

Chemistry-climate feedback of atmospheric methane in a methane emission flux driven chemistry-climate model

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Abstract.

The chemical sink of atmospheric methane (CH_4) depends on the temperature and on the chemical composition. Here, we assess the feedback on atmospheric CH_4 induced by changes of the chemical sink in a warming climate using a CH_4 emission flux driven setup of the chemistry-climate model EMAC, in which the chemical feedback of CH_4 mixing ratios
5 can evolve explicitly. We perform idealized perturbation simulations driven either by increased carbon dioxide (CO_2) mixing ratios, or by increased CH_4 emission fluxes. The CH_4 emission flux perturbation leads to a large increase of CH_4 mixing ratios. Remarkably, the factor by which the CH_4 mixing ratio increases is larger than the increase factor of the emission flux, because the atmospheric lifetime of CH_4 is extended.

In contrast, the individual effect of the global surface air temperature (GSAT) increase is to shorten the CH_4 lifetime, which
10 results in a significant reduction of CH_4 mixing ratios in our setup. The corresponding radiative feedback is estimated at $-0.041 \text{ W m}^{-2} \text{ K}^{-1}$ and $-0.089 \text{ W m}^{-2} \text{ K}^{-1}$ for the CO_2 and CH_4 perturbation, respectively. The explicit response of CH_4 mixing ratios leads to secondary feedbacks on the hydroxyl radical (OH) and ozone (O_3). Firstly, the OH response includes the CH_4 - OH feedback, which enhances the CH_4 lifetime change, and, secondly, the formation of tropospheric O_3 is reduced. Our CH_4 perturbation induces the same response of GSAT per effective radiative forcing (ERF) as the CO_2 perturbation, which
15 supports the applicability of the ERF framework for CH_4 .

1 Introduction

Methane (CH_4) is, after carbon dioxide (CO_2), the second most important anthropogenic greenhouse gas (GHG). Compared to CO_2 , CH_4 has a larger radiative efficiency (Forster et al., 2021) and a shorter atmospheric lifetime of about 10 years (e.g., Prather et al., 2012; Stevenson et al., 2020). Therefore, reducing atmospheric CH_4 mixing ratios is considered an important
20 measure to mitigate climate change on a decadal time scale (Saunio et al., 2016; Collins et al., 2018; Ocko et al., 2021; Staniasek et al., 2022). The relative short atmospheric lifetime of CH_4 is a consequence of the fact that CH_4 is a chemically active species. According to Saunio et al. (2020), the most important sink of atmospheric CH_4 is oxidation by the hydroxyl

radical (OH). Thus, understanding the chemical mechanisms underlying CH₄ oxidation is crucial when assessing its climate impact and mitigation options.

25 Besides its direct radiative effect, indirect contributions from ozone (O₃) and stratospheric water vapour (H₂O) enhance the effective radiative forcing (ERF) of CH₄ (Shindell et al., 2005, 2009; Stevenson et al., 2013; Winterstein et al., 2019; Thornhill et al., 2021b; O'Connor et al., 2022). In addition to its climate impact, tropospheric O₃ poses harmful effects on human health (Nuvolone et al., 2018) and on vegetation (Ashmore, 2005). Therefore, mitigation options involving CH₄ emission reductions have beneficial effects on air quality (Shindell et al., 2012; Staniaszek et al., 2022) and plant productivity (Sitch et al., 2007). In
30 addition to the effects on O₃ and H₂O, CH₄ oxidation reduces OH, which feeds back onto its own atmospheric lifetime (e.g., Winterstein et al., 2019) and affects the rate of formation of secondary aerosols leading to a shift in the aerosol-size distribution. The latter, in turn, influences aerosol-radiation interactions and aerosol-cloud interactions, and is considered another indirect contribution to the ERF of CH₄ (Kurtén et al., 2011; O'Connor et al., 2022).

Next to its importance for indirect contributions to the ERF, CH₄ oxidation largely constrains the atmospheric lifetime of
35 CH₄ and, thus, together with the magnitude of the emissions, its direct radiative effect. The atmospheric lifetime of CH₄ is not constant, but depends on the temperature and on the chemical background, which determines the abundance of its sink reactants, especially OH. OH is influenced by a multitude of factors (e.g., Voulgarakis et al., 2013; Stevenson et al., 2020). Among others, meteorological factors such as humidity and temperature influence the abundance of OH. Hence, climate feedbacks of the chemical sink of CH₄ and thereby its lifetime are to be expected. More precisely, the CH₄ lifetime is projected to shorten as a
40 result of tropospheric warming (Voulgarakis et al., 2013; Stecher et al., 2021; Heimann et al., 2020; Thornhill et al., 2021a). To date, only a limited number of studies have assessed the corresponding response of CH₄ mixing ratios directly (Heimann et al., 2020). Even though efforts are ongoing to employ chemistry-climate models (CCMs) in a CH₄ emission flux driven model setup (Shindell et al., 2013; He et al., 2020; Folberth et al., 2022), it is still common practice to prescribe CH₄ mixing ratios at the lower boundary. For instance, the latter method was pursued in the Aerosol Chemistry Model Intercomparison Project
45 (AerChemMIP; Collins et al., 2017), which was endorsed in the Coupled-Model Intercomparison Project 6 (CMIP6; Eyring et al., 2016), that, in turn, built the basis for the last report of the Intergovernmental Panel on Climate Change (IPCC, 2021).

When CH₄ mixing ratios are prescribed at the surface, the CH₄ adjustment to changes of the chemical sink is suppressed in the troposphere, and can be only derived offline from the atmospheric lifetime change (Dietmüller et al., 2014; Heinze et al., 2019; Thornhill et al., 2021a). This offline method, however, suppresses indirect feedbacks induced by the CH₄ response.
50 Firstly, when CH₄ mixing ratios are free to evolve, the resulting CH₄ response alters the atmospheric CH₄ lifetime, which in turn leads to further changes of the CH₄ mixing ratios. The derivation of the CH₄ response from the lifetime change usually accounts for this effect by including a constant CH₄-OH feedback factor f (Heinze et al., 2019; Thornhill et al., 2021a) so that the equilibrium CH₄ mixing ratio [CH₄]_{eq} is estimated as (e.g., Stevenson et al., 2020)

$$[\text{CH}_4]_{\text{eq}} = [\text{CH}_4]_{\text{ref}} \left(\frac{\tau_{\text{exp}}}{\tau_{\text{ref}}} \right)^f, \quad (1)$$

55 where [CH₄]_{ref} is the reference CH₄ mixing ratio and τ_{ref} and τ_{exp} are the reference and perturbed atmospheric lifetimes of CH₄, respectively. Estimates of f are in the range of 1.19 to 1.55 (Fiore et al., 2009; Voulgarakis et al., 2013; Stevenson et al.,

2013; Thornhill et al., 2021b; Stevenson et al., 2020; Sand et al., 2023). Holmes (2018) found that f can vary geographically and seasonally, and that it strengthens with an increasing CH_4 burden. Secondly, the subsequent CH_4 response affects other chemical constituents such as O_3 . This effect is also sometimes accounted for by scaling the sensitivity of O_3 towards CH_4 perturbations with the expected CH_4 response (Fiore et al., 2009; Thornhill et al., 2021b). However, previous studies that assessed the climate feedback of O_3 and the corresponding implication for the global surface air temperature (GSAT) response did not, or only rudimentarily, account for the interaction between changes of O_3 and CH_4 (Dietmüller et al., 2014; Nowack et al., 2015; Marsh et al., 2016; Li and Newman, 2023). As for O_3 alone the latter studies indicate that its feedback reduces the resulting GSAT response, or in other words that it is a negative feedback. The magnitude of this feedback, however, is highly model dependent.

In this study, we use a CH_4 emission flux driven setup of the CCM ECHAM/MESSy Atmospheric Chemistry (EMAC; Jöckel et al., 2016) to explicitly simulate the response of atmospheric CH_4 mixing ratios resulting from changes in the chemical sink and in CH_4 emissions. We perform idealized perturbation simulations with either increased CO_2 mixing ratios (with CO_2 being an inert GHG), or increased CH_4 emission fluxes. The CH_4 perturbation affects the chemical composition directly, whereas the CO_2 perturbation influences the chemical composition only indirectly, e.g. through the temperature change. From the simulation results we assess the change in CH_4 mixing ratios and its implications for OH and O_3 . In addition to the CH_4 feedback, GSAT changes induce other processes that influence O_3 . For instance, temperature changes affect chemical reaction rates, emissions of precursor species from natural sources, circulation, or the abundance of H_2O (e.g., Stevenson et al., 2006; Chiodo et al., 2018; Abalos et al., 2020; Griffiths et al., 2021; Zanis et al., 2022). Therefore, we apply an attribution method for O_3 (TAGGING; Grewe et al., 2017; Rieger et al., 2018) to identify and quantify the importance of individual source categories that influence tropospheric O_3 under tropospheric warming.

Our analysis is based on the ERF conceptual framework (Shine et al., 2003; Hansen et al., 2005; Ramaswamy et al., 2018; Forster et al., 2021), which means that the so-called fast and (slow) climate responses are assessed separately. The fast response represents the part of the full response that develops, on short time scales, independent of the corresponding GSAT change, whereas the climate response represents the isolated effect of the GSAT change. There is no formal time scale that separates the fast and slow responses, but they are distinguished conceptually by the dependence on the GSAT response, which is coupled to the (slow) response of the ocean. It is noteworthy that the CH_4 adjustment that follows the increase of CH_4 emission fluxes evolves on the time scale of decades, whereas typical physical (rapid) adjustments evolve on the time scale of weeks or months (e.g., Smith et al., 2018). We derive ERF and the fast response from simulations with prescribed sea surface temperatures (SSTs) and sea ice concentrations (SICs) as recommended by Forster et al. (2016). The climate response is assessed as the difference between the response in a simulation coupled to a mixed layer ocean model and the respective fast response. Analogously, we assess (rapid radiative) adjustments as the radiative effects corresponding to changes in the fast response and (slow climate) feedbacks as the radiative effects corresponding to changes in the climate response.

The paper is structured as follows. Section 2 explains the simulation set-up (Sect. 2.1.), as well as the TAGGING method to attribute O_3 to individual source categories (Sect. 2.2.), and the method to derive the radiative effects corresponding to composition changes of individual species (Sect. 2.3.). Additionally, Sect. 2.3. introduces the theoretical framework for radiative

forcing and climate sensitivity. Section 3 presents the simulation results. In Sect. 3.1. and 3.2., we present composition changes in the CO₂ and CH₄ perturbation simulations, respectively. In Sect. 3.3., the corresponding radiative effects are addressed. We conclude with a general discussion and summary of our findings in Sect. 4. Parts of the paper are based on the PhD thesis of the first author (Stecher, 2024).

2 Methods

2.1 Model description and simulation strategy

We use the modular CCM ECHAM/MESSy Atmospheric Chemistry (EMAC; Jöckel et al., 2016) in version 2.55.2. All simulations are performed at a resolution of T42L90MA, i.e. at a triangular (T) truncation at wave number 42 of the spectral dynamical core, corresponding to a quadratic Gaussian grid of approximately $2.8^\circ \times 2.8^\circ$ resolution in latitude and longitude and 90 vertical levels, with the uppermost level centered around 0.01 hPa. The simulations are performed as time slices, which means that the same boundary conditions are repeated cyclically for each simulation year. The boundary conditions, i.e. prescribed emissions and mixing ratios of well-mixed GHGs, represent the year 2010. The quasi-biennial oscillation (QBO) is nudged following the method of Giorgetta and Bengtsson (1999) as described by Jöckel et al. (2016), which introduces some interannual variability. The simulation set-up builds on previous studies assessing the impact of enhanced CH₄ mixing ratios with EMAC (Winterstein et al., 2019; Stecher et al., 2021), with the important advance that for the present study EMAC is used in a CH₄ emission flux driven setup, which means that CH₄ emission fluxes instead of CH₄ mixing ratios are prescribed at the lower boundary. The CH₄ emission fluxes are prescribed as offline emission fluxes, i.e. there are no feedbacks on CH₄ emission fluxes from natural sources such as wetlands or permafrost, which are expected to change in a changing climate (e.g., O'Connor et al., 2010; Dean et al., 2018).

The applied CH₄ emission inventory is an inverse optimized inventory for the EMAC model (Frank, 2018). For the two reference simulations (see Tab. 1 and text below), monthly mean emissions of the year 2010 are repeated cyclically and scaled by a globally constant factor of 1.08, which corresponds to total annual mean emissions of 625.3 Tg(CH₄) a⁻¹. The scaling was applied to bring the simulated CH₄ surface mixing ratios closer to observations. As the tropospheric mean CH₄ lifetime is about 10 years (e.g., Prather et al., 2012; Stevenson et al., 2020), the CH₄ mixing ratios of the year 2010 result not only from CH₄ emissions of the year 2010, but also from emissions of the years before. Therefore, it can not be expected that the cyclic repetition of CH₄ emissions of the year 2010 results in CH₄ mixing ratios that represent the year 2010 exactly. Applying the scaling, the resulting global mean CH₄ surface mixing ratio is 1.82 ppmv for both reference simulations. This is in close agreement with observational estimates for the years 2010 and 2012 of 1.80 and 1.81 ppmv by the National Oceanic and Atmospheric Administration Earth System Research Laboratories (NOAA/ESRL) (Lan et al., 2023), and 1.81 and 1.82 ppmv by the WMO World Data Centre for Greenhouse Gases (WMO, 2022). The estimates of NOAA/ESRL tend to be lower, as only unpolluted marine surface sites contribute to the global estimate. The chemical sink reactions of CH₄ with OH, excited oxygen (O(¹D)) and chlorine (Cl), and CH₄ photolysis are interactively accounted for by the MESSy submodels Module Efficiently Calculating the Chemistry of the Atmosphere (MECCA; Sander et al. (2019)) and JVAL (Sander et al., 2014). Oxidation by OH

dominates the tropospheric CH₄ sink, so that the reaction with Cl accounts for only 0.23% of the total chemical tropospheric CH₄ loss (see Tab. S1 in the supplement). Therefore, we focus on CH₄ lifetime changes with respect to oxidation by OH. In addition to the sink reactions of CH₄, the chemical mechanism covers the basic chemistry of O₃, OH, hydroperoxyl (HO₂), nitrogen oxides, alkanes and alkenes up to four C-atoms, and isoprene (C₅H₈). Further, halogen chemistry of bromine and chlorine species is included. Alkynes, aromatics and mercury are not considered. In total, the used mechanism covers 265 gas-phase, 82 photolysis and 12 heterogeneous reactions of 160 species. The chemical feedback on H₂O modifies the prognostic specific humidity, and vice versa. The soil sink of CH₄ is included by the submodel DDEP (Kerkweg et al., 2006a), which uses a prescribed deposition rate (Spahni et al., 2011; Curry, 2007) that is scaled to the actual CH₄ mixing ratio in the corresponding grid box. On average, the global soil sink is 27.6 Tg(CH₄) a⁻¹ for both reference simulation.

Precursor emissions of O₃, in particular nitrogen oxides NO and NO₂ (NO_x), non-methane hydrocarbons (NMHCs), and carbon monoxide (CO), are treated as described by Jöckel et al. (2016). Anthropogenic emissions of these species are prescribed from the MACCity inventory (Lamarque et al., 2010; Granier et al., 2011; Diehl et al., 2012), whereby the (mostly monthly resolved) emission fluxes of the year 2010 are repeated cyclically. In addition, climatologies of biogenic emissions of NMHCs and CO are prescribed from the Global Emissions Initiative (GEIA). Natural emissions of NO_x from lightning, NO_x and C₅H₈ from biogenic sources, as well as the exchange of chemical species between the atmosphere and ocean are parameterized. For lightning NO_x the parameterization of Grewe et al. (2001) is used in the MESSy submodel LNOX (Tost et al., 2007). The 20-year mean global emissions from lightning NO_x are 5.2 Tg(N) a⁻¹ for both reference simulations (see Tab. 3). Interactive biogenic emissions of soil NO_x and C₅H₈ are calculated by the submodel ONEMIS (Kerkweg et al., 2006b). On average, biogenic NO_x emissions are 6 Tg(N) a⁻¹ and biogenic C₅H₈ emissions are about 307 Tg(C) a⁻¹ for both reference simulations (see Tab. 3). The atmosphere-ocean exchange of the chemical species C₅H₈, dimethyl sulfide (DMS) and methanol (CH₃OH) is parameterized using the submodel AIRSEA (Pozzer et al., 2006). The mixing ratios of CO₂, nitrous oxide (N₂O) and ozone depleting substances (ODS) are prescribed at the lower boundary using monthly mean values of the year 2010 (Meinshausen et al., 2011; Carpenter et al., 2018). For the radiation, a CFC-11 equivalent is calculated lumping additional radiatively active ODS via radiative efficiencies following the approach by Meinshausen et al. (2017). For the short-lived halocarbons CHCl₂Br, CHClBr₂ and CH₂ClBr, as well as CH₂Br₂ and CHBr₃ surface emissions are prescribed from Warwick et al. (2006) and Liang et al. (2010), respectively.

Table 1 summarizes the performed simulations. The simulations REF-SSTfix and REF-SSTvar serve as references for the experiment simulations and represent year 2010 conditions. REF-SSTfix is performed using prescribed SSTs and SICs, whereas for REF-SSTvar a mixed layer ocean (MLO) model is coupled (MESSy submodel MLOCEAN, Kunze et al. (2014); original ECHAM5 code by Roeckner et al. (1995), described in the ECHAM5 documentation (Chap. 6.3 – 6.5 in Roeckner et al., 2003)). The prescribed multi-year monthly mean climatology of SSTs and SIC is an observations based estimate of the years 2000 to 2009 from the Met Office Hadley Center (Rayner et al., 2003). The same climatology was used by Winterstein et al. (2019). Appendix C of Stecher (2024) provides a comparison of the two reference simulations. Overall, the simulation REF-SSTvar reproduces the simulation REF-SSTfix well. The largest differences are in the Southern Hemisphere (SH) polar region,

where the MLO model tends to underestimate the sea ice area of the prescribed climatology, which has been noted for a similar application of the MLOCEAN submodel as well (Stecher et al., 2021).

The perturbation simulations ERFCO₂ and ERFCH₄ are performed with the same prescribed climatology of SSTs and SICs as REF-SSTfix to assess the so-called fast response and to quantify the ERF and the adjustments following the fixed SST method (e.g., Forster et al., 2016). ERF is defined as the top of atmosphere (TOA) net radiative flux change between the experiment and the reference simulation. The perturbations of CO₂ and CH₄ are scaled to result in ERFs of similar magnitude, because for a most fair comparison of the climate sensitivity parameters of different perturbation agents, the respective forcings need to be at the same order of magnitude as the climate sensitivity, as it can be dependent on the magnitude of the forcing (e.g., Hansen et al., 2005; Dietmüller et al., 2014). The ERF is targeted to be large enough to cause statistically significant and interpretable feedbacks (Forster et al., 2016), and small enough to be reached with still realistically large perturbations of CO₂ and CH₄ (Dietmüller et al., 2014; Winterstein et al., 2019). Perturbations of $1.35 \times \text{CO}_2$ mixing ratios and $2.75 \times \text{CH}_4$ surface emission fluxes result in ERFs of $1.61 \pm 0.16 \text{ W m}^{-2}$ and $1.72 \pm 0.17 \text{ W m}^{-2}$, respectively (see Tab. 4). The scaling of $1.35 \times \text{CO}_2$ mixing ratios or $2.75 \times \text{CH}_4$ surface emission fluxes is applied to all CO₂ and CH₄ perturbation experiments, respectively. ECCCO₂ and ECCCH₄ are so-called equilibrium climate change simulations. In these simulations the MLO model accounts for the response of SSTs and SICs. Therefore, the effect of GSAT driven feedbacks is included in these simulations.

In the following, we assess the so-called fast response as the difference between ERFCO₂ or ERFCH₄ and REF-SSTfix, and the full response as the difference between ECCCO₂ or ECCCH₄ and REF-SSTvar. The difference between the full and the fast response is assessed as the climate response, which represents the isolated effect of the GSAT change. Similarly, adjustments and feedbacks are defined as the radiative effects corresponding to the fast response and the climate response, respectively. For the analysis, results of 20 simulated years after the spin-up period are used. The spin-up ensures that a quasi-equilibrium is reached and is, therefore, different for the individual simulations according to the simulation set-up. For ERFCH₄ the longest spin-up period of 90 years, for ECCCO₂ and ECCCH₄ 50 years, respectively, and for ERFCO₂ 25 years were necessary. Time series of the global mean surface CH₄, the total atmospheric masses of CH₄ and O₃, the TOA radiation balance, and GSAT (for the MLO simulations) were monitored to decide whether an equilibrium is reached. In addition, we assessed the spin-up of the mass of CH₄ of the simulation ERFCH₄ in more detail. A curve fit was applied to the spin-up period to derive the atmospheric mass of CH₄ in equilibrium. The mass of CH₄ follows the exponential function of the form $a - b \cdot \exp(-t/c)$ closely. The mass of CH₄ in the last year of the spin-up, simulation year 90, is about 0.5% smaller than the derived equilibrium estimate (parameter a), and therefore spun-up sufficiently well (see Fig. S14). The derived perturbation lifetime (parameter c) is 21.6 years. We note that the perturbation lifetime is larger than that of the CH₄ emission reduction experiment by Staniaszek et al. (2022). As the perturbation lifetime increases with increasing CH₄ burden (Holmes, 2018), this can be expected. In addition, model differences and the magnitude of the emission change might play a role.

Table 1. Overview of performed simulations. REF indicates that the respective reference is used, which is 388.4 ppmv for the global mean surface mixing ratio of CO₂, and 625.3 Tg(CH₄) a⁻¹ for the CH₄ surface emissions. The prescribed multi-year monthly mean climatology of SSTs and SIC is based on an observations based estimate of the years 2000 to 2009 from the Met Office Hadley Center (Rayner et al., 2003).

simulation name	SST + SIC	CO ₂ VMR	CH ₄ surface emissions
REF-SSTfix	prescribed	REF	REF
REF-SSTvar	MLO	REF	REF
ERFCO ₂	prescribed	REF×1.35	REF
ECCCO ₂	MLO	REF×1.35	REF
ERFCH ₄	prescribed	REF	REF×2.75
ECCCH ₄	MLO	REF	REF×2.75

In this study, the CH₄ lifetime is calculated according to Jöckel et al. (2016) as

$$\tau_{CH_4} = \frac{\sum_{b \in B} m_{CH_4}}{\sum_{b \in B} k_{CH_4+OH}(T) \cdot c_{air}(T, p, q) \cdot x_{OH} \cdot m_{CH_4}}, \quad (2)$$

with m_{CH_4} being the mass of CH₄ in [kg], $k_{CH_4+OH}(T)$ the temperature T dependent reaction rate coefficient of the reaction CH₄ + OH → products in [cm³ s⁻¹], c_{air} the concentration of air in [cm⁻³] and x_{OH} the mole fraction of OH in [mol mol⁻¹] in all grid boxes $b \in B$. B is the region, for which the lifetime should be calculated, e.g. all grid boxes below the tropopause for the mean tropospheric lifetime. For the CH₄ lifetime calculation a climatological tropopause, defined as $tp_{clim} = 300 \text{ hPa} - 215 \text{ hPa} \cdot \cos^2(\phi)$, with ϕ being the latitude in degrees north, is used as recommended by Lawrence et al. (2001). The reaction rate coefficient $k_{CH_4+OH}(T)$ is calculated as in the applied kinetic equation system (submodel MECCA), i.e. as

$$k_{CH_4+OH}(T) = 1.85 \times 10^{-20} \cdot T^{2.82} \cdot \exp\left(-\frac{987}{T}\right). \quad (3)$$

2.2 TAGGING

The TAGGING method (Grewe et al., 2017; Rieger et al., 2018) quantifies the contributions of individual source categories to the mixing ratios of tagged tracers. Tagged tracers are O₃, CO, reactive nitrogen compounds (NO_y), peroxyacyl nitrate (PAN), NMHCs, OH, and HO₂. For computational reasons NMHCs and NO_y are considered with a family approach. For these species or families of species the individual contributions of emission categories or source processes are calculated. In this study O₃ production from the following categories is considered:

- through photolysis of molecular oxygen (O₂) in the stratosphere (*O₃ stratosphere*),

- from emissions of lightning NO_x (O_3 *lightning*),
- from biogenic precursor emissions, mainly soil NO_x and C_5H_8 , (O_3 *biogenic*),
- 210 – from products of the CH_4 decomposition (O_3 *CH₄*),
- from products of the N_2O decomposition (O_3 *N₂O*),
- from biomass burning precursor emissions (O_3 *biomass burning*)
- and from anthropogenic precursor emissions (O_3 *anthropogenic*).

The categories are the same as defined by Grewe et al. (2017), except for the category O_3 *anthropogenic*, which, in our study,
 215 combines O_3 production from all anthropogenic emissions, i.e. of the sectors industry, road traffic, shipping and aviation.

The tagged tracers (i.e. the individual contributions) undergo the same processes as the corresponding total species. These are transport, emissions, dry and wet deposition, and chemical production and loss (see Grewe et al. (2017) for details). For the short-lived species OH and HO_2 a steady-state between chemical production and loss is assumed (Rieger et al., 2018). The chemical reaction rates are taken from the submodel MECCA. Effective production and loss is taken into account for
 220 O_3 , meaning that production and loss terms from a family, which includes all fast exchanges between O_3 and other chemical species, are considered. The diagnostic tool *ProdLoss* (Grewe et al., 2017) is used to identify all reactions that contribute to effective O_3 production and loss in the applied chemical mechanism. The reaction rates of effective O_3 production and loss are then manually grouped into O_3 production and loss rates, depending on which tagged species contributes to O_3 production or loss.

225 2.3 Quantification of individual radiative effects

The assessment of radiative effects in this study follows the ERF framework. This means that (rapid radiative) adjustments, which are defined as the TOA net radiative flux change corresponding to changes in the fast response, i.e. independent from GSAT changes, are accounted for as part of the forcing. Thus, ERF is given as the sum of instantaneous radiative forcing (IRF), defined as the net radiative flux change at TOA excluding any adjustment, and the sum of all individual adjustments A_i (e.g.,
 230 Smith et al., 2018)

$$ERF = IRF + \sum_i A_i. \quad (4)$$

Consistently, (slow climate) feedbacks are defined as the TOA net radiative flux change induced by atmospheric parameter changes that correspond to the gradually changing GSAT. These feedbacks act to reduce or enhance the associated GSAT change (ΔT) and determine the climate sensitivity parameter λ (units: $\text{K} / (\text{W m}^{-2})$), which is the proportionality constant that
 235 relates the equilibrium change of GSAT to the ERF as

$$\Delta T = \lambda \cdot ERF. \quad (5)$$

The feedback parameter α is the negative inverse of the climate sensitivity parameter λ ($\alpha = -\frac{1}{\lambda}$; units: $\text{W m}^{-2} \text{K}^{-1}$). The feedback parameter quantifies the net radiative flux change at TOA for a given change in GSAT. Under the assumption of linearity it can be decomposed into the radiative contributions of individual processes affected by the change in GSAT, i.e. the individual feedback parameters α_i , so that (e.g., Forster et al., 2021)

$$\alpha = \sum_i \alpha_i = \sum_i \frac{\partial N}{\partial x_i} \frac{dx_i}{dT}, \quad (6)$$

where N is the radiative flux change at TOA induced by the change of an individual variable of the Earth system x_i .

We quantify adjustments and feedbacks corresponding to composition changes of CO_2 , CH_4 , O_3 and stratospheric H_2O following the method used by Winterstein et al. (2019) and Stecher et al. (2021): Additional simulations are performed with EMAC using the option for multiple diagnostic radiation calls (Dietmüller et al., 2016; Nützel et al., 2024). These simulations are performed (for the sake of saving computational resources) without interactive chemistry, but with prescribed climatologies for the radiatively active trace gases CH_4 , CO_2 , O_3 , N_2O and the chlorofluorocarbons (CFCs) from the simulations REF-SSTfix or REF-SSTvar. SSTs and SICs are prescribed using the same observational based climatology as used for REF-SSTfix (Rayner et al., 2003). Thus, the background climate of the simulations represents reference conditions. The additional simulations are run over 2 years each (plus 1 year spin-up).

In these simulations the first radiation call, P, provides the radiative heating rates that drive the base model, whereas the other radiation calls, D1, D2, ... , are purely diagnostic. The radiation call D1 serves as the reference for the perturbations and receives identical input as P, except for the specific humidity, for which a monthly mean climatology from the respective reference simulation (REF-SSTfix or REF-SSTvar) is used instead of the prognostic specific humidity from the base model. This is necessary, because the radiation calls to calculate the radiative effect of H_2O use monthly mean climatologies of the specific humidity from the sensitivity simulations (see below), and therefore need to be compared to a radiation call, that uses a monthly mean climatology of specific humidity instead of the prognostic, highly variable, specific humidity.

In the other radiation calls (D2, D3, ...) either CO_2 , CH_4 , O_3 or the specific humidity is replaced by a monthly mean climatology from the sensitivity simulation (either ERFCO₂, ECCCO₂, ERFCH₄ or ECCCH₄) to calculate the corresponding radiative effect. For example, to derive the radiative effect of the full response of CH_4 of the CO_2 perturbation, the reference CH_4 climatology in D1 is replaced by the monthly mean CH_4 climatology from ECCCO₂ in D2. For O_3 and the specific humidity the radiative effects of changes in the troposphere and in the stratosphere are derived separately. The diagnostic radiation calls include the stratospheric temperature adjustment induced by the respective perturbation following the method of Stuber et al. (2001). Therefore, the radiative effect corresponding to CH_4 (CO_2) from the simulation ERFCH₄ (ERFCO₂) represents stratospheric adjusted radiative forcing (SARF), i.e. the direct radiative effect of the perturbation including the associated stratospheric temperature adjustment. To define the region in which the stratospheric temperature adjustment is applied, as well as to separate tropospheric and stratospheric radiative effects of O_3 and the specific humidity, the climatological tropopause tp_{clim} is used consistently with the CH_4 lifetime calculation (see Sect 2.1).

There is one methodological difference compared to Winterstein et al. (2019) and Stecher et al. (2021). They used the climatological specified humidity directly in the first prognostic radiation call, which then served as the reference for the

perturbed calls. However, here it was decided to use the prognostic specific humidity in the first radiation call as it is consistent with the model's background meteorology, e.g. the cloud cover. The influence on the calculated radiative effects was tested and found to be up to 1.02% (or 0.004 W m^{-2}) with the maximum deviation for the perturbations of specific humidity, which is negligible in comparison to other uncertainties.

275 3 Results

3.1 Methane and ozone composition changes following $1.35 \times \text{CO}_2$ perturbation

In this section, we present the simulation results of the $1.35 \times \text{CO}_2$ perturbation. Figure 1 shows the annual zonal mean composition changes of CH_4 mixing ratios in the simulations ERFCO₂ (fast response) and ECCCO₂ (full response), and their difference, which is interpreted as the climate response. The fast response is dominated by increasing CH_4 mixing ratios in the upper stratosphere and mesosphere. In this region, the cooling to be expected from the CO_2 increase (see Fig. S1 in the supplement) leads to the prolongation of the CH_4 lifetime. The stratospheric CH_4 loss by reaction with OH, Cl, and $\text{O}(^1\text{D})$ is reduced by about 2% (see Tab. S1 in the supplement). A similar effect has been noted by Dietmüller et al. (2014). In the fast response, tropospheric CH_4 shows a slight increase below 2%.

In contrast to the fast response, the full response shows a significant reduction of CH_4 mixing ratios in the troposphere and lower stratosphere. As CH_4 emission fluxes are prescribed in the simulation set-up and cannot respond to changes in meteorology or composition, any feedback on natural CH_4 emissions (e.g., Dean et al., 2018) is suppressed. Therefore, the decrease of CH_4 mixing ratios results from enhanced chemical decomposition of CH_4 , mainly by the oxidation with OH. The tropospheric CH_4 lifetime with respect to oxidation by OH shortens by about 7 months (0.56 a or 7.4 %, see Tab. 2). This shortening is a combined result of the direct influence of the temperature on the reaction rate coefficient and of an enhanced abundance of OH. Tropospheric warming increases OH mixing ratios throughout the troposphere with the maximum increase in the tropics (see Fig. S3 in the supplement). Firstly, emissions from lightning NO_x increase by about 0.3 Tg(N) a^{-1} in the climate response (see Tab. 3), which leads to enhanced production of OH. To estimate the effect on the CH_4 lifetime, we use the multi-model mean sensitivity of the CH_4 lifetime towards lightning NO_x emission change of $-4.8\% (\text{Tg(N) a}^{-1})^{-1}$ from Thornhill et al. (2021a), which suggest a shortening of the CH_4 lifetime due to lightning NO_x emissions by 1.4%. Additionally, the increase in the tropospheric humidity associated with higher temperatures leads to enhanced production of OH.

In addition to the reduction in the troposphere, the CH_4 mixing ratios decrease also in the lower stratosphere as part of the full response. As the reaction partners of CH_4 , namely OH, Cl and $\text{O}(^1\text{D})$, do not show any significant response in the lower stratosphere (see Fig. S3 for OH), and the stratospheric CH_4 loss does not change (see Tab. S1 in the supplement), the decrease is likely a transport effect. Tropospheric air masses with reduced CH_4 mixing ratios compared to the reference simulation enter the stratosphere by the upwelling branch of the Brewer-Dobson-Circulation. Tropical upwelling is enhanced in the climate response (see Fig. S13 in the supplement). Dietmüller et al. (2014) noted an increase of CH_4 mixing ratios throughout the stratosphere as a result of $2 \times \text{CO}_2$ due to stratospheric cooling and thereby a slower CH_4 oxidation. In addition, enhanced tropical upwelling transports CH_4 enriched air in the stratosphere more efficiently. In our setup, the reduction of tropospheric

CH₄, which is suppressed in the set-up of Dietmüller et al. (2014) as CH₄ mixing ratios are prescribed at the lower boundary, dominates the latter two processes.

Previous studies also found that tropospheric warming leads to increasing OH mixing ratios and correspondingly to the shortening of the CH₄ lifetime (e.g., Voulgarakis et al., 2013; Dietmüller et al., 2014; Heimann et al., 2020; Stecher et al., 2021; Thornhill et al., 2021a). The novelty of our study is that the associated reduction of CH₄ mixing ratios is simulated explicitly, which was assessed by only a small number of studies so far (Heimann et al., 2020). In our CO₂ perturbation experiment, the CH₄ lifetime change per unit change of GSAT is -0.51 a K⁻¹ or -6.7 % K⁻¹.

Voulgarakis et al. (2013) addressed the sensitivity of the CH₄ lifetime towards climate change in the Atmospheric Chemistry and Climate Modeling Intercomparison Project (ACCMIP) model ensemble. In the respective sensitivity simulations the boundary conditions for SSTs, SICs and CO₂ were set to RCP8.5 conditions for the years 2030 or 2100, while all other boundary conditions were representative of the year 2000. They found sensitivities of the tropospheric CH₄ lifetime of -0.31 ± 0.14 a K⁻¹ (-3.2 ± 1.0 % K⁻¹) and -0.34 ± 0.12 a K⁻¹ (-3.4 ± 0.8 % K⁻¹) for the year 2030 and the year 2100 experiments, respectively¹. The CMIP6 AerChemMIP model ensemble as analyzed by Thornhill et al. (2021a) suggests a sensitivity of the whole-atmosphere CH₄ lifetime towards climate change of -0.6 ± 4.5 % K⁻¹ assessed from abrupt 4× pre-industrial CO₂ experiments. The large intermodel spread results from one model that shows an extension of CH₄ lifetime as a result to 4×CO₂. The three models showing a shortening of CH₄ lifetime suggest a sensitivity of -3.2 ± 0.8 % K⁻¹ in close agreement with Voulgarakis et al. (2013).

Our study indicates a larger sensitivity of the CH₄ lifetime towards climate change compared to Voulgarakis et al. (2013) and Thornhill et al. (2021a). Possible reasons are the different magnitudes of the perturbations, differences in the simulation set-ups, or the explicit treatment of the CH₄ feedback in our study. The similar estimates for the years 2030 and 2100, corresponding to 1.14 K and 4.76 K change of GSAT, respectively², by Voulgarakis et al. (2013) suggest that the sensitivity is not highly dependent on the magnitude of the perturbation. Furthermore, the set-ups of individual models in Voulgarakis et al. (2013) and Thornhill et al. (2021a) differ, e.g. with respect to the level of complexity of the chemical mechanism, whether interactive aerosol is used, or through the different treatment of natural O₃ precursor emissions. Nevertheless, the present estimate is larger than the estimates of all individual models in Voulgarakis et al. (2013) and Thornhill et al. (2021a), except for two models which do not parameterize the effect of stratospheric O₃ on photolysis rates below, which is taken into account here. In the simulation set-ups analyzed by Voulgarakis et al. (2013) and Thornhill et al. (2021a) CH₄ mixing ratios are prescribed at the lower boundary in all models, except for the GISS-E2-R model analyzed by Voulgarakis et al. (2013). The lifetime response per unit temperature change derived from GISS-E2-R is comparably weak. GISS-E2-R calculates wetland emissions of CH₄ online, presumably also for the climate sensitivity experiments, which makes it difficult to compare the CH₄ lifetime response in this model to our study. Nevertheless, compared to the other models, the explicit treatment of the CH₄ feedback in our set-up allows for a subsequent feedback on OH and correspondingly for a self-feedback on the CH₄ lifetime, which can explain the enhanced sensitivity of the CH₄ lifetime towards climate change.

¹Relative estimates were calculated from estimates given in Tables 1 and 4 of Voulgarakis et al. (2013)

²Multi-model mean changes of GSAT were calculated from the estimates given in Table 4 of Voulgarakis et al. (2013).

If the CH₄ mixing ratio can not adapt to changes in its lifetime, the corresponding CH₄ equilibrium mixing ratio can be estimated using Eq. 1. The feedback factor f in the equation accounts for the CH₄-OH feedback. In our CH₄ emission driven simulation the CH₄-OH feedback is implicitly included in the simulated response of OH and the CH₄ lifetime, so that using
340 Eq. 1 with $f > 1$ applies the CH₄-OH feedback twice in this case. Eq. 1 indicates a global mean CH₄ equilibrium mixing ratio in the range of 1.61 to 1.66 parts per million volume (ppmv) for $f = [1.19, 1.55]$ for the present changes of the CH₄ lifetime. Thus, it suggests a larger reduction than simulated by the model, which adjusts to a global mean CH₄ equilibrium mixing ratio of 1.69 ppmv (see Tab. 2). However, if the feedback factor is not applied ($f=1$), Eq. 1 gives 1.68 ppmv, which is in close agreement with the simulated response of CH₄ mixing ratios.

345 The corresponding response of O₃ is shown in Figure 2. The fast response is dominated by O₃ increases of up to 8% in the middle and upper stratosphere. In these regions, CO₂ induced stratospheric cooling causes slower chemical O₃ depletion (e.g., Rind et al., 1998; Rosenfield et al., 2002; Portmann and Solomon, 2007; Dietmüller et al., 2014; Chiodo et al., 2018). In the lowermost stratosphere, O₃ mixing ratios decrease by up to 4%. This decrease can be explained by the so-called reversed self-healing (Rosenfield et al., 2002; Portmann and Solomon, 2007), which describes the effect that increasing O₃ above leads to a
350 reduction of ultraviolet radiation that reaches the lower stratosphere and consequently to reduced photochemical production of O₃. The effect of transport from the troposphere into the stratosphere is expected to play a minor role in the fast response, as the strength of tropical up-welling is largely determined by the response of SSTs (Garny et al., 2011; Butchart, 2014). The fast response of tropospheric O₃ is smaller than 2%.

The climate response of O₃ is dominated by a reduction of up to 10% in the lowermost tropical stratosphere (see Fig. 2 (c)).
355 Enhanced tropical up-welling transports tropospheric O₃ poor air from the troposphere into the stratosphere more efficiently. This is a robust feature across CCMs (Dietmüller et al., 2014; Nowack et al., 2015; Marsh et al., 2016; Chiodo et al., 2018). In the troposphere, O₃ mixing ratios decrease by up to 6% in the tropics close to the surface and decrease slightly in the upper tropical troposphere.

The pattern of the full response of stratospheric O₃ is qualitatively consistent with previous studies of O₃ changes resulting
360 from a CO₂ perturbation (Dietmüller et al., 2014; Nowack et al., 2015; Marsh et al., 2016; Nowack et al., 2018; Chiodo et al., 2018; Thornhill et al., 2021a). However, the tropospheric response is different here. Most studies using various CCMs consistently show an increase of O₃ in the tropical upper troposphere as part of the full response (Dietmüller et al., 2014; Nowack et al., 2015; Marsh et al., 2016; Nowack et al., 2018; Chiodo et al., 2018). In the studies by Dietmüller et al. (2014) and Nowack et al. (2015, 2018), and presumably also in the studies by Marsh et al. (2016) and Chiodo et al. (2018), CH₄ mixing
365 ratios are prescribed at the lower boundary. Consequently, the negative CH₄ feedback as discussed above can not evolve. This can lead to an overestimation of O₃ produced from products of the CH₄ oxidation and is consistent with the positive response of O₃ in the upper tropical troposphere. In particular, the comparison with the study by Dietmüller et al. (2014) indicates an effect of the CH₄ feedback on O₃ because the EMAC model was used as well in that study.

Using the MESSy submodel TAGGING (Grewe et al., 2017; Rieger et al., 2018) the tropospheric O₃ response is attributed
370 to individual source categories representing different processes of O₃ production. Consistent with the small fast response of total tropospheric O₃ (Fig. 2 (a)), the corresponding response of the individual categories is below 0.5% of the total reference

O_3 for all categories, except for O_3 *stratosphere* (see Fig. S5 in the supplement). The response of the category O_3 *stratosphere* confirms that less O_3 is produced via photolysis in the lower tropical stratosphere. Additionally, it indicates enhanced transport from the stratosphere into the troposphere in middle and higher latitudes of the Northern Hemisphere (NH).

375 Figure 3 shows the climate response of individual O_3 source categories presented as the difference between the fast and full response of each category in percentage points (p.p.)

$$\Delta O_{3, \text{cat. climate response}} = \left(\frac{O_{3, \text{cat. ECC}} - O_{3, \text{cat. REF}}}{O_{3, \text{total. REF}}} \right) - \left(\frac{O_{3, \text{cat. ERF}} - O_{3, \text{cat. REF}}}{O_{3, \text{total. REF}}} \right). \quad (7)$$

The presentation relative to the total reference O_3 allows to directly compare the responses of the individual categories to the relative response of total O_3 as shown in Fig. 2 (c) and Fig. 3 (a).

380 The climate response of the category O_3 *stratosphere* shows significantly enhanced transport of stratospheric O_3 into the troposphere in both hemispheres. In the extratropical middle troposphere, O_3 mixing ratios increase by up to 1.5% relative to the total reference O_3 in the full response, which is the largest positive contribution to the total tropospheric O_3 response. This supports current knowledge, as enhanced entry of stratospheric O_3 under increasing GHG concentrations has been a robust feature in CCMs (Abalos et al., 2020). The category O_3 *stratosphere* is also the largest contributor to the strong reduction in the

385 lowermost stratosphere. The category O_3 *lightning* shows a significant increase of up to 1.25% relative to total reference O_3 in the middle tropical troposphere. This is consistent with an increase of lightning NO_x emissions by about 0.3 Tg(N) a^{-1} globally (see Tab. 3). Lightning NO_x is emitted mainly in the upper tropical troposphere where convection is strongest (not shown). Biogenic emissions of NO_x and C_5H_8 increase in the full response as well. Biogenic C_5H_8 emissions increase strongest in the Amazon region and the Congo river basin, whereas biogenic NO_x emissions increase over land in the tropics and mid

390 latitudes (not shown). However, the zonal mean climate response of O_3 *biogenic* is mostly not significant due to competing effects of enhanced precursor emissions and of enhanced chemical loss with H_2O . An enhanced sink of O_3 via the reaction of $\text{O}(^1\text{D})$ with H_2O , which leads to effective O_3 loss, is expected in a warmer and moister troposphere (e.g., Stevenson et al., 2006). The spatial distribution of the tropospheric O_3 column shows mainly a reduction over the tropical ocean (see Fig. S7 in the supplement), which is also reflected by the significant reduction between the equator and 30° N in the zonal mean

395 (Fig. 3 (d)). Locally over regions with increasing precursor emissions, e.g. over the Amazon region and the Congo river basin, the tropospheric O_3 column increases in the category O_3 *biogenic* (see Fig. S7 in the supplement). Anthropogenic and biomass burning emissions are prescribed and are therefore not affected by the CO_2 increase. In these categories, decreasing O_3 from enhanced loss or reduced O_3 production efficiency is shown. The reduction of O_3 *anthropogenic* is most pronounced over the tropical ocean, where a decline of O_3 due to enhanced loss via H_2O is expected (Stevenson et al., 2006; Zanis et al.,

400 2022). The effect of the reduction of O_3 *biomass burning* on total O_3 is small, since also its absolute contribution is small. In addition to the enhanced sink, reduced O_3 production per emitted NO_x could play a role in the latter two categories as O_3 precursor emissions from natural categories increase. The category O_3 *CH₄* shows a reduction throughout the troposphere. This is consistent with the reduction of CH_4 mixing ratios, as in the new equilibrium fewer products of the CH_4 oxidation are available for O_3 production resulting in reduced O_3 production in this category. Further, enhanced chemical loss can contribute

405 to the reduction of this category. In the upper tropical troposphere the increase in lightning NO_x emissions counteracts the

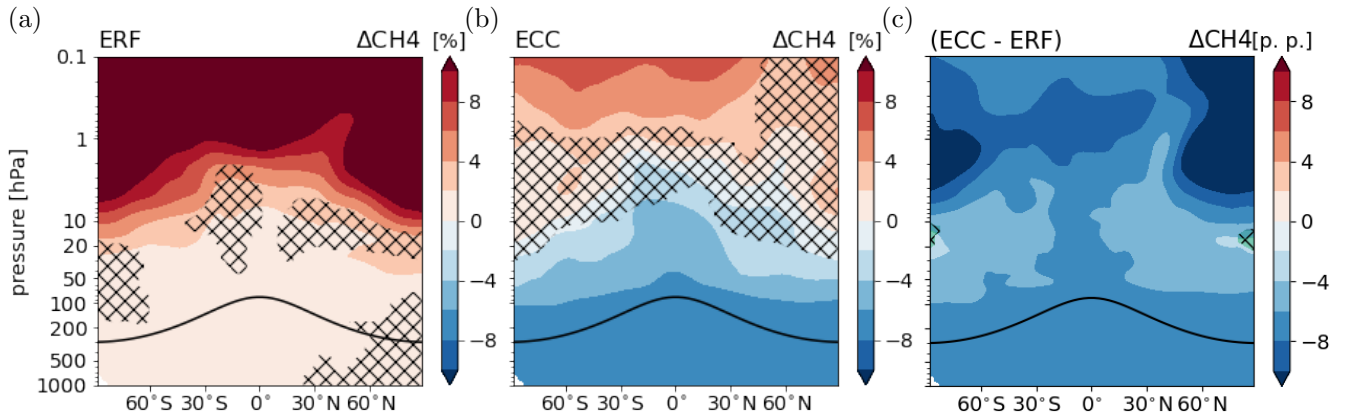


Figure 1. CH₄ response following the CO₂ perturbation: Relative differences between the annual zonal mean CH₄ mixing ratios of sensitivity simulations (a) ERF_{CO₂} (fast response) and (b) ECCO_{CO₂} (full response) and their respective reference simulation in [%]. (c) Climate response as difference between the CH₄ responses in panels (a) and (b) in [percentage points (p.p.)]. Non-hatched areas are significant on the 95% confidence level according to a Welch's test based on annual mean values. The solid black line indicates the location of the climatological tropopause.

Table 2. Global annual mean values of tropospheric CH₄ lifetime with respect to oxidation by OH, and CH₄ surface volume mixing ratio for the performed simulations.

	Trop. CH ₄ lifetime [a]	CH ₄ surface VMR [ppmv]
REF-SSTfix	7.59 ± 0.03	1.82 ± 0.00
REF-SSTvar	7.58 ± 0.03	1.82 ± 0.00
ERFCO ₂	7.59 ± 0.03	1.82 ± 0.00
ECCCO ₂	7.02 ± 0.05	1.69 ± 0.00
ERFCH ₄	14.48 ± 0.04	8.66 ± 0.01
ECCCH ₄	13.20 ± 0.08	8.05 ± 0.01

The values after the ± are the corresponding interannual standard deviations based on 20 annual mean values, which are listed to estimate the year to year variability.

effect of the CH₄ decrease by providing enhanced levels of NO_x, which react with the products of the CH₄ oxidation more efficiently. The climate response of O₃ CH₄ is not significant in this region. The climate response in the category O₃ N₂O shows significant decreases in the lower stratosphere and troposphere. In the stratosphere, N₂O mixing ratios increase (not shown) indicating less N₂O decomposition (Dietmüller et al., 2014). Thereby, less nitrogen oxide (NO) is produced to form O₃, which is consistent with the decrease of O₃ formed from N₂O decomposition.

Table 3. Global annual mean emissions of NO_x from lightning, NO_x from biogenic sources, and C_5H_8 from biogenic sources.

	Lightning NO_x [Tg(N) a^{-1}]	Biogenic NO_x [Tg(N) a^{-1}]	Biogenic C_5H_8 [Tg(C) a^{-1}]
REF-SSTfix	5.2 ± 0.1	6.0 ± 0.0	307 ± 3
REF-SSTvar	5.2 ± 0.1	6.0 ± 0.0	306 ± 4
ERFCO ₂	5.3 ± 0.1	6.0 ± 0.0	307 ± 4
ECCCO ₂	5.6 ± 0.1	6.4 ± 0.0	338 ± 6
ERFCH ₄	4.9 ± 0.1	6.0 ± 0.0	306 ± 3
ECCCH ₄	5.1 ± 0.1	6.4 ± 0.0	337 ± 5

The values after the $\pm$ are the corresponding interannual standard deviations based on 20 annual mean values, which are listed to estimate the year to year variability. The model calculated biogenic C_5H_8 emissions are scaled by a factor of 0.6 before being added to the atmospheric C_5H_8 tracer (see Jöckel et al., 2016). The values shown here include the scaling.

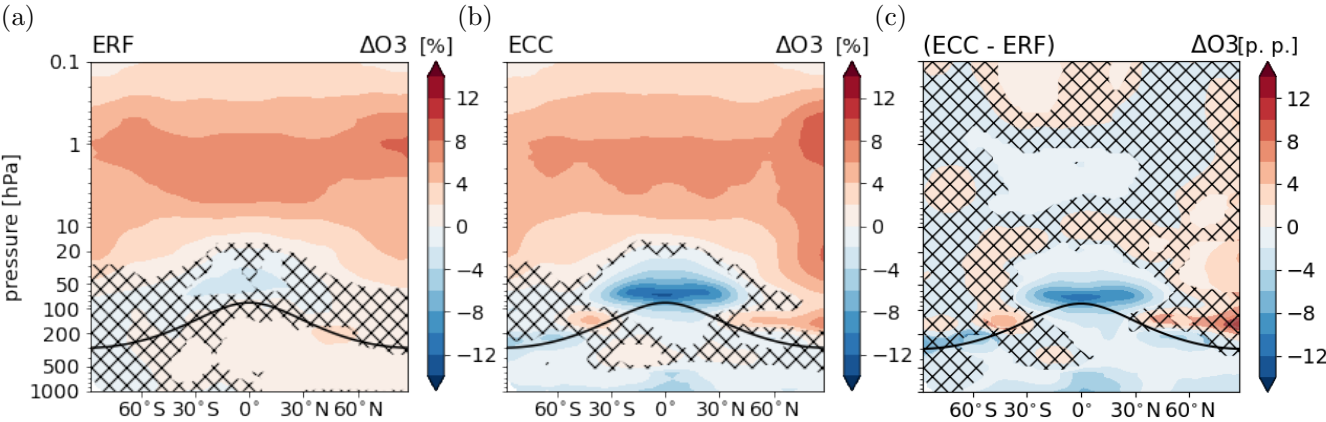


Figure 2. Same as Fig. 1, but for O_3 .

3.2 Methane and ozone composition changes following $2.75 \times \text{CH}_4$ emission flux perturbation

In this section, we present the simulation results of the $2.75 \times \text{CH}_4$ emission flux perturbation. Figure 4 shows the zonal mean distribution of CH_4 mixing ratios of the reference simulation REF-SSTfix and of the two simulations with CH_4 emission fluxes increased by a globally constant factor of 2.75. As expected, CH_4 mixing ratios increase everywhere in the fast response shown in Fig. 4 (b). Hereby, the increase factor of CH_4 mixing ratios is even larger than the increase factor of the emission fluxes. Tab. 2 shows that an increase of CH_4 emissions by a factor of 2.75 results in an increase in the global mean surface CH_4 mixing ratio by a factor of 4.76. This is caused by a large extension of the tropospheric CH_4 lifetime by about 7 years (see Tab. 2). The CH_4 increase reduces the tropospheric OH mixing ratios by up to 60% (see Fig. S3 in the supplement), thereby extending the CH_4 lifetime.

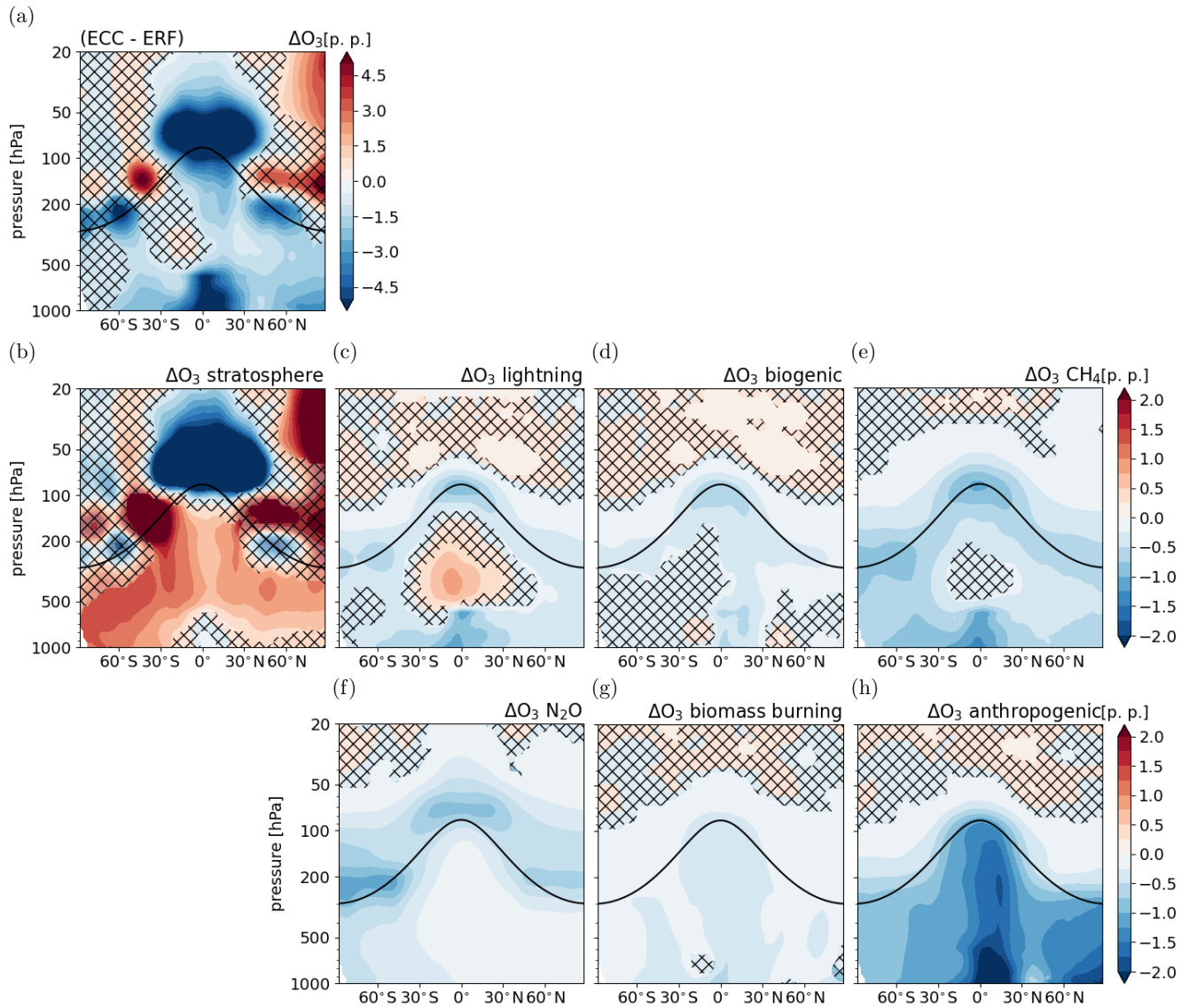


Figure 3. Climate response of tropospheric O_3 following the CO_2 perturbation: (a) response of total O_3 (same as Fig. 2 (c), but differently scaled color levels to better compare with the response in the individual source categories), (b) - (h) response of O_3 in individual categories relative to total reference O_3 ($\Delta O_{3cat, climate response} = (\frac{O_{3cat,ECC} - O_{3cat,REF}}{O_{3total,REF}}) - (\frac{O_{3cat,ERF} - O_{3cat,REF}}{O_{3total,REF}})$). Non-hatched areas are significant on the 95% confidence level according to a Welch's test based on annual mean values. The solid black line indicates the location of the climatological tropopause.

420 A similar effect was found by Winterstein et al. (2019) who analyzed the fast response of $2\times$ and $5\times CH_4$ surface mixing ratios in a set-up with prescribed CH_4 surface mixing ratios also using EMAC. The magnitude of the present CH_4 perturbation is comparable to their $5\times CH_4$ experiment. In particular, to reach the prescribed CH_4 surface mixing ratios a pseudo surface

emission flux is diagnosed in their set-up. The increase factor of the pseudo flux that corresponds to an increase of $5 \times \text{CH}_4$ is 2.75 (Stecher et al., 2021), exactly the increase factor of CH_4 surface emissions used in our study. Thus, in our study the increase of emission fluxes results in a close to fivefold increase in the CH_4 surface mixing ratio. The global mean reference CH_4 mixing ratio and the corresponding pseudo emission flux are slightly lower in Winterstein et al. (2019), namely about 1.8 ppmv and $567.7 \text{ Tg}(\text{CH}_4) \text{ a}^{-1}$. Additionally, the spatial distribution of their diagnosed pseudo flux is different and might be unrealistic. The latter two points explain, why the increase factor of CH_4 mixing ratios is not exactly the same in our study. Nevertheless, the results suggest that the relation between the increase in CH_4 emissions and mixing ratios at the lower boundary is consistent, if either the emissions or the mixing ratios are increased.

We derive the feedback factor f (see Eq. 1) from ERF CH_4 using two approaches. Firstly, it is calculated from Eq. 12 by Holmes (2018) as $f = \frac{\ln(m_1/m_0)}{\ln(E_1/E_0)}$. Secondly, it is derived from a curve fit of the function $m(t) = m_0 * [2.75^f + (2.75 - 2.75^f) * \exp(-t/(f * \tau))]$ (Holmes, 2018) of the spin-up of the atmospheric mass of CH_4 using the yearly mean CH_4 lifetime with respect to OH oxidation for τ (see Fig. S14). Both approaches suggest $f = 1.55$. However, the derived f is not expected to be representative for CH_4 perturbations of EMAC close to present-day conditions because f increases with increasing CH_4 burden (Holmes, 2018). This might also explain why our estimate of f is at the upper end of previous estimates (Fiore et al., 2009; Voulgarakis et al., 2013; Stevenson et al., 2013; Thornhill et al., 2021b; Stevenson et al., 2020; Sand et al., 2023).

In the stratosphere, CH_4 loss by OH is enhanced due to an increase in stratospheric HO_x , whereas CH_4 loss by Cl is reduced (see Tab. S1 in the supplement). Overall, chemical stratospheric CH_4 loss is increased by 17.5%. However, the increase of CH_4 mixing ratios is larger than the increase factor of surface emissions of 2.75 in the whole stratosphere as well.

In the full response, as shown in Fig. 4 (c), CH_4 mixing ratios are lower in comparison to the fast response, as shown in Fig. 4 (b). Similar as in the climate response following the CO_2 perturbation, higher tropospheric temperatures lead to increased production of OH (see Fig. S3 in the supplement). Additionally, the temperature dependent reaction rate coefficient leads to a faster CH_4 oxidation. The corresponding sensitivity of the CH_4 lifetime per unit change of GSAT is -1.09 a K^{-1} or $-7.6\% \text{ K}^{-1}$ (relative to the lifetime in ERF CH_4). Both, the absolute and the relative sensitivity, are larger compared to the CO_2 perturbation experiment, which is possibly caused by the different CH_4 conditions in the respective fast responses (ERF CO_2 and ERF CH_4).

Stecher et al. (2021) analyzed the climate response of the $2 \times$ and $5 \times$ CH_4 surface mixing ratio experiments corresponding to Winterstein et al. (2019). The sensitivity of CH_4 lifetime per unit change of GSAT corresponding to their $5 \times \text{CH}_4$ surface mixing ratio perturbation is $\frac{-1.17 \text{ a}}{1.28 \text{ K}} = -0.91 \text{ a K}^{-1}$, which corresponds to a relative change of $-5.9\% \text{ K}^{-1}$ (relative to the lifetime in their fast response), and is thus less pronounced than the respective value of our study. The major difference between the simulation set-ups is that tropospheric CH_4 mixing ratios can not respond to the lifetime response in the set-up of Stecher et al. (2021). This suggests that in the present study the sensitivity of CH_4 lifetime towards climate change is enhanced, because the CH_4 -OH feedback is included in the response of OH and, therefore, in the CH_4 lifetime. The same is indicated by the results of the CO_2 perturbation as discussed above.

The response of O_3 is shown in Fig. 5. In the fast response (panel (a)), O_3 mixing ratios increase significantly throughout the troposphere with a maximum increase of up to 60% in the upper tropical troposphere. The CH_4 perturbation leads to enhanced O_3 formation by enhanced production of O_3 precursor species through CH_4 oxidation. In the stratosphere, radiatively induced

cooling (a rapid adjustment) leads to O₃ increases in the middle stratosphere. Above 1 hPa, O₃ mixing ratios decrease due to enhanced catalytic depletion by odd hydrogen (HO_x). HO_x is increased by enhanced production of stratospheric H₂O caused by CH₄ oxidation (see Fig. S2 in the supplement) and also by enhanced formation via the sink reaction of CH₄ with O(¹D). In the lower tropical stratosphere O₃ decreases, which can be explained by the reversed self-healing effect (Rosenfield et al., 2002; Portmann and Solomon, 2007), which is also effective for the CO₂ perturbation (see above). The fast response of O₃ is consistent with the fast response evolving in the comparable 5×CH₄ surface mixing ratio experiment (Winterstein et al., 2019), as the same processes are effective, which are explained in more detail by Winterstein et al. (2019).

Fig. 6 shows the fast response of individual O₃ categories derived using the TAGGING submodel. Shown is the difference between ERFCH₄ and REF-SSTfix of one category relative to the total reference O₃

$$\Delta O_{3cat} = \frac{O_{3cat,ERF} - O_{3cat,REF}}{O_{3total,REF}},$$

allowing a direct comparison with the relative response of total O₃. The O₃ mixing ratios increase in all categories except for the category O₃ *stratosphere*. This category shows reduced O₃ production through photolysis of O₂ in the lower stratosphere consistent with the reverse self-healing effect. The increase is strongest in the category O₃ *CH₄*, as the CH₄ increase directly leads to the formation of O₃. The increase of this category is most pronounced in the upper tropical troposphere and reaches up to 30% relative to the total reference O₃. The larger abundance of NMHCs and CO also affects O₃ production of the other categories as their reaction with precursors from other categories, in particular NO_x, leads to enhanced O₃ production in the category O₃ *CH₄*, but also in the other categories. This effect is largest for the category O₃ *lightning*, which shows O₃ increases of up to 20% relative to the total reference O₃, even though emissions of lightning NO_x decrease by 0.3 Tg(N) a⁻¹ globally in the simulation ERFCH₄ compared to REF-SSTfix (see Tab. 3). The CH₄ perturbation leads to upper tropospheric/lower stratospheric warming peaking at around 100 hPa in the tropics (see Fig. S1 in the supplement). The higher static stability leads to less convection and thereby to decreasing lightning NO_x emissions. Upper troposphere/lower stratosphere warming following increased CH₄ has been already noted elsewhere and is expected to be even more pronounced if shortwave (SW) absorption by CH₄ is accounted for in the simulation set-up (Modak et al., 2018; Allen et al., 2023). Nevertheless, the enhanced abundance of precursors from CH₄ oxidation lead to enhanced O₃ production in this category. The category showing the third most pronounced increase is O₃ *anthropogenic*. Here, the increase of up to 15% relative to the total reference O₃ is most pronounced in the lower NH, where the contribution of O₃ *anthropogenic* to total O₃ is largest.

The climate response of O₃ shown as the difference between full and fast response (see Fig. 5 (c)) represents the isolated effect of the GSAT response on O₃. It shows a strong reduction of O₃ mixing ratios in the lower tropical stratosphere, which is caused by enhanced tropical up-welling (consistent with the CO₂ simulation). In the Northern polar lower stratosphere, O₃ mixing ratios are enhanced pointing towards strengthened poleward and downward transport (i.e. strengthening of the Brewer-Dobson circulation, see Fig. S13 in the supplement) of stratospheric air masses. In the Southern polar tropopause region the rise of the tropopause in the climate response leads to a large O₃ reduction. This process is also apparent in the NH, albeit less pronounced. Apart from that, the full response of O₃ in the stratosphere is mainly caused by the fast response. The climate response of tropospheric O₃ shows a reduction, except for the tropical middle troposphere, where the response shows a weak,

not significant, increase in the zonal mean. In this region, enhanced emissions of lightning NO_x lead to enhanced O_3 formation (see also discussion of TAGGING results below). The climate response of O_3 is strikingly similar with the climate response pattern resulting from the CO_2 perturbation (see Fig. 2 (c)), even though the fast response is different. The spatial distribution of the climate response of surface O_3 is likewise similar for the CO_2 and the CH_4 perturbation (see Fig. S4).

The similarity of the climate response patterns of O_3 resulting from CO_2 and CH_4 perturbations has been also noted by Stecher et al. (2021). However, the O_3 climate response resulting from their $5\times\text{CH}_4$ mixing ratio increase shows a significant increase of O_3 in the tropical middle troposphere. As already stated, the main difference between their set-up and ours is that the feedback on CH_4 mixing ratios, and thereby also any secondary effects on O_3 , is suppressed. As for the CO_2 perturbation, the reduction of CH_4 mixing ratios feeds back on O_3 .

Fig. 7 shows the climate response of individual O_3 source categories. It is calculated using Eq. 7 in accordance with the corresponding analysis of the CO_2 perturbation. The patterns of the climate response of the individual categories are overall consistent with those of the CO_2 perturbation.

The category O_3 *stratosphere* increases in the troposphere, indicating enhanced transport of stratospheric O_3 into the troposphere. The increase is significant everywhere, except for the extratropical SH and the lower tropical troposphere. This category contributes strongest to the reduction of O_3 in the lower tropical stratosphere. The category O_3 *lightning* shows increases in the tropical middle troposphere resulting from an increase of the lightning NO_x emissions by 0.2 Tg(N) a^{-1} in ECCCH₄ compared to ERFCH₄ (see Tab. 3) and decreases in the lower troposphere. Biogenic NO_x emissions increase by $0.37 \text{ Tg(N) a}^{-1}$ and biogenic C_5H_8 emissions increase by about 30 Tg(C) a^{-1} as reaction to climate change (see Tab. 3). However, the zonal mean climate response of O_3 in this category is mostly not significant and shows a decrease in the lower tropical and upper NH troposphere (see Fig. 7 (d)). The tropospheric O_3 columns in this category increase locally over the Amazon region and the Congo river basin, where biogenic emissions of C_5H_8 increase strongest, and decrease mostly over the tropical ocean (see Fig. S9 in the supplement). As already mentioned, the sink of O_3 via the reaction of $\text{O}(^1\text{D})$ with H_2O is expected to strengthen in a warmer and moister troposphere. Similar as for the CO_2 perturbation, the effects of increased O_3 precursor emissions and the enhanced chemical sink due to a larger abundance of tropospheric H_2O compete in this category. The category O_3 *CH₄* decreases everywhere in the zonal mean, except for the tropical middle troposphere. The reduction is consistent with the reduction of CH_4 mixing ratios in the climate response, which leads to a reduced formation of O_3 . In addition, the enhanced chemical sink leads to further reduction of O_3 . The increase in the tropical middle troposphere coincides with the maximum increase of O_3 production from lightning NO_x emissions, which indicates that enhanced NO_x from lightning reacts with products of the CH_4 oxidation resulting in an increased O_3 production in both categories. The corresponding response of the tropospheric O_3 columns is not significant in the tropics, because of the counteracting responses in the lower and middle troposphere, but shows a significant decrease in the extra-tropics (see Fig. S9 in the supplement). The categories with prescribed O_3 precursor emissions, O_3 *biomass burning* and O_3 *anthropogenic*, show decreased O_3 mixing ratios throughout the troposphere (see Fig. 7 (g) and (h)), consistently with the climate response resulting from the CO_2 perturbation. Additionally, reduced O_3 production per emitted molecule NO_x can play a role as O_3 precursor emissions of natural categories increase.

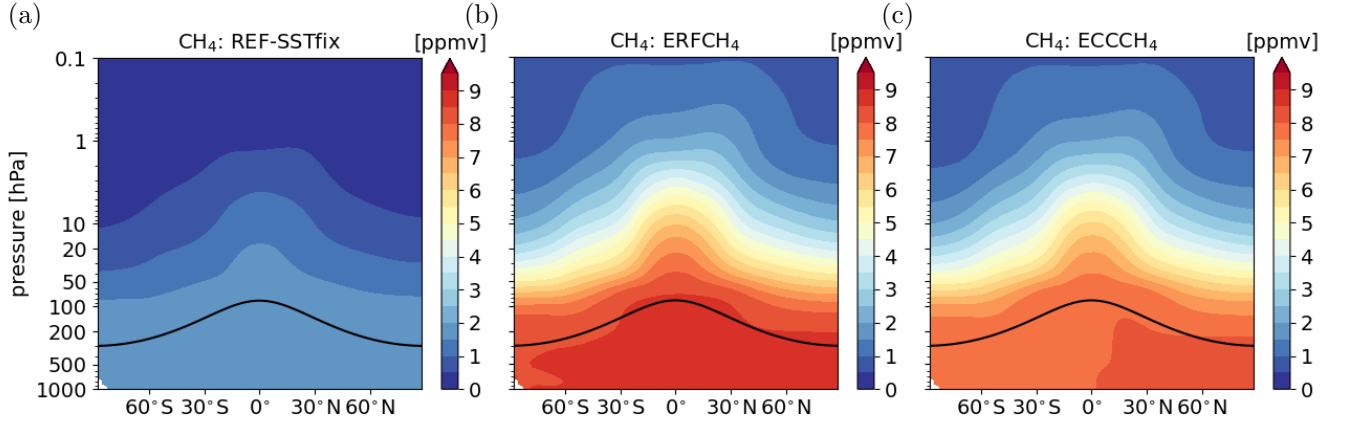


Figure 4. Annual zonal mean distribution of CH₄ mixing ratios in simulation (a) REF-SSTfix, (b) ERFCH₄ (fast response) and (c) ECCCH₄ (full response) in [ppmv].

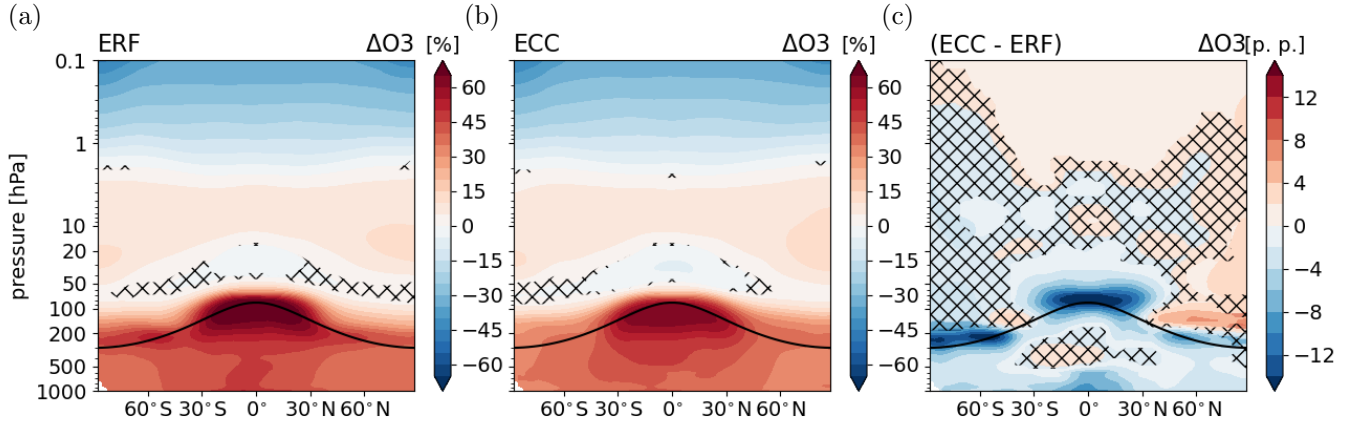


Figure 5. O₃ response following the CH₄ perturbation (same as Fig. 2, but for the CH₄ perturbation): Relative differences between the annual zonal mean O₃ mixing ratios of sensitivity simulations (a) ERFCH₄ (fast response) and (b) ECCCH₄ (full response) and their respective reference simulation in [%]. (c) Climate response as difference between the O₃ responses in panels (a) and (b) in [percentage points (p.p.)]. Non-hatched areas are significant on the 95% confidence level according to a Welch's test based on annual mean values. The solid black line indicates the location of the climatological tropopause.

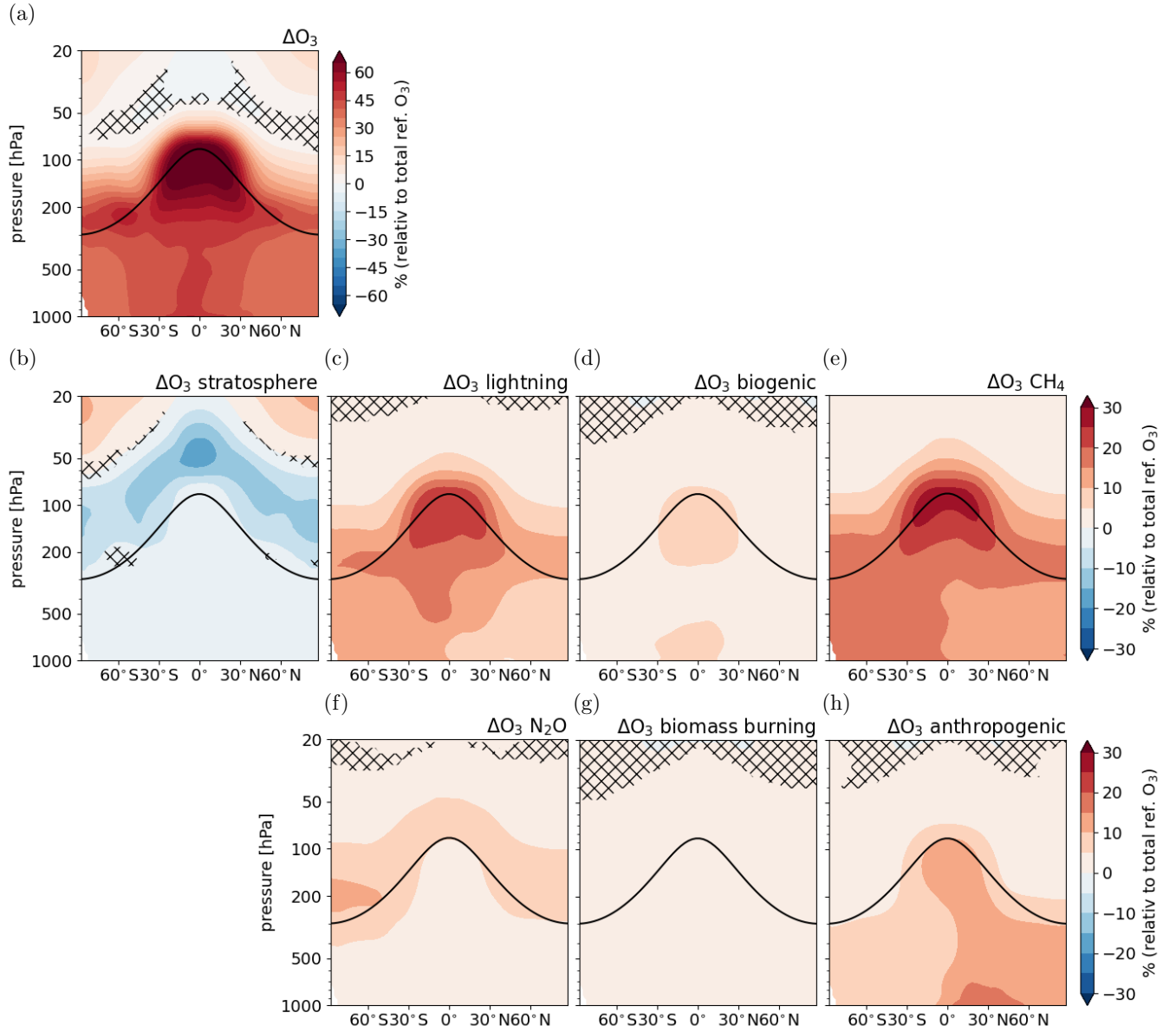


Figure 6. Fast response of tropospheric O_3 following the CH_4 perturbation: (a) response of total O_3 (same as Fig. 4 (a), but differently scaled colour levels to better compare with the response in the individual categories), (b) - (h) response of O_3 in individual source categories relative to total reference O_3 ($\Delta O_{3,cat} = \frac{O_{3,cat,ERF} - O_{3,cat,REF}}{O_{3,total,REF}}$). Non-hatched areas are significant on the 95% confidence level according to a Welch's test based on annual mean values. The solid black line indicates the location of the climatological tropopause.

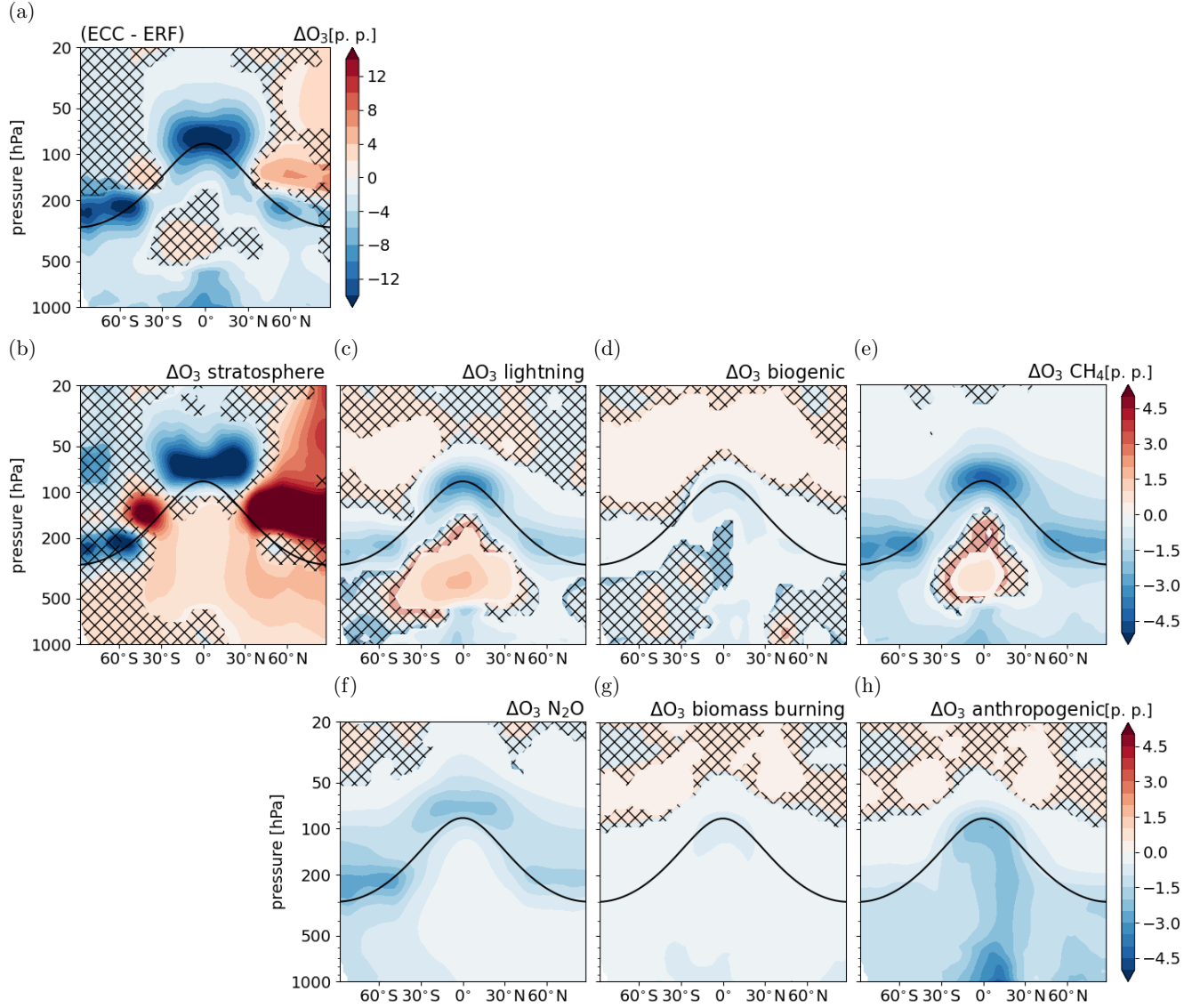


Figure 7. Climate response of tropospheric O_3 following the CH_4 perturbation (same as Fig. 3, but for the CH_4 perturbation): (a) response of total O_3 (same as Fig. 5 (c), but differently scaled colour levels to better compare with the response in the individual categories), (b) - (h) response of O_3 in individual source categories relative to total reference O_3 ($\Delta O_{3cat, climate response} = (\frac{O_{3cat,ECC} - O_{3cat,REF}}{O_{3total,REF}}) - (\frac{O_{3cat,ERF} - O_{3cat,REF}}{O_{3total,REF}})$). Non-hatched areas are significant on the 95% confidence level according to a Welch's test based on annual mean values. The solid black line indicates the location of the climatological tropopause.

3.3 Radiative effects and climate sensitivity

Table 4 shows results for the total SARF, ERF, Δ GSAT and the associated climate sensitivity parameters λ , as well as individual radiative effects corresponding to the composition changes of CH₄, O₃ and stratospheric H₂O. ERF includes physical and chemical adjustments, whereas SARF represents the radiative effect of the CO₂ or CH₄ composition change and the corresponding stratospheric temperature adjustment only.

For the CO₂ perturbation, the estimate of ERF is smaller than SARF, but the difference is not significant due to the large statistical uncertainty associated with ERF (e.g, Forster et al., 2016). Along with this, the climate sensitivity parameter based on ERF, λ_{ERF} , is larger compared to λ_{SARF} , but the difference is not statistically significant either. In contrast, for the CH₄ perturbation, the estimate of ERF of $1.72 \pm 0.17 \text{ W m}^{-2}$ is considerably larger than SARF, which is estimated at 0.51 W m^{-2} . The estimate of SARF reproduces the result of the comparable $5 \times \text{CH}_4$ mixing ratios experiment with the EMAC model (Winterstein et al., 2019). However, the radiative effect of CH₄ is known to be underestimated by the used radiative transfer scheme (Winterstein et al., 2019; Nützel et al., 2024). For instance, using the formula by Etminan et al. (2016)³ for the present CH₄ perturbation a SARF of about 1.7 W m^{-2} is derived. The underestimation of the radiative effect of CH₄ affects the estimate of ERF as well. Under the assumption that all other adjustments remain the same, only the direct contribution of CH₄ is exchanged, which results in an ERF of about 2.9 W m^{-2} . This considerably larger ERF suggests a correspondingly larger response of GSAT as well.

As illustrated by Tab. 4, chemical adjustments play a minor role for the CO₂ perturbation. The fast response of stratospheric O₃ induces a negative adjustment of -0.034 W m^{-2} , whereas the fast response of tropospheric O₃ induces a positive adjustment of 0.012 W m^{-2} . The adjustment of tropospheric CH₄ is negligible, whereas stratospheric CH₄ induces a small positive adjustment due to its increase in the stratosphere and associated local radiative cooling. H₂O increases in the lowermost stratosphere by up to 5% (see Fig. S2 in the supplement), which leads to a positive adjustment of 0.015 W m^{-2} . The change of H₂O in the lowermost stratosphere is largely driven by a change of the tropical cold point temperature (CPT) (see Fig. S10). For the CO₂ perturbation, chemical production of H₂O in the stratosphere is slightly reduced up to about 2 hPa. Thus, the adjustment of stratospheric H₂O is unlikely to be chemically induced. To summarize, interactive chemistry dampens the ERF of the CO₂ perturbation by about -1.3%, mainly by the effect of stratospheric O₃.

For the CH₄ perturbation, chemical adjustments of O₃ and stratospheric H₂O are important contributions to the ERF. The adjustment of tropospheric O₃ is 0.64 W m^{-2} , and that of stratospheric O₃ is 0.16 W m^{-2} . In addition, the adjustment of stratospheric H₂O is estimated at 0.51 W m^{-2} . The CH₄ perturbation leads to relative increases of H₂O up to 250% in the upper stratosphere and mesosphere (see Fig. S2 in the supplement) because the increased abundance of CH₄ leads to enhanced production of H₂O by CH₄ oxidation. Additionally, warming of the tropical cold point (see Fig. S9) leads to reduced dehydration of upwelling air parcels, and thus to an increased abundance of H₂O in the lower stratosphere. The zonal mean warming of the tropical cold point is 1.5 K and thereby more pronounced than in the respective CO₂ experiment. The CH₄

³The CH₄ mixing ratios of simulation ERFCH₄ are outside of the range tested to derive the formula of Etminan et al. (2016), but the formula can still provide a rough estimate for the CH₄ radiative effect.

perturbation induces a direct radiative heating at the tropical cold point of up to 1 K (see Fig. S12 in the supplement), and the response of stratospheric O₃ leads to additional radiative heating of about 1.5 K in this region (see Fig. S12 in the supplement).
 560 To summarize, the adjustments of O₃ and stratospheric H₂O enhance the ERF of the CH₄ perturbation by 1.31 W m⁻². The estimates of the adjustments of O₃ and stratospheric H₂O are consistent with the results of the comparable 5×CH₄ mixing ratios experiment (Winterstein et al., 2019, see also column 3 in Tab. 4).

The feedback parameters represent the radiative effects induced by changes in composition related to the climate response, i.e. to the isolated effect of GSAT changes. They are, as usual, given in W m⁻² K⁻¹, i.e., normalized by the corresponding
 565 GSAT response. For both perturbation types, CO₂ and CH₄, the feedbacks of CH₄ and O₃ are negative, which means that they dampen the resulting temperature change. The feedback parameter corresponding to the CH₄ reduction in the CO₂ perturbation experiment is -0.025 W m⁻² K⁻¹. As already mentioned, it is known that the direct radiative effect of CH₄ is underestimated by the used radiative transfer scheme (Winterstein et al., 2019; Nützel et al., 2024). Therefore, we additionally calculate the feedback parameter for the same change of CH₄ mixing ratios, but with the PSrad radiation scheme (Pincus and Stevens, 2013;
 570 Nützel et al., 2024), using otherwise the same methodology (see Sect. 2.3). With PSrad, the CH₄ feedback is estimated at -0.041 W m⁻² K⁻¹ implying a more pronounced negative radiative feedback. Applying the formula of Etminan et al. (2016) for the change of CH₄ mixing ratio diagnosed from the simulation suggests a radiative effect of -0.059 W m⁻², which corresponds to a feedback parameter of -0.054 W m⁻² K⁻¹. Previous estimates of the CH₄ feedback have been derived offline from the change of atmospheric CH₄ lifetime, and range from -0.014±0.067 W m⁻² K⁻¹ (Thornhill et al., 2021a, if the estimates for
 575 changes of biogenic volatile organic compounds, lightning NO_x and meteorology are combined⁴), -0.03±0.01 W m⁻² K⁻¹ (Heinze et al., 2019) to -0.036 W m⁻² K⁻¹ (Dietmüller et al., 2014). Our estimate using the PSrad scheme is at the upper end of previous estimates, but in the range of estimates from individual models analyzed by Thornhill et al. (2021a).

For the CH₄ perturbation, the feedback associated with the reduction of CH₄ mixing ratios in the full response in comparison to the fast response is -0.019 W m⁻² K⁻¹. Using the PSrad radiation scheme with otherwise the same method, the feedback pa-
 580 rameter is estimated at -0.089 W m⁻² K⁻¹ suggesting a clearly larger influence. The radiative feedback of CH₄ corresponding to the 5× CH₄ mixing ratio experiment (Winterstein et al., 2019; Stecher et al., 2021) does not include the reduction of CH₄ in the troposphere. The corresponding feedback parameter indicates a small positive feedback, caused by the larger mixing ratios of CH₄ in the stratosphere in the full response compared to the fast response (Stecher et al., 2021).

The feedback parameters corresponding to O₃ changes in the troposphere and stratosphere are both negative and add to
 585 total feedback parameters of -0.039 W m⁻² K⁻¹ for the CO₂ perturbation, and -0.054 W m⁻² K⁻¹ for the CH₄ perturbation. Previous studies of the O₃ feedback resulting from CO₂ perturbations have assessed the full response in contrast to the climate response. The feedback parameter corresponding to the full response, i.e. including the adjustment, is -0.059 W m⁻² K⁻¹ in our study. Previous estimates range from -0.015 W m⁻² K⁻¹ and -0.022 W m⁻² K⁻¹ (Dietmüller et al., 2014), -0.018 W m⁻² K⁻¹ (Marsh et al., 2016), -0.046±0.018 W m⁻² K⁻¹ (Thornhill et al., 2021a), to -0.12 W m⁻² K⁻¹ (Nowack et al., 2015, if a
 590 corresponding GSAT response of 5.75 K is assumed). The feedback parameter of total O₃ in the present study lies in the

⁴If the model CESM2-WACCM, which projects a prolongation of CH₄ lifetime with climate change, is excluded, the CH₄ feedback is estimated at -0.053±0.010 W m⁻² K⁻¹. The given uncertainties are standard deviations across models.

range of previous estimates, but, notably, is more pronounced than the estimate by Dietmüller et al. (2014), who also used the EMAC model. Part of the difference can be explained by the different sign of the feedback of tropospheric O₃. Dietmüller et al. (2014) found a positive feedback parameter of 0.008 W m⁻² K⁻¹ to 0.009 W m⁻² K⁻¹ for tropospheric O₃ compared to the negative feedback parameter in this study. The reduction of tropospheric CH₄ mixing ratios leads to reduced O₃ production and thereby modifies the response of O₃ as discussed above. This indirect effect on O₃ is a consequence of applying emission fluxes instead of a prescribed lower boundary mixing ratio for CH₄. In addition, also the negative feedback of stratospheric O₃ is more pronounced in this study, which might be explained by the different magnitude of the perturbations. Dietmüller et al. (2014) noted differences between their 2× and 4×CO₂ experiments. Therefore, deviations for the 1.35×CO₂ in this study can be expected. In addition, the different vertical resolution of the simulation set-ups might affect the response of stratospheric O₃. The results of the 5×CH₄ mixing ratio experiment by Stecher et al. (2021) do not indicate a significant feedback of total O₃. This suggests that the reduction of CH₄ mixing ratios in the full response drives the negative O₃ feedback.

As explained above, the scaling factors of the CO₂ and CH₄ increase are chosen so that the resulting ERFs are comparable to allow an optimal comparison of the climate sensitivity of the two perturbation types, as the latter can depend on the magnitude of the radiative perturbation (e.g., Hansen et al., 2005; Dietmüller et al., 2014). The estimates of the climate sensitivity parameter based on ERF, λ_{ERF} , are identical for the CO₂ and CH₄ perturbations of this study. In contrast, the climate sensitivity parameters based on SARF, λ_{SARF} , differ significantly between the CH₄ and the CO₂ perturbation. This finding confirms the results of previous studies that the climate sensitivity is in general less dependent on the type of perturbation for ERF (e.g., Richardson et al., 2019). The use of λ_{ERF} as climate sensitivity parameter to obtain an efficacy close to unity for the CH₄ perturbation is more important in this study compared to Richardson et al. (2019), because of the effect of interactive chemistry, which leads to larger differences between SARF and ERF for the CH₄ perturbation.

The estimate of λ_{ERF} of 0.68 ± 0.08 K / (W m⁻²) is smaller than the corresponding estimate of the 5×CH₄ mixing ratio experiment of 0.72 ± 0.07 K / (W m⁻²) (Stecher et al., 2021). This suggests a reduction of the climate sensitivity parameter caused by the explicit simulation of the CH₄ reduction which would be physically consistent with the negative feedbacks of O₃ and CH₄ in this study. The difference between the two estimates is, however, not statistically significant.

4 Discussion and Conclusions

In this study, we assess the feedback of atmospheric CH₄ resulting from changes in its chemical sink, which is mainly by oxidation with OH and, which is influenced by temperature and the chemical composition of the atmosphere. We present results from numerical simulations with the CCM EMAC perturbed by either 1.35×CO₂ mixing ratio or 2.75×CH₄ emission flux increase. The scaling factors were chosen to reach a comparable ERF for both perturbation agents. EMAC is used in a CH₄ emission flux driven setup, which allows the atmospheric CH₄ mixing ratio to adjust to changes of the chemical sink without constraints.

The increase of CH₄ emissions by a globally constant factor of 2.75 corresponds to an increase of the global mean CH₄ surface mixing ratio by a factor of 4.76. The larger increase of the CH₄ mixing ratio compared to the emissions is caused

Table 4. Estimates of total SARF, ERF, Δ GSAT and the corresponding climate sensitivity parameters λ , as well as adjustments and feedbacks of individual composition changes of CH₄, O₃ and stratospheric H₂O. ERF includes physical and chemical adjustments, whereas SARF represents the radiative effect of the CO₂ or CH₄ composition change and the corresponding stratospheric temperature adjustment only. The climate sensitivity parameters λ_{SARF} and λ_{ERF} are calculated using SARF or ERF, respectively. Adjustments are calculated as the radiative flux changes of the fast response (in W m⁻²). Feedbacks are calculated as the difference of radiative flux changes between the full and the fast response divided by the corresponding change of global surface air temperature Δ GSAT (in W m⁻² K⁻¹). The radiative effects of individual composition changes include the corresponding stratospheric temperature adjustment (Stuber et al., 2001). All radiative estimates are evaluated at TOA. In addition, the estimates of the 5×CH₄ volume mixing ratio experiments analyzed by Winterstein et al. (2019) and Stecher et al. (2021) are shown in the third column.

Perturbation		1.35×CO ₂ VMR ERFCO ₂ / ECCCO ₂	2.75×CH ₄ emissions ERFCH ₄ / ECCCH ₄	5×CH ₄ VMR (Winterstein et al., 2019; Stecher et al., 2021)
SARF	[W m ⁻²]	1.71	0.51	0.51
ERF	[W m ⁻²]	1.61±0.16	1.72±0.17	1.79±0.17
Δ GSAT	[K]	1.09±0.06	1.17±0.06	1.28±0.04
λ_{SARF}	[K / W m ⁻²]	0.64±0.03	2.30±0.11	2.49±0.08
λ_{ERF}	[K / W m ⁻²]	0.68±0.07	0.68±0.08	0.72±0.07
<u>Adjustments</u> [W m ⁻²]				
O ₃ trop.		0.012	0.64	0.56
O ₃ strat.		-0.034	0.16	0.20
O ₃ total		-0.022	0.81	0.76
CH ₄		<0.001	-	-
H ₂ O strat.		0.015	0.51	0.55
<u>Feedbacks</u> [W m ⁻² K ⁻¹]				
O ₃ trop.		-0.023	-0.029	0.005
O ₃ strat.		-0.016	-0.025	-0.006
O ₃ total		-0.039	-0.054	-0.001
CH ₄		-0.025	-0.019	0.004
CH ₄ using PSrad		-0.041	-0.089	-
H ₂ O strat.		0.15	0.11	0.079

Values after the $\pm$ sign are $2\times$ the standard error of the mean calculated on the basis of 20 annual mean values, which approximate the corresponding 95% confidence intervals. The standard errors for the climate sensitivity parameters are calculated from the standard error of the corresponding radiative forcing std_err_{RF} and the standard error of Δ GSAT $std_err_{\Delta GSAT}$, as $std_err_{\lambda} = (\sqrt{\frac{std_err_{RF}^2}{RF^2} + \frac{std_err_{\Delta GSAT}^2}{\Delta GSAT^2}} \cdot \frac{\Delta GSAT}{RF})$. The method to derive stratospheric adjusted radiative estimates does not account for interannual variability, which is why no uncertainty estimates are provided for the respective estimates.

by a strong reduction of tropospheric OH, which leads to the extension of the tropospheric CH₄ lifetime. A similar effect was found by Winterstein et al. (2019), who analyzed the response of 5×CH₄ mixing ratios using a comparable set-up of the EMAC

model, but with prescribed CH₄ surface mixing ratios. In particular, to reach the 5×CH₄ mixing ratio increase, a pseudo surface emission flux is calculated in their set-up. The increase factor of the pseudo flux that corresponds to an increase of 5×CH₄ is 2.75 (Stecher et al., 2021), exactly the scaling factor of CH₄ surface emissions used in this study. To summarize, reduced chemical decomposition enhances the increase of the CH₄ mixing ratios compared to the emissions. The relation between the increase of CH₄ mixing ratios and CH₄ emissions appears to be robust, if either the mixing ratio or the emissions are increased.

We separately assess the so-called fast response in CO₂ and CH₄ perturbation simulations with prescribed SSTs and SICs, and the full response in simulations coupled to a MLO model. The CO₂ perturbation affects the chemical composition only indirectly through temperature changes. In the fast response, radiatively induced cooling in the stratosphere causes slower chemical depletion and leads therefore to increasing mixing ratios of O₃ and CH₄. In particular, our results show that the well-known increase of upper and middle stratospheric O₃ (e.g., Dietmüller et al., 2014; Nowack et al., 2015; Marsh et al., 2016; Chiodo et al., 2018) is part of the fast response, and not related to the associated tropospheric warming. The CH₄ emission increase directly influences the chemical composition in the troposphere and stratosphere. The fast response patterns of O₃ and stratospheric water vapour are consistent to the changes following the 5×CH₄ mixing ratio increase (Winterstein et al., 2019) as expected from the comparable magnitude of CH₄ mixing ratio increase.

Despite the different effect on the chemical composition in the fast response, the isolated effect of GSAT changes induced by either the CO₂ or the CH₄ increase is consistent. Tropospheric warming shortens the atmospheric lifetime of CH₄. The corresponding reduction of CH₄ mixing ratios is explicitly simulated by the used CH₄ emission flux driven set-up. The explicit reduction of CH₄ mixing ratios allows for secondary feedbacks on OH and O₃.

Firstly, the CH₄ lifetime response implicitly includes the CH₄-OH feedback. The sensitivities of the CH₄ lifetime per unit change of GSAT are -6.7 % K⁻¹ for 1.35×CO₂ and -7.6 % K⁻¹ for 2.75×CH₄, which is larger compared to previous CCM results using prescribed CH₄ mixing ratios at the lower boundary (Voulgarakis et al., 2013; Thornhill et al., 2021a; Stecher et al., 2021). The results of the comparable CH₄ increase experiment with prescribed CH₄ surface mixing ratios (Stecher et al., 2021) provide a clear indication that the lifetime change per temperature change is larger in the CH₄ emission driven set-up. A comparable CO₂ increase simulation using EMAC with prescribed CH₄ surface mixing ratios is not available, but the comparison to the results of other CCMs (Voulgarakis et al., 2013; Thornhill et al., 2021a) indicates the same effect (see Sect. 3.1). Estimates of the CH₄ lifetime change per temperature change from other CCMs driven by prescribed CH₄ emission fluxes would be helpful to verify the influence of CH₄ emission fluxes in comparison to prescribing CH₄ at the lower boundary. Additionally, the multi-model differences of the CH₄ lifetime change per unit change of GSAT are large (Voulgarakis et al., 2013; Thornhill et al., 2021a) and it would be valuable to identify reasons behind CCM differences in future studies.

Secondly, the reduction of CH₄ mixing ratios results in reduced formation of O₃ in the troposphere. This leads to substantial differences in the climate response of tropospheric O₃ between this study and previous work using prescribed CH₄ mixing ratios at the lower boundary (Dietmüller et al., 2014; Nowack et al., 2015; Marsh et al., 2016; Nowack et al., 2018; Chiodo et al., 2018; Stecher et al., 2021). The latter studies consistently show an increase of O₃ mixing ratios in the tropical upper troposphere, whereas in this study the response is either insignificantly weak or indicates a reduction of O₃ mixing ratios in this region. An attribution method is used to identify and quantify the processes that influence tropospheric O₃ under

climate change: Stronger stratosphere - troposphere exchange and larger natural emissions of O_3 precursors lead to increases in tropospheric O_3 , whereas enhanced chemical loss caused by the increased tropospheric humidity and the reduction of CH_4 mixing ratios lead to decreases. The contribution of the individual processes depend on the representation of the process of the model. For instance, the representation of O_3 precursor emissions from natural sources is model dependent (e.g., Voulgarakis et al., 2013; Stevenson et al., 2020; Zanis et al., 2022). The climate response of lightning NO_x emissions is uncertain so that even the sign of the projected change depends on the used parameterization (Finney et al., 2016, 2018; Zanis et al., 2022). This has implications for the climate response of tropospheric O_3 , for which changed lightning NO_x emissions are found to be an important contribution. Most schemes used in CCMs to date project increasing lightning NO_x emissions in response to tropospheric warming (Voulgarakis et al., 2013; Finney et al., 2016), which is in accordance with the results of this study, whereas a more sophisticated lightning NO_x parameterization indicates a decrease of lightning NO_x emissions (Finney et al., 2018). The spatial distribution of increases of biogenic C_5H_8 emissions over the Amazonian region and the Congo river basin are in qualitative agreement with the climate response of biogenic emissions simulated by other CCMs (Zanis et al., 2022, see their Fig. S6). We expect the contribution of biogenic emission changes on O_3 to be more important than diagnosed by the used version of the TAGGING method, as it underestimates the influence of C_5H_8 emissions on the diagnostic tracer O_3 biogenic. The NMHC emissions are scaled by the number of C-atoms in the molecule, i.e. 5 for C_5H_8 , before they are added to the NMHC family tracer, which was not done in the case of the online calculated biogenic C_5H_8 emissions. We expect that this issue influences the quantitative response of the category O_3 from biogenic sources, more precisely that changes of O_3 biogenic caused by changes in C_5H_8 emissions are underestimated. However, we do not expect that the response patterns and general findings would change. Therefore, and due to the computational costs of the simulations, it was decided to not repeat the simulations. We also want to stress that this issue affects the diagnostic TAGGING results only, but not the total O_3 response. Furthermore, biogenic emissions of C_5H_8 depend on the underlying vegetation, which is expected to interact with changes in e.g. climate, atmospheric CO_2 abundance, tropospheric O_3 or land use change (e.g., Zhou et al., 2018; Vella et al., 2023), but such interactions are not included in the used set-up. In addition, droughts can inhibit the substrate supply and thereby reduce biogenic C_5H_8 emissions (e.g., Wang et al., 2022). A respective representation of the impact of droughts on C_5H_8 emissions is not included in the used model version.

We calculate the radiative effects that correspond to the composition changes of CH_4 , O_3 and stratospheric H_2O . Our results confirm that chemical adjustments of O_3 and stratospheric H_2O are important contributions to the ERF of the CH_4 perturbation. Therefore, ERF is significantly larger than SARF, which represents the direct radiative effect of CH_4 including the associated stratospheric temperature adjustment. The individual adjustments are in agreement with the estimates of the $5 \times CH_4$ mixing ratio experiment (Winterstein et al., 2019).

Chemical adjustments play a minor role in the CO_2 case. Here, stratospheric O_3 induces a negative adjustment, which reduces the ERF by about -1.3%. Previous studies defined the full response of O_3 as its feedback (Dietmüller et al., 2014; Nowack et al., 2015; Marsh et al., 2016). Our results show that under the ERF framework large parts of the stratospheric O_3 change is to be regarded as an adjustment. Further, our results do not indicate that ERF is significantly different from SARF for

695 the CO₂ perturbation, which is in accordance to simulation results, which account for physical adjustments only (Smith et al., 2018).

The scaling of the CO₂ and the CH₄ perturbations in this study are chosen so that the resulting ERFs are of similar magnitude. This allows an optimal comparison of the climate sensitivity parameters as these can depend on the magnitude of the perturbation (e.g., Hansen et al., 2005; Dietmüller et al., 2014). Our results suggest an efficacy of unity for the CH₄ perturbation
700 when the climate sensitivity parameters are based on ERF. The climate sensitivity parameters based on SARF differ significantly between the CO₂ and the CH₄ increase, because of the large effect of chemical adjustments for the CH₄ perturbation. Thereby, our results support the finding that the climate sensitivity is in general less dependent on the type of perturbation for the ERF framework (e.g., Richardson et al., 2019). The multi-model mean efficacy based on ERF using the fixed SST method for a 3×CH₄ perturbation analyzed by Richardson et al. (2019) is slightly less than 1, with a spread of individual models of
705 0.56–1.15. In their study, the efficacy based on SARF is slightly less than 1 as well. In our study, the efficacy based on SARF is significantly larger than 1, i.e. about 3.6, because of the effect of chemical adjustments, which is not included in the estimate of Richardson et al. (2019).

The feedbacks corresponding to tropospheric O₃ changes in the full response are negative in contrast to previous estimates derived with the EMAC model with prescribed CH₄ mixing ratios at the lower boundary (Dietmüller et al., 2014;
710 Stecher et al., 2021). As mentioned above, the explicit reduction of CH₄ mixing ratios allows for secondary feedbacks on O₃ to evolve and leads, more precisely, to reduced O₃ formation, which is also reflected by the negative radiative feedback. Furthermore, the feedback parameter of tropospheric O₃ derived from the multi-model mean analyzed by Stevenson et al. (2006) does not account for the CH₄ chemistry-climate feedback. The corresponding feedback parameter has been estimated at $-0.007 \pm 0.009 \text{ W m}^{-2} \text{ K}^{-1}$ by Heinze et al. (2019).

715 The reduction of CH₄ mixing ratios in the climate response induces a negative feedback parameter, which is estimated at $-0.025 \text{ W m}^{-2} \text{ K}^{-1}$ for the CO₂ perturbation, and at $-0.019 \text{ W m}^{-2} \text{ K}^{-1}$ for the CH₄ perturbation using the default radiative transfer scheme of EMAC. However, it is known that this radiative transfer scheme underestimates the direct radiative effect of CH₄ (Winterstein et al., 2019; Nützel et al., 2024). Therefore, we derive the radiative feedback also with the PSrad radiation scheme (Pincus and Stevens, 2013; Nützel et al., 2024), which suggests a clearly more pronounced feedback parameters of
720 $-0.041 \text{ W m}^{-2} \text{ K}^{-1}$ for the CO₂ perturbation, and of $-0.089 \text{ W m}^{-2} \text{ K}^{-1}$ for the CH₄ perturbation. The PSrad feedback parameters are in the range of previous individual model estimates derived from CH₄ lifetime changes (Dietmüller et al., 2014; Heinze et al., 2019; Thornhill et al., 2021a).

Further, the default radiation scheme used in EMAC so far does not account for absorption of CH₄ in the solar SW spectrum. Recent studies have shown that accounting for SW absorption by CH₄ influences adjustment and feedback processes of, e.g.
725 clouds (Smith et al., 2018; Modak et al., 2018; Allen et al., 2023, 2024). For an improved representation of the radiative effect of CH₄ in future studies, the PSrad radiation scheme (Pincus and Stevens, 2013) is now available for use in online EMAC simulations (Nützel et al., 2024).

This study focuses on the role of CH₄ for interactions between the gas-phase chemistry and climate change. However, further processes can also play a role, which are not accounted for by the used simulation set-up. For instance, chemistry-aerosol-cloud

730 coupling was identified to contribute to the ERF of CH₄ perturbations (Kurtén et al., 2011; O'Connor et al., 2022) and might therefore also influence the corresponding climate response. In addition, natural emission sources of CH₄, e.g. from wetlands or permafrost, have the potential to increase in a warming climate (e.g., O'Connor et al., 2010; Dean et al., 2018). For instance, the results of Thornhill et al. (2021a) suggest that the negative radiative effect corresponding to the shortening of the CH₄ lifetime is offset by the positive radiative effect of CH₄ emission increases from wetlands in response to a 4×CO₂ perturbation. The net effect of feedbacks on the gas-phase chemistry and on natural emissions influences the effect of associated secondary feedbacks, e.g. regarding the formation of O₃.

To conclude, the atmospheric abundance CH₄, and therefore its potential as a greenhouse gas, is linked to a number of complex interactions. This makes the assessment of the climate feedback of CH₄ and its indirect effects a non trivial undertaking, which requires comprehensive chemistry-climate simulations. The novelty of this study is that the feedback on CH₄ mixing ratios to changes of its chemical sink, and thereby also associated secondary feedbacks on OH and O₃, are accounted for explicitly, which is recommended to be adopted for further studies on chemical feedbacks.

Code and data availability. The Modular Earth Submodel System (MESSy; doi: 10.5281/zenodo.8360186) is continuously further developed and applied by a consortium of institutions. The usage of MESSy and access to the source code is licenced 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 Website (<http://www.messy-interface.org>). The simulation results presented here are based on MESSy version 2.55.2 (The MESSy Consortium, 2021). Furthermore the exact code version used to produce the simulation results is archived at the German Climate Computing Center (DKRZ) and can be made available to members of the MESSy community upon request. The simulation results are available at the DKRZ DOKU long term archive under https://www.wdc-climate.de/ui/entry?acronym=DKRZ_LTA_1132_ds00001 (Stecher et al., 2024). The HadISST data (Rayner et al., 2003) are available from www.metoffice.gov.uk/hadobs (last access 16 September 2024).

Author contributions. FW and MP developed the concept of the study. LS performed the model simulations, analyzed the data and created the figures with significant contributions regarding the interpretation and evaluation of the model results from all coauthors. LS prepared the original draft and all authors contributed to the writing and reviewing of the manuscript.

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