Dear Editor,

We revised manuscript acp-2014-76 (Atmos. Chem. Phys. Discuss., 14, 5535–5560, 2014) in accordance with the comments by the two referees and the short comment by M. E. Jenkin. Comments and responses can be found in the author responses in the online discussion. The abstract remains unchanged.

The following changes were made in the text:

Referee #1

1) Page 5542, lines 15, 17, 21: c_{OH} was replaced by f_{OH} as recommended.

2) Page 5546, line 22: „no likely" was replaced by „not likely a".

3) Page 5540, line 24: We added one sentence explaining the background correction of measured k_{OH}: "The reported k_{OH} were corrected for wall losses within the instrument that account for loss rate coefficients of typically 1.5 s^{-1} (Nehr et al., 2012). "

4) Page 5545, line 25 ff: We extended the discussion section on the differences between high and low NO conditions as requested (also by referee #2):

"The agreement between P_{OH} and D_{OH} was slightly better at high NO concentrations. However, this difference should be treated with caution considering the experimental uncertainties and the fact that OH destruction and production rates were greater by a factor of about four under high-NO conditions, mainly caused by greater OH and NO concentrations. Possible reasons for these discrepancies are measurement artefacts and additional OH recycling processes.
Regarding the NO measurements, no problems are expected during low and high NO conditions because both concentration ranges were covered by regular calibrations using test gases. HO_2 concentrations were comparable during high and low NO conditions because HO_2 formation and destruction rates were both increased at increased NO. The same applies to RO_2 concentrations and associated potential difficulties regarding RO_2-HO_2 interferences (see Appendix). k_{OH} was also similar at high and low NO conditions and recycling of OH from HO_2 was too slow at high NO to influence the k_{OH} measurements. An unaccounted primary OH source that is specific for SAPHIR is also unlikely because that would have its greatest effect during the zero air periods when the OH budget was closed (red points in Figs. 3 and 4). However, after addition of an OH reactant under low NO conditions, OH drops strongly making these measurements more challenging. An unaccounted offset in the OH measurements could produce the observed mismatch between OH production and destruction rates, independent of the nature of the added reactant. That could explain why the ratios for CO and aromatics were mostly greater than unity under low NO conditions. In previous LIF-DOAS comparisons no such offset in the OH LIF measurements was found as mentioned above. But it has to be taken into account that also DOAS measurements are more difficult at low OH concentrations.
The differences of the ratios could also be caused by additional OH recycling via HO_2 + RO_2 reactions that gain importance under low-NO conditions. Such radical-radical reactions... "

5) Page 5544, line 27: „... and the same rate constant k_9 were used for the calculations" was added as recommended.

6) Page 5547, line 20 ff: The Appendix was revised as recommended. We included a short introduction to explain the RO_2 interference issue and rephrased lines 7-12 on page 5548. The first part of the Appendix on page now reads:

"The LIF technique can only detect OH radicals. Measurements of HO_2 and RO_2 radicals by LIF work via conversion to OH upon addition of NO. The HO_2-to-OH conversion is direct and can be made shortly before the excitation of OH within the expansion of the sample gas (Holland et al., 2003). In contrast, RO_2 has to be converted to HO_2 first which requires at least one additional O_2 reaction following the RO_2 + NO reaction. This RO_2-to-HO_2 conversion is accomplished in a pre-reactor (Fuchs et al., 2008). The different reaction times thus allow a distinction between OH from HO_2 and RO_2. However, dependent on the nature of the RO2 radicals this distinction is not complete because some RO_2 produce HO_2 too rapidly. Therefore, LIF HO_2 measurements, $[HO_2^*]$, have to be corrected for the concentration of a number of interfering RO_2 radicals ...."

7) Page 5558, caption of Table A1: „but not discriminable" was added to clarify that LIF cannot distinguish the different RO_2 species.

8) Figure enhancements: The recommended enhancement of Fig. 1 was not made because it will be enlarged anyway to fit the final upright ACP format (see revised manuscript). Fig. 2 was split into two parts that can be increased to fill a full page width each for better visibility.

Referee #2:

1) Page 5544, line 9: we included the following sentences to explain why CO was chosen as a reference compound: „CO was selected as a reference compound because its photochemistry is comparatively simple. It is unreactive towards all gas-phase species except OH and the only known product of this reaction is HO_2 under the conditions employed."
Moreover, we included a new figure (Fig. 2 of the revised version) with a collection of all OH production and destruction rates obtained in the CO experiments.

2) Table 1: We included experiment temperatures in Tab. 1.

3) Page 5545, line 25 ff: We revised the discussion on the differences between low and high NO experiments, see under Referee #1, 4).

4) Fig. 1: We put in a vertical line to indicate the injection of the aromatic, as recommended. See under Referee #1, 8) regarding figure enhancements.

5) Fig. 1: We included O_3 and NO_2 data in Fig. 1 as recommended.

Short comment by Mike Jenkin:

In response to the short comment, the paragraph in the Discussion section starting on page 5546, line 2, was revised and extended:

"The differences of the ratios could also be caused by additional OH recycling via HO_2 + RO_2 reactions that gain importance under low-NO conditions. Such radical-radical reactions that are usually thought to produce non-radical products can lead to enhanced OH recycling as

shown by recent laboratory studies for reactions of carbonyl-containing RO_2 radicals with HO_2 (Hasson et al., 2004; Jenkin et al., 2007, 2008, 2010; Dillon and Crowley, 2008; Hasson et al., 2012; Gross et al., 2014). Recently also OH formation for the reaction of HO_2 with bicyclic peroxy radicals from aromatic precursors was proposed with a rate constant k_9 as used in the previous section. This rate constant corresponds to an OH yield of about 0.5 (Birdsall et al., 2010; Birdsall and Elrod, 2011) in agreement with a conservative upper limit of 0.5 estimated previously for bicyclic peroxy radicals from benzene (Jenkin et al., 2007). However, this upper limit may have to be scaled down further in view of recent results (Jenkin, 2014) and consequently the importance of this OH source is highly speculative. In our present work, the influence of the HO_2 + RO_2 reactions could only roughly be quantified in P_{OH} by using the measured total RO_2 concentrations and the estimated rate constant k_9 from the literature. Despite these uncertainties the small effects were found to have the right magnitude and to go in the right direction. Our data are therefore not in contradiction with the proposed additional OH recycling but cannot confirm it quantitatively. In any case, RO_2 + HO_2 reactions played a minor role for the OH budget even under the low-NO conditions of this work."

Citations Jenkin et al., 2008, 2010, 2014; Hasson et al., 2012 and Gross et al., 2014 were added.