



# Analysis of global methane changes after the 1991 Pinatubo volcanic eruption

N. Bândă<sup>1,2</sup>, M. Krol<sup>3,4,1</sup>, M. van Weele<sup>2</sup>, T. van Noije<sup>2</sup>, and T. Röckmann<sup>1</sup>

<sup>1</sup>Institute for Marine and Atmospheric Research Utrecht, Utrecht University, Utrecht, The Netherlands

<sup>2</sup>Royal Netherlands Meteorological Institute (KNMI), De Bilt, The Netherlands

<sup>3</sup>Dept. of Meteorology and Air Quality, Wageningen University and Research Center, Wageningen, The Netherlands

<sup>4</sup>Netherlands Institute for Space Research (SRON), Utrecht, The Netherlands

Correspondence to: N. Bândă (n.l.banda@uu.nl)

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**Abstract.** The global methane (CH<sub>4</sub>) growth rate showed large variations after the eruption of Mount Pinatubo in June 1991. Both sources and sinks of tropospheric CH<sub>4</sub> were altered following the eruption, by feedback processes between climate and tropospheric photochemistry. Such processes include Ultra Violet (UV) radiative changes due to the presence of volcanic sulfur dioxide (SO<sub>2</sub>) and sulphate aerosols in the stratosphere, and due to stratospheric ozone depletion. Changes in temperature and water vapour in the following years caused changes in tropospheric chemistry, as well as in natural emissions. We present a sensitivity study that investigates the relative effects that these processes had on tropospheric CH<sub>4</sub> concentrations, using a simple one-dimensional chemistry model representative for the global tropospheric column. To infer the changes in UV radiative fluxes, the chemistry model is coupled to a radiative transfer model. We find that the overall effect of natural processes after the eruption on the CH<sub>4</sub> growth rate is dominated by the reduction in CH<sub>4</sub> lifetime due to stratospheric ozone depletion. However, all the other processes are found to have non-negligible effects, and should therefore be taken into account in order to obtain a good estimate of CH<sub>4</sub> concentrations after Pinatubo. We find that the overall effect was a small initial increase in the CH<sub>4</sub> growth rate after the eruption, followed by a decrease of about 7 ppb yr<sup>-1</sup> by mid-1993. When changes in anthropogenic emissions are employed according to emission inventories, an additional decrease of about 5 ppb yr<sup>-1</sup> in the CH<sub>4</sub> growth rate is obtained between the years 1991 and 1993. The results using the simplified single column model are in good qualitative agree-

ment with observed changes in the CH<sub>4</sub> growth rate. Further analysis, taking into account changes in the dynamics of the atmosphere, variations in emissions from biomass burning, and in biogenic emissions of non-methane volatile organic compounds (NMVOC), requires the use of a full three-dimensional model.

## 1 Introduction

CH<sub>4</sub> is the second most abundant anthropogenic greenhouse gas in the atmosphere after CO<sub>2</sub>. Its concentration in the atmosphere has increased since preindustrial times by a factor of 2.5 (Dlugokencky et al., 2011). A good understanding of the processes responsible for variations in the CH<sub>4</sub> concentration is needed for making future predictions and developing mitigation strategies. However, the evolution of the CH<sub>4</sub> concentrations observed in the background atmosphere in the past three decades is not fully understood (Montzka et al., 2011a). The growth rate of CH<sub>4</sub> was generally positive and showed a decreasing trend during the 80s and 90s, with year to year fluctuations (Dlugokencky et al., 2003). As shown in Fig. 7, particularly large fluctuations were observed in the years following the eruption of Mount Pinatubo in 1991 (Dlugokencky et al., 1994, 1996; Bekki and Law, 1997; Butler et al., 2004; Bousquet et al., 2006). After a peak of about 16 ppb yr<sup>-1</sup> near the time of the eruption, the globally averaged CH<sub>4</sub> growth rate dropped to -2 ppb yr<sup>-1</sup> in late 1992, remaining negative for the second half of the year 1992 (Dlugokencky et al., 2003). A subsequent recovery of

the growth rate to  $7 \text{ ppb yr}^{-1}$  was observed by the end of 1993.

Changes in the global  $\text{CH}_4$  concentration are determined by either changes in  $\text{CH}_4$  emissions or by changes in the  $\text{CH}_4$  lifetime.  $\text{CH}_4$  is emitted from both natural sources (e.g. wetlands, oceans and geological seeps) and anthropogenic sources (e.g. agriculture, fossil fuel exploitation, waste treatment and biomass burning). The lifetime of  $\text{CH}_4$  in the atmosphere is determined by the reaction of  $\text{CH}_4$  with the hydroxyl radical (OH) in the troposphere, by the uptake of  $\text{CH}_4$  by soils and by the destruction of  $\text{CH}_4$  in the stratosphere. The main sink is, however, the reaction with OH, the other processes contributing by only 10–15 % to the  $\text{CH}_4$  loss (Prather et al., 2001; Spahni et al., 2011). Atmospheric levels of OH are determined by tropospheric photolysis reactions driven by the incident solar UV radiation, by water vapour levels, and by non-linear tropospheric chemistry. Because OH reacts with these species, its abundance is sensitive to atmospheric concentrations of  $\text{CH}_4$ , nitrogen oxides ( $\text{NO}_x$ ), carbon monoxide (CO) and NMVOC. Montzka et al. (2011b) showed by inversions of methyl chloroform that global tropospheric OH is relatively stable to perturbations, having an interannual variability of  $2.3 \pm 1.5 \%$  for the period 1998 to 2007. Such a small variability was shown to be consistent with the small interannual variability in  $\text{CH}_4$  concentrations. In a previous study, Prinn et al. (2005) found an interannual variability in tropospheric OH of 7 to 9 % for the period 1978 to 2004. On a decadal timescale, a possible small positive trend in OH of the order of  $0.2 \%$   $\text{yr}^{-1}$  for the period 1985 to 2000, and higher after the year 2000, has been suggested by inversions of  $\text{CH}_4$  and  $\delta^{13}\text{C}\text{-CH}_4$  (Monteil et al., 2011, scenario P2).

The eruption of Mount Pinatubo triggered a multitude of photochemical effects (McCormick et al., 1995), including feedbacks between climate and atmospheric photochemistry, which contributed to the observed evolution of the  $\text{CH}_4$  concentrations. The different processes had both positive and negative impacts on the  $\text{CH}_4$  growth rate, affecting  $\text{CH}_4$  emissions and the  $\text{CH}_4$  lifetime. From satellite observations it is estimated that the eruption emitted about  $18 \pm 4 \text{ Tg SO}_2$  (Guo et al., 2004a). Volcanic  $\text{SO}_2$  absorbs UV radiation between 290 nm and 330 nm, thus its presence in the stratosphere would lead to a decrease in ozone photolysis in the troposphere (Dlugokencky et al., 1996). Since OH formation in the troposphere depends on the photolysis of ozone to  $\text{O}(^1\text{D})$ , the UV absorption by  $\text{SO}_2$  would lead to a longer  $\text{CH}_4$  lifetime.  $\text{SO}_2$  stayed in the stratosphere for a few months, forming sulphate aerosols with an e-folding time of 23–25 days (Guo et al., 2004a). Enhanced sulphate aerosols were observed by the SAGE II satellite instrument for up to 4 yr after the eruption at heights between 15 and 30 km with a maximum globally averaged aerosol optical depth (AOD) at 550 nm of approximately  $\tau = 0.15$  about 7 months after the eruption (Russell et al., 1996; Thomason et al., 1997). Scattering of solar radiation by sulphate aerosols would lead

to a further reduction of photolysis frequencies in the troposphere, thus to a longer  $\text{CH}_4$  lifetime. Particles of ash emitted directly by the eruption would also absorb and scatter solar radiation, determining a similar effect on  $\text{CH}_4$  lifetime. However, because of their lifetime of only a few days, they are considered to have a negligible global impact (Guo et al., 2004b; Niemeier et al., 2009) and are not included in our study.

Another secondary effect on the  $\text{CH}_4$  lifetime is triggered by the destruction of stratospheric ozone on sulphate aerosols. A maximum global ozone depletion of 5 % was observed by TOMS about two years after the eruption (Chipperfield et al., 2003). Changes of similar magnitude have been obtained in modelling studies (Kinnison et al., 1994; Bekki and Pyle, 1994), and were attributed to enhanced heterogeneous ozone-depleting reactions on sulphate aerosols and changes in circulation due to stratospheric aerosol heating. Stratospheric ozone loss would lead to an increase of UV radiation in the troposphere, and thus to a higher OH abundance and a shorter  $\text{CH}_4$  lifetime.

The eventual fate of the volcanic sulfur is deposition to the surface. The modelling results of Gauci et al. (2008) indicate that deposition of  $122 \text{ Tg SO}_2$  emitted by the Laki eruption led to a decrease of  $8.8 \text{ Tg yr}^{-1}$  in  $\text{CH}_4$  emissions from wetlands in the two years following the eruption. As a rough estimate assuming linearity, the Pinatubo eruption would lead to  $1.3 \text{ Tg}$  decrease in the emissions. We consider this effect to be small and do not investigate it further here.

Other effects of the eruption on  $\text{CH}_4$  concentrations have occurred because of temperature changes after the eruption (Bekki and Law, 1997). The scattering of shortwave radiation by aerosols led to an increase in the reflected solar radiation of up to  $10 \text{ W m}^{-2}$  at the top of the atmosphere (Bender et al., 2010). This affected tropospheric temperatures, leading to an observed global cooling of up to 0.45 K in the two years following the eruption (Free and Angell, 2002). Bender et al. (2010) show that ten general circulation models give a maximum decrease of 0.5 K in response to the observed changes in the shortwave radiative flux after the eruption. They attribute the 0.05 K difference between models and observations to the coinciding El Niño event.

Temperature perturbations trigger changes in the chemical composition of the atmosphere, as well as in natural sources related to biogenic activity. A decrease in temperature would generally slow down photochemical transformations. In particular, the slowdown of the reaction between  $\text{CH}_4$  and OH would lead to higher tropospheric  $\text{CH}_4$  concentrations (Bekki and Law, 1997). Soden et al. (2002) found that the cooling after the eruption is associated to a maximum global decrease of 3 % in the water vapour column in both observations and model simulations. Less water vapour in the troposphere would imply less OH formation by photolysis of ozone, because the reaction between  $\text{O}(^1\text{D})$  and water becomes less likely. This would increase the  $\text{CH}_4$  lifetime, leading to  $\text{CH}_4$  build-up in the atmosphere.

Natural emissions from wetlands, accounting for about 30% of the total emissions in the year 2004 (Spahni et al., 2011), are sensitive to temperature and soil moisture changes. Furthermore, natural emissions of NMVOC are known to be temperature dependent (Guenther et al., 1993). A decrease in the surface temperature would result in reductions in both CH<sub>4</sub> emissions from wetlands and biogenic NMVOC emissions. Biogenic emissions of NMVOC are also dependent on the amount of photosynthetically active radiation (PAR) reaching the surface (Guenther et al., 1993). Decrease in PAR fluxes because of enhanced aerosol scattering would further decrease these emissions. While a reduction in CH<sub>4</sub> emissions directly impacts CH<sub>4</sub> concentrations, a decrease in NMVOC emissions may affect OH, and thus impose an indirect impact on the CH<sub>4</sub> lifetime.

The eruption of Pinatubo also changed the dynamics of the atmosphere, which might have influenced OH and CH<sub>4</sub> concentrations. It was inferred in the 4-box modelling study of Schauffler and Daniel (1994) that heating of the stratosphere may increase the exchange between the stratosphere and the troposphere, leading to a decrease in tropospheric CH<sub>4</sub> concentrations. Lowe et al. (1997) suggest that a large effect of enhanced stratosphere-troposphere exchange would be inconsistent with the decrease in observed  $\delta^{13}\text{C}$  in this period. However, other isotope data from this period do not support a strong decrease in  $\delta^{13}\text{C}$  between 1991 and 1992 (Quay et al., 1999).

Although the processes presented above are known to have contributed to the evolution of the CH<sub>4</sub> growth rate after the Pinatubo eruption, their relative magnitudes are not yet totally resolved. CH<sub>4</sub> observations show the net outcome of these processes and other processes not related to the eruption, such as changes in anthropogenic emissions. The growth rate changes after the eruption have been attributed in other studies to changes in either sources or sinks. Dlugokencky et al. (1996) show that the evolution of CH<sub>4</sub> and CO in 1991 and early 1992 is consistent with a decrease in OH for up to one year after the eruption. They relate this decrease in OH to an attenuation of the UV flux due to the presence of SO<sub>2</sub> and sulphate in the stratosphere. Additionally, Dlugokencky et al. (1994) relate the decrease in CH<sub>4</sub> growth rate in 1992 to a decrease in anthropogenic emissions due to the collapse of the Soviet Union. The modelling study of Bekki and Law (1997) shows that temperature-related effects had a significant impact on the growth rate of CH<sub>4</sub> in 1991–1992. They find that reduced emissions from wetlands may partly or fully explain the reduced growth rate in 1992. The inverse modelling study of Butler et al. (2004) reveals a global source-sink imbalance of +27 Tg CH<sub>4</sub> for the year 1991 and –19 Tg for the year 1992. In their inverse modelling studies, Bousquet et al. (2006) and Wang et al. (2004) both find a decrease in wetland emissions of 20–25 Tg between 1991 and 1993. Bousquet et al. (2006) also find reductions in the biomass burning and anthropogenic emissions, as well as in the OH sink for this period. In contrast, Wang et al.

(2004) postulate an increase in OH due to reduced stratospheric ozone. Using a two-dimensional model, Bekki et al. (1994) also conclude that half of the CH<sub>4</sub> growth rate reduction in 1992 can be attributed to the effect of decreased stratospheric ozone. In the modelling study of Telford et al. (2010) it is found that natural isoprene emissions have a minimum in early 1993, yielding an increase in the CH<sub>4</sub> sink of 5 Tg yr<sup>-1</sup>. Telford et al. (2010) also show that variations in meteorology lead to a decrease in the CH<sub>4</sub> sink of up to 14 Tg yr<sup>-1</sup>, mainly due to changes in temperature and water vapour following the eruption. To our knowledge, no complete study has been made to include all competing effects of the Pinatubo eruption and to analyse the processes responsible for OH and CH<sub>4</sub> growth rate variations. Quantifying these processes may help us gain a better understanding of the CH<sub>4</sub> budget and, consequently, to make better predictions of the future atmospheric burdens.

In this sensitivity study we will use a simplified tropospheric column chemistry model as a first step to assess the changes in the CH<sub>4</sub> growth rate after the Pinatubo eruption and the relative contributions of the various processes. First, we will analyse how the equilibrium state of the chemical system changes when varying individual conditions (emissions, photolysis frequencies, water vapor). The impact on the tropospheric steady state gives us an idea about the drivers of CH<sub>4</sub> and OH concentrations, and about the relative magnitude of different processes. Next, we allow the system to respond to transient perturbations. The response of CH<sub>4</sub> concentrations to natural changes after the eruption will be contrasted to their response to changes in anthropogenic emissions. Due to obvious limitations of a single column model, the effect of changes in the dynamics of the atmosphere cannot be studied here. Additionally, because of the high sensitivity of OH to isoprene emissions in our model (see Sect. 3.1.1), we do not include the effect of changes in NMVOC emissions.

A detailed description of the column chemistry model is presented in Sect. 2. In Sect. 3.1 we show sensitivities of the model, and evaluate its performance in representing the global atmosphere in the period 1890–2005. We show our results on steady-state and transient CH<sub>4</sub> changes after Pinatubo in Sect. 3.2, and conclusions are drawn in Sect. 4.

## 2 Model setup

The model used in this study is a one-dimensional column chemistry model, coupled to the radiation model TUV (Madronich (1993), <http://cprm.acd.ucar.edu/Models/TUV/>). The chemistry model can be used both in steady-state and transient versions. The effects of atmospheric perturbations on photolysis frequencies are calculated with the radiative transfer model TUV, and then employed in the chemistry model.

**Table 1.** Reactions included in the model. Reaction rate coefficients are the ones described in Huijnen et al. (2010), except for photolysis rates, which are computed using TUV.

Reactants	Products
$O_3 + h\nu$	$2 \times OH$
$NO_2 + h\nu$	$O_3 + NO$
$O_3 + NO$	$NO_2$
$O_3 + OH$	$HO_2$
$O_3 + HO_2$	$OH$
$HO_2 + HO_2$	
$HO_2 + OH$	
$HO_2 + NO$	$OH + NO_2$
$NO_2 + OH$	
$CO + OH$	$HO_2$
$CH_4 + OH$	$0.9 \times CO + RO_2$
$RH + OH$	$0.35 \times CO + RO_2$
$RO_2 + NO$	$NO_2 + y \times HO_2$
$RO_2 + HO_2$	
$RO_2 + RO_2$	

## 2.1 The column chemistry model

In this exploratory study we use a strongly simplified model that represents the troposphere in 10 vertical layers of 1.5 km thickness each. The chemical scheme employs 8 chemical species, of which 5 are transported between adjacent layers ( $O_3$ ,  $NO_x$ ,  $CH_4$ ,  $CO$ ,  $RH$ ).  $OH$ ,  $HO_2$  and  $RO_2$  are not transported, but calculated in steady state with the longer-lived transported species. Here  $RH$  stands for NMVOC, and  $RO_2$  for peroxy-radicals formed from NMVOC and  $CH_4$  oxidation.

Vertical transport is defined by vertical diffusion coefficients of  $10 \text{ m}^2 \text{ s}^{-1}$  between the first two layers (at 1.5 km),  $5 \text{ m}^2 \text{ s}^{-1}$  between the second and 3rd layers (at 3 km) and  $2 \text{ m}^2 \text{ s}^{-1}$  higher up. No flux to the stratosphere is considered except for ozone and  $CH_4$ . For ozone, we fix the concentration in the upper layer (at 13.5 km) at 148 ppb. A flux of  $40 \text{ Tg yr}^{-1}$  to the stratosphere is considered for  $CH_4$ , following Prather et al. (2001).

The chemical reactions included are presented in Table 1. We run the model with all-day all-year averaged reaction rate coefficients and photolysis frequencies. The 0.9 CO yield from  $CH_4$  oxidation is comparable to that found by complex 3-D global chemistry models (Shindell et al., 2006). The yield of CO from the oxidation of NMVOC varies strongly between species (Grant et al., 2010). We use here a global CO yield from NMVOC of 0.35.  $CH_4$  oxidation produces  $CH_3O_2$ , which may react with  $NO$ , yielding at least one molecule of  $HO_2$  through all the reaction pathways.  $CH_3O_2$  is included in the model as  $RO_2$ , together with other compounds produced from NMVOC oxidation. Thus we consider an  $HO_2$  yield  $y$  from the reaction of  $RO_2$  and  $NO$ , equal to the ratio between the  $CH_3O_2$  production from  $CH_4$  and the total

$RO_2$  production. For computational reasons, we use a global yield determined from a steady-state assumption. The rate of production of  $CH_3O_2$  from  $CH_4$  oxidation is equal to the rate of loss of  $CH_4$  in this reaction. Assuming steady state, this is equal to the emission rate of  $CH_4$  ( $E_{CH_4}$ ). Similarly, the rate of  $RO_2$  production from NMVOC is equal to the emission rate of NMVOC ( $E_{RH}$ ). Therefore the  $HO_2$  yield  $y$  from the reaction of  $RO_2$  and  $NO$  is taken as  $\frac{E_{CH_4}}{E_{CH_4} + E_{RH}}$ .

Dry deposition of ozone and  $NO_2$  are included with a deposition velocity of  $1.0 \times 10^{-3} \text{ m s}^{-1}$ . An additional loss of  $NO_2$  through heterogeneous reactions is considered, with a deposition velocity of  $1.5 \times 10^{-4} \text{ m s}^{-1}$  throughout the column.

A time-dependent version of the chemistry model performs transient simulations using the Euler Backward Iterative scheme with a time step of one hour.

## 2.2 Photolysis frequencies

The TUV model version 4.1 is used to calculate the effects of  $SO_2$ , aerosols and ozone column on tropospheric photolysis frequencies. Yearly averaged photolysis frequencies are calculated by averaging daily mean photolysis frequencies at  $30^\circ\text{N}$  for the 15th of the months of March, June, September and December. This latitude band is used because photochemistry is most active in the tropics, and is chosen such that  $CH_4$  concentrations and lifetime are realistically reproduced.

For the base scenario, the climatological aerosol profile of Elterman (1968) is used, with an aerosol single scattering albedo of 0.99.

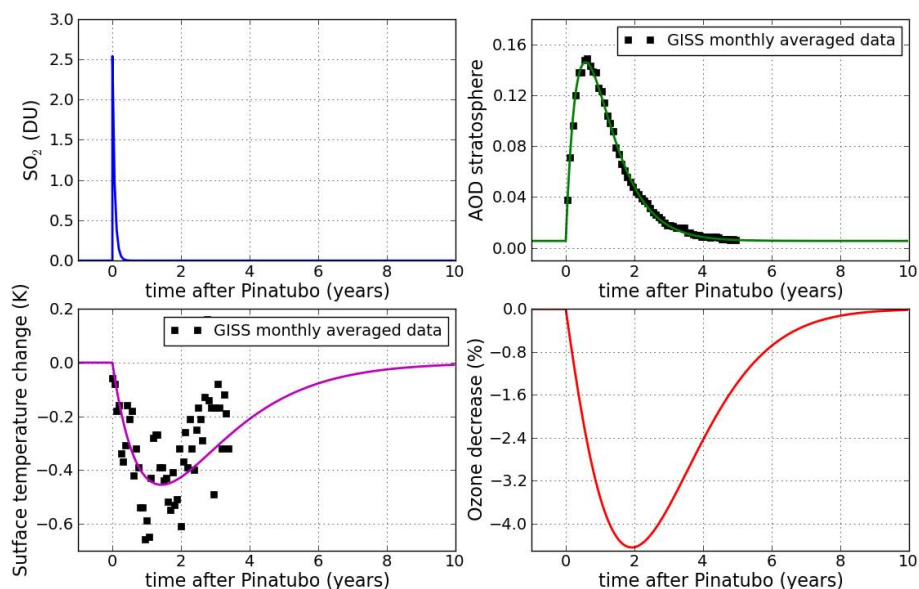
## 2.3 Emissions and atmospheric parameters

Global anthropogenic emissions for  $NO_x$ ,  $CO$ ,  $CH_4$  and NMVOCs are taken from EDGAR 4.1 yearly values for the years 1970–2005 (European Commission and Joint Research Centre (JRC)/Netherlands Environmental Assessment Agency (PBL), 2010), and EDGAR-HYDE decadal emissions for the years 1890–1970 (Van Aardenne et al., 2001). Natural emissions used are described in Huijnen et al. (2010), except for  $CH_4$  emissions, which are taken from Spahni et al. (2011) posterior values for the year 2004. The evolution of  $CH_4$  emissions implemented in the model is shown in Fig. 4. In addition to surface  $NO_x$  emissions, we add yearly  $6.3 \text{ Tg N}$  of  $NO_x$  from lightning (Huijnen et al., 2010), evenly distributed throughout the column in terms of mixing ratios.

Profiles of temperature, water vapour, ozone, and air density for  $30^\circ\text{N}$  were derived from the global 3-D chemistry transport model TM5 (Huijnen et al., 2010) driven by ERA-Interim meteorological fields (Dee et al., 2011) for the year 2005. These are applied both in TUV and in the column chemistry model. The ozone columns for the four months used here are respectively 302, 294, 283 and 270 Dobson Units (DU).

**Table 2.** Setup of the Pinatubo simulations. AOD = aerosol optical depth; DU = Dobson Unit.

Simulation name	Changes implemented in TUV	Changes implemented in the column chemistry model
SO <sub>2</sub>	2.54 DU of SO <sub>2</sub> between 15 and 30 km altitude	Changes in photolysis frequencies from TUV
Aerosol	0.15 AOD due to Pinatubo between 15 and 30 km altitude	Changes in photolysis frequencies from TUV
Ozone	5 % ozone column decrease	Changes in photolysis frequencies from TUV
Temp Rates		Changed reaction rate coefficients due to temperature
H <sub>2</sub> O		Changes in water vapour profile due to changed temperature profile
CH <sub>4</sub> Emis		Changes in CH <sub>4</sub> emissions from wetlands due to temperature
Temp All		Changes in reaction rate coefficients, water vapour and CH <sub>4</sub> emissions due to temperature

**Fig. 1.** Time evolution of the forcings, as implemented in the model. Squares represent monthly averaged GISS data (Hansen et al., 2005, 2010).

## 2.4 Implementation of Pinatubo perturbations

We define two sets of simulations. First, we evaluate the change in the model state due to individual natural perturbations after the eruption, in order to distinguish the most important drivers of CH<sub>4</sub> concentrations. In the second set of simulations we also include variations in anthropogenic CH<sub>4</sub> sources, with the aim to reproduce the evolution of the global CH<sub>4</sub> concentration in the early 1990s.

In the first set of simulations, we define the base simulation as the 1990 equilibrium situation. Next, the change in the model state due to the natural perturbations after Pinatubo is evaluated as a steady-state and as a transient response. The perturbations implemented in TUV and the column chemistry model are summarised in Table 2. In these sensitivity experiments, we assume constant anthropogenic and biomass burning emissions.

To compute the perturbations in photolysis frequencies after Pinatubo in TUV, we implement single forcings of 5% decrease in ozone column, 2.54 DU increase in SO<sub>2</sub>, equivalent to 18.5 Tg SO<sub>2</sub>, and 0.15 increase in AOD. SO<sub>2</sub> and aerosols are considered to be evenly distributed in our atmospheric column between 15 and 30 km altitude. In the column chemistry model, the perturbations in photolysis frequencies are then scaled with the magnitudes of the forcings, thus assuming that the effects of these processes are linear. In addition, we assume additivity between the different processes by adding the perturbations in photolysis frequencies when more than one process is considered. We tested the effect of this assumption on our results by performing two simulations: one in which we used photolysis rates calculated with TUV by implementing all the forcings at the same time, and one in which we implemented each forcing separately and assumed additivity. The difference in the CH<sub>4</sub> steady-state concentration between the two simulations is 0.5 ppb, which is small compared to the magnitude of the perturbations related to the eruption.

The time evolution of the forcings assumed in the column chemistry model is based on observed values, and is shown in Fig. 1. For  $\text{SO}_2$ , an exponential decay with an e-folding time of 24 days is considered, as found by Guo et al. (2004a), and a starting global mean concentration of 2.54 DU directly after the eruption. For the aerosol optical thickness, we use the Goddard Institute for Space Studies (GISS) monthly averaged values (Hansen et al., 2005), based on SAGE II satellite data. Surface temperature is taken from GISS analysis data (Hansen et al., 2010). The global mean GISS data for AOD and temperature are interpolated in the 4.5 and 3.5 yr following the eruption, respectively. The resulting evolutions have a peak at approximately 7 and 15 months after the eruption, respectively, and then a smooth decay, which is extrapolated for 10 yr. To a 0.5 K temperature decrease at the surface, we associate a tropospheric temperature change of 0.5 K decrease below 214.4 hPa, and a 1 K increase at 87.7 hPa, following the observations from Free and Angell (2002), and interpolate between these values. These profile changes are then scaled with the magnitude of the surface temperature change. For ozone decrease, we use an evolution that has a peak of 4.5 % 2 yr after the eruption and then decays to 0, following the results of Randel et al. (1995).

The water vapour profile as a function of temperature change is evaluated using the Clausius-Clapeyron equation, assuming constant relative humidity. Variations in emissions of  $\text{CH}_4$  from wetlands due to temperature are calculated using the  $Q_{10}$  temperature dependence relation (Dunfield et al., 1993), with a  $Q_{10}$  value of 2. For a temperature decrease of 0.5 K, we find that  $\text{CH}_4$  wetland emissions decrease from  $171.8 \text{ Tg yr}^{-1}$  to  $165.9 \text{ Tg yr}^{-1}$ .

The second set contains two additional transient simulations, which enable us to compare the magnitude of natural effects after the eruption to that of variations in anthropogenic sources. In both simulations we employ yearly anthropogenic emissions from EDGAR 4.1, while keeping the biomass burning emissions constant at 1990 values. In the first simulation, natural emissions and atmospheric parameters are kept constant. In the second one we also include the natural forcings after the eruption. These simulations are performed starting from the steady state in the year 1890, using EDGAR-HYDE and EDGAR 4.1 emissions for the spin-up period between 1890 and 1990.

## 2.5 Methyl chloroform model

For validating the transient OH concentrations obtained with our column chemistry model, we perform an offline simulation of methyl chloroform (MCF) for the period 1988 to 2005. We use the same column model, with only one chemical tracer, MCF.

The MCF emissions used are the same as described in Montzka et al. (2011b). The main sink of MCF is the reaction with OH in the troposphere. We use OH fields from each time step of the transient simulation for the period 1890 to 2005

**Table 3.** Yearly emissions for 1890 and 1990 implemented in the model. Emission units are given in parentheses.

Species (unit)	1890	1990
$\text{CH}_4$ ( $\text{Tg yr}^{-1}$ )	278	512
$\text{NO}_x$ ( $\text{Tg N yr}^{-1}$ )	22.7	47.6
CO ( $\text{Tg yr}^{-1}$ )	460	1177
NMVOC ( $\text{Tg C yr}^{-1}$ )	707	808

(the first simulation of the second set), and a temperature-dependent reaction rate as given in JPL 2011 (Sander et al., 2011). Additional stratospheric and ocean sinks are considered with lifetimes of 38 and 80 yr, respectively. These are in the range of values found by Krol and Lelieveld (2003).

We use an initial condition in 1988 of 115 ppt throughout the column.

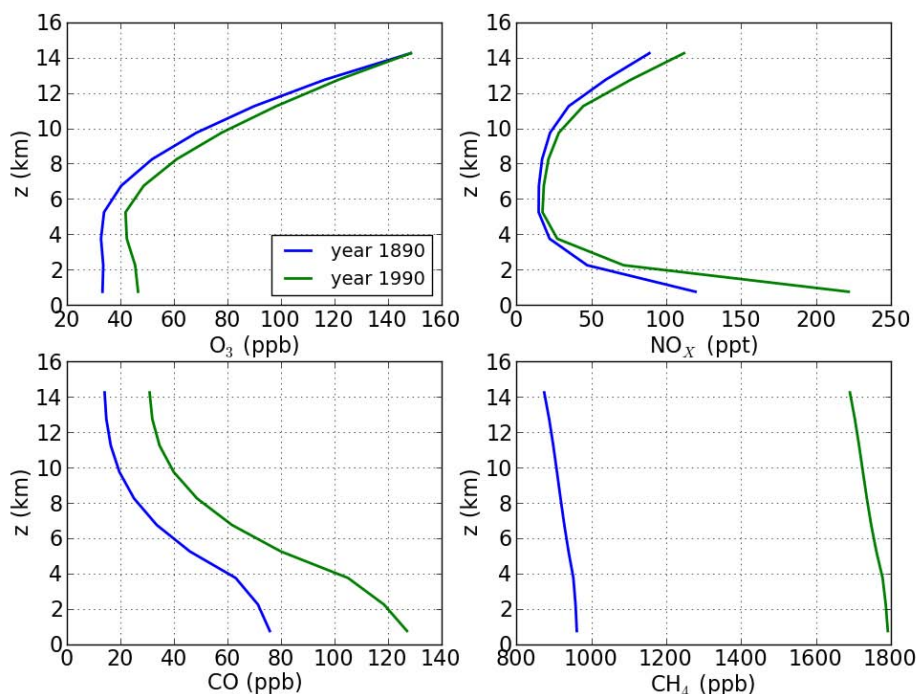
## 3 Results and discussion

### 3.1 Model evaluation

Even though the model presented above contains many simplifications, we will show that it performs reasonably well in representing the global state of the troposphere.

Figure 2 presents the steady-state profiles for  $\text{CH}_4$ ,  $\text{O}_3$ ,  $\text{NO}_x$ , and CO obtained by the column chemistry model for the years 1890 and 1990. The yearly emission values used are shown in Table 3.  $\text{CH}_4$  decreases with altitude by about 100 ppb throughout the troposphere in the year 1990. CO mixing ratios for the same year decrease with altitude from 125 ppb at the surface to 30 ppb near the tropopause. The  $\text{NO}_x$  profile has the typical C-shape due to the production of  $\text{NO}_x$  by lightning throughout the column and the longer lifetime of  $\text{NO}_x$  in the upper troposphere. Ozone mixing ratios decrease with altitude in the first few kilometers, and then increase towards the stratosphere.

Between the years 1890 and 1990, we find increases in ozone, CO and  $\text{CH}_4$ , which are more pronounced near the surface due to increases in emissions of ozone precursors, CO and  $\text{CH}_4$ . For  $\text{NO}_x$  we find increases both near the surface, because of increased emissions, as well as near the tropopause, due to an increase in the  $\text{NO}_x$  lifetime at this altitude. This is consistent with a decrease in OH in the upper troposphere due to higher  $\text{CH}_4$  concentrations. In the study of Wang and Jacob (1998), zonal averaged profiles for ozone, OH,  $\text{NO}_x$  and CO are computed using a three-dimensional model of tropospheric chemistry for preindustrial and year 1990 conditions. Concentrations of ozone and  $\text{NO}_x$  near the surface are somewhat higher in our model, possibly due to the fact that no differentiation is made between land and ocean in our simplified single column model. Our model finds a higher CO variability throughout the column, which may be caused by the fact that we did not



**Fig. 2.** Vertical profiles of ozone,  $\text{NO}_x$ , CO, and  $\text{CH}_4$  obtained with the one dimensional model for the years 1890 and 1990.

**Table 4.** Comparison of trace gas budgets for the global troposphere obtained with our one-dimensional model, with the results from other models. Numbers in  $\text{Tg yr}^{-1}$ , unless otherwise specified.

	Stevenson et al. (2006), S1 scenario	Shindell et al. (2006)	Williams et al. (2012)	One-dimensional model
Ozone chemical production	$5110 \pm 606$		4729	6117
Ozone chemical loss	$4668 \pm 727$			5009
Ozone deposition	$1003 \pm 200$		863	1349
Ozone stratospheric exchange	$552 \pm 168$		274	241
Ozone burden (Tg)	$344 \pm 39$		320	448
Ozone lifetime (days)	$22.3 \pm 2$		23.4	25.7
OH ( $\text{molec cm}^{-3}$ )		$11.3 \pm 1.7$		9.5
OH production from photolysis			1663	2061
OH chemical production			3522	3519
CO chemical production		$1505 \pm 236$	1314	1400
CO burden (Tg)			322	368
CO lifetime (days)			48.3	52.1
$\text{CH}_4$ lifetime (yrs)	$8.76 \pm 1.32$	$9.7 \pm 1.7$	8.35	8.2

formulate a convective redistribution of the column. In terms of changes in concentrations between the preindustrial setup and the year 1990, our model finds generally lower relative changes than the study of Wang and Jacob for  $\text{O}_3$ ,  $\text{NO}_x$  and CO, possibly due to the different emission sets that are used. However, the 30 % increase in OH that we find in the lowest 1.5 km of the model, and about 20 % decrease between 6 and 12 km altitude compare well with their study.

In Table 4, we compare the ozone, OH and CO budgets given by our model for the year 1990 to global budgets

found by several 3-dimensional chemistry transport models presented in Williams et al. (2012); Stevenson et al. (2006); Shindell et al. (2006). Overall, our model falls within the uncertainties of these models in terms of OH and CO burdens and budgets. CO and  $\text{CH}_4$  lifetimes are also modeled realistically, certainly when one considers the huge simplifications of the chemical system and the simplified representation of the global atmosphere. Ozone burden, production, and deposition are high compared to full 3-D models. These are more representative of tropical values than global ones, likely due

to the choice of tropical conditions to represent the global troposphere. For the same reason, ozone stratospheric inflow is quite low. This is because most ozone inflow occurs in the extratropics (Gettelman et al., 2011), while our model column is in the tropics.

### 3.1.1 Model sensitivities

We further evaluate the sensitivity of the model to parameters involved in this study, i.e. to CH<sub>4</sub> and isoprene emissions, ozone column, temperature and water vapour (Table 5). We compare the sensitivities of our model to sensitivities of 2-D and 3-D models present in literature. Except for the sensitivity to CH<sub>4</sub> emissions, these studies evaluate other sensitivities while keeping CH<sub>4</sub> concentrations fixed, or by looking at timescales of a few years. Because of the CH<sub>4</sub> lifetime of about 8 yr, the feedback of CH<sub>4</sub> concentrations on its own lifetime is ineffective on such a short period. Therefore we also calculate these sensitivities while keeping CH<sub>4</sub> concentrations fixed.

The effect of CH<sub>4</sub> emission changes on the CH<sub>4</sub> concentrations is enhanced by the feedback via the CH<sub>4</sub> lifetime. To describe this process, a feedback factor  $a$  is defined as  $a = 1/(1 - \frac{d \ln \tau}{d \ln \text{CH}_4})$ , following Voulgarakis et al. (2012). Here  $\tau$  stands for the CH<sub>4</sub> lifetime, and the small offsets  $d \ln \text{CH}_4$  and  $d \ln \tau$  are determined by a small perturbation in CH<sub>4</sub> emissions. We find that  $a$  has a value of 1.45 for the year 1990, which compares well with the best estimate of the Third Assessment Report of the IPCC (Prather et al., 2001), and falls well in the range found in the model intercomparison study of Voulgarakis et al. (2012).

Another sensitivity that is important to our study is the sensitivity of CH<sub>4</sub> to changes in the ozone column. In the two-dimensional modelling study of Bekki and Pyle (1994), a 6% increase in OH is found due to a 6% decrease in stratospheric ozone between the years 1991 and 1993. We find that a 6% decrease in ozone column leads to a 6.4% enhancement in OH, which compares well to their results. Other studies that assess the sensitivity of CH<sub>4</sub> and OH to ozone column changes find lower sensitivities (Camp et al., 2001; Fuglestedt et al., 1994). However, the ozone perturbations in these studies are dominated by the middle and high latitudes, where ozone photolysis and CH<sub>4</sub> oxidation are less important. After the Pinatubo eruption, both low and high latitude ozone columns were affected (Chipperfield et al., 2003). Therefore we consider it more appropriate to compare our results to Bekki and Pyle (1994).

To test the sensitivity of our model to climate, we used a temperature increase of 1 K throughout the column, and computed the corresponding change in humidity using the Clausius-Clapeyron equation. The CH<sub>4</sub> lifetime change of  $-0.49 \text{ yr K}^{-1}$  in our model is somewhat larger than the multimodel mean of  $-0.31 \pm 0.14 \text{ yr K}^{-1}$  found in Voulgarakis et al. (2012). However, we do not include changes in stratospheric ozone related to temperature. We use observed

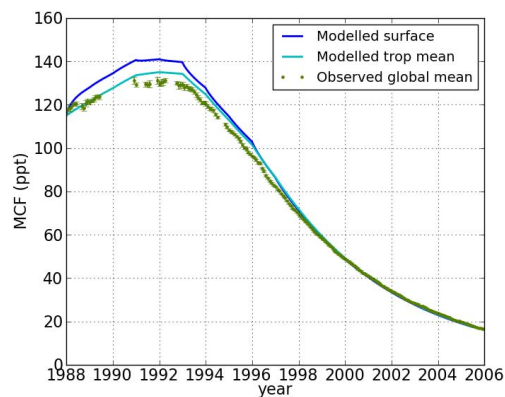


Fig. 3. Observed and modeled evolution of methyl chloroform surface and tropospheric mean mixing ratios between 1988 and 2006.

changes in stratospheric ozone, and the effect of temperature on ozone concentrations is included in the observations. The two models used in Voulgarakis et al. (2012) that also do not include this feedback give higher sensitivities to temperature, of  $-0.4$  and  $-0.57 \text{ yr K}^{-1}$ . Therefore we consider our model to respond to temperature changes in a similar manner as global chemistry models.

Telford et al. (2010) found a maximum decrease in isoprene emissions of 9% due to lower temperature and lower PAR fluxes in the year 1992 due to the presence of aerosols in the stratosphere. They find a corresponding 1% increase in OH tropospheric burden. We test the sensitivity of our model to such a perturbation in isoprene emissions, and find that our model is two times more sensitive. We attribute this again to our one-column approach, in which we cannot account for horizontal transport. Isoprene reacts rapidly with OH, and regions with large and small isoprene emissions are present in the true atmosphere. Furthermore, our simplified chemistry scheme is not well suited to explore the sensitivity to changing NMVOC emissions. A more recent study shows that the effect of aerosols on isoprene emissions is smaller if diffuse and direct radiation is treated separately (Wilton et al., 2011). We conclude therefore that the calculated feedback of NMVOC emissions on OH is highly uncertain, and we decide not to include it in further simulations. We simply note that decreases (increases) in NMVOC emissions probably lead to more (less) OH and a shorter (higher) CH<sub>4</sub> lifetime.

### 3.1.2 Evaluation of CH<sub>4</sub> and methyl chloroform concentrations

The results on MCF surface and tropospheric mean mixing ratios are shown in Fig. 3. We compare our simulation results to the observations-based global mean mixing ratios, computed by averaging the GAGE/AGAGE data at the stations Mace Head, California, Barbados, Samoa, and Cape Grim.



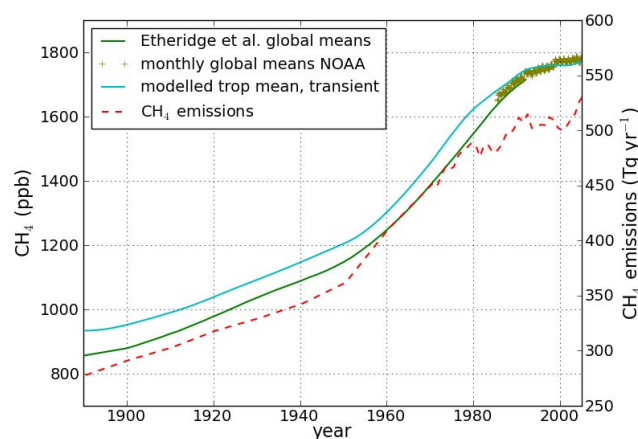
**Table 5.** Sensitivities and feedback factors of our column chemistry model and comparison to literature.

Sensitivity	1-D model	Value in literature	Study
Feedback factor between CH <sub>4</sub> emissions and CH <sub>4</sub> concentrations	1.45	1.4 1.23–1.69	IPCC TAR, Prather et al. (2001) Voulgarakis et al. (2012)
Change in tropospheric OH due to a 6 % increase in ozone column (%)	6.4	6	Bekki and Pyle (1994)
Change in CH <sub>4</sub> lifetime due to a 1 K increase in global temperature (yr K <sup>-1</sup> )	-0.49	-0.31 ± 0.14	Voulgarakis et al. (2012)
Change in tropospheric OH due to a 9 % decrease in isoprene emissions (%)	1.9	1.	Telford et al. (2010)

The modelled total lifetime of MCF is 4.6 yr and the lifetime with respect to OH is 5.7 yr, in agreement with other studies (Krol and Lelieveld, 2003; Prinn et al., 2005). When we sample the model at the surface in the period in which MCF emissions were significant (1988–1998), the model is seen to overestimate the observed mixing ratios. This is related to differences in the sampling of the model and the observations. Observations are generally taken in remote areas, away from the emissions, in order to be representative for the global burden. In our one-dimensional model, the sampling is done in the surface grid box, where the emissions are also put in. Therefore a tropospheric mean sampling of the model is in better correspondence with the observations. This is confirmed by the fact that our modelled tropospheric mean MCF mixing ratios are in very good agreement with GAGE/AGAGE observations. A tropospheric mean sampling of the model will be used in the rest of the paper.

The results for CH<sub>4</sub> concentrations from the first simulation of the second set, as defined in Sect. 2.4, are shown in Fig. 4. They are compared to global means for the period 1890 to 1990, calculated from ice core measurements in Etheridge et al. (1998). Following the same procedure as used in Etheridge et al. (1998), we estimate global mean mixing ratios for the period 1985 to 2005 based on the monthly means from the GLOBALVIEW-CH<sub>4</sub> (2009) data from the stations Alert and South Pole. The global mean is therefore computed as the mixing ratio at South Pole plus 37 % of the inter-polar difference. Modelled CH<sub>4</sub> mixing ratios generally follow the decadal trends in CH<sub>4</sub> emissions, with a delay of about 10 yr due to the CH<sub>4</sub> lifetime. The stabilization of the concentrations towards the end of the simulation period is a phenomenon that is also present in the observations (Dlugokencky et al., 2003).

Compared to the observations, our model follows quite well the trends in CH<sub>4</sub> mixing ratios, but generally overestimates CH<sub>4</sub> mixing ratios by up to 50 ppb. We expect this to happen in the first decades of the simulation, because the starting point represents a steady state, while the system might not have been in equilibrium in the year 1890. The concentration continues to be overestimated until 1990, pointing either to an overestimation of the CH<sub>4</sub> emissions



**Fig. 4.** Observed and modeled evolution of CH<sub>4</sub> mixing ratios between 1890 and 2005. Observation-based global means are calculated by Etheridge et al. (1998) based on ice-core data (green line), and more recent global means are calculated using measurements at South Pole and Alert NOAA stations (green crosses). CH<sub>4</sub> emissions implemented in the model are also shown (red dotted line, with scale on the right axis) (Van Aardenne et al., 2001; Spahni et al., 2011).

or of the CH<sub>4</sub> lifetime in this period. These results are only based on changing anthropogenic emissions (NO<sub>x</sub>, CO, CH<sub>4</sub>, NMVOC) for the simulated period, and there are several possible explanations for the differences between modelled and observed concentrations. Firstly, processes not included here, such as changes in stratospheric ozone, temperatures and possible trends in natural and biomass burning emissions can have a significant impact on CH<sub>4</sub> concentrations. Secondly, we are not able to represent high and low NO<sub>x</sub> regions in our column chemistry model. For this reason, our model might misrepresent the sensitivity of CH<sub>4</sub> concentrations to NO<sub>x</sub> and NMVOC emissions. Finally, we use a fixed CO yield from NMVOC oxidation for the simulated period. This yield varies among species and among NO<sub>x</sub> pollution environments, therefore we would expect it to change on a centennial scale. However, the chosen model setup captures the observed range of CH<sub>4</sub> concentrations in the period 1990–2005, which is the period we are interested in.

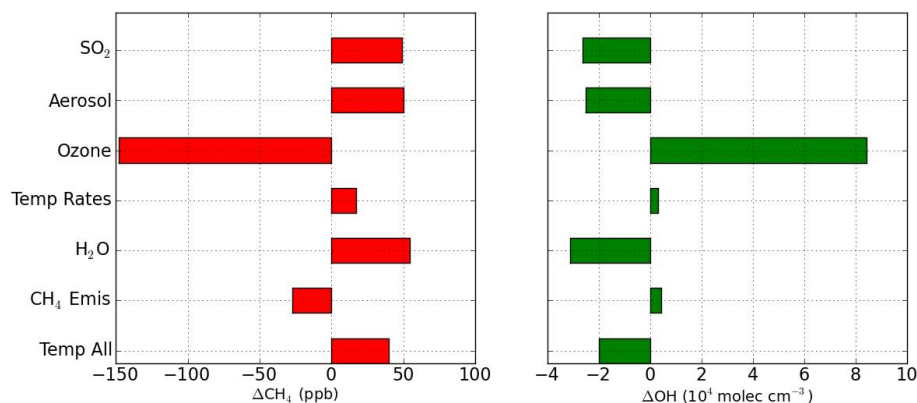


Fig. 5. CH<sub>4</sub> and OH steady-state changes due to various Pinatubo forcings.

We conclude that our model properly represents the global budgets and lifetimes of the different species, and is able to reproduce the mean state of the atmosphere in the 1990s. The sensitivities relevant for this study are reasonably represented. However, the model is too simplified to capture variations of CH<sub>4</sub> on a centennial scale, or vertical profiles of different species present in the model. Our sensitivity tests also show that the sensitivity of the model to NMVOC emissions is overestimated.

## 3.2 The Pinatubo eruption

### 3.2.1 Steady-state perturbations

We first examine the effect of each of the forcings of the Pinatubo eruption described in Table 2 on the CH<sub>4</sub> equilibrium concentration, using the maximum magnitude of each forcing. The differences in tropospheric CH<sub>4</sub> and OH between each simulation and the “base” simulation are shown in Fig. 5.

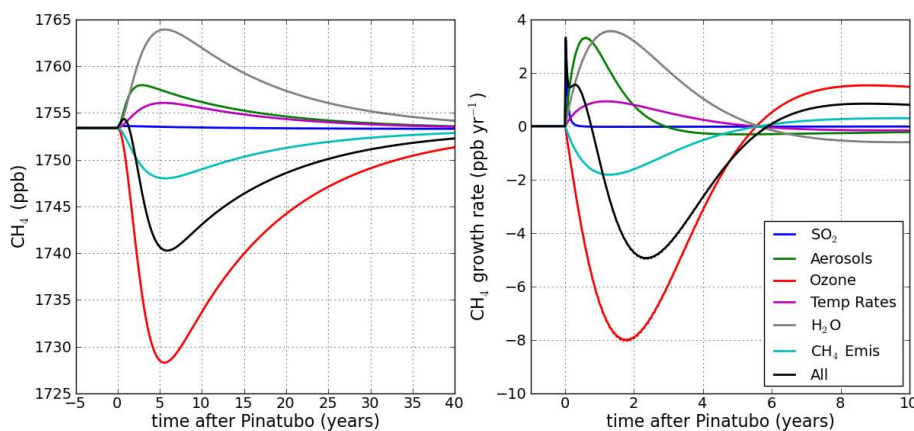
We find that the 5 % reduction in ozone column has the largest effect on the tropospheric mean CH<sub>4</sub> equilibrium mixing ratio, decreasing it by 125 ppb. SO<sub>2</sub>, aerosol and water vapour changes all increase the CH<sub>4</sub> steady-state by 48 to 55 ppb. The effects of temperature decrease on CH<sub>4</sub> emissions and reaction rates have smaller impacts on the simulated steady-state mixing ratios, of 27 and 17 ppb respectively. The temperature-related processes, that is “Temp Rates”, “H<sub>2</sub>O” and “CH<sub>4</sub> Emis”, partly cancel each other, resulting in an overall increase of 40 ppb.

Except for the effects of changed CH<sub>4</sub> emissions and changed reaction rates, the effects on CH<sub>4</sub> are strongly correlated to effects on OH of the same relative magnitude and of opposite sign. The OH response to decreasing CH<sub>4</sub> emissions reflects the effectiveness of the feedback factor introduced in the previous section. Changed reaction rates due to tropospheric cooling lead to a small increase in OH, because of the slower oxidation rate of CH<sub>4</sub>.

### 3.2.2 Evolution of transient concentrations and growth rate

The modelled transient evolution of CH<sub>4</sub> mixing ratios due to individual natural perturbations following the eruption, and including their overall effect, are shown in Fig. 6a. When all natural effects are included, the tropospheric mean CH<sub>4</sub> mixing ratio slightly increases for 9 months after the eruption. Afterwards it decreases, reaching a maximum decrease of 13 ppb about 6 yr after the eruption. The magnitudes of the perturbations in transient concentrations are smaller than the effects on the steady states, occurring at different moments in time after the eruption and on different timescales. Because the CH<sub>4</sub> lifetime is about 8 yr, the concentration at one moment in time shows an integrated effect of its source-sink imbalance in the previous years. Therefore not only the magnitude, but also the duration of the perturbation plays an important role in determining its effect on CH<sub>4</sub> concentrations. The recovery time to the initial concentration is much longer compared to the recovery time of the perturbations applied. The SO<sub>2</sub> effect is hardly observed in the transient concentrations, because of its short duration. All the other processes affect the CH<sub>4</sub> concentration for up to 40 yr after the eruption.

We calculate the CH<sub>4</sub> growth rate by differentiating the transient mixing ratios. The overall effect of the natural forcings after Pinatubo on the tropospheric CH<sub>4</sub> growth rate (Fig. 6b) is a positive jump of 3 ppb yr<sup>-1</sup> due to UV absorption by SO<sub>2</sub> immediately after the eruption. The effect decreases, but remains positive for about 9 months after the eruption, due to the presence of SO<sub>2</sub> and sulphate aerosols in the stratosphere. After that, the effect on the CH<sub>4</sub> growth rate is dominated by the forcing exerted by ozone depletion, partly counteracted by decreased water vapour. The overall effect of natural forcings on CH<sub>4</sub> growth rate experiences a minimum of -5 ppb yr<sup>-1</sup> about 2 yr after the eruption. The growth rate increases afterwards, reaching zero about 6 yr after the eruption, when the effect on the transient CH<sub>4</sub> mixing ratios is at a minimum (Fig. 6a). The slow recovery of the



**Fig. 6.** Effect of the different Pinatubo forcings on the temporal evolution of the tropospheric mean  $\text{CH}_4$  mixing ratio and growth rate.

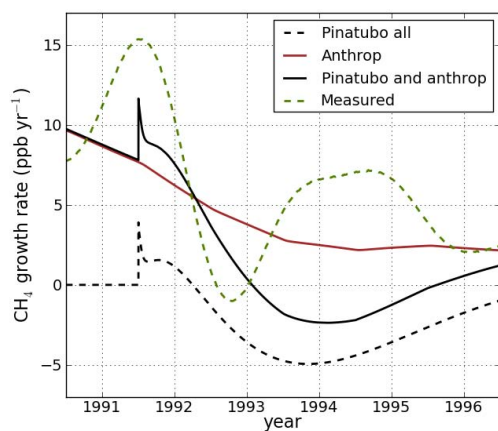
concentrations to the steady state is marked by a small positive growth rate of less than  $1 \text{ ppb yr}^{-1}$ . The shape of the growth rate evolution reflects the annual imbalance between  $\text{CH}_4$  sources and sinks.

We find a positive  $\text{CH}_4$  growth rate for about 9 months after the eruption. The effect of temperature on the reaction rates is small in this period, and the temperature effect on emissions leads to a negative growth rate. Therefore we can only relate this positive growth rate to a decrease in OH, as also suggested by Dlugokencky et al. (1996). The large effect of ozone depletion which follows compares well with the results of Bekki et al. (1994). They report a  $7 \text{ ppb yr}^{-1}$  decrease in growth rate from spring 1991 to autumn 1992 due to ozone depletion. The drop in  $\text{CH}_4$  growth rate due to ozone depletion in our model is associated with a 5% increase in OH. This is consistent with the findings of Wang et al. (2004) of a global drop in OH of  $10^5 \text{ molec cm}^{-3}$ , equivalent to 7%, between the end of 1991 and beginning of 1994. Using the same parametric model, but keeping stratospheric ozone constant, they find much smaller variability in OH in this period, on the order of 1–2%. Similar to our results, Bousquet et al. (2006) find an increase in the OH sink until the beginning of 1992, and then a subsequent decrease in 1992 and 1993. However, they find different magnitudes of these changes compared to our study, leading to an overall increase in the OH sink between 1991 and 1993. The magnitude of the temperature-related effects that we find compares well with the estimate from Bekki and Law (1997). We find a maximum of  $6 \text{ Tg yr}^{-1}$  change in wetland emissions after the eruption. This is similar to the bottom up estimate of about  $5 \text{ Tg yr}^{-1}$  shown in Spahni et al. (2011) Fig. 8a, but a few times lower than the maximum anomaly of about  $40 \text{ Tg yr}^{-1}$  found in the inverse modelling study of Bousquet et al. (2006). Our lower estimate might be partly due to the fact that we considered changes in  $\text{CH}_4$  emissions solely due to temperature.  $\text{CH}_4$  emissions also depend on spatial and temporal changes in soil moisture and precipitation, which have been observed after the eruption (Spahni et al., 2011).

Changes in wetland extent were also shown to have a large impact on the interannual variability in  $\text{CH}_4$  emissions from wetlands (Ringeval et al., 2010), which is also not taken into account in the study of Spahni et al. (2011) for the years 1991 and 1992. In addition, we consider a global  $Q_{10}$  factor of 2, while this factor was shown to be dependent on ecosystem type, with a range of measured values between 1.6 and 16 (Dunfield et al., 1993; Valentine et al., 1994).

The results show that stratospheric ozone changes had a large impact on  $\text{CH}_4$  growth rate after the eruption. The WMO 2003 report (Chipperfield et al., 2003) shows that the total ozone in the atmosphere decreased between the years 1991 and 1993 by about 5%. Similar numbers are found when excluding the high latitudes (for  $60^\circ \text{ S}–60^\circ \text{ N}$ ), or when looking only at the tropical region ( $25^\circ \text{ S}–25^\circ \text{ N}$ ). This change was caused partly by natural variability, including an increase in the solar activity in this period, and partly by processes related to the eruption. Therefore, after removing the effects of the solar cycle and QBO, a decrease of 2% to 3% is found in the measured total ozone between 1991 and 1993.  $\text{CH}_4$  measurements are affected by changes in the ozone column, irrespective of their cause. For this reason, we used here a maximum decrease of 4.5% in the ozone column, representative for  $60^\circ \text{ S}–60^\circ \text{ N}$ , which includes solar variability. To distinguish the change in  $\text{CH}_4$  concentrations due to changes in ozone related to the eruption, a smaller perturbation should be considered.

The modelled  $\text{CH}_4$  growth rate from the second set of simulations, when varying anthropogenic emissions of  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{NO}_x$  and NMVOC, is shown in Fig. 7. These simulations have a starting point in 1890, producing a more realistic growth rate at the moment of the eruption of  $10 \text{ ppb yr}^{-1}$ . Results for the full length of the simulation, without including the post-Pinatubo perturbations, are shown in Fig. 4. We compare our results with the observations-based global mean growth rate, obtained by globally averaging the  $\text{CH}_4$  reference marine boundary layer matrix from GLOBALVIEW- $\text{CH}_4$  (2009), and deseasonalising it using



**Fig. 7.** Modelled growth rate evolution after the Pinatubo eruption including variations due to anthropogenic emissions, and the combined signal from natural and anthropogenic changes. The black dotted line shows the growth rate evolution obtained in the first set of simulations, including all natural forcings (the same as the black line in Fig. 6b). Also shown is the measured globally averaged growth rate obtained using the reference marine boundary layer matrix from GLOBALVIEW-CH<sub>4</sub> (2009).

the software provided by NOAA (based on Thoning and Tans (1989)). CH<sub>4</sub> anthropogenic emissions were relatively stable in the years 1990 to 2000, while anthropogenic NO<sub>x</sub> emissions increased and CO emissions decreased. Therefore we find a generally decreasing trend in CH<sub>4</sub> growth rate due to a decrease in CH<sub>4</sub> lifetime, when only variations in anthropogenic emissions are taken into account.

When both variations in anthropogenic emissions and natural forcings are included in the model, a similar range of values is found for the modelled and observed growth rates in the years 1991 to 1996. These values vary between more than 10 ppb yr<sup>-1</sup> and slightly negative values of up to -2 ppb yr<sup>-1</sup>. Decreased anthropogenic CH<sub>4</sub> emissions between the years 1991 and 1993 are found to contribute by an additional 5 ppb yr<sup>-1</sup> to the drop in CH<sub>4</sub> growth rate in this period, in agreement with previous studies (Dlugokencky et al., 1994; Bousquet et al., 2006). The timing of the minimum growth rate after the eruption is modelled about 15 months later than that observed. This minimum is found by a complex balance between the different forcings, being later than the minimum in any of the individual forcings applied. Therefore the discrepancy between the timing of the modelled minimum and of the observed one might be related to the simplified evolution of the temperature and ozone changes applied, or the fact that some sources of variability (see below) are not taken into account. This might also explain the fact that the increased growth rate in 1994 is not captured in our simplified simulations.

By comparing the sum of the “Pinatubo all” and “Anthrop” curves to the growth rate evolution when including both Pinatubo forcings and changes in anthropogenic emissions, we find that the effect of nonlinearity on growth rates is less than 10%.

Since our study is an idealised sensitivity study, there are many possible reasons for differences between the modelled and the observed growth rate. Firstly, many processes known to determine CH<sub>4</sub> variability are not included here. These include changes in biomass burning emissions (Bousquet et al., 2006), isoprene emissions (Telford et al., 2010) and variability in wetland emissions due to atmospheric changes related to the El Niño Southern Oscillation (ENSO) cycle (Hodson et al., 2011). Secondly, differences may result from the different sampling of the model and the observations, as already mentioned in Sect. 3.1.2. The interpolation procedure used to obtain the observed global CH<sub>4</sub> growth rate curve can also smoothen out some sudden variations in the CH<sub>4</sub> growth rate, such as the jump due to the SO<sub>2</sub> injected by the eruption. Finally, there are uncertainties related to our model setup, on which we elaborate further below.

In order to show that our results are robust with respect to the parameters used in the model, a series of sensitivity tests was performed. We tested different temperature and water vapour profiles, a higher value for the CO yield from the oxidation of NMVOC, including NMVOC recycling, and increased vertical mixing. Although the effect on the modelled CH<sub>4</sub> concentrations in the last century may be on the order of 100 ppb (results not shown), the effect on the growth rate evolution after the eruption is less than 10%. Changing the temperature by -2.5 K to +1 K and simultaneously changing the water vapour profile according to the Clausius-Clapeyron equation lead to changes in the CH<sub>4</sub> growth rate results of less than 0.1 ppb yr<sup>-1</sup>. Similar results are obtained when changing the CO yield from NMVOC to 0.5 instead of 0.35, or when doubling the vertical mixing coefficients. Including a 0.25 yield of HO<sub>2</sub> from the oxidation of NMVOC in the presence of NO<sub>x</sub> leads to a higher growth rate minimum after the eruption by 0.3 ppb yr<sup>-1</sup>. We estimate therefore a maximum error of 10% in the modelled growth rate due to uncertainties in the model parameters.

Horizontal distributions of the modelled forcings can play an important role for the overall effect on the CH<sub>4</sub> growth rate, and cannot be simulated in our column model. This may cause additional uncertainties in our results. For example, we expect to overestimate the effect of SO<sub>2</sub>, by inferring an instant homogenisation of the emissions. In reality, high concentrations were found close to the emission point after the eruption, and the short lifetime of SO<sub>2</sub> limited this effect to low latitudes (Guo et al., 2004a). Changes in stratospheric aerosol, ozone and temperature have been observed globally, but with different magnitudes at different latitudes. Since CH<sub>4</sub> oxidation is more important in the tropics, processes that are relatively stronger in the tropics will have a higher impact on the CH<sub>4</sub> lifetime.

## 4 Conclusions

We have implemented a column chemistry model, and tested its performance in representing the mean state of the atmosphere. Although we acknowledge that our model is simplified and difficult to apply in a globally-averaged fashion, it allowed us to quantify for the first time the combined effect of radiation and temperature-related effects after the Pinatubo eruption on the CH<sub>4</sub> growth rate, including feedbacks on the CH<sub>4</sub> lifetime. The results show that full recovery of transient CH<sub>4</sub> concentrations from these perturbations takes about 40 yr.

Using this simple approach, we are able to explain a large part of the observed drop in CH<sub>4</sub> growth rate after the eruption of Pinatubo. We conclude that a multitude of emission and lifetime effects contributed to the observed growth rate variations following the eruption, as has been suggested by previous inverse modelling studies (Bousquet et al., 2006; Wang et al., 2004). We find that about 7 ppb yr<sup>-1</sup> of the observed 17 ppb yr<sup>-1</sup> can be explained by natural processes after the eruption. The dominating effects operate through tropospheric photolysis rates, with an important contribution from ozone depletion. This shows the importance of stratospheric-tropospheric couplings, and that a good representation of stratospheric chemistry is needed in order to model accurately CH<sub>4</sub> concentrations. We also find that the decrease in anthropogenic emissions between 1991 and 1993 contributed by 5 ppb yr<sup>-1</sup> to the decreased CH<sub>4</sub> growth rate in 1993. The remaining 5 ppb yr<sup>-1</sup> of the observed drop in CH<sub>4</sub> growth rate remains unexplained, and might be related to changes in emissions from biomass burning or changes in biogenic NMVOC emissions.

Our model has the advantage of simplicity; however, there are processes that cannot be represented, such as horizontal transport and changes in the dynamics of the atmosphere. Additionally, we did not consider the spatial distribution of CH<sub>4</sub> emissions. Using a global vegetation model would allow better estimates of the response of natural emissions to changes in temperature, precipitation and radiation. Therefore, a three dimensional chemistry transport model coupled with a climate model will be used to perform future experiments.

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