**SUPLEMENTARY INFORMATION (CAPTIONS)**

Figure S1. Correlation between: Top: $O_3$ measured with the passive dosimeters and an UV photometry analyser; middle: $NO_2$ measured with the passive dosimeters and a chemiluminiscence analyser; bottom: $O_3$ measured with the PO3M sensor and an UV photometry analyser.

Figure S2. Instrumentation pack for tethered balloon measurements.

Figure S3. Comparison between the nano particle sizer (two units) used in the tethered balloon with the reference scanning mobility particle sizer.

Figure S4. Instrumentation pack for free sounding measurements.

Figure S5. Geopotential and temperature at 850 hPa (left) and 500 hPa (center). Potential temperature (K) of the atmospheric sounding in Barcelona (WMO 08190) at 12:00 UTC (right). Meteorological figures are reported for 03/07/2015 (top) and 14/07/2015 (bottom).

Figure S6. 8-h $PM_{2.5}$ chemical components at VIC station during 10-17/07/2015. White: 16:00-24:00 UTC; blue: 00:00-08:00 UTC, yellow: 08:00-16:00 UTC.

Figure S7. Data from the free sounding measurements (at VIC) of temperature, relative humidity, and particle number concentrations performed from 10:00 to 11:30 UTC on 16/07/2015. Red lines identifies the limit between diferrent atospheric layers. The 3 daily shadowed bars indicate the 3 8h periods sampled.

Figure S8.Spatial variability of the monthly July $O_3$ and $O_X$ concentrations recorded in the study area at the XVPCA air quality monitoring network and with the passive dosimeters.

Table S1. Name, acronym, type, coordinates and measurements for each of the stations of the regional air quality network (XVPCA).

Table S2. Details of vertical measurements performed with the balloon and the miniaturised instrumentation at VIC.

Table S3. Location of the meteorological stations.

Table S1.

| STATION | TYPE | COORDINATES | | HEIGHT | ONLINE MEASUREMENTS | OFFLINE MEASUREMENTS |
|---|---|---|---|---|---|---|
| | | Lat (°N) | Long (°E) | (m.a.s.l.) | | |
| Agullana (AGU) | Rural, Background | 42.39 | 2.84 | 166 | $O_3$ | |
| Alcover (ALC) | Rural, Industry | 41.28 | 1.18 | 243 | $O_3$, NO, $NO_2$, CO, $SO_2$, $H_2S$ | |
| Amposta (AMP) | Suburban, Background | 40.71 | 0.58 | 8 | $O_3$, NO, $NO_2$, CO, $SO_2$, $PM_{10}$ | $C_6H_6$ |
| Badalona (BAD) | Urban, Traffic | 41.44 | 2.23 | 6 | $O_3$, NO, $NO_2$, $SO_2$, | |
| Barcelona Gràcia (BCN-G) | Urban, Traffic | 41.40 | 2.15 | 75 | $O_3$, NO, $NO_2$, $SO_2$, $C_6H_6$ | $PM_{10}$, $PM_{2.5}$, As, B(a)p, Cd, Ni, Pb, $C_6H_6$ |
| Barcelona Poblenou (BCN-PBN) | Urban, Traffic | 41.40 | 2.20 | 12 | $O_3$, NO, $NO_2$, $SO_2$ | $PM_{10}$, $PM_{2.5}$, As, B(a)p, Cd, Ni, Pb, $C_6H_6$ |
| Barcelona Palau Reial (PLR) | Urban, Background | 41.39 | 2.11 | 81 | $O_3$, NO, $NO_2$, CO, $SO_2$ | |
| Barcelona Ciutadella (CTL) | Urban, Background | 41.39 | 2.19 | 5 | $O_3$, NO, $NO_2$ | |
| Begur (BEG) | Rural, Background | 41.95 | 3.02 | 200 | $O_3$ | $C_6H_6$ |
| Bellver de Cerdanya (BdC) | Rural, Background | 42.37 | 1.78 | 1060 | $O_3$, NO, $NO_2$, $PM_{10}$ | $PM_{10}$, $PM_{2.5}$, As, B(a)p, Cd, Ni, Pb, $C_6H_6$ |
| Berga (VER) | Suburban, background | 42.10 | 1.85 | 661 | $O_3$, NO, $NO_2$, CO, $SO_2$, $PM_{10}$ | $PM_{10}$, $PM_{2.5}$, As, B(a)p, Cd, Ni, Pb, $C_6H_6$ |
| Constantí (CON) | Suburban, Industry | 41.16 | 1.22 | 87 | $O_3$, NO, $NO_2$, CO, $SO_2$ | $PM_{10}$, $PM_{2.5}$, As, B(a)p, Cd, Ni, Pb, $C_6H_6$, HCl |
| El Prat de Llobregat (EPLL) | Suburban, Traffic | 41.32 | 2.08 | 7 | $O_3$, NO, $NO_2$, $SO_2$, $H_2S$ | $PM_{10}$, $PM_{2.5}$, Pb, $C_6H_6$ |
| Els Guiamets | Rural, Background | 41.10 | 0.76 | 220 | $O_3$ | |
| Gandesa (GAN) | Rural, Background | 41.06 | 0.44 | 368 | $O_3$ | |
| Gavà (GAV) | Suburban, Background | 41.30 | 1.99 | 25 | $O_3$, NO, $NO_2$, CO, $SO_2$ | $PM_{10}$, $PM_{2.5}$, Pb |
| Granollers (GRA) | Urban, Traffic | 41.60 | 2.29 | 140 | $O_3$, NO, $NO_2$ | $PM_{10}$, $PM_{2.5}$, B(a)p |
| Igualada (IGU) | Suburban, Industry | 41.58 | 1.63 | 284 | $O_3$, NO, $NO_2$, CO, $SO_2$, $H_2S$ | $PM_{10}$, As, B(a)p, Cd, Ni, Pb |
| Juneda (JUN) | Rural, Background | 41.55 | 0.83 | 255 | $O_3$, NO, $NO_2$ | $PM_{10}$ |
| L'Hospitalet | Urban, Traffic | 41.37 | 2.11 | 20 | NO, $NO_2$, $PM_{10}$ | $PM_{10}$, $PM_{2.5}$ |
| La Sènia (LSE) | Rural, Background | 40.64 | 0.29 | 428 | $O_3$ | $PM_{10}$, $PM_{2.5}$ |
| Lleida (LLE) | Urban, Traffic | 41.62 | 0.62 | 220 | $O_3$, NO, $NO_2$, CO, $SO_2$, $PM_{10}$ | $PM_{10}$, $PM_{2.5}$, As, B(a)p, Cd, Ni, Pb, $C_6H_6$ |
| Manlleu (MAN) | Suburban, Background | 42.01 | 2.29 | 460 | $O_3$, NO, $NO_2$, $SO_2$ | $PM_{10}$, As, B(a)p, Cd, Ni, Pb |
| Manresa (MNR) | Urban, Traffic | 41.73 | 1.83 | 238 | $O_3$, NO, $NO_2$, CO, $SO_2$ | $PM_{10}$, $C_6H_6$ |
| Mataró (MAT) | Urban, Background | 41.54 | 2.44 | 40 | $O_3$, NO, $NO_2$, CO, $SO_2$ | $PM_{10}$, $C_6H_6$ |
| Montcada (MON) | Suburban, Industry | 41.48 | 2.19 | 33 | $O_3$, NO, $NO_2$, $SO_2$, $PM_{10}$ | |
| Montsec (MSC) | Rural, Background | 42.05 | 0.73 | 1570 | $O_3$, NO, $NO_2$, CO, $SO_2$, $PM_{10}$, $PM_{2.5}$ | |
| Montseny (MSY) | Rural, Background | 41.78 | 2.38 | 720 | $O_3$, NO, $NO_2$, CO, $SO_2$ | |
| Pardines (PAR) | Rural, Background | 42.31 | 2.21 | 1226 | $O_3$ | |
| Ponts (PON) | Rural, Background | 41.91 | 1.19 | 370 | $O_3$ | $PM_{10}$, $C_6H_6$ |
| Reus (REU) | Suburban, Traffic | 41.15 | 1.12 | 110 | $O_3$, NO, $NO_2$, CO, $SO_2$, $H_2S$, $PM_{10}$ | $PM_{10}$, As, Cd, Ni, Pb, $C_6H_6$ |
| Rubí (RUB) | Suburban, Background | 41.49 | 2.03 | 200 | $O_3$, NO, $NO_2$, CO, $SO_2$, $PM_{10}$ | $PM_{10}$, $PM_{2.5}$, $C_6H_6$ |
| Sabadell (SAB) | Urban, Traffic | 41.56 | 2.10 | 190 | $O_3$, NO, $NO_2$ | $PM_{10}$, $PM_{2.5}$, $C_6H_6$ |
| Sant Celoni (SCE) | Suburban, Industry | 41.69 | 2.50 | 155 | $O_3$, NO, $NO_2$, CO, $SO_2$, $H_2S$, $PM_{10}$ | $PM_{10}$, B(a)p, $C_6H_6$ |
| Sort (SOR) | Rural, Background | 42.41 | 1.13 | 692 | $O_3$ | $PM_{10}$ |
| St Adrià Besòs (SAD) | Suburban, Traffic | 41.42 | 2.22 | 9 | $O_3$, NO, $NO_2$, $PM_{10}$ | $PM_{10}$, $PM_{2.5}$ |
| St Cugat del Vallès (SCV) | Urban, Background | 41.48 | 2.09 | 124 | $O_3$, NO, $NO_2$ | $PM_{10}$ |
| St Vicenç dels Horts (SVH) | Suburban, Industry | 41.39 | 2.01 | 22 | $O_3$, NO, $NO_2$, $SO_2$ | |
| S.M. Palautordera (SMPT) | Rural, Background | 41.70 | 2.45 | 208 | $O_3$ | $PM_{2.5}$ |
| Sta Pau (STP) | Rural, Background | 41.96 | 3.21 | 496 | $O_3$ | |
| Tarragona (TARR) | Urban, Background | 41.12 | 1.24 | 14 | $O_3$, NO, $NO_2$, CO, $SO_2$, $H_2S$ | $C_6H_6$ |

| | | | | | | |
|---|---|---|---|---|---|---|
| Terrassa (TERR) | Urban, Traffic | 41.56 | 2.01 | 277 | $O_3$, NO, $NO_2$, CO, $SO_2$ | $PM_{10}$ |
| Tona (TON) | Rural, Background | 41.86 | 2.23 | 620 | $O_3$, NO, $NO_2$ | $C_6H_6$ |
| Vic (VIC) | Suburban, Background | 41.92 | 2.26 | 498 | $O_3$ | $PM_{2.5}$, $C_6H_6$ |
| Viladecans (VLC) | Suburban, Traffic | 41.31 | 2.01 | 14 | $O_3$, NO, $NO_2$, CO, $SO_2$ | $PM_{10}$, $PM_{2.5}$, $C_6H_6$ |
| Vilafranca Penedès (VLP) | Suburban, Background | 41.35 | 1.69 | 200 | $O_3$, NO, $NO_2$, $PM_{10}$ | $C_6H_6$ |
| Vilanova i la Geltrú (VLG) | Urban, Traffic | 41.22 | 1.72 | 22 | $O_3$, NO, $NO_2$, $PM_{10}$ | $C_6H_6$ |
| Vila-Seca (VSE) | Suburban, Industry | 41.11 | 1.15 | 60 | $O_3$, NO, $NO_2$, CO, $SO_2$, $H_2S$, $PM_{10}$, $PM_{2.5}$ | $PM_{10}$, As, Cd, Ni, Pb, $C_6H_6$ |

Table S2.

| Date | Start (UTC) | End (UTC) | Direction | Height (m a.s.l.) | Instrumentation |
|---|---|---|---|---|---|
| 14/07/2015 | 07:06 | 08:21 | ascending | 520-1452 | CPC-$O_3$ |
| | 13:49 | 15:03 | ascending | 520-871 | SMPS-$O_3$ |
| 15/07/2015 | 07:07 | 07:36 | ascending | 520-1262 | SMPS-$O_3$ |
| | 07:36 | 08:22 | descending | 1262-520 | SMPS-$O_3$ |
| | 08:37 | 09:04 | ascending | 520-1069 | SMPS-$O_3$ |
| 16/07/2015 | 06:28 | 06:35 | ascending | 520-736 | SMPS-$O_3$ |
| | 06:35 | 07:23 | constant height | 709-736 | SMPS-$O_3$ |
| | 07:23 | 07:26 | ascending | 714-859 | SMPS-$O_3$ |
| | 07:26 | 09:40 | constant height | 860-870 | SMPS-$O_3$ |
| | 09:40 | 10:10 | ascending | 870-1350 | SMPS-$O_3$ |
| 17/07/2015 | 07:39 | 07:52 | ascending | 545-1002 | CPC-$O_3$ |
| | 07:52 | 08:29 | constant height | 999-1009 | CPC-$O_3$ |
| | 08:29 | 08:40 | descending | 999-607 | CPC-$O_3$ |
| | 08:40 | 09:25 | constant height | 599-610 | CPC-$O_3$ |
| | 09:42 | 10:51 | ascending | 517-1548 | CPC-$O_3$ |

Table S3.

| **Meteo station** | **Latitude (°N)** | **Longitude** | **Height (m a.s.l.)** |
|---|---|---|---|
| Gurb | 41.95 | 2.23 | 509 |
| Muntanyola | 41.88 | 2.18 | 816 |
| Parets del Vallès | 41.57 | 2.23 | 123 |
| Núria | 42.40 | 2.16 | 1971 |
| Sant Cugat del Vallès | 41.48 | 2.08 | 158 |
| Barcelona - el Raval | 41.38 | 2.17 | 33 |
| Barcelona - Zona Universitària | 41.38 | 2.11 | 79 |
| Castell d'Aro | 41.81 | 3.03 | 14 |
| Oliola | 41.88 | 1.15 | 443 |
| Montseny | 41.78 | 2.36 | 720 |
| Montsec | 42.05 | 0.73 | 1570 |
| Ponts | 41.91 | 1.19 | 363 |

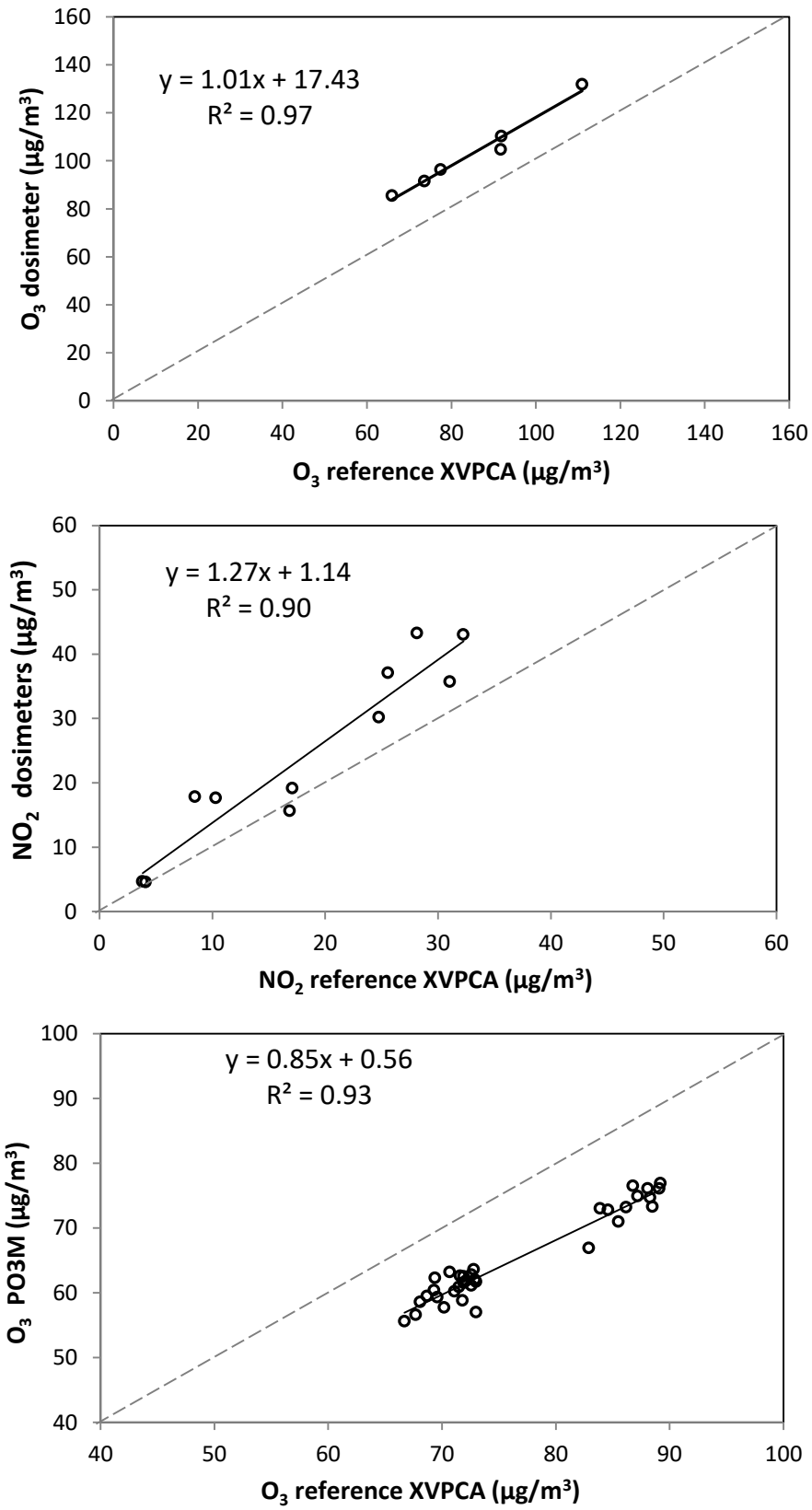
y = 1.01x + 17.43
R² = 0.97
O3 dosimeter (µg/m3)
O3 reference XVPCA (µg/m3)
y = 1.27x + 1.14
R² = 0.90
NO2 dosimeters (µg/m3)
NO2 reference XVPCA (µg/m3)
y = 0.85x + 0.56
R² = 0.93
O3 PO3M (µg/m3)
O3 reference XVPCA (µg/m3)

Figure S1.

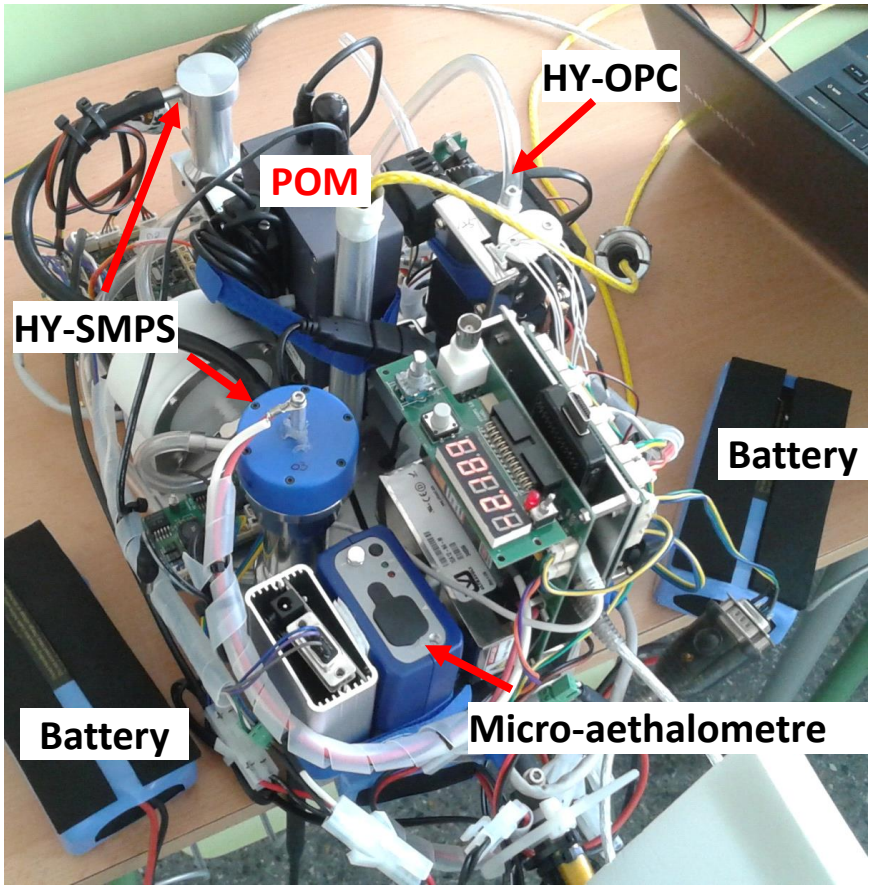


Figure S2.

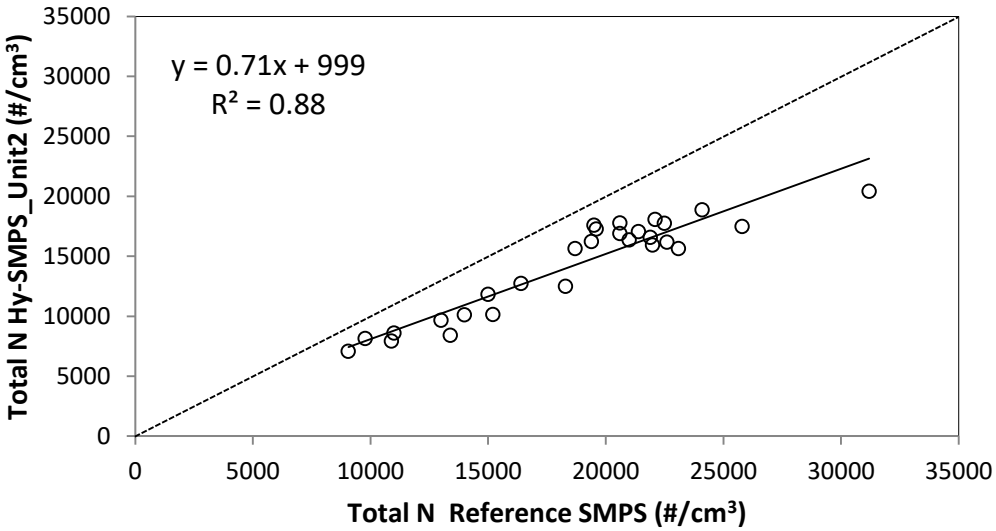


Figure S3.

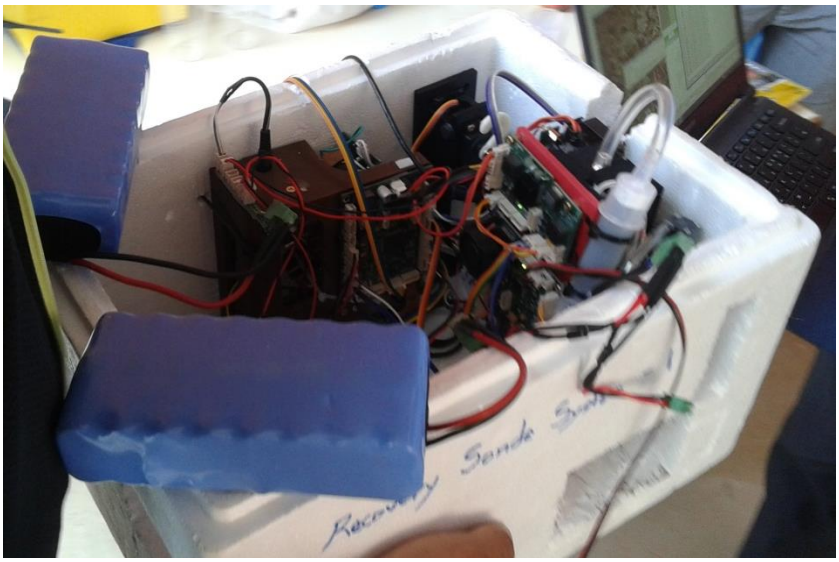

Figure S4.

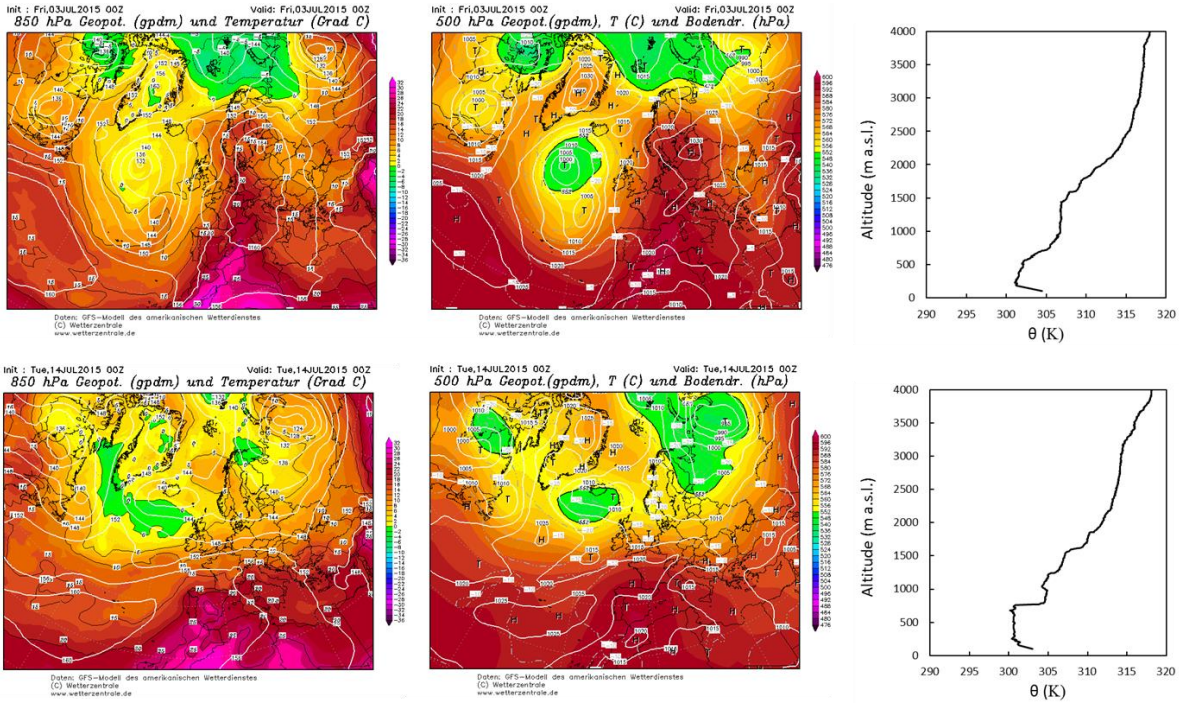


Figure S5.

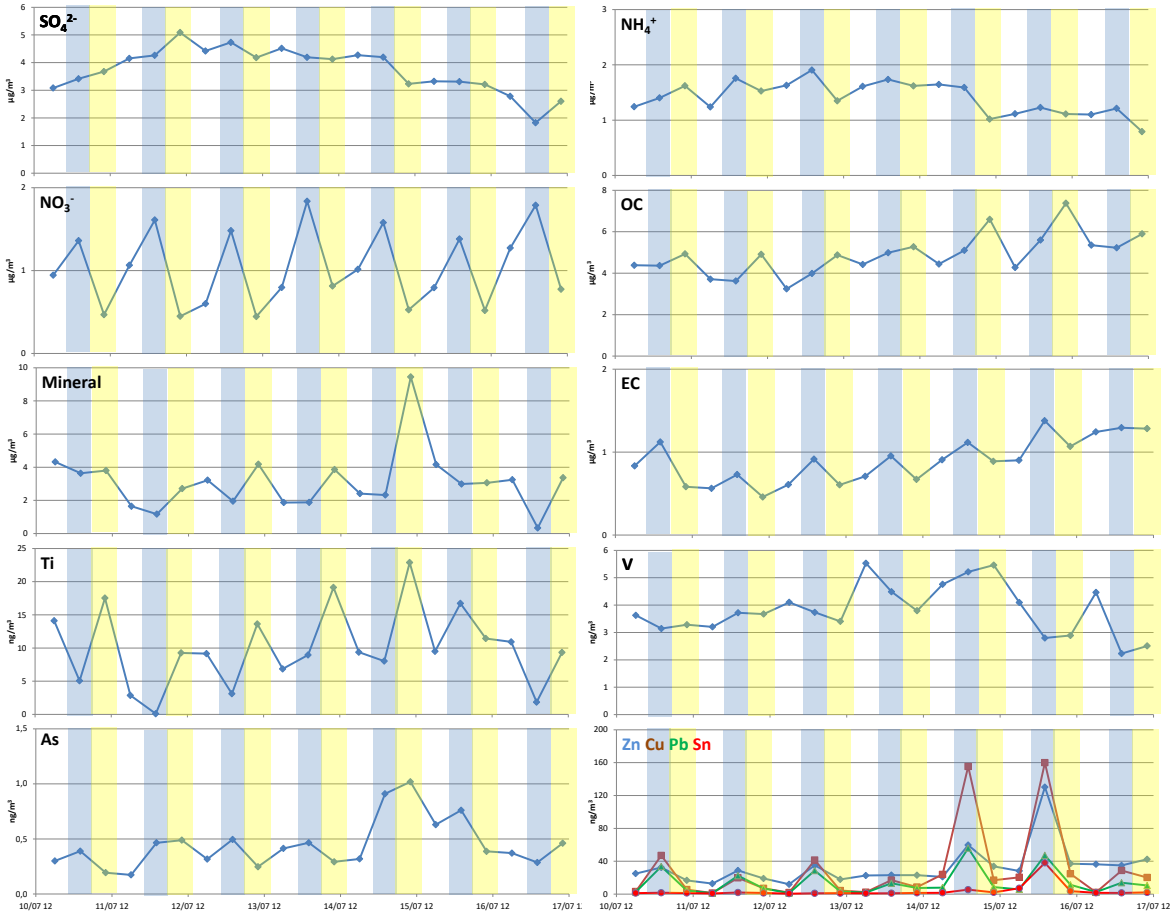
SO4 2-
NH4 +
NO3 -
OC
Mineral
EC
Ti
V
As
Zn Cu Pb Sn
µg/m³
ng/m³
10/07 12
11/07 12
12/07 12
13/07 12
14/07 12
15/07 12
16/07 12
17/07 12

Figure S6

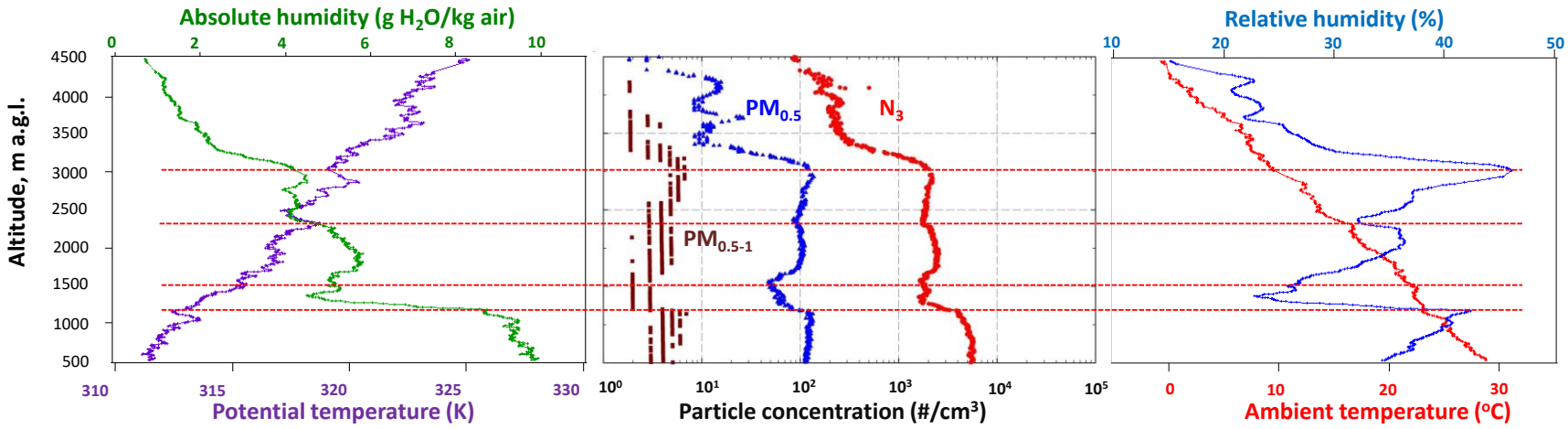
Absolute humidity (g H2O/kg air)
0
2
4
6
8
10
Altitude, m a.g.l.
4500
4000
3500
3000
2500
2000
1500
1000
500
310
315
320
325
330
Potential temperature (K)
PM0.5
N3
PM0.5-1
10⁰
10¹
10²
10³
10⁴
10⁵
Particle concentration (#/cm³)
Relative humidity (%)
10
20
30
40
50
0
10
20
30
Ambient temperature (°C)

Figure S7.

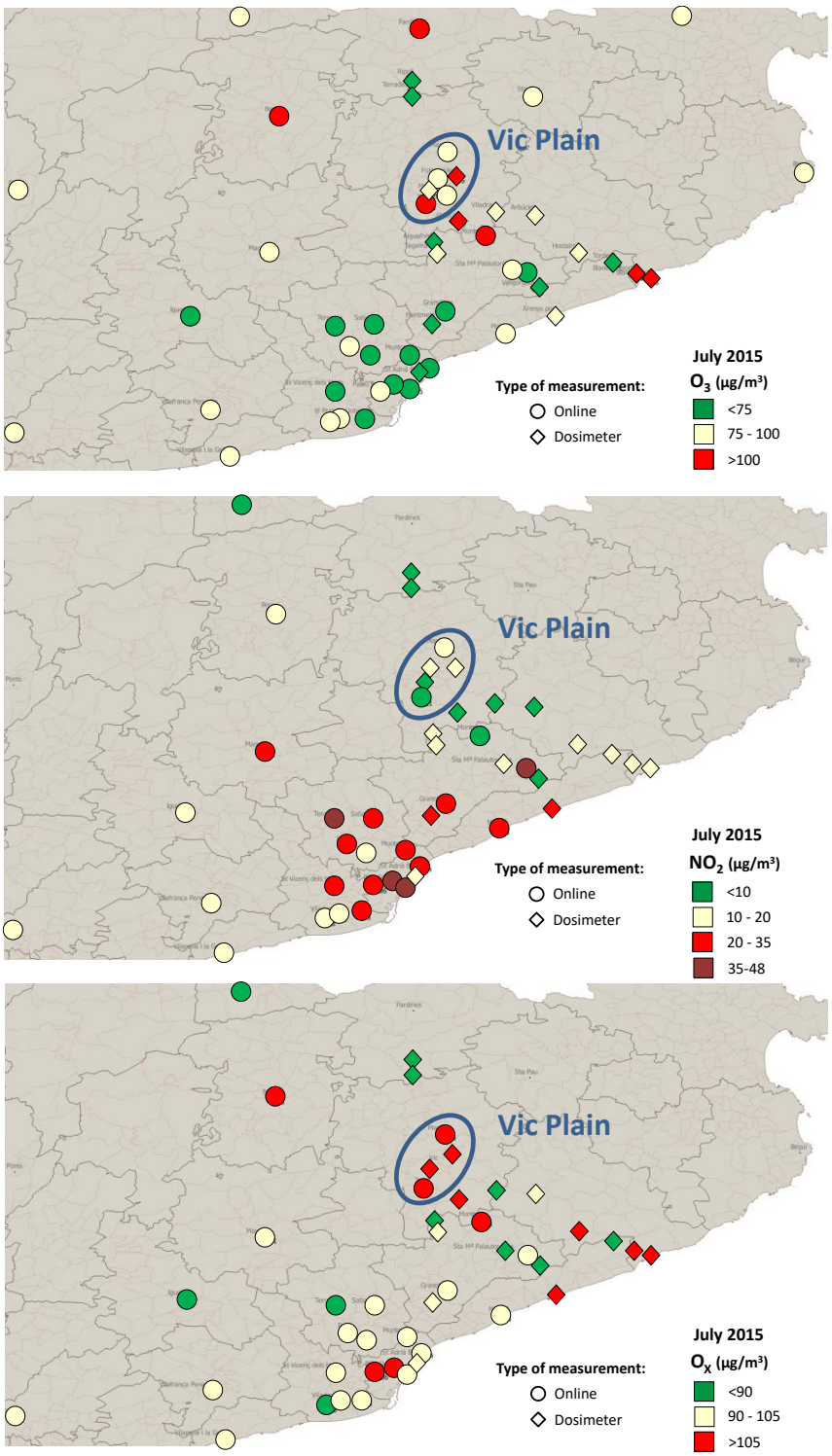
Vic Plain
July 2015
$O_3$ (µg/m³)
Type of measurement:
Online
Dosimeter
<75
75 - 100
>100
Vic Plain
July 2015
$NO_2$ (µg/m³)
Type of measurement:
Online
Dosimeter
<10
10 - 20
20 - 35
35-48
Vic Plain
July 2015
$O_X$ (µg/m³)
Type of measurement:
Online
Dosimeter
<90
90 - 105
>105

Figure S8.