Implication of extreme atmospheric methane concentrations for chemistry-climate connections

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Abstract. Methane (CH₄) is the second most important greenhouse gas, which atmospheric concentration is influenced by human activities. In this study, numerical simulations with a chemistry-climate model (CCM) are performed aiming to assess possible consequences of significantly enhanced CH₄ concentrations in the Earth’s atmosphere for the climate.

We analyze experiments with 2xCH₄ and 5xCH₄ present day (2010) mixing ratio and its quasi-instantaneous chemical impact on the atmosphere. The massive increase in CH₄ strongly influences the tropospheric chemistry by reducing the hydroxyl radical (OH) abundance and thereby extending the CH₄ lifetime as well as the residence time of other chemical pollutants. The region above the tropopause is impacted by a substantial rise in stratospheric water vapor (SWV). The stratospheric ozone (O₃) column increases overall, but SWV induced stratospheric cooling also leads to a enhanced ozone depletion in the Antarctic lower stratosphere. Regional patterns of ozone change are affected by modification of stratospheric dynamics, i.e. increased tropical up-welling and stronger meridional transport towards the polar regions. We calculate the net radiative impact (RI) of the 2xCH₄ experiment to be 0.69 W/m² and for the 5xCH₄ experiment to be 1.79 W/m². A substantial part of the RI is contributed by chemically induced O₃ and SWV changes, in line with previous radiative forcing estimates.

To our knowledge this is the first numerical study using a CCM with respect to two/fivefold CH₄ concentrations and it is therefore an overdue analysis as it emphasizes the impact of possible strong future CH₄ emissions on atmospheric chemistry and its feedback on climate.

1 Introduction

Methane (CH₄) is a potent greenhouse gas (GHG), subject to strong anthropogenic emissions that contribute substantially to global warming. It is not just by itself a radiatively active gas but is chemically active as well, strongly influencing the chemical composition of the atmosphere. Beyond that its sources are prone to temperature and it is generally expected that climate change (i.e. surface warming) will lead to enhanced CH₄ emissions, accelerating the temperature rise. For instance additional CH₄ emissions are expected from wetlands due to climate-driven changes (Gedney et al., 2004; Zhang et al., 2017; Ma et al., 2017). Moreover, a large quantity of CH₄ is stored as methane hydrate not only in permafrost soil but also in the sea floor. Permafrost soil stores about a hundredfold of the current CH₄ burden in the atmosphere and oceanic methane hydrates...
store even a thousandfold (IPCC, 2013). Current estimates indicate that GHG emissions from thawing permafrost soils could represent a major terrestrial biogeochemical feedback to climate change over the coming decades (Comyn-Platt et al., 2018).

At the same time, it is under debate whether a possible strong release of CH$_4$ from thawing permafrost in the Arctic region could potentially force an abrupt climate change (as discussed by O’Connor et al., 2010). At present, the release of methane hydrate from reservoirs is highly uncertain as well as the magnitude of future natural and anthropogenic emissions of methane. Increasing surface temperatures cause enhanced CH$_4$ emissions from thawing permafrost soils to the atmosphere, but the amount is currently poorly constrained (Hayes et al., 2014; Schaefer et al., 2014; Koven et al., 2015; Schuur et al., 2015). For instance, Dean et al. (2018) stated that there is basically no significant increase of Arctic methane emissions at the moment, though it may increase towards the end of the 21st century.

Nevertheless, permafrost thaw could potentially release trapped CH$_4$ and transform frozen soil to wetland areas, which would then add to Arctic CH$_4$ emissions. Moreover, ongoing heating of the Arctic sea surface temperature (SST) will also enhance future CH$_4$ production in the ocean, and a reduction of sea ice concentration (SIC) may increase the direct transfer of CH$_4$ from the ocean to the atmosphere. In particular, enhanced SST can increase the production of CH$_4$ as permafrost underlying the continental shelf begins to thaw (Miller et al., 2018). How a changing climate will impact future CH$_4$ emissions remains a topic of debate in atmospheric science, since emissions from the most climate sensitive CH$_4$ sources, i.e. wetlands, are difficult to quantify precisely.

Although there remain important knowledge gaps about the magnitude of CH$_4$ emissions, it is important to improve our understanding of how strongly future CH$_4$ emissions may impact our atmosphere and the environment. About 90% of the emitted CH$_4$ is removed in the troposphere. A change in tropospheric CH$_4$ concentration affects the oxidizing capacity of the atmosphere, modifies ozone in the troposphere and influences the CH$_4$ lifetime itself (e.g. Saunois et al., 2016; Frank, 2018; Holmes, 2018). Additionally, it also influences the stratosphere. For example, enhanced CH$_4$ emissions will lead to increased abundance of stratospheric water vapor (SWV) and by this strongly influence stratospheric ozone (O$_3$) (Stenke and Grewe, 2005; Revell et al., 2016).

To assess the direct and indirect effects of severely enhanced CH$_4$ emissions on atmospheric composition and Earth climate, numerical model studies are able to support investigations such as to identify potential signatures impacting climate change. So far only a limited amount of numerical studies are available concerning the impact of very strong CH$_4$ emissions. Exemplary, the effect of twofold CH$_4$ was investigated in a 1D radiative-convective climate model by Owens et al. (1982) and by MacKay and Khalil (1991). Shang et al. (2015) used a Chemical Transport model (CTM) but doubled CH$_4$ emission over China only. Other CTM studies have focused on recent changes and fluctuations of the atmospheric CH$_4$ concentration (e.g. Dalsøren et al., 2016) or have tried to explain CH$_4$ trends, which is a challenge because of important uncertainties in the global CH$_4$ budget, i.e. the balance of surface sources and atmospheric and surface sinks (Saunois et al., 2016). Furthermore, CTMs are limited in assessing climate change related issues, because they do not include the feedback between chemistry and dynamics. Smith et al. (2018) investigated the fast radiative feedbacks (adjustments) in a 3×CH$_4$ simulation without considering the chemical feedback effects. This investigation includes only physical components of the atmosphere, like direct cloud, water vapor and
temperature adjustments, and the total radiative adjustment result in a value near zero. This example even more motivates an assessment of simulations that include chemically driven atmospheric adjustments to increases of CH₄.

To our knowledge studies using data derived from chemistry-climate model (CCM) simulations including extreme CH₄ emissions (i.e. beyond current and near-future amounts) are not available so far. A CCM is an atmospheric global circulation model that is interactively coupled to a detailed chemistry module. In contrast to CTMs, in CCMs the simulated concentrations of the radiatively active gases are used for the calculations of net heating rates. Changes in the abundance of these gases due to chemistry and advection influence heating rates and, consequently, variables describing atmospheric dynamics. This creates a dynamical-chemical coupling in which the chemistry influences the dynamics and vice versa. Since CH₄ influences other trace gases due to its oxidation products as well as the removal of hydroxyl radical (OH), a comprehensive chemistry module is necessary. In simulations with doubled carbon dioxide (CO₂), in contrast, the feedback on climate and chemistry is induced only by its radiative impact. Apart from accounting for the direct radiative impact of CH₄ the use of a CCM is strongly desired, since the atmospheric CH₄ chemical feedback is a key process for understanding the variations in atmospheric CH₄ and its effects on other chemical constituents of the atmosphere (Holmes, 2018).

The present work is the first study investigating atmospheric effects due to extreme CH₄ emissions with such a CCM. Idealized simulations of significantly enhanced CH₄ concentrations are performed, i.e. twofold (2xCH₄) and fivefold (5xCH₄) enhanced CH₄ concentrations compared to present day condition, allowing to assess possible future consequences for atmospheric composition considering chemical feedback processes. In a first step, which is described in this paper, we conducted CCM simulations without interactive ocean coupling, i.e. the surface conditions regarding SST and SIC are prescribed (suppressed surface temperature feedback). Equivalent to the work of Smith et al. (2018), the results can be interpreted as rapid adjustments to a sudden CH₄ enhancement before the ocean reacts to the perturbation, which would occur on a by far larger time scale.

In this study we will use the ECHAM/MESSy Atmospheric Chemistry (EMAC) CCM (Jöckel et al., 2016) assessing the range of atmospheric responses by abrupt increases of CH₄ concentrations. A short description of EMAC is given in Section 2 as well as an explanation of the simulation strategy. In Section 3 the reference simulation representing near-present day condition is briefly evaluated with observations (Subsect. 3.1) and a discussion of the impact of twofold and fivefold increased CH₄ concentrations in respective scenario simulations is presented in Subsect. 3.2. In the final Section 4 we draw some conclusions from our investigation and give a brief outline for follow-up investigations.

## 2 Description of the model and simulation strategy

We use the EMAC model in the version 2.52 (Jöckel et al., 2010) and operate it at a resolution of T42L90MA corresponding to a quadratic Gaussian grid of approx. 2.8° x 2.8° in latitude and longitude with 90 levels up to 0.01 hPa. More details on the Modular Earth Submodel System (MESSy) can be found in Jöckel et al. (2016).

We conducted one reference simulation (REF) and two sensitivity simulations (S1 and S2) as 20-year time slice simulations representing in general year 2010 conditions. Monthly SST and SIC are thereby repeatedly prescribed, representing a climato-
logical annual cycle of the years 2000–2009 based on global analyses of Rayner et al. (2003). An at least 10-year long spin-up simulation preceding each simulation (likewise time slice) ensures quasi steady state conditions, but has been neglected in the evaluation. The spin-up started with initial conditions using a restart file representing the year 2010 of a reference simulation with so called specified dynamics (SD) of the Earth System Chemistry integrated Modelling (ESClMo) project (Jöckel et al., 2016). To reduce the length of the spin up of the sensitivity simulations we started those using twofold and fivefold CH$_4$ mixing ratios compared to the initialization of the reference, respectively.

The lower boundary condition of CH$_4$ in the reference simulation, i.e. the CH$_4$ surface mixing ratio, is prescribed by Newtonian relaxation (i.e. nudged) following a zonal mean estimate from the National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL) based on observations of CH$_4$ surface mixing ratios. These observations are provided by the Advanced Global Atmospheric Gases Experiment (AGAGE; http://agage.eas.gatech.edu) and National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL; http://www.esrl.noaa.gov). The mean surface mixing ratio is about 1.8 parts per million volume (ppmv). The two sensitivity simulations (S1 and S2) are carried out nudged at the surface to a twofold CH$_4$ surface mixing ratio (compared to the present day reference) being about 3.6 ppmv and a fivefold CH$_4$ surface mixing ratio being 9.0 ppmv, respectively. Although this does not correspond to an equivalent increase in the surface fluxes, it scales the surface mixing ratio directly to the intended value, as has been done in similar studies (see Kirner et al., 2015; Forster et al., 2016; Smith et al., 2018). To put the chosen scaling factors in perspective, a surface mixing ratio of 3.6 ppmv (similar to the doubling above) will be reached according to the Representative Concentration Pathways (RCP) 8.5 scenario towards the end of the 21st century (Riahi et al., 2007). The RCP 8.5 is the so called baseline climate change scenario, which does not employ any climate mitigation target (Riahi et al., 2011). Other prescribed conditions (SST, SIC, CO$_2$ etc.) of the sensitivity simulations S1 and S2 are identical to REF. Particularly all other GHG concentrations and online simulated emissions represent 2010 conditions.

In the following, changes and feedbacks are assessed by comparing the reference simulation REF with S1 and S2, with focus on changes in the simulated chemically and radiatively active trace gases. To quantify the associated radiative impact (RI), the EMAC option for multiple radiation calls is employed (Dietmüller et al., 2016) in a separate additional simulation, which allows to estimate individual components of the total radiative impact. This simulation is run for one year (plus one year spin-up) and uses climatological 20 year means of the species of interest, namely CH$_4$, O$_3$ and SWV. The results corresponding to one of the previously introduced experiments are indicated by the associated simulations name and a asterixs (i.e. REF*, S1* and S2*).

3 Discussion of results

3.1 Evaluation of the reference simulation

The reference simulation REF is set up to represent conditions comparable to the near-present atmospheric conditions in 2010. To ensure that this simulation is sufficiently realistic, the simulation results of CH$_4$ mixing ratio in the troposphere and the
stratosphere are compared to data derived from atmospheric observations indicated below. These observations are independent to the data sets used for the lower boundary condition, to ensure an objective evaluation.

For a detailed assessment of the performance of EMAC in general and how EMAC compares to observations (e.g. regarding temperature and ozone) we refer to Jöckel et al. (2016). This publication also includes an evaluation of transient simulations regarding CH$_4$ in the Upper Troposphere and Lower Stratosphere (UTLS) using measurements of the Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container (CARIBIC) project, which indicates a good representation with relative differences of less than 5%.

In general, observed surface mixing ratios of CH$_4$ indicate a north-south gradient with larger CH$_4$ mixing ratios in the Northern Hemisphere (NH) mostly due to large wetland regions and anthropogenic sources on the northern continents. This north-south gradient is by design (nudging to observation based zonal mean surface mixing ratios) apparent in the simulation data as well. The simulated gradient of the model is compared to observations during a ship cruise of the research vessel Polarstern (Klappenbach et al., 2015, see Supplement Fig. S1). The simulation results reproduce the observed north-south gradient of the ship cruise qualitatively well, although an offset of about 0.055 ppmv exists. Note that the observations in the Polarstern were conducted in 2014, while the simulation represents 2010 conditions. Global CH$_4$ surface mixing ratios have risen between 2010 and 2014 by about 0.030 ppmv, which explains a large part of the offset.

Additionally, the average vertical CH$_4$ profile of the REF simulation is evaluated using balloon borne measurements from Röckmann et al. (2011). The CH$_4$ mixing ratio in the troposphere is approximately constant as a result of well-mixed tropospheric conditions. Above the tropopause the mixing ratio of CH$_4$ decreases with altitude. This vertical gradient apparent in the balloon borne observations is reasonably reproduced in REF (see Supplement Fig. S2).

Furthermore, a general comparison of zonally averaged CH$_4$ mixing ratio above the tropopause of REF is done with observations from the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) instrument mounted on the ENVISAT satellite (Fischer et al., 2008). The zonally averaged CH$_4$ MIPAS climatology (2002–2012) in Plieninger (2017) corresponds qualitatively and quantitatively to our simulation results in Figure 1a.

Our simulation represents the observed CH$_4$ mixing ratios in the stratosphere and mesosphere and also shows the apparent double bulge in the upper stratosphere with slightly higher values in the NH.

Overall, the agreement of the reference simulation results with observations turned out to be sufficient for the purpose of our intended study. In the next section we compare the reference simulation with the two sensitivity simulations, to present the general impact of strongly enhanced CH$_4$ concentrations.

3.2 Impact of twofold and fivefold increased CH$_4$ concentrations

In this sub-section we investigate the impact of twofold and fivefold surface CH$_4$ mixing ratio on the chemical composition of the atmosphere and analyze the new chemical equilibrium after a sufficient spin up.

Since SST and SIC are prescribed, any possible feedback on tropospheric temperature is largely suppressed in the present simulations. Therefore, in this study we are only considering rapidly evolving chemical feedback effects including respective radiative adjustments and temperature adjustments in the stratosphere.
Figure 1. Annual zonal mean of absolute CH$_4$ mixing ratios (in parts per billion volume (ppbv)) of reference (REF) (a), S1 (b) and S2 (c). Note the different color scales.

Figure 2. CH$_4$ lifetime calculated according to equation 1 versus the corresponding scaling factor applied to the reference lower boundary condition in the respective simulation: REF (1.0), S1 (2.0), S2 (5.0).

The oxidation capacity of the atmosphere is often measured in terms of the CH$_4$ lifetime (Karlsdóttir and Isaksen, 2000; Dentener et al., 2003; Naik et al., 2013; Voulgarakis et al., 2013). In this study we calculate the tropospheric CH$_4$ lifetime according to Jöckel et al. (2006) as

$$
\tau_{CH_4} = \frac{\sum_{b \in B} M_{CH_4}}{\sum_{b \in B} k_{CH_4+OH}(T) \cdot c_{air}(T,p,q) \cdot OH \cdot M_{CH_4}},
$$

(1)

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Figure 3. Difference between the annual zonal mean CH$_4$ of the simulations S1 relative to the twofold and S2 relative to the fivefold annual zonal mean of the reference in (%).

with $M_{CH_4}$ being the mass of methane in kg, $T$ the temperature, $p$ the pressure and $q$ the specific humidity, all depending on time and the specific box $b \in B$, with $B$ being the set of all considered grid boxes, e.g. all boxes which lie below the tropopause. $k_{CH_4 + OH}(T)$ is the reaction coefficient of the reaction CH$_4$ + OH $\rightarrow$ products in [molec. s$^{-1}$]. $c_{air}(T, p, q)$ is the concentration of air in [molec. cm$^{-3}$] and $OH$ the mole fraction of OH in one mole of the chemical tracer per one mole of air (mol mol$^{-1}$)$_{dry\ air}$.

Our calculations yield a nearly linear increase of tropospheric CH$_4$ lifetime with respect to the CH$_4$ scaling in the sensitivity simulations (see Fig. 2). It is known that the tropospheric CH$_4$ lifetime is anti-correlated with OH concentration (Montzka et al., 2011). The strongly enhanced CH$_4$ mixing ratios reduce the atmospheric OH mixing ratio, which leads to a longer (tropospheric) CH$_4$ lifetime. It is not sure that the quasi-linear behavior will hold for even larger or smaller scaling factors, since the chemistry determining the OH abundance is highly non-linear. There are also not enough data points (sensitivity simulations) for a definite proposition on strictly linear dependence. Nevertheless, we assume that these results give evidence that in the troposphere CH$_4$ and OH for the given range are almost linearly anti-correlated. The simulations clearly show that increasing CH$_4$ emissions increase the residence time of CH$_4$ in the atmosphere and therefore its global warming potential (GWP).

Next, we investigate the impact of CH$_4$ concentration increases on changes in CH$_4$ depletion, thus analyzing possible non-linearities in the chemical cycles. For this we compare both sensitivity simulation results with the reference CH$_4$ mixing ratio multiplied by 2 and 5, respectively, as is shown in Fig. 3. This approach makes it possible to see where CH$_4$ is impacted by non-linear processes, hence where the twofolding (fivefolding) at the surface does not lead to an equal increase in the upper layers in the steady state.
In both sensitivity simulations, the troposphere is largely controlled by the nudging at the lower boundary due to turbulent mixing. In this area the differences of the sensitivity simulations and the scaled reference simulation are near-zero (though slightly positive). Larger CH$_4$ mixing ratios reduce its most important sink reactant in the troposphere, namely OH, which leads to a reduction of the CH$_4$ depletion compared to the reference.

The n-fold methane concentrations at the surface do not generate a likewise n-fold methane concentration throughout the upper stratosphere. In the sensitivity simulation with twofold (fivefold) CH$_4$, lower CH$_4$ values of about 5% (10%) are found between 50 and 1 hPa compared to the corresponding n-folded reference. Identically prescribed SST in all three model simulations determines to a large extent the forcing of atmospheric dynamics and also constrains to a large part the stratosphere (see Garny, 2010). Therefore, modified atmospheric circulation patterns are unlikely the cause of these changes in stratospheric CH$_4$ mixing ratios.

An explanation for the relatively strong relative depletion in CH$_4$ in the upper stratosphere could be the change of the reaction rates for the CH$_4$ decomposition via OH and chlorine (Cl), which are both temperature dependent. However, since the stratosphere cools in the sensitivity simulations (as will be discussed below) this also cannot explain the simulated reduced CH$_4$ content in the stratosphere. Nevertheless, the deviation of a linear signal in stratospheric CH$_4$ mixing ratio gives evidence that more CH$_4$ in the upper stratosphere is destroyed due to secondary feedbacks caused by changes in the chemical composition of the stratosphere (particular O$_3$, SWV and OH) and will be discussed in the paragraphs below.

The OH concentration in the atmosphere is determined by its precursors, which are water vapour (H$_2$O) and O$_3$, the photolysis rate of O$_3$, as well as by its sinks, which are mostly CH$_4$ and carbon monoxide (CO). The decline of OH in the troposphere
Figure 5. Comparison of the relative changes (%) in annual zonal mean H$_2$O mixing ratio of the sensitivity simulations S1 and S2 (two- and fivefold CH$_4$, respectively) compared to the reference REF. Non-stippled areas are significant on a 95% confidence level according to a two sided Welch's test.

by 20 – 30% in the S1 simulation compared to REF (see Fig. 4) is caused, as stated above, by the increased sink via CH$_4$. In the stratosphere, however, OH increases by about 30% in the twofold CH$_4$ case (S1) and by 60 – 80% in the fivefold CH$_4$ case (S2, see Fig. 4). The mixing ratio of OH increases especially in the upper stratosphere at higher latitudes and fits to the decline in CH$_4$ in the same regions (see Fig. 3). However, increases in CH$_4$ mixing ratios influence the abundance of OH precursors, namely H$_2$O and O$_3$ via direct and secondary chemical effects and thereby feedback on the production of the CH$_4$ associated sink OH.

Oxidation of CH$_4$ in the stratosphere produces additional H$_2$O and is therefore an important source for SWV (Hein et al., 2001; Rohs et al., 2006; Frank et al., 2018). The enhanced CH$_4$ mixing ratios in the stratosphere cause a steady increase of SWV with height in both sensitivity simulations as indicated by Fig. 5. In the twofold CH$_4$ case (S1) the amount of H$_2$O is enhanced by up to 50% in the middle and higher stratosphere, in the fivefold experiment (S2) the SWV increases by more than 250%.

The chemical changes indicated above influence the atmospheric temperature. However, since the SST is prescribed, the temperature response is largely suppressed in the troposphere. Confirmation gives Fig. 6, where only a small change in tropospheric temperature is detected in both sensitivity simulations (S1 & S2). The stratosphere, however, shows larger changes in temperature. It can adjust to the perturbation since its temperature is mostly controlled by local radiative heating from trace gases and changing dynamics.

Around the tropopause there is a slight warming in the twofold CH$_4$ case (S1), which is reaching values of up to +3 K in the fivefold case (S2, see Fig. 6). Elsewhere in the stratosphere, however, the higher abundance of CH$_4$ induces a stratospheric
cooling in our simulations. The twofold CH$_4$ mixing ratios in S1 lead to a stratospheric cooling of about $-1$–$-2$ K and a mesospheric cooling of up to $-5$ K. The results of the simulation with fivefold CH$_4$ mixing ratios indicate a cooling of about $-3$ K in the stratosphere and more than $-10$ K in the mesosphere.

As will be shown below, these temperature changes are mainly induced by the radiative impact of CH$_4$ in the stratosphere and mesosphere and by the changes in atmospheric chemistry due to enhanced chemically reactive CH$_4$.

Furthermore, the extreme CH$_4$ concentrations prescribed in our sensitivity simulations have an impact the vertical profile of O$_3$. Concentrations of O$_3$ increase between 50 and 5 hPa (see Fig. 7) and decrease above. There is also a decrease between 50 hPa and 20 hPa in the tropics and between 100 hPa and 50 hPa at the southern pole.

The pattern of ozone reduction in the lowermost tropical stratosphere is typical for an enhanced tropical up-welling, which transports ozone depleted air from the upper troposphere to the lower stratosphere (Deckert and Dameris, 2008; Dietmüller et al., 2014). Although the main factor for such a strengthening, namely the SST, is prescribed, the increase in the GHG CH$_4$ alone can also lead to an enhanced tropical up-welling (Garny et al., 2011). A similar pattern in stratospheric ozone changes due to CH$_4$ increases (i.e. increase between 2000 and 2040–2049 according to the Intergovernmental Panel on Climate Change (IPCC) A1B greenhouse gas scenario) has been shown by Kirner et al. (2015). Nonetheless, we expect the impact on the tropospheric up-welling to intensify further in simulations, where the SSTs can adjust to the CH$_4$ induced climate change.

In the middle stratosphere the O$_3$ production/depletion is influenced by the increased SWV and the corresponding stratospheric cooling, which restrains the reaction rates of O$_3$ depleting catalytic cycles (Portmann and Solomon, 2007; Braesicke et al., 2013). Furthermore, Excited oxygen (O($^1$D)) is depleted by increased abundances of H$_2$O, which reduce the sink of O$_3$.
Figure 7. Comparison of the relative changes (%) in annual zonal mean O₃ mixing ratio of the sensitivity simulations S1 and S2 (two- and fivefold CH₄, respectively) compared to the reference REF. Non-stippled areas are significant on a 95% confidence level according to a two-sided Welch’s test.

and eventually lead to increased O₃ abundances. Above 2 hPa, increases in OH facilitate O₃ destruction in the upper stratosphere and mesosphere (Kirner et al., 2015). Beyond that, there are inter-hemispheric differences in O₃ mixing ratios in the polar regions (increased O₃ at the polar middle stratosphere at about 30 hPa) that are an indication for a strengthening of the meridional transport towards the poles in the extreme case of 5xCH₄ (see Supplement Fig. S4). In southern winter (Supplement Fig. S4 upper right) this transport is suppressed by the polar vortex and is forming a corona of increased O₃ mixing ratios outside the polar vortex. The stratospheric cooling also leads to enhanced forming of polar stratospheric clouds (PSCs) during the southern hemispheric winter and therefore to enhanced O₃ depletion in the southern lower stratosphere (see Supplement Fig. S3 c and S4 c), (Dameris, 2010). The severity of the depletion does barely increase from S1 to S2, which may be explained by a saturation effect reached with respect of additional PSCs.

Overall, the twofold CH₄ mixing ratio with respect to 2010 is found to induce a radiative impact (RI) of about 0.69 Watt per square meter (W/m²) in the twofold case (S1) and a RI of about 1.79 W/m² in the fivefold case (S2). The RI is calculated by the difference of the sum of long-wave and short-wave radiation at the top of the atmosphere between the reference and the respective sensitivity simulation. As the simulations are performed with prescribed SST, this net RI has the character of an effective radiative forcing (ERF), (Forster et al., 2016). It includes the RI of CH₄ itself, as well as rapid adjustments from physical and chemical processes. The chemical processes specifically include changes in SWV and O₃ and have been quantified by estimating their individual RIs (including stratospheric temperature adjustments) with the EMAC submodel RAD (Dietmüller et al., 2016) in a separate simulation resulting in estimates corresponding to the reference simulation REF* and the sensitivity simulations S1* and S2* (see 2 for a detailed explanation on the simulation).
Table 1. An estimation of separate RI in [W/m$^2$] of the changes in the chemical species CH$_4$, SWV and O$_3$. Values are calculated using the RAD submodel (Dietmüller et al., 2016) in a separate simulation using 20 years climatologies of the individual species. Solely values of the totals are directly calculated from the presented simulations R1, S1 and S2.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>CH$_4$</th>
<th>SWV</th>
<th>O$_3$</th>
<th>chemical RI</th>
<th>physical RI$^1$</th>
<th>total RI</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1* (2xCH$_4$)</td>
<td>0.23</td>
<td>0.15</td>
<td>0.27</td>
<td>0.66</td>
<td>0.03</td>
<td>0.69</td>
</tr>
<tr>
<td>S2* (5xCH$_4$)</td>
<td>0.51</td>
<td>0.55</td>
<td>0.76</td>
<td>1.82</td>
<td>-0.03</td>
<td>1.79</td>
</tr>
</tbody>
</table>

$^1$ total RI = chem. RI.

The twofolding and fivefolding CH$_4$ enhancements in the sensitivity simulations S1 and S2 correspond to a net increase of surface CH$_4$ of 1800 ppbv and 7200 ppbv, respectively. For example, the increase of the surface CH$_4$ mixing ratio from 1750 (pre-industrial) to 2011 has led to a ERF of 0.48 W/m$^2$±0.1 W/m$^2$ (IPCC, 2013, Chap. 8, Tab. 8.2), which corresponds to a net increase of surface CH$_4$ of about 1100 ppbv. The net increase of twofold CH$_4$ mixing ratios (S1) is larger than the increase since pre-industrial times. Thus, at first glance, the net RI calculated in this study seems consistent with the value in the IPCC and previous estimates from other models for a tripled CH$_4$ concentration (assumed +3534 ppbv) (Forster et al., 2016; Smith et al., 2018), which are for example for HadGEM2 1 W/m$^2$ and for CESM1 1.4 W/m$^2$.

However, those previous estimates do not account for contributions from O$_3$ and stratospheric H$_2$O changes (see also Smith et al. (2018)). Only by looking at the direct RI simulations of individual species a clearer picture emerges (see Table 1). The individual RIs of the chemical variations is once more reasonable compared with similar calculations of the IPCC (Chapter 8, Figure 8.17). We detect comparably low values for the RI of CH$_4$, a feature which has been reported before for the ECHAM5 radiation module (Löhmann et al., 2010). As a residuum of the sum of chemically induced RI (Table 1) and the ERF, we estimate a pure physical RI of 0.03 W/m$^2$ (S1*, 2xCH$_4$) and -0.03 W/m$^2$ (S2*, 5xCH$_4$), respectively, i.e., small contributions that compare very well to the results of Smith et al. (2018).

The separation of the individual RI in the main contributing species allows to further identify the individual contribution to temperature adjustments in the stratosphere (see Supplement Fig. S5 and S6). The stratosphere cools by about $-1.5$ to $-2$ K mostly due to SWV (up to $-1.4$ K). This cooling is amplified by the increased CH$_4$ and tropospheric O$_3$, but reduced by increased stratospheric O$_3$ in the area between roughly 20 hPa and 1 hPa. This induces a dipole pattern in the total temperature change (warming in the lower stratosphere, cooling in the middle stratosphere, warming in the upper stratosphere and cooling in the mesosphere, see Supplement Fig. S5 and S6). Only a minor contribution to the stratospheric temperature change is contributed by tropospheric H$_2$O, as to be expected. The difference between the pure RI of all trace gas changes (Figs. S5a, S6a) and the net stratospheric temperature change (Fig. 6) is small, indicating a dominating role of radiative effects in forcing the temperature response in S1 and S2.
4 Conclusions

The present study summarizes the quasi-instantaneous chemical adjustments of the atmosphere in response to a very strong increase in atmospheric CH$_4$. We emphasize that the applied doubling of present day CH$_4$ surface mixing ratios is not unrealistic as it is even part of the RCP 8.5 scenario. Considering further feedbacks with still uncertain quantitative consequences, it is indeed possible that the presented changes in the atmospheric chemistry will be faced by upcoming generations.

For the range of CH$_4$ concentrations covered in this study we find that the CH$_4$ lifetime increases quasi-linearly with enhanced surface mixing ratios. This is ascribed to a strong reduction of OH, which is the main sink of CH$_4$ in the troposphere. We conclude that the strong reduction of OH will also influence other radiatively active, air quality relevant, and ozone depleting substances in the troposphere. The radical OH is the most important atmospheric detergent and its reduction will enhance the residence time of these substances as well as of CH$_4$, and thereby increase the global radiative burden.

Additionally, induced by CH$_4$ oxidation, SWV will increase substantially. This leads to stratospheric cooling, which in turn influences stratospheric chemistry and (to a less degree) dynamics. In particular it will lead to an increase in total O$_3$ column (not shown) nearly on the whole globe. Only in the antarctic spring it causes a strengthening of the ozone depletion.

The rapid radiative adjustments of O$_3$ and SWV are both positive and thus increase the radiative forcing directly induced by CH$_4$, consistent with Fig. 8.17 of IPCC (2013). However, the direct CH$_4$ radiative impact is considerably low biased in the simulations, apparently through a systematic error in the radiation module. This bias remains masked if only the effective radiative forcing of the twofold and fivefold CH$_4$ simulations is considered. Individual radiative impact estimates also help interpreting the net stratospheric temperature change in the CH$_4$ increase simulations. It reveals that the main part of the overall temperature pattern is controlled by cooling from stratospheric H$_2$O.

Since the SSTs are prescribed in the present simulations, tropospheric temperatures and atmospheric dynamics do not represent the situation after adaption of the ocean. This also prohibits the calculation of climate sensitivity parameters. In a future study similar CCM simulations with a mixed layer ocean will be carried out and the contribution of feedbacks associated with SST changes will be investigated accordingly.

**Code and data availability.** The Modular Earth Submodel System (MESSy) is continuously developed and applied by a consortium of institutions. The usage of MESSy and access to the source code is licensed to all affiliates of institutions, which are members of the MESSy Consortium. Institutions can become a member of the MESSy Consortium by signing the MESSy Memorandum of Understanding. More information can be found on the MESSy Consortium Web-site (http://www.messy-interface.org).

**Author contributions.** The simulations were set-up and carried out by P. J. and F. W.. F. T. analyzed the data and compiled the results. M. D. and F. W. structured and composed the manuscript. M. P. and F. W. contrived and calculated the radiative impact. P. J. and M. P. contributed to the text.
Competing interests. The authors declare that they have no conflict of interest.

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