# Influence of aromatics on tropospheric gas-phase composition

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We present an assessment of the impacts of aromatics on tropospheric gas-phase chemistry, using the general circulation model EMAC (ECHAM5/MESSy Atmospheric Chemistry). We employ a comprehensive kinetic model to represent the oxidation of the monocyclic aromatics benzene, toluene, xylenes, phenol, styrene, ethylbenzene, trimethylbenzenes, benzaldehyde and lumped higher aromatics ($>C_9$).
Significant regional changes are identified for several species. For instance, glyoxal increases by 130 % in Europe and 260 % in East Asia, respectively. Large increases in $HCHO$ are also predicted in these regions. In general, the influence of aromatics is particularly evident in areas with high concentrations of $NO_x$, with increases up to 12 % in $O_3$ and 17 % in $OH$.

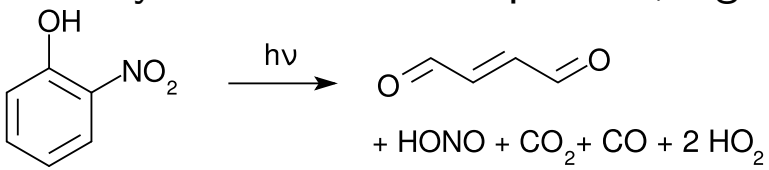
Globally, net changes are minor when aromatics are considered, partially because of compensating effects between high- and low-$NO_x$ regions. The tropospheric burden of $CO$ increases by about 6 %, and those of $OH$, and $NO_x$ ($NO + NO_2$) decrease between 3 % and 9 %. The largest change (+36 %) is seen for glyoxal. In contrast to other studies the net change in tropospheric ozone is predicted to be negative, -3 % globally. This change is larger in the northern hemisphere where models usually show positive biases. The reaction with phenoxy radicals is a significant loss for ozone, about 200-300 $Tg/yr$.
Our results indicate that aromatics can strongly influence tropospheric chemistry on a regional scale. An analysis of the main model uncertainties related to oxidation and emissions suggests that the impact of aromatics may even be significantly larger.

# Introduction

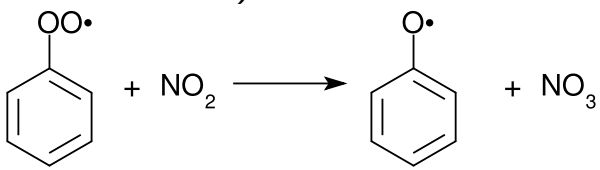
- Aromatics are a subset of unsaturated organic compounds.
- Aromatic compounds are found in continental areas, especially in industrialized urban and semi-urban regions.
- Many aromatics are toxic.
- Emissions are primarily anthropogenic, related to fuel combustion, and leakage from fuels and solvents.
- Emissions from biomass burning play a secondary role, but can be important on a regional scale.
- Biogenic emissions are only relevant for toluene.
- Aromatic compounds are removed from the atmosphere mainly via chemical oxidation.
- Due to their high reactivities, aromatics have short atmospheric lifetimes ranging from hours to a few days.
- Their oxidation is mainly controlled by the $\mathrm{OH}$ radical but they also react with $\mathrm{NO_3}$ and $\mathrm{O_3}$.

# The chemistry mechanism

- Chemistry calculated with MECCA module (Sander et al., 2019).
- The reactions of aromatics are based on a reduced version of the MCM (`http://mcm.leeds.ac.uk`).
- The mechanism contains the monocyclic aromatic compounds benzene, toluene, xylenes (lumped), phenol, styrene, ethylbenzene, trimethylbenzenes (lumped), benzaldehydes, and lumped higher aromatics ($>C_9$).
- Additional reactions in our mechanism (not in MCM):
  - Photolysis of several nitrophenols, e.g.:




  - Photolysis of benzaldehyde updated according to UV/VIS spectrum recommended by IUPAC, producing $C_6H_5O_2$, $HO_2$ and $CO$.
  - Reactions of several phenyl peroxy compounds with $NO_2$ (Jagiella and Zabel, 2007):



# The global model

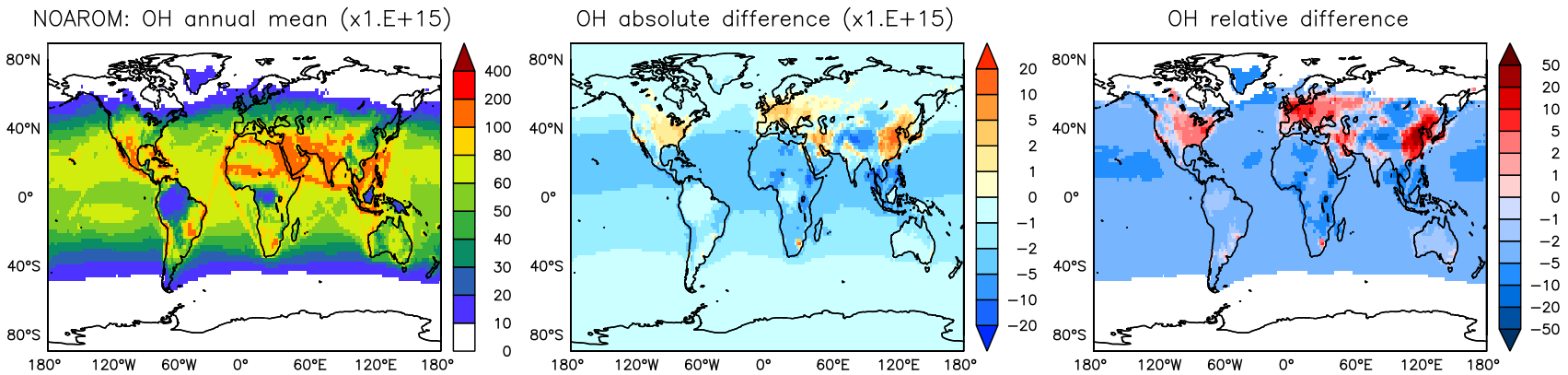
- GCM: ECHAM5/MESSy Atmospheric Chemistry (EMAC) model, version 2.53 (Jöckel et al., 2010).
- T63L31 resolution ($1.9° \times 1.9°$, 31 vertical levels from the surface to 10 hPa)
- Total global annual emissions are 29.4 $\mathrm{TgC/a}$:

| Species | total ($\mathrm{TgC/a}$) | anthropogenic (EDGAR) | biomass burning (BIOBURN) | biogenic (MEGAN) |
|---|---|---|---|---|
| Benzene | 4.417 | 70 % | 30 % | |
| Toluene | 5.888 | 82 % | 13 % | 5 % |
| Xylenes | 5.664 | 96 % | 4 % | |
| Ethylbenzene | 1.961 | 74 % | 26 % | |
| Benzaldehyde | 1.382 | 92 % | 6 % | 2 % |
| Phenol | 2.559 | 43 % | 57 % | |
| Styrene | 1.596 | 91 % | 9 % | |
| Trimethylbenzenes | 0.906 | 94 % | 6 % | |
| Higher aromatics | 4.980 | 48 % | 52 % | |

- Simulated period from 2009 (spin-up) to 2010.
- Sensitivity studies:
  - *AROM*: Base run, includes aromatic emissions and chemistry
  - *NOAROM*: Identical to *AROM* but without aromatics.
  - *ONLYMCM*: No chemical reactions on top of the MCM.

# Results for surface OH

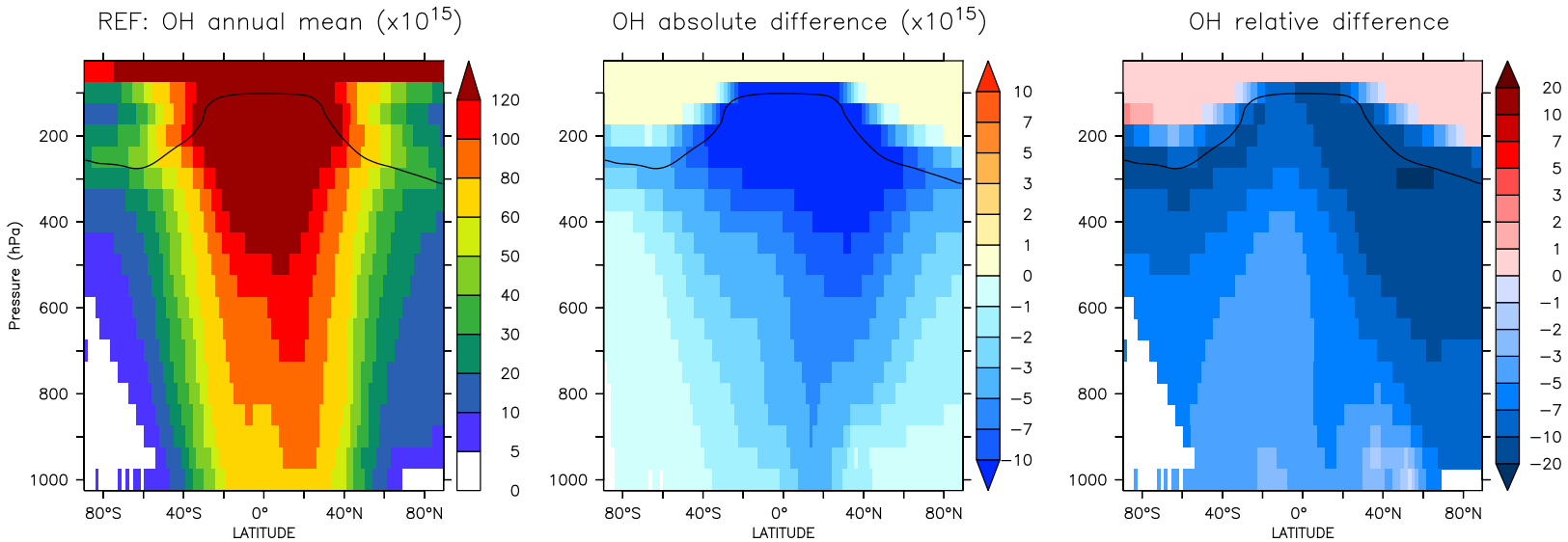
- Globally, aromatics decrease OH for two reasons:
  - The direct reaction with aromatics consumes OH.
  - Additional CO resulting from the degradation of aromatics represents an increased sink for OH.
- In high-$NO_x$ regions (eastern Asia, Europe, and the east coast of the US), however, OH increases:
  - The increase is mainly caused by the reaction of NO with $HO_2$.
  - Although the aromatics decrease $NO_x$ in these areas, the chemical system remains in the high-$NO_x$ regime.




Annual average OH at the surface. Left: Mixing ratios in the *NOAROM* simulation. Middle: Absolute difference *AROM*-*NOAROM*. Right: Relative difference *AROM*/*NOAROM*-1 in % (shown only where OH is above 0.01 pmol/mol).

# Results for tropospheric OH

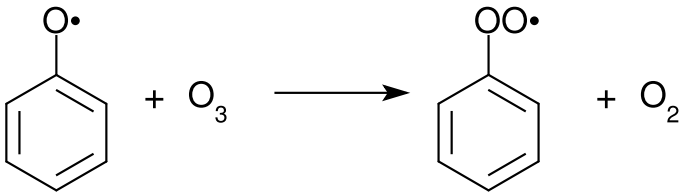
- Globally, aromatics in the troposphere reduce OH by 7.7 %.
- Annual zonal mean changes of OH are most pronounced in the northern hemispheric upper troposphere.
- This helps bringing the model-simulated inter-hemispheric OH asymmetry closer to that derived from observations.

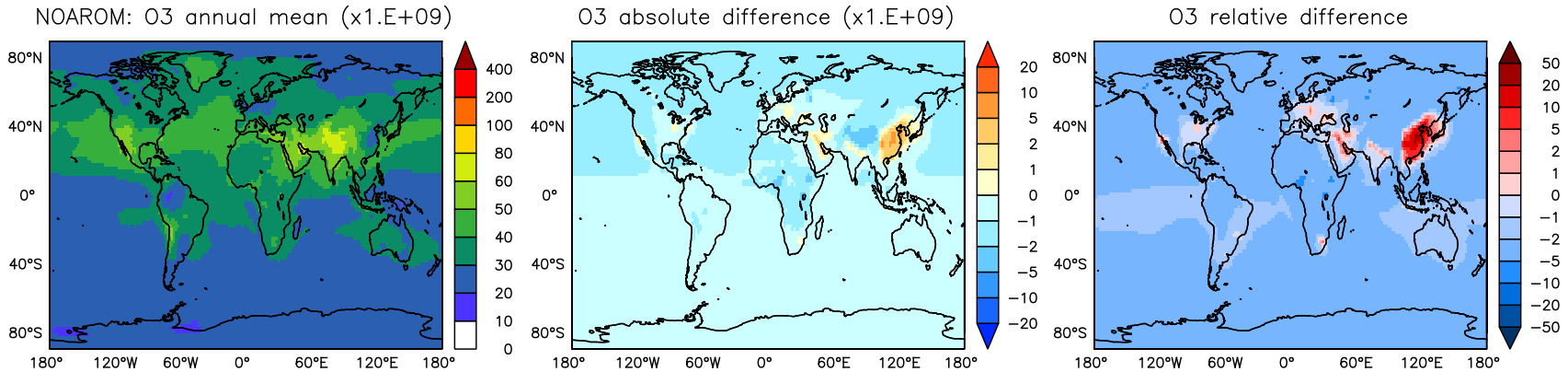



Annual average zonal mean OH. Left: Mixing ratios in the *NOAROM* simulation. Middle: Absolute difference *AROM*-*NOAROM*. Right: Relative difference *AROM*/*NOAROM*-1 in %. The solid line between 100 and 300 hPa depicts the mean tropopause level.

# Results for surface $O_3$

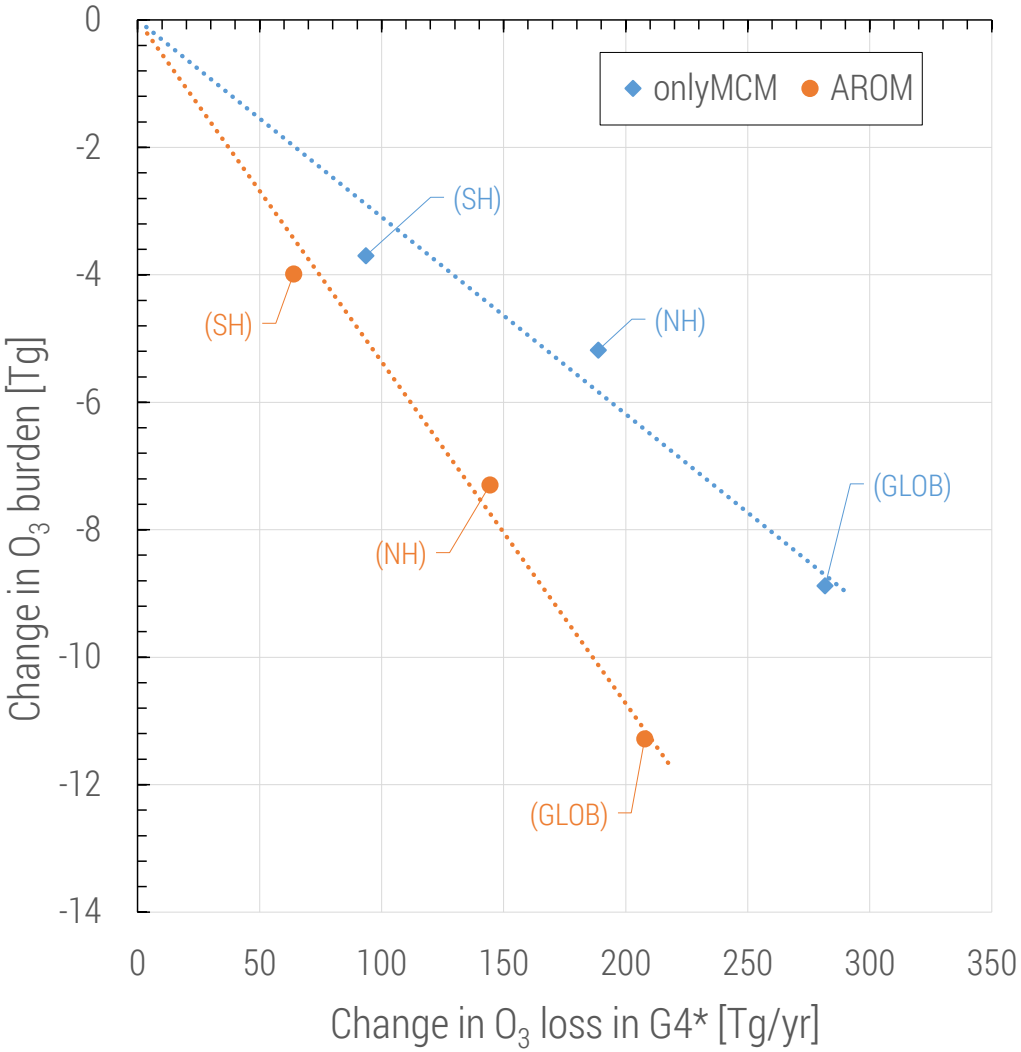
- Globally, the introduction of aromatics decreases tropospheric $O_3$ by 3 %.
- Similar to OH, an increase of $O_3$ is only seen in high-$NO_x$ regions.
- Phenoxy radicals are an important sink for ozone:




Annual average $O_3$ at the surface. Left: Mixing ratios in the *NOAROM* simulation. Middle: Absolute difference *AROM*-*NOAROM*. Right: Relative difference *AROM*/*NOAROM*-1 in %.

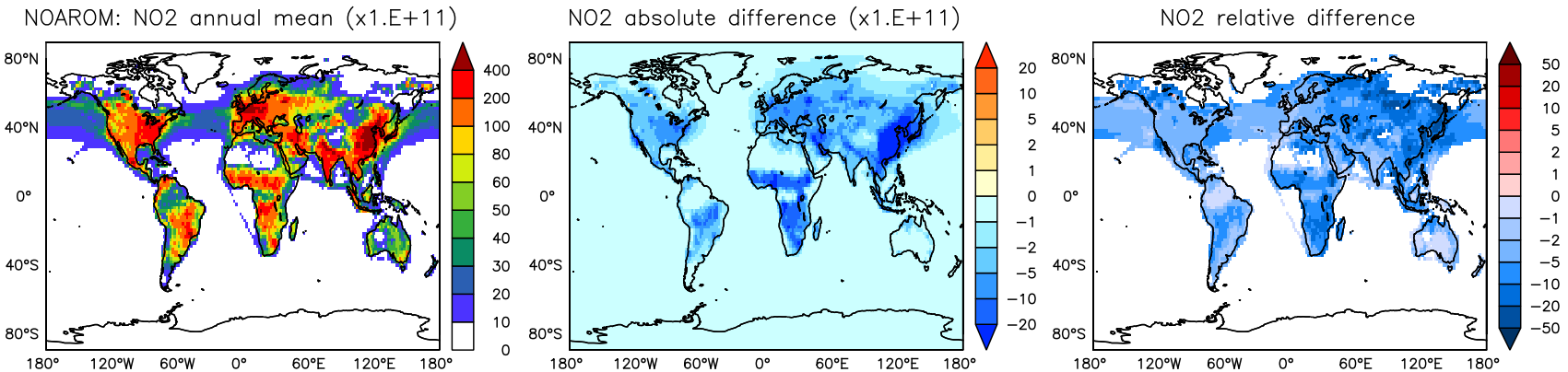
# Results for tropospheric $O_3$




Change in tropospheric ozone burden versus change in ozone loss for organic reactions (G4*) in MECCA. Global (GLOB) and hemispheric (NH, SH) results are shown for *onlyMCM* (blue) and *AROM* (orange).

# Results for $NO_x$

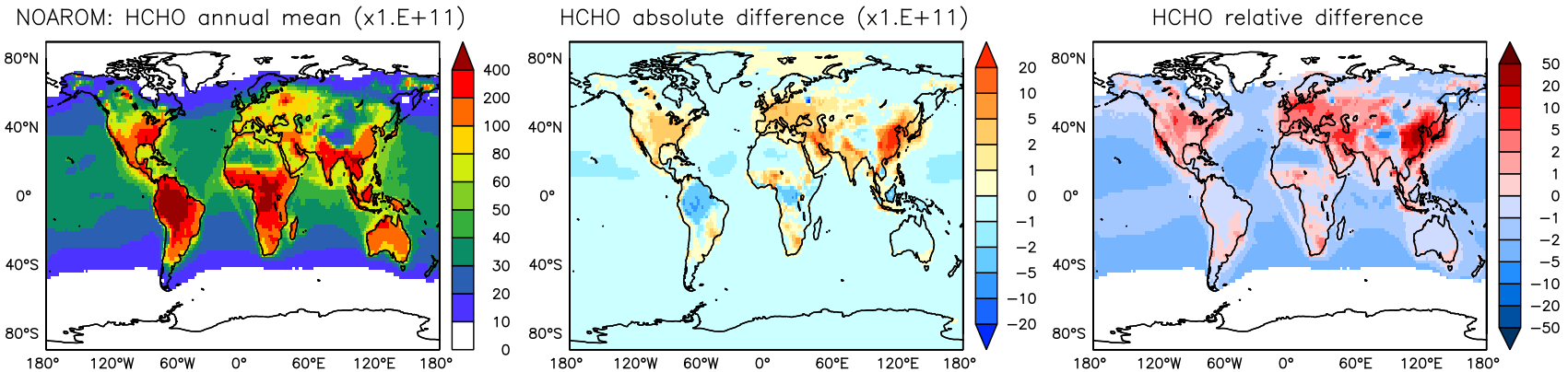
- Aromatics decrease the annual mean $NO_x$ at the surface.
- Nitrogen-containing aromatics are formed, e.g., nitrophenols.




Annual average $NO_2$ at the surface. Left: Mixing ratios in the *NOAROM* simulation. Middle: Absolute difference *AROM*-*NOAROM*. Right: Relative difference *AROM*/*NOAROM*-1 in % (shown only where $NO_2$ is above 100 pmol/mol).

# Results for aldehydes

- Small change of $\mathrm{HCHO}$ on global average.
- Increased $\mathrm{HCHO}$ in east Asia and Europe.
- Depletion of $\mathrm{HCHO}$ in the Amazon region, where its concentrations are high.

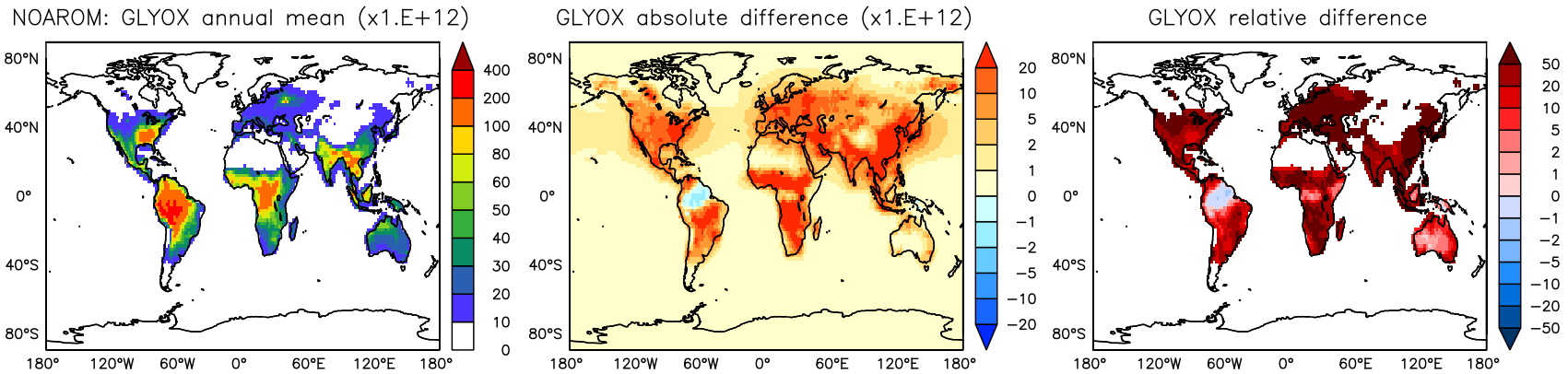



Annual average $\mathrm{HCHO}$ at the surface. Left: Mixing ratios in the *NOAROM* simulation. Middle: Absolute difference *AROM*-*NOAROM*. Right: Relative difference *AROM*/*NOAROM*-1 in % (shown only where $\mathrm{HCHO}$ is above 100 pmol/mol).

- Comparing *AROM* to *ONLYMCM*, benzaldehyde ($\mathrm{C_6H_5CHO}$) decreases by more than 50 % when the updated photolysis is used.

# Results for $\alpha$-dicarbonyls

- Global increase of glyoxal by 36 % due to aromatics.
- Very large increase of glyoxal in continental areas.
- About 10-20 % increase of glyoxal in the lower troposphere, which can be important for secondary organic aerosol (SOA) formation via cloud processing.




Annual average glyoxal at the surface. Left: Mixing ratios in the *NOAROM* simulation. Middle: Absolute difference *AROM*-*NOAROM*. Right: Relative difference *AROM*/*NOAROM*-1 in % (shown only where glyoxal is above 10 pmol/mol).

- Similar results for methyl glyoxal.

# Model uncertainties

- Reaction of the phenoxy radical ($C_6H_5O$) with ozone:
  - The temperature-dependence of the rate constant is not known.
  - We use the same rate constant also for substituted phenoxy radicals.
  - The product phenyl peroxy radical ($C_6H_5O_2$) has not been found experimentally (yet?).
- Chemistry of aromatics inside cloud droplets is not considered.
- Emissions:
  - Recent study by Andreae (2019) indicates that biomass burning emissions of aromatics could be higher.
  - Our one-year simulation cannot capture inter-annual variability, e.g., peat fire emissions were low in 2010.

# Summary: Impact of aromatics

- Large global changes for glyoxal and methyl glyoxal.
- Small importance for other species on the global scale.
- Significant changes on a regional scale, especially in East Asia where emissions are high.
- Reduced $\mathrm{OH}$ in free troposphere, especially in the northern hemisphere.
- Impact on global $\mathrm{O_3}$ is negative, not positive.
- Regions with high $\mathrm{NO_x}$ concentrations show increases of $\mathrm{OH}$ and $\mathrm{O_3}$.
- Given the uncertainties in the oxidation mechanism and emissions, our results may underestimate the impact of aromatics.

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