**Table S1. WRF model physics options and parametrizations.**

| Option | Setup |
|---|---|
| Initialization | ERA5 |
| Shortwave radiation | MM5 |
| Longwave radiation | GFDL |
| Land-surface model | Noah LSM |
| Microphysics scheme | WSM6 |
| PBL Scheme | Boulac |
| Surface Layer option | Monin-Obukhov |
| Cumulus Parametrization | No |
| Urban Physics | BEP (Building Environment Parameterization) |
| Nudging | No |

**Table S2. Horizontal dimensions and resolution of WRF and CMAQ modeling domains.**

| Domains | Geographic area | WRF X-Y dimensions (grid cells) | CMAQ X-Y dimensions (grid cells) | Horizontal resolution (km) |
|---|---|---|---|---|
| D1 | Europe | 560 x 496 | 459 x 406 | 12 |
| D2 | Iberian Peninsula | 384 x 312 | 300 x 240 | 4 |
| D3 | Greater Madrid area | 256 x 256 | 136 x 144 | 1 |

**Table S3. Compliance objectives of Directive 2008/50/EC and those defined by the World Health Organization (WHO) in relation to the pollutant analyzed.**

| Average time | $O_3$ ($\mu g\ m^{-3}$) | |
|---|---|---|
| | **R.D 102/2011** | **OMS** |
| Maximum daily eight-hour mean | **120 $\mu g\ m^{-3}$** not to be exceeded on more than 25 days per calendar year averaged over three years | **100 $\mu g\ m^{-3}$** 3-4 exceedance days per year |
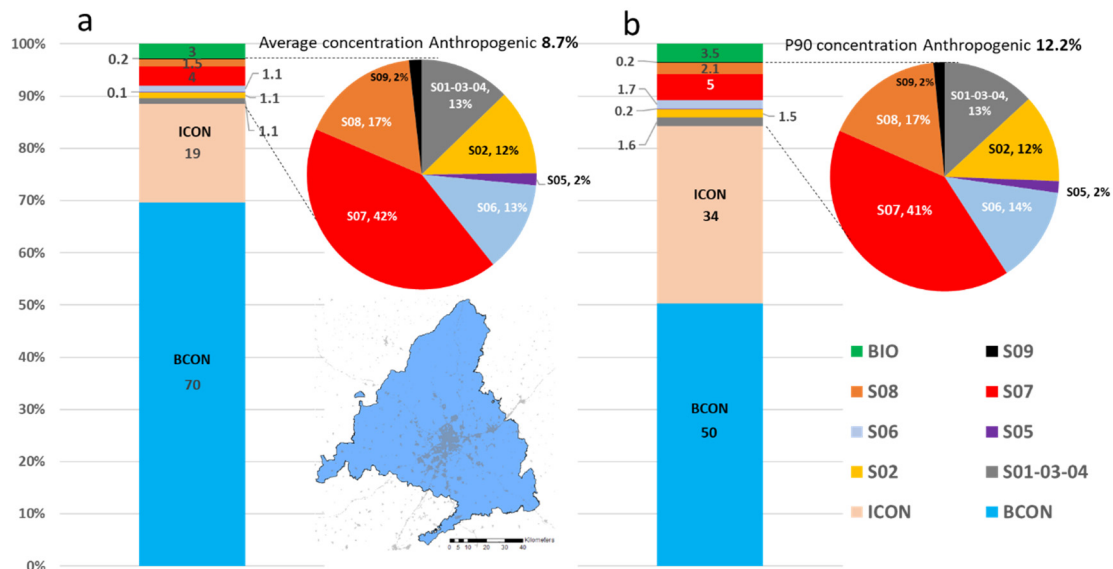
**Figure S1.** Spatially-averaged source apportionment (%) over the whole Madrid Region for (a) O₃ monthly mean and (b) 90$^{th}$ percentile O₃ concentration.
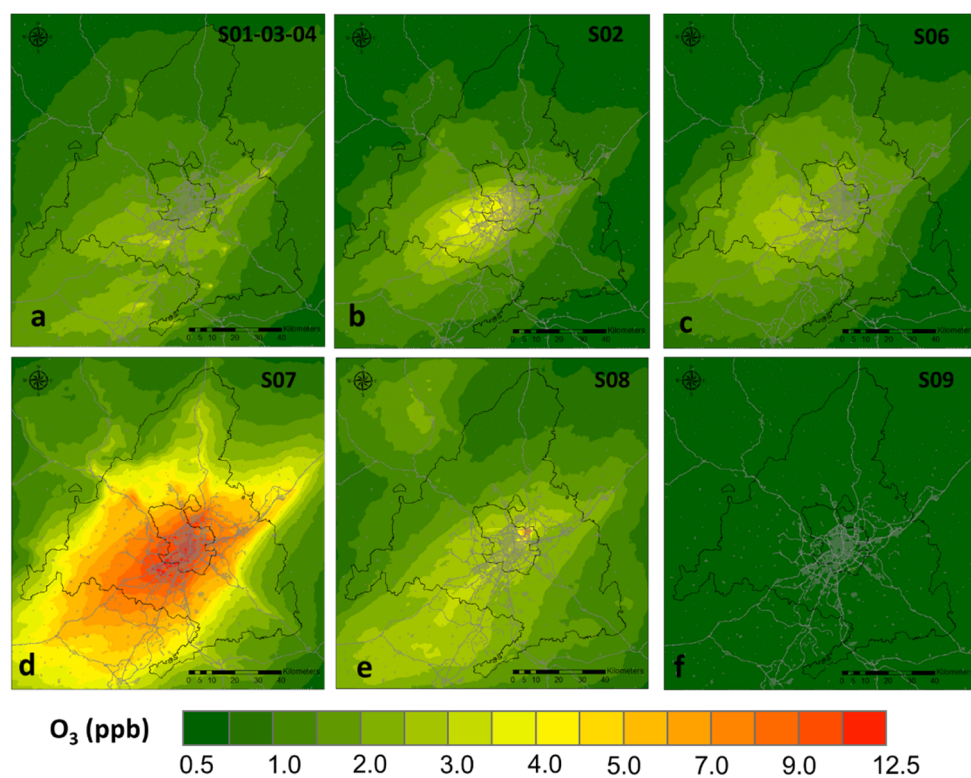
**Figure S2.** Absolute contribution to the 90$^{th}$ percentile of O₃ concentration of the main emitting sectors.
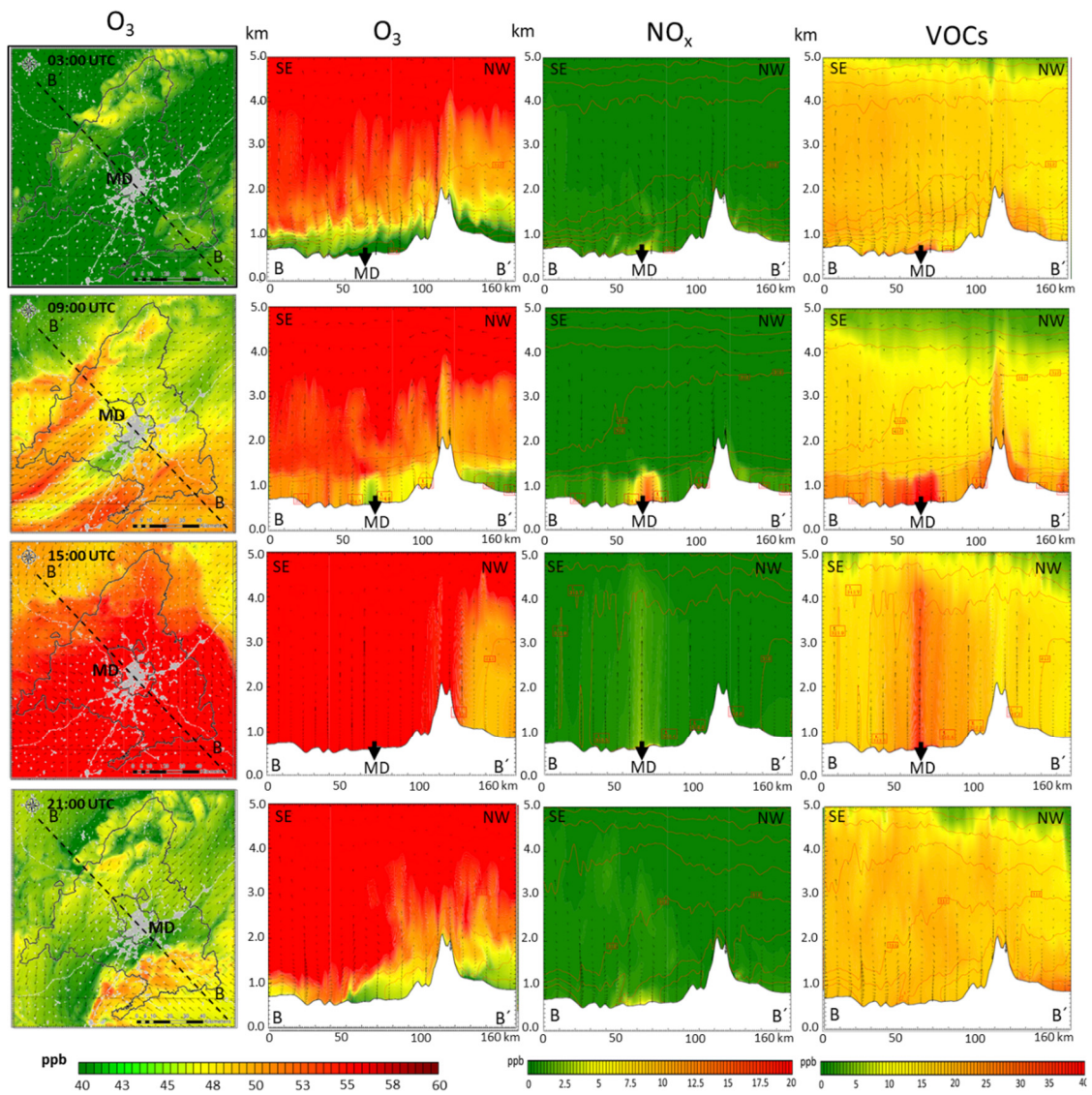
**Figure S3. Accumulation period: hourly concentration during July 27th. From left to right, plan view and SE-NW cross section (up to 5 km height) O₃ concentrations (ppb), NOx (ppb) and VOCs (ppb) at 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.**
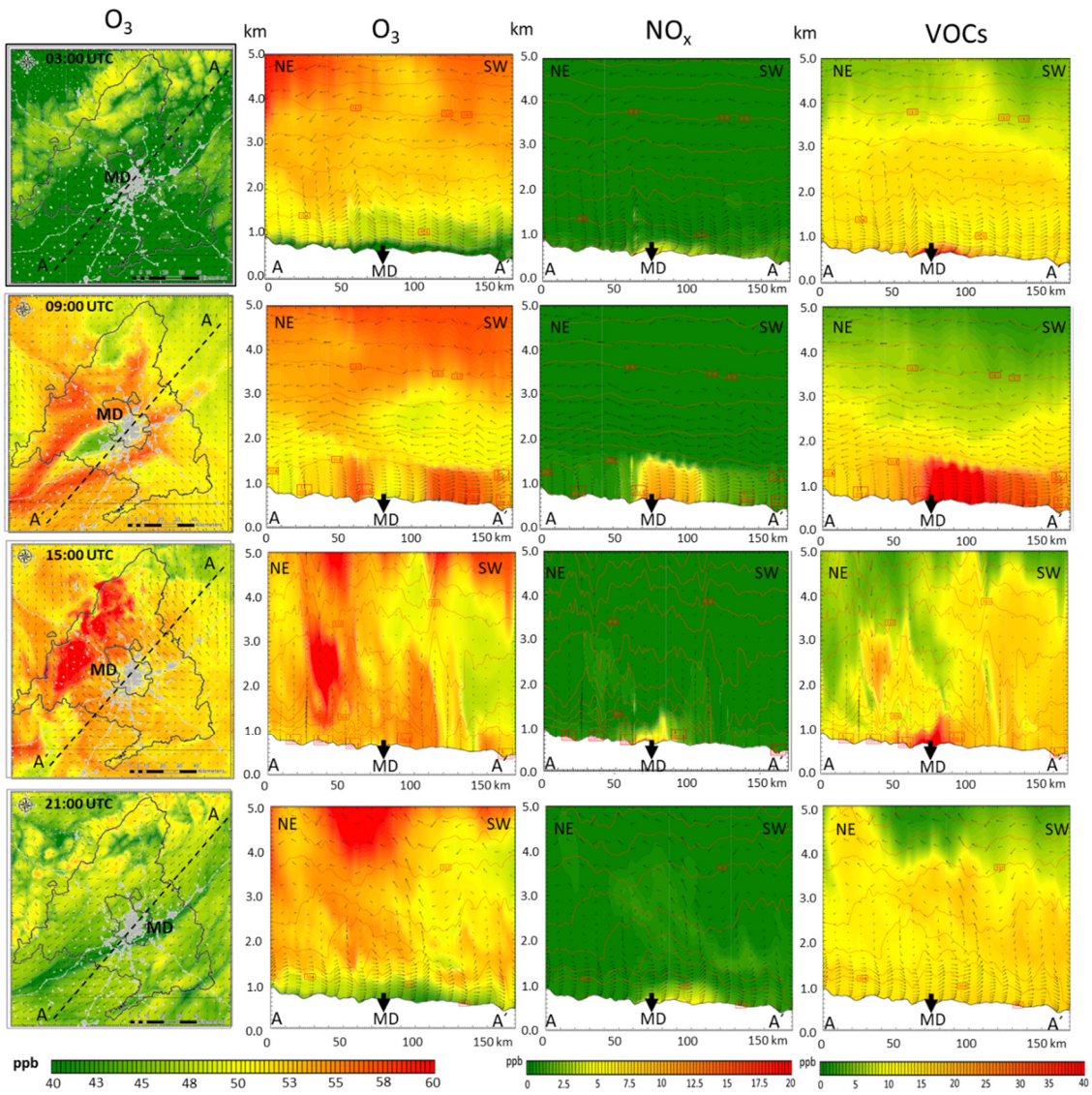
**Figure S4. Accumulation period: hourly concentration during July 6th. From left to right, plan view and NE-SW cross section (up to 5 km height) O₃ concentrations (ppb), NOx (ppb) and VOCs (ppb) at 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.**
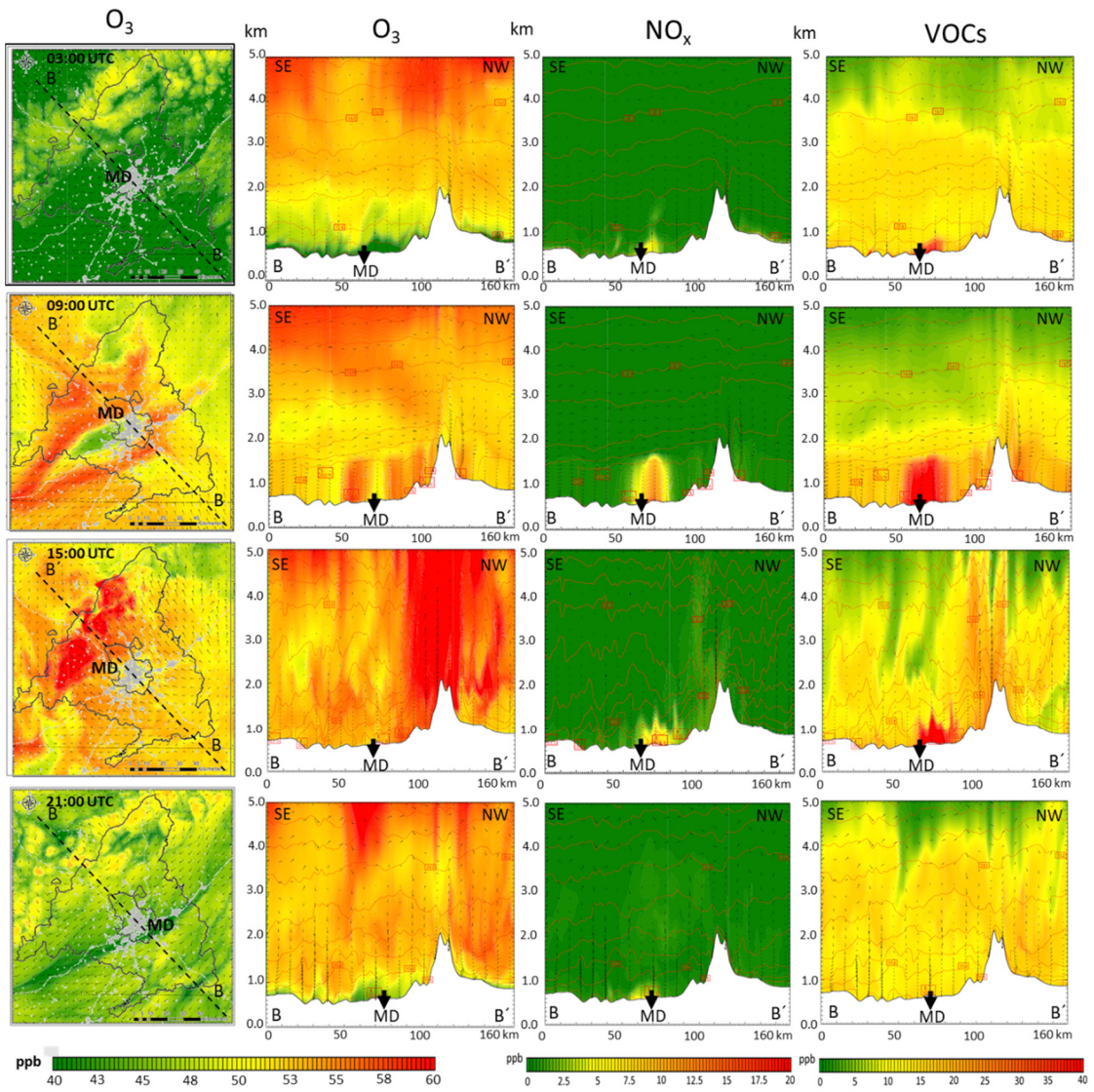
**Figure S5. Accumulation period: hourly concentration during July 6th. From left to right, plan view and SE-NW cross section (up to 5 km height) O₃ concentrations (ppb), NOx (ppb) and VOCs (ppb) at 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.**
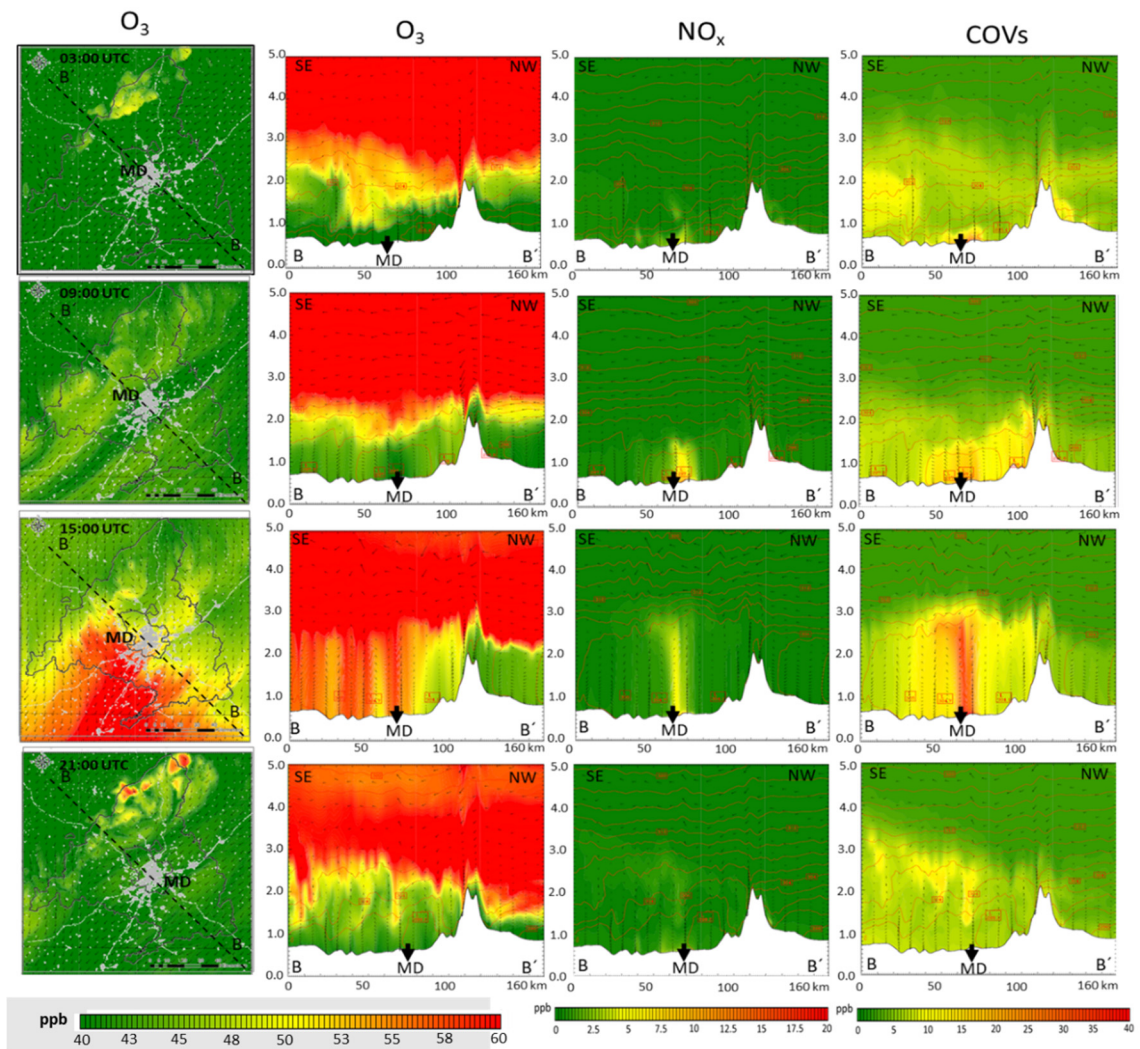
**Figure S6. Advection period: hourly concentration during July 13th. From left to right, plan view and SE-NW cross section (up to 5 km height) O₃ concentrations (ppb), NOx (ppb) and VOCs (ppb) at 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.**
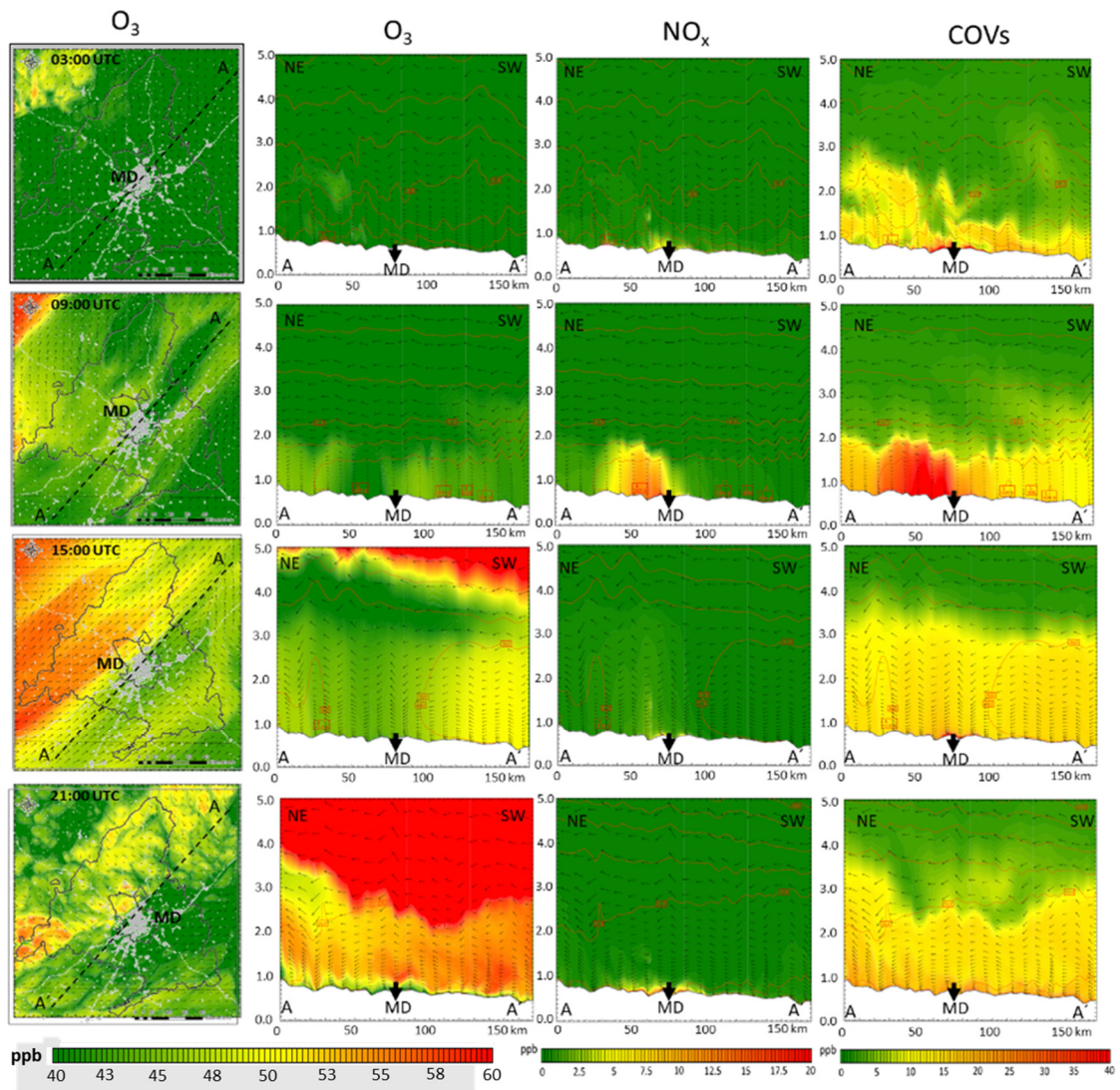
**Figure S7. Advection period: hourly concentration during July 20th. From left to right, plan view and NE-SW cross section (up to 5 km height) O₃ concentrations (ppb), NOx (ppb) and VOCs (ppb) at 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.**
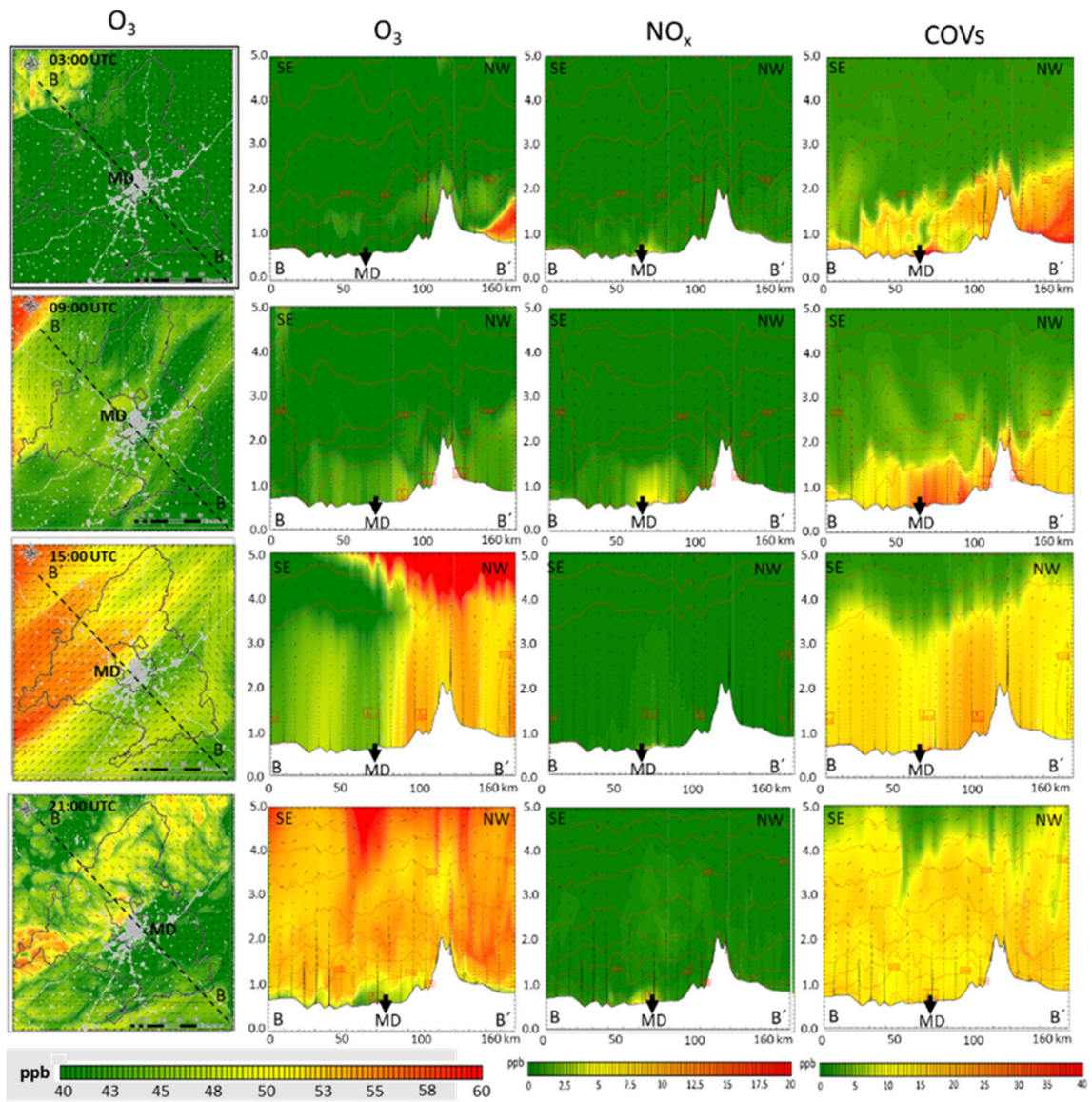
**Figure S8. Advection period: hourly concentration during July 20th. From left to right, plan view and SE-NW cross section (up to 5 km height) O₃ concentrations (ppb), NOx (ppb) and VOCs (ppb) at 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.**
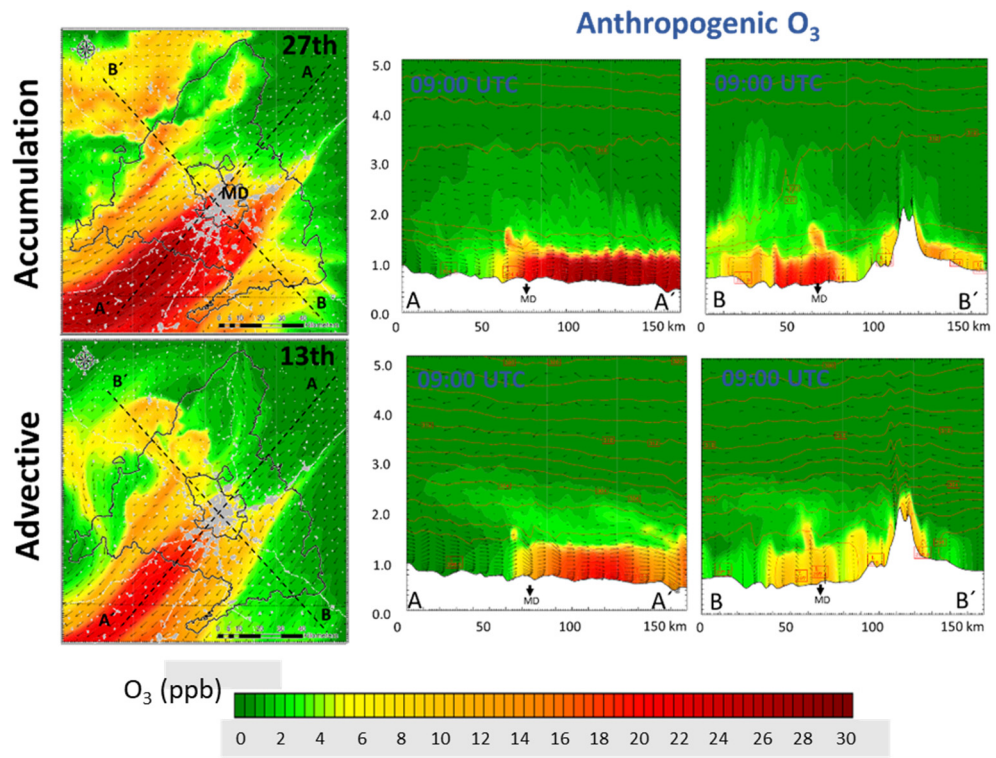
**Figure S9. O₃ concentration (ppb) at 09:00 UTC for July 27th (accumulation period) and July 13th (advective period). From left to right, plan view, NE-SW and SE-NW cross sections (up to 5 km height). MD = Madrid City.**
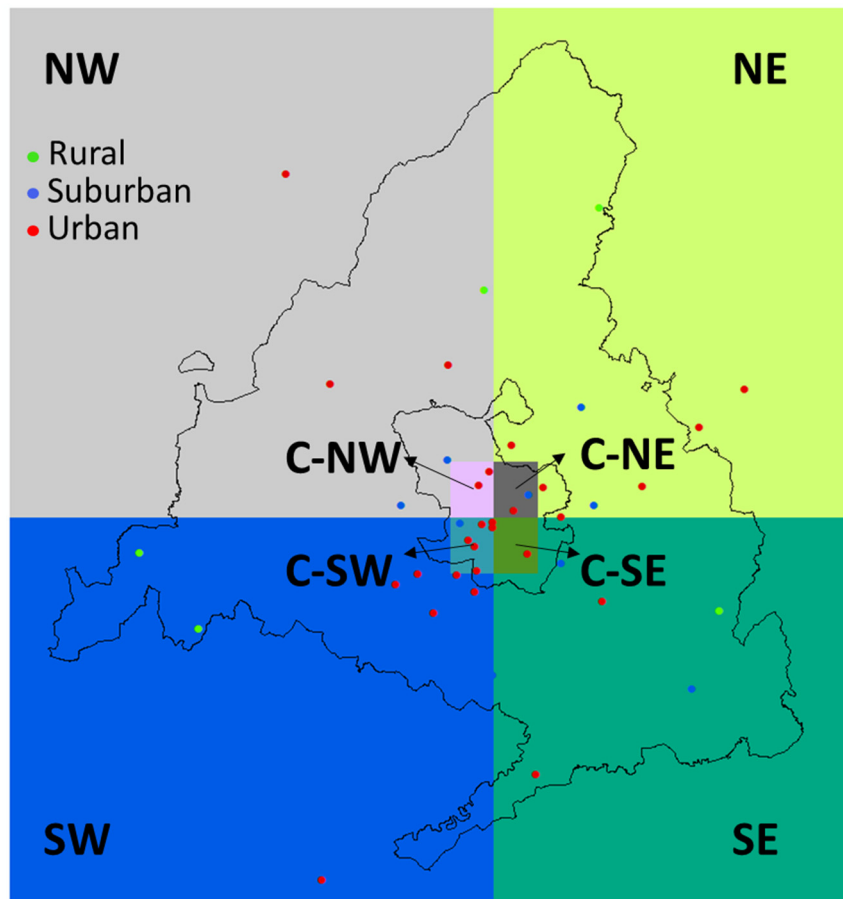
**Figure S10. Geographical division (quadrants) of the study area for the analysis of individual monitoring station locations**
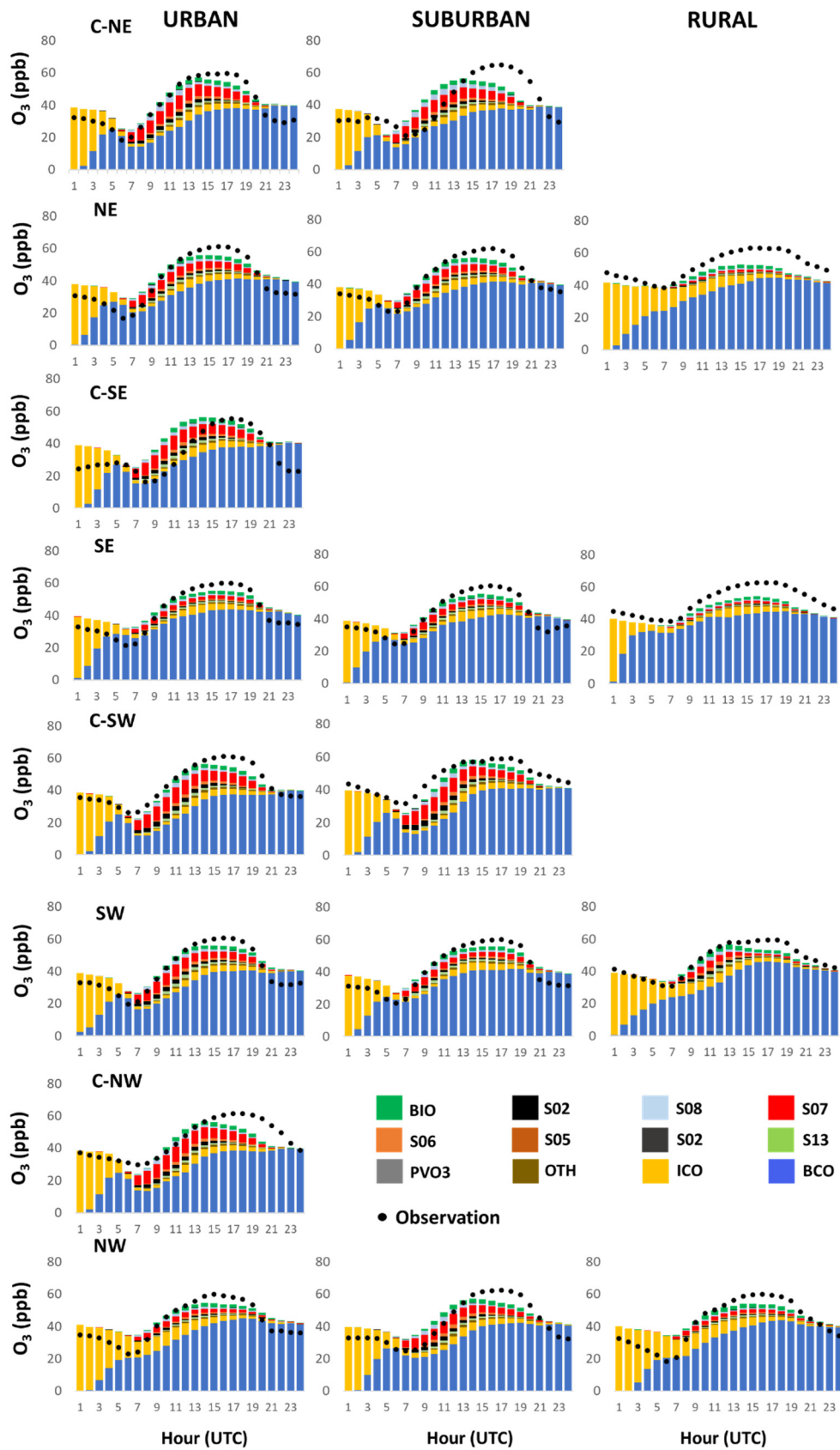
**Figure S11. Hourly contribution (ppb) for the monthly average at the location of monitoring sites by geographical quadrant.**
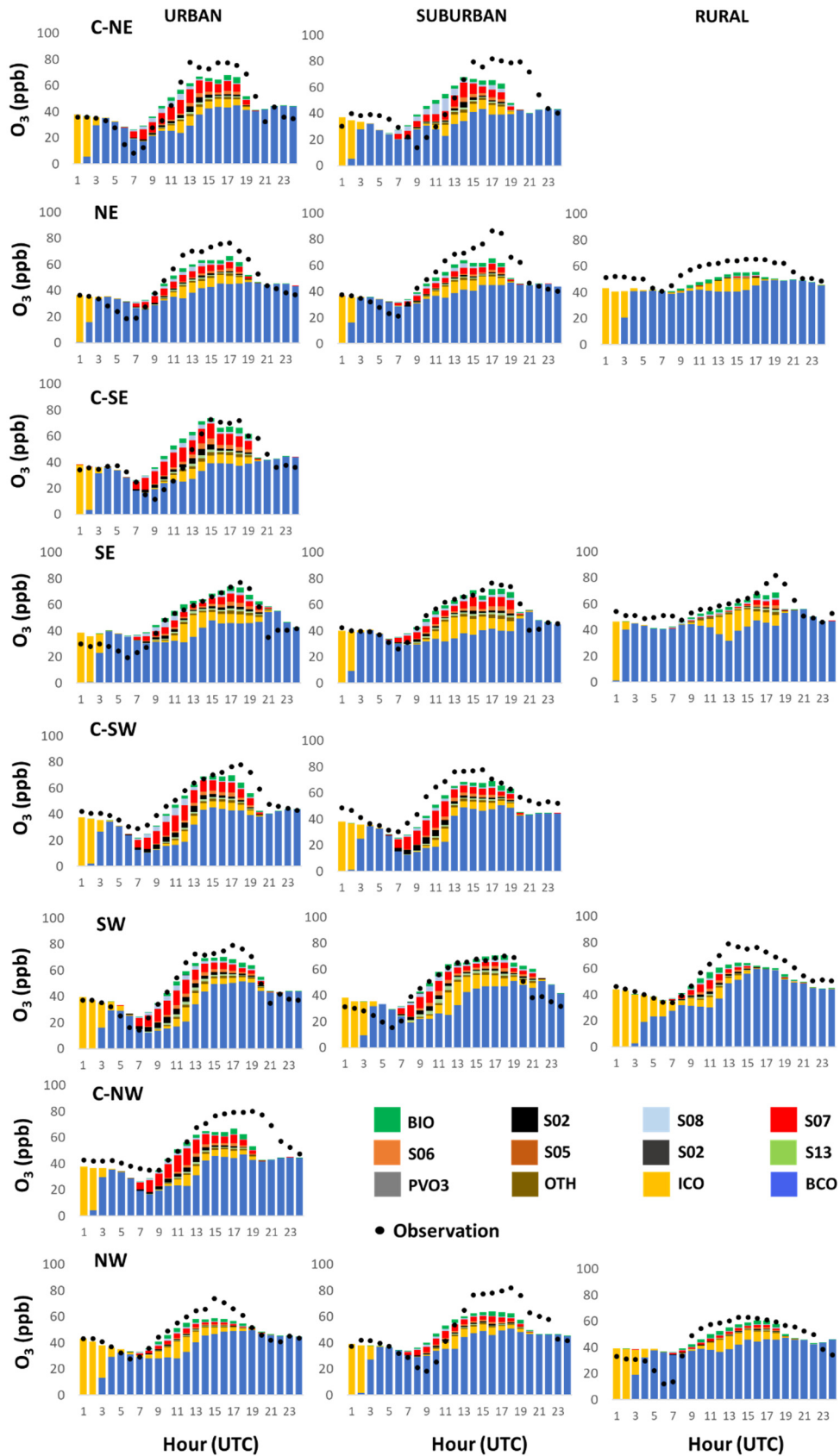
**Figure S12. Hourly contribution (ppb) for July 27th, 2016 at the location of monitoring sites by geographical quadrant.**
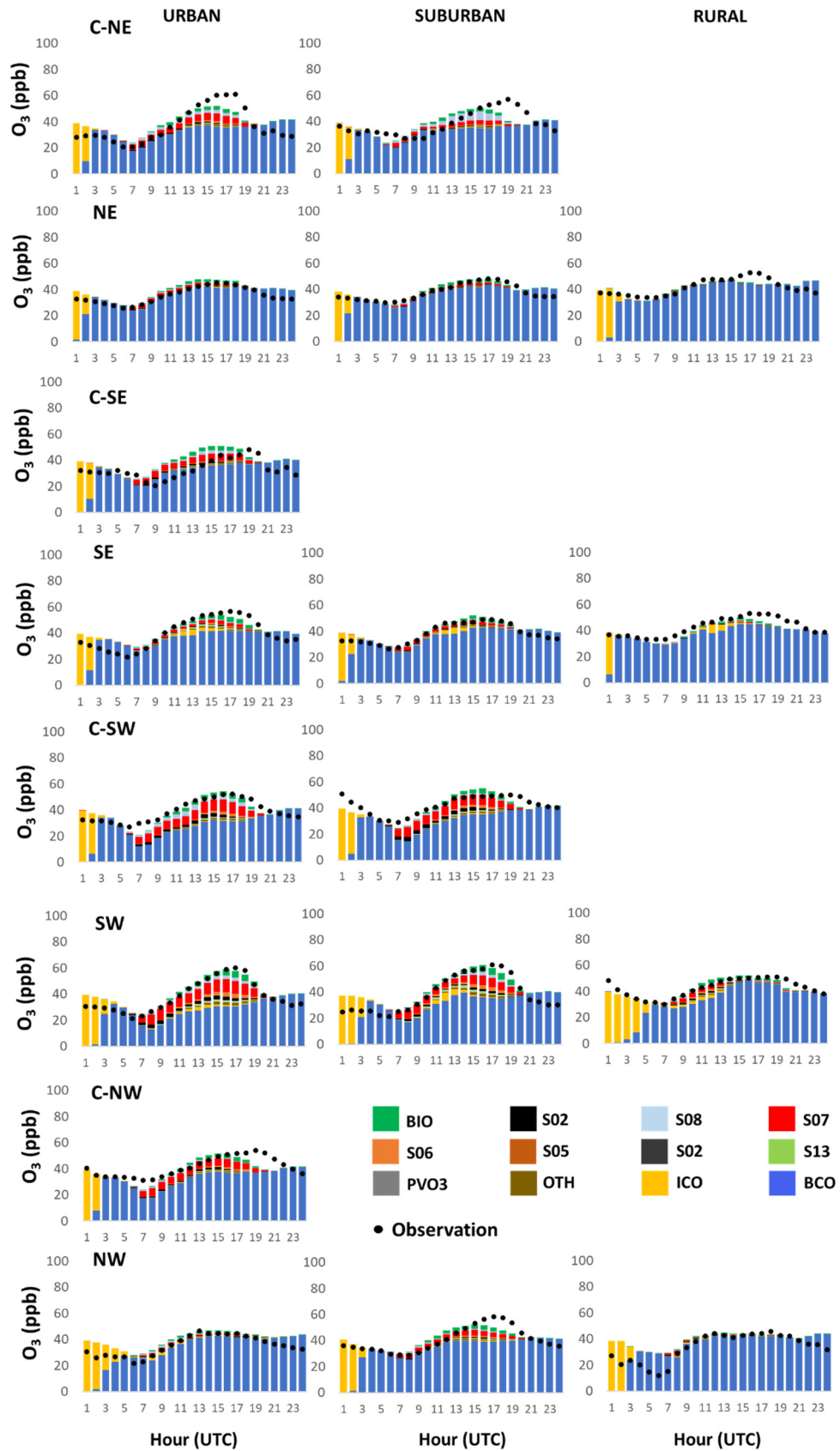
**Figure S13. Hourly contribution (ppb) for July 13<sup>th</sup>, 2016 at the location of monitoring sites by geographical quadrant.**

**Table S4. Model performance statistics by station type for O₃ concentration.**

| Station | FAC2 | MB (µg m⁻³) | MGE (µg m⁻³) | NMB | NMGE | RMSE (µg m⁻³) | r | IOA |
|---|---|---|---|---|---|---|---|---|
| Industrial | 0.95 | 7.82 | 14.53 | 0.10 | 0.18 | 18.67 | 0.84 | 0.70 |
| Rural | 0.98 | -2.88 | 13.79 | -0.03 | 0.14 | 17.72 | 0.79 | 0.67 |
| Suburban | 0.93 | 3.75 | 17.75 | 0.05 | 0.21 | 23.55 | 0.76 | 0.68 |
| Urban background | 0.87 | 10.56 | 22.35 | 0.15 | 0.29 | 29.03 | 0.67 | 0.61 |
| Urban traffic | 0.85 | 12.91 | 21.33 | 0.18 | 0.29 | 27.97 | 0.74 | 0.62 |

**Table S5. Model performance statistics by station for O₃ concentration.**

| STATION | TYPE | FAC2 | MB (µgm⁻³) | MGE (µgm⁻³) | NMB | RMSE (µgm⁻³) | r | IOA |
|---|---|---|---|---|---|---|---|---|
| ARGANDA DEL REY | Industrial | 0.956 | 5.8 | 14.6 | 0.1 | 18.6 | 0.84 | 0.72 |
| FUENLABRADA | Industrial | 0.948 | 9.9 | 14.4 | 0.1 | 18.7 | 0.84 | 0.69 |
| VILLA DEL PRADO | Rural | 0.985 | 0.8 | 11.8 | 0.0 | 15.3 | 0.82 | 0.72 |
| SAN MARTIN DE VALDEIGLESIAS | Rural | 0.997 | 0.0 | 10.5 | 0.0 | 13.7 | 0.80 | 0.71 |
| ORUSCO DE TAJUŇA | Rural | 1.000 | 10.0 | 12.7 | 0.1 | 16.1 | 0.84 | 0.66 |
| GUADALIX DE LA SIERRA | Rural | 0.924 | 7.6 | 17.9 | 0.1 | 22.7 | 0.79 | 0.67 |
| EL ATAZAR | Rural | 0.996 | 11.2 | 16.1 | 0.1 | 20.7 | 0.69 | 0.58 |
| ALGETE | Suburban | 1.000 | 4.4 | 13.1 | 0.1 | 17.2 | 0.81 | 0.72 |
| LA SAGRA | Suburban | 0.940 | 7.3 | 14.5 | 0.1 | 20.0 | 0.81 | 0.71 |
| MOSTOLES | Suburban | 0.940 | 8.1 | 15.5 | 0.1 | 20.6 | 0.83 | 0.71 |
| MAJADAHONDA | Suburban | 0.962 | 2.7 | 15.7 | 0.0 | 21.4 | 0.81 | 0.71 |
| VALDEMORO | Suburban | 0.910 | 6.7 | 16.0 | 0.1 | 22.1 | 0.80 | 0.71 |
| RIVAS VACIAMADRID | Suburban | 0.913 | 7.0 | 17.3 | 0.1 | 23.0 | 0.81 | 0.70 |
| TORREJON DE ARDOZ | Suburban | 0.901 | 10.0 | 17.6 | 0.1 | 23.6 | 0.82 | 0.70 |
| AZUQUECA DE HENARES | Suburban | 0.948 | 3.6 | 16.8 | 0.0 | 21.6 | 0.78 | 0.70 |
| TOLEDO2 | Suburban | 0.954 | 0.9 | 16.3 | 0.0 | 22.0 | 0.72 | 0.69 |
| ARANJUEZ | Suburban | 0.910 | 9.3 | 16.7 | 0.1 | 22.5 | 0.77 | 0.67 |
| EL PARDO | Suburban | 0.922 | 0.2 | 22.2 | 0.0 | 28.0 | 0.74 | 0.65 |
| CASA DE CAMPO | Suburban | 0.942 | 1.7 | 20.1 | 0.0 | 26.7 | 0.61 | 0.63 |
| JUAN CARLOS I | Suburban | 0.895 | 4.6 | 24.2 | 0.1 | 31.0 | 0.61 | 0.63 |
| ALCORCON | Urban Background | 0.958 | 4.8 | 14.6 | 0.1 | 19.7 | 0.83 | 0.73 |
| GUADALAJARA | Urban Background | 0.935 | 7.4 | 15.6 | 0.1 | 21.4 | 0.77 | 0.70 |
| TRES OLIVOS | Urban Background | 0.921 | 4.0 | 22.8 | 0.0 | 29.2 | 0.66 | 0.63 |
| VILLAVERDE | Urban Background | 0.863 | 13.1 | 22.2 | 0.2 | 29.4 | 0.66 | 0.61 |
| FAROLILLO | Urban Background | 0.883 | 5.8 | 22.4 | 0.1 | 29.7 | 0.62 | 0.62 |
| RETIRO | Urban Background | 0.860 | 11.9 | 23.0 | 0.2 | 29.3 | 0.64 | 0.60 |
| BARAJAS PUEBLO | Urban Background | 0.809 | 11.2 | 25.1 | 0.2 | 32.2 | 0.65 | 0.62 |
| ARTURO SORIA | Urban Background | 0.838 | 15.4 | 23.2 | 0.2 | 29.8 | 0.63 | 0.57 |
| ENSANCHE DE VALLECAS | Urban Background | 0.876 | 16.0 | 24.6 | 0.2 | 32.6 | 0.64 | 0.58 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| PLAZA DEL CARMEN | Urban Background | 0.723 | 24.0 | 29.9 | 0.4 | 37.0 | 0.59 | 0.47 |
| SEGOVIA 2 | Traffic | 0.973 | 3.5 | 13.6 | 0.0 | 17.0 | 0.84 | 0.71 |
| VILLAREJO DE SALVANES | Traffic | 0.992 | 3.1 | 10.6 | 0.0 | 14.6 | 0.78 | 0.71 |
| COLMENAR VIEJO | Traffic | 0.992 | 0.8 | 13.0 | 0.0 | 17.3 | 0.78 | 0.70 |
| ALCOBENDAS | Traffic | 0.928 | 0.8 | 17.8 | 0.0 | 23.6 | 0.80 | 0.70 |
| GETAFE | Traffic | 0.916 | 8.8 | 16.9 | 0.1 | 23.1 | 0.80 | 0.70 |
| ALCALA DE HENARES | Traffic | 0.866 | 10.0 | 19.3 | 0.1 | 25.0 | 0.83 | 0.69 |
| LEGANES | Traffic | 0.871 | 12.4 | 18.4 | 0.2 | 25.7 | 0.79 | 0.68 |
| BARRIO DEL PILAR | Traffic | 0.881 | 9.0 | 20.9 | 0.1 | 28.2 | 0.64 | 0.62 |
| COSLADA | Traffic | 0.792 | 18.9 | 24.8 | 0.3 | 31.2 | 0.80 | 0.61 |
| COLLADO VILLALBA | Traffic | 0.784 | 19.3 | 23.6 | 0.3 | 31.7 | 0.73 | 0.59 |
| ESCUELAS AGUIRRE | Traffic | 0.830 | 16.5 | 23.7 | 0.2 | 29.9 | 0.63 | 0.54 |
| PZ. FERNANDEZ LADREDA | Traffic | 0.798 | 22.1 | 26.7 | 0.3 | 33.4 | 0.63 | 0.48 |