

Ref#1

This paper discusses global OH. The paper is well-written and reads smoothly. Illustrations and supplement give a large amount of interesting information. Basically, the paper describes the update of the Mainz-Isoprene-Mechanism (MIM) to MOM and additionally studies the primary formation of OH, the OH recycling (secondary OH formation) as well as HO₂. Having read the paper with great pleasure, I looked back and wondered what I learned. This uncovered several fundamental weaknesses of the paper, which are outlined below:

(1) How does MOM change the OH budget?

The paper concentrates on the current model, run for 2013. But I would like to know fundamental things like: By how much did OH increase by including low-NO_x recycling?

Is the OH abundance still compliant with the CH₄ lifetime and/or methyl chloroform analysis?

Reply:

We performed sensitivity simulations to determine the role of MOM in the OH budget, as indicated in our reply in the ACPD discussion, to answer the questions of Ref#1. These sensitivity simulations address the three principal OH recycling mechanisms. In Sect. 2 we discuss the new aspects of MOM relative to previous model versions. We added Fig. 11 and the following text to Sect. 6 (plus 3 sentences in the conclusions):

“To estimate the contributions of the three recycling mechanisms (NO_x, O_x, OVOC) to global OH and r , we performed sensitivity simulations, switching them off one-by-one. By excluding OH recycling by NO_x, the global mean OH concentration declines from 11.3×10^5 to 2.7×10^5 molecules/cm³, i.e., a reduction by 76%, while τ_{CH_4} increases from 8.5 to 21.6 years, r reduces from 67% to 42%, and the global mean production of OH drops from 4.8 to 2.8 ppbv/day. This result corroborates the great importance of this mechanism, and the sensitivity of global OH to NO_x abundance. The latter is also illustrated by Fig. 11, which shows zonal mean OH concentrations by the reference simulation and by excluding the three OH recycling mechanisms one-by-one. The NO_x mechanism clearly has the largest impact on global OH. Fig. 11 also shows that model calculated OH exhibits near-interhemispheric parity in the FT, while the NO_x mechanism leads to relatively more OH in the NH, primarily in the subtropical boundary layer. From Fig. 11 we see that the OH concentrations generated by the different mechanisms do not add up to the reference simulation, because they are complementary and partly compensate the recycling of deactivated mechanisms.

The strength of the O_x mechanism comes second in magnitude, as its omission leads to a drop in global OH from 11.3×10^5 to 5.9×10^5 molecules/cm³, i.e., a reduction by 48%, while τ_{CH_4} increases from 8.5 to 15.0 years, r reduces from 67% to 52%, and the global mean production of OH decreases from 4.8 to 3.4 ppbv/day. The overall strength of the OVOC mechanism is relatively weakest of the three. When we switch it off, global OH decreases from 11.3×10^5 to 9.7×10^5 molecules/cm³, i.e., a reduction by 14%, while τ_{CH_4} increases from 8.5 to 9.7 years, r reduces from 67% to 61%, and the global mean production of OH decreases from 4.8 to 4.2 ppbv/day. Note that in the latter sensitivity simulation we include OH recycling from HO₂ that is produced through OVOC chemistry, which would otherwise contribute to the NO_x and O_x mechanisms. The OH formation through HO₂, produced in the breakdown of VOC, accounts for about half the OH recycling by the OVOC mechanism.”

We extended the discussion about the CH₄ and methyl chloroform lifetime in Sect. 5 as follows:

“Our estimate of the mean lifetime of CH₄ due to oxidation by tropospheric OH (τ_{CH_4}) is 8.5 years, being within the multi-model calculated 1σ standard deviation of the mean of 9.7 ± 1.5 years presented by Naik et al. (2013), though towards the lower end of the range. Notice that this figure does not include uptake of CH₄ by soils and stratospheric loss by OH, O(¹D) and chlorine radicals, which together make up about 10% of the total CH₄ sink. The 17 models that participated in the model inter-comparison by Naik et al. (2013) show a range of 7.1 – 14.0 years, while the multi-model mean of 9.7 years was considered to be 5-10% higher than observation-derived estimates.

One reason for our τ_{CH_4} estimate being toward the lower end of the range may be that Naik et al. (2013) refer to the year 2000, whereas we applied an emission inventory for the year 2010, i.e., after a

period when NO_x concentrations increased particularly rapidly in Asia (Schneider and van der A., 2012) and CO concentrations decreased, most significantly in the Northern Hemisphere (Worden et al., 2013; Yoon and Pozzer, 2014). These trends in NO_x and CO may have contributed to a shift within HO_x from HO_2 to OH. Further, Naik et al. (2013) defined the tropospheric domain as extending from the surface up to 200 hPa, whereas we diagnose the tropopause height. In effect Naik et al. include part of the extratropical lower stratosphere, where τ_{CH_4} is about a century. Another reason is that our MOM mechanism more efficiently recycles OH than other VOC chemistry schemes applied in global models. This is supported by our calculation of the MCF lifetime of 5.1 years, which compares with 5.7 ± 0.9 years by Naik et al. (2013), based on a range of 4.1 – 8.4 years among the 17 participating models.”

(2) Why should we, apart from the OH budget, also analyze the HO_2 budget?

The paper analyses the HO_2 budget, but without much motivation. Concerning OH, one could argue that this is the “cleansing agent” of our atmosphere. Why HO_2 , not RO_2 , or other short-lived species of which the abundances are determined by local chemistry?

Reply: The HO_2 budget is included because the main OH conversions in atmospheric chemistry directly relate to HO_2 (e.g., reactions with NO_x , CO). HO_2 is critically important for OH recycling, which is central in our paper. Field and laboratory measurements often address both OH and HO_2 , e.g., by reporting ratios. By providing global concentration distributions and budgets of both molecules, we may help guide and interpret radical measurements, while the resulting data in turn provide important constraints for HO_x and OH studies. To meet the comment of Ref#1, we removed the HO_2 budget calculations from Table 1. In the revised manuscript we have added the following text in Sect. 4:

“Since conversions between HO_2 and OH play a key role in OH recycling, we address the budget of HO_x ($OH+HO_2$), which is dominated by HO_2 . Field and laboratory measurements often address both OH and HO_2 .”

(3) The paper discusses concepts like “tele-connections” and “buffering” without proper definitions

Maybe the largest complaint from my side. Earlier work by the authors introduced the “recycling probability”, which has at least a proper definition (the probability that OH, once formed, is recycled). However, buffering and tele-connection have not been defined in the paper and hence give freedom to use these terms for everything that is or cannot be fully quantified.

I suggest that the authors at least define and quantify terms like “buffering”. One handle could be to actually use perturbations (e.g. the transition from MIM to MOM) to investigate where OH is “buffered”. My further remarks below identify parts of the text where the text was specifically vague.

Reply: We agree that these concepts could be defined more clearly. The concept “tele-connection” is not centrally important in the present context and has been removed from the revised manuscript. However, the concept “buffering” is important and is defined by adding the following text to the introduction:

“Lelieveld et al. (2002) performed perturbation simulations of NO_x and CH_4 to compute the impact on OH. This showed that at an OH recycling probability of 60% or higher, these perturbations have negligible influence on OH (their Fig. 6). Therefore, at $r > 60\%$ the atmospheric chemical system can be considered as buffered.”

Like stated above, the paper lacks quantitative analysis. In section 4 the HO_2 budget is discussed, however, with very little justification (rather vague statements appear: “transport processes influence HO_x through longer-lived precursors and reservoir species such as O_3 and OVOC”). The authors write: “Our results suggest that HO_x is highest over tropical... and OH sinks are large”. This would call for an analysis in terms of the main photochemical path-ways (i.e. RH, CO shifting the HO_x balance towards HO_2/RO_2 , and NO/O_3 shifting the balance back through $NO/O_3 + HO_2$ OH + NO_2 , some hints of this analysis in line 26, page 7). Certainly it must be possible to provide a somewhat deeper analysis! Without such an analysis I see very little motivation to show the HO_2 budget in such detail. One driver would be the availability of atmospheric observations of HO_2 , but

this is handled by one reference in a short sentence.

Reply: For the HO₂ budget, see above. We agree that it would be interesting to study photochemical pathways, however, without losing scope and our global view of OH, as indicated in the title. Since OH and HO₂ are often studied together for good reason, it makes sense to present both. For example, the lifetime of HO₂ helps evaluate the efficiency of OH recycling, which has been made more explicit in the revised manuscript. We believe that providing the budget and distribution of HO₂ helps appreciate that of OH.

We have deepened the analysis of OH recycling mechanisms by presenting sensitivity simulations of the three main photochemical pathways, also mentioning the contribution of HO₂ in OH recycling in VOC chemistry, and by adding and discussing Fig. 11 (text, see above). In the last paragraphs of Sect. 6 we have added quantitative information about the OH recycling mechanisms.

Moreover, many statements are made from which the quantitative nature is unclear. Is this speculation, on backed by calculations? Examples: Page 6, lines 26-30: “is partly related to...are a near source aloft” Page 7, lines 28-31: “The efficient atmospheric transport...across altitudes”

Reply: The interpretation of these results does not necessarily needs to be quantitative and builds on prior articles. This paper aims at conceptual understanding of the atmospheric oxidation efficiency. Certainly this is not speculation. In the revision we refer to previous work that shows the important role of lightning over Central Africa: Tost, H., P. Jöckel and J. Lelieveld (2007) Lightning and convection parameterizations – uncertainties in global modeling. Atmos. Chem. Phys. 7, 4553-4568. For the role of stratosphere – troposphere exchange of ozone we refer to Lelieveld, J. and F.J. Dentener (2000) What controls tropospheric ozone? J. Geophys. Res. 105, 3531-3551, and for the marine boundary layer to De Laat, A.T.J. and J. Lelieveld (2000) Diurnal ozone cycle in the marine boundary layer. J. Geophys. Res. 105, 11547-11559.

Vague statements are also given on page 9, lines 7-9: The effective (?) difference in oxidation capacity (is this OH or HO_x, how defined?)...is a factor of ten, which is close to the extra-tropical seasonal cycle of HO_x. This is smaller than..., indicative of the important role of secondary (OH) formation. With this statement, the authors seem to suggest that the gradient in OH is linked to the extra-tropical seasonal cycle of HO_x, and smaller than the gradient in primary production. It took me a while, however, to decipher this sentence, and once again miss some kind of “interpretation framework” that would deepen general understanding. The main message seems to be that the seasonal cycle in OH is smaller in magnitude than the seasonal cycle in primary OH formation, a statement that is not totally surprising but for now lacks quantitative explanation and seems poorly connected to concepts like buffering.

Reply: The bottom line is that OH recycling can partly compensate the lack of primary OH production in locations and seasons where actinic radiation or water vapor concentrations are low. For clarity we changed the sentence into:

“The effective range in the mean OH concentration and τ_{CH_4} between the high- and the low-latitude troposphere is about a factor ten, which is close to the OH and HO₂ range between the summer and winter at high latitudes. This is much smaller than the low-to-high latitude gradients and the seasonal cycle of primary OH formation, indicative of the important role of secondary formation”.

Other remarks:

Page 4: Results have been evaluated (page 4, line 22): references are of 2010, after which substantial updates took place in isoprene chemistry. So that must have been different results? Please be clear about validation. The CO and O₃ comparisons in the supplement do not look very convincing.

Reply: With the three sensitivity simulations indicated above, the role of isoprene and VOC chemistry has become much clearer. We will submit a comprehensive ACP manuscript about the new isoprene chemistry soon (Taraborrelli et al., in preparation), and have updated the references. Part of the new scheme has recently been published by Cabrera-Perez et al. (2016), also using MOM. We have

extended the part on validation, e.g., by comparing with OH measurements and OH reactivity over tropical forests and by discussing the calculated MCF lifetime (see above).

Page 2, line 23: P,S, and G have unit (moles / year), please provide.

Reply: done.

Page 2, line 32: “observation-based studies”. I think it is good to mention specifically that this is based on methyl chloroform, because this suggests “OH observation-based studies”.

Reply: done.

Page 4, line 11: “in future”. This suggests that this study is based on the complete mechanism. Please say so directly, and mention that this is computationally heavy, and prevents multi-year simulations (i.e. restricting the current study to one year at T42/L31 resolution).

Reply: done.

Page 4, line 27: natural VOC emissions are 747-789 TgC/year, but we are discussion 2013 results only. So, it would be correct to give only the 2013 value here.

Reply: done.

Page 5, line 11: “may be relevant”. I would prefer “are relevant”.

Reply: done.

Page 5, line 18: “mean tropospheric OH”: unclear how troposphere is defined (from the supplement it is clear that a dynamical tropopause is calculated).

Reply: done.

Page 6, line 1: “being the main reason”. I wonder if this is true. OH in the extra-tropics is much lower than in the tropics. I cannot assess the NH/SH in the tropics, but the influence of “ITCZ”-weighting suggests a leading role of tropical OH.

Reply: This is correct, as shown in previous publications. This is also illustrated by Fig. 1.

Page 6, top paragraph. This is now rather confusing. The numbers quoted seem to refer to volume-weighted OH, which puts unrealistic weight on the stratosphere, leading to OH-parity in the integrated atmosphere. This is likely due to parity in the sinks (CO, CH₄, etc.) which show much less NH/SH differences in the stratosphere. But I would argue that the mass (or CH₄/MCF weighted) OH is the quantity to be analyzed here (see paper Lawrence et al., 2001). Table S15 clearly shows the impact of the selected weighting procedure.

Reply: It is common practice to provide the volume weighted OH. To prevent interpretation issues we also give the other metrics suggested by Lawrence et al. (2001). To prevent unrealistic weight on the stratosphere we concentrate on the troposphere and present results for the lower stratosphere separately.

Page 8, line 30-31 and further: Here the authors suggest that the slow rate of SO₂ + OH “serves a purpose in the Earth system” (??). This is rather vague again. What I get from it is that, if the reaction rate would be faster at low temperatures, tropical volcanic eruptions would deplete OH completely around the tropopause. This, in turn, would be a threat to the ozone layer, because O₃ destroying halocarbons (natural, anthropogenic?) would freely pass the tropopause. If the authors want to suggest that the ozone layer would not have been formed with a faster SO₂ + OH reaction rate

in cold conditions in a volcanically-active early Earth, they could simply quantify the impact in their model. Without further elaboration, this side note is clearly out of scope here.

Reply: The paragraph has been removed in the revised manuscript.

Page 9, lines 31-31: G is the same over the continent as over the oceans, and this would show that OH is buffered through processes in the FT. Figure 7 misses units (mol/m²/year?). This statement implies that the contrast in G of MBL and CBL is large, but these plots are not provided in the supplement. The text mentions that G is on average 3x larger in the CBL than in the MBL, and likely the S-term in G dominates, because the contrast in P is small. Nevertheless, the authors write on page 10, line 7, that S is similar over oceans and continents (in contrast to what figure 7 shows). Page 10, line 13. This actually contributes to OH buffering. Since there is no actual definition of what “buffering” is, this remains a vague statement. A definition on internet says: “Something that lessens or absorbs the shock of an impact.” In the context of OH being driven by primary and secondary formation pathways, I do not see how the “impact” is defined. Only if anything reducing primary production (O₃, radiation, water vapor) would result in enhanced recycling of OH, I would see a buffer. A proper definition and analysis of the “buffer” concept would greatly enhance the readability of the paper.

Reply: We have included units (ppbv/day), and relate the buffering to the definition that is given in the introduction of the revised manuscript (r > 60%). We agree that the sentence on land-ocean contrasts was confusing, now replaced by:

“At low latitudes G is much higher over continents than oceans, related to strong OH recycling, while at high latitudes longitudinal gradients are small, also between oceans and continents in the NH (Fig. 7).”

Page 10, line 24. Is the R² defined for the log-scale or the linear scale? This suggests linear.

Reply: Correct, this refers to a linear relationship between variables.

Page 10, line 29. Here a new concept is introduced, named a recycling efficiency, defined as (S-P)/G. Together with $G = S + P$ and $r = 1 - P/G$, it seems to me that this representation is abundant, and further complicates the discussion. The information in the left and right panels of figure 9 is therefore similar. I would suggest to avoid further definitions.

Reply: In the revised manuscript we have removed the recycling efficiency (left panels of Fig. 9).

Page 11, line 4: “The chemical buffering mechanisms include the dominant though self-limiting effect of NO_x on OH formation in polluted air.” Closer to a definition, but now introducing “chemical” and presumably also “transport-related” buffers. It has been shown that at high NO_x levels, the chemical system can enter a “run-away” regime (so definitely not buffered), in which fresh NO consumes O₃ and the formed NO₂ reacts with OH. Given the large grid-cells in EMAC, this effect will likely not occur, but bringing this mechanism as a chemical buffering mechanism seems incorrect to me. Again, the paper would profit from a clear definition and interpretation framework addressing “buffering”.

Reply: Runaway conditions have been shown in box modeling studies, while in the real atmosphere such conditions are not observed as they are quickly diluted by transport and mixing processes. This illustrates the importance of transport and mixing. Such conditions would also have reduced OH recycling probability and therefore not qualify as buffered. Please realize that even a buffered system can be perturbed so heavily that the buffering capacity is exceeded. Even if runaway conditions would occur locally, they would be of short duration and not relevant globally. In the revised manuscript we have provided an unambiguous definition of buffering.

Page 11, discussion figure 10. Now it seems that “r” is defined as “buffer”, because figure 10 illustrates how OH is buffered on the local and global scales. Further the authors write: “the complementarity of the three mechanisms is remarkable”. Is this not the case by definition as “r” is being decomposed?

Reply: In the revised manuscript we removed the word remarkable and use “r” to define buffering, as indicated above. The text has been revised to:

“Fig. 10 illustrates how OH is buffered both on local and global scales. It shows the fractional contributions of the NO_x, O_x and OVOC mechanisms to the overall recycling probability r, and indicates that the three mechanisms are complementary.”

Page 12, line 15: “Physical-chemical tele-connections”. How are these defined? I am not a fan of the word “teleconnection” because it refers to something that is only vaguely understood (we see a correlation at large distances, but we do not really understand precisely why this correlation is present). In this case atmospheric transport mixes long-lived gases through the atmosphere (O₃, CO, CH₄, PAN,...) thereby influencing remote regions with “signals” of photochemistry that occurred e.g. over regions with high natural or anthropogenic emissions (e.g. last sentence of the manuscript). This is well-understood, operates on short and long distances, and is therefore definitely not a tele-connection.

Reply: We removed reference to tele-connections in the revised manuscript.

Ref#2

This interesting and well written paper describes sources and recycling of OH and HO₂ in the EMAC model. In a few places, I found the text could benefit from clarification, and I think some additions/revisions are needed. A full budget of OH is not presented, and the three ‘OH recycling’ mechanisms are not well defined. I also found it a bit surprising that no comparison with measured values was included. The modelled methane lifetime seems quite short compared to the accepted value – this is a common feature of models, but it goes unmentioned (and I think the comparison with the real world gets worse as more recycling mechanisms are added). Direct comparison to OH/HO₂ measurements is also not evident – we are directed to other papers and the model web-site (p4 122-23), but these papers seem (from their titles) to evaluate other aspects of the model, not HO_x, and I couldn’t find any mention of the EMAC model version on the web-site. Some statements in the text appear unsubstantiated or a bit over-blown (see specific comments below). Having said all that, I think if these comments and those listed below are adequately addressed, this paper will make a very useful addition to the literature and should be accepted for publication.

In the revised manuscript we added a full OH budget, more clearly define the three OH recycling mechanisms, and extended the discussion of OH model/measurement results over tropical forest. As also requested by ref#1, we expanded the discussion on the lifetime of methane, indicating potential discrepancies with other work. Sect. 5 has been amended as follows:

“Our estimate of the tropospheric mean lifetime of CH₄ due to oxidation by OH (τ_{CH_4}) is 8.5 years, being within the multi-model calculated 1 σ standard deviation of the mean of 9.7 \pm 1.5 years presented by Naik et al. (2013), though towards the lower end of the range. Notice that this figure does not include uptake of CH₄ by soils and stratospheric loss by OH, O(¹D) and chlorine radicals, which together make up about 10% of the total CH₄ sink. The 17 models that participated in the model inter-comparison by Naik et al. (2013) show a range of 7.1 – 14.0 years, while the multi-model mean of 9.7 years was considered to be 5-10% higher than observation-derived estimates.

One reason for our τ_{CH_4} estimate being toward the lower end of the range may be that Naik et al. (2013) refer to the year 2000, whereas we applied an emission inventory for the year 2010, i.e., after a period when NO_x concentrations increased particularly rapidly in Asia (Schneider and van der A., 2012) and CO concentrations decreased, most significantly in the Northern Hemisphere (Worden et al., 2013; Yoon and Pozzer, 2014). These trends in NO_x and CO may have contributed to a shift within HO_x from HO₂ to OH. Further, Naik et al. (2013) defined the tropospheric domain as extending from the surface up to 200 hPa, whereas we diagnose the tropopause height. In effect Naik et al. include part of the extratropical lower stratosphere, where τ_{CH_4} is about a century. Another reason is that our MOM mechanism more efficiently recycles OH than other chemical schemes applied in global models. This is supported by our calculation of the MCF lifetime of 5.1 years, which compares with 5.7 \pm 0.9 years by Naik et al. (2013), based on a range of 4.1 – 8.4 years among the 17 participating models.”

With respect to OH over the forest, we added the following text:

“In the BL over tropical forests OH concentrations are comparatively low, about 10 \times 10⁵ to 20 \times 10⁵ molecules/cm³, in agreement with OH measurements in South America and Southeast Asia (Kubistin et al., 2010; Pugh et al., 2010; Whalley et al., 2011).”

We will submit a comprehensive ACP manuscript about the new biogenic VOC chemistry soon (Taraborrelli et al., in preparation), while one on the new anthropogenic aromatics chemistry has been published by Cabrera-Perez et al. (2016) who also use MOM.

Specific comments
P1 126 Spivakovsky

Reply: changed.

P2 14 combine, not recombine

Reply: changed.

P2 17 This sentence implies RH features in the previous equation(s), but it doesn't?

Reply: has been reformulated.

P2 123 I find the definition of 'r' ($= 1 - P/G$) a bit obscure. Isn't $r = S/G$ clearer?

Reply: In our paper of Lelieveld et al (2002) we defined the recycling probability r by solving the differential equation dOH/dt with a Taylor series expansion. We would like to maintain this definition for consistency.

P3 Paragraph from 129 onwards. This paragraph is perhaps not immediately comprehensible to most readers. I suggest you try and make it a bit less technical/more accessible.

Reply: We changed it into:

“An important pathway in isoprene chemistry, basic to the recycling of OH, is isomerization through H-migration within oxygenated reaction products, leading to photo-labile hydroperoxy-aldehydes (HPALD), as reviewed by Vereecken and Francisco (2012).”

P4 112 ...notably FOR carbon...

Reply: changed.

P4 130 ...in SOME previous... (Not all previous atmospheric chemistry-transport models have had to artificially reduce natural VOC emissions.)

Reply: changed.

P5 111 may be -> are

Reply: changed.

P7 113 Plane -> Plain

Reply: changed.

P7 125 "...tropospheric production of HO₂ – and thus HO_x..." I don't think this follows. Isn't most HO₂ production associated with OH destruction (i.e. HO_x recycling, e.g., R3 and R4)? Production of HO_x is thus only primary production of either OH or HO₂ (i.e. from R1/R2 and HCHO photolysis), whereas production of HO₂ is dominated by conversion of OH to HO₂. Thus production of HO_x and production of HO₂ are quite different.

Reply: changed.

P8 111 Dividing better than 'relating'.

Reply: changed.

P8 123 I wondered what "strongly underestimated" meant here (it is rather non-specific). I would say normally something that is strongly underestimated is 50% or less of its correct value. From your budget in Figure 6, if the VOC reactions were simplified/not included, I don't think OH reactivity would be underestimated by as much as 50%. So I think you are being over-dramatic and non-quantitative, which is unhelpful.

Reply: Actually we are not exaggerating, as Mogensen et al (2015) identified "missing OH reactivity" in the boreal forest to be about 65% and Whalley et al. (2011) and Nölscher et al. (2016) up to a

factor 10 in the tropical forest. We have added the references to Mogensen et al. and Whalley et al. and the numeric value of a factor of 10 to the revised manuscript.

P8 I29 ‘...indicates that air masses that traverse the TTL into the stratosphere have been largely cleansed from compounds that react with OH’. This seems like overstatement – aren’t CO and CH₄ the two main compounds that react with OH in the troposphere? I don’t think TTL air is ‘largely cleansed’ of these two gases?

Reply: The formulation has been changed into:

“While this is largely related to low temperatures and reduced reaction rates, it also indicates that air masses that traverse the tropical transition layer into the stratosphere are cleansed from reactive compounds that are removed by OH, for example organo-halogen compounds that could damage the ozone layer.”

P8 I30 onwards. The ‘side note’ about SO₂, OH, halocarbons and stratospheric O₃ seems a bit odd.

Reply: Also in view of the critical remarks by Ref#1 this paragraph has been removed.

P9 I3 onwards. The discussion of the methane lifetime (to oxidation by OH) of 8.5 years in the model should also be compared to observational estimates (e.g., Prather et al., 2012: 11.2 ± 1.3 yr). Pretty much all models, and EMAC with MOM seems not to be an exception, apparently underestimate the methane lifetime. Do we have any idea why this is? It seems that we need less OH in model’s atmospheres, but by adding new OH sources from recycling this discrepancy gets worse. Doesn’t this suggest that models are missing something fundamental about OH?

Reply: Prather et al. (2012) derive a CH₄ lifetime of 9.1±0.9 yr, and indicate this is 5% higher than the multi-model mean, as presented in the IPCC (2007) AR4 assessment, being 8.7±1.3 yr. Our estimate is somewhat less (8.5 yr) but still consistent. Prather et al. (2012) relate their CH₄ lifetime to that of methyl chloroform, hence also associated with uncertainty. For example, it is not well known how much methyl chloroform is exchanged with the oceans. Calibrating global OH to a “standard” remains to be a problem, also in view of OH and methyl chloroform distributions. We will probably have to live with some uncertainty, which we nevertheless hope to reduce further in a collaboration project with Wageningen University (Maarten Krol) and NOAA-ESRL (Steve Montzka). In the revised manuscript we have expanded the text as indicated in our reply to the first comments, which discusses the methane lifetime.

P9 I31 ‘...over the oceans G is the same as over the continents.’ G is defined earlier (p2 I23) as ‘gross OH formation’. I am unclear whether you mean G over the oceans as a whole compared to G over the continents as a whole, or if you mean per unit area. Obviously this makes a big difference.

Reply: We have replaced the ambiguous formulation with the following sentence:

“At low latitudes G is much higher over continents than oceans, related to strong OH recycling, while at high latitudes longitudinal gradients are small, also between oceans and continents in the NH (Fig. 7).”

P10 I7 ‘...S is also the same over the oceans and continents...’ Same query as previous.

Reply: This has been changed into:

“Consequently, on average S is also the same over oceans and continents,...”

P10 I11 ‘...P declines steeply with solar radiation and water vapor.’ Figure 7 show that P declines steeply with increasing altitude (ignoring the stratosphere) and latitude. Water vapor declines with increasing latitude and altitude (so that’s OK). Solar radiation declines with increasing latitude, but increases with increasing altitude. So the relationship of P with solar radiation seems more complex than stated.

Reply: We have reformulated into:

“Comparison of the middle and lower panels in Fig. 7 shows that spatial gradients of P and S can be rather different, e.g., towards high latitudes with P falling off with solar radiation and water vapor, while the latter also declines with altitude.”

P10 I30 ‘is subordinate to’ -> is less than?

Reply: changed into “less than”

P11 I1-2 Isn't ‘r’ larger in the extra-tropics mainly just because P is small?

Reply: We changed the sentence into (added “relatively”):

“Fig. 9 shows that r is relatively larger in the extra-tropics than in the tropics, and largest at high latitudes.”

P11 I2 The last sentence is true for the MBL but not the CBL, so it is incorrect for the BL as a whole.

Reply: Has been corrected.

P11 I4-13 Some clarification of what is exactly meant by the NO_x, O₃ and OVOC ‘mechanisms’ of OH recycling is needed. The earlier reaction equations and discussion is very good and useful, but I am not completely clear on which reactions make up each mechanism.

Reply: In the revised manuscript we have more clearly defined the three recycling mechanisms, notably in the Introduction and by referring to Fig. 6. For example, referring to Fig. 6 we mention in the revised text:

“S is subdivided into contributions by the NO_x mechanism (R7, blue), the O_x mechanism (R11 and R12; green and yellow, respectively) and all OH recycling in VOC chemistry, the OVOC mechanism (red).”

P11 I13 Do you mean from the FT to the BL (rather than ‘transport in the FT’)?

Reply: We have changed the sentence into:

“Hence the O_x mechanism depends on replenishment of O₃ through transport in the FT and subsequent mixing into the BL.”

P11 I17 ‘The complementarity of the three mechanisms is remarkable.’ Is it? Don't they have to add up to 100% by definition? Figure 10 is certainly interesting, but I am not sure it is ‘remarkable’. As suggested earlier, clearer definitions of the three mechanisms would help the discussion.

Reply: We have deleted the word remarkable, and have more clearly defined the three mechanisms through reference to Fig. 6.

P12 I4 Have you demonstrated in this paper that including MOM ‘increases OH reactivity’? I can believe this is the case, but I don't think you present evidence of what the OH reactivity was in the model before you included MOM.

Reply: In the revised manuscript we refer to Nölscher et al. (2016).

P12 I13 I note your reference to ‘measurement campaigns’. There is no comparison with observations in this paper, which seems like an oversight. Can you demonstrate that modelled OH is improved and compares well to reality?

Reply: In the past our model simulated OH over the tropical forest was a factor of 2-3 too low compared to measurements, whereas with MOM the agreement has much improved. This will be discussed in detail by Taraborrelli et al. (in preparation), and has been partly discussed in Cabrera-

Perez et al. (2016). In the revised manuscript we have included the following text:

“Modeled OH concentrations over the tropical forest are about $1-2 \times 10^6$ molecules/cm³, in agreement with OH measurements in South America and Southeast Asia (Kubistin et al., 2010; Pugh et al., 2010; Whalley et al., 2011).”

P18 Table 1. The caption doesn't adequately describe the table – which contains fluxes for HO_x primary production (O₁D+H₂O), recycling (NO+HO₂, O₃+HO₂, photolysis reactions) and loss (H₂O₂ deposition). This table could be more comprehensive, and describe the full OH and HO₂ budgets, i.e. include all the primary sources, OH to HO₂ inter-conversions, and sinks (e.g., Derwent, 1996). The sources and sinks should balance (this is not obvious from the current table). If this were done, it could also clarify the definitions of the three mechanisms, as suggested earlier.

Reply: We assume ref#2 refers to Fig. 1 in Derwent (1996), which is similarly structured to Fig. 2 in Lelieveld et al. (2002). In the revised manuscript we have completed Table 1 with sources and sinks of OH, to present a full budget (and checked that sources and sinks balance).

We changed the caption into:

“Global, annual mean tropospheric source and sink fluxes of OH (Tmol/yr). Sources and sinks are also specified for the boundary layer and free troposphere.”

P19 Figure 1 (and all zonal mean plots). It looks like surface pressures go up to 1000 hPa everywhere, but that can't be the case over Antarctica (etc.). Is the vertical scale really pressure?

Reply: This is correct. Hence the lower levels over Antarctica in the zonal plots are white. Since we are presenting zonal averages some areas up to 1000 hPa occur almost everywhere, except Antarctica.

P21 Figure 6. Related to my comments on Table 1 – I note the caption says 'Main' production terms of OH... Wouldn't a figure that shows all the OH sources be more useful?

Reply: Considering the comprehensive chemistry scheme in MOM, the figure would become complicated in the VOC part of the pies. The aim of such a figure is to provide an overview of the main production terms, i.e., primary formation and the three main OH recycling mechanisms. For the more detailed description of the OVOC fluxes of OH we refer to Taraborrelli et al. (this will be the main topic of that paper). We have provided additional discussion on the three recycling mechanisms in Sect. 6, which fits to Fig. 6 and Table 1.

P24 Figure 9. The text defines recycling efficiency as (S-P)/G. This allows it to take on negative values (where P>S). I find this a bit confusing, as efficiency normally refers to a number between 0-100%. The recycling probability (S/G) does just go from 0-100%. I'm not sure you need both quantities?

Reply: In the revised manuscript we have removed the recycling efficiency (left panel of Fig. 9).

P25 Figure 10. Again, clear definitions of the three mechanisms are needed.

Reply: This has been remedied in the revised manuscript.

Ref#3

This paper discusses the global OH atmospheric chemistry and analyzes the levels and chemical properties and the recycling of OH and HO₂ using the global modelling system EMAC. The paper reads smoothly at the most part, providing a lot of information on the chemistry of OH, and an abundance of results both in the main manuscript and the supplementary material.

General Comments

The abstract should be more precise on what the main findings of this work are. The predecessor model as well as the previously assumed amounts of secondary sources should be specifically mentioned here.

Reply: We have added the following to the abstract:

“By accounting for the complete breakdown products of higher VOCs, MOM is mass conserving, and calculates substantially higher OH reactivity from VOC oxidation compared to predecessor models. Whereas previously P and S were found to be of similar magnitude, the present work indicates that S may be twice as large, mostly due to OH recycling in the free troposphere. ... With an OH recycling probability of about 67%, global OH is buffered and not sensitive to perturbations by natural or anthropogenic emission changes.”

The terms “buffering” and “buffered” are used throughout the manuscript without proper definition given. Even after reading the entire manuscript it remains uncertain what the OH buffer actually is. The entire manuscript is based on the calculations made using an unpublished chemical mechanism (MOM) which is an update of a previous mechanism (MIM) using as reference a manuscript that is in preparation. Even though the full mechanism is included in the Supplementary material of the manuscript, a comparison of the model results using the updated mechanism to results of the previous mechanism and a more detailed comparison to measurements is needed. Also a better more complete budget analysis as well as a comparison and highlight of the differences between the two versions is clearly missing, especially since the authors give relative results such as “higher”, or “compared to predecessor models”.

Reply: We have added the following definition of buffering to the introduction, and evaluate our results accordingly:

“Lelieveld et al. (2002) applied perturbation simulations of NO_x and CH₄ to compute the impact on OH. This showed that at an OH recycling probability of 60% or higher, these perturbations have negligible influence on OH (their Fig. 6). Therefore, we argue that at $r > 60\%$ the atmospheric chemical system can be considered as buffered.”

In the revised manuscript we have presented a more complete budget (Table 1) and compare results with previous work.

The model description is rather short and feels incomplete. The EMAC modeling system is a complex system with a variety of options. The specific sub models used as well as the input used for the present study (i.e. emissions) should be clearly mentioned in the manuscript even if there is a small analysis in the supplementary material. The choice of RCP8.5 that suggests no further emission control also seems strange as it is often used to simulate the worst-case scenario. Even if in the year of interest (2013) the differences from the other scenarios are small, it still is an interesting choice and one that normally should be justified.

Reply: In the revised manuscript we provide additional model description, based the model version published by Jöckel et al. (2010), with modifications that have been documented by Yoon and Pozzer (2014) and Cabrera-Perez et al. (2016), who also used MOM.

Page 17 of the supplement provides a detailed list of emission fluxes applied in the model. While the RCP8.5 scenario is a business-as-usual scenario for CO₂ emissions, it is more conservative for reactive trace gases and generally conceived as more realistic than the other scenarios. In Sect. 2 we have added a description of the RCP8.5 scenario and included additional model description and references.

Finally I would suggest that a label is added by the colorbar of all figures, indicating the depicted property/substance and the units. This would make the interpretation of the figures quite easier.

Reply: In the revised manuscript we have added labels to the figures.

Specific Comments

P1, L10: ...may be significant... ! change to something more precise, or explain the reason that they might not be significant.

In all the reactions: Add the radical sign (dot) where necessary.

Reply: We have added the following sentences:

“Whereas previously P and S were found to be of similar magnitude, the present work indicates that S may be twice as large, mostly due to OH recycling in the free troposphere. ... With an OH recycling probability of about 67%, global OH is buffered and not sensitive to perturbations by natural or anthropogenic emission changes.”

While adding dots to radicals is generally good practice in chemistry, it is not common in atmospheric chemistry publications. One would have to do it with OH, but also other radicals, which can become problematic for larger molecules. We have added the following to the text:

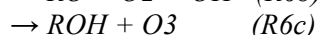
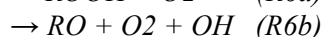
“Note that the formal notation of hydroxyl is HO[·], with one unpaired electron on the oxygen atom. For brevity we omit the dot and use the notation OH, and similarly for other radicals.”

P3, L25: R6 does not directly produce OH, hence a more clear explanation of how OH is produced is needed.

Reply: We have added the complete list of reaction channels for R6, and changed



into



and on p.3 line 25 we refer to R6b.

P3, L26: While in polluted air peroxy.... ! While in polluted air, peroxy...

Reply: the comma does not belong here; has been changed

P4, L15: By interconnected, do you mean coupled? If yes, the more used (and easier to understand) term should be used. If not, please give a definition of what an interconnected sub model is.

Reply: replaced by coupled.

P4, L27/28: Since only one year of results is presented (2013), why is a range of emitted quantities provided?

Reply: We have performed a 4-year simulation and only show the last year. In the 4-year period the online calculated emissions vary somewhat. We have specified this in the revised manuscript.

P5, L24/25 and elsewhere in the manuscript: Add the 105 term to the first number of all ranges.

Reply: done

P5, L27: Give the numbers calculated by Patra et al., since the discussion is based on them.

Reply: Patra et al. conclude inter-hemispheric parity (is in the title of their publication).

P7, L4: Reaction R1 of the manuscript should be referenced here.

Reply: done

P7, L7/8 and figure 2 caption: scaled down by a factor of 20.

Reply: mentioned in the figure (units added)

P7, L28/29: O3 from the stratosphere and O3 from photochemically... ! O3 from both the stratosphere and photochemically...

Reply: has been changed

P12, L15: The Physical-chemical tele-connections is here used without prior definition. Please give a clear definition.

Reply: In the revised manuscript we refrained from using the work tele-connection.

Figure 5: Add the OH reactivity zonal means (latitudinal) since the height distribution is mentioned during the discussion in section 5.

Reply: done

Figure 6: Enlarge the third panel of the figure since it is quite difficult to read the numbers in it. Also review the percentages given here since the numbers (as they are provided now) do not add up: e.g. for the OVOCs (red) the FT is 12% and the BL 19%. Multiplied by the 86% and 14% ratios respectively it gives a total of 13% (12.98) in the troposphere, where you present 12%. Maybe give the numbers with at least one decimal point so that the math comes out correct.

Reply: We have enlarged the numbers in the third panel for readability and double-checked the numbers; slight inconsistencies may arise from truncation, which should not be a problem, but in the table the OH budget is closed. Additional decimal numbers would suggest a level of accuracy that does not do justice to the meaning of our results, which aims at conceptual understanding of OH recycling.

Global tropospheric hydroxyl distribution, budget and reactivity

J. Lelieveld¹, S. Gromov¹, A. Pozzer¹, and D. Taraborrelli¹

¹Max Planck Institute for Chemistry, P.O. Box 3060, 55020 Mainz, Germany

Correspondence to: J. Lelieveld (jos.lelieveld@mpic.de)

5 **Abstract.** The self-cleaning or oxidation capacity of the atmosphere is principally controlled by hydroxyl (OH) radicals in the troposphere. Hydroxyl has primary (*P*) and secondary (*S*) sources, the former through the photo-dissociation of ozone, the latter through OH recycling in radical reaction chains. We used the recent Mainz Organics Mechanism (MOM) to advance volatile organic carbon (VOC) chemistry in the general circulation model EMAC, and show that *S* is larger than previously assumed. By accounting for the complete breakdown and intermediate products of higher VOCs, MOM is mass
10 conserving, and calculates substantially higher OH reactivity from VOC oxidation compared to predecessor models. Whereas previously *P* and *S* were found to be of similar magnitude, the present work indicates that *S* may be twice as large, mostly due to OH recycling in the free troposphere. Further, we find that nighttime OH formation may be significant in the polluted subtropical boundary layer in summer. With a mean OH recycling probability of about 67%, global OH is buffered and not sensitive to perturbations by natural or anthropogenic emission changes. Complementary OH formation mechanisms
15 in pristine and polluted environments in the continental and marine troposphere, connected through long-range transport of O₃, maintain stable global OH levels.

1 Introduction

The removal of most natural and anthropogenic gases from the atmosphere, important for air quality, the ozone layer and climate, takes place through their oxidation by hydroxyl (OH) radicals in the troposphere. The central role of tropospheric
20 OH in the atmospheric oxidation capacity (or efficiency) has been recognized since the early 1970s (Levy, 1971; Crutzen, 1973; Logan et al., 1981, Ehhalt et al., 1991). The primary OH formation rate (*P*) depends on the photo-dissociation of ozone (O₃) by ultraviolet (UV) sunlight – with a wavelength of the photon (*hν*) shorter than 330 nm – in the presence of water vapor



(Note that the formal notation of hydroxyl is HO·, indicating one unpaired electron on the oxygen atom. For brevity we omit the dot and use the notation OH, and similarly for other radicals.) Since the stratospheric ozone layer in the tropics is relatively thin, UV radiation is less strongly attenuated compared to the extra-tropics, and also because the solar zenith angle

and water vapor concentrations are relatively high, zonal OH is highest at low latitudes in the lower to middle troposphere (Crutzen and Zimmermann, 1991; Spivakovski et al., 2000).

The OH radicals attack reduced and partly oxidized gases such as methane (CH₄), non-methane volatile organic compounds (VOCs) and carbon monoxide (CO), so that these gases only occur in trace amounts, e.g.,

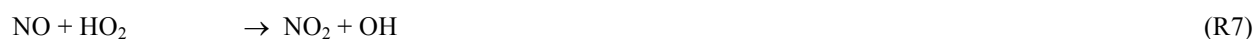


where M is an air molecule that removes excess energy from reaction intermediates by collisional dissipation. Because OH is highly reactive it has an average tropospheric lifetime of about 1-2 seconds. After the initial OH reaction (R3) peroxy radicals are produced (R4), which can combine to form peroxides



RH is a VOC that produces a radical R upon H-extraction by OH, e.g., an alkyl radical, that reacts with O₂ to form RO₂.

15 After formation of a peroxide the reaction chains can either propagate or terminate, the latter by deposition. Propagation of the chain leads to higher generation reaction products and secondary OH formation (*S*), which can be understood as OH recycling. For example, the photolysis of ROOH leads to OH production. In air that is directly influenced by pollution emissions *S* is largely controlled by nitrogen oxides (NO+NO₂=NO_x)



20 **This reaction, referred to as the NO_x recycling mechanism of OH,** also leads to ozone production through photo-dissociation of NO₂ by ultraviolet and visible light



25 However, in strongly polluted air NO₂ can locally be a large OH sink, and in such environments the net effect of NO_x on OH is self-limiting through the reaction



Conversely, under low-NO_x conditions, mostly in pristine air, secondary OH formation by other mechanisms is important



30 **These reactions are referred to as O_x recycling mechanism of OH.** In prior work we suggested that the strong growth of air pollution since industrialization, especially in the 20th century, has drastically changed OH production and loss rates, but that globally the balance between *P* and *S* changed little (Lelieveld et al., 2002). This is associated with a relatively constant OH recycling probability *r*, defined as $r = 1 - P/G$, in which *G* is gross OH formation ($G=P+S$); *P*, *S* and *G* have unit moles/year.

We computed that globally r changed little since pre-industrial times, remaining at about 50%. Thus, in the past century G (the atmospheric oxidation power) kept pace with the growing OH sink related to the emissions of reduced and partly oxidized pollution gases. Lelieveld et al. (2002) performed perturbation simulations, applying pulse emissions of NO_x and CH_4 , to compute the impact on OH. This showed that at an OH recycling probability of 60% or higher, these perturbations have negligible influence on OH (their Fig. 6). Therefore, at $r > 60\%$ the atmospheric chemical system can be considered to be buffered.

While globally r has remained approximately constant, the mean tropospheric OH concentration and the lifetime of CH_4 (τ_{CH_4}) have also changed comparatively little, for example within a spread of about 15% calculated by a 17-member ensemble of atmospheric chemistry-transport models (Naik et al., 2013). Despite substantial differences in OH concentrations and τ_{CH_4} among the models, simulations of emission scenarios according to several Representative Concentration Pathways indicate that future OH changes will probably also be small, i.e., well within 10% (Voulgarakis et al., 2013). We interpret the relative constancy of r , mean OH and τ_{CH_4} as indication that global OH is buffered against perturbations. This is corroborated by studies based on observations of methyl chloroform, with known sources and OH reaction as the main sink, showing small inter-annual variability of global OH and small inter-hemispheric difference in OH (Krol and Lelieveld, 2003; Montzka et al., 2011; Patra et al., 2014).

For our previous estimates of P and S we used a chemistry-transport model with the Carbon Bond Mechanism (CBM) to represent non-hydrocarbon chemistry (Houweling et al., 1998). This mechanism aggregates organic compounds into categories of species according to molecular groups, and has been successfully used to simulate ozone concentrations with air quality models (Stockwell et al., 2012). However, such chemical schemes are not mass-conserving, e.g., for carbon, and are optimized for conditions in which NO_x dominates r , while in low- NO_x environments other mechanisms may be important, for example through the chemistry of non-methane VOCs emitted by vegetation (Lelieveld et al., 2008), as reviewed by Vereecken and Francisco (2012), Stone et al. (2012) and Monks et al. (2015). A limitation of the CBM and other, similar mechanisms is that 2nd and higher generation reaction products are lumped or ignored for computational efficiency, whereas they can contribute importantly to OH recycling and ozone chemistry (Butler et al., 2011; Taraborrelli et al., 2012).

Here we apply the Mainz Organics Mechanism (MOM) that accounts for recent developments in atmospheric VOC chemistry (Taraborrelli et al., manuscript in preparation). The MOM is a further development of the Mainz Isoprene Mechanism (Taraborrelli et al., 2009, 2012). In addition to isoprene, MOM computes the chemistry of saturated and unsaturated hydrocarbons, including terpenes and aromatics (Cabrera-Perez et al., 2016). We use it to estimate the role of radical production through reactions of oxidized VOC, referred to as OVOC recycling mechanism of OH, being contrasted with the NO_x and O_x recycling mechanisms of OH. Based on this scheme, implemented in the atmospheric chemistry – general circulation model EMAC, we provide an update of global OH calculations, sources, sinks, tropospheric distributions, OH reactivity, the lifetime of CH_4 and CO, and discuss implications for atmospheric chemistry. We contrast the boundary layer and free troposphere (BL and FT), the Northern and Southern Hemisphere (NH and SH) and the tropics and extra-

tropics. We show that complementary OH recycling mechanisms in terrestrial, marine, pristine and polluted environments, inter-connected through atmospheric transport, sustain stable levels of hydroxyl in the global troposphere.

2 VOC chemistry and model description

To reconcile observations of high OH concentrations over the Amazon rainforest with models that predicted low OH concentrations, we have proposed that the chemistry of isoprene recycles OH, e.g., involving organic peroxy radicals (Lelieveld et al., 2008). Progress on such reactions was reported by Taraborrelli et al. (2012) and incorporated in a predecessor version of the present chemistry scheme. Laboratory experimental results by Groß et al. (2014a,b) provided additional evidence and insight into this type of chemistry, indicating that OH formation via reaction R6b ($\text{RO}_2 + \text{HO}_2$) had previously been underestimated significantly. While in polluted air peroxy radicals preferentially react with NO, in pristine, low- NO_x conditions over the rain forest, e.g., in the Amazon, isoprene degradation leads to hydroxy-hydroperoxides, which can reform OH upon further oxidation (Paulot et al., 2009).

An important pathway in isoprene chemistry, basic to the recycling of OH, is isomerization through H-migration within oxygenated reaction products, leading to photo-labile hydroperoxy-aldehydes (HPALD), as reviewed by Vereecken and Francisco (2012). While a high rate of 1,5-H-shifts that we have assumed previously (Taraborrelli et al., 2012) was not confirmed experimentally, these and especially 1,4-H- and 1,6-H-shifts have nevertheless shown to be key intermediaries in OH recycling (Crounse et al., 2012, 2013; Fuchs et al., 2014; Peeters et al., 2014). Next to HPALD, unsaturated hydroperoxyaldehydes, e.g., peroxyacylaldehydes (PACALD), were shown to be relevant (Peeters et al., 2014). Higher generation reaction products include several organic peroxides that produce OH upon photo-dissociation, which need to be accounted for in atmospheric chemistry models to reproduce field and reaction chamber observations (Nölscher et al., 2014).

These reactions have been included into the Mainz Organics Mechanism (MOM), being an extension and update of the Mainz Isoprene Mechanism, v.2 (Taraborrelli et al., 2009, 2012). The scheme, which accounts for about 630 compounds and 1630 reactions, makes use of rate constant estimation methods similarly to and in some cases like the Master Chemical Mechanism by Jenkin et al. (2015) (<http://mcm.leeds.ac.uk/MCM>), and recommendations by the Task Group on Atmospheric Chemical Kinetic Data Evaluation (<http://iupac.pole-ether.fr>), in addition to our own evaluation of recent literature. For the present work we applied the full scheme (Cabrera-Perez et al., 2016), which is computationally demanding and precludes that we apply high spatial resolution of the model for extended time periods. For computational efficiency in global and regional models, the scheme will be condensed in future (Taraborrelli et al., in preparation). In contrast to some previous chemistry mechanisms in atmospheric models, MOM accounts for higher generation reaction products and is mass conserving (notably for carbon containing reaction products from VOC oxidation).

The MOM has been included into the ECHAM/MESSy Atmospheric Chemistry (EMAC) general circulation model. The core atmospheric general circulation model is ECHAM5 (Roeckner et al., 2006), coupled with the Modular Earth Sub-model System, of which we have applied MESSy2 version 2.42 (Jöckel et al., 2010). EMAC sub-models represent

5 tropospheric and stratospheric processes and their interaction with oceans, land and human influences, and describe emissions, radiative processes, atmospheric multiphase chemistry, aerosol and deposition mechanisms (Jöckel et al., 2005, 2006; Sander et al., 2005, 2011, 2014; Kerkweg et al., 2006; Tost et al., 2006, 2007a; Pozzer et al., 2007, 2011; Pringle et al., 2010). We applied the EMAC model at T42/L31 spatial resolution, i.e., at a spherical spectral truncation of T42 and a quadratic Gaussian grid spacing of about 2.8 degrees latitude and longitude, and 31 hybrid terrain following – pressure levels up to 10 hPa.

10 Results have been evaluated against observations (Pozzer et al., 2010, 2012; de Meij et al., 2012; Christoudias and Lelieveld, 2013; Elshorbany et al., 2014; Yoon and Pozzer, 2014; Cabrera-Perez et al., 2016; for additional references, see <http://www.messy-interface.org>). Here we present results based on emission fluxes and meteorology representative of the year 2013, mostly annual means unless specifically mentioned otherwise. Tests of the present model version indicate minor changes, e.g., in intermediately long-lived compounds such as O₃ and CO, compared to previous versions. N₂O and CH₄ concentrations have been prescribed at the surface based on observations. Anthropogenic emissions have been based on the RCP8.5 emission scenario (Riahi et al., 2007; van Vuuren et al., 2011; Meinshausen et al., 2011). The scenario was tested by Granier et al. (2011), indicating that it realistically represents the source strengths of pollutants after the year 2000. The RCP8.5 scenario was also applied by Cabrera-Perez et al. (2016), in which the emissions and chemistry of aromatic compounds has been described. Natural emissions of higher VOCs are interactively calculated, amounting to 760 TgC/yr, with a four year range of 747–789 TgC/yr (including about 73%, or 546–578 TgC/yr, of isoprene) (Guenther et al., 2012), and anthropogenic emissions of saturated, unsaturated and aromatic compounds amount to 105 TgC/yr. These flux integrals are in carbon equivalent. It should be mentioned that in previous generation atmospheric chemistry-transport models VOC emissions have been artificially reduced to prevent the collapse of OH concentrations in regions of strong natural sources, i.e., at high-VOC and low-NO_x conditions (Arneth et al., 2010).

20 To analyze model production and sink pathways of OH and HO₂, including multiple radical recycling, and compute fluxes of reactants and intermediate products, we used the kinetic chemistry tagging technique of Gromov et al. (2010). The scheme computes detailed turnover rates of selected tracers, in this case OH, HO₂, O₃, CO, aldehydes, peroxides and others, in various parts of the MOM chemistry scheme within EMAC. With limited additional computational load the extensive budgeting allows characterization of OH sources and sinks, while the diagnostic calculations are decoupled from the regular chemistry scheme.

30 Here we present a selection of results, focusing on annual and large-scale averages to characterize global OH. The Supplement presents supporting tables and figures for the interested reader. Pages S1-S14 illustrate time sequences (Hovmöller plots), seasonal differences and results for different atmospheric environments and reservoirs such as the boundary layer (BL) and free troposphere (FT), to distinguish continental from marine boundary layers (CBL and MBL), the lower troposphere from the tropopause region and the lower stratosphere. These supplementary results focus on distributions of OH and HO₂, and lifetimes of different species, notably OH, HO₂, CO and CH₄, and include figures of global OH reactivity which are relevant for the discussion in Sect. 5. Page S15 presents details on the global OH budget, relevant for

Sect. 6. The Supplement also includes scatter plots between observations and model results of CO and O₃ at the surface for the year 2013 (S16), a table with details of VOC emission fluxes applied in EMAC (S17), and the complete mechanism of MOM, including a list of all chemical species (S18 and following). Model calculated global datasets of OH concentrations and other trace gases are available upon request.

5 3 Global OH distribution

In agreement with previous studies our model calculations show highest OH concentrations in the tropical troposphere (Fig. 1). Globally, mean tropospheric OH is 11.3×10^5 molecules/cm³, close to the multi-model mean of $11.1 \pm 1.6 \times 10^5$ molecules/cm³ derived by Naik et al. (2013) for the year 2000. Note that these are volume weighted means. Following the recommendation by Lawrence et al. (2001) we also calculated the air mass weighted (11.1×10^5 molecules/cm³), CH₄ weighted (12.4×10^5 molecules/cm³) and methyl chloroform (MCF) weighted means (12.3×10^5 molecules/cm³), though henceforth primarily report volume weighted mean values.

The calculated tropical tropospheric average is 14.6×10^5 molecules/cm³ (between Tropics of Cancer and Capricorn), with the NH and SH extra-tropical averages being 9.1 and 6.6×10^5 molecules/cm³, respectively. Our model indicates more OH north of the Equator compared to the south, 12.1×10^5 and 10.1×10^5 molecules/cm³, respectively. Hence the NH/SH ratio is 1.20, being towards the low end of the multi-model estimate of 1.28 ± 0.10 by Naik et al. (2013), though deviating from inter-hemispheric parity derived by Patra et al. (2014) based on the analysis of MCF (CH₃CCl₃) measurements.

For the air mass, CH₄ and MCF weighted means we find NH/SH ratios of 1.25, 1.30 and 1.25, respectively. Part of the discrepancy with Patra et al. (2014) may be related to the seasonally varying position of the Inter-Tropical Convergence Zone (ITCZ), which effectively separates the meteorological NH from the SH. The position of the ITCZ, on average a few degrees north of the equator in the region of highest OH, can influence these calculations, both in models and MCF analyses. If we correct for this, the volume weighted NH/SH ratio of OH decreases from 1.20 to 1.13. In the extra-tropics our model calculates 28% less OH in the SH compared to the NH, being the main reason for the model calculated inter-hemispheric OH disparity. The difference is even larger between the Arctic and Antarctic regions (defined by the polar circles), as the calculated mean OH concentration is 50% lower in the latter. However, if we also include the lower stratosphere (up to 10 hPa) we find near-interhemispheric parity of OH, i.e., 5% more in the NH and only 2% more based on the ITCZ metric. Considering the importance of the stratosphere as an MCF reservoir to the troposphere in recent years (Krol and Lelieveld, 2003), and possible inter-hemispheric differences in the age-of-air in the middle atmosphere, these aspects should be investigated further with a model version that accounts for the atmosphere from the surface to the mesosphere, to investigate the importance for MCF analyses and inferred OH distributions.

Fig. 1 illustrates that high OH concentrations in the tropics can extend up to the tropopause, with a main OH maximum below 300-400 hPa and a second maximum between 200 and 150 hPa. Note that the tropopause in the tropics is defined using temperature and in the extra-tropics potential vorticity gradients (2 PV units). The oxidative conditions throughout the

tropical troposphere limit the flux of reduced and partly oxidized gases (e.g., reactive halocarbons, sulfur and nitrogen gases) into the stratosphere through their chemical conversion into products that are removed by deposition processes. Near the cold tropical tropopause reaction products, such as low-volatile acids, can be removed by adsorption to sedimenting ice particles that also dehydrate the air that ascends into the stratosphere (Lelieveld et al., 2007). Due to the slow ascent rates of air parcels in the tropical tropopause region (tropical transition layer), pollutant gases are extensively exposed to oxidation by OH for several weeks to months. This mechanism protects the ozone layer from O₃ depleting substances that could be transported from the troposphere, at least to the extent that they react with OH.

In the global troposphere annual column average OH ranges from 1.0×10^5 to 22.0×10^5 molecules/cm³, i.e., between high and low latitudes, respectively (Fig. 1). This range is determined by the meridional OH gradient in the FT, since about 85% of tropospheric OH formation takes place in the FT, which dominates the global OH distribution (detailed below). In the BL the range is much larger, 0.3×10^5 to 44.0×10^5 molecules/cm³, as OH is affected by variable surface emissions. The subordinate role of the BL in the global OH load and distribution is conspicuous, for example from the OH maximum in the BL over the Middle East and OH minima over the Central African and Amazon forests (Fig. S1 of Supplement), which do not appear in the tropospheric column average OH concentrations, as the latter follow the OH distribution in the FT (Fig. 1).

In the BL over tropical forests OH concentrations are comparatively low, about 10×10^5 to 20×10^5 molecules/cm³, in agreement with OH measurements in South America and Southeast Asia (Kubistin et al., 2010; Pugh et al., 2010; Whalley et al., 2011), while in the FT in these regions OH concentrations are several times higher. High OH in the tropical FT is partly related to the combination of emissions from vegetation with NO_x from lightning in deep thunderstorm clouds. This is most prominent over Central Africa where deep convection and lightning are relatively intense (Fig. 1, left panel). The latter was corroborated by comparing our model with lightning observations (Tost et al., 2007b). The chemical mechanisms that control OH in the BL and FT are connected through vertical transport and mixing, which balances formation and loss in the column, i.e., near the surface VOCs are a net sink of OH while their reaction products are a net OH source aloft.

In the NH extra-tropics mean OH in the MBL approximately equals that in the CBL, i.e., in the zonal direction. As shown previously, this is related to the transport and mixing of oxidants (primarily O₃) and precursor gases (e.g., NO_x and partially oxidized volatile organic compounds, OVOCs) from polluted regions across the Atlantic and Pacific Oceans (Lelieveld et al., 2002). In the SH, on the other hand, where anthropogenic NO_x sources and related transports are much weaker, mean OH in the CBL is about 15% higher compared to the MBL. In the extra-tropical troposphere as a whole, OH gradients in the longitudinal direction are typically small (Fig. 1), related to relatively rapid exchanges by zonal winds in transient synoptic weather systems.

While primary OH formation (R1,2) during daytime is controlled by photo-dissociation of O₃, there are additional sources that can be relevant at night. This includes reactions of O₃ with unsaturated hydrocarbons and aromatic compounds in polluted air and with terpenes emitted by vegetation. Fig. 2 shows nighttime OH in the boundary layer during January and July to illustrate the strong seasonal dependency. While the color coding is the same as Fig. 1, the concentrations are scaled by a factor 20. On a global scale, OH concentrations in the BL at night are nearly two orders of magnitude lower than during

the day, and in the FT diel differences are even larger. Therefore, nighttime OH does not significantly influence the atmospheric oxidation capacity and the lifetimes of CH₄ and CO. Nevertheless, Fig. 2 shows several hotspots, mostly in the subtropical BL in the NH during summer, where nighttime OH can exceed 10⁵ molecules/cm³ and could contribute to chemical processes including new particle formation. These regions include the Western USA, the Mediterranean and Middle East, the Indo-Gangetic Plain and Eastern China.

4 Global HO_x distribution

Since conversions between HO₂ and OH play a key role in OH recycling, we address the budget of HO_x (OH+HO₂), which is dominated by HO₂. Field and laboratory measurements often address both OH and HO₂. Fig. 3 shows the annual HO₂ concentration distribution, the counterpart of OH in Fig. 1. We find that in the BL annual mean HO₂ ranges from 0.1 to 6.4×10⁸ molecules/cm³ globally, whereas in the FT as a whole this is only 0.2 to 1.1×10⁸ molecules/cm³. Even though the mean lifetime of HO₂ in the troposphere of 1.5 minutes is much longer than of OH (factor 60), both OH and HO₂ are locally controlled by chemistry. Transport processes influence HO_x through longer-lived precursor and reservoir species such as O₃ and OVOCs. Whereas OH in the BL over the tropical forests is relatively low, HO₂ is relatively high, about 5×10⁸ molecules/cm³, i.e., 2 to 3 orders of magnitude higher than OH, consistent with observations (Kubistin et al., 2010). Our results suggest that from a global perspective HO_x is highest over the tropical forests, where photochemistry is very active and OH sources and sinks are large. Localized HO_x maxima are also found in the polluted CBL where reactive VOC and NO_x emissions are strong, e.g., by the petroleum industry north of the Mexican Gulf and near the Persian Gulf.

On a global scale the tropospheric production of HO_x is dominated by that in the FT. In the FT HO_x is subject to long-range transport of relatively long-lived source and sink gases such as O₃ and CO, whereby the latter redistributes OH into HO₂ within HO_x, whereas in the BL local emissions of short-lived VOCs and NO_x are more relevant. The efficient atmospheric transport of longer-lived gases, such as O₃ from both the stratosphere and photochemically polluted regions, helps buffer the OH formation in regions where oxidant is depleted, such as the MBL (Lelieveld and Dentener, 2000; de Laat and Lelieveld, 2000). Within the tropospheric column, convection and entrainment of O₃ rich air from the FT into the BL play a key role in the exchange of oxidant, which reduces vertical gradients, and balances HO_x production and loss processes across altitudes.

We calculate a global tropospheric average HO₂ concentration of 0.6×10⁸ molecules/cm³. We find roughly the same average concentrations in the tropical and NH extra-tropical troposphere, and slightly less in the SH extra-tropics (0.5×10⁸ molecules/cm³). Thus the mean tropospheric HO₂ (and HO_x) concentrations in these tropical and extra-tropical reservoirs are very similar. Nevertheless, in the SH the mean HO₂ concentration in the CBL is about a factor 2 higher compared to the MBL, associated with strong VOC emissions by vegetation subject to intense photochemistry. In the NH mean HO₂ is comparable between the MBL and CBL, due to the widespread impact of air pollution, as explained above. The seasonal differences in tropospheric HO_x at middle and high latitudes can be large though, i.e., about an order of magnitude between

summer and winter. The seasonality of primary OH formation, which is proportional to solar radiation intensity, is even larger. In Sec. 6 we discuss that the low primary formation in winter is partly compensated by secondary OH formation, being less dependent on sunlight, which reduces latitudinal and seasonal OH contrasts.

5 Trace gas lifetimes and OH reactivity

5 The average tropospheric lifetime of OH (τ_{OH}) is 1.5s, calculated by dividing the annual averages of the volume-weighted OH burden and the total photochemical sink rate. Fig. 4 presents the spatial distribution of τ_{OH} . Unlike the OH concentration, τ_{OH} does not exhibit a strong seasonal cycle, being nearly absent in the tropics and the FT. Only in the CBL over Siberia, around 60°N, seasonal differences can reach a factor 5, related to the annual variability of VOC emissions by boreal forest (Siberian taiga). The tropospheric mean τ_{OH} in the NH is 1.4s and in the SH 1.6s. In the MBL mean τ_{OH} is about 0.7s, in the
10 CBL about 0.3s. The longest τ_{OH} is found near the tropical tropopause (10-20s) where OH reactivity (the inverse of τ_{OH}) is thus below 0.1 s⁻¹. While this is largely related to low temperatures and reduced reaction rates, it also indicates that air masses that traverse the tropical transition layer into the stratosphere are cleansed from reactive compounds that are removed by OH, for example organo-halogen compounds that could damage the ozone layer. In the NH mean tropospheric OH reactivity is 0.7 s⁻¹, and in the SH 0.6 s⁻¹. The seasonality of τ_{HO_2} is more pronounced than of τ_{OH} ; τ_{HO_2} is longest in the cold
15 season and over Antarctica, up to 10 minutes. In the MBL τ_{HO_2} is on average 1.3 minutes, in the CBL 0.5 and in the FT 1.7 minutes.

We find that τ_{OH} is generally shortest over the tropical forest, followed by the boreal forest, coincident with the spatial distribution of total OH reactivity, i.e., the inverse of τ_{OH} , shown in Fig. 5. Near the Earth's surface the OH reactivity varies from about 0.5 s⁻¹ over Antarctica, due to reaction of OH with CH₄ and CO in clean and cold air, to more than 100 s⁻¹ over
20 the Amazon rainforest in the dry season due to relatively strong isoprene sources, complemented by biomass burning emissions. This modeled OH reactivity range seems realistic in comparison to observations, whereas previous models – as well as measurement techniques – that did not account for all VOC reaction intermediates, strongly underestimated OH reactivity, i.e., up to a factor of ten (Walley et al., 2011; Mogensen et al., 2015; Nölscher et al., 2016). This topic will be studied in greater detail in a follow-up publication where we address the reactive carbon budget in different environments,
25 evaluated against measurements, including secondary organic aerosols (Tsimpidi et al., 2016).

Our estimate of the mean lifetime of CH₄ due to oxidation by tropospheric OH (τ_{CH_4}) is 8.5 years, which is within the multi-model calculated 1 σ standard deviation of the mean of 9.7 \pm 1.5 years presented by Naik et al. (2013), though towards the lower end of the range. Notice that this figure does not include uptake of CH₄ by soils and stratospheric loss by OH, O(¹D) and chlorine radicals, which together make up about 10% of the total CH₄ sink. The 17 models that participated in the
30 model inter-comparison by Naik et al. (2013) show a range of 7.1 – 14.0 years, while the multi-model mean of 9.7 years was considered to be 5-10% higher than observation-derived estimates.

One reason for our τ_{CH_4} estimate being toward the lower end of the range may be that Naik et al. (2013) refer to the year 2000, whereas we applied an emission inventory for the year 2010, i.e., after a period when NO_x concentrations increased particularly rapidly in Asia (Schneider and van der A., 2012) and CO concentrations decreased, most significantly in the Northern Hemisphere (Worden et al., 2013; Yoon and Pozzer, 2014). These trends in NO_x and CO may have contributed to a shift within HO_x from HO_2 to OH. Further, Naik et al. (2013) defined the tropospheric domain as extending from the surface up to 200 hPa, whereas we diagnose the tropopause height. In effect Naik et al. include part of the extratropical lower stratosphere, where τ_{CH_4} is about a century. Another reason is that our MOM mechanism more efficiently recycles OH than other VOC chemistry schemes applied in global models. This is supported by our calculation of the MCF lifetime of 5.1 years, which compares with 5.7 ± 0.9 years by Naik et al. (2013), based on a range of 4.1 – 8.4 years among the 17 participating models.

We calculate that at the tropopause and the poles τ_{CH_4} is longest, about a century. The mean τ_{CH_4} in the extra-tropics is 13.8 years and in the inner tropics 6.1 years. The mean τ_{CH_4} in the BL is 4.9 and in the FT 9.1 years. The effective range in the mean OH concentration and τ_{CH_4} between the high- and the low-latitude troposphere is about a factor ten, which is close to the OH and HO_2 range between the summer and winter at high latitudes. This is much smaller than the low-to-high latitude gradients and the seasonal cycle of primary OH formation, indicative of the important role of secondary formation (Sec. 6). The NH/SH ratio of τ_{CH_4} is 0.77. Similar differences and latitude contrasts are found for the lifetime of tropospheric CO (τ_{CO}) due to reaction with OH. In the tropics τ_{CO} is on average about 38 days, in the NH extra-tropics 65 days, in the SH extra-tropics 86 days, and the NH/SH ratio of τ_{CO} is 0.87.

6 Radical budget and recycling probability

Fig. 6 presents a summary of global, annual mean HO_x production terms in the troposphere, also listed in Table 1, which gives an overview of sources and sinks. Primary OH formation by reactions R1,2 (P , purple), amounts to 84 Tmol/yr, of which about 85% takes place in the FT. We find that gross OH formation (G) and HO_2 production in the FT also account for about 85% of the tropospheric total. Secondary OH formation (S) in the troposphere adds up to 167 Tmol/yr, i.e., 67% of G , the latter being 251 Tmol/yr. S is subdivided into contributions by the NO_x mechanism (R7, blue), the O_x mechanism (R11 and R12; green and yellow, respectively) and the OH recycling in VOC chemistry, the OVOC mechanism (red). The result that $r > 60\%$ indicates that global OH is buffered, i.e., not sensitive to chemical perturbations. Fig. 6 illustrates that the fractional contributions by the different production terms in the FT equal those in the troposphere as a whole. It is not surprising that the FT is the dominant reservoir in atmospheric oxidation as it contains 6-7 times more mass than the BL, though it shows that OH formation is rather evenly distributed between different environments within the troposphere, in spite of differences in precursors species and pollution levels.

On a global scale, the relative magnitudes of different OH production terms in the BL and FT are similar (Fig. 6), though the OVOC mechanism (red) is somewhat larger, and the O_x mechanism (green and yellow) somewhat smaller than in

the FT. The contribution by the NO_x mechanism, i.e., R7 (NO+HO₂, blue), is marginally smaller in the BL (30%) than the FT (31%), in spite that large areas in the BL are more directly influenced by anthropogenic NO_x emissions. As explained above, the contribution of NO_x to OH recycling can be locally self-limiting, e.g., in the strongly polluted BL, while some NO_x – partly as reservoir gases like organic nitrates – can escape to the FT where relatively lower concentrations can be effective in OH production. Examples of NO_x reservoir gases in MOM are alkyl nitrates with carbonyls, e.g., nitroxyacetone (NOA) and the nitrate of methyl ethyl ketone.

By comparing gross OH formation G between different regions we find that it is about twice as high in the tropics than the extra-tropics, and 16% lower in the SH than the NH. The upper panel of Fig. 7 presents G in ppbv/day (the lower panels P and S), with a global annual average in the troposphere of 4.8 ppbv/day. At low latitudes G is much higher over continents than oceans, related to strong OH recycling, while at high latitudes longitudinal gradients are small, also between oceans and continents in the NH (Fig. 7). Since emissions that affect OH largely occur on land, the latter underscores that on a large scale OH is buffered through processes in the FT. Regional maxima of G are found over the Amazon, Central Africa and southeastern Asia, and smaller areas north of the Mexican Gulf in the USA, Central America and Indonesia (Fig. 7). Over the Amazon and Central Africa we find a relatively high G up to the tropopause, related to deep convection and lightning NO_x over regions that are rich in natural VOCs. Within the BL G can vary greatly, e.g., being on average more than 3 times larger in the CBL than in the MBL. Comparing P between different regions we find that it is 37% higher in the tropics compared to the subtropics, while on average it is the same over oceans and continents.

Consequently, average S is also the same over oceans and continents; though below we underscore that the underlying chemical mechanisms can be very different. In the SH extra-tropics P is about 40% lower than in the NH, mostly associated with the lower abundance of tropospheric O₃ in the SH. This inter-hemispheric asymmetry is manifest in the middle panels of Fig. 7. Comparison of the middle and lower panels in Fig. 7 shows that spatial gradients of P and S can be rather different, e.g., towards high latitudes with P falling off with solar radiation and water vapor, while P also declines with altitude. In these regions gradients of S are weaker than of P . This actually contributes to OH buffering, as the relatively low rate of P is partly compensated by S . This mechanism also acts seasonally, i.e., S is relatively more important in winter.

Rohrer et al. (2006, 2014) emphasized the tight linear relationship between tropospheric OH and UV radiation in Germany and China, expressed by measurements of OH and the photo-dissociation frequency of O₃ ($J(O^1D)$). While the relationship with sunlight is also evident from our results, the interpretation is not straightforward because P also depends on O₃ and H₂O, and S on many other factors. For example, in the tropics P has a maximum in the lower troposphere and a minimum in the upper troposphere where the UV intensity is higher, related to dependencies of the $J(O^1D)$ quantum yield and H₂O on temperature. Hence the slope of the regression is different. Furthermore, S is not contingent on $J(O^1D)$ and is generally less strongly dependent on solar radiation.

This is illustrated by Fig. 8, indicating that sometimes a tight linear relationship with $J(O^1D)$ is found, e.g., for P in the BL, but that the relationship with S in the BL is less compact, while in the FT S can deviate from linearity at low UV intensity. Based on a global sample size of 1.45 million pairs from our model calculations, we find a high correlation

$R^2=0.94$ between P and $J(O^1D)$, and a lower correlation $R^2=0.80$ between S and $J(O^1D)$. While the mean slope for P is 0.99 (intercept close to zero), it is 0.46 for S (intercept about 0.3). Therefore, there is no unique relationship between OH and UV radiation as it depends on the relative importance of P , S and the different mechanisms that contribute to S .

Fig. 9 illustrates the efficiency at which OH is recycled, i.e., the recycling probability $r=1-P/G$. We find relatively large differences between tropospheric reservoirs, e.g., between the CBL and MBL, and also between the tropics and extra-tropics. When S is smaller than P , r is below 50% (yellow). However, if we consider the troposphere as a whole, S exceeds P everywhere due to the predominance of OH recycling in the FT. In the low latitude MBL r is lowest, indicative of a relatively high sensitivity to perturbations such as large-scale variations and trends in CH_4 and CO. This is not the case in the continental troposphere where natural VOCs play an important role in OH recycling. Fig. 9 shows that r is relatively larger in the extra-tropics than in the tropics, and largest at high latitudes. In the MBL the recycling efficiency and r anti-correlate with latitude and therefore with solar radiation intensity.

The chemical buffering mechanisms include the dominant though self-limiting effect of NO_x on OH formation in polluted air, the latter through reaction R10, which is an important sink of both NO_2 and OH when concentrations are high (NO_x mechanism; blue in Fig. 6). In unpolluted, low- NO_x conditions the OVOC mechanism acts through competition of unsaturated peroxide and carbonyl sinks, e.g., hydroperoxide-aldehyde (HPALD) in isoprene chemistry (red in Fig. 6). When OH is high, HPALD reacts with OH, whereas at low OH photo-dissociation takes the upper hand through the formation of peroxy-acid aldehyde (PACALD), which produces OH. Over land OH is generally buffered by the NO_x and OVOC mechanisms, illustrated by values of r well over 50% (Fig. 9). However, remote from NO_x and VOC sources in the BL over the tropical and subtropical oceans r can be below 40%. In these environments OH recycling depends on the O_x mechanism (green plus yellow in Fig. 6), which has limited efficiency because R11 (O_3+HO_2) is a net oxidant sink. Hence the O_x mechanism depends on replenishment of O_3 through transport in the FT and subsequent mixing into the BL.

Differences in S between tropospheric reservoirs, e.g., the CBL, MBL, tropics and extra-tropics, are associated with these three principal OH recycling mechanisms, to various degrees related to natural and anthropogenic VOC and NO_x emissions. Fig. 10 illustrates how OH is buffered both on local and global scales. It shows the fractional contributions of the NO_x , O_x and OVOC mechanisms to the overall recycling probability r , and indicates that the three mechanisms are complementary. The NO_x mechanism dominates in the NH, especially in polluted air at middle latitudes, and most strongly over the continents. In the SH over the continents, in low- NO_x air, the OVOC mechanism dominates. In the marine environment – except the pollution outflow regions over the Atlantic and Pacific Oceans – the O_x mechanism predominates. Seasonal complementarity of the three mechanisms is most significant at high latitudes, especially in the BL. Whereas in summer the O_x mechanism is most efficient, and to a lesser degree also the NO_x mechanism, in winter the OVOC mechanism maintains OH formation, being least dependent on solar radiation.

To estimate the contributions of the three recycling mechanisms (NO_x , O_x , OVOC) to global OH and r , we performed sensitivity simulations, switching them off one-by-one. By excluding OH recycling by NO_x , the global mean OH concentration declines from 11.3×10^5 to 2.7×10^5 molecules/cm³, i.e., a reduction by 76%, while τ_{CH_4} increases from 8.5 to

21.6 years, r reduces from 67% to 42%, and the global mean production of OH drops from 4.8 to 2.8 ppbv/day. This result corroborates the great importance of this mechanism, and the sensitivity of global OH to NO_x abundance. The latter is illustrated by Fig. 11, which shows zonal mean OH concentrations by the reference simulation and by excluding the three OH recycling mechanisms one-by-one. The NO_x mechanism clearly has the largest impact on global OH. Fig. 11 also shows that model calculated OH exhibits near-interhemispheric parity in the FT, while the NO_x mechanism leads to relatively more OH in the NH, primarily in the subtropical boundary layer. From Fig. 11 we see that the OH concentrations generated by the different mechanisms do not add up to the reference simulation, as they are complementary and partly compensate the recycling of deactivated mechanisms.

The strength of the O_x mechanism comes second in magnitude, as its omission leads to a drop in global OH from 11.3×10^5 to 5.9×10^5 molecules/cm³, i.e., a reduction by 48%, while τ_{CH_4} increases from 8.5 to 15.0 years, r reduces from 67% to 52%, and the global mean production of OH decreases from 4.8 to 3.4 ppbv/day. The overall strength of the OVOC mechanism is relatively weakest of the three. When we switch it off, global OH decreases from 11.3×10^5 to 9.7×10^5 molecules/cm³, i.e., a reduction by 14%, while τ_{CH_4} increases from 8.5 to 9.7 years, r reduces from 67% to 61%, and the global mean production of OH decreases from 4.8 to 4.2 ppbv/day. Note that in the latter sensitivity simulation we include OH recycling from HO_2 that is produced through OVOC chemistry, which would otherwise contribute to the NO_x and O_x mechanisms. The OH formation through HO_2 , produced in the breakdown of VOC, accounts for about half the OH recycling by the OVOC mechanism.

7 Conclusions

The atmospheric oxidation capacity is generally not sensitive to perturbations that may arise from variations or trends in emissions of natural and anthropogenic origin. This is illustrated by global OH calculations with a large number of chemistry-transport models (Naik et al., 2013; Voulgarakis et al., 2013), where differences between models are larger than between pre-industrial, present and future emission scenarios calculated by the same models. This suggests that model physics and chemistry formulations have a greater impact on calculations of global OH than applying different emission scenarios of source and sink gases. Results from the EMAC atmospheric chemistry – general circulation model illustrate how a combination of tropospheric chemistry and transport mechanisms buffer OH on a range of scales.

The EMAC model includes the recent Mainz Organics Mechanism (MOM) to comprehensively account for VOC chemistry, including higher generation reaction products, leading to a closed atmospheric budget of reactive carbon. The more realistic description of emissions and complex VOC chemistry in MOM compared to previous models substantially increases OH reactivity, bringing it close to measurements (Nölscher et al., 2016). We also find that in the polluted CBL, notably in the subtropical NH during summer, nighttime VOC chemistry initiated by O_3 can produce OH concentrations in excess of 10^5 molecules/cm³, which may be relevant for particle nucleation, for example. Nevertheless, nighttime OH does not contribute significantly to the global atmospheric oxidation capacity (e.g., τ_{CH_4} and τ_{CO}).

Global mean OH concentrations in the BL equal those in the FT and thus the troposphere as a whole (11.3×10^5 molecules/cm³). Tropospheric column averaged OH concentrations are highest in the tropics, especially over the Amazon, Central Africa and Southeast Asia. Concentrations of HO_x (OH+HO₂) are highest in the CBL over the Amazon, Central Africa, Southeast Asia, and some smaller regions over North Australia, the USA north of the Mexican Gulf and near the Persian Gulf. The latter is related to emissions from the petroleum industry in photochemically polluted air.

While measurement campaigns often focus on the BL, the global distribution and variability of OH and HO_x are dominated by the FT. Long-distance transport processes and OH recycling are most efficient in the FT, whereas BL chemistry is more sensitive to local impacts of reactive carbon emissions. Chemical processes during transport in the FT play an important role in global OH buffering through oxidant transport, notably of ozone. The FT connects with the BL through convective mixing by clouds (latent heating) and entrainment by the diurnal evolution of the BL (sensible heating). The latter is more effective in the continental than in the marine environment.

While HO_x concentrations can diverge strongly over the globe, especially in the BL and between seasons, annual averages in the troposphere vary little, e.g., between the tropics and extra-tropics and between hemispheres. Tropospheric OH is buffered through complementary primary and secondary formation mechanisms throughout seasons, latitudes and altitudes. Globally, secondary OH formation exceeds primary formation – through reactions R1,2 – by about a factor two, leading to an OH recycling probability of 67%, hence global OH is not sensitive to perturbations by natural or anthropogenic emission changes. We find that primary OH formation is tightly related to solar UV radiation intensity, whereas this is much less the case for secondary OH formation. There are three principal pathways of secondary OH formation: the NO_x, O_x and OVOC mechanisms.

The NO_x mechanism predominates in anthropogenically influenced environments, causing photochemical smog, and outcompetes the OVOC mechanism concomitant with VOC emissions from vegetation. The NO_x mechanism contributes greatly to global mean OH. When we switch it off in the model global OH declines by 76% and τ_{CH_4} increases by a factor of 2.5. In regions where NO_x is low the photochemistry of natural VOCs, through the breakdown of OVOC and their reaction products, can govern radical recycling and maintain the atmospheric oxidation capacity associated with undisturbed atmosphere-biosphere interactions. While the OVOC mechanism is important for OH production over forests, excluding it reduces global OH by 14%. In regions where both NO_x and VOC concentrations are low, e.g., in the remote marine environment and at high latitudes, OH recycling strongly depends on the O_x mechanism. When we switch it off global mean OH drops by 48%.

Recycling mechanisms of OH are important near emission sources of NO_x and VOCs in regions of active photochemistry in the BL, but especially in remote areas and the FT where photochemistry is less active. On large scales ozone is a key buffer of OH. To a lesser degree NO_x reservoir species (e.g., organic nitrates) also play a role. On smaller scales H₂O₂ and OVOCs that release OH upon further reaction and photo-dissociation (e.g., organic peroxides and carbonyls) are important. The short-lived reservoir species govern OH sources and sinks within the column. Ozone, with a lifetime of several weeks in the FT, is central to the atmospheric oxidation capacity through long-distance transport, either

from the stratosphere or from photochemically polluted regions, through primary OH formation and OH recycling in natural and anthropogenically influenced atmospheres.

References

- Arnth, A., Harrison, S.P., Zaehle, S., Tsigaridis, K., Menon, S., Bartlein, P.J., Feichter, J., Korhola, A., Kulmala, M.,
5 O'Donnell, D., Schurgers, G., Sorvari, S., and Vesala, T.: Terrestrial biogeochemical feedbacks in the climate system, *Nature Geosci.*, 3, 525-532, 2010.
- Butler, T.M., Lawrence, M.G., Taraborrelli, D., and Lelieveld, J.: Tagged ozone production potential (TOPP) of volatile organic compounds, *Atmos. Environ.*, 45, 4082-4090, 2011.
- Cabrera-Perez, D., Taraborrelli, D., Sander, R., and Pozzer, A.: Global atmospheric budget of simple monocyclic aromatic
10 compounds, *Atmos. Chem. Phys.*, 16, 6931-6947, 2016.
- Christoudias, T., and Lelieveld, J.: Modelling the global atmospheric transport and deposition of radionuclides from the Fukushima Dai-ichi nuclear accident, *Atmos. Chem. Phys.*, 13, 1425-1438, 2013.
- Crouse, J.D., Knap, H.C., Ørnsø, K.B., Jørgensen, S., Paulot, F., Kjaergaard, G.G., and Wennberg, P.O.: Atmospheric fate
15 of methacrolein. 1. Peroxy radical isomerization following addition of OH and O₂, *J. Phys. Chem., A*, 116, 5756-5762, 2012.
- Crouse, J.D., Nielsen, L.B., Jørgensen, S., Kjaergaard, H.G., and Wennberg, P.O.: Autoxidation of organic compounds in the atmosphere, *J. Phys. Chem. Lett.*, 4, 3513-3520, 2013.
- Crutzen, P.J.: The role of NO and NO₂ in the chemistry of the troposphere and the stratosphere, *Annu. Rev. Earth. Planet. Sci.*, 7, 443-472, 1979.
- 20 Crutzen, P.J., and Zimmermann, P.H.: The changing photochemistry of the troposphere, *Tellus*, 43AB, 136-151, 1991.
- De Laat, A.T.J., and Lelieveld, J.: Diurnal ozone cycle in the marine boundary layer, *J. Geophys. Res.*, 105, 11547-11559, 2000.
- De Meij, A., Pozzer, A., Pringle, K.J., Tost, H., and Lelieveld, J.: EMAC model evaluation and analysis of atmospheric aerosol properties and distribution, *Atmos. Res.*, 114-115, 38-69, 2012.
- 25 Ehhalt, D.H., Dorn, H.-P., and Poppe, D.: The chemistry of the hydroxyl radical in the troposphere, *Proc. Roy. Soc. Edinburgh, Ser. B.*, 97, 17-34, 1991.
- Elshorbany, Y.F., Crutzen, P., Steil, B., Pozzer, A., and Lelieveld, J.: Global and regional impacts of HONO on the chemical composition of clouds and aerosols, *Atmos. Chem. Phys.*, 14, 1167-1184, 2014.
- Fuchs, H., Acir, I.-H., Bohn, B., Brauers, T., Dorn, H.-P., Häseler, R., Hofzumahaus, A., Holland, F., Kaminski M., Li, X.,
30 Lu, K., Lutz, A., Nehr, S., Rohrer, F., Tillmann, R., Wegener, R., and Wahner, A., OH regeneration from methacrolein oxidation investigated in the atmosphere simulation chamber SAPHIR, *Atmos. Chem. Phys.*, 14, 7895-7908, 2014.

- Granier, C., Bessagnet, B., Bond, T., D'Angiola, A., van der Gon, H.D., Frost, G.J., Heil, A., Kaiser, J.W., Kinne, S., Klimont, Z., Kloster, S., Lamarque, J.-F., Liousse, C., Masui, T., Meleux, F., Mieville, A., Ohara, T., Raut, J.-C., Riahi, K., Schultz, M.G., Smith, S. J., Thompson, A., van Aardenne, J., van der Werf, G.R., and van Vuuren, D.P.: Evolution of anthropogenic and biomass burning emissions of air pollutants at global and regional scales during the 1980-2010 period, *Clim. Change*, 109, 163-190, 2011.
- 5 Groß, C.B.M., Dillon, T.J., Schuster, G., Lelieveld, J., and Crowley, J.N., Direct kinetic study of OH and O₃ formation in the reaction of CH₃C(O)O₂ with HO₂, *J. Phys. Chem., A*, 118, 974-985, 2014a.
- Groß, C.B.M., Dillon, T.J., and Crowley, J.N., Pressure dependent OH yields in the reactions of CH₃CO and HOCH₂CO with O₂, *Phys. Chem. Chem. Phys.*, 16, 10990-10998, 2014b.
- 10 Gromov, S., Jöckel, P., Sander, R., and Brenninkmeijer, C.A.M.: A kinetic chemistry tagging technique and its application to modelling the stable isotopic composition of atmospheric trace gases, *Geosci. Model Dev.*, 3, 337-364, 2010.
- Guenther, A.B., Jiang, X., Heald, C.L., Sakulyanontvittaya, T., Duhl, T., Emmons, L.K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geosci. Model Dev.*, 5, 1471-1492, 2012.
- 15 Houweling, S., Dentener, F., and Lelieveld, J.: The impact of non-methane hydrocarbon compounds on tropospheric photochemistry, *J. Geophys. Res.*, 103, 10673-10696, 1998.
- Jenkin, M.E., Young, J.C., and Rickard, A.R.: The MCM v3.3.1 degradation scheme for isoprene, *Atmos. Chem. Phys.*, 15, 11433-11459, 2015.
- Jöckel, P., Sander, R., Kerkweg, A., Tost, H., and Lelieveld, J.: Technical Note: The Modular Earth Submodel System (MESSy) - a new approach towards Earth System Modeling, *Atmos. Chem. Phys.*, 5, 433-444, 2005.
- 20 Jöckel, P., Tost, H., Pozzer, A., Brühl, C., Buchholz, J., Ganzeveld, L., Hoor, P., Kerkweg, A., Lawrence, M.G., Sander, R., Steil, B., Stiller, G., Tanarhte, M., Taraborrelli, D., van Aardenne, J., and Lelieveld, J.: The atmospheric chemistry general circulation model ECHAM5/MESSy: Consistent simulation of ozone from the surface to the mesosphere, *Atmos. Chem. Phys.*, 6, 5067-5104, 2006.
- 25 Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., Baumgaertner, A., Gromov, S., and Kern, B.: Development cycle 2 of the Modular Earth Submodel System (MESSy2), *Geoscientific Model Development*, 3, 717-752, 2010.
- Kerkweg, A., Sander, R., Tost, H., and P. Jöckel: Technical Note: Implementation of prescribed (OFFLEM), calculated (ONLEM), and pseudo-emissions (TNUDGE) of chemical species in the Modular Earth Submodel System (MESSy), *Atmos. Chem. Phys.*, 6, 3603-3609, 2006.
- 30 Krol, M., and Lelieveld, J.: Can the variability in tropospheric OH be deduced from measurements of 1,1,1-trichloroethane (methyl chloroform)? *J. Geophys. Res.*, 108, 4125, doi:10.1029/2002JD002423, 2003.
- Kubistin, D., Harder, H., Martinez, M., Rudolf, M., Sander, R., Bozem, H., Eerdeken, G., Fischer, H., Gurk, C., Klüpfel, T., Königstedt, R., Parchatka, U., Schiller, C.L., Stickler, A., Taraborrelli, D., Williams, J., and Lelieveld, J.: Hydroxyl

- radicals in the tropical troposphere over the Suriname rainforest: comparison of measurements with the box model MECCA, *Atmos. Chem. Phys.*, 10, 9705-9728, 2010.
- Lawrence, M.G., Jöckel, P., and von Kuhlmann, R.: What does the global mean OH concentration tell us? *Atmos. Chem. Phys.*, 1, 37-49, 2001.
- 5 Lelieveld, J., and Dentener, F.J.: What controls tropospheric ozone? *J. Geophys. Res.*, 105, 3531-3551, 2000.
- Lelieveld, J., Peters, W., Dentener, F.J., and Krol: M. Stability of tropospheric hydroxyl chemistry, *J. Geophys. Res.*, 107, 10.1029/2002JD002272, 2002.
- Lelieveld, J., Brühl, C., Jöckel, P., Steil, B., Crutzen, P.J., Fischer, H., Giorgetta, M.A., Hoor, P., Lawrence, M.G., Sausen, R., and Tost, H.: Stratospheric dryness: model simulations and satellite observations, *Atmos. Chem. Phys.*, 7, 1313-1332, 2007.
- 10 Lelieveld, J., Butler, T.M., Crowley, J.N., Dillon, T.J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M.G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a forest, *Nature*, 452, 737-740, 2008.
- Levy II, H.: Normal atmosphere: large radical and formaldehyde concentrations predicted, *Science*, 173, 141-143, 1971.
- 15 Logan, J.A., Prather, M.J., Wofsy, S.C., and McElroy, M.B.: Tropospheric chemistry: A global perspective, *J. Geophys. Res.*, 86, 7210-7354, 1981.
- Meinshausen, M., Smith, S. J., Calvin, K., Daniel, J. S., Kainuma, M.L.T., Lamarque, J.-F., Matsumoto, K., Montzka, S.A., Raper, S.C.B., Riahi, K., Thomson, A., Velders, G.J.M., and van Vuuren, D.P.P.: The RCP greenhouse gas concentrations and their extensions from 1765 to 2300, *Clim. Change*, 109, 213-241, 2011.
- 20 Mogensen, D., Gierens, R., Crowley, J.N., Keronen, P., Smolander, S., Sogachev, A., Nölscher, A.C., Zhou, L., Kulmala, M., Tang, J., Williams, J., and Boy, M.: Simulations of atmospheric OH, O₃ and NO₃ reactivities within and above the boreal forest, *Atmos. Chem. Phys.*, 15, 3909-3932, 2015.
- Monks, P.S., Archibald, A.T., Colette, A., Cooper, O., Coyle, M., Derwent, R., Fowler, D., Granier, C., Law, K.S., Mills, G.E., Stevenson, D.S., Tarasova, O., Thouret, V., von Schneidmesser, E., Sommariva, R., Wild, O., and Williams, M.L.: Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer, *Atmos. Chem. Phys.*, 15, 8889-8973, 2015.
- 25 Montzka, S., Krol, M., Dlugokencky, E., Hall, B., Jöckel, P., and Lelieveld, J.: Small inter-annual variability of global atmospheric hydroxyl, *Science*, 331, 67-69, 2011.
- Naik, V., Voulgarakis, A., Fiore, A.M., Horowitz, L.W., Lamarque, J.-F., Lin, M., Prather, M.J., Young, J., Bergmann, D., Cameron-Smith, P.J., Cionni, I., Collins, W.J., Dalsøren, S.B., Doherty, R., Eyring, V., Faluvegi, G., Folberth, G.A., Josse, B., Lee, Y.H., MacKenzie, I.A., Nagashima, T., van Noije, T.P.C., Plummer, D.A., Righi, M., Rumbold, S.T., Skeie, R., Shindell, D.T., Stevenson, D.S., Strode, S., Sudo, K., Szopa, S., and Zeng, G.: Preindustrial to present-day changes in tropospheric hydroxyl radical and methane lifetime from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), *Atmos. Chem. Phys.*, 13, 5277-5298, 2013.
- 30

- Nölscher, A.C., Butler, T., Auld, J., Veres, P., Muñoz, A., Taraborrelli, D., Vereecken, L., Lelieveld, J., and Williams, J.: Using total OH reactivity to assess isoprene photooxidation via measurement and model, *Atmos. Environ.*, 89, 453-463, 2014.
- 5 Nölscher, A.C., Yanez-Serrano, A.M., Wolff, S., Carioca de Araujo, A., Lavric, J.V., Kesselmeier, J., and Williams, J.: Unexpected seasonality in quantity and composition of Amazon rainforest air reactivity, *Nat. Commun.*, 7:10383, doi: 10.1038/ncomms10383, 2016.
- 10 Patra P.K., Krol, M.C., Montzka, S.A., Arnold, T., Atlas, E.L., Lintner, B.R., Stephens, B.B., Xiang, B., Elkins, J.W., Fraser, P.J., Ghosh, A., Hints, E.J., Hurst, D.F., Ishijima, K., Krummel, P.B., Miller, B.R., Miyazaki, K., Moore, F.L., Mühle, J., O'Doherty, S., Prinn, R.G., Steele, L.P., Takigawa, M., Wang, H.J., Weiss, R.F., Wofsy, S.C., and Young, D.: Observational evidence for interhemispheric hydroxyl-radical parity, *Nature*, 513, 219-223, 2014.
- Paulot, F., Crouse, J.D., Kjaergaard, H.G., Kürten, A., St. Clair, J.M., Seinfeld, J.H., Wennberg, P.O., Unexpected epoxide formation in the gas-phase photooxidation of isoprene, *Science*, 325, 730-733, 2009.
- Peeters, J., Müller, J.-F., Stavrou, T., and Nguyen, V.S., Hydroxyl radical Recycling in isoprene oxidation driven by hydrogen bonding and hydrogen tunneling: The upgraded LIM1 mechanism, *J. Phys. Chem., A*, 118, 8625-8643, 2014.
- 15 Pozzer, A., Jöckel, P., Tost, H., Sander, R., Ganzeveld, L., Kerkweg, A., and Lelieveld, J.: Simulating organic species with the global atmospheric chemistry general circulation model ECHAM5/MESy1: a comparison of model results with observations, *Atmos. Chem. Phys.*, 7, 2527-2550, 2007.
- Pozzer, A., Pollmann, J., Taraborrelli, D., Jöckel, P., Helmig, D., Tans, P., Hueber, J., and Lelieveld, J.: Observed and simulated global distribution and budget of atmospheric C₂-C₅ alkanes, *Atmos. Chem. Phys.*, 10, 4403-4422, 2010.
- 20 Pozzer, A., Jöckel, P., Kern, B., and Haak, H.: The atmosphere-ocean general circulation model EMAC-MPIOM, *Geosci. Model Dev.*, 4, 771-784, 2011.
- Pozzer, A., de Meij, A., Pringle, K.J., Tost, H., Doering, U.M., van Aardenne, J., and Lelieveld, J.: Distributions and regional budgets of aerosols and their precursors simulated with the EMAC chemistry-climate model, *Atmos. Chem. Phys.*, 12, 961-987, 2012.
- 25 Pringle, K.J., Tost, H., Metzger, S., Steil, B., Giannadaki, D., Nenes, A., Fountoukis, C., Stier, P., Vignati, E., and Lelieveld, J.: Description and evaluation of GMXe: A new aerosol submodel for global simulations (v1), *Geosci. Model Develop.*, 3, 391-412, 2010.
- Pugh, T.A.M., MacKenzie, A.R., Hewitt, C.N., Langford, B., Edwards, P.M., Furneaux, K.L., Heard, D.E., Hopkins, J.R., Jones, C.E., Karunaharan, A., Lee, J., Mills, G., Misztal, P., Moller, S., Monks, P.S., and Whalley, L.K.: Simulating atmospheric composition over a South-East Asian tropical rainforest: performance of a chemistry box model, *Atmos. Chem. Phys.*, 10, 279-298, 2010.
- 30 Riahi, K., Grubler, A., and Nakicenovic, N.: Scenarios of longterm socio-economic and environmental development under climate stabilization, *Technol. Forecast. Soc.*, 74, 887-935, 2007.

- Roeckner, E., Brokopf, R., Esch, M., Giorgetta, M., Hagemann, S., Kornblüh, Manzini, L. E., Schlese, U., and Schulzweida, U.: Sensitivity of simulated climate to horizontal and vertical resolution in the ECHAM5 atmosphere model, *J. Climate*, 19, 3771-3791, 2006.
- 5 Rohrer, F., and Berresheim, H.: Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, *Nature*, 442, 184-187, 2006.
- Rohrer, F., Lu, K., Hofzumahaus, A., Bohn, B., Brauers, T., Chang, C.-C., Fuchs, H., Häsel, R., Holland, F., Hu, M., Kita, K., Kondo, Y., Li, X., Lou, S., Oebel, A., Shao, M., Zeng, L., Zhu, T., Zhang, Y., and Wahner, A.: Maximum efficiency in the hydroxyl-radical-based self-cleansing of the troposphere, *Nature Geosci.*, 7, 559-563.
- 10 Sander, R., Kerkweg, A., Jöckel, P., and Lelieveld, J.: Technical Note: The new comprehensive atmospheric chemistry module MECCA, *Atmos. Chem. Phys.*, 5, 445-450, 2005.
- Sander, R., Baumgaertner, A., Gromov, S., Harder, H., Jöckel, P., Kerkweg, A., Kubistin, D., Regelin, E., Riede, H., Sandu, A., Taraborrelli, D., Tost, H., and Xie, Z.-Q.: The atmospheric chemistry box model CAABA/MECCA-3.0, *Geosci. Model Dev.*, 4, 373-380, 2011.
- 15 Schneider, P., and van der A, R.J.: A global single-sensor analysis of 2002–2011 tropospheric nitrogen dioxide trends observed from space, *J. Geophys. Res.*, 117, D16309, doi:10.1029/2012JD017571, 2012.
- Sander, R., Jöckel, P., Kirner, O., Kunert, A.T., Landgraf, J., and Pozzer, A.: The photolysis module JVAL-14, compatible with the MESSy standard, and the JVal PreProcessor (JVPP), *Geosci. Model Dev.*, 7, 2653-2662, 2014.
- Spivakovsky, C.M., Logan, J.A., Montzka, S.A., Balkanski, Y.J., Foreman-Fowler, M., Jones, D.B. A., Horowitz, L.A., Fusco, A.C., Brenninkmeijer, C.A.M., Prather, M.J., Wofsy, S.C., and McElroy, M.B.: Three-dimensional climatological distribution of tropospheric OH: Update and evaluation, *J. Geophys. Res.*, 105, 8931-8980, 2000.
- 20 Stockwell, W.R., Lawson, C.V., Saunders, E., and Goliff, W.S.: A review of tropospheric atmospheric chemistry and gas-phase chemical mechanisms for air quality modeling, *Atmosphere*, 3, 1-32, 2012.
- Stone, D., Whalley, L.K., and Heard, D.E.: Tropospheric OH and HO₂ radicals: field measurements and model comparisons, *Chem. Soc. Rev.*, 41, 6348-6404, 2012.
- 25 Taraborrelli, D., Lawrence, M., Butler, T., Sander, R., and Lelieveld, J.: Mainz Isoprene Mechanism 2 (MIM2): an isoprene oxidation mechanism for regional and global atmospheric modeling, *Atmos. Chem. Phys.*, 9, 2751-2777, 2009.
- Taraborrelli, D., Lawrence, M.G., Crowley, J.N., Dillon, T.J., Gromov, S., Groß, C.B.M., Vereecken, L., and Lelieveld, J.: Hydroxyl radical buffered by isoprene oxidation over tropical forests. *Nature Geosci.* 5, 190-193, 2012.
- Tost, H., Jöckel, P., Kerkweg, A., Sander, R., and Lelieveld, J.: Technical Note: A new comprehensive SCAVenging submodel for global atmospheric chemistry modelling, *Atmos. Chem. Phys.*, 6, 565-574, 2006.
- 30 Tost, H., Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., and Lelieveld, J.: Global cloud and precipitation chemistry and wet deposition: tropospheric model simulations with ECHAM5/MESSy1, *Atmos. Chem. Phys.*, 7, 2733-2757, 2007a.
- Tost, H., Jöckel, P., and Lelieveld, J.: Lightning and convection parameterisations – uncertainties in global modelling, *Atmos. Chem. Phys.*, 7, 4553-4568, 2007b.

- Tsimpidi, A.P., Karydis, V.A., Pandis, S.N., and Lelieveld, J.: Global combustion sources of organic aerosols: Model comparison with 84 AMS factor analysis data sets, *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2015-989, 2016.
- van Vuuren, D. P., Edmonds, J.A., Kainuma, M., Riahi, K., Thomson, A.M., Hibbard, K., Hurtt, G. C., Kram, T., Krey, V., Lamarque, J.-F., Masui, T., Nakicenovic, M.M.N., Smith, S.J., and Rose, S.: The representative concentration pathways: an overview, *Clim. Change*, 109, 5-31, 2011.
- Vereecken, L., and Francisco, J.S., Theoretical studies of atmospheric reaction mechanisms in the troposphere, *Chem. Soc. Rev.*, 41, 6259-6293, 2012.
- Voulgarakis, A., Naik, V., Lamarque, J.-F., Shindell, D.T., Young, P.J., Prather, M.J., Wild, O., Field, R.D., Bergmann, D., Cameron-Smith, P., Cionni, I., Collins, W.J., Dalsøren, S.B., Doherty, R.M., Eyring, V., Faluvegi, G., Folberth, G.A., Horowitz, L.W., Josse, B., MacKenzie, I.A., Nagashima, T., Plummer, D.A., Righi, M., Rumbold, S.T., Stevenson, D.S., Strode, S.A., Sudo, K., Szopa, S., and Zeng, G.: Analysis of present day and future OH and methane lifetime in the ACCMIP simulations, *Atmos. Chem. Phys.*, 13, 2563-2587, 2013.
- Whalley, L.K., Edwards, P.M., Furneaux, K.L., Goddard, A., Ingham, T., Evans, M.J., Stone, D., Hopkins, J.R., Jones, C.E., Karunaharan, A., Lee, J.D., Lewis, A.C., Monks, P.S., Moller, S.J., and Heard, D.E.: Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest, *Atmos. Chem. Phys.*, 11, 7223-7233, 2011.
- Worden, H.M., Deeter, M.N., Frankenberg, C., George, M., Nichitiu, F., Worden, J., Aben, I., Bowman, K.W., Clerbaux, C., Coheur, P.F., de Laat, A.T.J., Detweiler, R., Drummond, J.R., Edwards, D.P., Gille, J.C., Hurtmans, D., Luo, M., Martinez-Alonso, S., Massie, S., Pfister, G., and Warner, J.X.: Decadal record of satellite carbon monoxide observations, *Atmos. Chem. Phys.*, 13, 837-850, 2013.
- Yoon, J., and Pozzer, A.: Model-simulated trend of surface carbon monoxide for the 2001–2010 decade, *Atmos. Chem. Phys.*, 14, 10465-10482, 2014.

Table 1. Global, annual mean tropospheric source and sink fluxes of OH (Tmol/yr). Sources and sinks are also specified for the boundary layer and free troposphere.

Sources/Sinks	BL	FT	Troposphere
O(¹ D)+H ₂ O	12.5	71.5	84.0 (33%)
NO+HO ₂	10.4	66.2	76.6 (30%)
O ₃ +HO ₂	3.5	30.9	34.4 (14%)
H ₂ O ₂ +hν	2.3	22.5	24.8 (10%)
OVOCs, ROOH+hν	6.6	24.8	31.4 (13%)
<i>Total OH sources</i>	35.3	215.9	251.2
OH+HO_y¹	4.8	41.4	46.2 (18%)
OH+NO_y²	0.8	3.3	4.1 (1.5%)
OH+CH₄	4.1	25.7	29.8 (12%)
OH+CO	9.6	88.2	97.8 (39%)
OH+other C₁VOC³	5.7	31.3	37.0 (15%)
OH+C₂₊VOC⁴	10.3	24.4	34.7 (14%)
Rest	0.4	1.2	1.6 (0.5%)
Total OH sinks	35.7	215.5	251.2

¹ H₂, O₃, H₂O₂, radical-radical reactions

² NO, NO₂, HNO₂, HNO₃, HNO₄, ammonia, N-reaction products

5 ³ VOC with one C-atom (excl. CH₄), incl. CH₃OH, C₁-reaction products

⁴ VOC with ≥2 C-atoms, C₂₊-reaction products

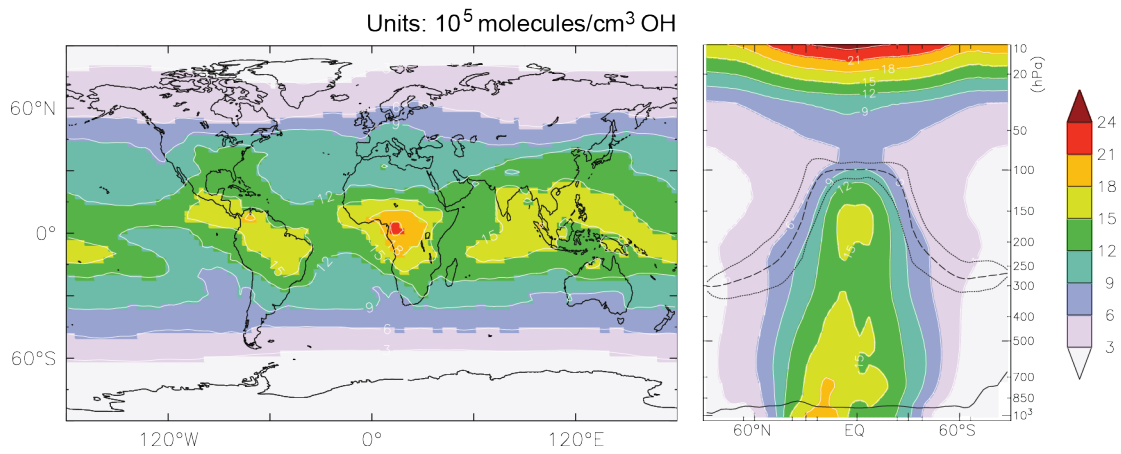


Figure 1: Global OH in 10^5 molecules/cm³. Left: tropospheric, annual mean. Right: zonal, annual mean up to 10 hPa. The lower solid line indicates the average boundary layer height, the upper dashed line the mean tropopause and the solid lines the annual minimum and maximum tropopause height.

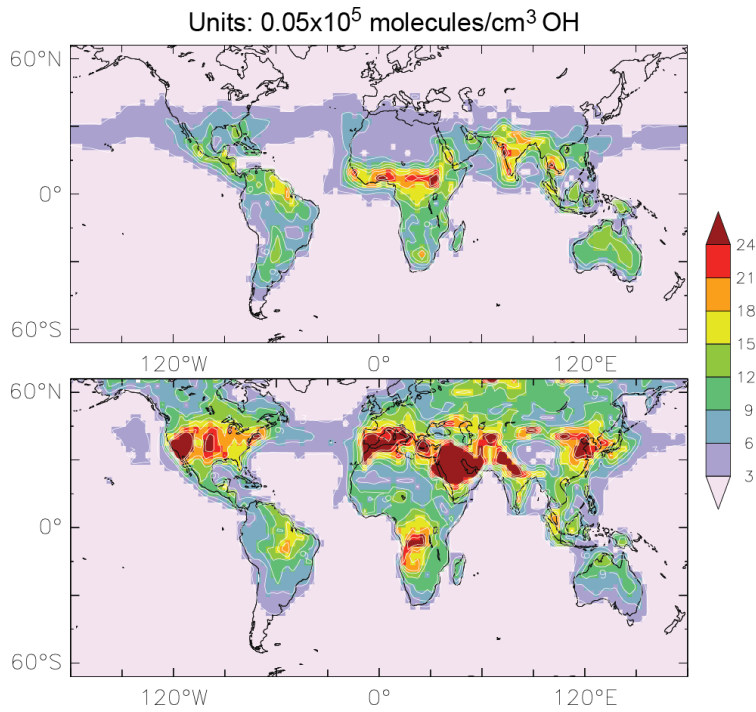
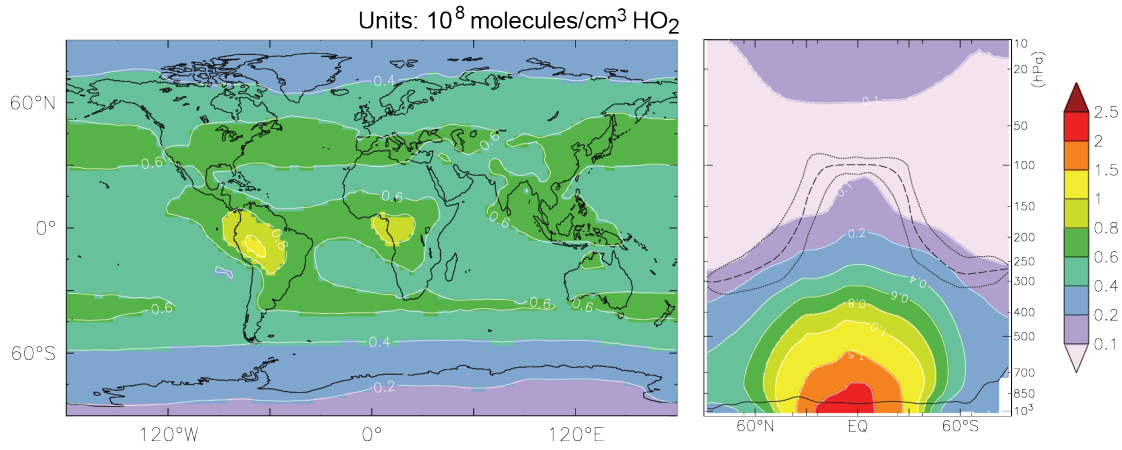
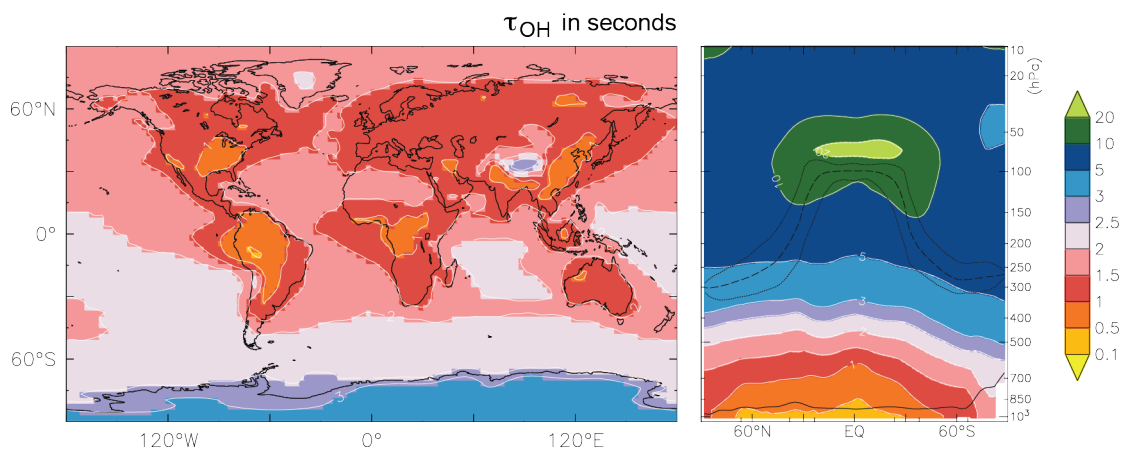


Figure 2: Nighttime OH in the boundary layer in January (top) and July (bottom). Color coding is the same as Fig. 1, but concentrations are scaled by a factor 20 ($\times 0.05 \times 10^5$ molecules/cm³).



5

Figure 3: As Fig. 1 for HO₂ in 10^8 molecules/cm³ in the troposphere (left) and up to 10 hPa (right).



10

Figure 4: As Fig. 1 for the OH lifetime (τ_{OH} , seconds) in the troposphere (left) and up to 10 hPa (right).

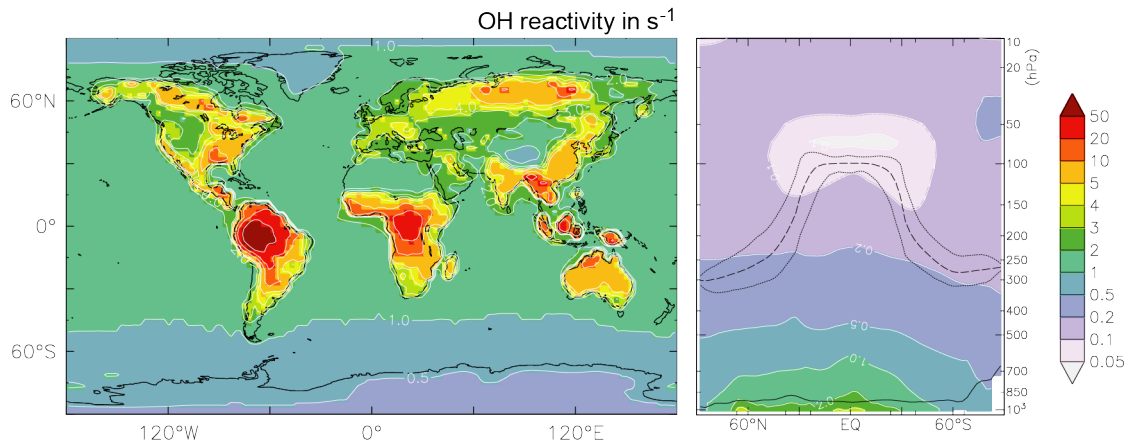


Figure 5: Annual mean OH reactivity near the Earth's surface in s^{-1} .

5

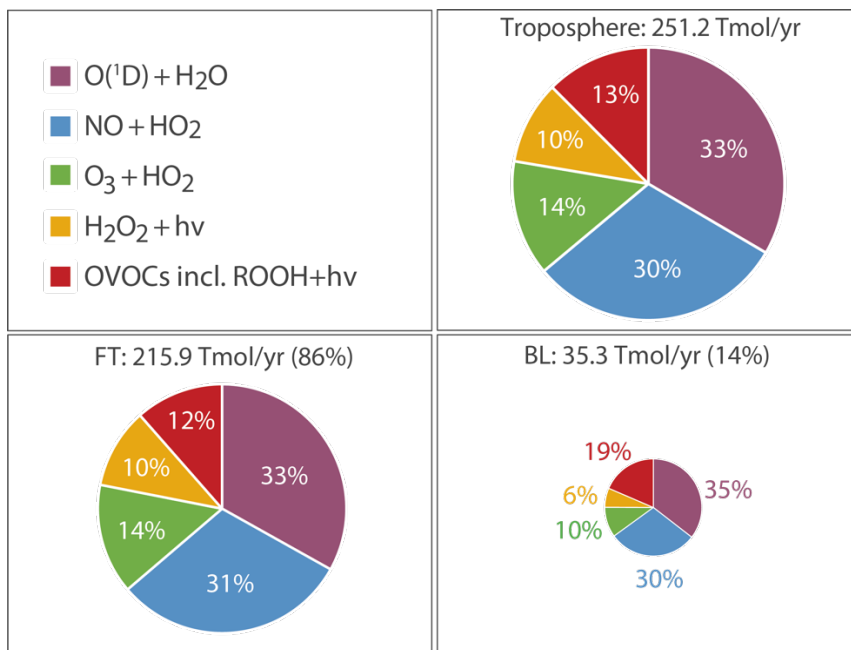
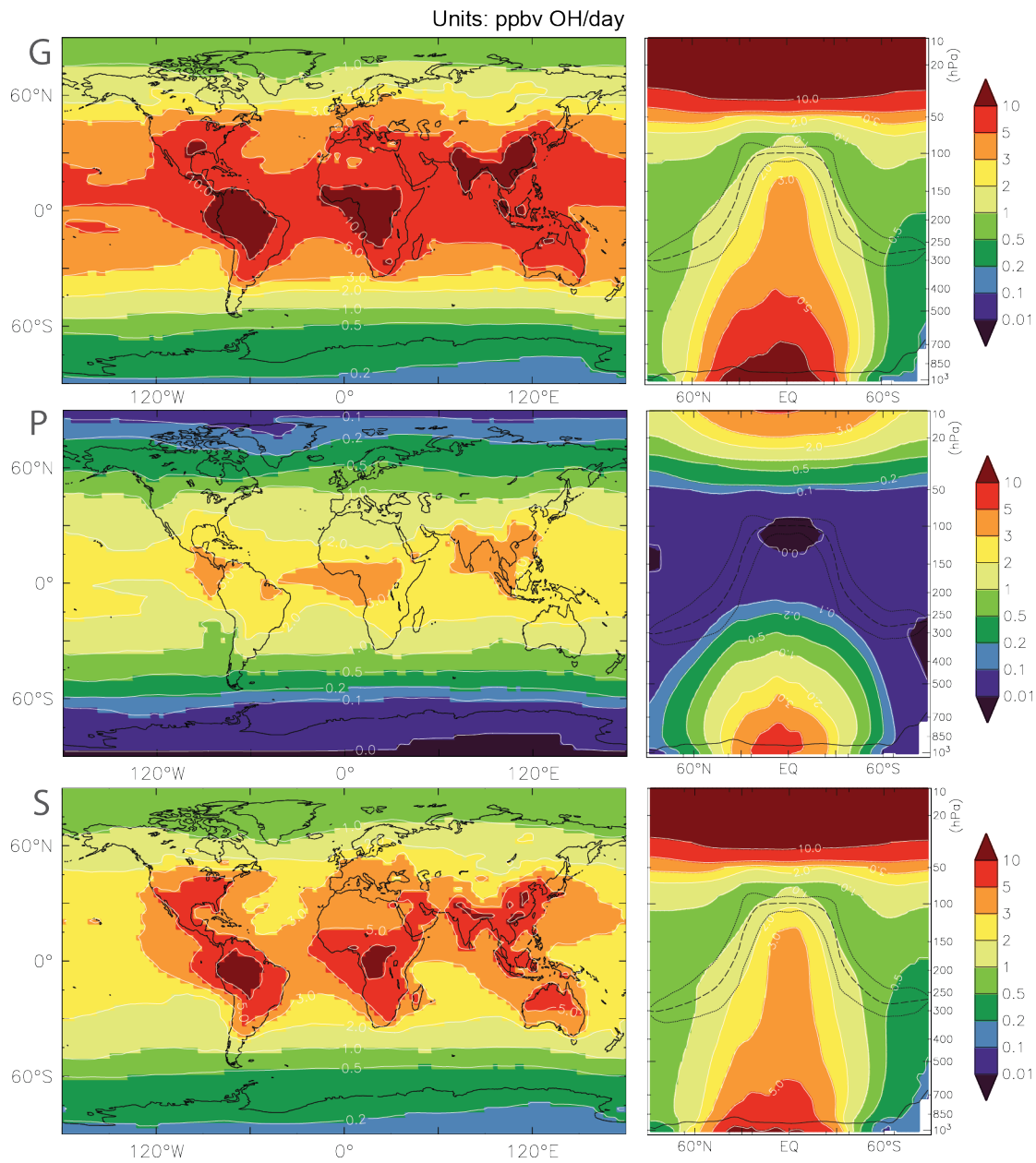


Figure 6: Main production terms of OH (Tmol/year) in the troposphere (top right), free troposphere (bottom left) and boundary layer (bottom right). The sizes of the lower two graphs are proportional to the upper right graph, reflecting the percentages of G in parentheses. We distinguish P (purple) from S , the latter made up of the NO_x mechanism (blue), the O_x mechanism (yellow and green) and the OVOC mechanism (red).



5 **Figure 7:** Annual mean OH formation in the troposphere (left) and up to 10 hPa (right). The top panels show total (*G*), the middle panels primary (*P*) and the bottom panels secondary (*S*) OH formation (in ppbv/day).

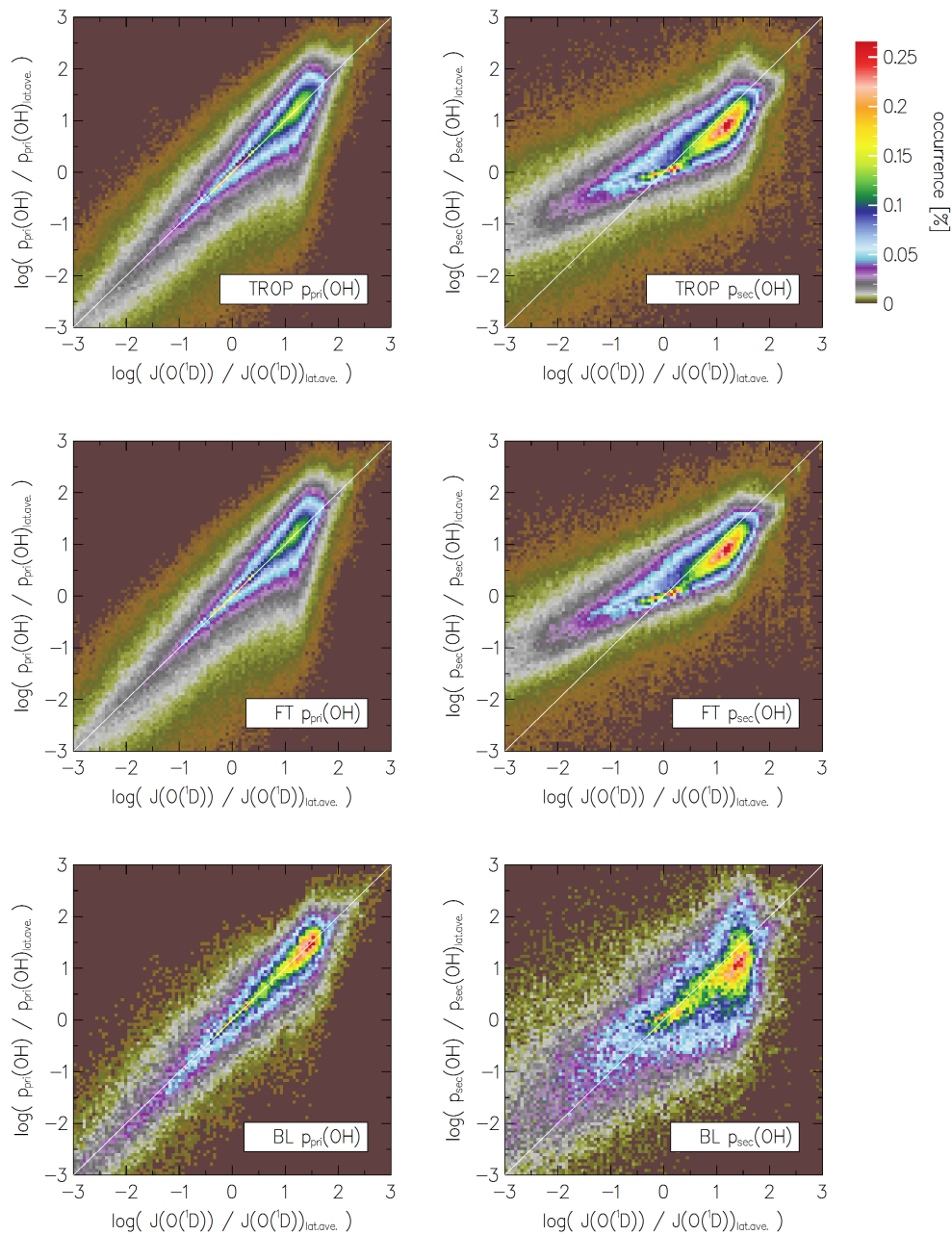
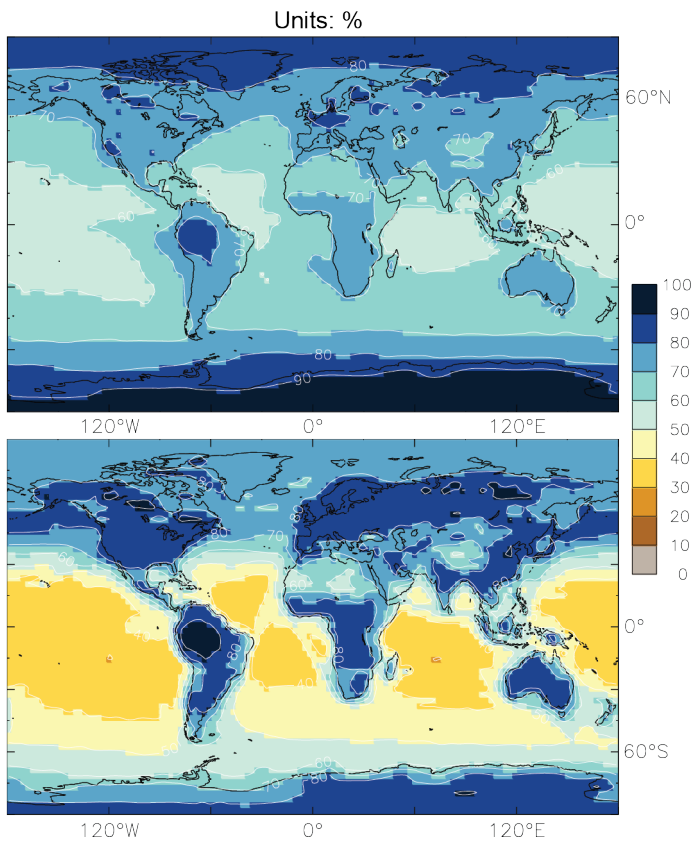


Figure 8: Correlation diagrams, showing P and S on the Y-axes as a function of the photo-dissociation rate of O_3 by R1, $J(O^1D)$, on the X-axes. Please notice the log/log scale. P is shown in the left panels and S in the right panels, in the 5 troposphere (top), FT (middle) and BL (bottom).



5 **Figure 9:** Annual mean OH recycling efficiency (left, in %), and the OH recycling probability (right, r in %) in the troposphere (top) and the BL (bottom).

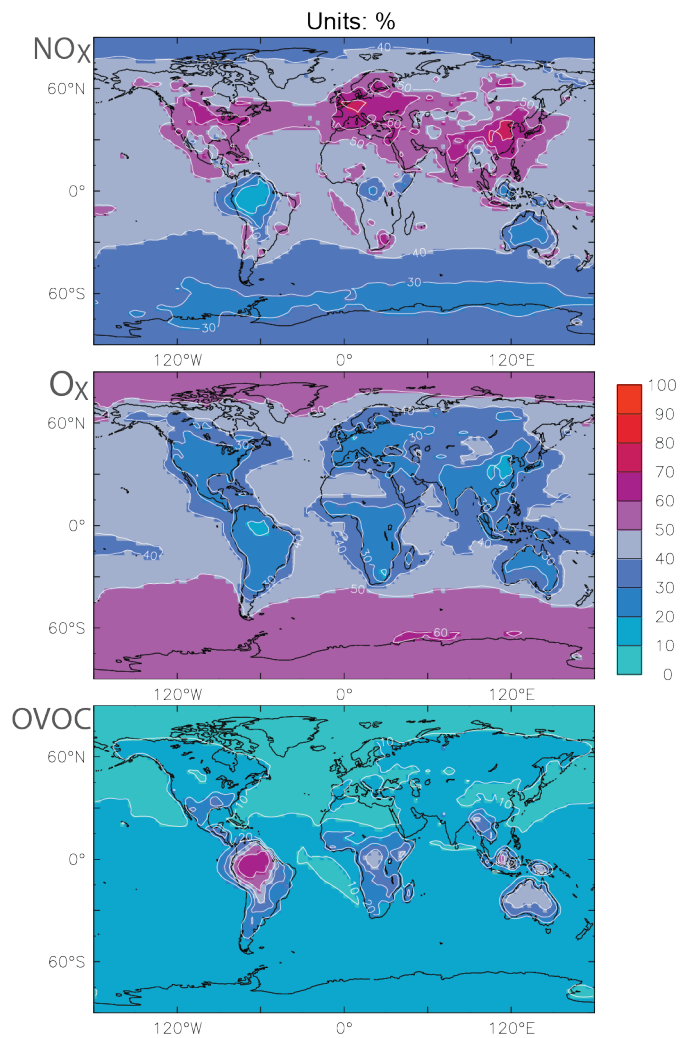


Figure 10: Fractional contributions to the OH recycling probability (% of r) in the troposphere by the NO_x (top), O_x (middle) and OVOC (bottom) mechanisms (sum of 3 panels is 100%).

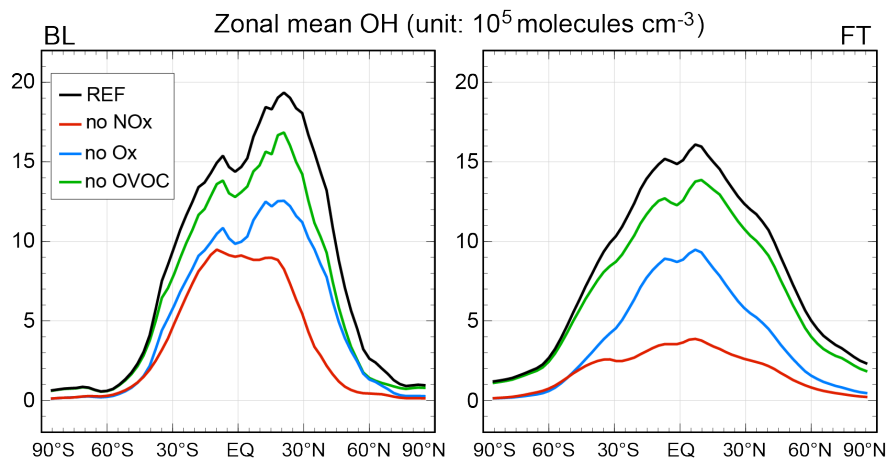


Figure 11: Zonal, annual mean OH concentrations calculated in the reference simulation (black) and by successively excluding OH recycling through the NO_x , O_x and OVOC mechanisms.

5