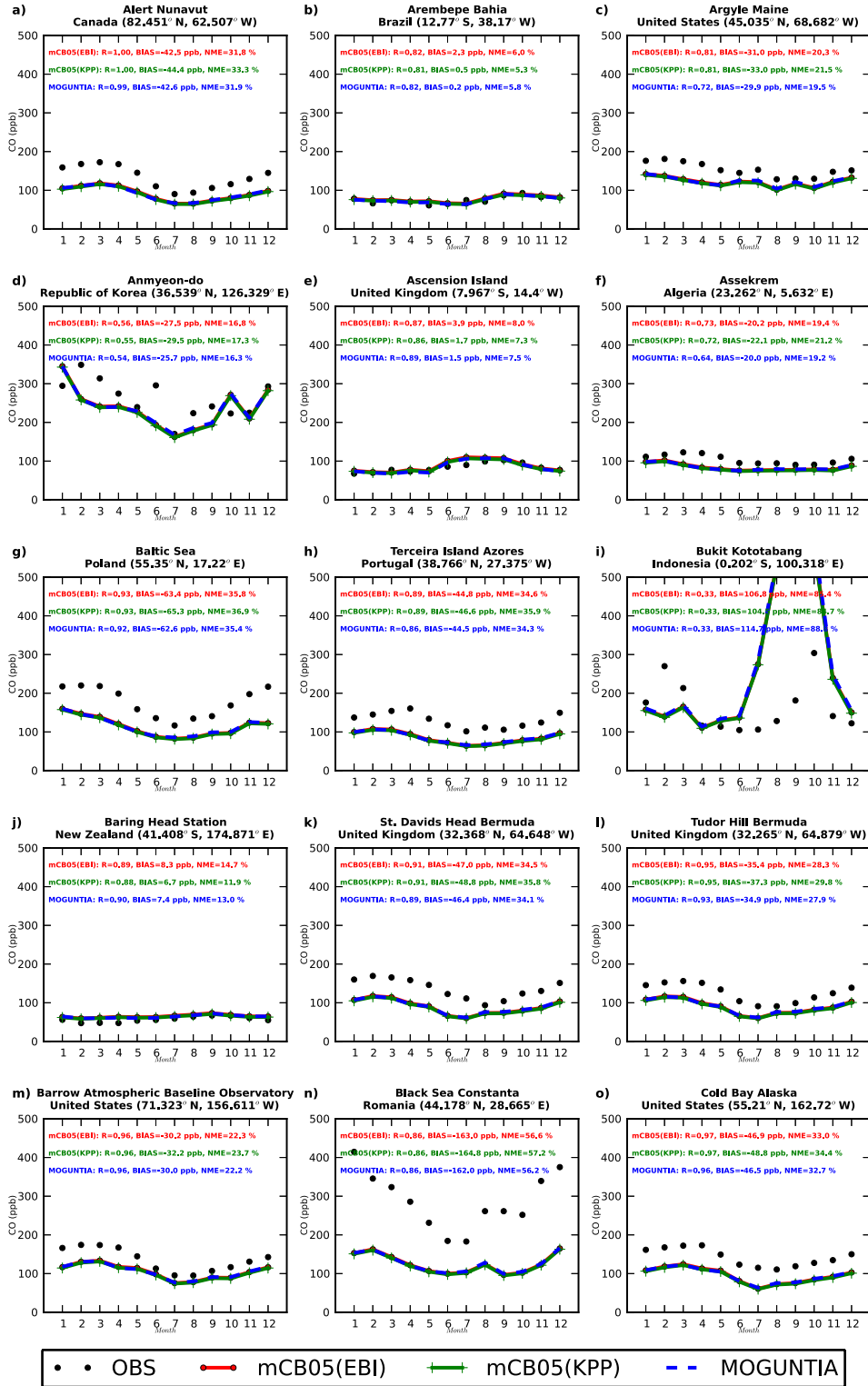
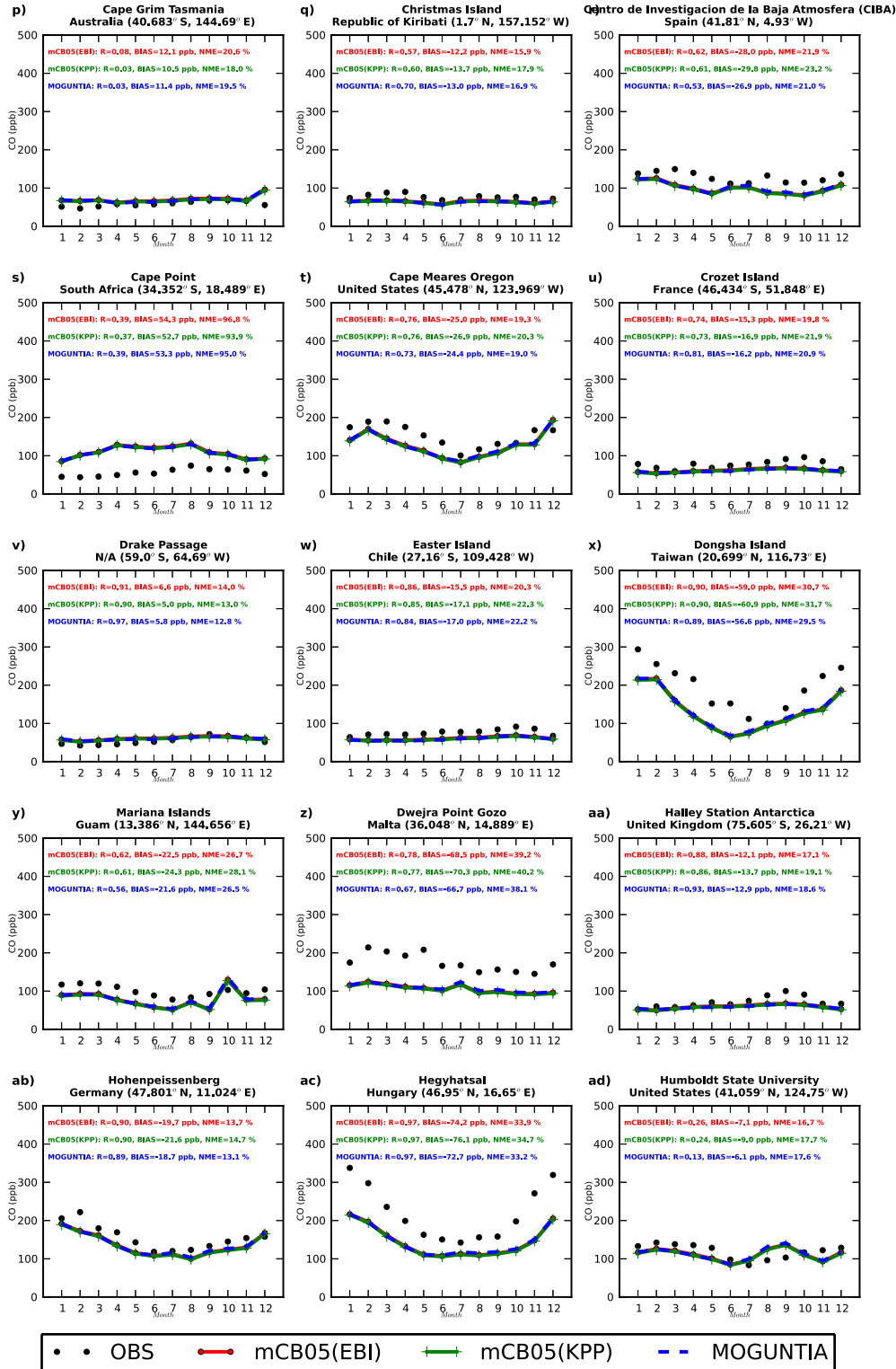


Figure S4: Comparison of monthly mean ozone sonde observations (black line) in ppb with model results (red-line for mCB05 configuration using the EBI solver, green-line for mCB05 configuration using the solver as generated by the KPP software and blue-line for MOGUNTIA configuration) at various stations around the globe, as obtained from the World Data Centre for Greenhouse Gases (WDCGG; <https://gaw.kishou.go.jp>), for the year 2006.

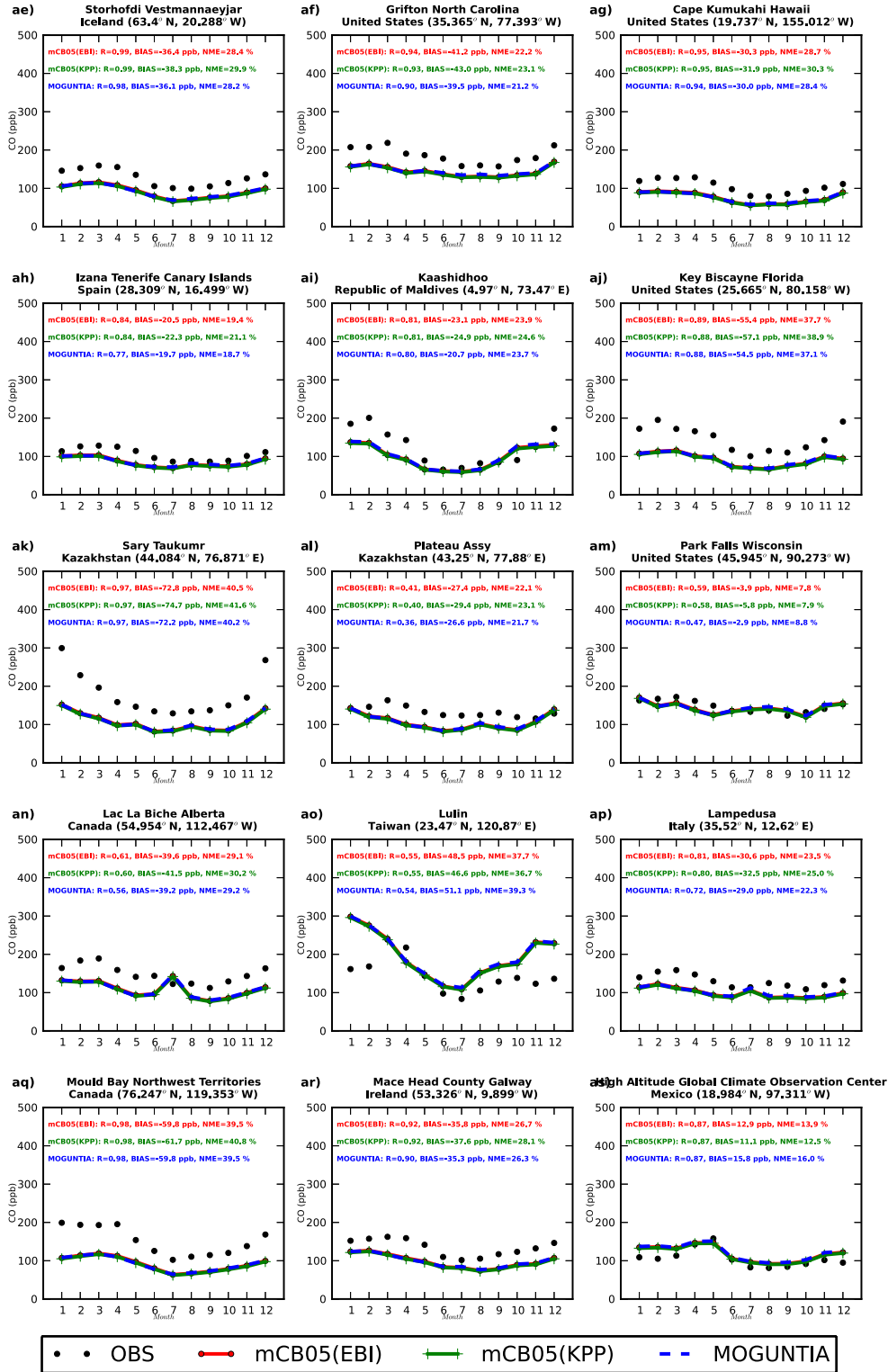


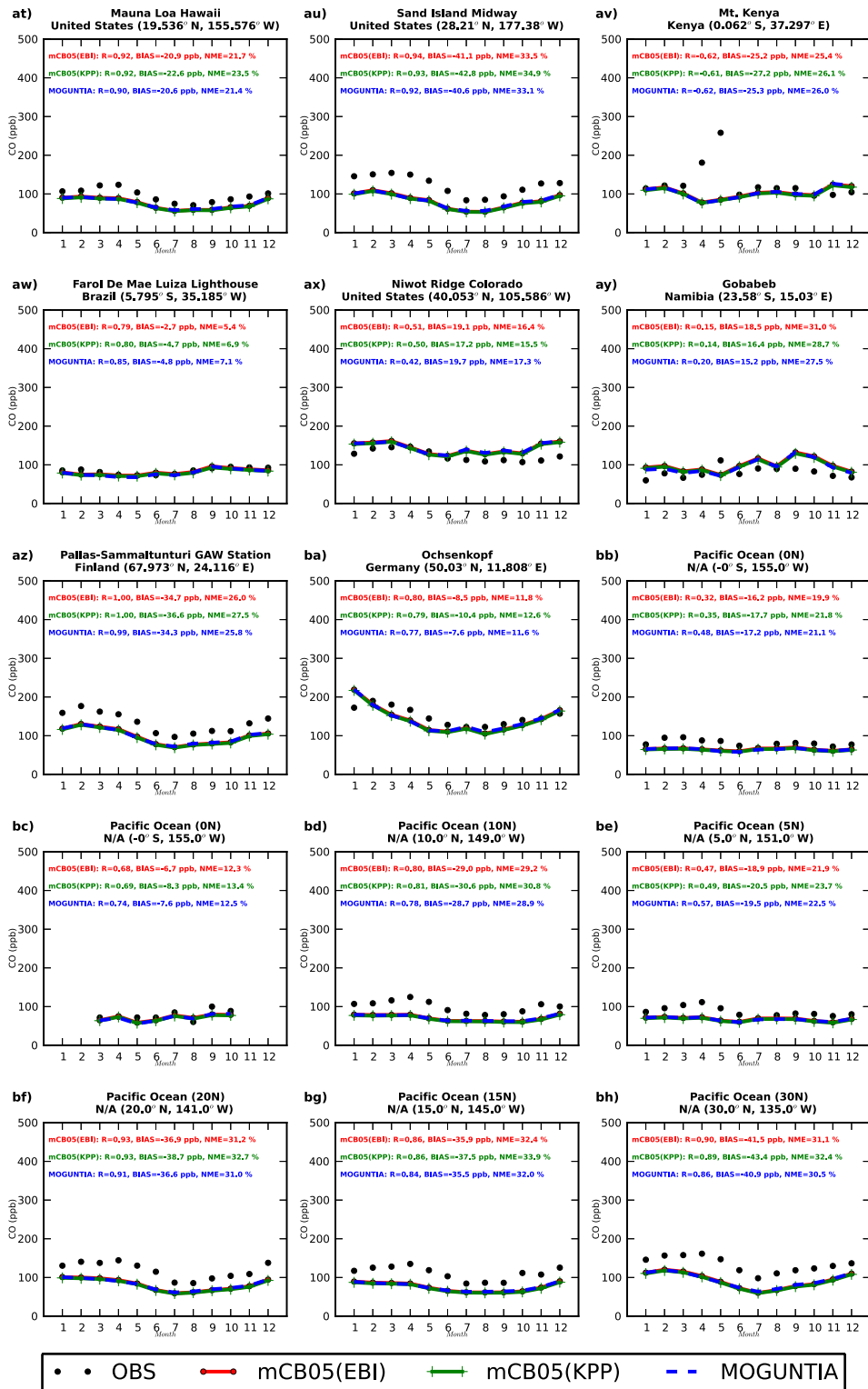
5 **Figure S5: Monthly mean comparisons of TM5-MP UTLS O<sub>3</sub> (top) and CO (bottom) mixing ratios (ppb) for the two chemistry schemes; mCB05(KPP) (blue line) and MOGUNTIA (red line), sampled at the measurement place and time against MOZAIC flight data (black line) between Frankfurt (50.0° N, 8.6° E) and Windhoek (22.5° S, 17.7° E) for April (left column) and October 2006 (right column). Data at pressures (P) lower than 300 hPa has been filtered out.**

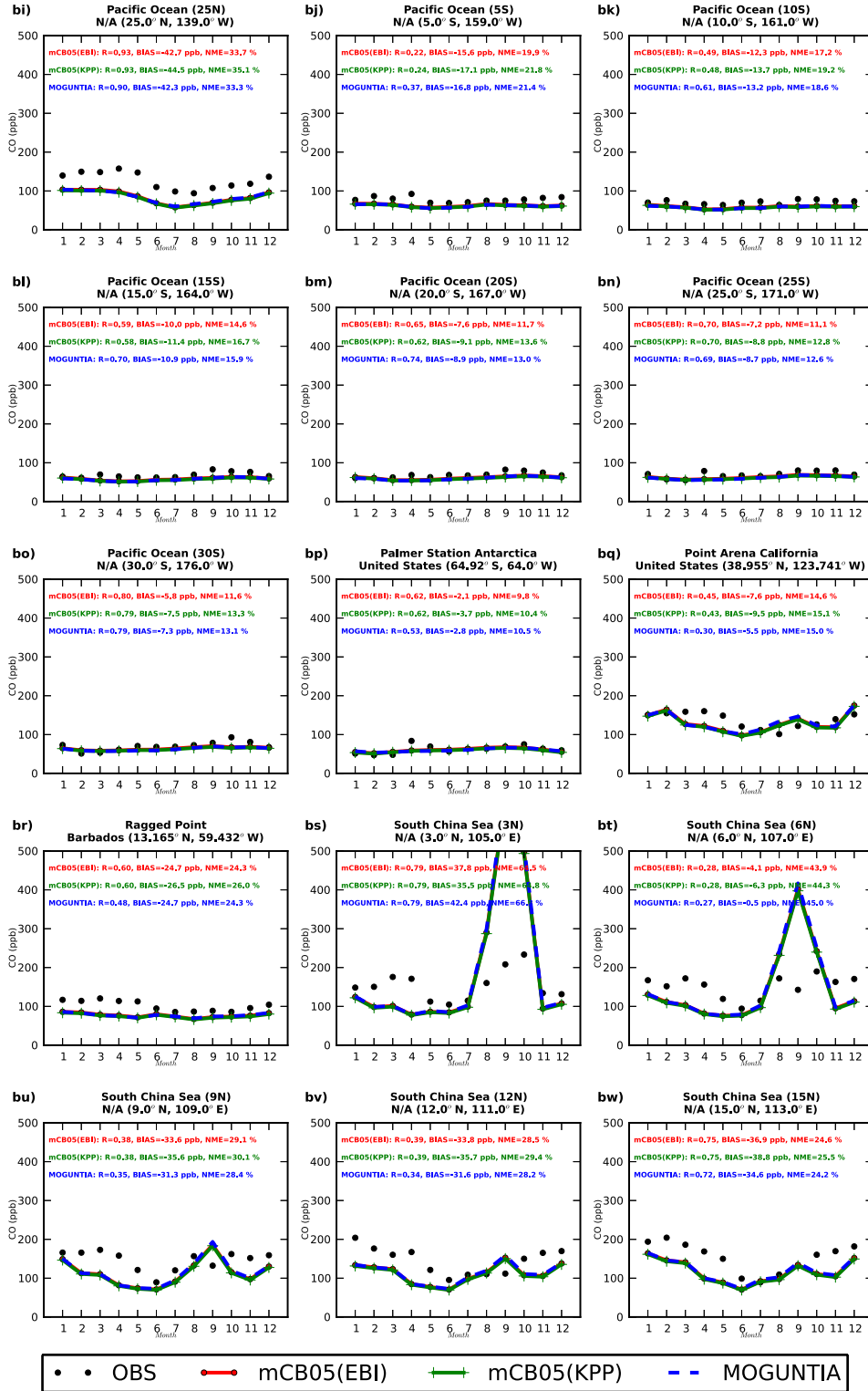


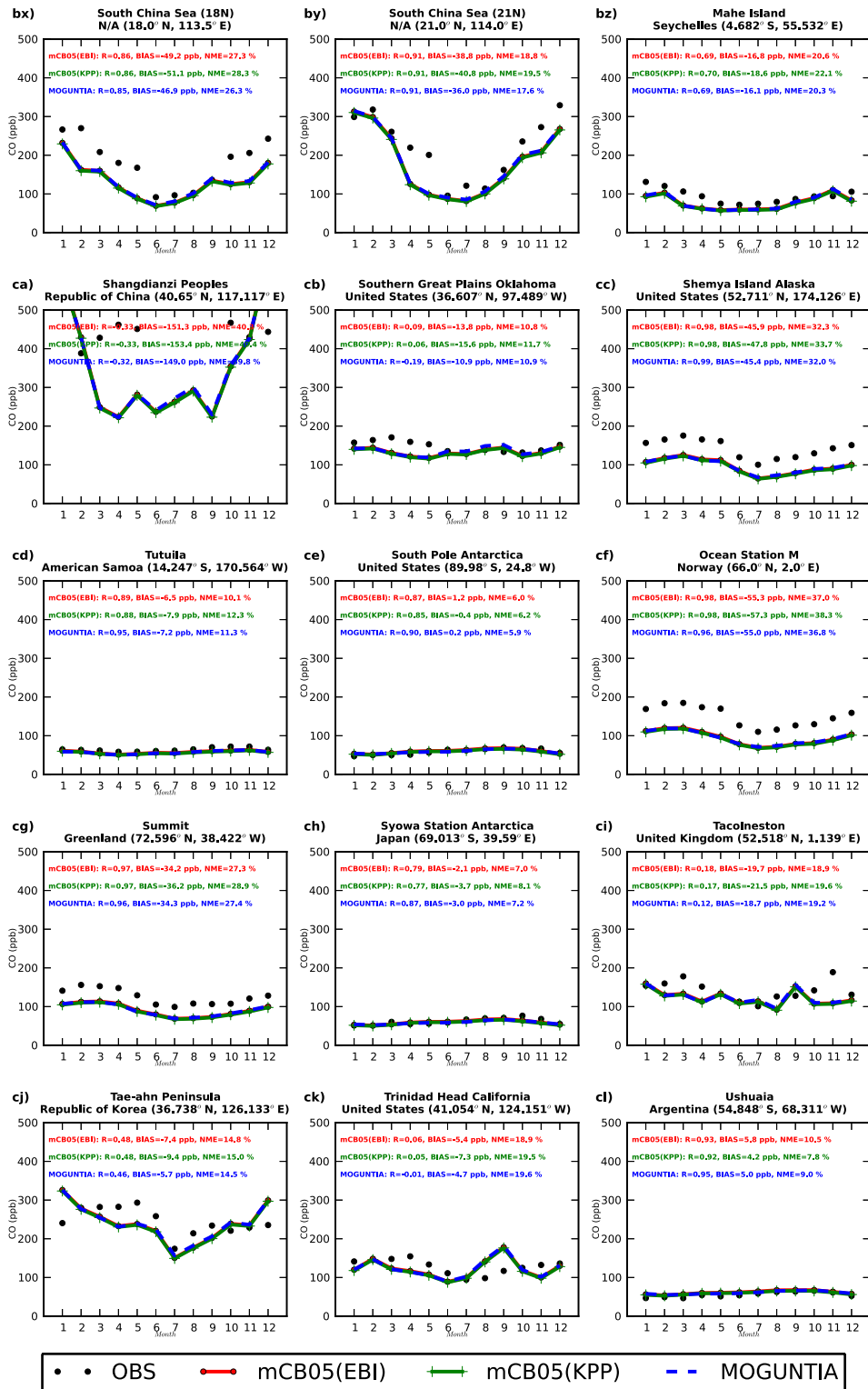












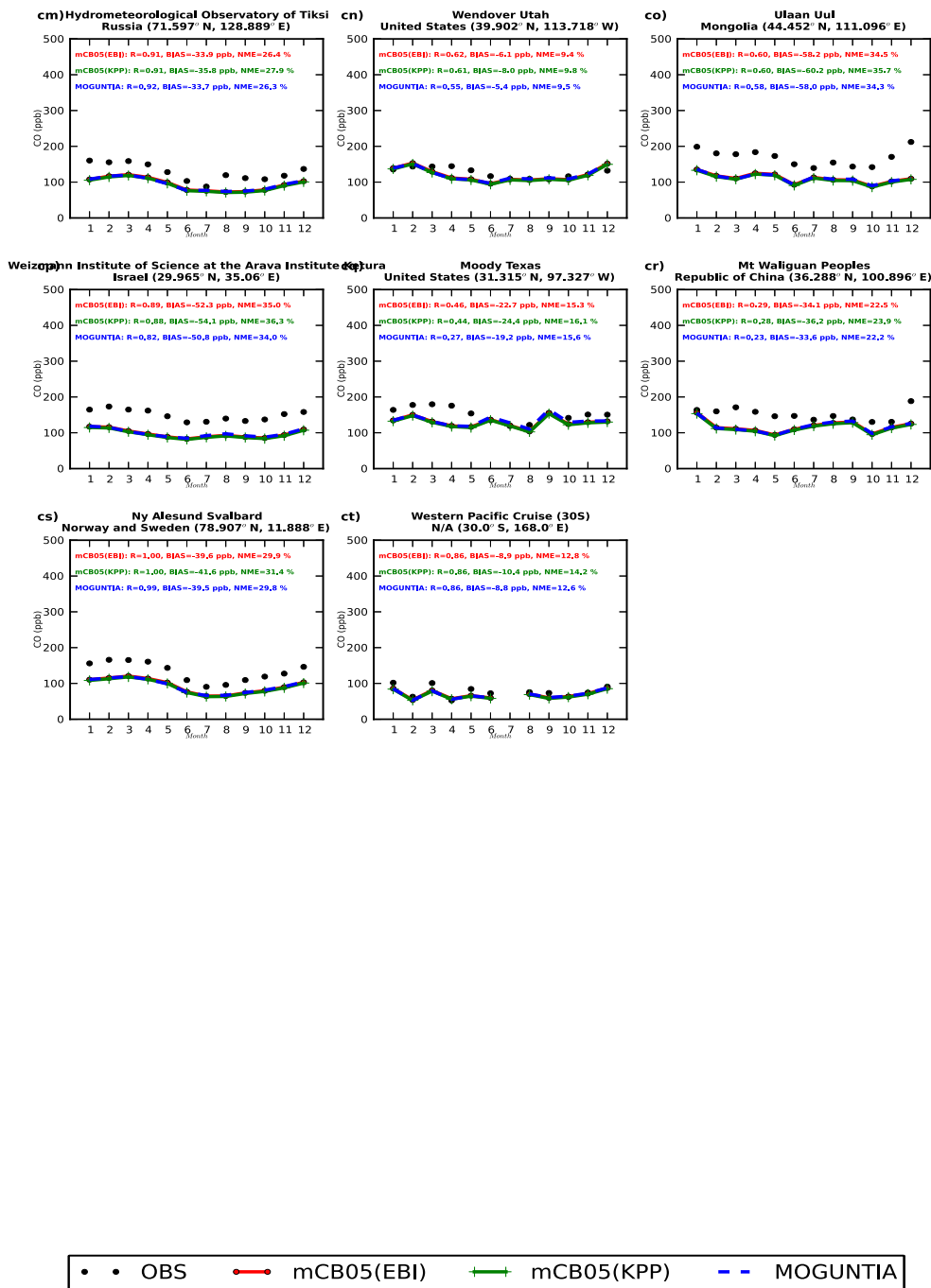


Figure S6: Comparison of monthly mean surface CO flask measurements (black dots) in ppb with model results (red-line for mCB05(EBI), green-line for mCB05(KPP) and blue-line for MOGUNTIA) at various stations around the globe, as obtained from NOAA database, for the year 2006.

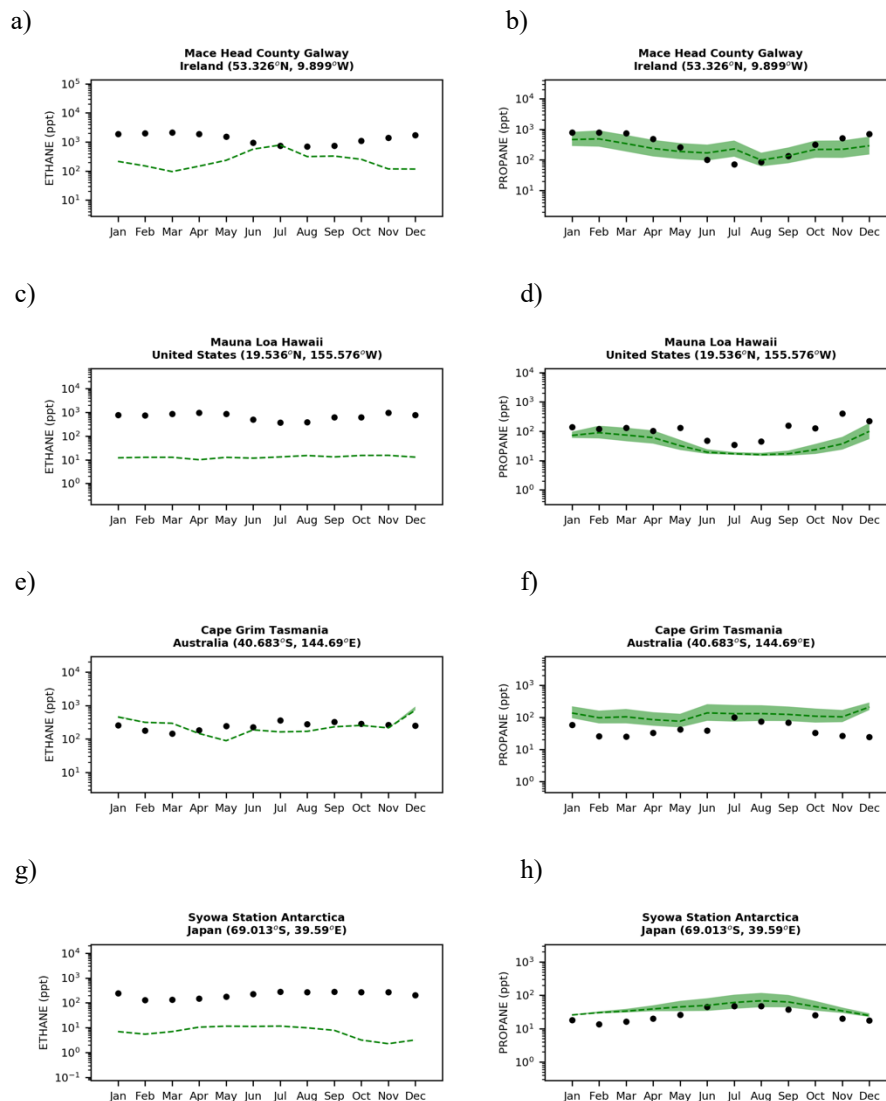
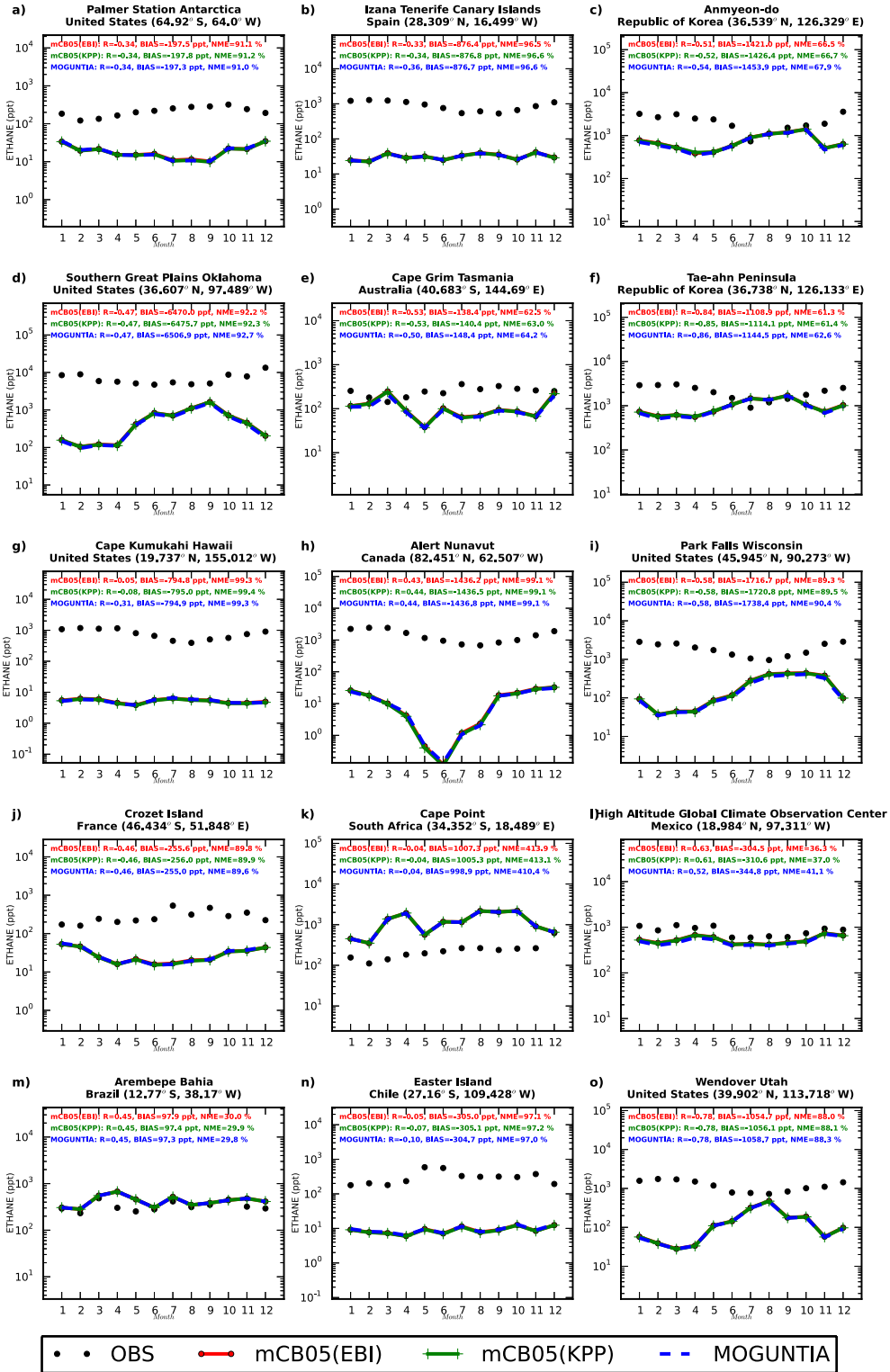
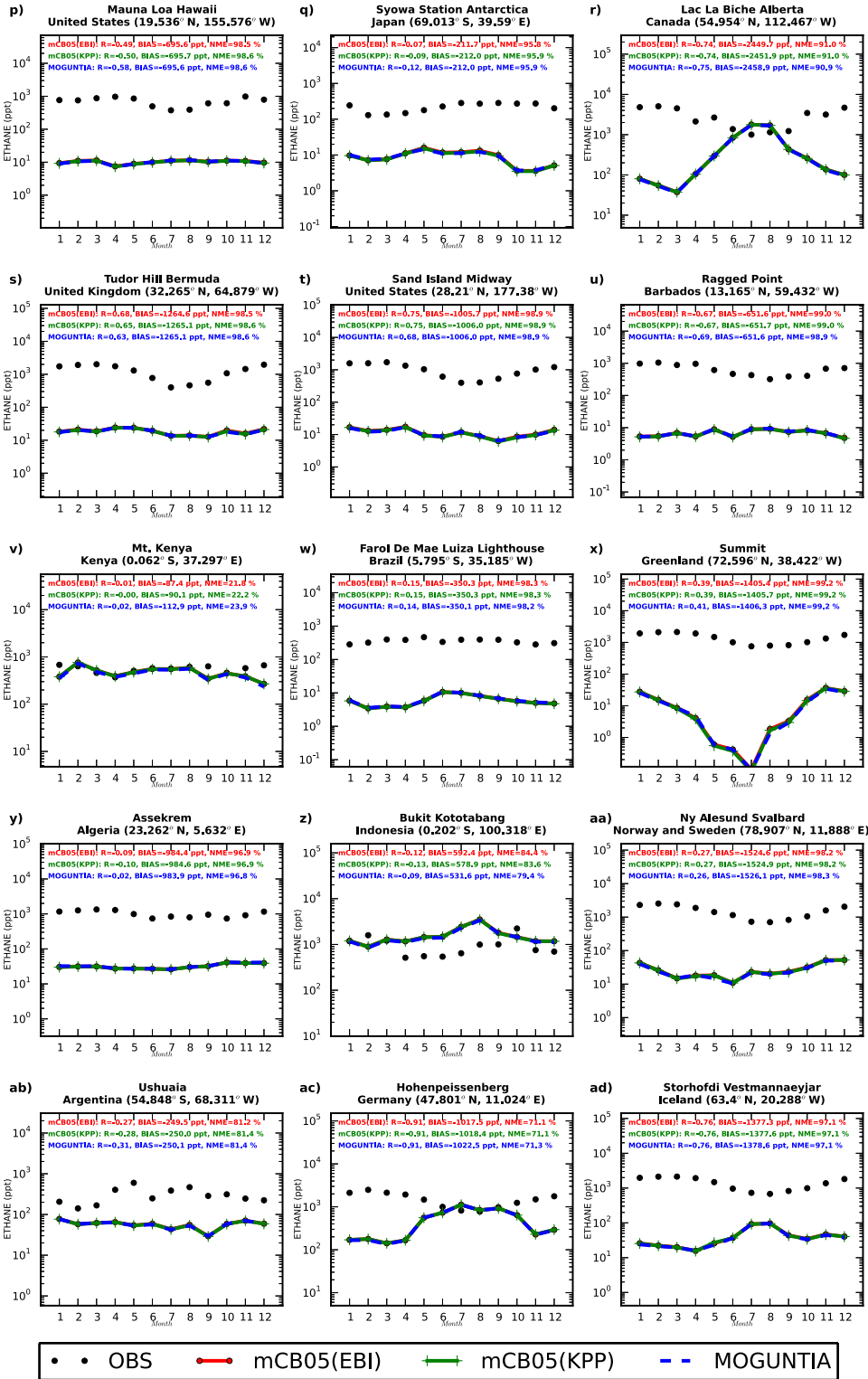
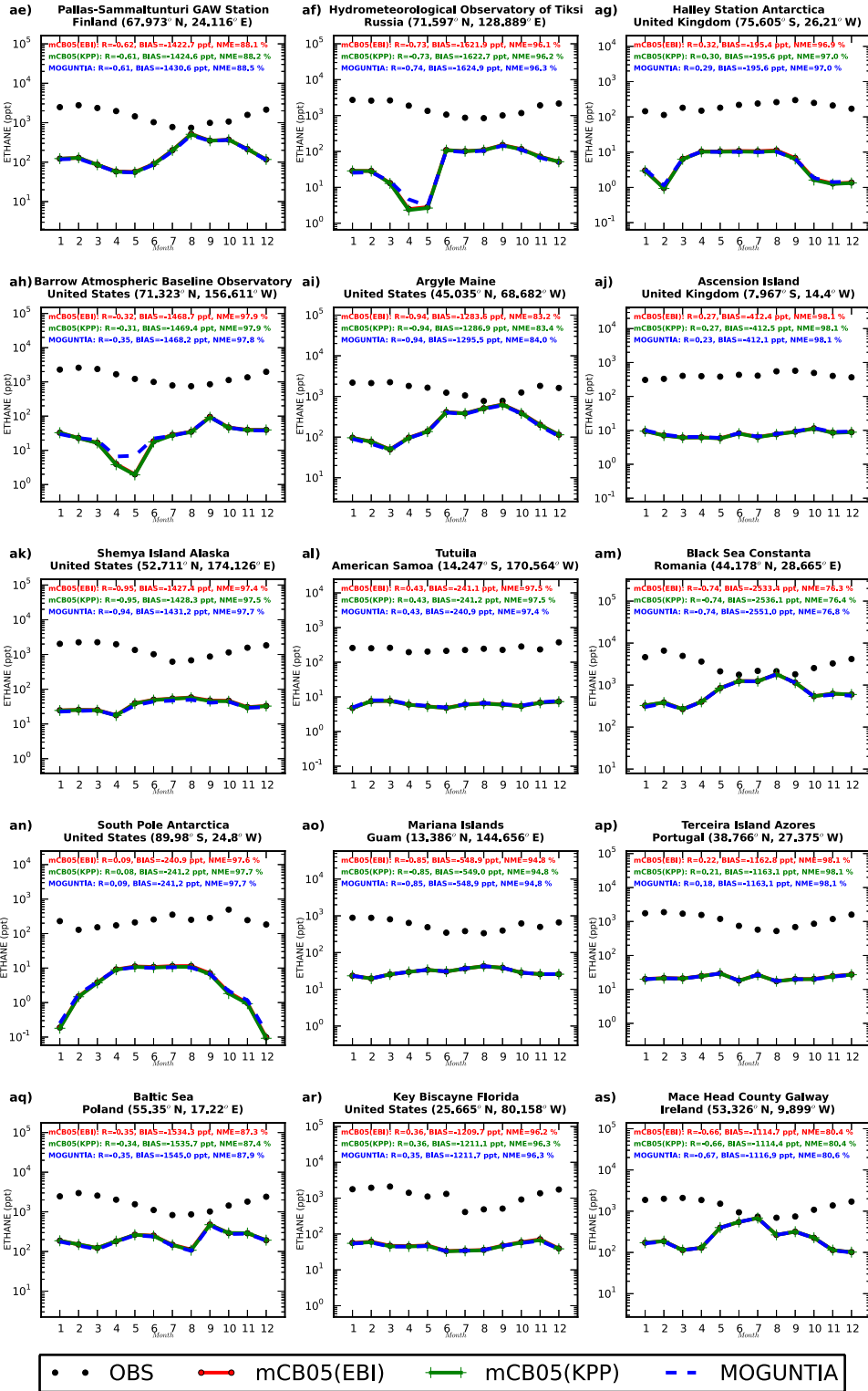


Figure S7: Monthly mean comparison of TM5-MP surface  $C_2H_6$  (left column) and  $C_3H_8$  (right column) using the base case emission scenario, doubling (2x) of the anthropogenic fossil fuel emissions, and quadrupling (4x) of the anthropogenic fossil fuel emissions of  $C_2H_6$  and  $C_3H_8$ , against flask measurements (black dots) in ppt for the MOGUNTIA chemistry scheme (green line), using co-located model output for 2006 sampled at the measurement times. Shaded areas indicate the range of model results due to the different emission strengths. For this sensitivity analysis, the model runs in  $3^\circ \times 2^\circ$  horizontal resolution in longitude by latitude, and 34 hybrid levels in the vertical.









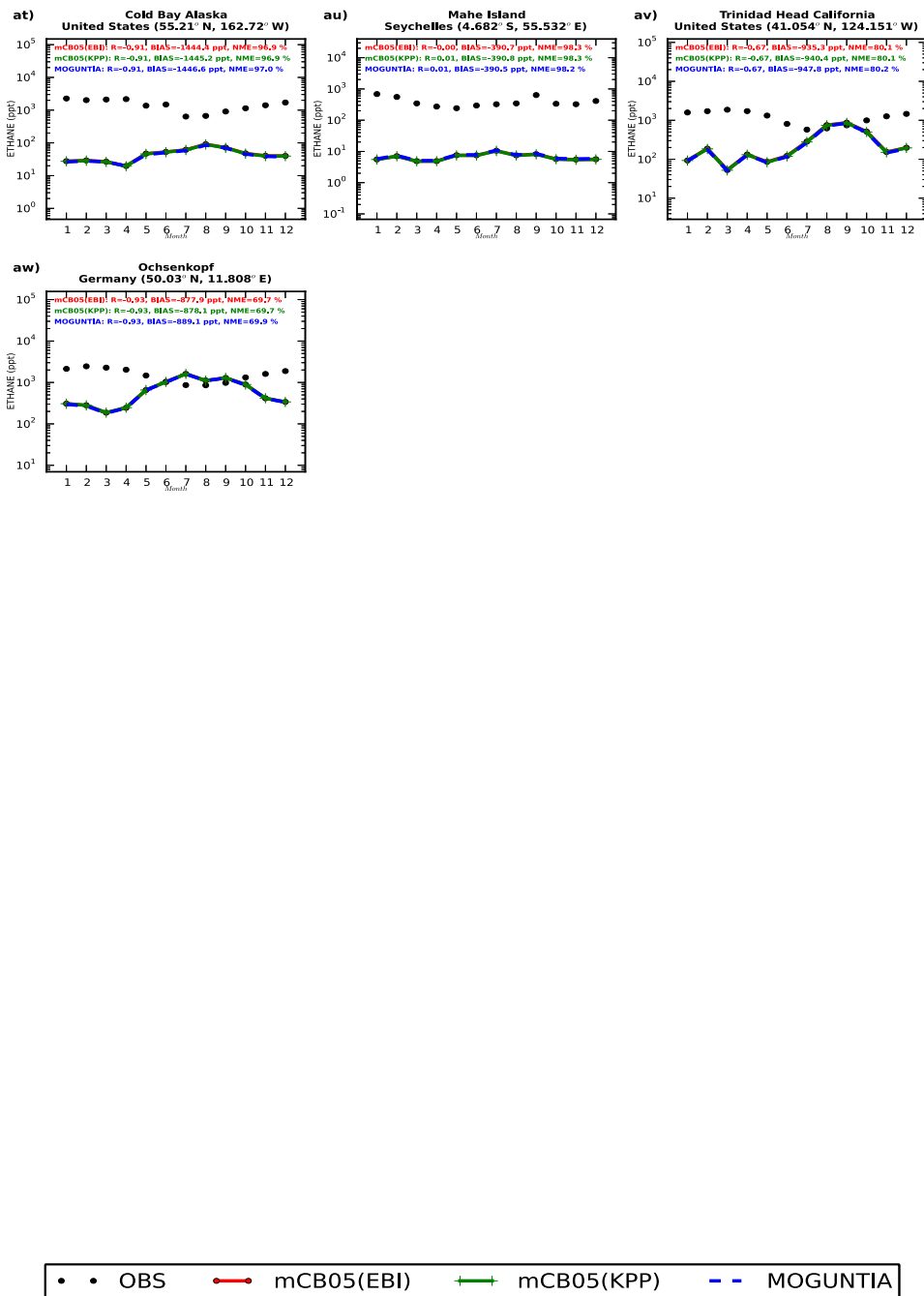
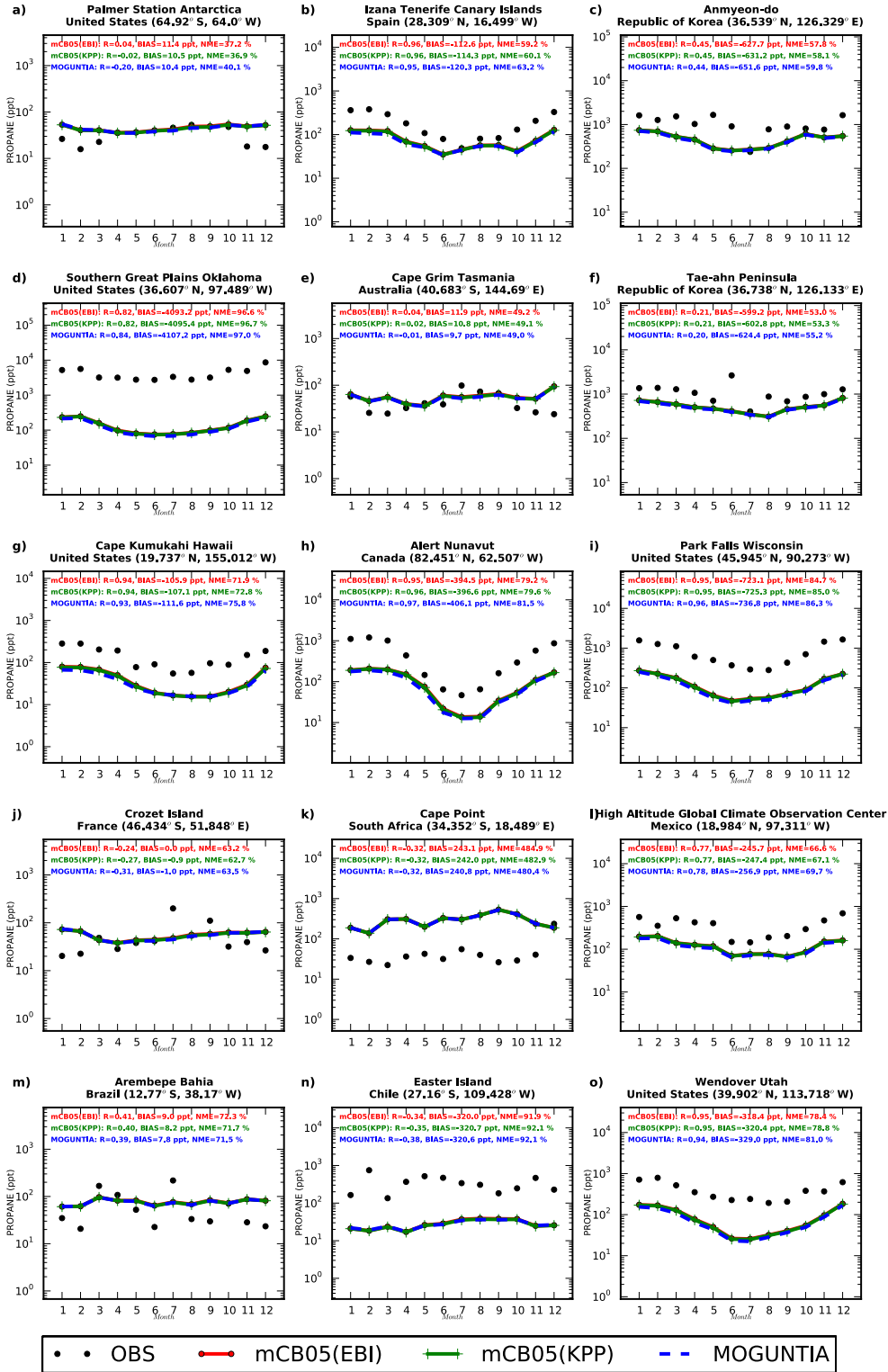
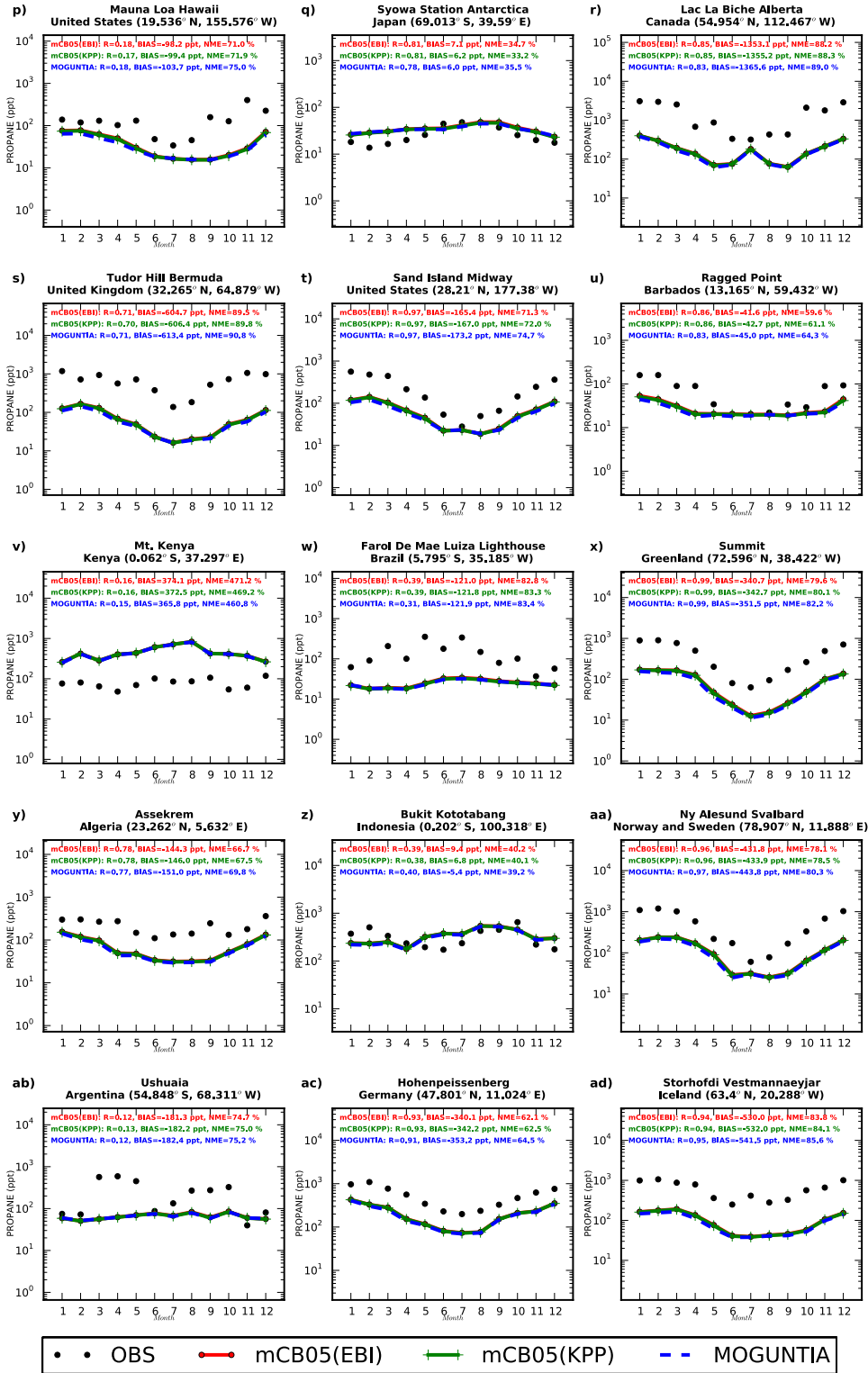
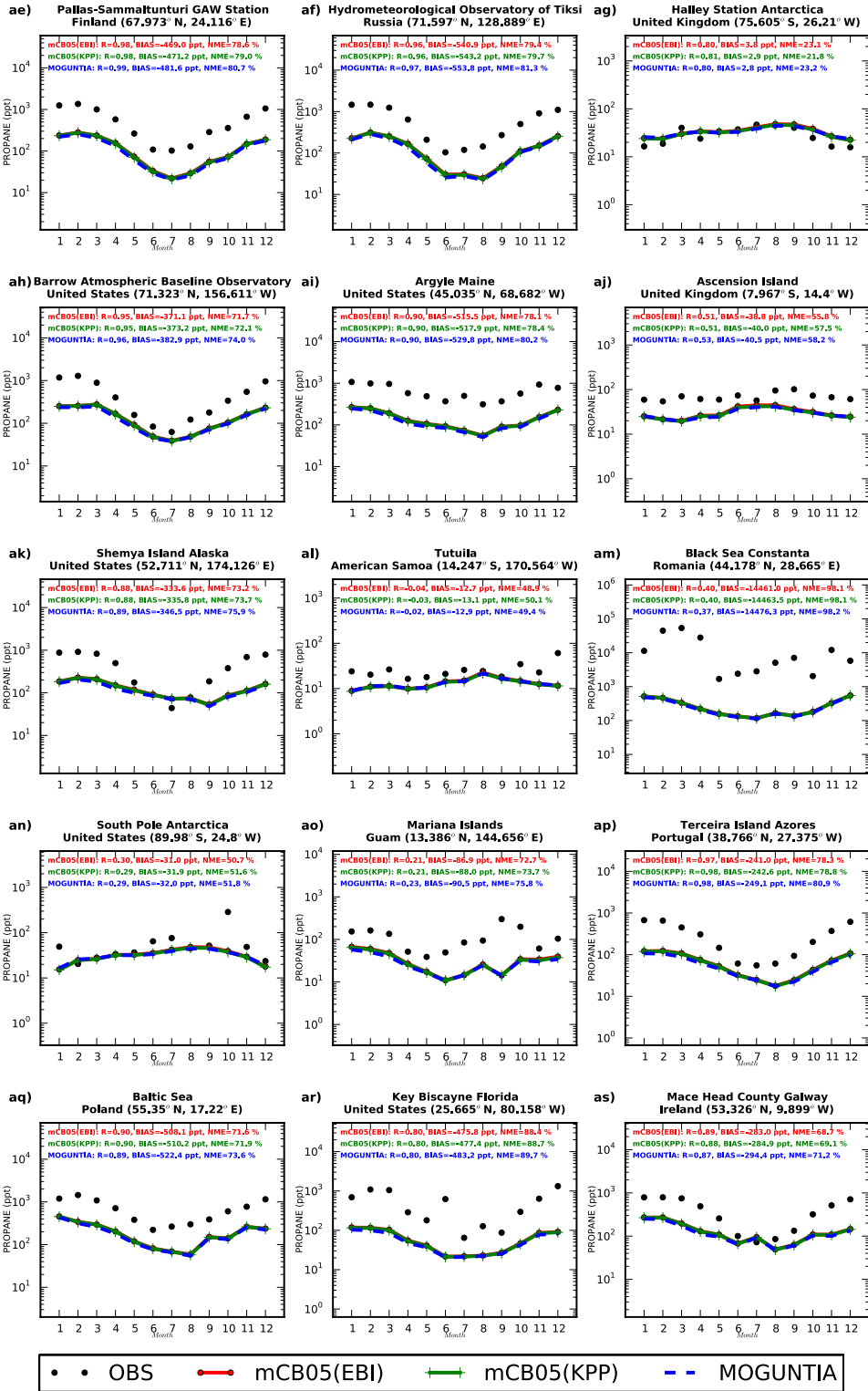


Figure S8: Comparison of monthly mean surface  $C_2H_6$  flask measurements (black dots) in ppt with model results (red-line for mCB05(EBI), green-line for mCB05(KPP) and blue-line for MOGUNTIA) at various stations around the globe, as obtained from NOAA database, for the year 2006.







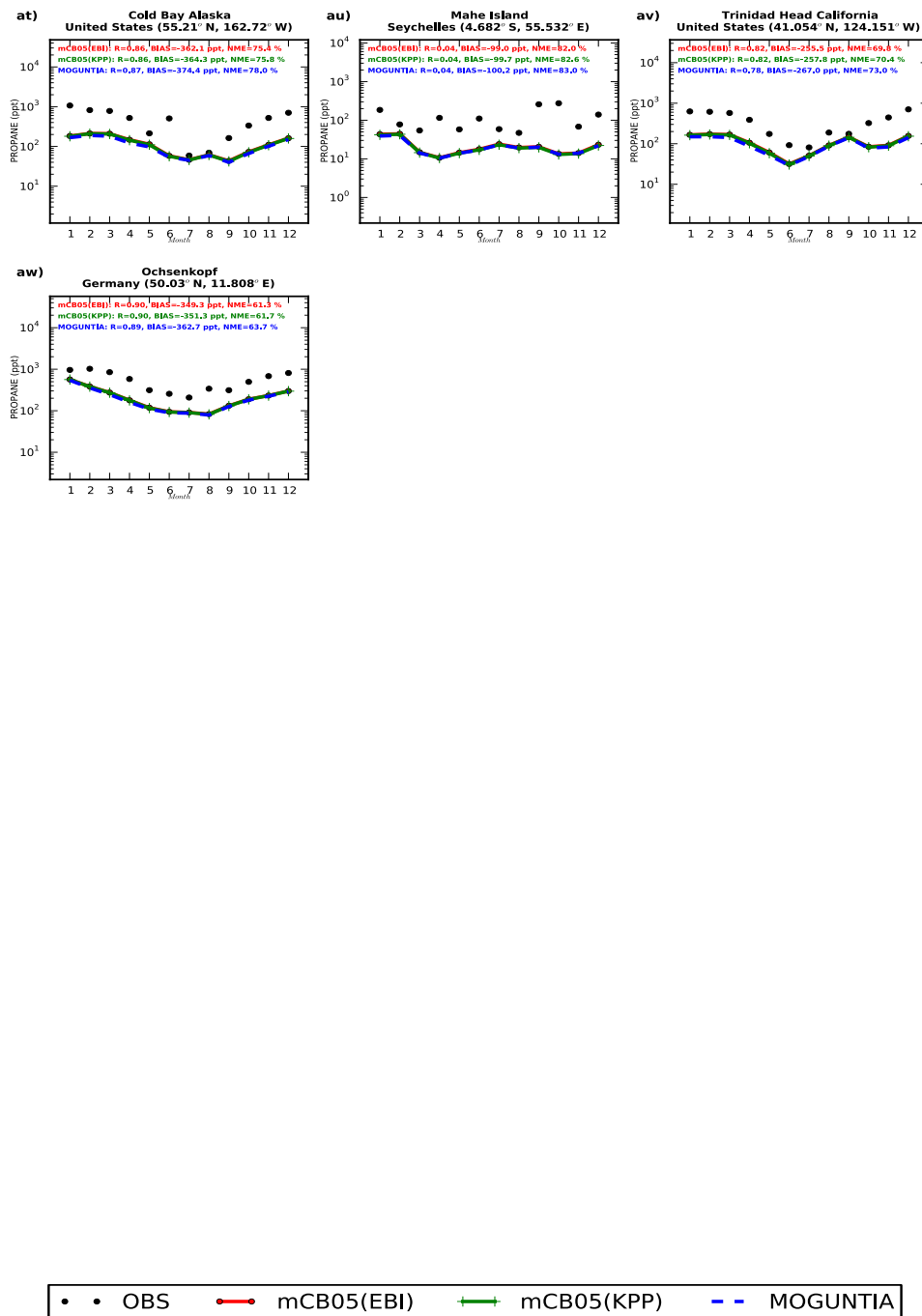
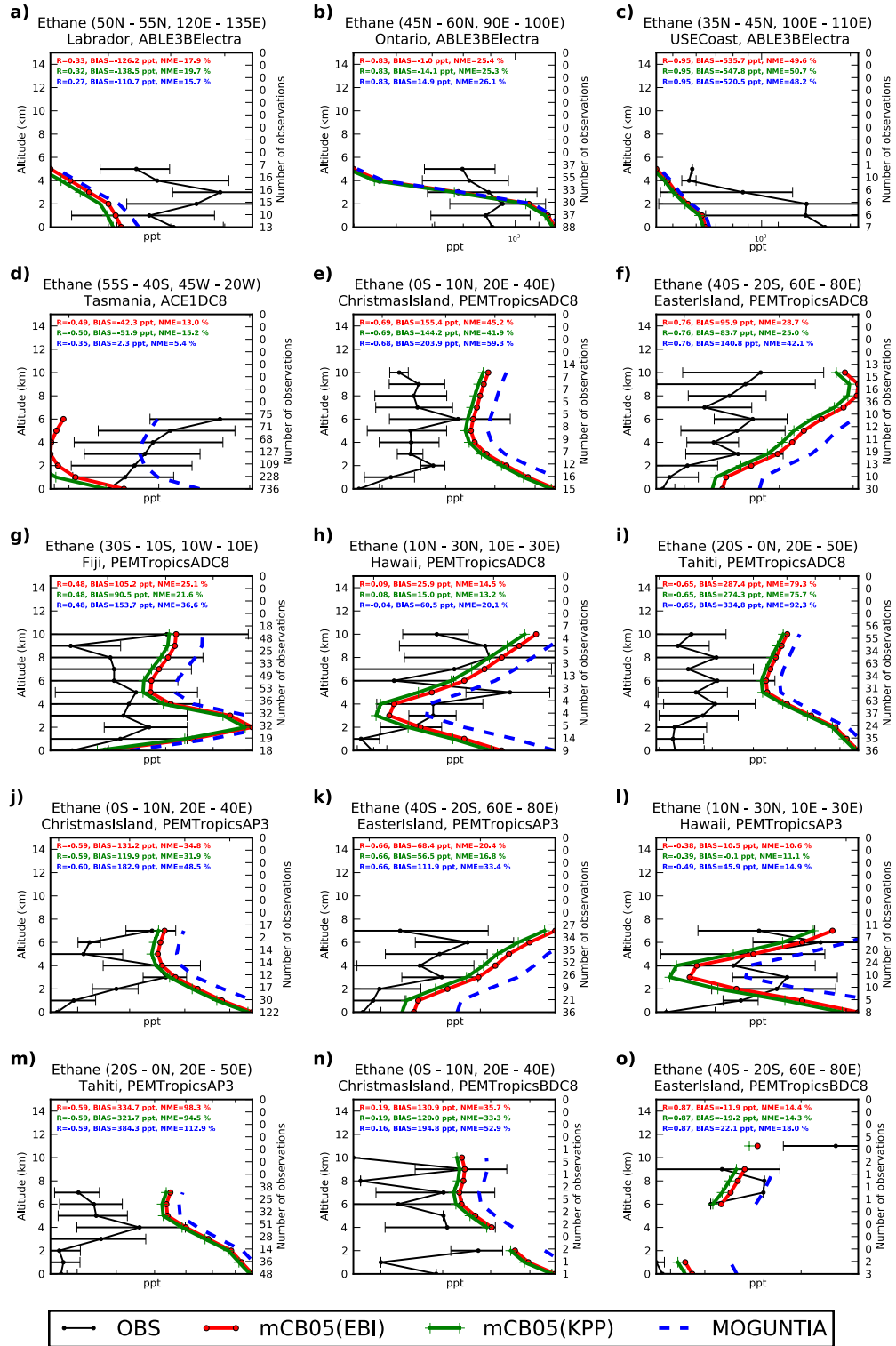
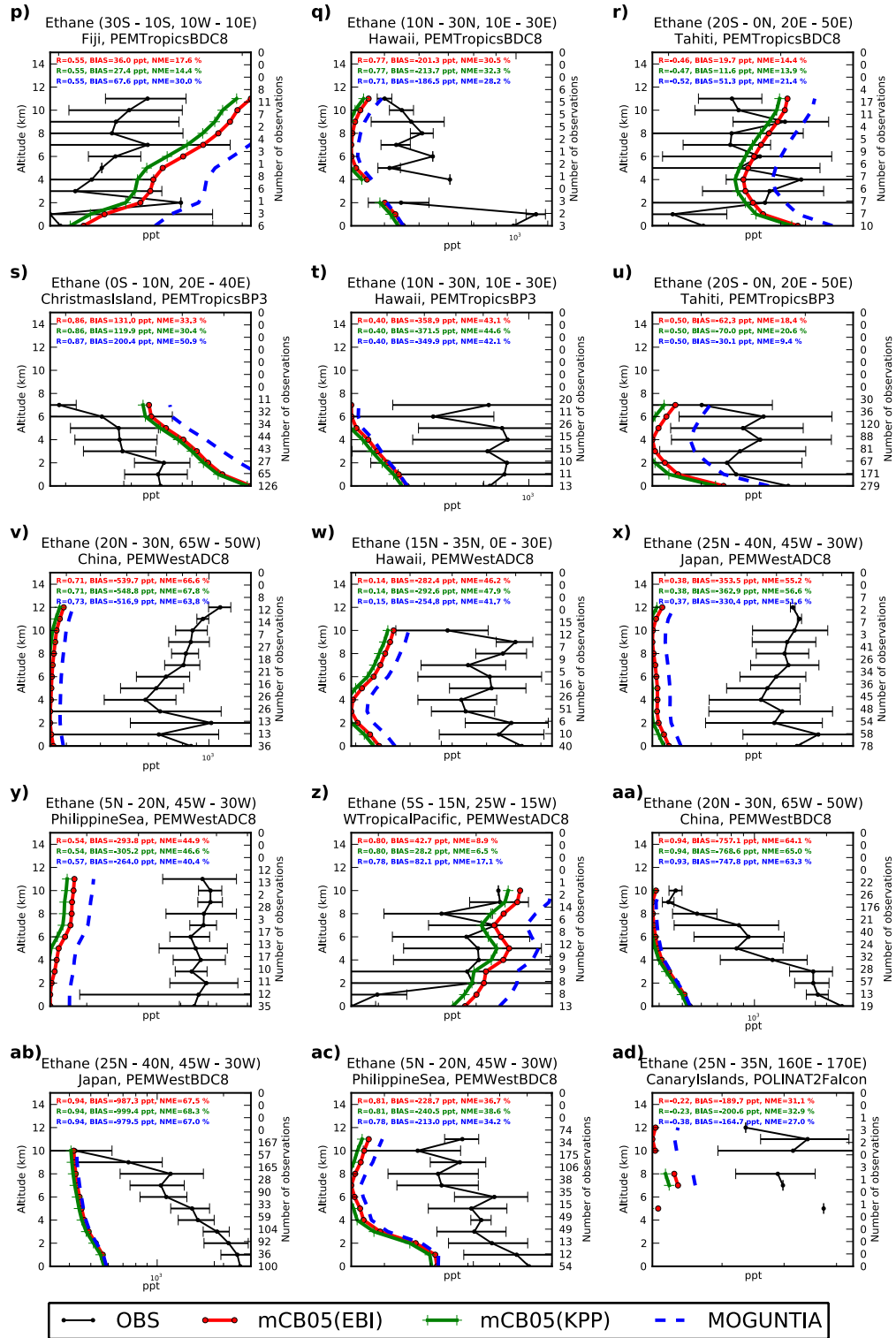
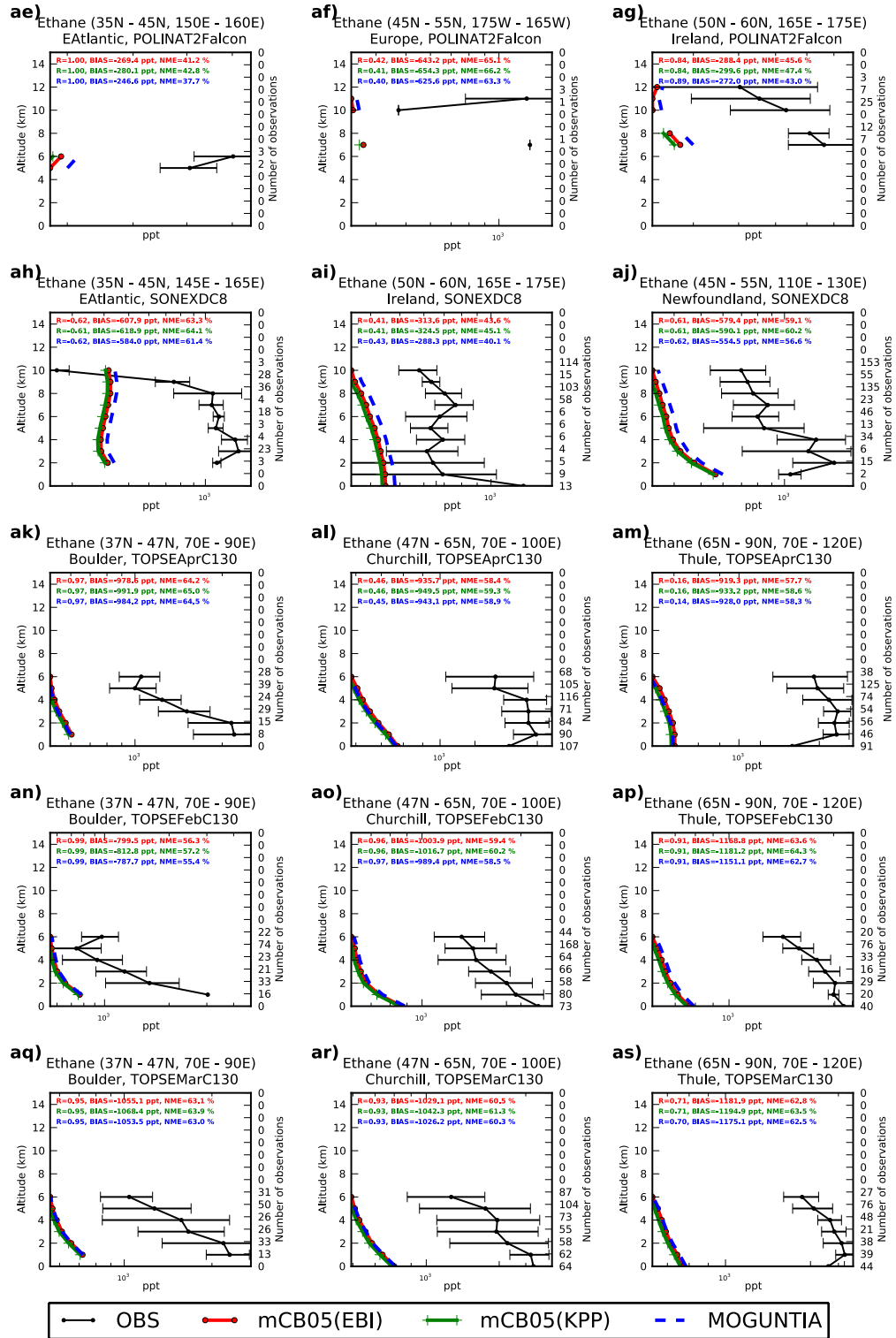


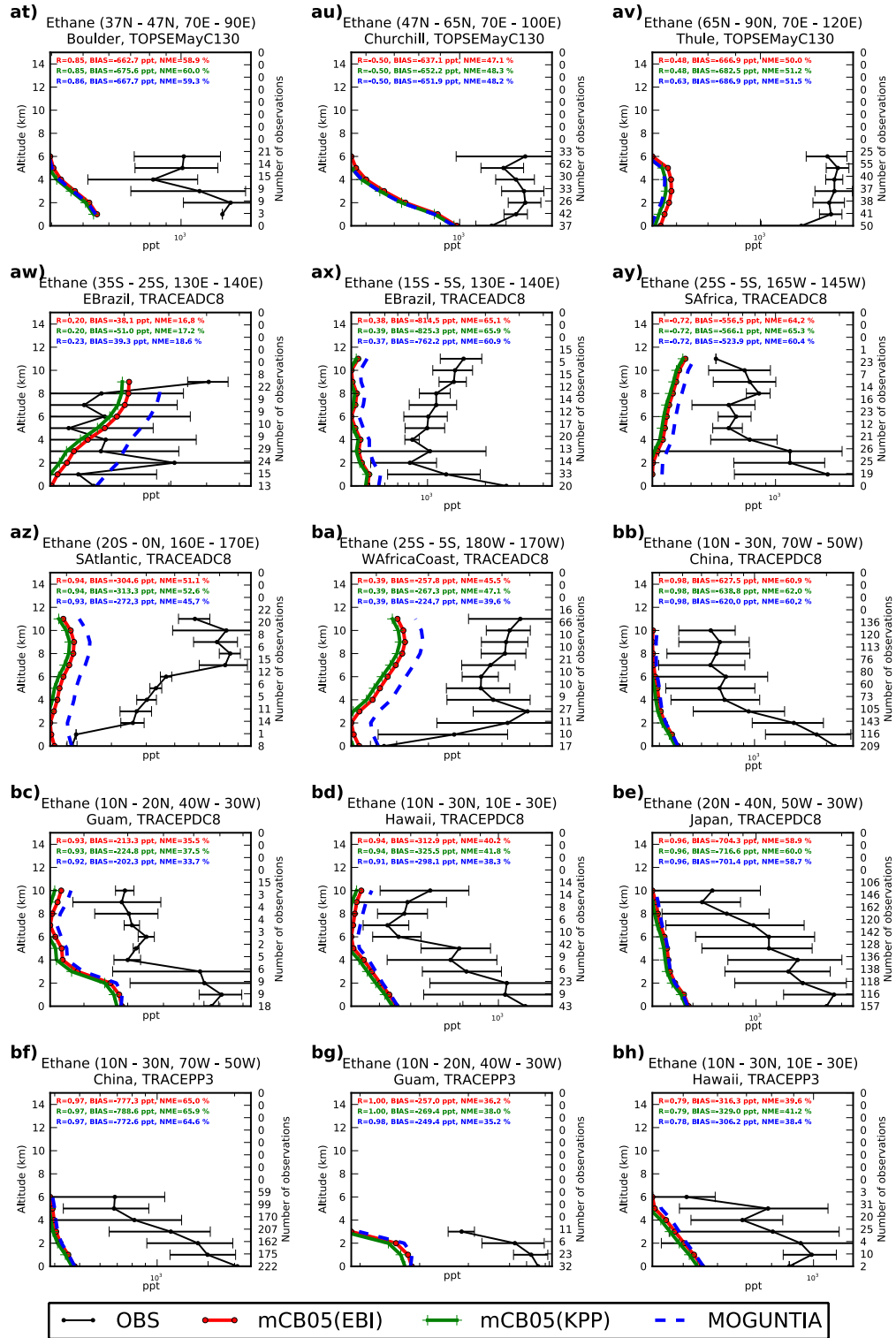
Figure S9: Comparison of monthly mean surface propane flask measurements (black dots) in ppb with model results (red-line for mCB05(EBI), green-line for mCB05(KPP) and blue-line for MOGUNTIA) at various stations around the globe, as obtained from NOAA database, for the year 2006.











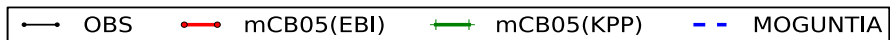
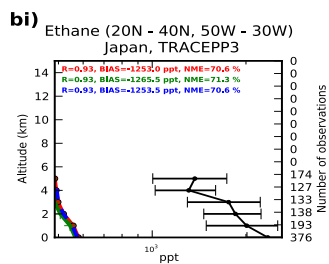
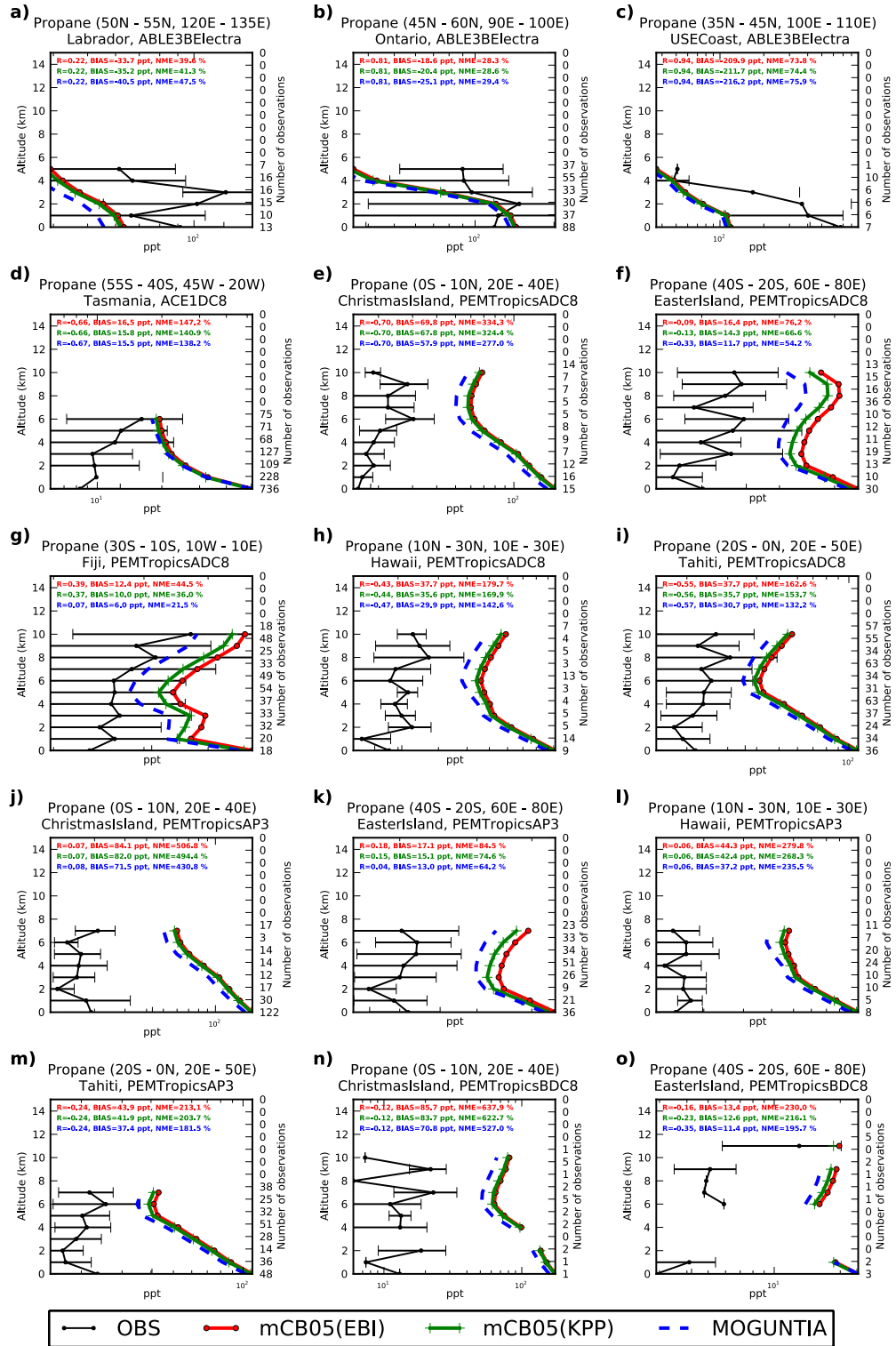
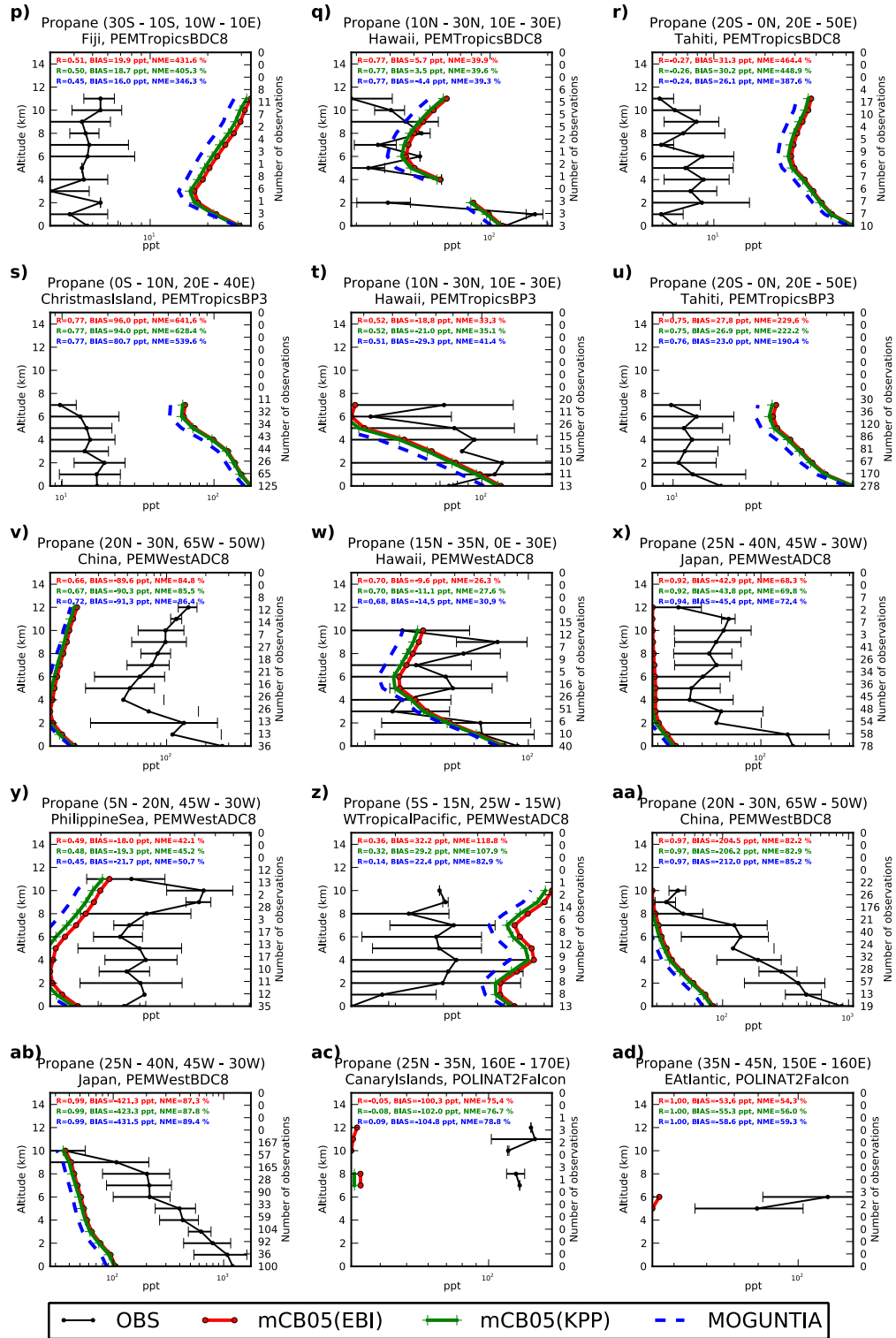
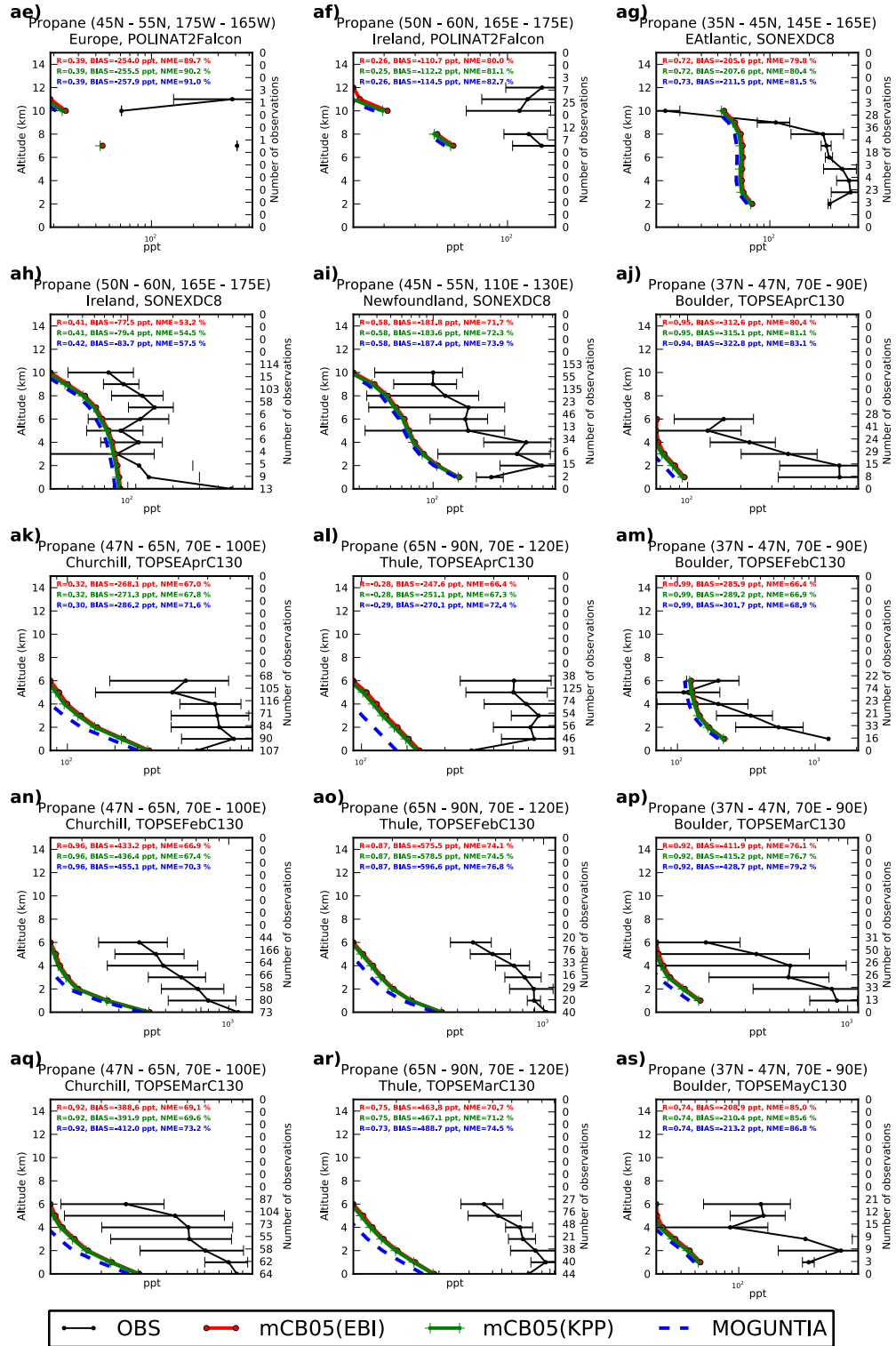
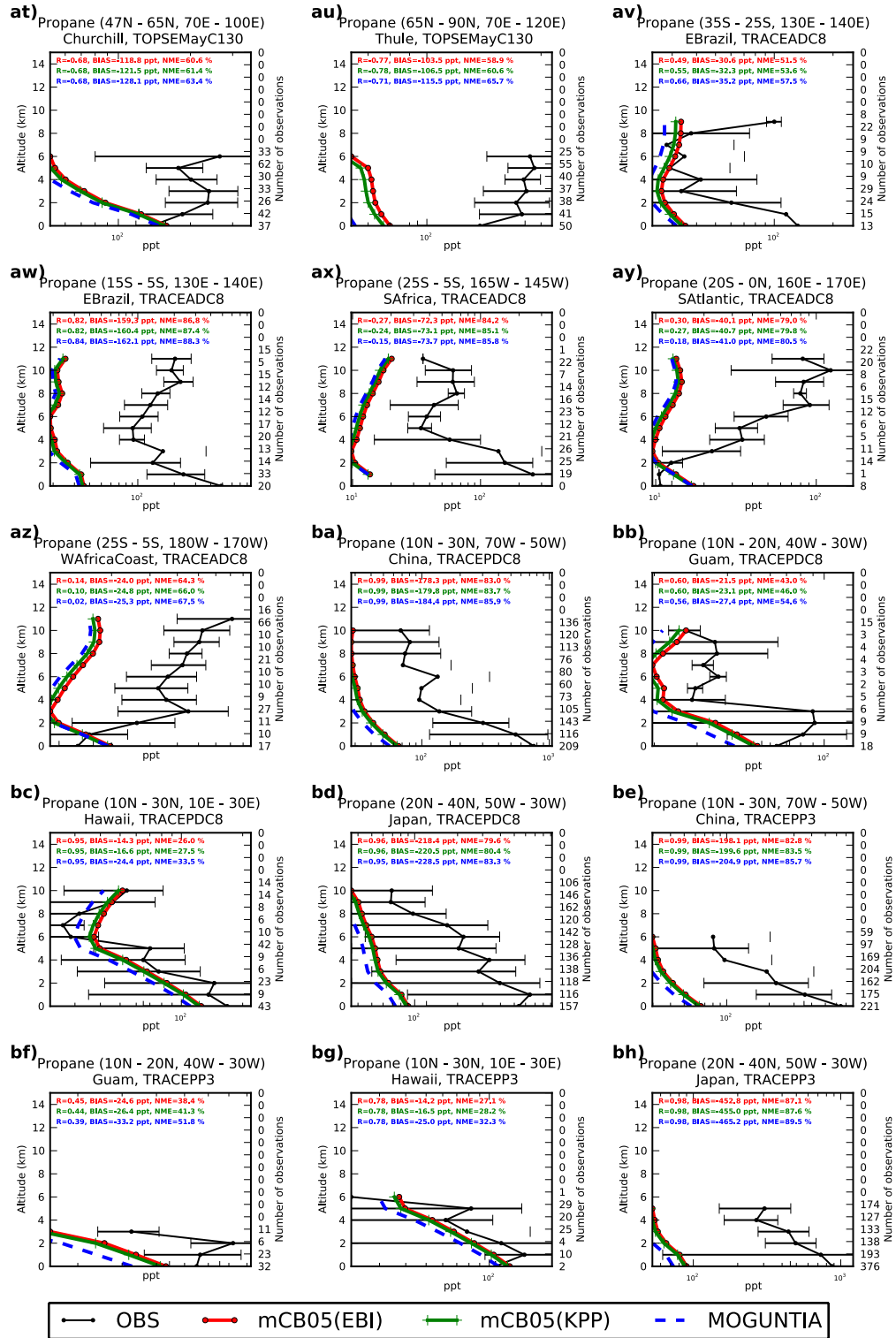


Figure S10: Comparison of TMS-MP vertical profiles (in km) of  $C_2H_6$  against aircraft observations (black line) in ppt with model results (red-line for mCB05(EBI), green-line for mCB05(KPP) and blue-line for MOGUNTIA), using co-located model output for 2006 sampled at the measurement times; error bars indicate the standard deviation. The numbers on the right vertical axis indicate the number of available measurements.









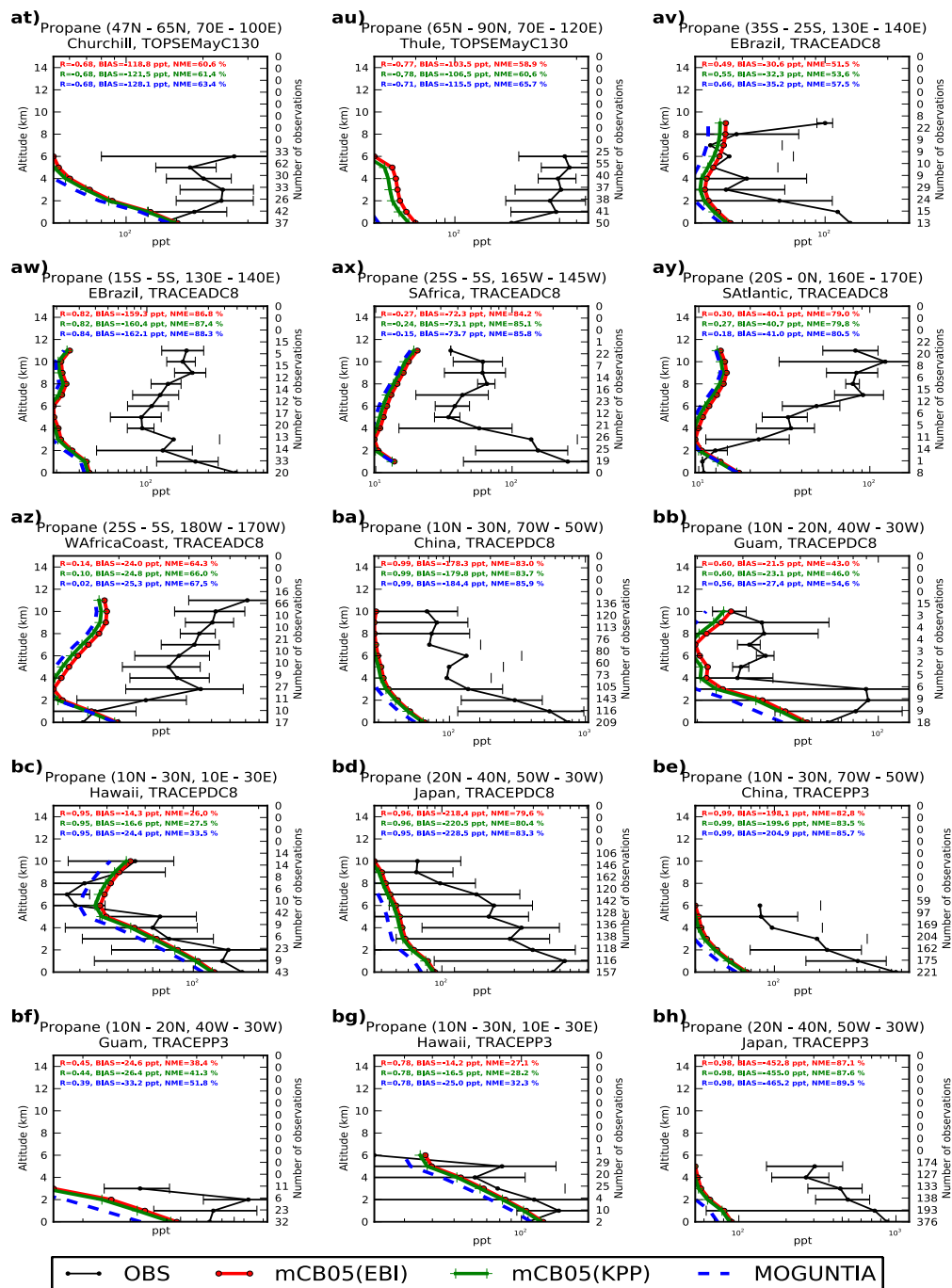
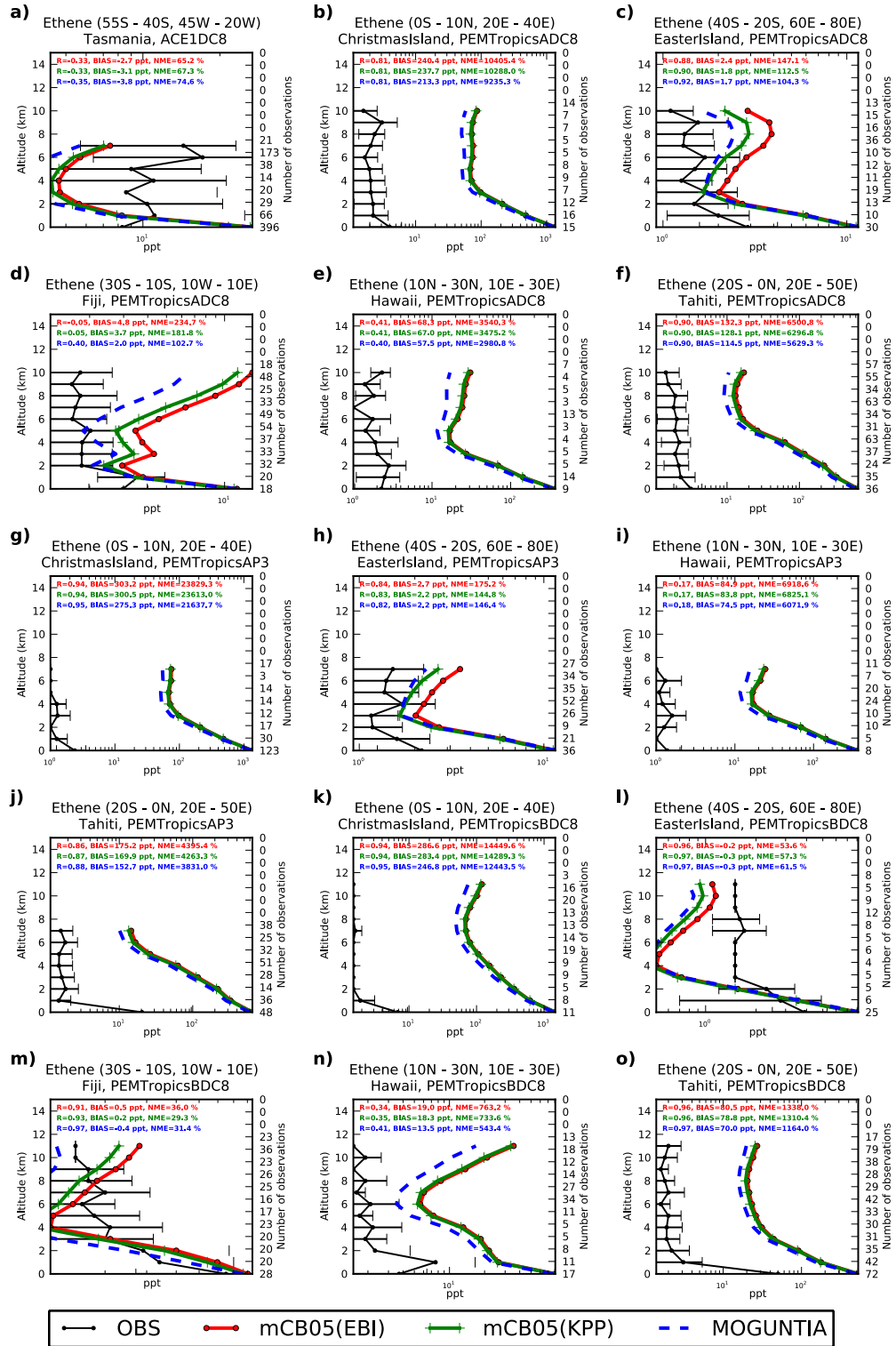
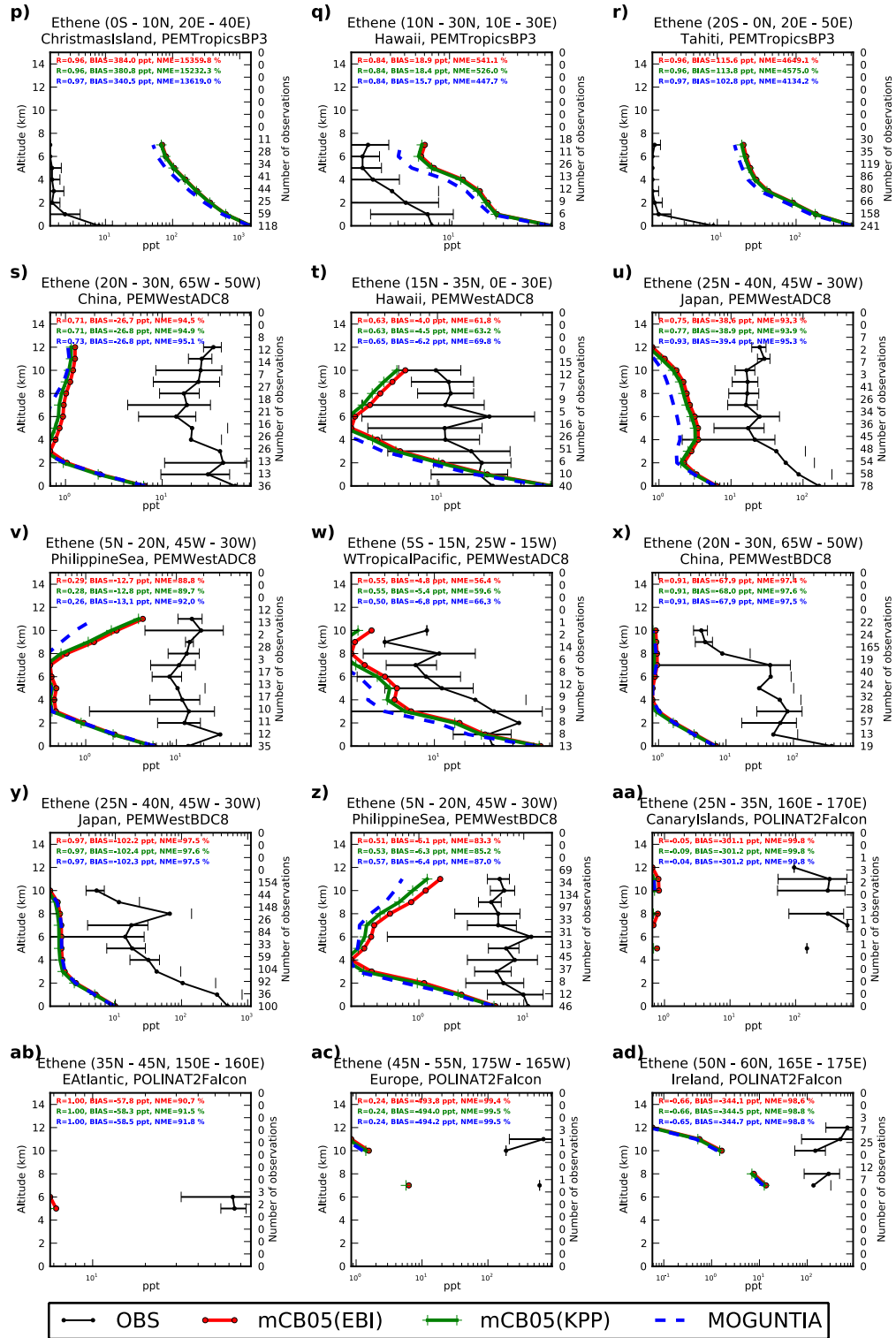
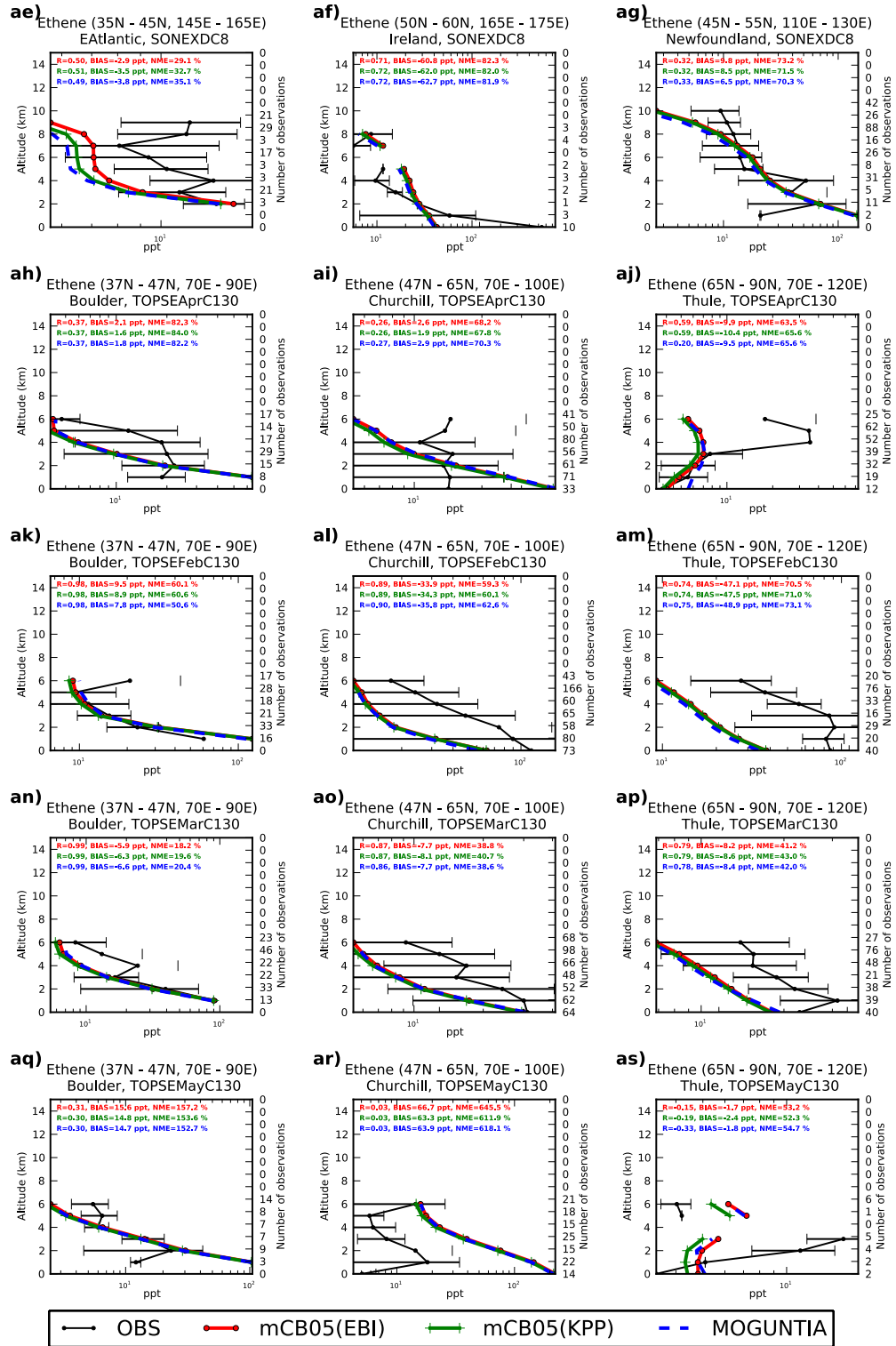


Figure S11: Comparison of TM5-MP vertical profiles (in km) of  $C_3H_8$  against aircraft observations (black line) in ppt, with model results (red-line for mCB05(EBI), green-line for mCB05(KPP) and blue-line for MOGUNTIA), using co-located model output for 2006 sampled at the measurement times; error bars indicate the standard deviation. The numbers on the right vertical axis indicate the number of available measurements.









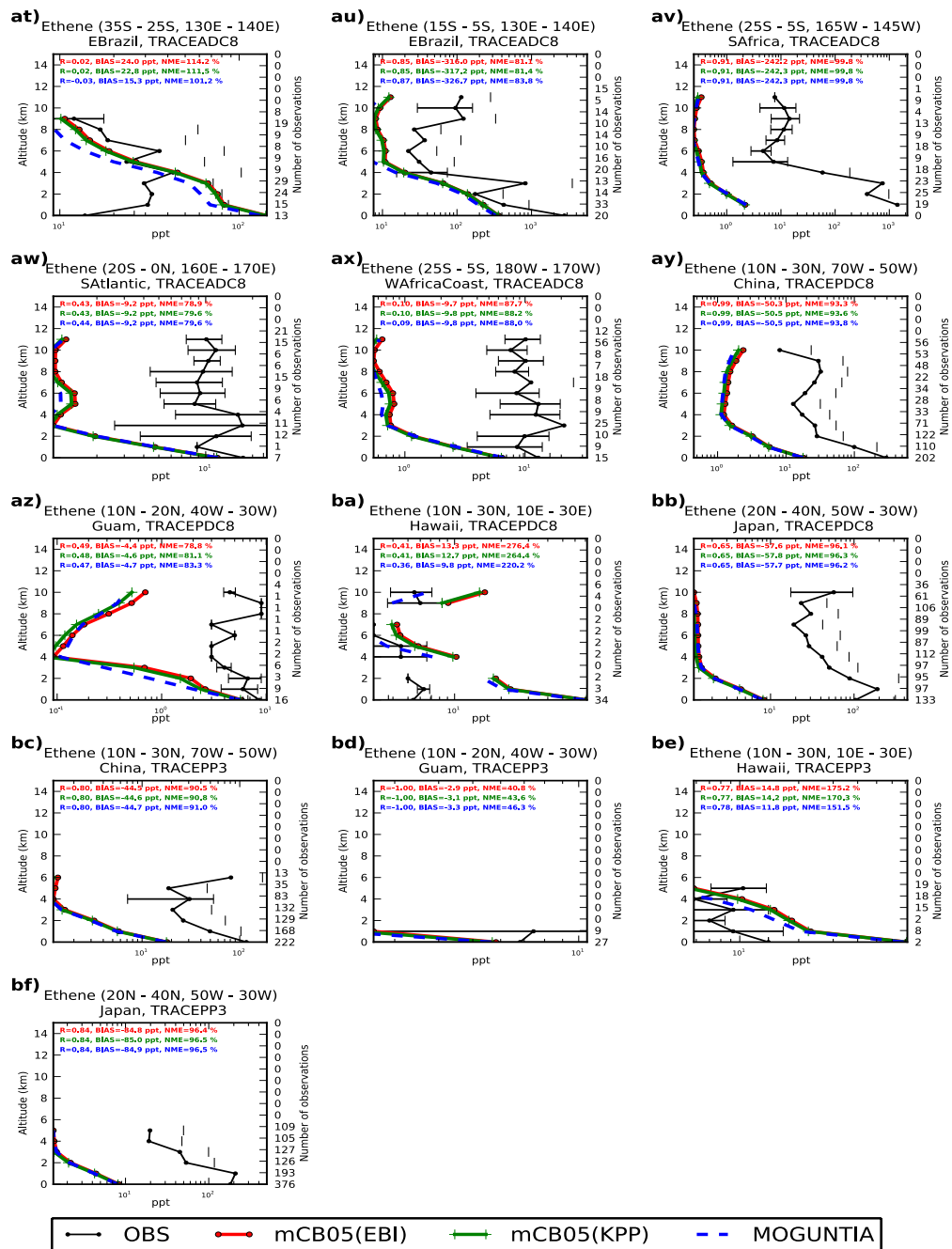
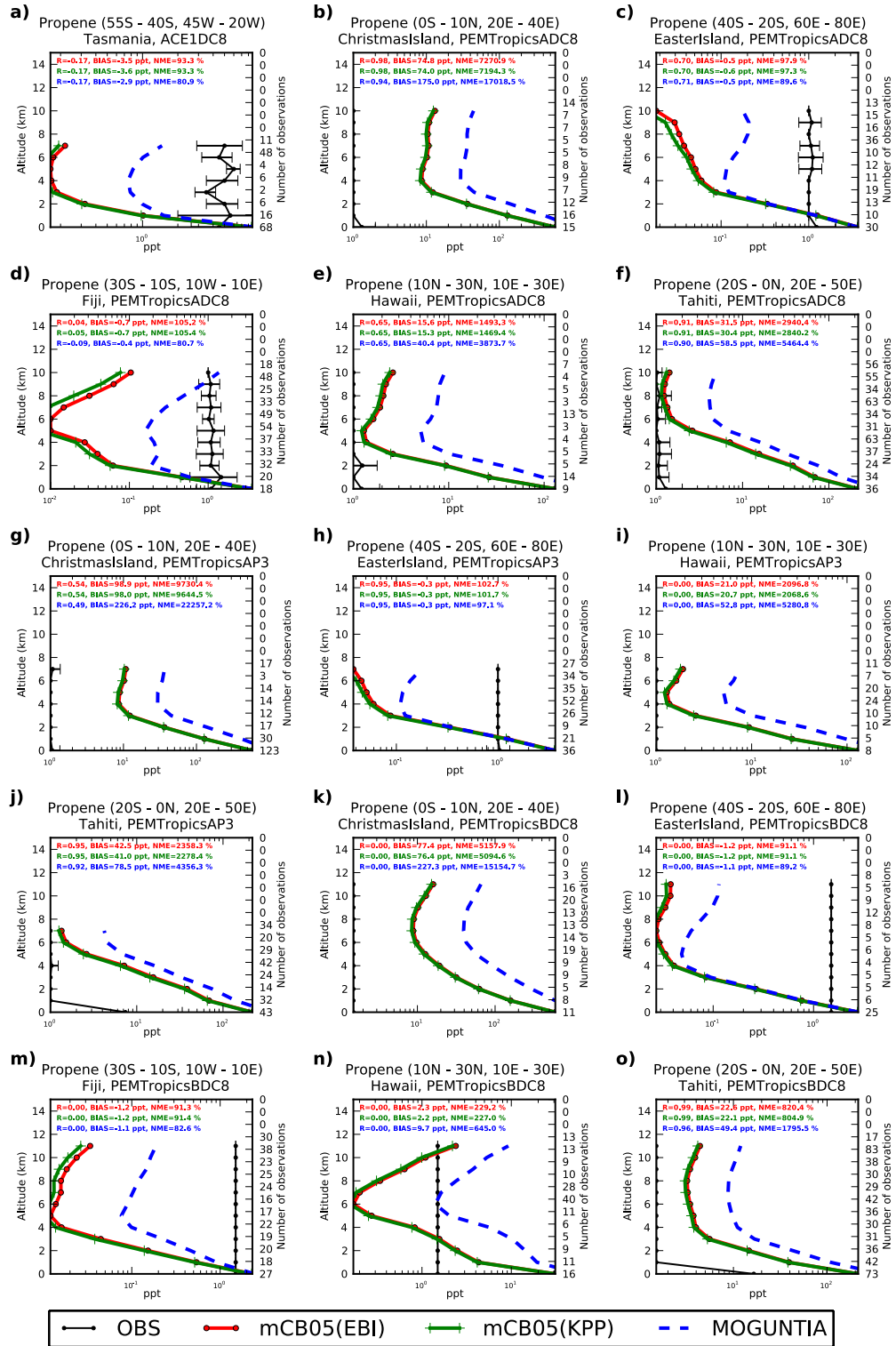
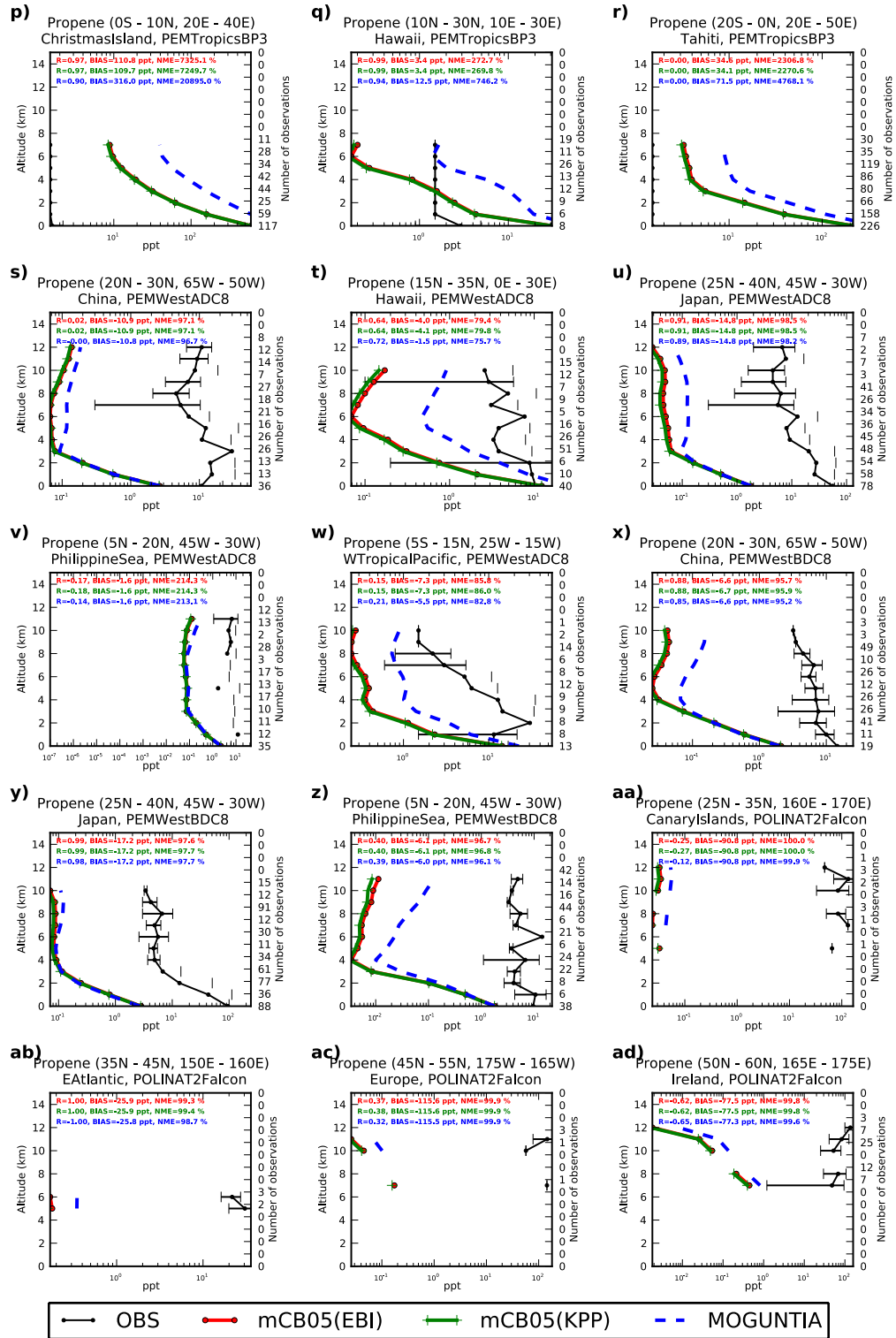
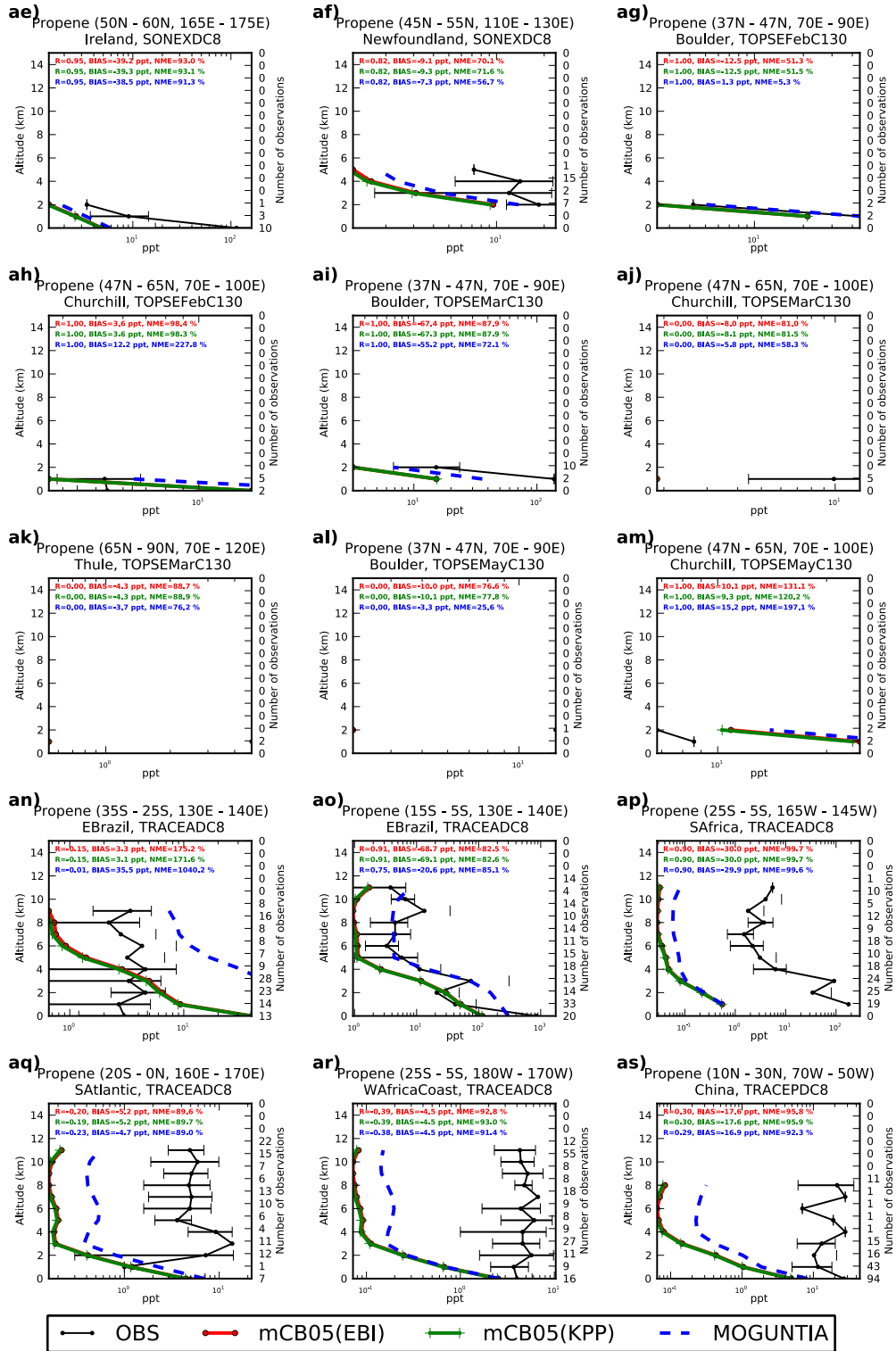


Figure S12: Comparison of TM5-MP vertical profiles (in km) of  $C_2H_2$  against aircraft observations (black line) in ppt, with model results (red-line for mCB05(EBI), green-line for mCB05(KPP) and blue-line for MOGUNTIA), using co-located model output for 2006 sampled at the measurement times; error bars indicate the standard deviation. The numbers on the right vertical axis indicate the number of available measurements.







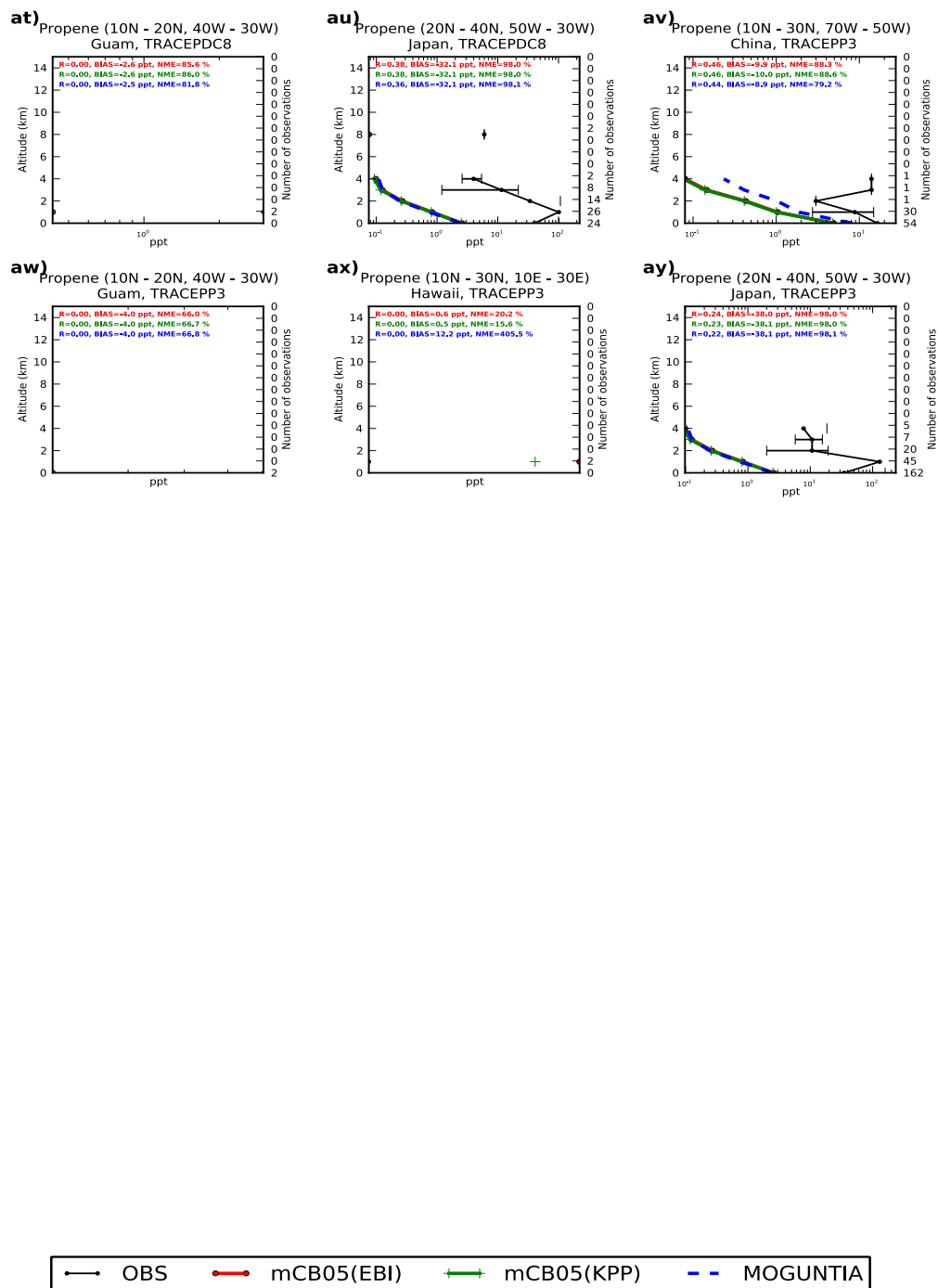


Figure S13: Comparison of TM5-MP vertical profiles (in km) of  $C_3H_6$  against aircraft observations (black line) in ppt, with model results (red-line for mCB05(EBI), green-line for mCB05(KPP) and blue-line for MOGUNTIA), using co-located model output for 2006 sampled at the measurement times; error bars indicate the standard deviation. The numbers on the right vertical axis indicate the number of available measurements.



## Supplementary References

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