

1 **Supplementary material to**

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3 **Radical budget analysis in a suburban European site**
4 **during the MEGAPOLI summer field campaign.**

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1 **Supplementary material S1: Description of OH and RO_x measurement modes,**
2 **calibration, estimation of precision and signal corrections.**

3
4 The reactants used for chemical conversion (³⁴SO₂, NO and NO₂) are injected into the reactor
5 through a set of injectors. Switching the reactant flows between the different injectors allows
6 measurements in four different modes: a background mode, two different OH radical
7 measurement modes and a RO₂ radical measurement mode. The two OH measurement modes
8 differ by the time used for the chemical conversion (see below). OH, RO₂ and H₂SO₄
9 measurements were performed by monitoring the peak intensities at m/z = 62 (NO₃⁻), m/z =
10 99 (H³⁴SO₄⁻) and m/z = 97 (H³²SO₄⁻). The detection of H³⁴SO₄⁻ and H³²SO₄⁻ corresponds to
11 the measurement of OH (or RO₂) and ambient H₂SO₄, respectively. Typically, 1 min
12 measurements for each OH or background detection mode consisted of 25 samples of 1 s at
13 m/z = 99 (OH) and 25 samples of 1s at m/z = 97 (H₂SO₄). Every 2 min OH measurements
14 included a 1 min OH signal and two 30 s background signals on both sides of the OH signal.
15 An OH detection sequence comprises 3 to 6 of OH measurement cycles of 2 min. At the end
16 of each OH detection sequence NO was switched to the corresponding injector for the
17 measurement of RO₂, typically for 1 min. For several periods the RO₂ measurements were
18 interrupted and the OH measurements were performed without addition of NO into the
19 reactor. No difference could be detected for the OH detection with NO or without it.

20 Calibration of the instrument was performed with a previously described calibration cell
21 [Kukui et al., 2008]. The calibration is based on production of controlled concentrations of
22 OH and RO₂ radicals in a turbulent flow reactor by photolysis of water vapour at 184.9 nm
23 [Heard and Pilling, 2003 and references herein; Faloon et al., 2004; Dusanter et al., 2008].
24 The concentration of the radicals generated in the turbulent flow is calculated from the
25 monitored photon flux and measured humidity. The ion peak intensities detected at m/z = 62
26 (I₆₂) and m/z = 99 (I₉₉) corresponding to the NO₃⁻ and H³⁴SO₄⁻ ions are related to the
27 concentrations of radicals R (R = OH or HO₂) produced in a calibration unit by the following
28 equation:

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$$[R] = CR \times \ln (1 + I_{97} / I_{62}) \quad (1)$$

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32 The calibration coefficients C_R can be derived from the estimated concentrations of radicals
33 produced in the flow tube, [R], and the measured I₉₇/I₆₂ ratio.

1 The overall accuracy of the calibration coefficients is estimated taking into account
2 uncertainties of all parameters used for calculation of the radical concentrations and the
3 precision of the I_{97}/I_{62} measurements [Kukui et al., 2008]. The main source of the calibration
4 uncertainty comes from the accuracy of estimation of the photon flux inside the reactor
5 depending in particular on the uncertainty of phototube sensitivity. The uncertainty (2σ) of the
6 OH calibration coefficient C_{OH} has been estimated to be 30%.

7 The calibration of HO_2 and CH_3O_2 was performed by adding CO or CH_4 into the calibration
8 cell photolysis reactor, converting OH to HO_2 or CH_3O_2 , respectively [Hanke et al., 2002;
9 Fuchs et al., 2008]. The HO_2 calibration coefficient was found to be 15% higher than that for
10 the CH_3O_2 . The total peroxy concentration was calculated with the calibration coefficient
11 average between HO_2 and CH_3O_2 , assuming that these radicals represented the major part of
12 the total peroxy radicals with approximately equal contribution. Accounting for an uncertainty
13 in the RO_2 composition, the calibration uncertainty (2σ) for the RO_2 measurements is
14 estimated to be 40% under MEGAPOLI conditions.

15 Precision of the OH and RO_2 measurements was estimated from the signals statistics during
16 the calibration measurements. For the 10 min averaged data the precision corresponding to a
17 standard random deviation was better than 10% for OH concentrations higher than 10^6
18 molecule cm^{-3} and better than 5% for RO_2 levels higher than 10^8 molecule cm^{-3} .

19 Accounting for the calibration uncertainties and measurement precision, the overall 2σ
20 uncertainty of the 10 min averaged measurements of OH and RO_2 is estimated to be 35% and
21 45%, respectively. The detection limit of 8×10^5 molecule cm^{-3} for one 2 min OH point was
22 calculated from the signal statistics in background mode at a signal to noise ratio of 3.

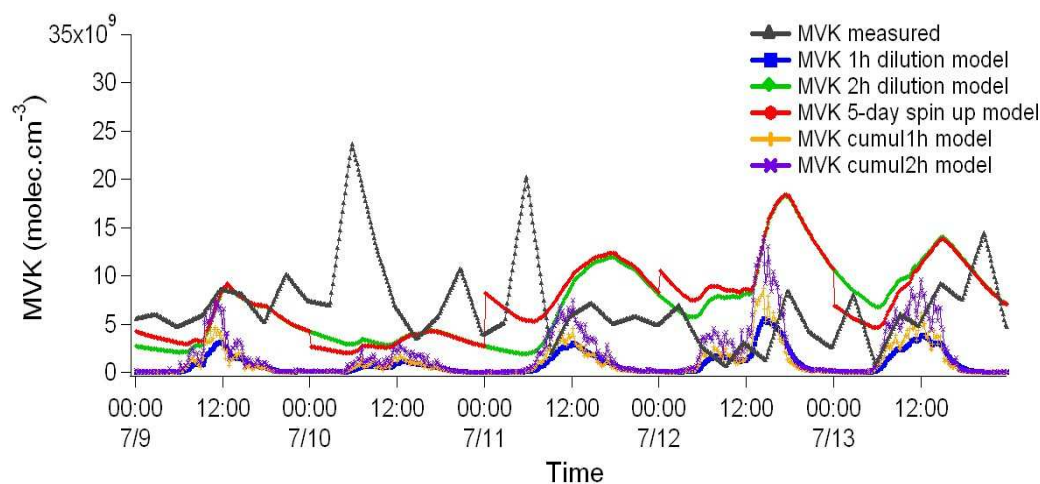
23 During the MEGAPOLI campaign rather high NO levels, up to 20 ppb, were encountered.
24 Under such conditions the OH measurements could be significantly influenced by a
25 contribution from the OH radical formed in the CCR via reaction of ambient HO_2 and NO
26 [Kukui et al., 2008]. The correction for this effect was made from a difference of the OH
27 signals measured using the “long” and the “short” modes (in preparation, will be submitted to
28 Atmos. Meas. Tech.). For most of the OH data the correction was less than 15%, but
29 sometimes under conditions of high NO_x it was as high as 35%. The correction for the
30 artificial OH formation added on average less than 5% to the overall OH measurements
31 uncertainty (2σ).

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1 **Supplementary material S2: Analysis of the estimation of unmeasured secondary VOCs**
2 **by the different versions of the model**

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4 To compare the measured secondary VOC with estimates made with the MCM model using
5 different scenarios, simulations have been performed by removing the Methyl-Vinyl Ketone
6 (MVK) constraints. The results of these simulations are shown in Fig. S2. The MVK has been
7 chosen because it usually represents a secondary product with no significant primary sources
8 and has a long lifetime (approximately 20h with OH [Cox et al., 1980]) and thus is a good
9 target species. The concentrations simulated with the various versions of the model match the
10 order of magnitude of the observed concentrations. However, no model version captures the
11 measured daily profile. The best model version can hardly be identified. However, the test
12 shows that the different model versions encompass non measured secondary species most of
13 the times.

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17 Figure S2: Observed [MVK] concentrations (black triangles) compared to concentrations
18 simulated with the three model versions used in this study: dilution model with corresponding
19 time of 1h (blue squares) and 2h (green diamonds) for the dilution loss terms, 5-day spin up
20 model (red circles) and model with 1h (orange pluses) or 2h (purple crosses) accumulation
21 for each 10 min time for the secondary unconstrained species.

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23 **Supplementary material S3: Discussion on the correlation between OH and J(O¹D)**

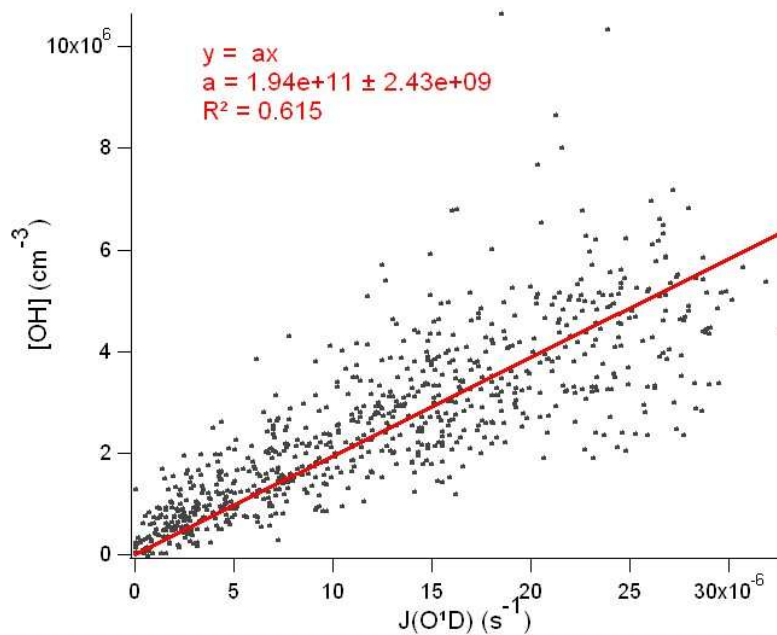
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25 As discussed in the section 4.1 of the article, the averaged diurnal variations of OH and
26 J(O¹D) show very similar behaviour. To quantify this relationship, the correlation between

1 OH and $J(O^1D)$ is shown in Fig. S3. As expected, a good correlation ($R^2 = 0.62$) was found
2 between OH and $J(O^1D)$. This correlation does not describe the direct dependency of OH on
3 photolysis frequency of ozone to O^1D but much more the general dependency of OH on
4 photolytic processes such as the photolysis of O_3 but also the photolysis of HONO, HCHO or
5 other aldehydes [Ehhalt and Rohrer, 2000; Holland et al., 2003]. The determination
6 coefficient R^2 is consistent with other studies [Creasey et al., 2001; Ren et al., 2005]. Better
7 correlations were found in rural environments during BERLIOZ [Holland et al., 2003] and
8 during a field campaign on an unpolluted site in northeastern Germany [Ehhalt and Rohrer,
9 2000] with correlation coefficient R^2 up to 0.8. In their analysis of OH data, Smith et al.
10 (2006) found that a power-dependence upon $J(O^1D)$, of the form $OH = a J(O^1D)^b$, resulted in
11 a better fit than a simple linear expression because the exponential parameter b incorporates
12 the influence of different photolytic OH sources including $J(NO_2)$ or $J(HONO)$. In our case,
13 no significant improvements of the correlation were found; R^2 being 0.62 for a linear
14 expression and 0.65 for a power expression.

15 The slope of this correlation from a linear regression fit is $1.94 \times 10^{11} \text{ s}^{-1} \text{ cm}^{-3}$ for this study
16 which is very close to the slope found during the BERLIOZ campaign [Holland et al., 2003]
17 although approximately twice lower than Ehhalt and Rohrer (2000) during the POP-CORN
18 campaign ($3.94 \times 10^{11} \text{ s}^{-1} \text{ cm}^{-3}$), both campaigns conducted in rural sites.

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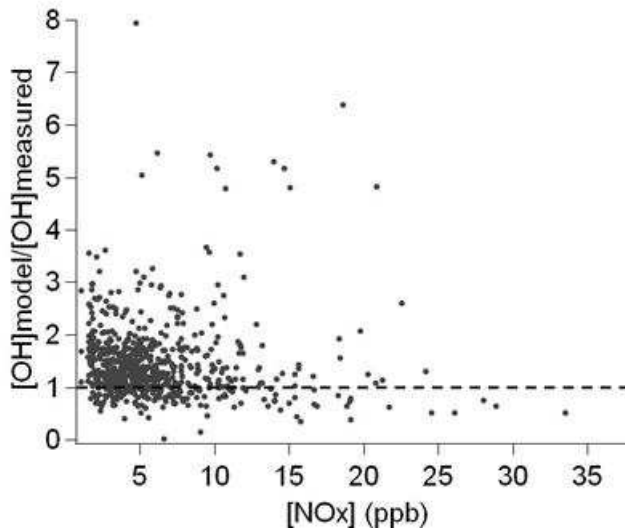
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22 Figure S3: Correlation between OH and $J(O^1D)$ during MEGAPOLI summer campaign, 09-26
23 July 2009. The correlation coefficient R^2 is 0.615 for the full data set of the studied period.

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Supplementary material S4: Variation of the modelled/measured OH concentration ratio with NO_x concentrations



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Figure S4: Variation of the ratio between modelled (with the 5-day spin up model version) and measured OH concentrations versus NO_x concentrations in ppb. The dotted line represents a ratio between modelled and measured OH concentrations of 1.

Supplementary material S5: Effect of the HO₂ and CH₃O₂ uptake on aerosol surfaces on simulated OH and RO₂ concentrations

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Simulations have been run adding an uptake of HO₂ and CH₃O₂ on aerosol surface to the 5-day spin up model. Owing to the short lifetime of OH (~1s), its uptake on aerosol surface is unlikely to affect its concentrations even with $\gamma = 1$ [Jacob, 2000], thus we have added only heterogeneous uptake of HO₂ and CH₃O₂ in the model which exhibit longer lifetimes. The heterogeneous uptake of these species is simulated using the free molecular approach described in [Sommariva et al., 2006]:

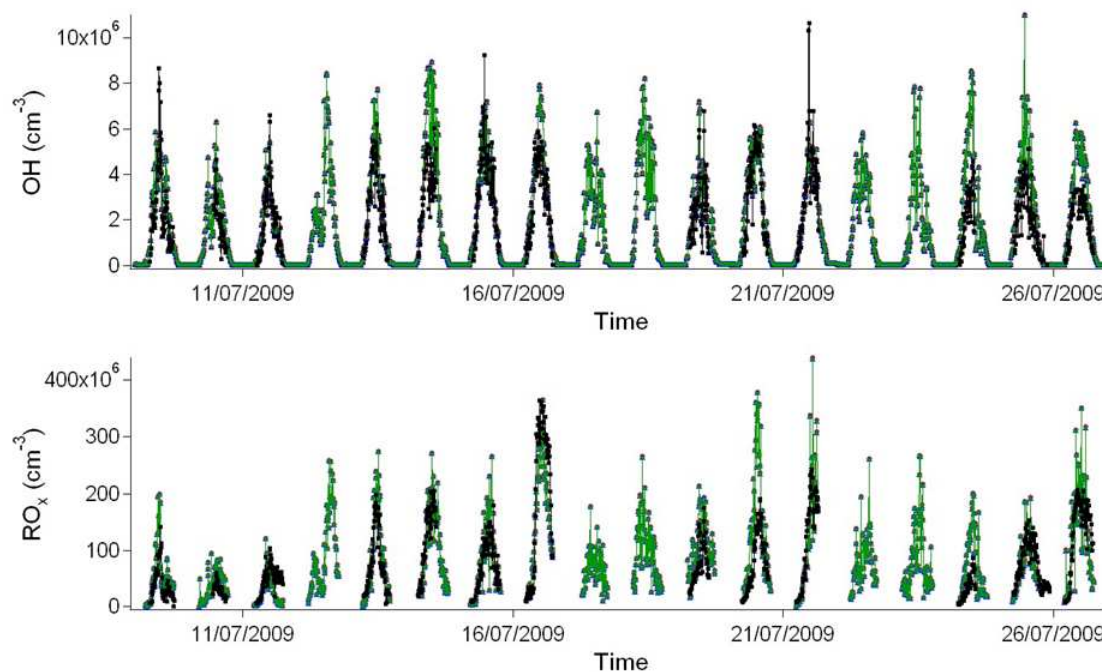
$$K_{\text{het}} = \frac{Ac\gamma}{4} \tag{2}$$

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Where A is the aerosol surface area, c is the mean molecular speed (cm s⁻¹) and γ is the reaction probability. The aerosol surface area was calculated using Aerosol Particle Sizer (APS) data. This instrument was deployed by the Paul Scherrer Institute team at the SIRTA observatory during the MEGAPOLI summer campaign. The mean aerosol surface area during

1 the study period was $2.3 \cdot 10^{-7} \text{ cm}^2 \text{ cm}^{-3}$. The reaction probability γ_{HO_2} is known to be
2 comprised in the range 0.1-1 [Jacob, 2000]. However, a recent study found γ_{HO_2} less than 0.01
3 for H_2SO_4 aerosols [Thornton and Abbatt, 2005]. We used two different values for the model
4 parameterization: 0.2 which is the value recommended in [Jacob, 2000] and 1 which is the
5 theoretical maximum. The reaction probability $\gamma_{\text{CH}_3\text{O}_2}$ used in the model was $3 \cdot 10^{-3}$
6 [Gershenson et al., 1995].

7 Under the conditions encountered during the MEGAPOLI summer campaign, the addition of
8 HOx uptake on the aerosol surface in our model does not lead to a significant improvement of
9 the simulated radical concentrations. The results of the model with the new scenarios
10 compared with the measurements are shown in Fig. S5 and the changes observed in the
11 simulated radical concentrations are shown in Fig. 13 in the article. Indeed, the major effect
12 was seen in predicted HO_2 concentrations with a reduction of 0.2% and 1.1% for a reaction
13 probability γ_{HO_2} of 0.2 and 1 respectively. The reduction of predicted OH and RO_2
14 concentrations were less important with only 0.1% and 0.4% for both OH and RO_2 for a
15 reaction probability γ_{HO_2} of 0.2 and 1 respectively. Thus, these decreases caused by the
16 addition of heterogeneous radical uptake in our model by far cannot resolve the
17 overestimation of simulated OH and RO_2 concentrations, since the aerosol surface area was
18 probably too small.



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21 Figure S5: Effect of heterogeneous uptake addition on OH and RO_2 concentrations. Black
22 squares represent the measurement, red circles represent the reference model, blue triangles

- 1 represent the base model + heterogeneous uptake with a reaction probability of 0.2 for HO₂
- 2 uptake and green diamonds represent the base model + HO_x heterogeneous uptake with a
- 3 reaction probability of 1 for HO₂ uptake. Because results are very similar, the red, the blue
- 4 and the green curves are difficult to discern.

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