Impact of the eruption of Mt. Pinatubo on the chemical composition of the stratosphere

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Abstract. This article describes the volcanic effect of the Mt. Pinatubo eruption in June 1991 on the ozone (O_3) and methane (CH_4) distribution in the stratosphere, as simulated with the chemistry-climate model EMAC (ECHAM/MESSy Atmospheric Chemistry, ECHAM5, version 5.3.02, MESSy, version 2.51). For the first time, the effects of volcanic heating and heterogeneous chemistry on the chemical composition, caused by the volcanic aerosol, are separated. Global model simulations over
5   the relevant period of the eruption from 1989 to 1997 with EMAC in T42L90MA resolution with specified dynamics and interactive chemistry were performed. The first simulation (VOL) contains the volcanic perturbation as additional aerosol load and thus simulates the interaction of the aerosol with the chemistry and the radiation. The second simulation (NOVOL) neglects the eruption and represents the undisturbed atmosphere. In the third simulation (CVOL) the volcanic aerosol only interacts with the heterogeneous chemistry, such that volcanic heating is omitted. The differences between the simulation results VOL-NOVOL
10 describe the total effect of the Mt. Pinatubo eruption on the chemical composition, VOL-CVOL the stratospheric heating effect and CVOL-NOVOL the chemical effect of the aerosol on the heterogeneous chemistry. The post volcanic stratosphere shows a decrease of the O_3 column in the tropics, and an increase in the mid-latitudes and polar regions, lasting roughly one year. This change in the ozone column is solely a result of the heating effect. The subsequent decrease of the ozone column is related to the chemical effect. The contribution of the catalytic loss cycles (NO_x, HO_x, ClO_x and BrO_x) on the depletion of O_3 is analysed
15 in detail. In the tropics, CH_4 increases in the upper stratosphere because of stronger vertical transport.

1   Introduction

Major volcanic eruptions in the tropics are able to inject material into the stratosphere and perturb the physical and the chemical states of the climate system for several years and longer (Robock, 2000; Thomas et al., 2009; Muthers et al., 2015). The emissions are mainly ash and sulphur in the form of SO_2, which oxidizes to sulphate in the stratosphere, and sulphate aerosols
20 are formed within weeks. The Mt. Pinatubo eruption in June 1991 decreased the tropical ozone column significantly, by 13-20 DU (Grant et al., 1992). Stratospheric ozone is a well studied greenhouse gas with a great public interest because it absorbs UV radiation and protects human health from harmful radiation. The abundance of ozone is mainly controlled by the production via photolysis and depletion by catalysts such as NO_x, ClO_x, BrO_x and HO_x (Solomon, 1999). The yearlong ozone production in the tropics and the transport via the Brewer-Dobson circulation (BDC) towards the polar regions, together with the ozone

depletion due to the temperature dependent PSC's (polar stratospheric clouds) and the resulting activation of chlorine, explain the global distribution of O_3.

The eruption of the Mt. Pinatubo on the 12th of June 1991 was one of the strongest volcanic eruptions in the 20th century (Thomas et al., 2009). It affected the chemical composition of the atmosphere considerably (Textor et al., 2004; von

5   Glasow et al., 2009; Poberaj et al., 2011; Aquila et al., 2013). The formed sulphate aerosols were rapidly zonally dispersed and transported into both hemispheres by the BDC. They absorb the solar radiation, resulting in a heating of the stratosphere and a cooling of the troposphere beneath (Labitzke and McCormick, 1992). Stenchikov et al. (1998) established that the near-infrared solar forcing mainly drives the stratospheric heating due to an increase in the atmospheric extinction by volcanic aerosol.

After the Mt. Pinatubo eruption, the temperature in the lower and middle stratosphere increased by up to 3.5 K at 30 hPa and

10   decreased by 0.5 K in the troposphere (Labitzke and McCormick, 1992; Self et al., 1999; Robock, 2000; von Glasow et al., 2009). The volcanic heating by the Mt. Pinatubo eruption lead to an increase of the vertical ascent by 20 % and subsequent polward transport of air from regions with low ozone and thus reduced the ozone column in the tropics (McCormick et al., 1995b; Dameris et al., 2005). Moreover, volcanic heating modifies the ozone budget via an acceleration of the temperature dependent heterogeneous reaction rates. Ozone measurements in the post-volcanic atmosphere of the Mt. Pinatubo eruption

15   showed a total ozone column decrease by 6-8 % in the tropics within a month after the eruption (Grant et al., 1992; Schoeberl et al., 1993a; McCormick et al., 1995b). McCormick et al. (1995b) figured out that the bulk of the ozone loss after the Mt. Pinatubo eruption appeared between 24-25 km with up to 20 %. The larger liquid aerosol surface accelerates the heterogeneous reactions and affects the O_3 chemistry, e.g. converting NO_x into HNO_3, provides and activates chlorine from reservoirs, and alters catalytic ozone destruction (Solomon et al., 1996; Solomon, 1999; Robock, 2000; Poberaj et al., 2011; Aquila et al.,

20   2013).

Modelling studies on the eruption of Mt. Pinatubo aim to understand which processes are responsible for the ozone changes and how these changes affect the dynamics. These studies differ with respect to the methodology. Rozanov et al. (2002) simulated the volcanic induced ozone depletion using a GCM including interactive chemistry and stratosphere-troposphere interactions. Two ensembles of free-running model simulations were performed. One ensemble simulates the volcanic aerosol,

25   hence including both, the chemical and dynamical effects, and the second set uses no volcanic forcing. Likewise, a set of free-running model simulations, but with a coupled atmosphere-ocean-chemistry model has been used by Muthers et al. (2015). They were also interested in the role of different climate settings (specific atmospheric composition of greenhouse gases) and performed corresponding sensitivity studies.

Aquila et al. (2013) used ensembles of 10 free-running model simulations representing either the case of full interaction of

30   volcanic aerosol with chemistry and radiation, with chemistry only, with radiation only and one simulation without the eruption effect. They could attribute the change in ozone to dynamical and chemical effects in the post Pinatubo period. Telford et al. (2009a) combined two nudged simulations and one free-running simulation in order to distinguish between chemical and dynamical effects on ozone of the Mt. Pinatubo eruption. Their first simulation nudged towards ERA-40 uses all aspects of the model with prescribed volcanic aerosol. The second nudged simulation is performed without the Pinatubo, but with an

35   unperturbed background aerosol. The difference between both lead to the so-called chemical effect on ozone. Admittedly,

the chemical effect of Telford et al. (2009b) is not purely chemical, because it still consists of both, a volcanic heating with subsequent influence on the stratospheric dynamics, and a perturbation of the heterogeneous chemistry. In our present study we separate Telford et al's alleged chemical effect into the heating through absorption by the volcanic aerosol and the pure chemical effect, the latter just developing from a change of the heterogeneous chemistry by the aerosol surface. In our study Telford et al's chemical effect is called combined effect. Muthers et al. (2015) also simulated the temperature driven effects decoupled from the chemical effect with a coupled atmosphere–ocean–chemistry–climate model, but did not separate the chemical effect of the heterogeneous chemistry from the heating effect of the volcanic heating.

Here, we performed global simulations of the eruption from 1989 to 1997 with specified dynamics and full chemistry with the chemistry-climate model EMAC. One simulation contains the volcanic perturbation as an additional aerosol load (VOL) and thus the full interaction of the aerosol with the chemistry and the radiation. In the second simulation, only the chemistry on the volcanic aerosols is accounted for (CVOL), and the third simulation neglects the eruption entirely and represents the undisturbed atmosphere (NOVOL). The differences of the simulation results (VOL-NOVOL) describe the combined effect of the Mt. Pinatubo eruption, (VOL-CVOL) of stratospheric heating effect only, and (CVOL-NOVOL) solely the effect of the chemistry due to the additional aerosol chemical effect. Moreover, the effect on the relevant chemical cycles is calculated between the CVOL and NOVOL simulations.

Section 2 provides a description of the chemistry-climate model EMAC, the setup of the simulations and the methodology of the analysis. Section 3 evaluates the EMAC results with the SWOOSH satellite measurements data set. Section 4 describes all relevant physical and chemical parameters, which are perturbed by the volcanic aerosol. Section 5 discusses the findings and provides an outlook on further studies. Section 6 summarises the most important results.

This is a follow-up study of Löffler et al. (2016), who analysed the perturbation of the stratospheric water vapour by the Mt. Pinatubo eruption. The motivation of this study is to differentiate the effect of the eruption on the chemical composition into:

1. the effect of stratospheric heating and subsequent changes in transport,

2. the pure chemical effect due to heterogeneous reactions on the volcanic aerosol and the modification of the relevant chemical cycles.

2 Model Simulations

2.1 Model Description

The European Centre for Medium-Range Weather Forecasts Hamburg – Modular Earth Submodel System (ECHAM/MESSy) Atmospheric Chemistry model (EMAC) is a numerical chemistry and climate simulation system that includes sub-models describing tropospheric and middle atmosphere processes and their interaction with oceans, land, and human influences (Jöckel et al., 2010, 2016). It uses the second version of the MESSy to link multi-institutional computer codes. The core atmospheric model is the 5th generation European Centre Hamburg general circulation model ECHAM (Roeckner et al., 2006). For the present study we applied EMAC (ECHAM5 version 5.3.02, MESSy version 2.51) in the T42L90MA resolution, i.e. with a

spherical truncation of T42 (corresponding to a quadratic Gaussian grid of ca. 2.8° × 2.8° in latitude and longitude) with 90 vertical hybrid pressure levels up to 0.01 hPa.
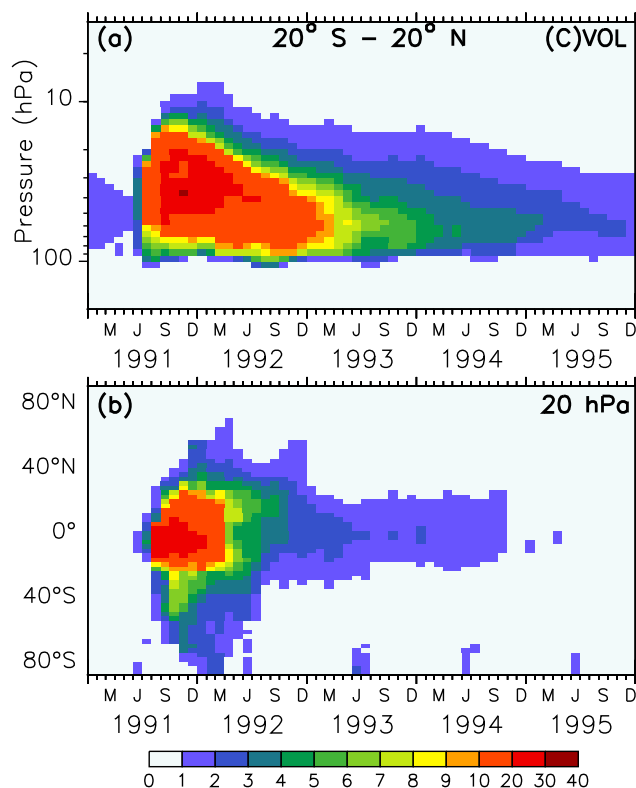
Figure 1. Colours show the monthly averaged liquid aerosol surface area density (10^{-8} cm^2cm^{-3}) of the volcanic sulfate aerosols in simulations VOL and CVOL in the stratosphere as tropical averaged vertical time series between 20° S and 20° N **(a)**, and as latitudinal time series at 20hPa **(b)**. The intervals of the colour scale are not equidistant.

The forcing of the volcano in the model is represented by the prescribed surface area density in time and space (Figures 1 and 2). Hence, volcanic aerosols in the simulations VOL and CVOL are not treated by an interactive aerosol module, but the volcanic aerosols are based on measurements from satellites. The aerosol data originate from the CCMI data set (Revell et al., 2017), which is based on SAGE II (Stratospheric Aerosol and Gas Experiment) extinction data. It uses a lognormal aerosol size distribution by means of the SAGE-4λ algorithm, which is compiled out of all four wavelengths (385, 452, 525, and 1024 nm) that are available in the SAGE II data set (Revell et al., 2017).

2.2 ESCiMo Consortial Simulations

The volcanic simulations of this study were performed like multiple simulations with different boundary conditions within the Earth System Chemistry integrated Modelling (ESCiMo) project (Jöckel et al., 2016). These model simulations were defined to improve the understanding of processes in the atmosphere and also to help answer questions related to climate change, ozone
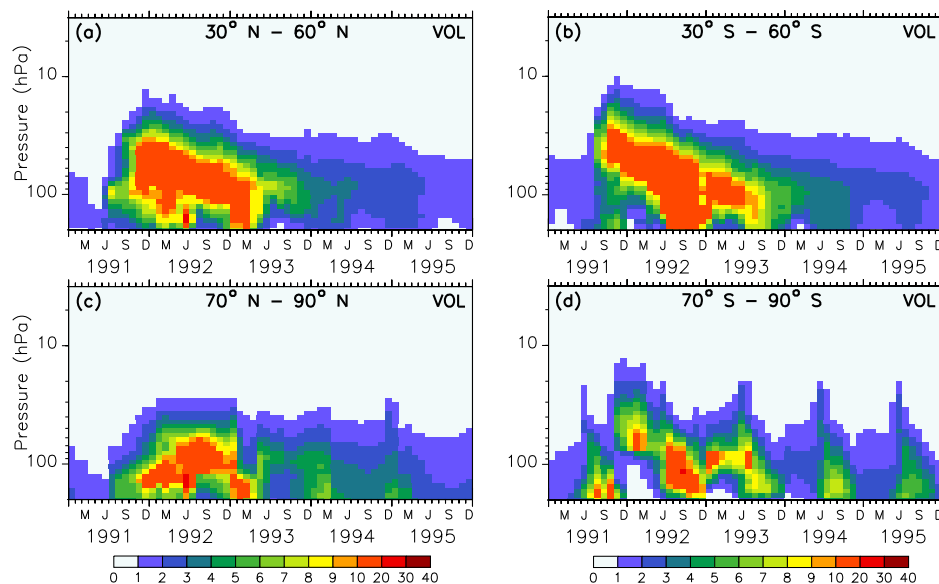
Figure 2. Colours show the monthly averaged liquid aerosol surface area density (10^{-8} cm^{2}cm^{-3}) of the volcanic sulfate aerosols used as boundary conditions in simulations VOL and CVOL in the stratosphere as averaged vertical time series in the mid-latitudes (**(a)** and **(b)**) and in the polar regions (**(c)** and **(d)**). The intervals of the colour scale are not equidistant.

depletion and air quality. Besides the scientific relevance, the obtained results are supposed to also have political and social impacts. This is especially important for the contribution to the WMO/UNEP (World Meteorological Organization/United Nations Environment Programme) ozone and IPCC (Intergovernmental Panel on Climate Change) climate assessments (WMO, 2019).

5 Here we employ these simulations and asses the impacts of the Mt. Pinatubo eruption on the atmospheric chemistry. In our study we focus on 3 simulations with specified dynamics. They are branched off from a specified dynamics hindcast simulation and are "nudged" with a Newtonian relaxation technique towards 6-hourly ERA-Interim reanalysis data from the ECMWF (European Centre for Medium-Range Weather Forecasts), which is available since 1979 (Dee et al., 2011). The Newtonian relaxation (nudging) is applied to the prognostic variables divergence, vorticity, temperature, and the (logarithm of the) surface

10 pressure in spectral space with relaxation times τ_x of 48, 6, 24, and 24 h, respectively. The global-mean temperature ($\overline{T}$) is not affected by the nudging technique, because we exclude nudging of the "wave-0" in spectral space. Moreover, the nudging is not applied uniformly in the vertical: the boundary layer and the stratosphere above 10 hPa are not nudged. The simulations VOL, CVOL and NOVOL span the years 1989 to 1997.

The set up (Table 1) is comparable with those of the EMAC simulations from Löffler et al. (2016). Again, VOL considers

15 the volcanic aerosols and its interaction with both, the radiation and the chemistry, and shows the combined effect of the volcanic eruption. NOVOL omits the volcanic eruption by using an unperturbed annual background aerosol from the year 2011. CVOL is the new set up in the course of the present study, because it considers the volcanic aerosols like VOL, but only

the heterogeneous reactions on the aerosol surface are affected, whereas the radiative transmission remains unaffected by the volcanic aerosols.

Simulation	Volcanic Aerosol	Aerosol Interaction
VOL	x	Radiation, Chemistry
CVOL	x	Chemistry
NOVOL	-	-

Table 1. Overview of the three simulations with their differences in model set-up in terms of the volcanic perturbation and its interactions.

2.3 Methodology

The results are presented as differences of monthly mean values between the simulations, with exceptions being denoted clearly. The goal is to separate the heating effect of volcanic aerosols from the chemical effect caused by the altered heterogeneous chemistry on the ozone distribution. The difference VOL-NOVOL shows the combined effect of the stratospheric temperature increase due to absorption by volcanic aerosols and the intensification of the heterogeneous reactions, due to an increase of the aerosol surface density. VOL-CVOL yields the stratospheric heating effect, which includes the absorption of solar radiation by the volcanic aerosol and changes in transport, as well as the secondary change of the temperature dependent heterogeneous reaction rates. The pure chemical effect induced by the larger aerosol surface can be separated by the difference of CVOL-NOVOL. The prescribed background aerosol in our NOVOL simulation is from the year 2011, which leads to small artefacts before and after the volcanic perturbation by Mt. Pinatubo. Due to the applied nudging, the temporal evolution of the synoptic conditions is similar in all 3 simulations. Therefore, a one-by-one comparison shows the volcanic perturbations and only a sub-synoptic noise. The production and loss rates of ozone are calculated off-line with the diagnostic tool *STratO3Bud* as described by Meul et al. (2014) and Grewe et al. (2017).

3 Comparison with Observations

The EMAC model has been evaluated intensively (Jöckel et al., 2006; Jöckel et al., 2010, 2016). In order to show the reliability of the simulated ozone distribution here, the volcanic simulation VOL is compared to the Stratospheric Water and OzOne Satellite Homogenized (SWOOSH) data set provided by NOAA (National Centers for Environmental Information, Davis et al. (2016)). This data set was constructed to investigate the variability and change of water vapour and ozone in the stratosphere. SWOOSH is a database of global long-term satellite O_3 and stratospheric water vapour (SWV) measurements presented on a vertical grid as monthly averages on pressure levels. The measurements from different satellite instruments, namely SAGE II, SAGE III, HALOE, UARS MLS and EOS Aura MLS, as well as from other merged data products have been combined. The spatial and temporal distribution of ozone in VOL corresponds to the SWOOSH data (Figure 3). The ozone layer between 5 and 20 hPa with mixing ratios of 10-12 ppmv, as well as the seasonal cycle, are well represented. With the Mt. Pinatubo
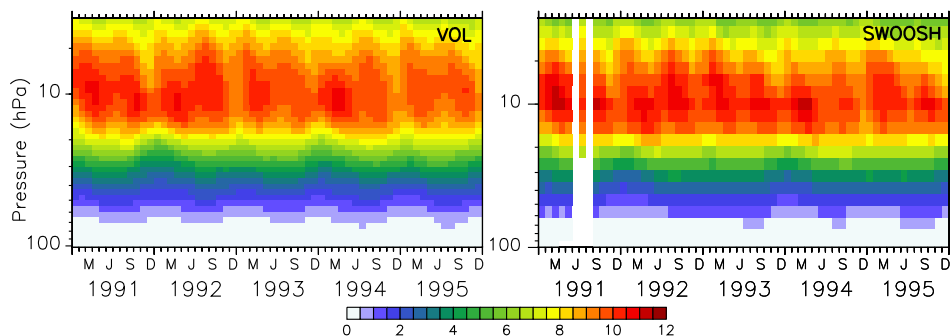
Figure 3. Colours show the absolute zonally and monthly averaged ozone mixing ratios (ppmv) at 10° N of the volcanic simulation VOL (left) and the SWOOSH satellite data set (right) for the period from 1991-1995 (Davis et al., 2016).

eruption in June 1991, the atmosphere was too opaque for reliable satellite measurements, and consequently, those months are marked with white stripes showing the data gap.

4 Results

We show in the results section the effect of the volcanic perturbation on temperature, on the vertical ozone column, on the
5   vertical distribution of ozone, the chemical cycles and the Polar stratospheric clouds (PSC). First, we investigate the temperature perturbation, because sulphate aerosols in the stratosphere increase the atmospheric extinction, resulting in a higher absorption of terrestrial (longwave) and solar (shortwave) radiation warming the stratosphere. Heterogeneous ozone chemistry is affected by the sulphate aerosols, which alter the ozone depletion cycles. Temperature changes at the tropopause perturb the cold point and alter the transport of SWV. An increase of the vertical transport also modifies methane. Since the ozone chemistry in
10   the polar regions is strongly affected by the formation of Polar Stratospheric Clouds (PSC), their behavior in a post volcanic stratosphere is analysed.

4.1 Temperature

The strongest heating due to absorption of radiation by volcanic aerosols is simulated in the tropics. Volcanic heating is directly caused by absorption through volcanic aerosols, and indirectly by a change in the chemical composition, which alters solar
15   absorption. The combined effect (Figure 4a) shows the strongest heating in the lower and middle stratosphere in December 1991. The vertical extent is congruent with the volcanic aerosol plume. The largest temperature increase occurs between 40-60 hPa in the tropical stratosphere. The central panel (VOL-CVOL) shows the direct heating due to absorption of solar radiation by volcanic aerosols. Here, the strongest heating occurs at the same height, but stronger with a maximum between 40° N and 40° S. The bottom panel displays the chemically caused change of temperature due to the changed chemical composition. It
20   results in a heating of up to 0.4 K in the upper stratosphere between 5 and 20 hPa and a cooling of up to 0.2 K between 30 and 70 hPa. More stratospheric ozone increases temperature due to more absorption of solar radiation and less ozone cools

the stratosphere. Thus, the main temperature change of this volcanic eruption arises mostly from the radiative properties of volcanic aerosols and less from the absorption of modified ozone.
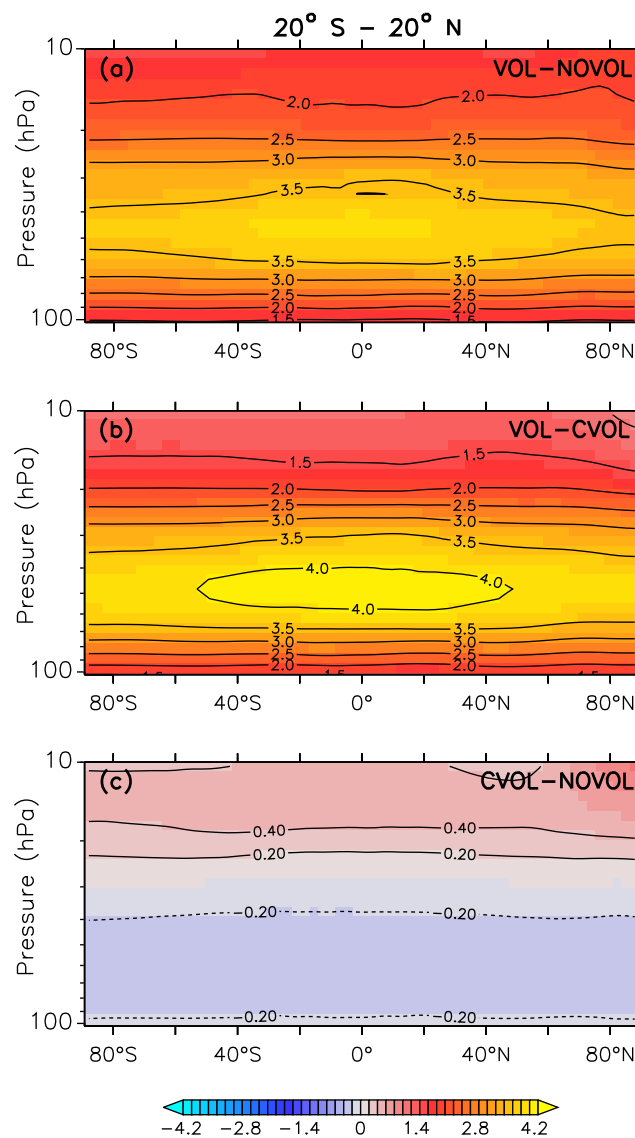
Figure 4. Monthly mean latitudinal cross sections of the zonally averaged stratospheric temperature difference (K) between the model simulations (CVOL and NOVOL) for December 1991. **(a)** shows the combined effect, **(b)** the heating effect and **(c)** the chemical effect. Black contours indicate the isothermal curves (K). Contour intervals are 0.5 K in **(a)** and **(b)**, and 0.2 K in **(c)**.
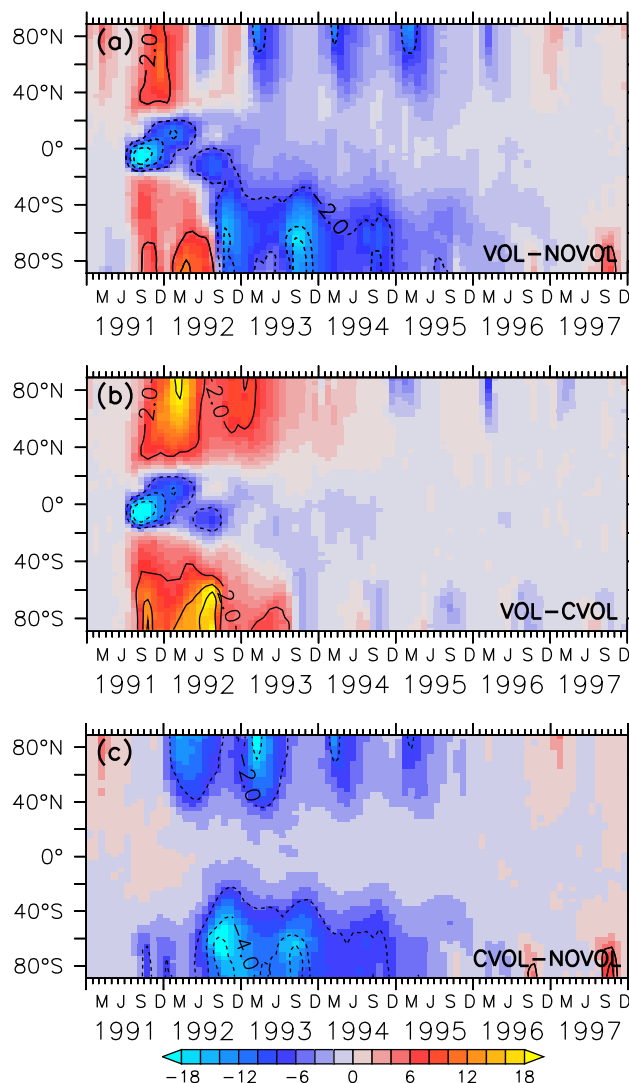
Figure 5. Colours show the differences of the zonal mean total ozone column (DU) as combined effect (VOL-NOVOL) **(a)**, heating effect (VOL-CVOL) **(b)**, and chemical effect (CVOL-NOVOL) **(c)** as a function of the latitude in degrees (°). Contours indicate the corresponding relative changes (%). Contour intervals are 2 %.

4.2 Total Ozone Column

Our simulations show that the total ozone column decreases in the first 12 months after the eruption of the Mt. Pinatubo by up to 18 DU (6 %) in the tropics (Figure 5a). In contrast, the mid latitudes and the polar regions experience an increase of the total ozone column by 8-12 DU (2 %), smaller in the southern than in the northern mid latitudes. In May 1992, an ozone reduction propagates towards the North Pole and in August 1992 a similar anomaly propagates towards the South Pole. The

combined effect **(a)** is the sum (VOL-CVOL)+(CVOL-NOVOL)=VOL-NOVOL of the heating **(b)** and chemical effect **(c)**, thus the change of the total ozone column is caused by a linear superposition of both effects (**b** and **c**) . The decrease of ozone in the tropics and the increase in the mid and higher latitudes in the first 2 years after the Mt. Pinatubo eruption are caused solely by the volcanic heating (Figure 5b), i.e. the increase in the BDC through the volcanic aerosol induced heating of the stratosphere
5 and a subsequent increase in transport of ozone. This result is in contradiction to Poberaj et al. (2011) and Aquila et al. (2013), who attributed the absence of ozone depletion in the southern hemisphere to interannual dynamic variability.

The ozone decrease by up to 4 % in the North Pole region and by up to 6 % in the South Pole region, starting in the respective spring seasons of 1992, is due to the chemical effect alone (Figure 5c).

Thus, the heating and chemical effect alter the ozone distribution in the mid-latitudes and in the polar regions in opposite
10 directions. Overall, the volcanic perturbation of the total ozone column lasts until the end of 1995. Some small artefacts at the poles in 1996 and 1997 arise from the used background aerosol in the NOVOL simulation (see section 2.3).

4.3 Vertical Ozone Distribution

The combined effect on ozone in the tropics is characterised by an increase of 5 % around 10 hPa and by a decrease of 15 % between 20-50 hPa (Figure 6a). This dipole structure appears in both, the heating (VOL-CVOL) and the chemical effect
15 (CVOL-NOVOL), and they sum up to the combined effect (VOL-NOVOL) (Kilian, 2018). The largest impact in the middle stratosphere is mostly attributed to the volcanic heating (Figure 6b). The perturbation of ozone lasts about 2 years. Volcanic heating by the aerosol modifies ozone via an increase of the vertical ascent by 20 % and subsequent transport to higher latitudes, which reduces the tropical ozone column (McCormick et al., 1995b; Dameris et al., 2005). The ozone increase at 10 hPa arises partly from the chemical effect (Figure 6c). As it will be more precisely explained in section 4.4, larger liquid aerosol surface
20 modifies the heterogeneous reactions and NO_x is converted into HNO_3. Thus, less NO_x is available and the catalytic ozone depletion via NO_x slows down. In accordance with Telford et al. (2009b), the chemical ozone decrease in the tropics is smaller than the dynamical effect, due to increased vertical transport (or heating effect).

In the extratropics, the combined O_3 perturbation also exhibits a dipole structure with an increase of O_3 between 10-30 hPa by up to 5 %, and a small decrease of ozone beneath, which lasts more than one year (Figure 7a). This increase mostly arises
25 from the chemical effect. Again, the NO_x cycle slows down so that less O_3 is depleted (see section 4.4). Interestingly, the heating effect and the chemical effect have counteracting influences on the ozone mixing ratio in the lower stratosphere, with an increase due to the volcanic heating, and a decrease in the same order of magnitude by the chemical effect (Figure 7b,c). A similar dipole pattern is also observed in the polar regions, where the perturbation of ozone is even larger than in the extratropics (Figure 8). Similary, the heating and chemical changes are counteracting with up to +/- 10 % at the North (Figures 8(**b**) and
30 (**c**)) and up to +/- 20 % at the South Pole ((**e**) and (**f**)), mostly between 100 and 300 hPa. In the polar regions the seasonal cycle of the ozone perturbation is large and the strongest effect appears during the respective spring season. The ozone decrease due to the chemical effect between 100-300 hPa lasts 4 years, whereas the ozone increase by the heating effect in the lower and middle stratosphere already disappears after one year. The next section describes, whether the chemical effect on ozone arises from a perturbation of the ozone production or the ozone loss, and how the net ozone production is affected.
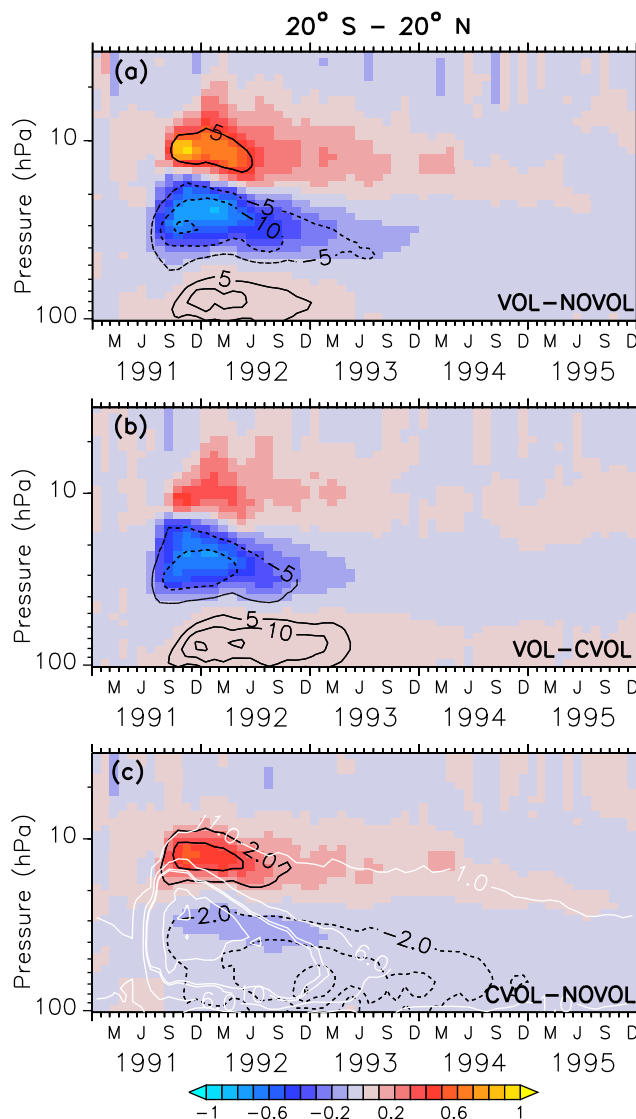
Figure 6. Zonally averaged differences of ozone mixing ratios (ppmv) between two simulation results, where **(a)** shows the combined effect (VOL-NOVOL), **(b)** the heating effect (VOL-CVOL), and **(c)** the chemical effect CVOL-NOVOL). Black contours indicate are the corresponding relative changes (%). Shown are averages in the tropics between 20° S and 20° N. Contour intervals are 5 % in the upper and central panel, and 2 % in the bottom panel. White contours in **(c)** show the liquid aerosol surface area density (10^{-8} cm^{2}cm^{-3}) in VOL and CVOL with intervals of 1, 5 and 10.

4.4   Ozone Budget of the Chemical Effect

In the following, we analyse the chemical effect (CVOL-NOVOL) on the O$_3$ budget for the tropics, the mid-latitudes and the polar regions (Figures 9 - 13). All presented results show the differences between CVOL and NOVOL of the O$_3$ production
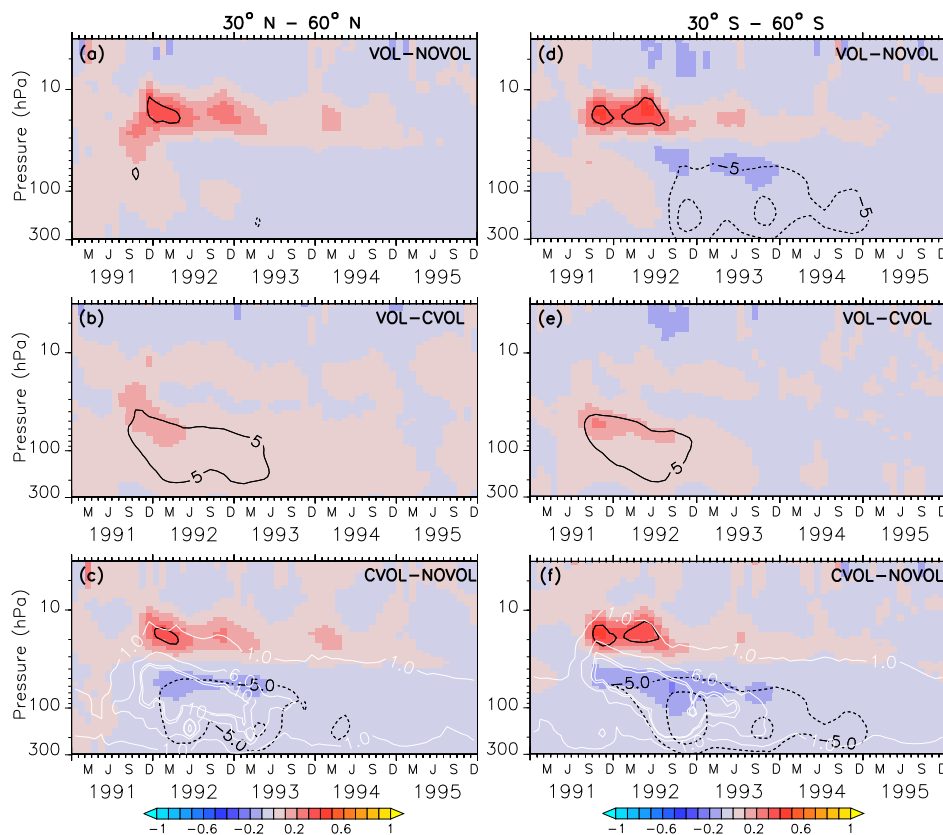
Figure 7. Zonally averaged differences of ozone mixing ratios (ppmv) between the simulations VOL - NOVOL **(a)** and **(d)**, VOL-CVOL **(b)** and **(e)** and CVOL-NOVOL **(c)** and **(f)**. Contours indicate the corresponding relative changes (%). Shown are averages over the mid latitudes 30° N - 60° N (left) and 30° S - 60° S (right). Contour intervals are 5 %. White contours in **(c)** show the liquid aerosol surface area density (10^{-8} $cm^2 cm^{-3}$) in VOL and CVOL with intervals of 1,5 and 10.

and loss rates given in mol/s. The shown vertical levels are selected according the largest perturbation of the O_3 mixing ratio (Figure 6). The O_3 loss rates are determined by different contributions of the catalytic cycles of NO_x, ClO_x, HO_x, O_x and BrO_x.

The increase of the O_3 mixing ratio in the tropics at 12 hPa (section 4.3) is explained by a strong decrease of the O_3 loss rate (Figure 9a). The O_3 gain is mostly compensated by a reduced O_3 production. The decrease of the O_3 production at 12 hPa is
5 caused by an increase of the chemical composition above, especially O_3, which dims the solar radiation and thus slows down the photolysis of oxygen and reduces the production of O_3 (Kilian, 2018). The strong reduction of the O_3 loss rate (Figure 9a) arises from a less active NO_x cycle (Figure 9b), because NO_x is transformed into the reservoir gas HNO_3 due to the enhanced liquid aerosol surface. On the other hand, HO_x, ClO_x and O_x cycles accelerate and thus partly counteract the NO_x cycle slow down towards a new chemical equilibrium. This leads to the increase of the O_3 mixing ratios at 12 hPa. The duration of the
10 disturbed ozone loss rates (Figure 9b) reflects the presence of the upper part of the volcanic aerosol cloud. At 30 hPa O_3 slightly decreases, because the HO_x, ClO_x and O_x cycle accelerate more than the NO_x cycle decelerates (Figure 9c).
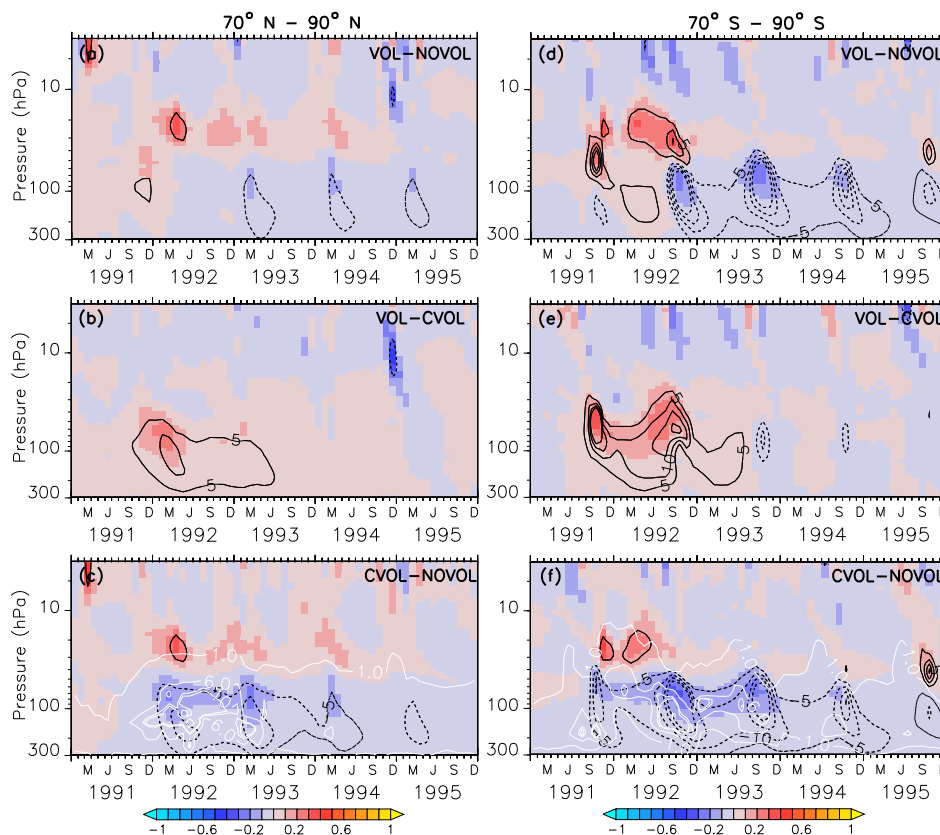
Figure 8. Zonally averaged differences of ozone mixing ratios (ppmv) between the simulations VOL - NOVOL **(a)** and **(d)**, VOL-CVOL **(b)** and **(e)** and CVOL-NOVOL **(c)** and **(f)**. Contours indicate the corresponding relative changes (%). Shown are averages over the mid latitudes 70° N - 90° N (left) and 70° S - 90° S (right). Contour intervals are 5 %. White contours in **(c)** show the liquid aerosol surface area density (10^{-8} cm^{2}cm^{-3}) in VOL and CVOL with intervals of 1, 5 and 10.

In the mid-latitudes of the northern hemisphere the strongest O$_3$ increase appears at 20 hPa. Again, this is caused by a change of the ozone loss and production due to the volcanic aerosol, although its order of magnitude is smaller than in the tropics (Figure 10a). However, the perturbation lasts longer. The differences of the production and loss rates in the southern mid-latitudes (Figure 10c) are half as large as in the tropics, but their duration is similar. The maxima in ozone loss rates correspond to the upper height limit of the volcanic cloud. The volcanic perturbation of the ozone budget lasts until spring 1993 on the northern hemisphere, and until summer 1992 on the southern hemisphere (Figure 11a,c). In each case, the decrease of the ozone loss rate can be attributed to a less active NO$_x$ cycle (Figure 11a,c) due to conversion of reactive NO$_x$ on the aerosol surface into HNO$_3$. Note that at this height the NO$_x$ cycle dominates the ozone depleting process.
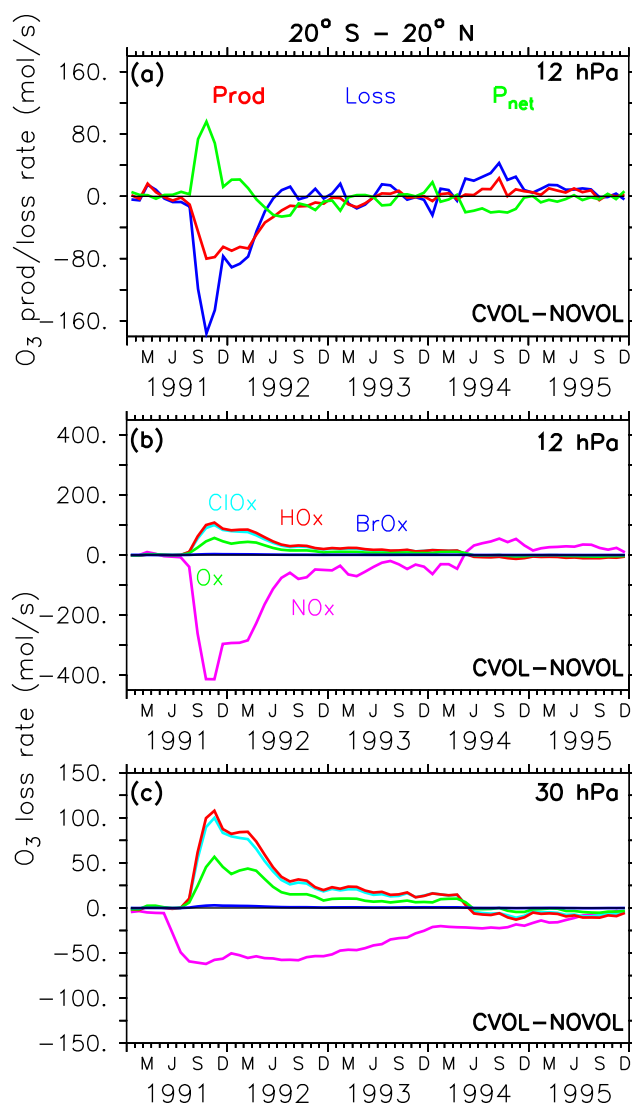
Figure 9. Differences (CVOL-NOVOL), i.e. chemical effect of ozone production (Prod) and loss (Loss) rates and corresponding net ozone production (P_{net} = Prod - Loss) **(a)** at 12 hPa. Differences (CVOL-NOVOL) of the ozone loss rates (mol/s) for each catalytic ozone loss cycle of CVOL-NOVOL at 12 hPa **(b)** and 30 hPa **(c)**. The shown level (12 hPa) is located in the maximum of the volcanic ozone perturbation. Shown are zonally averaged and latitudinally (20° S and 20° N) summed rates in mol/s.
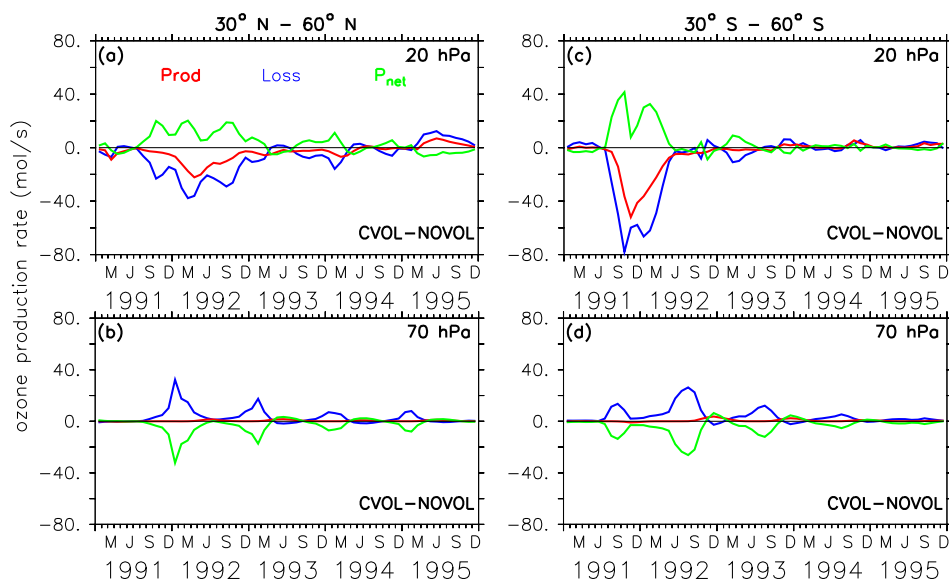
Figure 10. Differences (CVOL-NOVOL), i.e. chemical effect of ozone production (Prod) and loss (Loss) rates and corresponding net ozone production (P_{net} = Prod - Loss). **(a)** (20 hPa) and **(b)** (70 hPa) show zonally averaged and latitudinally (30° N and 60° N) summed rates in mol/s. **(c)** (20 hPa) and **(d)** (70 hPa) show zonally averaged and latitudinally (30° S and 60° S) summed rates in mol/s. The shown levels are located in the maximum of the volcanic ozone perturbation.
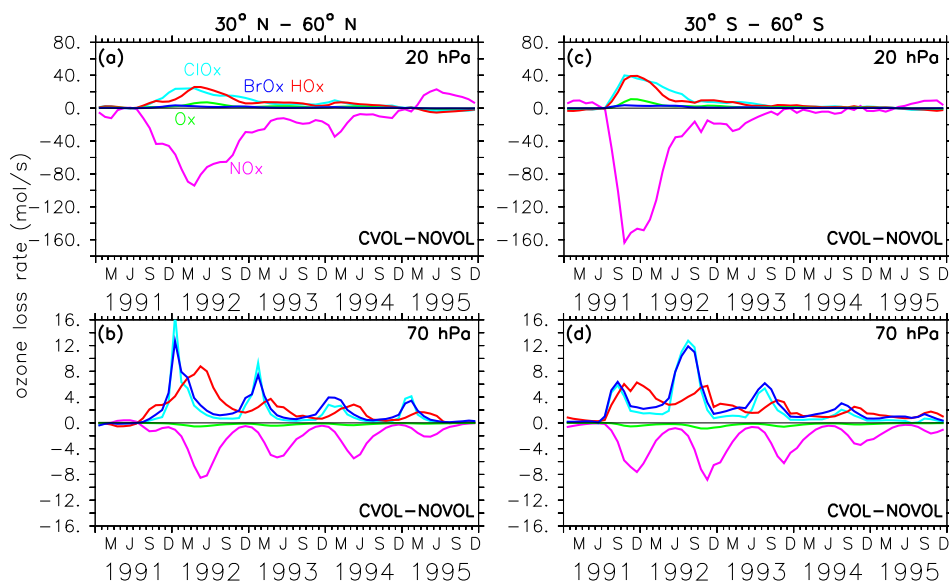
Figure 11. Differences (CVOL-NOVOL) of the ozone loss rates (mol/s) for each catalytic ozone loss cycle for the northern hemisphere at 20 hPa **(a)** and 70 hPa **(b)** and for the southern hemisphere **(c)** and **(d)**. These are monthly, zonally and latitudinally summed between 30° N - 60° N and 30° S - 60° S.
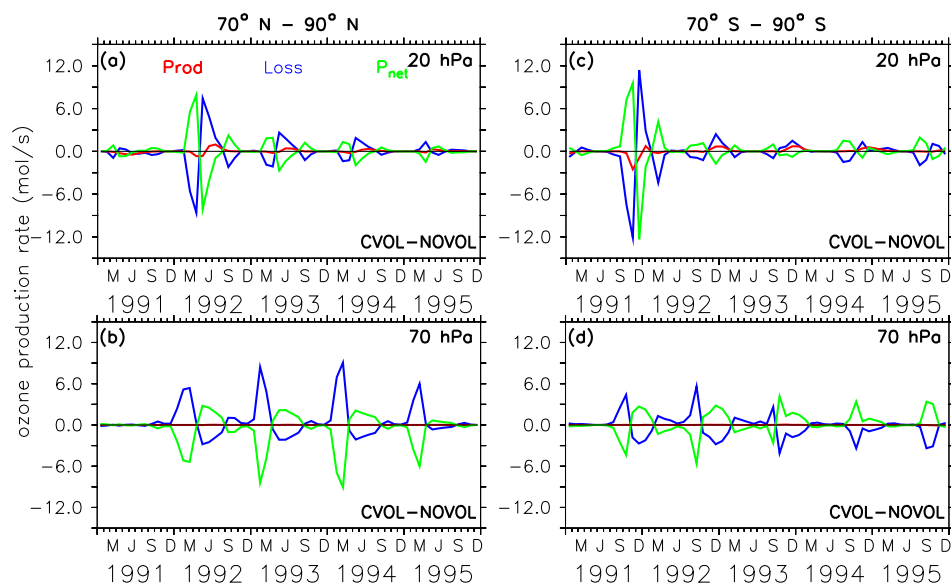
Figure 12. Differences (CVOL-NOVOL), i.e. chemical effect of ozone production (Prod) and loss (Loss) rates and corresponding net ozone production (P_{net} = Prod - Loss). **(a)** (20 hPa) and **(b)** (70 hPa) show zonally averaged and latitudinally (70° N and 90° N) summed rates in mol/s. **(c)** (20 hPa) and **(d)** (70 hPa) show zonally averaged and latitudinally (70° S and 90° S) summed rates in mol/s. The shown levels are located in the maximum of the volcanic ozone perturbation.
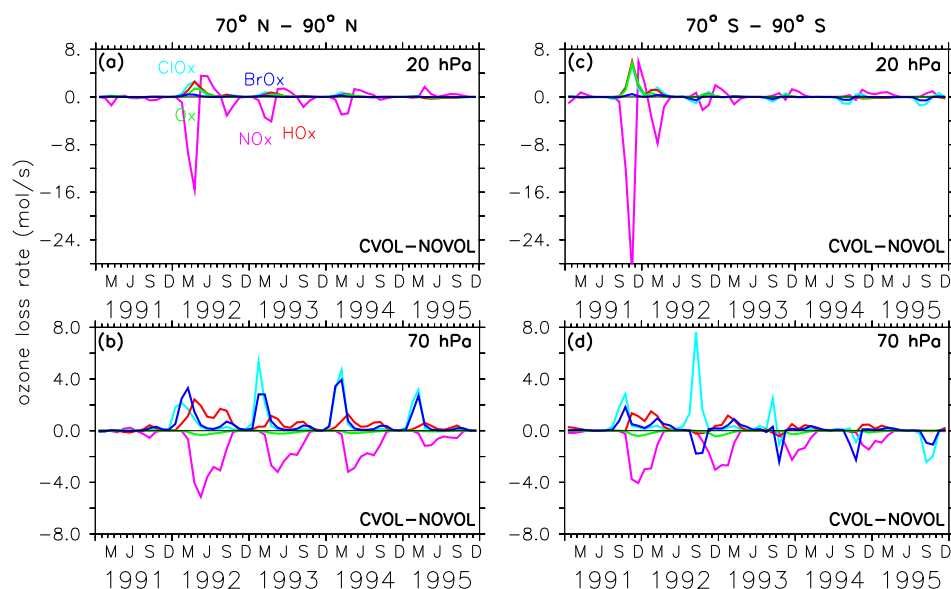
Figure 13. Differences (CVOL-NOVOL) of the ozone loss rates (mol/s) for each catalytic ozone loss cycle for the northern hemisphere at 25 hPa **(a)** and 70 hPa **(b)** and for the southern hemisphere **(c)** and **(d)**. These are monthly, zonally, and latitudinally summed between 70° N - 90° N and 70° S - 90° S.

In the mid-latitudes at 70 hPa the negative differences in the net ozone production (Figure 10b,d) arise solely from an increase in ozone loss rates and lead to the observed O_3 decrease in the lower stratosphere in the mid-latitudes. Moreover, a strong seasonal cycle with maximum loss rates in the respective winter is apparent. The seasonal increase in ozone loss rates is related to the predominance of the ClO_x and BrO_x cycle during the respective winter seasons. The presence of volcanic

5   aerosols lead to a conversion of NO_x into the reservoir HNO_3. Moreover, during the respective winter months with only minor sunlight, NO_x remains in the reservoir gas HNO_3. The reduction of NO_x accelerates the ClO_x and BrO_x cycle in depleting O_3. Below 20 km (50 hPa) in general the HO_x cycle is dominant in O_3 removal. Volcanic aerosols plus more water vapour (more OH) in summer increase the importance of the HO_x cycle. Together with more NO_x removal through the volcanic cloud, the relative importance of the HO_x cycle increases.

10   In the polar regions the ozone loss rates at 20 hPa also show a seasonal cycle with a strong decrease in the first respective spring season after the eruption, but followed by an abrupt increase in the following summer season (Figure 12a,c). The rapid decrease of the ozone loss rate, which is related to the first occurrence of the volcanic aerosol cloud in the north polar region in spring 1992 is 10 times smaller than in the mid-latitudes (Figure 10a,c and 12a,c). This abrupt change of sign is related to the beginning of solar insolation after the polar night. The strong reduction of O_3 loss rates are related to the decrease in the

15   NO_x cycle in summer, that is not compensated by the HO_x cycle as in the mid-latitudes (Figure 13a,c). At 20 hPa, and only in the first spring season after the eruption, and only in the south polar region, the O_x cycle becomes stronger in ozone depletion. The HO_x cycle shows a local minimum during the summer month (June and December).

The polar ozone decrease at 70 hPa is caused by an increase of the O_3 loss rate (Figure 12b,d). The responsible catalytic cycles have a similar seasonal variability as in the mid-latitudes (Figure 13b,d). Again, the efficiency of the NO_x cycle decreases,

20   which is halfway compensated by the HO_x cycle. The acceleration of the ClO_x and BrO_x cycles in springtime starts in 1992 especially at the North Pole. Note, that except for the first year after the eruption at the South Pole the BrO_x cycle is out of phase with the ClO_x cycle at 70 hPa. Probably, the deactivation of chlorine (Cl) and bromine (Br) atoms by a stronger polar vortex during the polar night is enhanced by the volcanic aerosol, and accelerates both cycles in spring.

4.4.1   Impact of the Polar Stratospheric Clouds

25   Next, the effects of the volcanic aerosol on the formation of PSCs are investigated. PSCs accelerate the heterogeneous chemistry, because fast chemical reactions take place on the PSC particles. During the polar night the strong isolated polar vortex prevents bonded chlorine atoms to deplete ozone. PSCs appear during the polar night at heights of 25-50 hPa, that is exactly where the largest increase of the aerosol surface occured. As soon as the first sunrays appear, Cl_2 is photolysed and Cl atoms destruct ozone. PSCs amplify the ozone destruction, because more particle surfaces are available for heterogeneous reactions.

30   More ozone destructive reactions occur at the surface of the PSC particles to form Cl_2 and Br_2. The volcanic heating increases the stratospheric temperature between 30-70 hPa by 3 K in the polar regions, implying that less PSCs form. Therefore, the heating effect (VOL-CVOL) shows less PSCs in both polar hemispheres. However, the chemical effect shows a temperature reduction in the lower stratosphere due to less ozone (Figure 8c,f), resulting in an enhanced formation of PSCs at the North and the South Pole (Figure 14, CVOL-NOVOL). At the North Pole, the PSC covered area increases between November 1991

and March 1992 (Figure 14,a, CVOL-NOVOL). At the South Pole the increase of the PSC area appears in the springtime, as well as in the autumn, when the first PSCs are formed (Figure 14,b, CVOL-NOVOL). Although we cannot quantitatively differentiate between the direct effect from PSC formation and the ozone destruction, it is likely that the latter contributes to the ozone depletion in the respective spring season by enhancing the ClO_x cycle at 70 hPa.
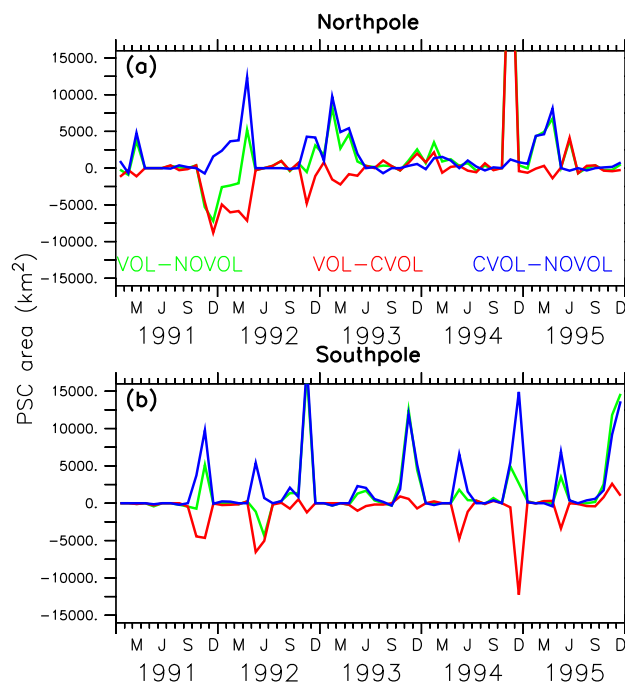
Figure 14. Differences of polar stratospheric cloud (PSC) covered area (km^2) at the Northpole **(a)** and Southpole **(b)** for the combined effect (green), the heating effect (red) and the chemical effect (blue).

4.5 Stratospheric Water Vapour

As already described in detail by Löffler et al. (2016), however without the separation of the heating and the chemical effect, we find that additional water vapour is transported into the stratosphere by the heating effect and less H_2O by the chemical effect. In the tropics, the transport of water vapour into the stratosphere is increased (Figure 15a, shown is the combined effect) due to volcanic heating of the stratosphere and subsequent upward movement of air masses. Both effects are related to a warming and to a cooling of the cold point temperature, due to the volcanic cloud, respectively (Figure 15a).

In the case of the chemical effect, which has not been considered by Löffler et al. (2016), the lower stratosphere is cooled by 0.4 K (due to less ozone) and less water vapour enters the stratosphere (Figure 15b). In September 1991 a negative SWV perturbation (outside the tape recorder) appears, following the volcanic plume (Figure 15b) in the first year after the eruption. This pattern is caused by sublimation of SWV into liquid and ice on the volcanic condensation nuclei. Thus, the total water content (water vapour + liquid + ice) remains constant.
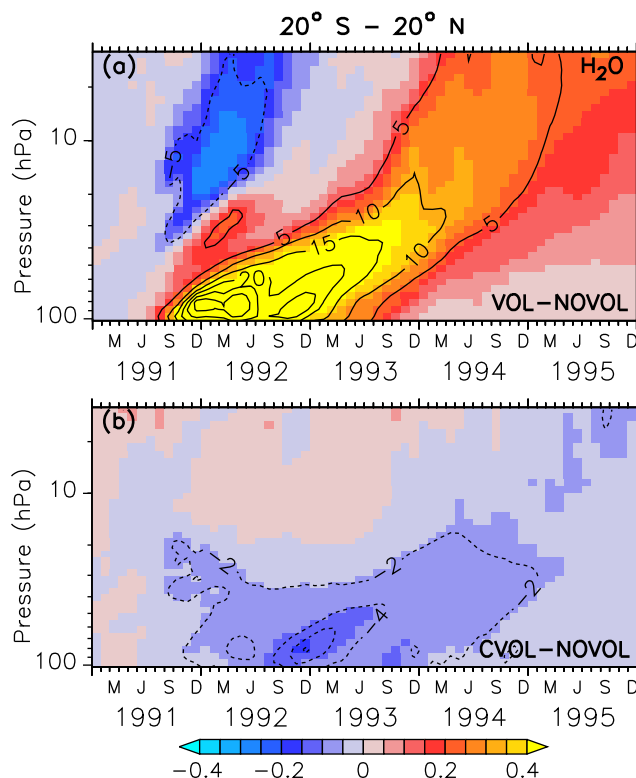
Figure 15. Zonally averaged differences of stratospheric water vapour (ppmv) between the simulations, where **(a)** shows the combined effect (VOL-NOVOL) and **(b)** the chemical effect (CVOL-NOVOL). The black contours show the relative change (%) of water vapour in comparison to NOVOL and CVOL, respectively. Shown are tropical averages (20° S - 20° N). Contour intervals are 5 % **(a)** and 2 % **(b)**.

4.6 Methane

Stratospheric methane (CH_4) is affected by the aerosols mainly due to the heating effect. Already 3 months after the eruption an increase of methane between 40 hPa and beyond 10 hPa can be noticed with changes of more than 80 ppbv, corresponding to a change of 10 % with respect to the absolute CH_4 in the unperturbed simulation NOVOL (Figure 16a). The upward propagating elevated values of CH_4 are the result of the enhanced tropical vertical ascent, which leads to a transport from relative methane rich air in the lower stratosphere into upper levels. The surplus of CH_4 is not depleted, which is an indicator that the stratospheric lifetime of CH_4 increased. In the lower stratosphere we find less CH_4 due to the volcanic eruption. The dipol pattern of the CH_4 perturbation spreads with time into the mid-latitudes (Figure 17a,b) and into the polar regions (Figure 17c,d). The increase of CH_4 in the tropical regions is partly transported by the deep branch of the BDC within a year to higher latitudes. But there is also a decrease of CH_4 partly transported by the lower branch of the BDC reaching mid-latitudes within the period of 1.5 - 3.5 years after the eruption.
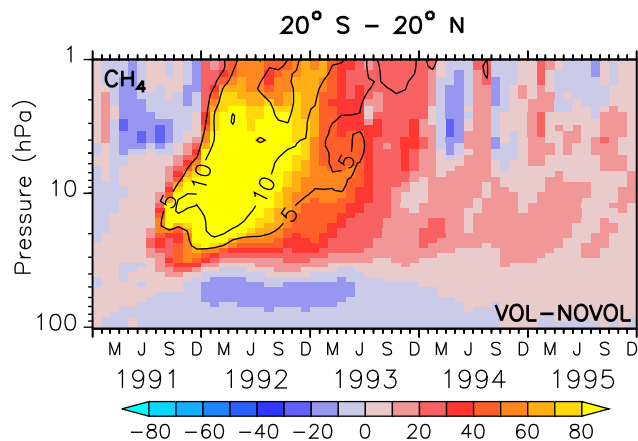
Figure 16. Zonally averaged differences of the methane mixing ratio (ppbv) for the combined effect (VOL-NOVOL). The black contours show the relative change (%) of methane in comparison to NOVOL. Shown are tropical averages (20° S - 20° N). Contour intervals are 5 %.
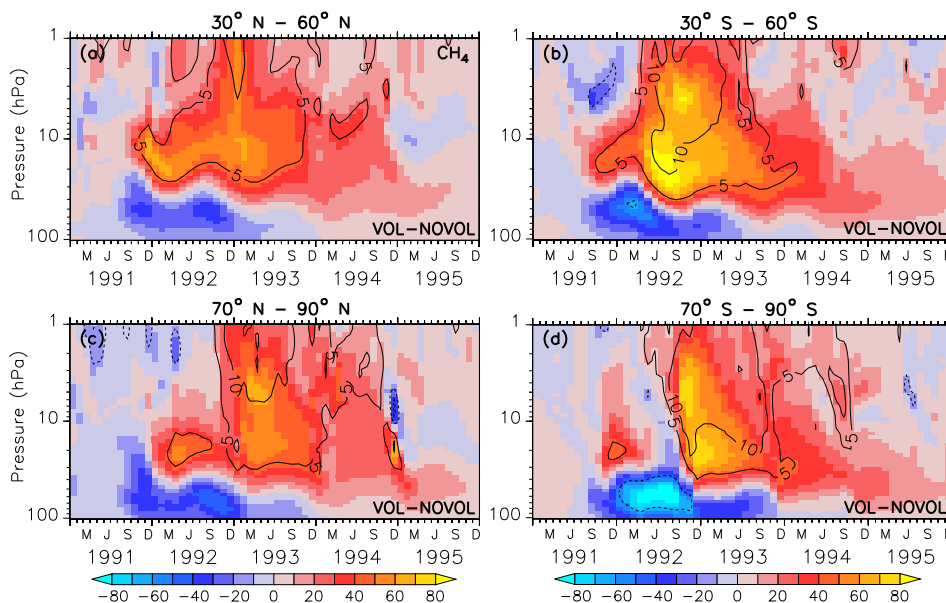
Figure 17. Zonally averaged differences of methane (ppbv) of the combined effect (VOL-NOVOL). The black contours show the relative change (%) of methane in VOL comparison to NOVOL, respectively. Shown are extratropical averages (**(a)** and **(b)**): 30° N - 60° N and 30° S - 60° S; **(c)** and **(d)** : 70° N - 90° N and 70° S - 90° S). Contour intervals are 5 %.

5 Discussion

The differences of the simulations (VOL-CVOL) separate the heating, and (CVOL-NOVOL) the chemical effect. In particular, we investigated the long- and shortwave heating effect of the volcanic aerosol on the temperature and transport, as well as

on ozone, SWV and CH_4. The simulation VOL of the ozone development after the eruption is in agreement with the satellite based SWOOSH data (Davis, 2016). The simulated volcanic heating of 3.5-4 K between 50-60 hPa in VOL agrees well with results from Labitzke and McCormick (1992), who observed a stratospheric heating at 50 hPa of 3-4.5 K in the tropics. Angell (1997a), who used radiosonde data, figured out a temperature increase of approximately 3-4 K between 30-50 hPa in late 1991.

5 Grant et al. (1992), Schoeberl et al. (1993b) and Angell (1997a) investigated total ozone column depletions of 5-8 % in the tropical region 6 months after the Mt. Pinatubo eruption. Our findings with up to 6 % column loss agree with these results and with measurements from the Mauna Loa observatory on Hawaii, showing a 5 % O_3 column loss, quite well (Randel et al., 1995). McCormick et al. (1995a) indicated the same order of magnitude from observation data with an ozone loss of 6-8 % over the Equator in the first several months after eruption. Grant et al. (1992) reported the absolute change of the ozone column

10 in the tropics to be 13-20 DU, which is in agreement with our study with decreases of 10-18 DU. Grant et al. (1992) and McCormick et al. (1995a) observed the largest tropical loss of ozone with 20 % between 24-25 km (25-30 hPa level), which is 5 % more than the perturbation in our study. Although the ozone production rates slow down (due to the local increase in ozone abundance), they might still be too high, because the simulated photolysis rates do not account for the presence of the volcanic aerosol.

15 The ozone change after a volcanic eruption is a combination of an ozone decrease of the vertical column in the tropics directly after the eruption, and ozone increase in the mid latitudes and polar regions in the first year after the eruption. Poberaj et al. (2011) reported a similar temporal behavior of the ozone decrease after the Mt. Pinatubo eruption. They quantified an ozone decrease of 3-4 % in the southern mid-latitudes. Telford et al. (2009b) reported a total ozone reduction of 10 DU averaged between 30-60° N and 12 DU between 30-60° S caused by the chemical effect. In general, the chemical effect on

20 ozone perturbation becomes more important at higher latitudes than the heating effect (Telford et al., 2009b).

Our results show that the the ozone increase in the extratropics in the year after the eruption can be solely attributed to the heating effect, i.e. the effect of increased transport of ozone with the BDC. Joshi and Shine (2003) simulated water vapour increases of 20-30 % in the tropics between 10°S-10°N after the Mt. Pinatubo eruption. Considine et al. (2001) simulated SWV and CH_4 anomalies between 0-10°N and showed increases of the vertical ascent in the tropical lower stratosphere of up

25 to 24 %. Referring to their figure 16b, they stated a positive SWV anomaly of 15-20 % starting in October 1991 following the tape recorder signal. Our study confirms these results quantitatively, and in terms of spatial and quantitative distribution. Furthermore, Considine et al. (2001) found increased values of CH_4 with 2 % at 10 hPa, which reached amplitudes of up to 10 % at 0.1 hPa. In our simulation, the largest relative methane anomalies caused by volcanic heating occur between 20 hPa and up to 1 hPa. Probably, this methane increase is predominantly caused by the stronger vertical ascent and less by secondary

30 chemical effects. We cannot explicitly differentiate in the heating effect between a stronger vertical transport and a smaller extent temperature influence on the chemistry. Winterstein et al. (2019) showed that the concentration of OH, which determines the lifetime of CH_4 is dependent of SWV and O_3. This leads us to the limitation of our study, namely that the perturbation of the chemical composition arises from a temperature induced enhancement of the transport and of the temperature dependent heteorogenoeus reaction rates (secondary effect). Both effects are included in the heating effect (VOL-CVOL), but can not be

35 separated in this study.

6 Summary

We presented an analysis with the focus on the changes of ozone, methane and water vapour, caused by the volcanic aerosols of the Mt. Pinatubo eruption in 1991 as simulated with the chemistry-climate model EMAC. We performed three specified dynamics simulations with prescribed volcanic aerosol, which differ with respect to the interaction between volcanic aerosol,

5   chemistry and radiation: VOL (volcanic aerosol: interaction with radiation AND heterogeneous chemistry), NOVOL (no volcanic aerosol) and CVOL (volcanic aerosol: interaction with chemistry, NO interaction with radiation). This enables the separation of the effect of volcanic heating on the atmospheric composition from the chemical effect, i.e. the effect of heterogeneous reaction rates on volcanic aerosols on the ozone distribution.

Although we use specified dynamics simulations, the effect of volcanic heating on the BDC is visible in an increase in
10   vertical velocity, especially in the tropics, with subsequent increased horizontal transport of heat and tracers with the BDC.

Further, the use of specified dynamics simulations allows us to eliminate the effect of the large-scale meteorology (e.g. QBO,ENSO) when the simulations are compared. This is important, as for instance the eruption of the Mt. Pinatubo coincided with a time period of strong upwelling in the tropics with related cooling. As a result, the observed tropopause temperatures were lower than expected through the eruption. This might also be the cause, why free-running models have a tendency to
15   overestimate the temperature response in the stratosphere. This is the fundamental difference to other studies on the effect of the Mt. Pinatubo eruption on the ozone distribution, as by Aquila et al. (2013) and by Muthers et al. (2015). They studied, among others, the contribution of interannual dynamical variability on the ozone distribution after the eruption.

The major finding in our study is that the chemical effect shows up globally as a dipole structure in the vertical ozone distribution with an ozone increase around 10-30 hPa and a decrease below down to the tropopause. These two vertical regions
20   are characterized by a different importance of the NO_x cycle.

The dominant chemical increase in ozone (1 year after the eruption around 10-30 hPa) is caused by a reduction of NO_x into HNO_3 on the volcanic aerosol, i.e. a slow down in the ozone depleting NO_x cycle.

The ozone decrease (in the lower stratosphere in mid- to high latitudes), however, is caused by an acceleration of the ozone depleting cycles ClO_x, BrO_x and HO_x as a result of the reduced NO_x cycle. Moreover, these chemical cycles show a strong
25   seasonal variablity in mid and high latitudes. SWV and CH_4 were increased by the heating effect by up to 25 % and 10 % in the tropics, respectively, and in contrast to O_3, for SWV and CH_4 the chemical effect has less importance.

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5 as well as for data processing and analysis. We thank Heidi Huntrieser and Volker Grewe for the internal review of our manuscript.

Data and Code availability

The simulation results and the computer code used here are archived at the German Climate Computing Center (DKRZ) and are available on request.

Author Contributions

10 MK analysed the data and wrote the manuscript. SB and PJ designed the experiments, performed the model simulations and contributed to the manuscript.

References

Angell, J.: Estimated Impact of Agung, El Chichon, and Pinatubo Volcanic Eruptions on Global and Regional total ozone after Adjustment for the QBO, Geophys. Res. Lett., 24, 647–650, 1997a.

Aquila, V., Oman, L. D., Stolarski, R., Douglass, A. R., and Newman, P. A.: The Response of Ozone and Nitrogen Dioxide to the Eruption of Mt. Pinatubo at Southern and Northern Midlatitudes, Journal of the Atmospheric Sciences, 70, 894–900, https://doi.org/10.1175/JAS-D-12-0143.1, https://doi.org/10.1175/JAS-D-12-0143.1, 2013.

Considine, D. B., Rosenfield, J. E., and Fleming, E. L.: An interactive model study of the influence of the Mount Pinatubo aerosol on stratospheric methane and water trends, Journal of Geophysical Research: Atmospheres, 106, 27 711–27 727, https://doi.org/10.1029/2001JD000331, https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2001JD000331, 2001.

Dameris, M., Grewe, V., Ponater, M., Deckert, R., Eyring, V., Mager, F., Matthes, S., Schnadt, C., Stenke, A., Steil, B., Brühl, C., and Giorgetta, M. A.: Long-term changes and variability in a transient simulation with a chemistry-climate model employing realistic forcing, Atmos. Chem. Phys., 5, 2121–2145, https://doi.org/10.5194/acp-5-2121-2005, https://www.atmos-chem-phys.net/5/2121/2005/, 2005.

Davis, S. M., Rosenlof, K. H., Hassler, B., Hurst, D. F., Read, W. G., Vömel, H., Selkirk, H., Fujiwara, M., and Damadeo, R.: The Stratospheric Water and Ozone Satellite Homogenized (SWOOSH) database: a long-term database for climate studies, Earth System Science Data, 8, 461–490, https://doi.org/10.5194/essd-8-461-2016, https://www.earth-syst-sci-data.net/8/461/2016/, 2016.

Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Hólm, E. V., Isaksen, L., Kållberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J.-J., Park, B.-K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J.-N., and Vitart, F.: The ERA-Interim reanalysis: configuration and performance of the data assimilation system, Quarterly Journal of the Royal Meteorological Society, 137, 553–597, https://doi.org/10.1002/qj.828, http://dx.doi.org/10.1002/qj.828, 2011.

Grant, W. B., Fishman, J., Browell, E. V., Brackett, V. G., Nganga, D., Minga, A., Cros, B., Veiga, R. E., Butler, C. F., Fenn, M. A., and Nowicki, G. D.: Observations of reduced ozone concentrations in the tropical stratosphere after the eruption of Mt. Pinatubo, Geophys. Res. Lett., 19, 1109–1112, https://doi.org/10.1029/92GL01153, http://dx.doi.org/10.1029/92GL01153, 1992.

Grewe, V., Tsati, E., Mertens, M., Frömming, C., and Jöckel, P.: Contribution of emissions to concentrations: the TAGGING 1.0 submodel based on the Modular Earth Submodel System (MESSy 2.52), Geoscientific Model Development, 10, 2615–2633, https://doi.org/10.5194/gmd-10-2615-2017, https://www.geosci-model-dev.net/10/2615/2017/, 2017.

Jöckel, P., Tost, H., Pozzer, A., Brühl, C., Buchholz, J., Ganzeveld, L., Hoor, P., Kerkweg, A., Lawrence, M. G., Sander, R., Steil, B., Stiller, G., Tanarhte, M., Taraborrelli, D., van Aardenne, J., and Lelieveld, J.: The atmospheric chemistry general circulation model ECHAM5/MESSy1: consistent simulation of ozone from the surface to the mesosphere, Atmos. Chem. Phys., 6, 5067–5104, https://doi.org/10.5194/acp-6-5067-2006, https://www.atmos-chem-phys.net/6/5067/2006/, 2006.

Joshi, M. and Shine, K.: A GCM Study of Volcanic Eruptions as a Cause of Increased Stratospheric Water Vapor, Journal of Climate, 16, https://doi.org/10.1175/1520-0442(2003)016<3525:AGSOVE>2.0.CO;2, 2003.

Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., Baumgaertner, A., Gromov, S., and Kern, B.: Development cycle 2 of the Modular Earth Submodel System (MESSy2), Geoscientific Model Development, 3, 717–752, https://doi.org/10.5194/gmd-3-717-2010, https://www.geosci-model-dev.net/3/717/2010/, 2010.

Jöckel, P., Tost, H., Pozzer, A., Kunze, M., Kirner, O., Brenninkmeijer, C. A. M., Brinkop, S., Cai, D. S., Dyroff, C., Eckstein, J., Frank, F., Garny, H., Gottschaldt, K.-D., Graf, P., Grewe, V., Kerkweg, A., Kern, B., Matthes, S., Mertens, M., Meul, S., Neumaier, M., Nützel, M., Oberländer-Hayn, S., Ruhnke, R., Runde, T., Sander, R., Scharffe, D., and Zahn, A.: Earth System Chemistry integrated Modelling (ESCiMo) with the Modular Earth Submodel System (MESSy) version 2.51, Geoscientific Model Development, 9, 1153–1200, https://doi.org/10.5194/gmd-9-1153-2016, https://www.geosci-model-dev.net/9/1153/2016/, 2016.

Kilian, M.: Impact of the eruption of Mt. Pinatubo on the chemical composition of the tropical atmosphere as simulated with EMAC, University of Innsbruck (LFU), Austria, http://diglib.uibk.ac.at/ulbtirolhs/content/titleinfo/2601841, 2018.

Labitzke, K. and McCormick, M. P.: Stratospheric temperature increases due to Pinatubo aerosols, Geophys. Res. Lett., 19, 207–210, https://doi.org/10.1029/91GL02940, http://dx.doi.org/10.1029/91GL02940, 1992.

Löffler, M., Brinkop, S., and Jöckel, P.: Impact of major volcanic eruptions on stratospheric water vapour, Atmos. Chem. Phys., 16, 6547–6562, https://doi.org/10.5194/acp-16-6547-2016, https://www.atmos-chem-phys.net/16/6547/2016/, 2016.

McCormick, M., Thomason, L., and Trepte, C.: Atmospheric effects of the Mt Pinatubo eruption, Nature, 373, 399–404, https://doi.org/10.1038/373399a0, 1995a.

McCormick, M., W. Thomason, L., and R. Trepte, C.: Atmospheric effects of the Mt Pinatubo eruption, Nature, 373, 399–404, 1995b.

Meul, S., Langematz, U., Oberländer, S., Garny, H., and Jöckel, P.: Chemical contribution to future tropical ozone change in the lower stratosphere, Atmos. Chem. Phys., 14, 2959–2971, https://doi.org/10.5194/acp-14-2959-2014, https://www.atmos-chem-phys.net/14/2959/2014/, 2014.

Muthers, S., Arfeuille, F., Raible, C. C., and Rozanov, E.: The impacts of volcanic aerosol on stratospheric ozone and the Northern Hemisphere polar vortex: separating radiative-dynamical changes from direct effects due to enhanced aerosol heterogeneous chemistry, Atmos. Chem. Phys., 15, 11461–11476, https://doi.org/10.5194/acp-15-11461-2015, https://www.atmos-chem-phys.net/15/11461/2015/, 2015.

Poberaj, C. S., Staehelin, J., and Brunner, D.: Missing Stratospheric Ozone Decrease at Southern Hemisphere Middle Latitudes after Mt. Pinatubo: A Dynamical Perspective, Journal of the Atmospheric Sciences, 68, 1922–1945, https://doi.org/10.1175/JAS-D-10-05004.1, https://doi.org/10.1175/JAS-D-10-05004.1, 2011.

Randel, W. J., Wu, F., Russell III, J. M., Waters, J. W., and Froidevaux, L.: Ozone and temperature changes in the stratosphere following the eruption of Mount Pinatubo, Journal of Geophysical Research: Atmospheres, 100, 16753–16764, https://doi.org/10.1029/95JD01001, https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/95JD01001, 1995.

Revell, L. E., Stenke, A., Luo, B., Kremser, S., Rozanov, E., Sukhodolov, T., and Peter, T.: Impacts of Mt Pinatubo volcanic aerosol on the tropical stratosphere in chemistry–climate model simulations using CCMI and CMIP6 stratospheric aerosol data, Atmos. Chem. Phys., 17, 13139–13150, https://doi.org/10.5194/acp-17-13139-2017, https://www.atmos-chem-phys.net/17/13139/2017/, 2017.

Robock, A.: Volcanic eruptions and climate, Reviews of Geophysics, 38, 191–219, https://doi.org/10.1029/1998RG000054, http://dx.doi.org/10.1029/1998RG000054, 2000.

Roeckner, E., Brokopf, R., Esch, M., Giorgetta, M., Hagemann, S., Kornblueh, L., Manzini, E., Schlese, U., and Schulzweida, U.: Sensitivity of Simulated Climate to Horizontal and Vertical Resolution in the ECHAM5 Atmosphere Model, Journal of Climate, 19, 3771–3791, https://doi.org/10.1175/JCLI3824.1, 2006.

Rozanov, V., Buchwitz, M., Eichmann, K.-U., de Beek, R., and Burrows, J.: Sciatran - a new radiative transfer model for geophysical applications in the 240–2400 NM spectral region: the pseudo-spherical version, Advances in Space Research, 29, 1831 – 1835, https://doi.org/https://doi.org/10.1016/S0273-1177(02)00095-9, http://www.sciencedirect.com/science/article/pii/S0273117702000959, 2002.

Schoeberl, M., Bhartia, P., Hilsenrath, E., and Torres, O.: Tropical ozone loss following the eruption of Mt. Pinatubo, Geophys. Res. Lett., 20, 29–32, 1993a.

Schoeberl, M., Bhartia, P., Hilsenrath, E., and Torres, O.: Tropical ozone loss following the eruption of Mt. Pinatubo, Geophys. Res. Lett., 20, https://doi.org/10.1029/92GL02637, 1993b.

5   Self, S., Zhao, J.-X., E. Holasek, R., C. Torres, R., and J. King, A.: The Atmospheric Impact of the 1991 Mount Pinatubo Eruption, pubs, 1999.

Solomon, S.: Stratospheric ozone depletion: A review of concepts and history, Reviews of Geophysics, 37, 275–316, https://doi.org/10.1029/1999RG900008, http://dx.doi.org/10.1029/1999RG900008, 1999.

Solomon, S., Portmann, R. W., Garcia, R. R., Thomason, L. W., Poole, L. R., and McCormick, M. P.: The role of aerosol varia-
10   tions in anthropogenic ozone depletion at northern midlatitudes, Journal of Geophysical Research: Atmospheres, 101, 6713–6727, https://doi.org/10.1029/95JD03353, https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/95JD03353, 1996.

Stenchikov, G. L., Kirchner, I., Robock, A., Graf, H.-F., Antuña, J. C., Grainger, R. G., Lambert, A., and Thomason, L.: Radia-
tive forcing from the 1991 Mount Pinatubo volcanic eruption, Journal of Geophysical Research: Atmospheres, 103, 13 837–13 857, https://doi.org/10.1029/98JD00693, https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/98JD00693, 1998.

15   Telford, P., Braesicke, P., Morgenstern, O., and Pyle, J.: Reassessment of causes of ozone column variability following the eruption of Mount Pinatubo using a nudged CCM, Atmos. Chem. Phys., 9, 4251–4260, https://doi.org/10.5194/acp-9-4251-2009, https://www.atmos-chem-phys.net/9/4251/2009/, 2009a.

Telford, P., Braesicke, P., Morgenstern, O., and Pyle, J.: Reassessment of causes of ozone column variability following the eruption of Mount Pinatubo using a nudged CCM, Atmos. Chem. Phys., 9, 4251–4260, https://doi.org/10.5194/acp-9-4251-2009, https://www.
20   atmos-chem-phys.net/9/4251/2009/, 2009b.

Textor, C., Graf, H.-F., Timmreck, C., and Robock, A.: Emissions from volcanoes, in: Emissions of Atmospheric Trace Compounds, edited by Granier, C., Artaxo, P., and Reeves, C. E., pp. 269–303, Springer Netherlands, Dordrecht, 2004.

Thomas, M. A., Giorgetta, M. A., Timmreck, C., Graf, H.-F., and Stenchikov, G.: Simulation of the climate impact of Mt. Pinatubo eruption using ECHAM5" Part 2: Sensitivity to the phase of the QBO and ENSO, Atmos. Chem. Phys., 9, 3001–3009, https://doi.org/10.5194/acp-
25   9-3001-2009, https://www.atmos-chem-phys.net/9/3001/2009/, 2009.

von Glasow, R., Bobrowski, N., and Kern, C.: The effects of volcanic eruptions on atmospheric chemistry, Chemical Geol-
ogy, 263, 131 – 142, https://doi.org/https://doi.org/10.1016/j.chemgeo.2008.08.020, http://www.sciencedirect.com/science/article/pii/
S0009254108003756, halogens in Volcanic Systems and Their Environmental Impacts, 2009.

Winterstein, F., Tanalski, F., Jöckel, P., Dameris, M., and Ponater, M.: Implication of extreme atmospheric methane concentrations for
30   chemistry-climate connections, Atmospheric Chemistry and Physics Discussions, pp. 1–18, https://doi.org/10.5194/acp-2019-41, 2019.

WMO: WMO Statement on the state of the global climate in 2018, Atmospheric Chemistry and Physics Discussions, pp. WMO– No. 1233, 2019.