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The Drivers of Atmospheric Methane Fluctuations over the Last Three Decades

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THE DRIVERS OF ATMOSPHERIC METHANE FLUCTUATIONS OVER THE LAST THREE DECADES

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MSc in Applied Physics EPFL
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THE DRIVERS OF ATMOSPHERIC METHANE FLUCTUATIONS OVER
THE LAST THREE DECADES

A thesis submitted to attain the degree of
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presented by

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ABSTRACT

Understanding the processes behind the observed methane fluctuations over the last three decades is crucial for reliable projections of future levels of atmospheric methane, the second most important greenhouse gas. After a period of continuous increase, the methane growth rate decreased from about 12 ppbv/yr in the 1980s to about 6 ppbv/yr in the 1990s. From 1999 to 2006 atmospheric methane concentrations reached a plateau, but since 2007, methane is on the rise again. Measurements of the carbon isotopes of methane suggest that an isotopic light source of methane related to biogenic processes is responsible for the increase. Although general nature of sources and sinks of methane are well known, their relative contributions to methane fluctuations are still subject to scientific debate.

The goal of this thesis is to disentangle the roles of changes in methane sources and in the main tropospheric methane sink, the reaction with the hydroxyl radical (OH), in determining the observed methane variations over the last three decades. In addition to covering the last three decades, this work pays special attention to the time period after the volcanic eruption of Mount Pinatubo in 1991 and the observed rise after 2007. Global chemistry-climate models (CCMs) are an ideal tool to investigate the atmospheric methane cycle and its interactions with atmospheric chemistry and climate in a self-consistent way.

In the framework of this thesis, model simulations with the CCM SOCOL have been performed, using a unique model set up. In contrast to the common approach of using prescribed mixing ratios as lower boundary conditions for methane, CH$_4$ emission fluxes were applied in SOCOL, which has only been done by a limited number of CCMs so far. In order to track the methane emissions from various source categories such as anthropogenic activities or wetlands and from different geographical regions, 48 diagnostic tracers were implemented into the model. To ensure best comparability with observational data the model was forced with prescribed meteorological fields from reanalysis data. In order to further constrain the simulated methane budget, a methyl chloroform tracer, commonly used as a proxy for OH variations, as well as two stable carbon isotopes of methane, namely $^{12}$CH$_4$ and $^{13}$CH$_4$, were employed in SOCOL.

In order to investigate the methane variations over the last three decades, four transient model simulations combining two different data sets for anthropogenic emissions (EDGAR4.2 and SCHWIETZKE) with two data sets for wetland emissions (LPJ-WSL and SDGVM), respectively, were performed. EDGAR4.2 and SCHWIETZKE differ in the reported total amount and temporal evolution of methane emissions from fossil fuel production, with SCHWIETZKE data set showing a more pronounced decrease over Eurasia after 1991 and a less steep increase in Chinese emissions after 2001. With respect to CH$_4$ emissions from wetlands, SDGVM shows larger total emissions.
mainly due to higher emissions over Northern Hemisphere high latitudes. This is a first time that atmospheric methane variations were investigated by such a combination of emission inventories. The inter-comparison of these four simulations allows for a unique evaluation of the applied emission data sets.

The implemented tracer diagnostic highlights the role of various methane sources in different time periods: before 1991 increasing anthropogenic emissions from Europe, China, and India contribute 60% of the total growth rate. The fall of the Soviet Union in 1991 led to a strong reduction in methane emissions from fossil fuel production in Europe and Siberia between 1990 and 1992, which is found to be responsible for the reduction in methane growth rate in the early 1990s. Furthermore, the simulations indicate that the drop in methane growth rate in the early 1990s is better reproduced by EDGAR4.2 while it is overestimated when using the SCHWIETZKE data set. All four simulations show a negative contribution to the methane growth rate from anthropogenic emissions over Europe up to the end of the runs in 2010, despite encompassing different trends in anthropogenic methane emissions. This decline is responsible for the plateau between 1999 and 2006, compensating increasing anthropogenic emissions from China, Africa, and India. All four simulations overestimate the increase in atmospheric methane after 2007 due to an overestimation of methane emissions from coal mining in China reported by both anthropogenic emissions inventories, despite a reduced emission rate reported by SCHWIETZKE.

Moreover, the two process-based models for natural emissions show different range of total emissions and variability in CH₄. This thesis shows that SDGVM overestimates inter-annual variability of Northern Hemispheric wetland emissions before 1990. Furthermore, the SDGVM data set shows more pronounced year-to-year regional differences in methane emissions which however compensate each other on a global scale. This study suggests that methane lifetime decreased by 8% during this period, due to the increase of tropospheric OH. While most of the increase occurred before 1996, the last 10 years show stable levels of tropospheric OH consistent with methyl chloroform studies.

In parallel to the fall of the Soviet Union, the strong volcanic eruption of Mount Pinatubo, Philippines, took place in June 1991, affecting the tropospheric methane budget in several ways. Using SDGVM overestimates the impact of the volcanic eruption because of a strong reduction in CH₄ emissions in Boreal Northern Hemisphere. Sensitivity runs, performed in order to investigate the main impacts influenced by the volcanic eruption on tropospheric methane, using LPJ-WSL, suggest that over 70% of the methane decrease in the second year following the volcanic eruption is due to reduced wetland emissions. The main contribution comes from tropical South America, where the reduced emissions are in first place driven by negative precipitation anomalies and less by the general surface cooling. In addition, pronounced stratospheric ozone depletion caused by massive stratospheric aerosols of volcanic origin leads to an increase in tropospheric ozone photolysis rates by about 4% suggesting enhanced OH production. However, global tropospheric cooling of around 0.3 K in the second year after the volcanic eruption leads to a reduced tropospheric humidity by roughly
3% and a slow down of the reaction between CH₄ and OH by 0.5%, both effects compensating the enhanced UV levels.

The anthropogenic emissions inventories used in the simulations have been shown to overestimate the increase in methane concentrations after 2007. Using the implemented tracers as only diagnostics renders a clear attribution of this rise to specific sources and regions difficult. However, the implemented isotope tracers can be used as a further constraint. Applying a reduced emission rate for coal mining emissions in China leads to a better agreement with both a slower increase in methane concentrations and decreasing trend in δ¹³C. Indeed, the model suggests that Chinese emissions were in reality only as important as anthropogenic emissions in India or in South America. Together, increasing emissions from these regions overcompensate decreasing fossil fuel emissions, an isotopically heavy source, over Eurasia and Northern America, better represented in the 2000s by SCHWIEETZKE. As anthropogenic emissions over India and South America origin mainly from agriculture, an isotopically lighter source, both changes are consistent with the observed decrease in δ¹³C.

As shown in this thesis model results are highly sensitive to the applied emission data sets. The best agreement in terms of spatial distribution and temporal evolution is found for the combination of SCHWIEETZKE and LPJ-WSL. Reducing uncertainties in emission inventories is an important prerequisite for reliable model studies on past methane fluctuations and for a better knowledge of atmospheric processes and feedbacks determining the methane budget. This is of special importance since the climate feedbacks are expected to increase natural emissions from wetlands as well as from thawing permafrost within the upcoming decades, which can hardly be controlled by technical measures.

From this thesis past methane fluctuations over the last three decades are analyzed as a transition between a world dominated by increasing fossil fuel emissions until the fall of the Soviet Union, leading to a global slowdown of methane growth rate. However, nowadays, the increasing methane emissions in developing countries, mostly dominated by agriculture, make methane on the rise again. Reducing its global concentration is then not only an energetic question but also a change in human lifestyle.
RESUME

Le méthane de l’atmosphère - le deuxième gaz à effet de serre après le dioxyde de carbone - a fluctué au cours des trente dernières années. Comprendre le phénomène est crucial pour pouvoir établir des niveaux prédictifs de ce gaz. Après avoir augmenté de manière constante, le taux de croissance du méthane a diminué de 12 ppbv/an dans les années 1980 à 6 ppbv/an la décennie suivante. Entre 1999 et 2006, les concentrations atmosphériques de méthane ont atteint un plateau, mais augmentent à nouveau depuis 2007. L’analyse des isotopes de carbone semble indiquer que cette hausse du méthane est due à une source isotopique légère de gaz provenant de processus biologiques. Les sources et les puits de méthane sont bien connus, cependant leur contribution relative aux fluctuations de ce gaz dans l’atmosphère font toujours l’objet de vifs débats.

Le but de cette thèse est de démêler les différents effets observés dans les variations historiques de méthane, notamment le rôle des variations des sources de méthane et celui de la réaction avec le radical hydroxyde (OH), son principal puit dans la troposphère. La période après l’éruption volcanique du Mont Pinatubo en 1991 et la hausse de méthane en 2007 ont fait l’objet d’études plus approfondies. Les modèles chimique et climatique à l’échelle planétaire constituent un outil idéal pour étudier la cycle du méthane et ses interactions avec la chimique atmosphérique et le climat de manière autonome.

Des simulations, basées sur le modèle à résolution planétaire climatique et chimique SOCOL, ont été réalisées en utilisant un développement unique du modèle. A la différence d’une approche plus commune consistant à utiliser la concentration du méthane comme condition aux bords, les flux d’émissions du méthane ont été appliqués dans SOCOL. 48 traceurs diagnostiques ont été implémentés afin de pister les émissions de méthane provenant de différentes sources telles que les activités humaines et les marécages, et de différentes régions géographiques. Pour que les données d’observations puissent être comparées, des données météorologiques issues d’une combinaison d’observation et de modélisation ont été réintroduits dans le modèle. Et pour encadrer d’avantage la simulation, le methyl chloroforme - un traceur couramment utilisé comme un substitut pour les variations d’OH - et les deux isotopes de carbone, $^{12}CH_4$ et $^{13}CH_4$, ont été pris en compte dans SOCOL.

Quatre simulations combinant quatre sets de données, deux sets pour les émissions humaines (EDGAR4.2 and SCHWIETZKE) et l’autre pour les marécages (LPJ-WSL and SDGVM), ont permis d’étudier les variations de méthane sur les trente dernières années. EDGAR4.2 and SCHWIETZKE se différencient par la valeur totale des émissions de méthane mais aussi dans leur évolution temporelle, et plus particulièrement SCHWIETZKE reporte une diminution plus importante des émissions humaines en Eurasie après 1991 ainsi qu’une plus faible augmentation des émissions en Chine.


Les émissions de marécages basées sur des modèles montrent différentes valeurs totales d’émissions ainsi que une variabilité différente. Cette thèse montre que SDGVM surestime la variabilité inter-annuelle des émissions de marécages dans les hautes latitudes de l’hémisphère nord, avant 1990. De plus, SDGVM montre des différences régionales plus prononcées qui néanmoins se compensent entre elles à l’échelle mondiale.

Cette étude met en évidence que la durée de vie du méthane a diminué de 8% sur les trente dernières années à cause de la hausse d’OH troposphérique. Même si la hausse a eu lieu majoritairement avant 1996, les dix dernières années connaissent des niveaux stables d’OH troposphérique comme le montrent les analyses du methyl chloroforme.

La violente éruption volcanique du Mont Pinatubo (Philippines) a eu lieu en juin 1991 - au même moment que la chute de l’Union soviétique - perturbant le budget du méthane atmosphérique de plusieurs manières. SDGVM, par une forte diminution des émissions de marécages dans l’hémisphère nord, surestime l’impact de cette éruption volcanique. Des tests de sensibilité montrent que 70% de la baisse de méthane observée dans la deuxième année après l’éruption volcanique sont dus à la diminution du méthane provenant des marécages, essentiellement en Amérique du Sud, au niveau des tropiques. Cette diminution est le résultat d’anomalies négatives des précipitations dans la région après l’éruption. De plus, la perte en ozone stratosphérique causée par l’apport massif d’aérosols volcaniques dans la stratosphère entraîne une augmentation du taux de photolyse de l’ozone dans la troposphère de 4%, suggérant une augmentation d’OH. Cependant, un refroidissement mondial de la troposphère d’environ 0.3 K dans la deuxième année après l’éruption volcanique entraîne une ré-
duction de l’humidité troposphérique d’environ 3% et un ralentissement de la réaction entre CH₄ et OH par 0.5%, ces deux effets compensant l’augmentation des niveaux d’ultraviolet.
Les résultats obtenus dépendent beaucoup du set de données d’émissions qui a été utilisé. La plus réaliste des combinaisons est obtenue en utilisant SCHWIEZKE and LPJ-WSL. Il est donc important de réduire les incertitudes dans les rapports d’émissions pour étudier au mieux les fluctuations passées du méthane et pour mieux comprendre les processus atmosphériques qui expliquent le bilan de ce gaz. C’est d’autant plus important car les sursauts climatiques risquent d’augmenter les émissions marécageuses ainsi que la fonte du permafrost dans les décennies à venir. Ce qu’aucune intervention technologique ne parviendra à contrôler.
Cette thèse a démontré que les variations de méthane depuis les trois dernières décennies sont vues comme une transition entre un monde dominé par l’augmentation des émissions d’énergies fossiles jusqu’à la chute du bloc soviétique, amenant à un ralentissement général de la croissance du méthane. Cependant, actuellement, l’augmentation de ces émissions dans les pays en développement, principalement provenant du secteur agricole, sont les raisons de la nouvelle augmentation du méthane. Réduire sa concentration globale n’est donc pas seulement une question énergétique mais également demande un changement des modes de vie humains.
CONTENTS

1 INTRODUCTION .......................... 2

2 METHANE IN THE ATMOSPHERE ........... 7
   2.1 Methane sources and sinks ................. 7
      2.1.1 Methane sources .......................... 7
      2.1.2 Methane sinks .......................... 8
      2.1.3 Differences between bottom-up and top-down approach for evaluating the methane budget .......................... 9
   2.2 Methane in the atmospheric chemistry ...................... 10
   2.3 Impact of methane on climate ...................... 11
   2.4 Isotopic signature of the methane sources ...................... 12
   2.5 Atmospheric methane distribution ...................... 14

3 MODEL DESCRIPTION AND DEVELOPMENT ......... 16
   3.1 The CCM SOCOL version 3 ...................... 16
      3.1.1 Description ...................... 16
      3.1.2 Experimental set up ...................... 18
   3.2 The nudging technique ...................... 20
      3.2.1 Description ...................... 20
      3.2.2 Impact of the nudging on SOCOLv3 ...................... 20
   3.3 New parameterization of the nitric acid washout ...................... 27
      3.3.1 Description of the new parameterization ...................... 29
      3.3.2 Impact of the new parameterization ...................... 31

4 UNDERSTANDING METHANE VARIATIONS OVER THE LAST THREE DECADES USING A CHEMISTRY-CLIMATE MODEL .......................... 36
   4.1 Introduction ...................... 37
   4.2 Methodology ...................... 38
      4.2.1 Chemistry-climate model SOCOLv3 ...................... 38
      4.2.2 Methane tracers ...................... 38
      4.2.3 Performed simulations ...................... 40
      4.2.4 Anthropogenic emissions ...................... 41
      4.2.5 Wetland emissions ...................... 43
   4.3 Results and Discussion ...................... 44
      4.3.1 Tropospheric OH ...................... 44
      4.3.2 Methane variations for different time periods ...................... 46
      4.3.3 Variations in OH and methane lifetime ...................... 52
   4.4 Conclusions ...................... 53

5 IMPACT OF THE VOLCANIC ERUPTION OF MOUNT PINATUBO ON TROPOSPHERIC METHANE .......... 55
   5.1 Introduction ...................... 56
   5.2 Methodology ...................... 57
## CONTENTS

5.2.1 Chemistry-climate model SOCOLv3 ........................................ 57
5.2.2 Tracer diagnostics .......................................................... 58
5.2.3 Performed simulations ..................................................... 59
5.2.4 Wetlands emissions ......................................................... 60
5.3 Results and Discussion ........................................................ 61
  5.3.1 Comparison with observations ........................................ 61
  5.3.2 Change in methane emissions from wetlands .................... 63
  5.3.3 Change in tropospheric methane due to the decrease in methane emissions from wetlands ......................... 65
  5.3.4 Change in tropospheric methane due to OH ..................... 68
5.4 Conclusions ................................................................. 70

6 THE DRIVERS OF ATMOSPHERIC METHANE INCREASE SINCE 2007 72
  6.1 Introduction ............................................................... 73
  6.2 Methodology .............................................................. 74
    6.2.1 Chemistry-climate model SOCOLv3 .............................. 75
    6.2.2 Performed simulations ............................................. 76
  6.3 Results and Discussion .................................................. 77
  6.4 Conclusions ............................................................... 84

7 GENERAL CONCLUSIONS AND OUTLOOK 88
  7.1 General conclusions ........................................................ 88
  7.2 Outlook ................................................................. 91

A IMPACT OF THE MAINZ ISOPRENE MECHANISM (MIM-1) ON SOCOLv3 94
  A.1 Impact on Tropospheric OH ............................................. 94
  A.2 Impact on methane lifetime ............................................ 94
  A.3 Impact on OH inter-hemispheric ratio ............................... 94

B IMPACT OF THE NUDGING TECHNICS ON THE SIMULATED TEMPERATURE AND ZONAL WIND: ADDITIONAL MATERIAL 97
  B.1 DJF, MAM, and SON for the temperature ......................... 97
  B.2 DJF, MAM, and SON for the zonal wind .......................... 97

C VISUALIZATION OF THE TRACER DIAGNOSTICS 101

BIBLIOGRAPHY 103
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Methane concentrations at different time periods.</td>
<td>3</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematic of the global methane cycle.</td>
<td>8</td>
</tr>
<tr>
<td>2.2</td>
<td>Contribution of methane sources based on the Top-Down (a) and Bottom-Up (b) approach based on Ciais et al., 2013.</td>
<td>10</td>
</tr>
<tr>
<td>2.3</td>
<td>Radiative Forcing of different atmospheric species between 1750 and 2011.</td>
<td>11</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematic of the global methane cycle.</td>
<td>12</td>
</tr>
<tr>
<td>2.5</td>
<td>Isotopic signature of the different methane sources.</td>
<td>13</td>
</tr>
<tr>
<td>2.6</td>
<td>Global trend of observed $\delta^{13}$C from Global Atmospheric Watch (GAW) stations (green points). The yellow points show $\delta^{13}$C from historic spline (HS). The grey shading shows the 1-$\sigma$ confidence interval. Figure from Schafer et al. (2016).</td>
<td>14</td>
</tr>
<tr>
<td>2.7</td>
<td>Methane atmospheric distribution.</td>
<td>15</td>
</tr>
<tr>
<td>3.1</td>
<td>Description of SOCOLv3 used in this thesis.</td>
<td>17</td>
</tr>
<tr>
<td>3.2</td>
<td>Correlation in time for the temperature for a simulation when only half of the spectral resolution is nudged (T21).</td>
<td>21</td>
</tr>
<tr>
<td>3.3</td>
<td>Zonal mean temperatures for the JJA season averaged over 1980-1989.</td>
<td>22</td>
</tr>
<tr>
<td>3.4</td>
<td>Probability Density Function (PDF) for the absolute difference (in K) between the nudged simulation and ERA-Interim.</td>
<td>23</td>
</tr>
<tr>
<td>3.5</td>
<td>Anomalies (in K) of global averaged deseasonalized temperature compared to the 1980-1989 period at 250 hPa (top plot) and 750 hPa (bottom plot) for the nudged simulation (red lines), free simulation (blue lines) and ERA-Interim (black lines). A 12-month running average had been performed to the temperature.</td>
<td>24</td>
</tr>
<tr>
<td>3.6</td>
<td>Same as Figure 3.3 for the zonal wind (in m/s).</td>
<td>25</td>
</tr>
<tr>
<td>3.7</td>
<td>Tape recorder signal averaged over 1992-2001.</td>
<td>26</td>
</tr>
<tr>
<td>3.8</td>
<td>Phase Amplitude and Phase Lag based on Figure 3.7.</td>
<td>27</td>
</tr>
<tr>
<td>3.9</td>
<td>Zonal precipitation for DJF and JJA averaged over 1980-1989.</td>
<td>28</td>
</tr>
<tr>
<td>3.10</td>
<td>Annual average North Atlantic Oscillation signal.</td>
<td>29</td>
</tr>
<tr>
<td>3.11</td>
<td>Zonal mean of annually averaged HNO$_3$ concentration for the new and old parameterization of nitric acid washout.</td>
<td>32</td>
</tr>
<tr>
<td>3.12</td>
<td>Tropospheric column (in molec.cm$^{-2}$) of HNO$_3$ from the IASI satellite. Tropospheric column of nitric acid from SOCOLv3 with the old and the new scheme.</td>
<td>32</td>
</tr>
<tr>
<td>3.13</td>
<td>Different processes involved in the new nitric acid washout scheme.</td>
<td>33</td>
</tr>
<tr>
<td>3.14</td>
<td>Absolute difference of HNO$_3$ concentrations (in ppbv) averaged over 1985-1987 between NEW SCHEME and CLOUDS, NEW SCHEME and PRECIP, and NEW SCHEME and AEROSOLS.</td>
<td>34</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>3.15</td>
<td>Relative change in concentration for CH\textsubscript{4}, OH, HNO\textsubscript{3}, CO, NO, NO\textsubscript{2}, HO\textsubscript{2} and O\textsubscript{3} averaged over different latitudes and altitude bands.</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>Definition of the methane tracers.</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>Relative contribution of methane sources.</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>Anomalies in anthropogenic emissions.</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>Anomalies in CH\textsubscript{4} emissions from wetlands.</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>Differences between SDGVM and LPJ-WSL in CH\textsubscript{4} emissions from wetlands.</td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>Tropospheric OH concentration compared to ACCMIP.</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>MCF decay rate and anomalies.</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>Simulated global methane concentrations as well as its growth rate compared to observations between 1980 and 2010.</td>
<td></td>
</tr>
<tr>
<td>4.9</td>
<td>Yearly averaged methane growth rate for different latitude bands.</td>
<td></td>
</tr>
<tr>
<td>4.10</td>
<td>Tracer diagnostics for the performed simulations.</td>
<td></td>
</tr>
<tr>
<td>4.11</td>
<td>Time series of simulated tropospheric methane lifetime.</td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>Time series of deseasonalized partial ozone column between 100 hPa and 1 hPa averaged over 60\textdegree N to 60\textdegree S between 1991 and 1995.</td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>Time series of anomalies in deseasonalized temperature (K) averaged over 1000 hPa–500 hPa compared to the 1990-1995 mean.</td>
<td></td>
</tr>
<tr>
<td>5.3</td>
<td>Relative anomalies in wetland extent, precipitation, from GPCP, and CH\textsubscript{4} emissions from wetlands.</td>
<td></td>
</tr>
<tr>
<td>5.4</td>
<td>Relative anomalies (in %) in wetland extent, temperature (in K), and CH\textsubscript{4} emissions from wetlands for the North America Boreal region, Europe region, and Eurasia Boreal region.</td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>Global tropospheric methane burden up to 500 hPa for nine methane tracers as well as total methane for REF simulations, NOPIN simulations, and WET simulation.</td>
<td></td>
</tr>
<tr>
<td>5.6</td>
<td>Absolute difference between WET and NOPIN of tropospheric methane burden for the methane tracers based on wetland emissions in the second year following the volcanic eruption.</td>
<td></td>
</tr>
<tr>
<td>5.7</td>
<td>Time series of global tropospheric methane burden, water vapor mixing ratio, ozone photolysis rate and simulated temperature up to 500 hPa from 1991 to May 1993 for the NOPIN ensemble, AER, and SST ensembles.</td>
<td></td>
</tr>
<tr>
<td>6.1</td>
<td>Relative change in methane concentration (in %) between the average over the years 2008-2010 and 2001-2003 for the various SOCOLv3 simulations.</td>
<td></td>
</tr>
<tr>
<td>6.2</td>
<td>Tracer diagnostics for the eight selected locations.</td>
<td></td>
</tr>
<tr>
<td>6.3</td>
<td>Simulated (colored lines) and observed (black lines) $\delta^{13}$C for the eight locations.</td>
<td></td>
</tr>
<tr>
<td>6.4</td>
<td>Calculated $\delta^{13}$C of the sources for different simulations.</td>
<td></td>
</tr>
<tr>
<td>Figure 6.5</td>
<td>Sum of emissions (in Tg/yr) for the 2001-2003 period and the 2008-2010 period for EDGAR4.2 and SCHWIETZKE for nine regions defined from the methane tracking.</td>
<td>83</td>
</tr>
<tr>
<td>Figure 7.1</td>
<td>Simulations performed with the FLEXPART Lagrangian model.</td>
<td>93</td>
</tr>
<tr>
<td>Figure A.1</td>
<td>Airmass-weighted average tropospheric OH.</td>
<td>95</td>
</tr>
<tr>
<td>Figure A.2</td>
<td>Same as A.1 but for tropospheric methane lifetime.</td>
<td>95</td>
</tr>
<tr>
<td>Figure A.3</td>
<td>Same as A.1 but for OH inter-hemispheric (Northern hemisphere versus southern hemisphere) ratio.</td>
<td>96</td>
</tr>
<tr>
<td>Figure B.1</td>
<td>Zonal mean temperature (in K) averaged over the DJF season.</td>
<td>97</td>
</tr>
<tr>
<td>Figure B.2</td>
<td>Same as Figure B.1 for MAM.</td>
<td>98</td>
</tr>
<tr>
<td>Figure B.3</td>
<td>Same as Figure B.1 for SON.</td>
<td>98</td>
</tr>
<tr>
<td>Figure B.4</td>
<td>Zonal wind (in m/s) averaged over the DJF season for the 1980-1989.</td>
<td>99</td>
</tr>
<tr>
<td>Figure B.5</td>
<td>Same as B.4 for MAM.</td>
<td>99</td>
</tr>
<tr>
<td>Figure B.6</td>
<td>Same as B.4 for SON.</td>
<td>100</td>
</tr>
<tr>
<td>Figure C.1</td>
<td>Methane concentrations at the surface (in ppbv) for total methane as well as three tracers, averaged over 200-2009.</td>
<td>101</td>
</tr>
<tr>
<td>Figure C.2</td>
<td>Global methane concentration at the surface (in ppbv) for total methane as well as the sum of the methane tracers.</td>
<td>102</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 1.1 Main Effects of the Mount Pinatubo volcanic eruption on tropospheric methane. + means an increase in tropospheric methane concentration and - a decrease. This table is based on the PhD thesis from Narcissa Bândă from University of Krol (the Netherlands). .................................................. 4

Table 3.1 Description of the boundary conditions used for the performed simulations ........................................................... 18

Table 3.2 Performed simulations for the evaluation of the nitric acid washout new parameterization. .............................................. 31

Table 4.1 Summary of applied methane emission fluxes by source type. .............................................................. 39

Table 5.1 Performed simulations for the time period 1990-1995. Each type of simulation is a 5 members ensemble of runs. .............. 59

Table 5.2 Summary of the source categories of emissions used as input for the methane boundary conditions in the simulations run by SOCOLv3. .............................................................. 60

Table 6.1 Summary of applied methane emission fluxes by source type. .............................................................. 74

Table 6.2 Isotopic signature of methane sources as well as the sink fractionation of $^{13}$CH$_4$ ............................................................. 76

Table 6.3 Description of the selected locations depending on their geographical situation in order to get different influences in methane variability .............................................................. 86
### ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACCMIP</td>
<td>Atmospheric Chemistry and Climate Model Intercomparison Project</td>
</tr>
<tr>
<td>CCM</td>
<td>Chemistry-Climate Model</td>
</tr>
<tr>
<td>CFC</td>
<td>Chlorofluorocarbon</td>
</tr>
<tr>
<td>CTM</td>
<td>Chemistry-Transport Model</td>
</tr>
<tr>
<td>ECHAM</td>
<td>European Centre Hamburg Model</td>
</tr>
<tr>
<td>ENSO</td>
<td>El-Niño Southern Oscillation</td>
</tr>
<tr>
<td>FLEXPART</td>
<td>FLEXible PARTicle dispersion model</td>
</tr>
<tr>
<td>GCM</td>
<td>General Circulation Model</td>
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<tr>
<td>GHG</td>
<td>Greenhouse Gas</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>LW</td>
<td>Long Wave</td>
</tr>
<tr>
<td>MCF</td>
<td>methyl chloroform</td>
</tr>
<tr>
<td>MEZON</td>
<td>Model for Evaluation of OZone trends</td>
</tr>
<tr>
<td>NH</td>
<td>Northern Hemisphere</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion. ppbv: parts per billion by volume</td>
</tr>
<tr>
<td>RF</td>
<td>Radiative Forcing</td>
</tr>
<tr>
<td>SH</td>
<td>Southern Hemisphere</td>
</tr>
<tr>
<td>SOCOL</td>
<td>modeling tools for studies of SOlar Climate Ozone Links</td>
</tr>
<tr>
<td>SST</td>
<td>Sea Surface Temperature</td>
</tr>
<tr>
<td>SW</td>
<td>Short Wave</td>
</tr>
<tr>
<td>WETCHIMP</td>
<td>WETland and wetland CH$_4$ Inter-Comparison of Models Project</td>
</tr>
</tbody>
</table>
INTRODUCTION

Human activities led to a general increase of greenhouse gases (GHGs) since the industrial revolution in the mid-18th century, which is extremely likely to be the cause of observed warming since the mid-20th century (IPCC, 2013 [70]). Understanding our climate has since become a challenging research area. The recent United Nations conference on climate change in Paris (COP 21), in December 2015, ended with a global agreement among the 195 countries to limit global warming to 2°C by the end of the century compared to pre-industrial levels. It can be only achieved by an immediate reduction in greenhouse gas emissions. Large attention has previously been given to carbon dioxide (CO2). Methane (CH4), the second most important GHG in terms of radiative forcing (Myhre et al., 2013 [93]), became in the recent years a major field of investigation. Its past fluctuations over the last three decades show a global not constant increase which remains unknown and needs to be better understood for predicting future methane levels and its impact on the climate. The aim of this thesis is to investigate in detailed methane past fluctuations over the last three decades. Ice cores observations (Etheridge et al., 1992 [45]) as well as surface based measurements (Dlugokencky et al., 1994 [32]; 1995 [38]; 1996 [33]; 1997 [34]; 1998 [35]; 2001 [36]; 2003 [37]; 2009 [30]) show a substantial increase in methane levels since 1850: from 830 parts per billion (ppb) to 1843 ppb today, unprecedented levels in the last 650,000 years (Spahni et al., 2005 [132]). This rise in CH4 is mainly due to stronger intensive farming as well as coal extraction, gas and oil production. Methane concentrations for different time periods are shown in Figure 1.1. Besides its direct GHG effect, methane indirectly has a positive climate change feedback via the formation of stratospheric water vapor and ozone, two other GHGs. Furthermore, methane reacts with the hydroxyl radical OH (the “cleaning agent”, responsible for reacting with atmospheric pollutants), which is methane’s main sink in the troposphere. A strong increase in methane concentrations, therefore, decreases the abundance of OH, leading to an increase in methane lifetime: its impact on climate becomes stronger. This relationship between OH and CH4 constitutes a key factor both for air quality and climate change. With a rather short 9-year atmospheric lifetime (Prather et al., 2012 [101]), methane is a good candidate for mitigating global warming for the next century. The last three decades show substantial fluctuations in methane (Figure 1.1c). A continuous global increase in methane is observed, increasing since 1984 at 12 ppbv/year, followed by a slowdown in the 1990s (6 ppbv/year), and a stabilization period from 1999 to 2006. Since 2007, methane has started increasing again (Rigby et al., 2008 [112]). The contribution of the various sources and sinks to the observed CH4 variations during this period is still under investigation. Declining fossil fuel emissions is the “most likely” reason to the decline in methane growth rate after 1991 (Dlugokencky et al., 1994 [32]). Decline in ethane, another atmospheric hydrocarbon, was also observed
via firn air measurements after the mid-1980s. As ethane and methane share the same fossil fuel emissions, an ethane/methane analogy estimates a decline in CH$_4$ fossil fuel emissions between 1980 and 2010 (Aydin et al., 2011 [5]; Simpson et al., 2012 [128]). Worthy et al. (2009) [152] inferred decreasing anthropogenic emissions in Europe and Siberia twice larger than previously reported from simulating methane concentration in Alert, Canada, from 1987 onwards.

In addition to the collapse of the Soviet Union, the volcanic eruption of Mount Pinatubo induced a massive injection of sulfur into the stratosphere (100 times higher than the average), increasing sulfate aerosols concentration, having an impact both on climate and atmospheric chemistry. Volcanic aerosols led to an enhanced scattering of short wave (SW) radiation by sulfate particles in the first year after the eruption (Bender et al., 2010 [11]). Furthermore, a cooling of the global temperature in the following
Table 1.1: Main Effects of the Mount Pinatubo volcanic eruption on tropospheric methane. + means an increase in tropospheric methane concentration and - a decrease. This table is based on the PhD thesis from Narcissa Bândă from University of Krol (the Netherlands).

<table>
<thead>
<tr>
<th>Processes</th>
<th>Impact on tropospheric methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV absorption by SO$_2$</td>
<td>+</td>
</tr>
<tr>
<td>UV scattering by sulfate aerosols</td>
<td>+</td>
</tr>
<tr>
<td>Stratospheric ozone depletion</td>
<td>-</td>
</tr>
<tr>
<td>Temperature effect on CH$_4$ + OH reaction rate</td>
<td>+</td>
</tr>
<tr>
<td>Water vapor decrease</td>
<td>+</td>
</tr>
<tr>
<td>Temperature effect on wetland emissions</td>
<td>-</td>
</tr>
</tbody>
</table>

two years was observed, more pronounced in the upper troposphere: a decrease of 0.3-0.45 K was measured at the surface and 0.6-0.8 K in the lower troposphere due to the volcanic eruption (Santer et al., 2001 [117]). Stratospheric ozone also suffered from this volcanic eruption: an increase of ozone transported from the tropics towards high-latitudes because of enhanced stratospheric heating because of the long wave (LW) radiation absorption by the sulfate particles (Aquila et al., 2013 [3]); but also an enhanced stratospheric ozone depletion via heterogeneous conversion of N$_2$O$_5$ to HNO$_3$, therefore less stratospheric NO$_2$, leading to more ozone destroyed by chlorine. Tropospheric methane was impacted by this eruption via different processes: the cooling of temperature leading to a slow down of the reaction rate between CH$_4$ and OH and a decrease in tropospheric water vapor column (3% observed, Soden et al., 2002 [129]), but also a decrease in CH$_4$ emissions from wetlands. The changes in UV radiation reaching the troposphere triggered by the stratospheric ozone depletion and the enhanced scattering by volcanic SO$_2$ also have an impact on tropospheric methane lifetime. The relative contribution of the different processes remains unclear (Dlugokencky et al., 1996 [33]; Bekki and Law 1997 [9]; Wang et al., 2004 [144]; Bousquet et al., 2006 [15]; Bândă et al., 2013 [6]; 2015 [8]; 2016 [7]). The different effects ant their impacts are summarized in Table 1.1.

The plateau in methane levels was also investigated. Using carbon isotopes (as methane can also be emitted as $^{13}$CH$_4$ with various importance depending on the source), this plateau was impacted as a result of reduced microbial production from rice emissions in Asia in Kai et al. (2011) [72]. However it had not been confirmed by the isotopic study including more observations sites than only one site over continental mountain station in the United States as representative of the entire Northern Hemisphere in Levin et al. (2012) [81]. The ratio of the contribution from natural wetland emissions and anthropogenic emissions is crucial to understand the methane variations since 2000 (Wang et al., 2004 [144]; Bousquet et al., 2006 [15]; 2011 [16]; Pison et al., 2013 [100]; Kirschke et al., 2013 [73]; Nisbet et al., 2014 [96]; Ghosh et al., 2015 [55]). The rise in atmospheric methane levels after 2007 is inferred to natural emissions from isotopic measurements, either from wetlands (Nisbet et al., 2014 [96]) or agriculture
(enteric fermentation from cows mainly, Schaefer et al., 2016 [119]), or a combination of increasing wetland and fossil fuel emissions but with unknown relative contribution (Kirschke et al, 2013 [73]).

In addition to the impact of the sources, the contribution of the sinks, and mainly OH, needs also to be better understood. Fiore et al. (2006) [52] estimated a decrease in methane lifetime by 2% between 1990 and 2004 due to increasing tropospheric OH concentrations. The factors driving this change remains unknown: increase in tropospheric water vapor mixing ratio (Dentener et al., 2003 [29]); increasing NOx (NO + NO2) emissions especially from Southeast Asia; and trends in photolysis rates (Wang et al., 2004 [144]). Using proxy tracers for global OH variations, long-term changes in OH were found to be small between 1998 to 2007 (Prinn et al., 2005 [103]; Montzka et al., 2011 [91]). An decrease in OH by 4% ± 14% was found in 2007 using modeling (Rigby et al., 2008 [112]), but not significant to explain the increase in methane.

In 1997-98, a strong El-Niño Southern Oscillation (ENSO) occurred. ENSO is a prolonged warming in the Eastern Pacific Ocean sea surface temperatures. This event led to a dry year, responsible for increasing wildfire emissions mainly over South East Asia in 1997 (Dlugokencky et al., 2001 [36]; Van der Werf et al., 2004 [139]; Bousquet et al., 2006 [15]), followed by wet and warm global conditions. Warmer as well as drier conditions are also expected to have an impact on methane emissions from wetlands, but globally compensated via a decrease in northern hemisphere regions and an increase in tropical emissions in 1997-98 (Bousquet et al., 2006 [15]). A possible decrease in OH concentration also took place, because of large emissions of carbon monoxide and other reactive carbon compounds via the enhanced wild fire emissions, as these species react with OH (Bousquet et al., 2006 [15]).

Former global model studies investigating methane fluctuations were performed on Chemistry-Transport Models (CTMs) (Fiore et al., 2006 [52]; Bândă et al., 2016 [7]), or with tropospheric General Circulation Models (GCMs) (Harder et al., 2007 [61]). These types of studies are driven by meteorological fields but do not consider feedback between circulation and atmospheric chemistry. Another tool is a Chemistry-Climate Model (CCM). However, recent studies performed with this type of model use prescribed mixing ratios for methane, without methane surface fluxes (Eyring et al., 2006 [50]; 2007 [48]; 2010 [49]; as well as the ACCMIP studies: Naik et al., 2013 [94]; Voulgarakis et al., 2013 [141]). The full methane cycle, including methane emissions reacting with interactive OH, is not simulated. There is a need to simulate the methane cycle to better represent methane fluctuations and, therefore, attribute the contribution of the different methane sources and sinks. Using CCMs also provide a useful tool to perform sensitivity simulations to investigate the influence of one specific driver, or study the sensitivity of the species to its emissions, by simulating different datasets. This is the approach done in this thesis with the CCM SOCOLv3 (Stenke et al., 2013 [134]).

The following questions are addressed by this thesis:

- Which processes are responsible for the observed CH4 variations over the last three decades?
• A specific event from the last three decades was the volcanic eruption of the Mount Pinatubo in June 1991. How did this strong eruption affect tropospheric methane?

• Observations of methane isotopes have become nowadays a standard tool to study methane fluctuations. How do simulated methane isotopes compare with observations? Moreover, can it be used to retrieve the driving factors of increasing methane after 2007 where isotopic studies show a global enrichment in methane from natural sources?

This thesis consists of 7 chapters. A background of atmospheric methane is given in Chapter 2. The description of the CCM SOCOLv3, the experimental set up, as well as an explanation of its development, is found in Chapter 3. Methane fluctuations over the last three decades is investigated via four different simulations performed with SOCOLv3 using different data to represent methane from anthropogenic emissions, as well as wetland sources (Chapter 4). The case study of Mount Pinatubo is detailed in Chapter 5 where sensitivity simulations are performed with SOCOLv3 to quantify the impact of wetlands emissions, as well as tropospheric OH on methane after the volcanic eruption. The study of the increase in methane after 2007 with an implemented isotope diagnostic for methane is given in Chapter 6. A summary of the thesis as well as ideas for possible research questions, as follow-up to this thesis, are presented in Chapter 7.
METHANE IN THE ATMOSPHERE

Methane (CH\textsubscript{4}) is a powerful greenhouse gas, representing however only 0.00018% of the atmospheric composition in volume. It appeared in early Earth’s history via release from a strong volcanic activity. About 3.5 billion years ago, atmospheric methane levels were 1000 times higher than present days concentrations. The appearance of cyanobacteria 2.7 billion years ago was also a source of methane, influenced by the origin of oxygen about 2 billion years ago, changing the methane cycle via its oxidation. The release of methane via natural emissions and its sink by the chemical reaction with OH, balanced methane levels until the preindustrial era. Since 1750, the rise of intensive farming, coal extraction, gas and oil production hastened to large quantities of methane and therefore increasing levels of CH\textsubscript{4} concentration. This section describes the methane in the atmosphere: its sources, its sinks as well as its impact on climate.

2.1 METHANE SOURCES AND SINKS

2.1.1 Methane sources

Methane is not formed in the atmosphere, but only emitted at the surface. Overall, slightly less than half of the emissions come from anthropogenic sources (46%) (Ciais et al., 2013 [23]). However, this number depends on the estimation technique (Ciais et al., 2013 [23]): here, the values are taken from the top-down approach averaged over 2000-2009 (see section 2.1.3). Natural emissions of fossil methane from geological sources, escaping from marine and land surface (geological gas seepage) or from land or submarine mud volcanoes represent a small part of total emissions (8%). On the other hand, human activities are responsible for 14% of emissions simply from the extraction of fossil fuel (coal and oil). Methane is also emitted via incomplete burning of fossil fuel (anthropogenic source) and plant biomass (natural source), both of which represent a small fraction of the emissions (6% in total).
Methanogenic bacteria generate methane by transforming organic matter into carbon dioxide and methane under anaerobic conditions (absence of oxygen). Wetlands are the main contributor of natural methane emissions from biogenic sources (32% of the total emissions and 63% of the natural emissions). Other natural emissions come from termites, wild animals and ocean hydrates (roughly 5%). Rice paddy agriculture, ruminant livestock, landfills, and waste management represent the anthropogenic part of these biogenic sources (29%). Improving technology led to modern landfill sites
2.1 Methane Sources and Sinks

Figure 2.1: Schematic of the global methane cycle. The values represent annual fluxes in Tg(CH$_4$)/year estimated for the 2000-2009 decade. Black arrows denote natural fluxes, red arrows anthropogenic fluxes and brown arrow a combined "natural and anthropogenic" fluxes (Ciais et al., 2013 [23]).

using impermeable liners and a capping layer to control the movement of the gas, which may then be collected, but still not sufficient enough to avoid emissions of methane. Freshwater emissions complete the natural emissions (6%)

2.1.2 Methane sinks

After being emitted, methane is chemically removed from the atmosphere. The main sink is tropospheric OH, which accounts for 87% of the total loss (Ciais et al., 2013 [23]). Furthermore, methane is removed via chemical reaction with chlorine in the stratosphere (8%) and stratospheric OH (5%). The atmospheric lifetime of a gas is defined by the ratio of the burden (Tg) to the mean global sink (Tg/year), at steady state (Bolin and Rhode, 1973 [14]). Methane lifetime with respect to tropospheric OH
is estimated at 11.2 ± 1.3 years. The lifetime of methane with respect to its other sinks is estimated at 120 ± 24 years for uptake by soils, 150 ± 50 years for stratospheric losses. Overall methane lifetime is then calculated using the full range of each separate lifetime and a value 9.25 years ± 0.6 years is estimated (Myhre et al., 2013 [93]).

2.1.3 Differences between bottom-up and top-down approach for evaluating the methane budget

Figure 2.2 summarizes the estimates in methane emissions for bottom-up and top-down approaches. These different methods show substantial differences in estimating both methane sources and sinks. For the 2000-2009 decade, the bottom-up approach estimates total methane emissions at 678 Tg/yr, in comparison to the 548 Tg/yr evaluated from the top-down approach. The main difference comes from the evaluation of natural emissions: 218 Tg/yr for the top-down and 347 Tg/yr for the bottom-up, averaged over the different studies taken into account in Ciais et al. (2013) [23].

The bottom-up approach is based on emission inventories. For anthropogenic sources, emissions are calculated for different sources via reports on flux measurements. For example, countries estimate the emissions from ruminants after measuring the emissions from a single ruminant and reporting the total number of ruminants. Bottom-up estimates of natural emissions includes process-based model (Kirchke et al., 2013 [73]). On the other hand, methane emissions can be retrieved from model inversions (top-down approach), i.e which emissions fit the best the atmospheric observations with a specific atmospheric transport model, including chemistry, prior estimates and their uncertainties (Kirchke et al., 2013 [73]). The treatment of OH in inverse models is crucial in order to retrieve methane emissions. As OH is the main sink of methane, a change in OH concentration has a direct impact on methane. However, OH is a very short lived species (lifetime of about 1 sec) and, therefore, it becomes difficult to observe global OH levels with high precision: its measurements on local scales cannot be used as approximation for global scales. OH can instead be taken from CCMs, or by modeling estimates using observations of ozone, H2O, [NO2 + NO + 2N2O5 + NO3 + HNO2 +HNO4], CO, hydrocarbons, temperature, and cloud optical depth (Spivakovsky et al., 2000 [133]). Large differences in OH exist among the CCMs (Naik et al., 2013 [94]), but an increase in tropospheric OH over the last three decades between 2% and 8 % is found (Fiore et al., 2006 [52]; Naik et al., 2013 [94]; Dalsoren et al., 2015 [27]). Observations of indirect species are used to derive OH variations, such as methyl chloroform (MCF). MCF was first used as a less toxic agent with emissions detected globally after 1974 (Lovelock et al., 1977 [83]). Its emissions decreased tremendously after the ratification of the Montreal Protocol on substances depleting ozone in 1987. Emission rates decreased rapidly at a low level since 1997 (around 10 Gg/year, McCulloch and Midgley, 2001 [87]). As natural emissions can be excluded (Krol and Lelieveld, 2003 [77]), and with a lifetime of approximatively 5 years (Prinn et al., 2005 [103]), the variations in MCF are impacted by its main sink OH. Therefore, global MCF observations gives a good indication of OH fluctuations after 1998, when
global emissions are not considered significant for MCF variations. These studies do not show large changes in OH after 1998 (Prinn et al., 2005 [103]; Montzka et al., 2011 [91]).

2.2 M ETHANE I N THE ATMOSPHERIC CHEMISTRY

Tropospheric methane reacts with OH in the troposphere, leading to the formation of CO$_2$ at the end of the oxidation chain (Fig. 2.3). This is part of the climate feedback of methane: an increase in methane levels lead to enhanced warming via its GHG effect but also indirectly via the CO$_2$ formation. The cycle starts with the reaction between CH$_4$ and OH.

$$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$$
Figure 2.3 shows different pathways for the methane oxidation chain, depending on NOx concentration. The nitrogen dioxide molecule formed is responsible for ozone production via its photolysis. The available oxygen atom then reacts with O2 to create ozone. Ozone photolysis is the primary source of tropospheric OH:

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad (\lambda < 320\text{nm})$$

OH is secondarily formed via the reaction between HO2 and NO, controlled by the formation of nitric acid (HNO3) via the reaction between OH and NO2. Nitric acid can be removed from the lower atmosphere via wet deposition.

CH3O2 can also react with HO2 to form methyl hydroperoxide, CH3OOH. It can further react with OH to form a catalytic cycle for the removal of OH and HO2, or create formaldehyde, HCHO, a first generation oxidation product of CH4 and many other hydrocarbons.

Each molecule of methane creates then a formaldehyde, leading to the formation of CO. Formaldehyde reacts via its photolysis or reaction with OH (Figure 2.3). Or CO reacts with OH as well to form CO2, the end product of methane oxidation.

The reaction of methane with Cl, occurring in the stratosphere, also create the methyl radical as well as the reservoir species hydrochloric acid (HCl). The increase with height in water vapor abundance observed in the stratosphere can be qualitatively explain by methane chemical destruction with OH (Brasseur and Solomon, 2006 [17]).

### 2.3 Impact of Methane on Climate

Methane is a greenhouse gas with a Global Warming Potential (GWP) 28 times higher than CO2 over a 100 years time horizon, or in other words, one tonne of methane is equivalent to 28 tonnes of carbon dioxide. With its increased concentration since pre-industrial times, methane has become the second most important GHG in terms of
2.4 Isotopic signature of the methane sources

The isotopic ratio of methane depends on its emission source. Specifically, the stable carbon isotope $^{13}\text{CH}_4$ can tell us about the type of source that led to an increase in $\text{CH}_4$, mainly after 2007 where observations of the isotopic ratio, $^{13}\text{CH}_4/^{12}\text{CH}_4$, show a global decrease indicating an increase in a biogenic source of methane, such as wetlands (Nisbet et al., 2014 [96]) (Fig. 2.6).

Depending on its sources, methane can be emitted with a larger or smaller ratio of its isotopes: mainly $^{13}\text{CH}_4$ and $\text{CH}_3\text{D}$. As the differences in isotopologue masses is small, it is often described as a ratio between the isotope and the standard methane.
molecule. For the stable carbon isotope $^{13}$C, it is defined as $\delta^{13}$C and its is calculated as follows:

$$\delta^{13}\text{C} = \left( \frac{^{13}\text{C}_{\text{sample}}}{^{12}\text{C}_{\text{sample}}} - 1 \right) \times 1000\%$$  \hspace{1cm} (1)

where the standard is defined as the isotopic ratio of Vienna Pee-Dee belemnite (PDB) (de Laeter et al., 2003 [156]). PDB was a fossil calcium carbonate from the Pee Dee formation in South Carolina, but the original material became exhausted decades ago (Gros et al., 2004 [58]). The same formula is used to evaluate $\delta$D, but relative to the Vienna Standard Mean Ocean Water (VSMOW).

Figure 2.5 summarizes the isotopic signature of different methane sources. Three main categories can be distinguished from this figure, based on $\delta^{13}$C: biogenic emissions, defined by rice paddies, wetlands, and ruminants in Fig. 2.5 (-55‰ to -70‰), thermogenic emissions, found as natural gas and coal mining in Fig. 2.5 (-25‰ to -55‰), and
pyrogenic emissions, biomass burning in Fig. 2.5 (~13‰ to -25‰). The categories come from the different pathways to produce methane. Biogenic emissions have two stage process. First bacteria produce methane via CO₂ reduction, or acetate fermentation, leading to methane depleted in ¹³C or D, respectively -170 to -250‰ for δD or -60 to 110‰ for δ¹³C, and less than -250‰ for δD and -50 to -65‰ for δ¹³C via the acetate fermentation (Gros et al., 2004). Before methane is released to the atmosphere, it is oxidized, which leads to a slightly enriched methane in ¹³C. Pyrogenic sources, mainly coming from biomass burning, show the smallest depletion in ¹³C, first due to a preferential selection of ¹²C from vegetation and the primary combustion of light hydrocarbons. The biogenic source shows the greatest depletion and thermogenic sources (comprising most of the fossil fuel emissions) the least depletion in ¹³C. ¹³CH₄ and ¹²CH₄ also differ as a result of the reaction with OH. The reaction rate between ¹²CH₄ methane and OH is about 0.5% faster than with ¹³CH₄ (Saueressig et al., 2001 [118]).

Figure 2.6: Global trend of observed δ¹³C from Global Atmospheric Watch (GAW) stations (green points). The yellow points show δ¹³C from historic spline. The grey shading shows the 1-σconfidence interval. Figure from Schafer et al. (2016).

2.5 ATMOSPHERIC METHANE DISTRIBUTION

With a lifetime of about a decade, methane emitted from the surface and is mixed in the troposphere. Therefore, local emissions have a global impact on methane variations. Methane has a higher concentration at the surface in the northern hemisphere,
where most emissions occur (Figure 2.7 a)). Because of its lifetime of around 10 years, methane does not significantly decrease with altitude and is well mixed in the troposphere. Decreasing temperature increases methane lifetime with altitude (observed as higher concentrations around 200 hPa in Figure 2.7). In higher altitudes, in the stratosphere, methane is also chemically removed mainly via its reaction with chlorine. Its reaction with the hydroxyl radical is leading to stratospheric water vapor formation, which is a positive climate change feedback, as water vapor is a GHG.
3.1 THE CCM SOCOL VERSION 3

3.1.1 Description

This thesis is based on the Chemistry-Climate Model SOCOLv3 (Figure 3.1). A detailed description is given in Stenke et al. (2013) [134]. It is based on the Middle Atmosphere General Circulation Model MA-ECHAM version 5.4 (Roeckner et al., 2003 [114]; Manzini et al., 2006 [84]) coupled to the chemical module of the CTM MEZON (Model for Evaluation of oZONe trends; Rozanov et al., 1999 [116], 2001 [115]; Egorova et al., 2001 [42], 2003 [41]; Hoyle, 2005 [69]; Schraner et al., 2008 [121]). The coupling is interactive by using the 3-dimensional fields of temperature and wind as well as the radiative forcing induced by water vapor, ozone, methane, nitrous oxide, and CFCs (chlorofluorocarbons). The dynamical time step is 15 minutes, also used for physical parameterizations, while the chemical scheme is only called every 2 hours for computational efficiency.

The GCM ECHAM5 was developed at the Max-Planck-Institute for Meteorology in Hamburg. It is a spectral general circulation model based on primitive equations with the prognostic variables temperature, vorticity, divergence, logarithm of surface pressure, humidity and cloud water. The advection of water vapor, cloud variables as well as chemical species is done via a flux-based mass-converting and shape-preserving transport scheme (Lin and Rood, 1996 [82]). The shortwave radiation considers 6 bands in the UV-visible range (180-250 nm; 250-440 nm; 440-690 nm) and near-IR range (690-1190 nm; 1190-2380 nm; 2380-4000 nm) (Cagnazzo et al., 2007 [20]). 16 bands are used for the longwave radiation. The full radiative transfer is calculated every 2h. The longwave fluxes are kept constant between two radiative calls while the shortwave fluxes are updated every 15 min (the dynamical time step) in order to take into account changes in the solar zenith angle (Stenke et al., 2013 [134]). MEZON considers 41 chemical species of the oxygen, hydrogen, nitrogen, chlorine and bromine groups. The chemical solver uses a Newton-Raphson iterative method. 140 gas phase reactions as well as 16 (stratospheric) heterogeneous reactions in/on aqueous sulfuric acid aerosols are represented in MEZON as well as three types of polar stratospheric clouds (PSCs).

Previous and current versions of SOCOLv3 show high levels of OH compared to other CCMs (see Appendix A and Chapter 4). OH is considered as the “oxidizing agent” of the atmosphere, reacting with various pollutants: methane, carbon monoxide (CO) as well as other Non-Methane Volatile Organic Compounds (NMVOCs). Previous model versions only included its reactions with methane and carbon monoxide (CO), leading to high OH concentrations, high ozone levels and low CO abundances. In order
to have a better representation of tropospheric chemistry, the Mainz Isoprene Mechanism MIM-1 was implemented into SOCOLv3 to take into account isoprene (C₅H₈), another hydrocarbon. The MIM comprises 16 organic species (degradation products of isoprene) as well as 44 chemical reactions (Poeschl et al., 2000 [104]). A description of the impact of this oxidation mechanism can be found in Appendix A. Moreover, a fraction of emissions of Non-Methane Volatile Organic Compound (NMVOC) is directly added to CO: 1.0 for anthropogenic, 0.31 for biomass burning and 0.31 for biogenic emissions of NMVOC is converted to CO. The impact of clouds on photolysis rates is taken into account by including a cloud modification factor, following Chang et al. (1987) [21].

SOCOLv3 is the first version of the SOCOL model that can be run in parallel mode. For this thesis simulations are carried out on the Euler cluster (“Erweiterbarer Umweltfreundlicher Leistungsfähiger ETH Rechner”) at the ETHZ. It is located at the CSCS data center in Locarno. Euler consists in 416 compute nodes from Hewlett-Packard connected via a high-speed InfiniBand FDR network. Each node contains two 12-core Intel Xeon CPUs (E5-2697v2, 2.7 GHz) and 64 GB of RAM, hence a total of 9984 pro-
Table 3.1: Description of the boundary conditions used for the performed simulations

<table>
<thead>
<tr>
<th>Variables</th>
<th>Requested input files</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenhouse Gases (CO$_2$ and N$_2$O)</td>
<td>Observations until 2005 then RCP 6.0 (Masui et al., 2011 [85])</td>
</tr>
<tr>
<td>Ozone Depleting Substances (ODSs)</td>
<td>Observations + A1 scenario from WMO (2011) [142]</td>
</tr>
<tr>
<td>Sea Surface Temperatures (SSTs)</td>
<td>Hadley centre SST data set (HadISST) (Rayner et al., 2003 [107])</td>
</tr>
<tr>
<td>Background and Volcanic Aerosol</td>
<td>SAGE 4λ dataset for the surface area density and the number density (Arfeuille et al., 2013 [4])</td>
</tr>
<tr>
<td>Solar Variability</td>
<td>Lean et al. (2005) [80]</td>
</tr>
<tr>
<td>Gas and aerosol Precursors</td>
<td>Observations until 2000 Lamarque et al. (2010) [78], then RCP6.0 (Masui et al., 2011 [85])</td>
</tr>
</tbody>
</table>

3.1.2 Experimental set up

The simulations performed for this thesis follow to a large extent the recommendations from the Chemistry-Climate Model Initiative (CCMI) (Eyring et al., 2013a [51]) (Table 3.1).

For all the simulations performed in this thesis, interactive lightning NOx emissions are calculated via a parameterization based on cloud top height (Price and Rind, 1992 [102]) with local scaling factors evaluated from the Lightning Imaging Sensor (LIS) and Optical Transient Detector (OTD) satellite observations (Christian et al., 2003 [22]). Simulations use emission fluxes for NOx, CO as well as NMVOCs. For biogenic isoprene, formaldehyde, and other NMVOC emissions a climatology is used for the year 2000 (based on Model of Emissions of Gases and Aerosols from Nature (Guenther et al., 2000 [59]) - MEGAN), while the biomass burning emissions follow those described by Lamarque et al. (2010) [78], and RCP 6.0 afterwards (Masui et al., 2011 [85]). Anthropogenic emissions of formaldehyde and other anthropogenic NMVOCs follow Lamarque et al. (2010) [78] until 2000, then RCP6.0 (Masui et al., 2011 [85]).

In addition to the CCMI boundary conditions, methane fluxes are used in these simulations in order to better represent the methane cycle. A detailed description is given...
in Chapter 4. Different source categories are considered: anthropogenic, wetlands, rice, biomass burning, as well as termites, wild animals, mud volcanoes, and ocean hydrates. The uptake by soils is taken into account via the climatology from Spahni et al. (2011) [130]: as it is scaled to a methane concentration of 1800 ppbv, the uptake by soils is adjusted to the simulated methane tracer. This uptake is calculated via the LPJ-WHYMe global dynamical vegetation model as negative emissions. The soil consumption is given by the microbial oxidation rate within the soil and the transport of methane into the soil (Spahni et al., 2011 [130]). These processes depend on soil moisture, temperature and texture. The uptake scheme from Curry et al. (2007) [25] is applied to the vegetation model.

The reaction between methane and OH is evaluated via the implementation of a methyl chloroform (MCF) tracer. Its emissions are implemented using the TransCom-CH4 dataset (Patra et al., 2010 [98]). Only its reaction with OH is considered for this tracer. As described in the Introduction section, MCF is used as proxy for OH variations. As many studies use MCF to evaluate OH fluctuations (e.g. Montzka et al., 2011 [91]; Holmes et al., 2013 [65]), its implementation into SOCOLv3 allowed OH-comparison from previous analyses.

48 tracers have been implemented into SOCOLv3 to investigate the relative importance of different methane source categories (anthropogenic, wetlands, rice, biomass burning, termites, wild animals, mud volcanoes, and ocean hydrates) from various geographical regions following the recommendations of the TransCom-CH4 project (Gurney et al., 2000 [60]). The definition of the tracers is given in Chapter 4 Figure 4.1. A map of 3 tracers can be found in Appendix C as a visualization of the implemented tracer diagnostics in terms of concentration, as well as the time series of global atmospheric concentration of methane at the surface compare to the concentration of the sum of all the tracers, to ensure good implementation of the diagnostics.

For this thesis new developments were done in SOCOLv3, described in this section. First, an accurate representation of tropospheric methane was needed in order to understand its variability, as well as a reduction of the model variability. Moreover, as this thesis was done in collaboration with the atmospheric modeling group at the EMPA Institute and a comparison with model results using the Lagrangian chemistry transport model (CTM) FLEXPART (Henne et al., 2010 [63]; Uglietti et al., 2011 [138]), it was decided to force the meteorological fields simulated in SOCOLv3. This was done using a nudging technique described in the next section. Another new development was elaborated to reduce the overestimation of tropospheric ozone, as described in Revell et al. (2015) [110]. A new scheme for the representation of HNO3 washout in the troposphere was implemented, as a potential factor of high values of NOx in the troposphere leading to more simulated ozone (see section 3.3).
3.2 THE NUDGING TECHNIQUE

3.2.1 Description

Nudging is used in ECHAM in order to correct any existing deviation between the model and observations. This is a relaxation mechanism defined by the following equation:

\[
\frac{d}{dt}(\epsilon_t - \zeta_t) = -\frac{1}{\tau}(\epsilon_t - \zeta_t)
\]

where \(\epsilon\) represents the simulated variable and \(\zeta\) the input variable for the dynamics, both of which are time dependent (\(t\) in the equation). \(\tau\) is the relaxation time. For the rest of the study the temperature, divergence, vorticity, and logarithm of the surface pressure are nudged, the prognostic variables in ECHAM. ERA-Interim (Dee et al., 2011 [28]) is used as input meteorological fields. In the nudged simulation the whole model domain is nudged, and the nudging is called every 6 hours. The nudging files were created by Sebastian Rast from MPI Hamburg.

Based on Jeuken et al., (1996) [71], the nudging set up is optimal when using these relaxation times: 12 hours for the temperature and the surface pressure, 48h for the divergence and 6h for the vorticity.

To confirm that the nudging is well implemented, a simulation can be performed where only half of the spectral core is nudged: for this thesis this means a simulation in T42 resolution where the zonal wave numbers from 0 to 21 are nudged. The correlation in time between the simulated temperature and the temperature from the input nudged files is shown in Fig. 3.2. There is a good correlation between the nudged part of the model and the input files from ERA-Interim. Where the nudging is not applied, however, the correlation decreases showing that the nudging technique is correctly implemented.

3.2.2 Impact of the nudging on SOCOLv3

This section presents a comparison between SOCOLv3 in free and nudged mode. As described earlier, the temperature, vorticity, divergence as well as the logarithm of the surface pressure are forced towards fields from ERA-Interim. This new development performed during this thesis was investigated first as a general evaluation of the model: impact on the nudged variables (temperature, winds) in terms of mean state and variability, impact on the transport in SOCOLv3 (upwelling transport as well as tropospheric convection). Therefore, comparisons for the above-mentioned variables are carried out throughout the atmosphere.

Two simulations are investigated in this section: one in nudged mode and the other in free mode with the same experimental set up otherwise, between 1980 and 1989. When a seasonal study is needed, only JJA is shown. The conclusions stated from the Northern Hemisphere summer season can be extrapolated to the others. The rest is described in Appendix B.
3.2 The Nudging Technique

Figure 3.2: Correlation in time for the temperature for a simulation when only half of the spectral resolution is nudged (T21). The y axis represent the zonal wave numbers (from 0 to 42). The x axis represents the total wave number.

3.2.2.1 Impact on Temperature

The zonal mean temperature in nudged mode shows less pronounced variability compared to the free mode (Figure 3.3) in terms of differences with ERA-Interim. The application of nudging leads to a colder troposphere and a warmer stratosphere compared to ERA-Interim. The nudging has a strong effect in the high latitudes in the upper troposphere lower stratosphere (UTLS) region as well as in the high stratosphere. Because of a lower tropopause in the high latitudes in both hemispheres (Fig. 3.3), the temperature in the lower stratosphere in these regions becomes warmer with the nudging. On the other hand, the temperature is much warmer in the free mode in the high latitudes of the southern hemisphere in the upper stratosphere, which might be due to a lower stratosphere and also a shift of the polar vortex towards mid latitudes (Figure 3.6).

The nudging also impacts the horizontal distribution of temperature. It can be seen by evaluating the Probability Density Function (PDF) of the difference between the simulations (nudged or free) and ERA-Interim at specific pressure levels (Figure 3.4). At 750 hPa, the mean difference is better for the free simulation (-0.63 K) compared to the nudged simulation (1.63 K). However, the spread of the distribution is reduced with nudging. The same is observed at 250 hPa, even if the mean temperature is signif-
Figure 3.3: Zonal mean temperature for the JJA season averaged over 1980-1989 for ERA-Interim (top). The bottom plots show the difference (in K) between the nudged mode and ERA-Interim (bottom left) and the free mode and ERA-Interim (bottom right). The black lines represent the averaged tropopause height for the nudged simulation (thick line) and the free mode (dashed line).

Not only the atmospheric temperature mean state was influenced by the nudging but also its variability in time. Figure 3.5 shows the anomalies (in K) of temperature compared to the 1980-1989 period. The nudging shows a slightly better agreement than the free mode compared to ERA-Interim at 750 hPa, especially in 1988. However, the free mode already agrees reasonably well with the reanalysis data. At 250 hPa, both the free and nudged simulations show discrepancies with ERA-Interim. Only the temperature anomalies in 1987-1988 are better reproduced when using nudging. This highlights again that the nudging technique is a relaxation technique (with a 12 hours relaxation time) and cannot force the simulated temperature to match ERA-Interim.

The implementation of nudging in SOCOLv3 led to a change in the temperature distribution. Overall the temperature goes towards the direction of ERA-Interim with the
nudging, but some differences remain. As this thesis focuses on near-surface methane changes, where the nudging simulation shows better agreement in terms of mean state as well as temperature variability, using the nudging helps to improve simulated temperature variability. As methane is influenced by temperature mainly via its reaction with OH, a simulation in nudged mode will help to reproduce the influence of temperature on methane surface fluctuations.

3.2.2.2 Impact on Zonal Winds

The divergence as well as vorticity of the wind are nudged in SOCOLv3. As for temperature, differences between the nudged and free simulations are expected for the wind field (Figure 3.6). The nudged simulation shows very good agreement with ERA-Interim, while the free simulation shows larger differences. In the nudged simulation the polar vortex shifts towards the mid-latitudes and decelerates. These changes have a minimal impact on near-surface methane variability. However, the impact of a change in zonal winds on tropospheric transport can have an impact and is described in the next section.
Figure 3.5: Anomalies (in K) of temperature compared to the 1980-1989 period at 250 hPa (top plot) and 750 hPa (bottom plot) for the nudged simulation (red lines), free simulation (blue lines) and ERA-Interim (black lines).

3.2.2.3 Impact on large-scale circulation

By affecting temperature and zonal winds, a change in the simulated circulation is expected. As SOCOLv3 is known for having a too-fast upwelling transport in the tropical stratosphere (Stenke et al., 2013), we may ask the question whether the nudging also affects large-scale circulation. The speed of the vertical upward transport within the tropical stratosphere due to the Brewer-Dobson Circulation (BDC) can be analyzed using the H2O tape recorder (Mote et al., 1996). The observed as well as simulated tape recorder are shown in Figure 3.7. The tape recorder in the nudged version compares better to the observations than the free simulation. A general slowing of the tropical upward motion is found when the nudging is applied, remaining however faster than observed (Figure 3.8). Horizontal mixing is also changed, as the relative amplitude decays less rapidly with altitude (Figures 3.7 and 3.8). The higher water vapor mixing ratios at 100 hPa simulated with the nudging is an indicator of the higher tropopause, also seen in Figure 3.3.

This section describes a change in general circulation patterns when applying the nudging technique. The influence of near-surface methane variability is limited, but is part of a general study of the impacts of nudging.
3.2.2.4 Changes in tropospheric advection and convection

This thesis aims to analyze near-surface methane variations. Methane emissions are released from the surface and transported in the troposphere. With a lifetime of slightly less than a decade (Prather et al., 2012 [101]), methane is well mixed in the troposphere (Figure 2.6 b)) and is therefore influenced by a change in vertical and horizontal transport. Indicators of possible changes in tropospheric convection and horizontal transport, such as zonal convective precipitation (Figure 3.9) and the North Atlantic Oscillation (NAO) (Figure 3.10) are used as examples to represent horizontal and vertical transport. SOCOLv3 simulates a correct precipitation pattern compared to the observations (Fig. 3.9). The nudged version does not show a significant improvement based on the change in precipitation (also described by Zhang et al., 2014 [154]). However, only the convective precipitation can be used as a proxy for convection and not the total precipitation. This is shown in Figure 3.9 together with the maximum height of convective cloud-top. Overall, there is an anti-correlation between the cloud-top height and convective precipitation. The nudged mode shows a general stronger convection in the tropics, responsible for higher precipitation, seen here mainly in JJA. The Northern Hemisphere (NH) shows overall more convection, also stronger in summer time, in the nudged mode.

The NAO represents a meteorological pattern defined by the difference between the
3.2 The Nudging Technique

Water Vapor anomaly time height sections (averaged from 10S to 10N)

Figure 3.7: Tape recorder signal averaged over 1992-2001: time-height sections of water vapor mixing ratio shown as the deviation from the mean profile, averaged between 10°N and 10°S for observations from HALOE (Gross and Russel, 2005 [57]), SOCOLv3 with a T31 spectral resolution and 39 vertical model levels (T31L39), in T42L39, in T42L90 and in T42L39 in nudged mode.

surface pressure over Iceland and the Azores. It essentially describes the strength and direction of westerly winds and storm tracks across the North Atlantic. A positive NAO indicates increased westerlies and cool summers and wet winters over Central Europe. On the other hand, a negative NAO means reduced westerlies and dry winters over Northern Europe and a shift of the storm track towards South Europe. Figure 3.10 shows that the nudged version of SOCOLv3 agrees better with the observations in terms of the NAO index, but the absolute values remains different. The interannual variability of horizontal transport in the NH troposphere is more accurately simulated when the nudging is applied.
3.3 New Parameterization of the Nitric Acid Washout

3.2.2.5 Conclusions on the nudging technique

Nudging was used for all the simulations in order to better represent the variability (mean states and temporal trends) in temperature as well as tropospheric transport, and therefore reducing model bias. These changes impacted both circulation and tropospheric transport, being more consistent with observations in terms of interannual variability. Simulating methane in nudged mode is therefore a better way to reproduce the fluctuations due to horizontal transport as well as change in temperature influencing the reaction rate between CH$_4$ and OH.

3.3 New Parameterization of the Nitric Acid Washout

Revell et al. (2015) [110] describe an overestimation of tropospheric ozone compared to observations (by up to 50% in the Northern Hemisphere). As NOx concentrations...
Figure 3.9: Zonal precipitation (in mm/day) for DJF (dashed lines) and JJA (thick lines) seasons averaged over 1980-1989, compared to the Global Precipitation Climatology Project (GPCP) observations (Adler et al., 2003) (top plot). Convective precipitation (thick lines, in mm/day) and maximum of the convective cloud tops (in hPa) (dashed lines) for the nudged (red lines) and free (blue lines) simulations averaged over JJA (middle plot) and DJF (bottom plots) seasons for the 1980-1980 period.
were also found to be highly biased (also by about 50% in the polluted regions of the northern hemisphere), a possible explanation suggested was a weak removal of NOx in the troposphere. NO2 reacts with OH to form nitric acid (HNO3) via a three body process (NO2 + OH + M → HNO3 + M). HNO3, highly soluble species, can then easily be washed out of the atmosphere, leading to reduced amount of NOx available for ozone production.

The current parameterization is based on a constant rate removal of HNO3: 2.5% is removed at every chemical time step, for each grid point up to 160 hPa. No consideration is made of the different processes responsible for nitric acid washout, as described in section 3.3.1

3.3.1 Description of the new parameterization

For the new parameterization three different physical processes responsible for nitric acid washout are taken into account: aerosol scavenging, as well as in-cloud and below cloud precipitation (rain and snow) washout.

Nitric acid is a highly soluble species (Seinfeld and Pandis, 2006 [125]). Therefore, it
can be assumed that nitric acid exists exclusively as nitrate in a cloud (Seinfeld and Pandis, 2006). The implementation takes into account the cloud fraction of a grid cell:

\[
\text{HNO}_3\text{(gas)} = \text{HNO}_3\text{(gas)} \times (1 - \text{cloud\_fraction})
\] (1)

Precipitation can also affect nitric acid washout. However, this process is highly uncertain as part of the removed HNO\(_3\) can be released from evaporating rain droplets. Based on Chang (1984), the removal coefficient depends on the precipitation rate following this formula:

\[
\lambda_\omega = 0.33 \times 10^{-4} R^{0.42} + 1.0 \times 10^{-4} R^{0.58} (s^{-1}) \] (2)

\[
\lambda_\omega = 0.88 \times 10^{-4} S^{0.33} + 1.9 \times 10^{-4} S^{0.64} (s^{-1}) \] (3)

where R represents the precipitation rate (in mm.h\(^{-1}\)) and S the snow fall rate (in mm.h\(^{-1}\)).

The HNO\(_3\) removal is evaluated at each chemical time step via:

\[
\text{HNO}_3\text{(gas)} = \text{HNO}_3\text{(gas)} \times \exp(-\lambda_\omega \Delta t).
\]

\(\Delta t\) represents the chemical time step (2 hours). This parameterization is only considered below the clouds and assumed constant from the surface to the cloud height. \(\lambda_\omega\) is based on equations (4) and (5).

The last process represents the washout via tropospheric aerosols. Nitric acid can be removed from the gas phase via its partitioning into the aerosol phase. The removal of gas phase nitric acid was implemented in collaboration with Dr. Beiping Luo and Dr. Jianxiong Sheng as follows:

\[
\text{HNO}_3\text{(gas)} = \text{HNO}_3\text{(gas)} \times \frac{1}{1 + 8.173 \times T \times x_H \times 10^{-5} \times \text{AVOL}}
\] (4)

T represents the temperature, \(x_H\) is the effective Henry’s constant, \(\text{AVOL}\) is the averaged volume of aerosols in the grid cell. Henry’s constant defines the part of a gas dissolved into the liquid phase and depends on pH. For this parameterization an average pH value of 4 was chosen to represent the troposphere. For more acid regions (where other acids are emitted, such as sulfuric acid, e.g. over polluted regions), a lower pH of 3 could be considered and therefore lead to an increasing partitioning from aerosols (personal discussion with Dr. Beiping Luo). However, as described in the next section, HNO\(_3\) removal via this process remains small compared to the in-cloud washout process because of the high solubility of HNO\(_3\). All tropospheric aerosols are assumed to be in the liquid phase.

Five different simulations of eight years were performed: a reference simulation representing the new washout parameterization, and four sensitivity simulations (Table 3.2): with the old scheme, without only in-cloud washout, below clouds precipitation washout, and without only the aerosols scavenging. The results based on these simulations are shown in the next section.
Table 3.2: Performed simulations for the evaluation of the nitric acid washout new parameterization.

<table>
<thead>
<tr>
<th>Simulations</th>
<th>Aerosols partitioning</th>
<th>In-cloud washout</th>
<th>Below-cloud precipitation</th>
<th>Old scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLD SCHEME</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>NEW SCHEME</td>
<td>✓ ✓ ✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AEROSOLS</td>
<td>✓ ✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CLOUD</td>
<td>✓ ✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PRECIP</td>
<td>✓ ✓</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3.2 Impact of the new parameterization

The new washout scheme results in global decreases of HNO$_3$ in the lower troposphere but higher concentrations in the upper troposphere (Figure 3.11), due to the use of the tropopause height as an upper limit of the parameterization and not 160 hPa, which correspond to stratospheric pressure levels in the high latitudes. The decrease in the lower troposphere (about 50% reduction in concentration up to 500 hPa) shows that the new washout scheme removes more nitric acid than previously, and is now in better agreement with satellite observations (Figure 3.12). However, looking at quantitative differences (Fig. 3.12) might be biased by different approaches in calculating tropospheric column (the stratospheric column was removed in Cooper et al. (2014) [24] from the GEOS-Chem 3D model) as well as different time periods (averaged over 1985-1987 for the SOCOLv3 simulations and 2008 for IASI). However, the new scheme shows an overall decrease in tropospheric HNO$_3$ in the gas phase, which reduces a positive bias of the nitric acid tropospheric column. The spatial distribution also agrees with Cooper et al. (2014) [24] with higher column above 20° N and lower values in the tropical regions. However, the tropospheric column nitric acid remains underestimated over the South Pacific, Atlantic and Indian oceans. As this effect already exists in the old scheme, a possible explanation for this low bias over South East Asia and the West Pacific also modeled in Cooper et al. (2014) [24] comes from the NOx emissions from lightning. The effect for SOCOLv3 is not investigated in the frame of this thesis.

The removal of gas phase nitric acid is dominated by the in-cloud washout (Fig. 3.14), as HNO$_3$ is a highly soluble species. Partitioning into the aerosol phase has a weak impact above 700 hPa, as most of the aerosols for the parameterization are found below 700 hPa (Figure 3.13 b)). In-cloud washout follows the averaged simulated cloud cover, as expected (3.13 a)). Higher removal is found in the Northern Hemisphere as higher concentrations are located here (Fig. 3.11). The impact of below-cloud washout
3.3 New Parameterization of the Nitric Acid Washout

Figure 3.11: Zonal mean of annually averaged HNO₃ concentration (in ppbv) for the new (left plot) and old (right plot) parameterization of nitric acid washout.

Figure 3.12: Tropospheric column (in molec.cm⁻²) of HNO₃ from the IASI satellite (top plot), from Cooper et al. (2014) [24]. Tropospheric column of nitric acid from SOCOLv3 with the old (middle plot) and the new scheme (bottom plot).

is less important and mostly efficient in the tropical region, where most of the precipitation occurs. A high removal is also found in the NH mid-latitudes during boreal summer time, mainly due to higher nitric acid concentration (Figures 3.14, 3.13 c) and
3.3 NEW PARAMETERIZATION OF THE NITRIC ACID WASHOUT

Figure 3.13: a): Zonal cloud fraction (black line, right y-axis) and absolute difference between NEW SCHEME and CLOUDS in zonal HNO₃ concentrations (in ppbv) (red line, left y-axis) averaged over 1985-1987. b): Zonal tropospheric aerosol concentrations (in kg/kg) taken into account in this parameterization. c): Absolute difference in HNO₃ concentrations (in ppbv) between NEW SCHEME and PRECIP averaged over DJF 1985-1987. The continuous black line represents the simulated tropopause height and the dashed line the constant 160 hPa pressure level. d): Same as c) but averaged over JJA 1985-1987.

d), and 3.9). The higher NOx tropospheric column found in polluted regions in Revell et al. (2015) [110] can also explain the higher values simulated in SOCOLv3 near the continental regions (Fig. 3.12).

A decrease in gas phase HNO₃ leads to a change in the distribution of various chemical species. Figure 3.15 summarizes the difference for several chemical species between the new and the old scheme averaged over different latitude bands and altitudes. There is a general decrease in HNO₃ concentration, leading to decreasing NO and NO₂ (because of the reaction between HNO₃ and OH as well as nitric acid photolysis). A decrease in ozone abundances is found in the tropics and Northern Hemisphere, as O₃ is mainly produced via the oxygen atom created by NO₂ photolysis. In contrast, ozone concentrations are higher in the Southern Hemisphere. There, the low NOx concentrations (30S-60S is mainly covered by oceans and remote from main pollution sources), ozone is chemically destroyed via its reaction with HO₂. Having less HNO₃
3.3 New Parameterization of the Nitric Acid Washout

Figure 3.14: Absolute difference of HNO$_3$ concentrations (in ppbv) averaged over 1985-1987 between NEW SCHEME and CLOUDS (left plot), NEW SCHEME and PRECIP (middle plot), and NEW SCHEME and AEROSOLS (right plot). The thick line represent the simulated tropopause height and the dashed line the constant 160 hPa pressure level.

Figure 3.15: Relative change in concentration for CH$_4$, OH, HNO$_3$, CO, NO, NO$_2$, HO$_2$ and O$_3$ averaged over different latitudes and altitude bands.
then involves less NO$_2$ and OH, products of its photolysis. If in the Northern Hemisphere the simulated decrease in OH (Figure 3.15) comes from less ozone resulting in reduced NOx concentrations, it is different in the Southern Hemisphere as NOx levels are low. Overall a decrease in the HOx (OH + HO$_2$) concentrations is simulated. Moreover, a decrease in OH concentrations leads to a reduction in methane oxidation and therefore an increase in methane abundance. An increase is also simulated for CO at all latitudes and altitudes. CO differs from methane as it is also produced via methane oxidation. A decrease in OH leads to a reduction in CO chemical reduction but also an increase of its production via methane oxidation. Seinfeld and Pandis (2006) [125] describe that the sink of CO via its reaction with OH is about 2.5 times higher than its production via methane oxidation. The increase in CO from Fig. 3.15 is therefore mainly an impact of simulated decreasing OH levels.

The decrease of ozone is found to be on the order of 5% in the Northern Hemisphere, considerably smaller than the 50% high bias seen in Revell et al. (2015) [110]. The new nitric acid washout therefore helps to reduce modeled ozone levels but is not enough to obtain a more realistic ozone tropospheric distribution.

The implementation of the new nitric acid washout led to a better representation of tropospheric HNO$_3$. A part of the HNO$_3$ in the liquid phase can be evaporated again (also when precipitation occurs), leading to a recycling of gas phase nitric acid (Gregoire et al., 1994 [56]). As this process is not taken into account in this new parameterization, it is suggested as a further development of this new approach. By taking into account the flux of downward liquid phase nitric acid the rate of HNO$_3$ evaporated again can be evaluated (personal communication with Beiping Luo). Moreover, all tropospheric aerosols were considered as liquid in this approach. A further step will be to distinguish between liquid and solid aerosols in the troposphere.

By reducing the biases in model mean state and trend uncertainties via the nudging technique and using a more accurate nitric acid washout helping to decrease high ozone (and therefore OH) tropospheric concentrations, the model more accurately reproduces methane trends over the last three decades.
We investigate the drivers of atmospheric methane variations from 1980 to 2010 by four transient simulations using the chemistry-climate model SOCOL with specified dynamics. Overall 48 diagnostic tracers allow the tracking of methane emitted from various source categories and geographical regions. Uncertainties in existing methane emission flux estimates were addressed by combining two data sets for wetland emissions based on process-based models (LPJ-WSL and SDGVM) with two anthropogenic emission inventories (EDGAR 4.2 and Schwietzke et al., 2014a [124]; Schwietzke et al., 2014b [125], called in this study SCHWIEZKE).

Increasing anthropogenic emissions in Europe, India and China are responsible for the observed methane increase from 1984 to 1991, contributing to 60% of the global growth rate. Decreasing anthropogenic emissions in Europe after 1991 are reflected by a slow-down of the global methane growth until 2000. Applying the SCHWIEZKE data set leads to an underestimation of the global methane growth rate after the collapse of the Soviet Union up to 2004. Observed short-term variations atmospheric methane after the eruption of Mount Pinatubo in 1991 and the strong El Niño 1997/98 are mainly driven by reduced wetland emissions in 1992 by 8 Tg (30 Tg for SDGVM) and mostly in tropical South America (boreal Eurasia and North America in SDGVM) according to LPJ-WSL, and high levels of biomass burning (30% of increase) in tropical Asia, respectively. After 2000 increasing anthropogenic emissions in China, India and South America are compensated by less anthropogenic emissions in Europe, resulting in near-zero methane growth. The reinforced methane increase after 2004 is overestimated in all model scenarios, from 230% to 380%, due to overly strong emission in China reported in both anthropogenic data sets.

In terms of CH₄ emissions from wetlands, SDGVM simulates higher levels of wetland emissions in North America as well as the Siberian region. Simulations indicate a too strong decrease in wetland emissions simulated by SDGVM after the Mount Pinatubo volcanic eruption.

Our simulated tropospheric methane lifetime decreases on average by 8% from 1980 to 2010, caused by increasing OH levels. Variations in simulated OH after 1998 inferred from a methyl chloroform tracer are consistent with observations, despite an overall too strong, but constant loss of methyl chloroform in the model.

Current atmospheric methane (CH$_4$) concentrations are 2.5 times higher than in pre-industrial times (Ciais et al., 2013 [23]). Methane has become the second most important greenhouse gas in terms of anthropogenic radiative forcing (Myhre et al., 2013 [93]). Global observations indicate remarkable fluctuations in the methane growth rate over the last three decades. The rather constant increase by 10.8 ppbv/yr from the beginning of regular measurements in the early 1980s until 1990 was followed by a reduced growth rate of 6.8 ppbv/yr in the 1990s. After 1999, global methane levels stayed constant for several years before they started rising again in 2007 (Kirschke et al., 2013 [73]).

The atmospheric methane budget is determined by its sources, both natural and anthropogenic, and its sinks, of which the chemical reaction with the hydroxyl (OH) radical in the troposphere is the most important. The contribution of sources and sinks on the methane variations is still under debate. Declining fossil fuel emissions in the former Soviet Union were found to be the "most likely" reason for the decline in methane growth rate after 1991 (Dlugokencky et al., 1991 [37]). By using an ethane/methane analogy, a decline in global fossil fuel emissions was also found between 1980 and 2010 (Aydin et al., 2011 [5]; Simpson et al., 2012 [128]). In addition to the collapse of the Soviet Union, the volcanic eruption of Mount Pinatubo also led to a change in methane growth rate via reduced wetlands emissions and a larger tropospheric OH sink (Bousquet et al., 2006 [15]; Bândă et al., 2013 [6]; Bândă et al., 2015 [8]; Bândă et al., 2016 [7]). The relative contributions of natural emissions from wetlands and anthropogenic emissions is determinant to understand methane variations from 2000 (Bousquet et al., 2006 [15]; Bousquet et al., 2011 [16]; Pison et al., 2013 [100]; Ghosh et al., 2015 [55]). The rise since 2007 also remains unclear. Increasing fossil fuel emissions, mainly in China, are discussed as possible explanation (Kirschke et al., 2013 [73]). Isotopic studies, however, attribute this increase to natural emissions from wetlands (Nisbet et al., 2014 [96]) or agriculture (Schaefer et al., 2016 [119]).

The impact of the main tropospheric methane sink, the reaction with the OH radical, is also heavily discussed. Methyl chloroform (MCF), an industrially produced substance with a relatively short atmospheric lifetime of around five years, that is banned by the Montreal Protocol, is commonly used to study OH variations. MCF observations indicate small OH variability for the period 1998-2007 (Montzka et al., 2011 [91]). However, Holmes et al. (2013) [65] suggest that the differences among observation networks must be better understood for MCF to be used as a constraint for OH variations. Using a 2-D twelve-box model, Rigby et al. (2008) [112] simulated an OH decrease from 2007 to 2008 by 4% ± 14%, but this decrease was not considered significant enough to explain the methane rise after 2007. In a longer timescale (1970-2012), Dalsoren et al. (2016) [26] found via a global chemistry transport model (CTM) an increase in the tropospheric OH concentration of 8%, due to a combination of chemical and meteorological factors, being responsible of a decrease in methane lifetime of the same order. This study analyzes methane variations over the last three decades using the Chemistry-Climate Model SOCOL. Methane emission fluxes are used as input in the performed
4.2 METHODOLOGY

4.2.1 Chemistry-climate model SOCOLv3

The study is based on simulations performed with the global chemistry-climate model SOCOLv3 (Stenke et al., 2013 [134]). It consists of the middle atmosphere version of the general circulation model ECHAM5 (Roeckner et al., 2003 [114]) and the chemistry transport model MEZON (Egorova et al., 2003 [41]). The coupling is interactive and done via the temperature, wind, and the radiative forcing induced by water vapor, ozone, methane, nitrous oxide, and chloroﬂuorocarbons. Chemical species are advected by a flux-form semi Lagrangian scheme (Lin and Rood, 1996 [82]). 41 chemical species, 140 gas-phase reactions, 46 photolysis reactions, 16 heterogeneous reactions (in the stratosphere), and 3 types of polar stratospheric clouds are considered in the chemical mechanism. Isoprene oxidation follows the Mainz Isoprene Mechanism (MIM-1, Poeschl et al., 2000 [104]), with 16 species and 44 additional chemical reactions. The radiation and chemical scheme is called every two hours while the dynamical processes and physical parameterizations are called every 15 minutes. A detailed description of the most current model version, which has been used in the present study, can be found in Revell et al. (2015) [110].

To ensure best comparability with observational data SOCOLv3 was run in nudged mode, meaning that the prognostic variables temperature, vorticity, divergence as well as the logarithm of the surface pressure were forced towards prescribed meteorological fields from ERA-Interim reanalysis data (Dee et al., 2011 [28]). All simulations were performed with T42 spectral resolution, which corresponds to a horizontal grid of approximatively $2.8^\circ \times 2.8^\circ$, as well as 39 vertical levels (a hybrid-sigma pressure coordinate system is used) from Earth’s surface to 0.01 hPa.

In contrast to most other chemistry-climate models, a so-called flux boundary condition was applied for methane. Eight different sources of methane have been taken into account and are summarized in Table 4.1. In addition, the uptake of methane by soils is taken into account using a climatology from Spahni et al. (2011) [130]. (Table 4.1).

4.2.2 Methane tracers

To investigate the relative importance of different methane source categories from various geographical regions, additional methane tracers were implemented into SOCOLv3. This approach separates methane into 48 tracers. We distinguish eight different source
4.2 Methodology

Table 4.1: Summary of applied methane emission fluxes by source type.

<table>
<thead>
<tr>
<th>Source category</th>
<th>Available emissions</th>
<th>Inventory</th>
<th>2000-2009 Global average (Tg/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthropogenic</td>
<td>1980 – 2010</td>
<td>EDGAR 4.2 database</td>
<td>283</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EC-JRC/PBL. EDGAR version 4.2.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>“SCHWIETZKE” database</td>
<td>301</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Schwietzke et al., (2014a) [124];</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Schwietzke et al., (2014b) [123]</td>
<td></td>
</tr>
<tr>
<td>Wetlands</td>
<td>1980 – 2010</td>
<td>LPJ-WSL</td>
<td>171</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zhang et al., (2015) [155]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1980-2009</td>
<td>SDGVM</td>
<td>211</td>
</tr>
<tr>
<td></td>
<td>2010: extension of 2009</td>
<td>Hopcroft et al., (2011) [66]</td>
<td></td>
</tr>
<tr>
<td>Rice</td>
<td>1993-2007</td>
<td>Hodson et al., (2011) [64]</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Climatology otherwise</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2010: Extension of 2009</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wild animals</td>
<td>Houweling et al., (1999) [68]</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Climatology</td>
<td>Patra et al., (2011) [97]</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Mud volcanoes</td>
<td>Patra et al., (2011) [97]</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Climatology</td>
<td>Etiopie and Milkov, (2004) [47]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ocean hydrates</td>
<td>Patra et al., (2011) [97]</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Climatology</td>
<td>Lambert and Schmidt, (1993) [79]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Termites</td>
<td>Patra et al., (2011) [97]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Climatology</td>
<td>Fung et al., (1991) [54]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Uptake by soils</td>
<td>Spahni et al., 2011 [130]</td>
<td>-25 1</td>
</tr>
</tbody>
</table>

1 Representative for a global average CH\(_4\) mixing ratio of 1800 ppb. Scaled to the actual simulated methane values during the model simulations

categories (Table 4.1). The distinction of the different regions follows the TransCom approach (Gurney et al., 2000 [60]). The different regions are summarized in Figure 4.1. The sum of the diagnostic methane tracers is forced to be equal to the prognostic methane tracer at every grid point and every chemical time step. The diagnostic tracers are initialized according to the total methane emissions in 1980.
To evaluate how realistically SOCOLv3 simulates tropospheric OH levels, we also implemented a methyl chloroform (MCF) tracer. MCF is mainly oxidized in the tro-
posphere via the reaction with OH. As MCF has no natural emissions and its anthropogenic emissions are well known (McCulloch et al., 1999 [88]), MCF is commonly used to diagnose OH variability (Montzka et al., 2011 [91]; Holmes et al., 2013 [65]). MCF emissions are taken from the TransCom-CH₄ experiment (Patra et al., 2011 [97]).

4.2.3 Performed simulations

Four different simulations were performed using combinations of the two anthropogenic and two wetland emissions datasets (see Table 4.1 for the chosen databases), allowing us to study the sensitivity of methane fluctuations to natural (from wetlands) and anthropogenic methane emissions. Other than these two main emissions categories several minor sources have been considered (Table 4.1). All the simulations cover the time period 1980 to 2010. Besides methane, the boundary conditions used for these simulations follow the specifications of the CCMI REF-C₁ simulation until the year 2000 and the REF-C₂ simulation afterwards (Eyring et al., 2013a [51]).

The simulations are defined for the rest of this study as follows: EDGAR-WSL (when using the combination of EDGAR4.2 anthropogenic inventory and LPJ-WSL CH₄ emissions from wetlands), EDGAR-SDGVM (combination of EDGAR4.2 and SDGVM); SCHWIETZKE-WSL (combination of the anthropogenic inventory based on Schwietzke et al., (2014a) [124]; Schwietzke et al. (2014b) [123] and LPJ-WSL); and SCHWIETZKE-SDGVM.

Since tropospheric OH concentrations as simulated by SOCOLv3 are at the upper edge of common chemistry-climate models (see Fig. 4.6), the following scaling emission factors are used to obtain equilibrium between methane sources and sinks during the model spin-up: 1.23 for EDGAR-WSL, 1.12 for EDGAR-SDGVM, 1.16 for SCHWIETZKE-WSL, 1.06 for SCHWIETZKE-SDGVM. The total of emissions used as model input, averaged over the 2000-2009 decade, are between 634 Tg/yr and 665.
Figure 4.2: Relative contribution of different methane source categories. Anthropogenic sources follow EDGAR4.2, wetland emissions are based on LPJ-WSL. Averaged over the period from 2000 to 2009. 14 categories from EDGAR4.2 have been selected: enteric fermentation (4A), fugitive from solid (1B1), gas production and distribution (1B2), industrial process and product use (2), manure management (4B), oil production and refineries (1B2b), residential (1A4), road transportation (1A3b), solid waste disposal (6A), wastewater (6B), non-road transportation (1A3_c_d_e), and fossil fuel fires (7A).

Tg/yr, and therefore within the range 542 Tg/yr to 852 Tg/yr reported by Kischke et al. (2013) [73].

4.2.4 Anthropogenic emissions

Two different bottom-up inventories were used in this study: EDGAR4.2 (Table 4.1) and a database based on Schwietzke et al. (2014a) [124] and Schwietzke et al. (2014b) [123], created and provided by Tonatiuh Nunez (personal communication, 2015).

Schwietzke et al. (2014a) [124] estimates natural gas emissions of methane for different Fugitive Emissions Rates (FER, % of dry production) scenarios, representing total natural gas industry emissions. New calculations of the FER per year were performed based on literature. For developed countries, (United States, Canada, Netherlands, United Kingdom, Norway, Australia, Italy, and Germany), the FER were evaluated based on the Inventory of U.S. Greenhouse Gas Emissions and Sinks. For Russia and Eastern Europe, large natural gas emissions before 1990 as well as the large decrease after the collapse of the Soviet Union were taken into account, based on local inventories (Reshetnikov et al., 2000 [109]; Dlugokencky et al. 1994a [32]). For developing countries, the FER were based on flaring efficiency (Elvidge et al., 2009 [44]; Schwietzke et al. 2014a [124]): the satellite-derived mass of flared gas [kg] per volume of oil produce (EIA International Agency Statistics, http://www.eia.gov/cfapps/ipdbproject/-
4.2 METHODOLOGY

IEDIndex3.cfm) were used as a proxy for the country’s yearly FER. Upper, lower and medium ranges of emissions were scaled to measurements of atmospheric methane and its stable carbon isotope ratio (Schwietzke et al., 2014b [123]). As this study mainly focuses on methane trends, and because total methane emissions are scaled (section 4.2.3), only the medium range of values was considered. Moreover, as this dataset provides data for natural gas and oil as well as coal mining emissions, only the corresponding categories in EDGAR4.2 (1B2, 1B2b and 1B1) are replaced to create the SCHWIETZKE database, as termed for the rest of the study.

Figure 4.3 compares the two inventories. SCHWIETZKE shows a stronger increase before 1991 and a more pronounced decrease afterwards, due to a stronger decrease in emissions in Europe and Siberia after the fall of the former Soviet Union. Between 1984 and 2000, SCHWIETZKE reports a decrease in anthropogenic emissions over Eurasia of 18 Tg/yr, compared to 7 Tg/yr for EDGAR4.2. Therefore, SCHWIETZKE is closer to the global decrease in fossil fuel emissions of 10-21 Tg/yr between 1984 and 2010 reported by Simpson et al., 2012 [128]. Moreover, Worthy et al., 2009 [152], in order to match the decline in methane concentrations in Alert, Canada, simulated a drop in anthropogenic emissions twice larger than reported in EDGAR4.2. The difference between SCHWIETZKE and EDDGAR4.2 after 1991, namely 22 Tg/yr and 15 Tg/yr between 1991 and 2000, comes close to their results. The reasons for these large differences in the Eurasian region remain unknown (Schwietzke et al., 2014a [124]): new technologies, decrease in energy consumption could be an explanation. In boreal Eurasia and North America, anthropogenic emissions reported by SCHWIETZKE are higher compared to EDGAR4.2 (Fig. 4.3). Anthropogenic emissions in China show a lower increase after 2004 in SCHWIETZKE: a linear slope of 2.2 Tg/yr per year from 2003 to 2008 compared to 2.6 Tg/yr per year for EDGAR4.2. Both trends are signifi-
4.2 Methodology

Figure 4.4: Anomalies (%) of global wetland emission fluxes with respect to the mean from 1980 to 2010 for LPJ-WSL (red line), SDGVM (blue line) and LPJ-WSL from Hodson et al. [64] (green line) models. MAIOLICA-I covers the period 1993-2007. Before and after, the 1990 values are used. MAIOLICA-I is used in the FLEXPART simulation.

...cantly larger than the trend estimate of 1.1 Tg/yr per year provided by Bergamaschi et al., 2013 [12] based on satellite observations. This increase is mainly due to coal mining emissions, as reported by the two inventories and Bergamaschi et al. (2013) [12].

4.2.5 Wetland emissions

Both vegetation models, SDGVM and LPJ-WSL, are part of the WETCHIMP intercomparison project (Wania et al., 2013 [147]; Melton et al., 2013 [89]). Here we applied an updated version of LPJ-WSL (Zhang et al. (2015) [155]). In contrast to other wetland models, which prescribe the wetland area, SDGVM and LPJ-WSL both include an online calculation of the wetland extent. Temperature and precipitation from the CRU3.1 reanalysis data (Harris et al., 2014 [62]) were used as input data.

The largest difference between both data sets is found after the volcanic eruption of Mount Pinatubo (Fig. 4.4): SDGVM reports a negative anomaly of 24% (corresponding to a decrease of about 30 Tg) in 1992, not supported in LPJ-WSL (negative anomaly of 6% or 8 Tg). The uncertainty in simulating the decrease in CH₄ emissions from wetlands is also discussed in Bândă et al., (2016) [7]. Using two inventories, ORCHIDEE (Krinner et al., 2005 [76]) and LP emissions from the Hydrogen, Methane and Nitrous oxide (HYMN) project (Spahni et al., 2011 [130]), a decrease of about 25 Tg is found with ORCHIDEE and similar for their LPJ version compared to LPJ-WSL. SDGVM simulates the strongest drop in wetlands northwards of 30°N, due to a decrease in wetlands extent, soil respiration and temperature (personal communication with Peter Hopcroft, 2016). This differs from LPJ-WSL which shows the largest change over the tropical region over South America caused by a negative precipitation anomaly.
Figure 4.5 describes differences in the spatial distribution from the two databases: SDGVM evaluates higher CH$_4$ emissions from wetlands (by slightly more than 20%), with the largest contribution from NH high latitudes during summer. Part of this difference can be related to the treatment of frozen soils: while LPJ-WSL does not allow any methane emissions from frozen soils, this is not the case in SDGVM. Moreover, in contrast to SDGVM, LPJ-WSL does not consider boreal lakes in the calculation of the wetland area (personal communication with Z. Zhang, 2016).

4.3 RESULTS AND DISCUSSION

4.3.1 Tropospheric OH

Tropospheric OH is the main sink of methane. Understanding the simulated OH distribution and its variability is therefore crucial for understanding methane fluctuations. Revell et al. (2015) [110] evaluated tropospheric ozone in SOCOLv3 and found a high bias in tropical regions and the northern hemisphere. At 500 hPa simulated ozone levels were up to 30 ppbv (50%) above observed levels, which is probably related to a simultaneous NOx high bias in the model. An ozone bias could lead to an overestimation of tropospheric OH, as it is primarily formed by ozone photolysis and recombination of the oxygen atom O(^1D) with water vapor.

Tropospheric OH levels show a wide spread among current CCMs, with SOCOLv3 lying at the upper edge of the range (Fig. 4.6). The ACCMIP models show on average an OH increase of 2.8%, while SOCOLv3 simulates an increase of about 7%. The OH trend in SOCOLv3 is comparable to a recent study by Dalsören et al. (2016) Dalsøren et al. [26], who simulated a tropospheric OH increase by 8% between 1985 and 2005 using the Oslo CTM3 and methane emission fluxes.

To evaluate our simulated OH variability, a MCF tracer was implemented in the SOCOLv3 simulation. Using the same approach as Montzka et al. (2011) Montzka et al. [91], MCF loss rate is calculated as follows:

$$k_t = -\ln(c_{t+6}/c_{t-6})$$  (1)
where $c_t$ is the global MCF concentration in month $t$. Observations are taken from the global mean AGAGE global network (Prinn et al., 2005 [103]). The five measurement sites (Cape Grim in Australia, Mace Head in Ireland, Ragged Point in Barbados, American Samoa and Trinidad Head in California) from the AGAGE measurements are taken into account and compared to the corresponding five SOCOLv3 grid points. Observations sites are available after 1996. However, because of decreasing MCF emissions before this period (from 718 Gg/yr to 24 Gg/yr between 1990 and 1998, McCulloch et Midgley, 2001 [87]), MCF decay rate is mostly due to this change in emissions and therefore extrapolations on OH variations are difficult.

After 1997 both observations and model results show rather constant MCF decay rate, with SOCOLv3 showing a constant offset compared to the observations (Fig. 4.7). This indicates a high bias in simulated tropospheric OH. However, as it remains constant in time (after 1998), its influence on methane trends should remain low. Figure 4.7 describes MCF anomalies inferred from its loss rate compared to the 1998-2007 average. Simulations and observations are in the same range of magnitude in terms of MCF anomalies (between -4% and 4% on average). The coarse horizontal resolution in the simulations could explain the small differences, as well as the low remaining MCF emissions. Holmes et al. (2013) [65] explains that half of the anomalies derived from MCF decay rate can be explained by abrupt MCF emission changes. Residual anthropogenic and high latitudes ocean MCF emissions between 2002 and 2004 are estimated to be 6 and 4 Gg/yr (Wennberg et al., 2004 [148]; Prinn et al., 2005 [103];
Figure 4.7: Left: MCF decay rate for EDGAR-WSL (red) and AGAGE network (blue) between 1998 and 2010. The lines represent the average over the five observations sites (Cape Grim in Australia, Mace Head in Ireland, Ragged Point in Barbados, American Samoa and Trinidad Head in California) from the AGAGE network and their corresponding grid points. The area represent the maximum and minimum values at each month over the five sites. Right: MCF anomalies inferred from the decay rate compared the 1998-2007 average.

Montzka et al., 2011 [91]; Holmes et al., 2013 [65]), in the range of the change in emissions required to explain the observed decay rate (4 Gg/yr, Holmes et al., 2013 [65]).

4.3.2 Methane variations for different time periods

In this section we evaluate the simulated methane concentrations and analyze the drivers of their interannual variability (Fig. 4.8, 4.9, and 4.10). Figure 4.8 compares simulated global mean methane concentrations near the surface with observations from the NOAA-ESRL global network (Dlugokencky et al., 2015 [31]), as well as its growth rate. Figure 4.9 shows the annual mean global methane growth rate for different latitude bands: 30°N-65°N; 30°S-30°N; and 30°S-65°S. Figure 4.10 decomposes the yearly growth rate into the ten most important methane tracers.

4.3.2.1 1984-1993

The NOAA-ESRL measurements are available for global analysis starting in 1984, and therefore this section starts when we are able to compare our simulations with the observations, in order to strengthen our statements. Before 1990, SOCOLv3 reproduces the observed growth rate. An excessive inter-annual variability is found when using SDGVM wetland emissions, especially in the Northern Hemisphere high latitudes (Fig. 4.9). Furthermore, a lower growth rate is found in the tropical and Southern Hemisphere extra-tropical regions with SDGVM for 1986 and 1987, when an El Niño event caused less precipitation in the tropics leading to lower wetland emissions (Hodson et al., 2011 [64]). SCHWIEZKE reports a stronger increase in anthropogenic emissions for this period, mainly in Europe and “boreal Eurasia”. Therefore, SCHWIEZKE-WSL (12.7 ppbv/yr) simulates a higher growth rate than EDGAR-WSL (10.0 ppbv/yr), and the same for SCHWIEZKE-SDGVM (10.9 ppbv/yr) compared to EDGAR-SDGVM (6.9 ppbv/yr). In EDGAR-WSL anthropogenic emissions in Europe,
Figure 4.8: Time series of global methane concentrations (in ppbv, top plot) as well as its growth rate (in ppbv/yr, bottom plot) at the surface between 1980 and 2010 for EDGAR-WSL (red line), EDGAR-SDGVM (blue line), SCHWIETZKE-WSL (dotted brown line), and SCHWIETZKE-SDGVM (dotted light blue line), and the simulation performed with FLEXPART (green line in the bottom plot) Global methane growth rate of FLEXPART starts in 1995 in order to avoid the missing signal after Pinatubo, as their wetland emissions start varying in 1993. Global average measurements from the NOAA-ESRL global network (Dlugokencky et al., 2015 [31]) are represented by the black lines. Growth rate was deseasonalized and a smoothed by applying a 6 month running average.

China and India contribute 60% of the total methane growth rate (Fig. 4.10). Tropical South America is the most important region in terms of wetland emissions (Fig. 4.5), accounting for 27% of the total methane growth rate in EDGAR-WSL and 38% in EDGAR-SDGVM.

For the 1988-1990 period, both EDGAR-WSL (9.8 ppbv/yr) and SCHWIETZKE-SDGVM (10.1 ppbv/yr) simulate a global methane growth rate comparable to the observations (10.3 ppbv/yr) (Fig. 4.8 and 4.9), despite opposing contributions from wetlands,
especially in Europa and boreal Eurasia. For these regions, SCHWIETZKE-SDGVM report an impact of 4.6 ppbv/yr average over 1988-1990, compared to -0.4 ppbv/yr in EDGAR-WSL. The positive contribution in SDGVM is compensated by decreasing emissions in Africa and boreal North America (not shown). This highlights the need to better constrain CH₄ emissions from wetlands, as simulations are very sensitive to the
chosen database. As already reported in the WETCHIMP inter-comparison (Melton et al., 2013 [89]) as well as in Kirschke et al., 2013 [73], wetland emission estimates show a large range of values which makes it difficult to accurately quantify the impact of CH$_4$ emissions from wetlands on methane variability.

The period 1991-1993 is a transition period for global methane, going from a growth rate of 15 ppbv/yr in mid-1991 to nearly zero during 1992, and partly recovering in 1993 (4.8 ppbv/yr) (Dlugokencky et al., 1994 [32] and Fig. 4.8). During this period two major events influenced global methane levels: the collapse of the former Soviet Union, responsible for a decrease in fossil fuel emissions over Eastern Europe (Dlugokencky et al., 2003 [37]; Aydin et al., 2011 [5]; Simpson et al., 2012 [128]); and the volcanic eruption of the Mount Pinatubo in June 1991, leading to a change in both the methane sources via reduced wetland emissions and in methane sink via increasing tropospheric OH sink in the two years following the eruption (Wang et al., 2004 [144]; Bousquet et al., 2006 [15]; Bândă et al., 2013 [6]; Bândă et al., 2015 [8]; Bândă et al., 2016 [7]). Both simulations using SDGVM obviously overestimate the decrease in global methane growth rate after 1992 (Fig. 4.8). As described in the previous section, SDGVM simulates a decrease by 30 Tg/yr in 1992, compared to 8 Tg/yr for WSL. SDGVM shows comparable values to former inverse modeling studies (Wang et al., 2004 [144]; Bousquet et al., 2006 [15]). In terms of OH sink, an increase of 3.5 Tg/yr is simulated between 1992 and 1990 with WSL and no change is found with SDGVM, when directly computed from SOCOLV3 OH fields. A stronger increase of 10 Tg/yr was found in Wang et al. (2004) [144], but decreases of 25 Tg/yr or 5 Tg/yr was simulated in Bousquet et al. (2006) [15] and Bândă et al., (2016) [7] for the same period. These studies use different approach to simulate OH: based on MCF (Bousquet et al., 2006 [15]); from CCMs (Wang et al., 2004 [144]); or interactive OH calculated via the TM5 CTM ( Bândă et al., 2016 [7]). From their OH concentrations Wang et al. (2004) [144] and Bousquet et al. (2006) [15] found a decrease in wetland emissions of 20 Tg in 1992 compared to 1990 and 35 Tg/yr in the first half of 1992, respectively. This highlights that large uncertainties remain on the contribution of both methane sources and sinks affected by the volcanic eruption ( Bândă et al., 2016 [7]).

In terms of anthropogenic emissions, EDGAR and SCHWIETZKE report a decrease of the Eurasian region of 5 and 5.2 ppbv/yr between 1991 and 1993. Therefore, the fall of the Soviet Union is responsible for about 50% of the methane decrease between 1991 and 1993. Wetlands are the second most important factor, accounting for 37% of the total change using WSL, followed by decreasing anthropogenic contributions from China and North America).

4.3.2.2 1993-2004

A major event taking place during this period is the 1997-98 El-Niño, responsible for a large increase in the observed global methane growth rate (Fig. 4.8). Biomass burning emissions in tropical Asia and boreal Eurasia are the most important contributors (Fig. 4.10). This is consistent with a strong increase in CH$_4$ emissions from biomass burning, reported in GFED3.1 (Van der Werf, 2010 [157]) as an increase of 26.4 Tg/yr in
global emissions in 1997 (corresponding to 155% based on the 2000-2009 global mean, Table 4.1) compared to 1996, followed by a decrease of 17.9 Tg/yr in 1998 (105%). The results of our model simulation are in agreement with a previous inversion modeling study by Bousquet et al. (2006) [15] and the CTM simulations by Dalsoren et al., (2016) [26].

In addition to the increase in biomass burning emissions, ENSO, by its extreme dry and warm followed by wet conditions also impacts CH₄ emissions from wetlands. Figure 4.5 suggests a small global negative anomaly in 1997 followed by a strong positive and also global anomaly of about 5% simulated by both inventories. Global wetland tracers between 1997 and 1998 increase by 1.3 ppbv/yr for EDGAR-WSL and 5.3 ppbv/yr for EDGAR-SDGVM, mainly due to an increase in emissions in tropical South America, as already suggested by Dlugokencky et al. (2001) [36], Bousquet et al. (2006) [15], Dalsoren et al. (2015) [27]. Moreover, a large contribution is given to the wetland emissions from the “NA_Boreal“ region in WSL, which is not supported by SDGVM. The boreal North America emissions in WSL improve agreement with observations (Fig. 4.9). Previous studies also confirm a positive change in wetland emissions in Northern Hemisphere high latitudes (Bousquet et al., 2006 [15], Dalsoren et al., 2015 [27]). In addition, El-Niño, by increasing CO emissions, also led to decreasing OH sink (Bousquet et al., 2006 [15]). The underestimation found in our case could be due to our overestimated OH levels (Section 4.3.1), which do not allow the large CO emissions of this period to remove OH enough.

The long-term trend during the 1993-2004 is affected by a strong negative contribution from anthropogenic emissions in the Eurasian region (Fig. 4.10). SCHWIETZKE reports a stronger decline in anthropogenic emissions in Europe and boreal Eurasia (Sect. 4.2.4), leading to an underestimation of global methane growth rate. EDGAR4.2 seems to better represent the change in emission fluxes during that period.

The plateau between 1999 and 2006 was investigated by former studies: a combination of increasing anthropogenic emissions and decreasing natural emissions was found to be a possible reason (Bousquet et al; 2006 [15]; Bousquet et al., 2011 [16]; Monteil et al., 2013 [90]). However, Pison et al. (2013) [100] found natural emissions either to decrease or to increase, depending on the modeling approach. The simulated plateau between 1999 and 2001, which is in good agreement with observations (Fig. 4.8 and 4.9), is explained by a compensation of negative contributions from anthropogenic emissions in Europe and positive contributions from anthropogenic emissions in Africa, China, India, and South America (Fig. 4.10). Using SDGVM leads to a stronger variability of wetland emissions between 1999 and 2001, however canceling each other out (Figure 4.10). A negative contribution from biomass burning emissions in Tropical Asia is also found to play a role during this period.

2002-2003 is marked by an observed positive anomaly (Fig. 4.8), more pronounced in the Northern Hemisphere (Fig. 4.9). Tracer diagnostics highlight in all simulations a significant contribution from biomass burning in tropical Asia (Fig. 4.10) and to a lesser extent tropical South America (not seen in Fig. 4.10), in agreement with previous studies (Simpson et al., 2006 [127]; van der Werf et al., 2010 [157]; Bergamaschi et al., 2013 [12]; Dalsoren et al., 2016 [26]).
4.3 RESULTS AND DISCUSSION

All our simulations overestimate the observed global methane growth rate after 2004 (Figures 4.8 and 4.9), by 2.3 to 3.8 (averaged over the 2004-2010 period). Differences are higher in the simulations using EDGAR4.2, highlighting the overestimation of coal mining emissions in China (Fig. 4.10), already discussed in Bergamaschi et al. (2013) [12]. SOCOLv3 is not able to reproduce the decrease in observed methane growth rate after 2004, mainly occurring in the Northern Hemisphere mid-latitudes (Fig. 4.9). The reasons for this sudden decrease remain unclear.

Because all simulations attribute too much to increasing anthropogenic emissions over China after 2004, identifying the drivers of methane increase after 2007 remains difficult. Using SCHWIETZKE-WSL helps to reduce the bias between observations and simulations at all latitudes (Fig. 4.9). This simulation shows a strong impact of anthropogenic emissions to explain increasing methane. A more detailed attention has been
given to the drivers of the increase in methane after 2007 and will be described in a combination paper.

4.3.3 Variations in OH and methane lifetime

Model performance in simulating OH was already discussed in section 4.3.1. Here, the trend in methane lifetime as well as trend in OH concentrations is analyzed in order to understand its impact on methane variations. Only the impact of OH is taken into account in this section, as this study mainly focuses on methane fluctuations at the surface, as the uptake of methane by soils remains a small part of methane sinks (2%) and a climatology is used for this effect (Table 4.1).

Figure 4.11 shows tropospheric methane lifetime between 1984 and 2010 as well as tropospheric OH concentrations. Overall, there is an anti-correlation between OH trends and variations in methane lifetime. The average over all the simulations shows decrease of 7% in tropospheric methane lifetime, comparable to Dalsoren et al. (2015) [27] using the Oslo CTM3 model (8%). However, a more pronounced decrease is found between 1990 and 2000 (5% and 2% respectively). As already mentioned, simulations with SDGVM show a lower lifetime, especially after the Pinatubo volcanic eruption, due to enhanced tropospheric OH concentrations, because of the low levels of methane (Fig. 4.8).

Absolute values are however lower (9.2 yr in their study in 2000 compared to 6.7 yr on average for our four simulations) in our simulations compared with Dalsoren et al. (2015) [27]. Simulated tropospheric methane lifetime are also lower compared to the ACCMIP inter-comparison: on average, ACCMIP reports a tropospheric methane lifetime of 9.7 years in 2000 (Naik et al., 2013 [94]). However, as mentioned in section 4.3.1, the range of values in ACCMIP goes from 7.1 to 14.0, and SOCOLv3 is in the lower limit. Section 4.3.1 has already shown that our simulated MCF variations after 1998 are in agreement with previous studies (Montzka et al., 2011 [91]; Holmes et al., 2013 [65]). Other forward models show an increase in tropospheric OH concentrations between the 1980 decade and the 2000 decade, but with a lower absolute value of about 2-3% (Fiore et al., 2006 [52]; Holmes et al., 2013 [65]; Naik et al. 2013 [94]). This could reflect a possible overestimation in increasing OH the years following the volcanic eruption of Mount Pinatubo. On the other hand, large increases in OH concentrations in the 1980 decade, followed by a substantial negative trend in the 1990s, are found by studies using MCF variations (Krol and Lelieveld, 2003 [77]), but these results were debated because of uncertainties in latitudinal gradient distribution of MCF emissions (Wang et al., 2008 [145]).

Using multi-linear regression approach, Dalsoren et al. (2016) [26] found with a robust result that methane lifetime is mainly driven by CO and NOx emissions, specific humidity, lightning NOx emissions, and ozone column. A similar approach would help to understand the drivers influencing simulated methane lifetime in SOCOLv3.
In this study we present four simulations performed with the CCM SOCOLv3 using methane fluxes as input and different inventories for CH$_4$ emissions from the anthropogenic and wetland sources. The relative impact of various sources and geographical regions is tracked and allow a unique quantification of methane sources on its fluctuations.

Different time periods are chosen. Between 1984 and 1991, the constant increase in methane growth rate is mainly affected by positive contribution of anthropogenic emissions over India, Europe, and China, independently of the chosen inventory for anthropogenic emissions: EDGAR4.2 and SCHWIEKZE. The observed decrease after 1991 is mainly impacted by decreasing fossil fuel emissions over Europe and Siberia, as well as decreasing wetland emissions mainly from the tropical South America region. The negative contribution of anthropogenic emissions over Europe after the collapse of Soviet Union remains important almost until the end of the simulations. Besides the 1997-1998 El-Niño period, where a strong contribution of biomass burning emissions over tropical Asia is found, the plateau of methane levels between 1991 and 2001 is found to be due to compensating negative contributions of anthropogenic emissions over Europe and positive contributions over India, South America, and China. If the plateau is observed until 2006, all the simulations miss the decrease in 2004, mainly observed in the Northern Hemisphere. Simulations using EDGAR4.2 strongly overestimate methane increase after 2007, due to a too strong contribution from coal mining emissions over China. Using SCHWIEKZE helps to get a smaller difference with the observations but the increase in anthropogenic emissions over China is still too high.
in this inventory. Furthermore, the decrease in Eurasian anthropogenic emissions after the collapse of the Soviet Union is overestimated in the 1990s in SCHWIEITZKE. The use of the stable carbon isotope of methane, $^{13}\text{CH}_4$ and its atmospheric ratio with $^{12}\text{CH}_4$, which could help to understand the drivers of increasing methane since 2007, is part of a more detailed study. Simulations using the two wetland data sets, LPJ-WSL and SDGVM, show significant differences in the impact of wetlands from various regions on global methane growth rate. SDGVM, simulating globally higher CH$_4$ emissions from wetlands, mainly from Northern Hemisphere high latitudes, show a stronger influence of wetlands. The interannual variability of different regions however globally partly compensate. In 1992, the decrease in CH$_4$ emissions from wetlands after the volcanic eruption of Mount Pinatubo estimated by SDGVM overestimate the impact on global methane growth rate compared to LPJ-WSL. Using two inventories for wetland emissions highlight the need to better constrain CH$_4$ emissions from wetlands in order to better represent the impact of wetlands on past methane fluctuations. For the same period, all the simulations show a decrease in methane lifetime mainly between 1990 and 2000, followed by stable levels. The implementation in SOCOLv3 of a MCF tracer shows a too strong removal by OH, due to overestimated OH levels. However, variations in MCF after 1998 infer small OH fluctuations, as expected from previous studies. A study of the potential drivers of methane lifetime, such as CO/NOx emissions, temperature, as the multi linear regression performed in Dalsoren et al. (2015) [27], will help to better understand variations of methane lifetime in SOCOLv3, as well as its impact on methane variations over the last three decades.
Observations show a strong drop in the global methane growth rate following the eruption of Mount Pinatubo, which could be caused by changes in methane sources and/or sink processes. Here we study the impact of the volcanic eruption on tropospheric methane with the 3D Chemistry-Climate Model (CCM) SOCOLv3. An implemented tracer diagnostics allows tracking of methane from different source categories and geographical regions. Our results indicate that over 70% of the methane change in the second year after the eruption is caused by a decrease in wetland emissions, mainly from tropical South America. In addition, the main sink of tropospheric methane, its reaction with the hydroxyl radical (OH), is affected by several opposing processes. The enhanced stratospheric aerosol burden leads to a more pronounced stratospheric ozone depletion, hence more UV radiation increasing tropospheric ozone photolysis rates by 4%, and therefore OH formation, resulting an a reduced methane lifetime. This effect is compensated by the global tropospheric cooling of around 0.25 K in the second year after the eruption, which slows down methane oxidation via the reaction with OH, leading to a prolonged lifetime of methane. Furthermore, the lower temperatures reduce OH formation due to less tropospheric water vapor.

This chapter is a paper in preparation: Coulon, A., Stenke, A., Zhang, Z., and Peter, T.: Impact of the volcanic eruption of Mount Pinatubo on tropospheric methane
5.1 INRODUCTION

Concentrations of methane (CH$_4$) in the atmosphere have more than doubled since pre-industrial times, from 720 ppbv to 1504 ppbv in 1978 (Etheridge et al., 1998 [46]), and then further to 1830 ppbv nowadays (WMO GHG Bulletin 10, 2014 [143]). Methane is the second most important greenhouse gas (GHG), responsible for about 17% of the total radiative forcing since pre-industrial times (Myhre et al., 2013 [93]). During the last three decades, its atmospheric levels revealed fluctuations which are not yet fully understood yet. The growth rate decreased from 12 ± 6 ppbv/yr in the 1980s to 6 ± 8 ppbv/yr in the 1990s, and even lower rates afterwards (Kirschke et al., 2013 [73]).

The volcanic eruption of Mount Pinatubo in June 1991 of the Philippines (15°N) had a significant impact on global atmospheric chemistry (Bekki et al., 1994 [10]; Dlugokencky et al., 1996 [33]). Methane observations show a decrease from 10 ppbv/yr to nearly zero in 1992 of global methane growth rate, followed by an increase in 1993 (Dlugokencky et al., 1996 [33]).

A volcanic eruption such as that Mount Pinatubo has a number of different effects on tropospheric photochemistry and methane variability. Recent results suggest an injection strength of about 7 Mt of sulfur into the stratosphere (mainly between 19 and 22 km), approximatively 100 times higher than the background value (Sheng et al., 2015 [126]), leading to enhanced stratospheric aerosols producing significant effects for a few years after the eruption (McCormick et al., 1995 [86]). Less UV radiations reach the troposphere because of enhanced stratospheric scattering (Dlugokencky et al., 1996 [33]). Furthermore, the volcanic aerosols lead to an enhanced depletion of stratospheric ozone caused by heterogeneous chemistry on the aerosol surfaces and by changes in atmospheric circulation caused by aerosol-induced IR-heating (Robock, 2000 [113]). The two effects lead to opposing impact on tropospheric methane. First, the enhanced UV absorption by SO$_2$ and scattering from sulfate aerosols reduce the tropospheric ozone photolysis and thus increase the methane lifetime due to less tropospheric OH. Using the three dimensional chemistry transport model TM5, Bândă et al., (2015) [8] estimated this effect to be responsible for a decrease of ~2% of tropospheric OH in the first two years following the volcanic eruption. Conversely, when SO$_2$ has been converted into aerosols, volcanic stratospheric aerosols cause higher ozone depletion via heterogeneous reactions taking place at the surface of aerosols. It allows more UV radiation to reach the troposphere and therefore, increase the tropospheric ozone photolysis rate and formation of the OH radical. Using a 2D box-model, Bekki et al., (1994) [10] attributed half of the decrease in CH$_4$ growth rates in 1992 to stratospheric ozone depletion. This effect has a large impact of post-Pinatubo tropospheric methane variability (Bândă et al., 2013 [6]; Bândă et al., 2016[7]).

The Mount Pinatubo volcanic eruption also involved a cooling of the global surface temperature of about 0.5 K (Dutton and Christy, 1992 [40]; McCormick et al., 1995 [86]), which affects tropospheric methane variability in three major ways. First, OH production decreases via a reduction in tropospheric water vapor concentration (by about 4% per 0.5 K). Second, a slowdown of the chemical reaction rate between methane and OH (by about 1% per 0.5 K). Third, a reduction in methane emissions due to re-
duced wetland productivity. Inverse modeling studies found a significant effect from wetlands emissions (Wang et al., 2004 [144]; Bousquet et al., 2006 [15]). However these studies show impact of OH of opposite sign: using methyl chloroform as a proxy for OH variations, Bousquet et al., (2006) [15] inferred a reduced OH sink of 30 Tg/yr between 1991 and 1993, while Wang et al. (2004) [144] found an increase by 5% for the same time period, by using OH fields from 3D models.

Volcanic eruptions may influence methane sources as well as species determining the OH in other ways. For instance, a decrease of the temperature might influence methane emissions from biomass burning. The RETRO database (Schultz et al., 2008 [122]) suggests a decrease of around 5 Tg (corresponding to a 23% change) of global methane emissions from biomass burning in 1993. However, there was previously a global increase from the same order between mid-1991 and 1992, because of an El-Niño Southern Oscillation (ENSO), correlated to increasing methane emissions from biomass burning. Telford et al. (2010) [136] found that a decrease in isoprene emissions due to the cooling impacted by the eruption led to enhanced tropospheric OH and therefore increased sink for methane of up to 5 Tg(CH₄)/yr. Furthermore, an increase in the exchange rate between stratosphere and troposphere due to the volcanic aerosol heating can influence tropospheric methane variations, as simulated by Schaufuller et al. (1994) [120]. In addition, the radiative impact of ash and water vapor injected in the stratosphere by the eruption, as well as the effect of sulfur on methane emissions from wetlands are considered to have minor impacts on methane growth rate (Bândă et al., 2016 [7]).

The Chemistry-Climate Model (CCM) SOCOL is used to perform simulations and quantify the impact of the following processes: change in methane emissions from wetlands, influence of stratospheric aerosols on tropospheric methane as well as the cooling of the troposphere. A tracer diagnostics is implemented in the model in order to attribute the changes in methane concentration to the variability at different regions in wetlands emissions, based on LPJ-WSL (Zhang et al., 2015 [155]) model. The method is described in Section 5.2. Comparison with observations, an explanation of the global decrease of the methane emissions from wetlands, a quantification of the amount of tropospheric methane lost due to this change in emissions as well as the change in methane due to the decrease of tropospheric temperature and the stratospheric ozone depletion is shown in Section 5.3. Conclusions are drawn in Section 5.4.

5.2 METHODOLOGY

5.2.1 Chemistry-climate model SOCOLv3

This study was performed using the global chemistry-climate model SOCOLv3 (Stenke et al., 2013 [134]). This model consists of the chemistry transport model (CTM) MEZON (Egorova et al., 2003 [41]) coupled to the middle atmosphere version of the general circulation model (GCM) ECHAM5 (Roeckner et al., 2003 [114]). All simulations were
done in T42 spectral resolution, which corresponds to a horizontal grid of about 2.8° × 2.8°. In the vertical a hybrid sigma-pressure coordinate system is used with 39 vertical levels from Earth’s surface up to 0.01 hPa (= 80 km). Dynamical processes are called in SOCOLv3, while radiative and chemical calculations are performed every two hours. Chemical species are advected by a flux-form semi-Lagrangian scheme (Lin and Rood, 1996 [82]). The standard chemical mechanism considers 41 chemical species of the oxygen, hydrogen, nitrogen, carbon, chlorine and bromine groups within 140 gas-phase reactions, 46 photolysis reactions, and 16 heterogeneous reactions. Isoprene oxidation is taken into account via the Mainz-Isoprene Mechanism (MIM-1), which includes 16 organic species (degradation products of isoprene) and further 44 chemical reactions (Poechl et al., 2000 [104]). To consider the contribution of certain NMVOCs to CO production, a certain fraction of NMVOC emissions is directly added to CO. In order to match total CO emissions provided by IPCC (Ehhalt et al., 2001 [43]), conversion factors are applied to NMVOC emissions: 1.0 for anthropogenic NMVOC emissions, 0.31 for biomass burning NMVOC emissions, and 0.831 for biogenic NMVOC emissions. More details are provided in Revell et al. (2015) [110]. Photolysis rates are calculated at every chemical time step using a look-up table approach (Rozanov et al., 1999[116]), including effects of the solar irradiance variability. The look-up tables provide photolysis rates as a function of O2 and O3 columns, meaning that the photolysis scheme sees interactive ozone. The impact of clouds on photolysis rates is accounted for by including a cloud modification factor, following Chang et al., (1987) [21]. For the present model study we used emission fluxes as lower boundary condition for methane to simulate the whole methane cycle in a self-consistent manner. The applied emission data sets for the different source categories are described in Section 1.2.3 and 1.2.4. The uptake of methane by soils and its subsequent oxidation is taken into account as negative emission using a climatological map of negative methane fluxes provided by Spahni et al. (2011) [130]. The climatology is given for an atmospheric concentration of 1800 ppbv. The actual uptake in then scaled to the actual methane concentration during the model simulation.

5.2.2 Tracer diagnostics

Besides the prognostic methane tracer, 48 diagnostic methane tracers, tracking methane emissions from various source categories and geographical regions, have been implemented into SOCOLv3. These tracers allow a quantification of the contribution of different methane sources to the total methane variability. The tracer definition follows the TransCom-CH4 approach (Gurney et al., 2000 [60]). 13 tracers, separated in different regions have been implemented to track methane emissions from wetlands, 11 for anthropogenic sources, 13 for biomass burning, 7 for rice emissions, and 4 tracers for minor sources: wild animals, mud volcanoes, ocean hydrates, and termites. The sum of the diagnostic methane is forced to be equal to the prognostic methane tracer.
Furthermore, these tracers are initialized via the ratio of emissions from the specifics source and region and the total emissions of CH$_4$ in 1980.

Table 5.1: Performed simulations for the time period 1990-1995. Each type of simulation is a 5 members ensemble of runs.

<table>
<thead>
<tr>
<th>Simulations</th>
<th>Wetlands emissions</th>
<th>Stratospheric aerosols</th>
<th>SSTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOPIN</td>
<td>1990</td>
<td>1990</td>
<td>1990</td>
</tr>
<tr>
<td>SST</td>
<td>1990</td>
<td>1990</td>
<td>1990-1995</td>
</tr>
</tbody>
</table>

5.2.3 Performed simulations

Five different ensemble (of 5 members each) simulations have been performed for understanding the impact of the volcanic eruption on tropospheric methane (Table 5.1). A referent simulation was performed from 1990 to 1995. In order to eliminate the influence of the volcanic eruption, a simulation was performed where the CH$_4$ emissions from wetland, the stratospheric aerosol layer as well as the sea-surface temperatures (SSTs) were kept constant to the 1990 values. Simulating constant wetland emissions do not take into account the effect of tropospheric colder temperatures as well as precipitation anomalies induced by the volcanic eruption. Constant stratospheric aerosol layer does not consider the enhanced stratospheric ozone depletion after the volcanic eruption and its impact on tropospheric OH. Furthermore, keeping SSTs to constant values before the volcanic eruption is not influenced by the tropospheric cooling as well as decreasing water vapor abundance in the troposphere. The impact of these different processes induced by the volcanic eruption of Mount Pinatubo and involved in tropospheric methane variations were disentangled using sensitivity simulations, where one of the parameter is varying between 1990 and 1995 (Table 5.1).

The sea-surface temperatures (SSTs) are provided by the U.K. Meteorological Office Hadley Centre (Rayner et al., 2003 [107]; Rayner et al., 2006 [108]). The stratospheric aerosols are based on the SAGE-4.5 satellite data (Arfeuille et al., 2013 [4]). The applied wetland emissions are described in the following section. All other boundary conditions, namely emissions of CO, NOx, and NMVOCs, concentrations of CO$_2$, N$_2$O and ozone depleting substances as well as total solar irradiance, are prescribed following the specifications of the IGAC/SPARC Chemistry-Climate Model Initiative (CCMI: Eyring et al., 2013 [51]).

Table 5.2 summarizes the applied emission data sets for methane.
Table 5.2: Summary of the source categories of emissions used as input for the methane boundary conditions in the simulations run by SOCOLv3.

<table>
<thead>
<tr>
<th>Source category</th>
<th>Available emissions</th>
<th>Inventory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthropogenic</td>
<td>1990 – 1995</td>
<td>EDGAR 4.2 database</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EC-JRC/PBL. EDGAR version 4.2.</td>
</tr>
<tr>
<td>Wetlands</td>
<td>1990 – 1995</td>
<td>LPJ-WSL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zhang et al., (2015) [155]</td>
</tr>
<tr>
<td>Rice</td>
<td>1993-1995</td>
<td>Hodson et al., (2011) [64]</td>
</tr>
<tr>
<td></td>
<td>Climatology otherwise</td>
<td></td>
</tr>
<tr>
<td>Biomass burning</td>
<td>1990 – 1995</td>
<td>RETRO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Schultz et al. (2008) [122]</td>
</tr>
<tr>
<td>Wild animals</td>
<td>Climatology</td>
<td>Houweling et al., (1999) [68]</td>
</tr>
<tr>
<td>Mud volcanoes</td>
<td>Climatology</td>
<td>Patra et al., (2011) [97]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Etioppe and Milkov, (2004) [47]</td>
</tr>
<tr>
<td>Ocean hydrates</td>
<td>Climatology</td>
<td>Patra et al., (2011) [97]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lambert and Schmidt, (1993) [79]</td>
</tr>
<tr>
<td>Termites</td>
<td>Climatology</td>
<td>Patra et al., (2011) [97]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fung et al., (1991) [54]</td>
</tr>
<tr>
<td>Uptake by soils</td>
<td>Climatology</td>
<td>Spahni et al., 2011 [130]</td>
</tr>
</tbody>
</table>

5.2.4 Wetlands emissions

For a better representation of the wetland fraction within a model grid box the hydrological inundation model TOPMODEL (Beven et al., 1984 [13]) is used in LPJ-WSL. It helps moreover to improve the spatial distributions of wetlands as well as their inter-annual variations (Zhang et al., 2015 [155]). The inundated area is constrained in LPJ-WSL using monthly values from the CRU3.1 reanalysis data: precipitation, mean temperature, cloud cover (Harris et al., 2014 [62]). 

CH₄ emissions are assumed to be emitted from areas where anaerobic conditions combined with decomposition of organic matter occur. The wetland CH₄ fluxes are modeled as linear function of wetland types (linked to an ecosystem scaling factor), wetland area extent and heterotrophic respiration (Hodson et al., 2011 [64]). These methane emissions are regulated by major biotic processes controlling substrate availability for methanogenesis, temperature and moisture dependence of microbial decomposition rate, as well as abiotic processes that influence the mean water table depth at each 0.5 degree grid cell with consideration of geomorphic controls at fine resolution (500m) within the grid cell (Zhang et al., 2015 [155]).
5.3 Results and Discussion

5.3.1 Comparison with observations

Before we disentangle the different effects of the eruption of Mount Pinatubo on tropospheric methane, simulated stratospheric ozone and tropospheric temperatures are evaluated by comparison with observations. Figure 5.1 describes deseasonalized ozone column integrated from 100 hPa to 1 hPa, averaged over 60°N to 60°S, from 1991 to 1995, scaled to January 1991, for the ensemble means REF, AER and NOPIN, as well as GOZCARDS satellite measurements (Froidevaux et al., 2015 [53]). Satellite observations show an increase in global ozone just after the volcanic eruption, mainly in the Southern Hemisphere (however not shown in Fig. 5.1), possibly due to an enhanced tropical upwelling and extra-tropical downwelling due to the heating from volcanic aerosols (Aquila et al., 2013 [3]). The increase is less pronounced in the simulations, resulting in a different response of the Brewer-Dobson Circulation (BDC) to the volcanic eruption by SOCOLv3. It could be due to compensating effect between transported ozone and both chemical production and destruction of O3. After 1992 observations as well as model simulations show a decrease in stratospheric ozone, leading to enhanced UV levels in the troposphere. The modeled decline in stratospheric ozone is more pronounced than in the observations. Enhanced heterogeneous reaction due to the volcanic aerosols could be a reason for this too pronounced simulated ozone depletion. A comparison between observed and simulated stratospheric NO2 could help to understand the chemical influence of the volcanic aerosols on ozone. More UV radia-
tions is expected to lead to higher OH formation in the troposphere (Bândă et al., 2015 [8]). Our simulations indicate an increase by about 4% in 92-mid 1993 in tropospheric ozone photolysis rate by comparing AER and NOPIN. Because of the simulated too strong stratospheric ozone depletion, an increase of only 2-3% for the same period should be expected (the relationship between increase in surface UV and ozone column reduction can be considered as linear for ozone column reduction of less than 5%, according to Vogelmann et al., 1992 [140]).

The tropospheric temperature response to the eruption of Mount Pinatubo is shown in Figure 5.2. The simulated tropospheric cooling follows the different reanalysis data, to reach an absolute cooling of 0.2 K compared to the 1990-1995 average, in good agreement with the selected reanalysis data (Fig. 5.2). However, a coinciding El Niño event partly offset the temperature decrease from the eruption. Removing this effect leads to a decrease of -0.6-0.8 K in the lower troposphere (Santer et al., 2001 [117]). Only the absolute change in temperature is considered for this study, which could lead to an underestimation of the impact of the tropospheric cooling only due to the volcanic eruption. The recovery after 1993 is found to be also in agreement with the reanalysis data, despite a slight overestimation in mid-1993.

Reduced tropospheric temperatures are expected to have an impact on tropospheric water vapor abundance. Simulations describe a decrease in water vapor of maximum 1.2% (late 1992) by comparing SST and NOPIN simulations. This is comparable to a decrease of 3% in observed tropospheric water vapor column at the same period (Soden et al., 2002 [129]). It should be noted that we averaged tropospheric water vapor concentration up to 500 hPa in our calculation, which could also explain the lower value.

Figure 5.2: Time series of anomalies in deseasonalized temperature (K) averaged over 1000 hPa–500 hPa compared to the 1990-1995 mean from the REF simulation (red line represents the ensemble mean, shaded area the minimum-maximum range) and reanalysis data: JRA55 (black double dotted-dashed line) (Kobayashi et al., 2015 [74]), ERA-Interim (black dashed line) (Dee et al., 2011 [28]), MERRA (black dotted line) (Rienecker et al., 2011 [111]), and MERRA-2 (dashed-dotted line) (Koster et al., 2015 [75]).
5.3 RESULTS AND DISCUSSION

Precipitation GPCP
Precipitation CRU3.1
Wetland extent CRU3.1
CH$_4$ emissions from wetland
Temperature CRU3.1

Figure 5.3: Relative anomalies (in %, left y axis) in wetland extent (blue line), precipitation from CRU3.1 (green line), from GPCP (dashed green line), and CH$_4$ emissions from wetlands (red line). The black lines represent the absolute anomaly in temperature (in K, right y axis). Nine regions are shown based on the implemented methane tracers. Anomalies are calculated with respect to the 1980-2010 mean.

5.3.2 Change in methane emissions from wetlands

The years following the Pinatubo volcanic eruption are characterized by decline of surface temperatures by about 0.5 K at the surface (Dutton and Christy, 1992 [40]) and a
decrease in precipitation over land for the October 1991-September 1992 period (Trenberth and Dai, 2007 [137]), both processes influencing wetlands area and the amount of emitted methane.

Figure 5.3 shows the anomalies in precipitation (both from CRU 3.1 data and the Global Precipitation Climatology Project, GPGP, Adler et al., 2003 [1]), temperature from CRU3.1, wetland extent, and methane emissions from wetlands as calculated by the Dynamical Global Vegetation Model (DGVM) LPJ-WSL. The nine regions shown in Fig. 5.3 correspond to the implemented tracer diagnostics.

The change in precipitation after Mount Pinatubo shows different patterns for different regions. Based on Figure 5.3, five regions show a negative anomaly in precipitation after the volcanic eruption: India, East Asia, South Africa, tropical South America, and tropical Asia. Only temperate South America shows a pronounced positive anomaly. As GPCP and CRU3.1 show similar patterns (Fig. 5.3), the statements from Trenberth and Dai [137], using GPCP observations to understand the impact of the volcanic eruption on global precipitation, can be applied for this study. They impact the severe drought occurring in these regions too strong to be only due to the 1991-92 El-Niño event, and can be attributed to the volcanic eruption to some extent.

Regions located in the Northern Hemisphere high latitudes are described in Fig. 5.4. In these regions the main driver for the change in CH₄ emissions from wetland is the temperature. When the soil is frozen, no CH₄ emissions is simulated by LPJ-WSL. A decrease in temperature in these regions could then lead to a decrease in CH₄ emissions from wetland, as more surface could stay cover by ice during summer time. Another effect is the efficiency of methane production via microbial sources, as it temperature dependent (Westermann et al., 1989 [149]). Figure 5.4 shows that the anomaly in temperature is 10% for boreal North America, 4% for Europe, and 8% for boreal Eurasia, corresponding to an absolute decrease of about 0.7 K. The regions located

![Figure 5.4: Relative anomalies (in %)) in wetland extent (blue), temperature (black, in K), and CH₄ emissions from wetlands (red line), for the North America Boreal region (left plot), Europe region (middle plot), and Eurasia Boreal region (right plot). Anomalies are compared to the 1980-2010 mean.](image-url)
in the tropics and Southern Hemisphere mid-latitudes (mainly South America, Africa and Eastern Asia) show a strong correlation between anomalies in precipitation and wetland extent, and therefore CH$_4$ emissions. LPJ-WSL simulates a decrease in global wetlands of 8.2 Tg/yr between 1992 and 1991 (corresponding to 5% of total emissions), close to the 8 Tg/yr from the LPJ model from the Hydrogen, Methane, and Nitrous Oxide (HYMN) project (Spahni et al., 2011 [130]) used in Bândã et al., (2016) [7]. However it is smaller than the 25 Tg/yr decrease in 1992 simulated by ORCHIDEE (Wania et al., 2013 [147]), corresponding of roughly 11% of the emissions.

The effect of sulfur deposition on wetlands, potentially decreasing CH$_4$ emissions from this source category, is not taken into account in this study, as it considered to be small compared to the other drivers, i.e. precipitation and temperature (Bândã et al., 2016 [7]).

### 5.3.3 Change in tropospheric methane due to the decrease in methane emissions from wetlands

The previous section highlighted a substantial decrease in methane emissions from wetlands in 1992. Comparing the difference in the tropospheric methane burden between REF and NOPIN and between WET and NOPIN (Fig. 5.5), respectively, shows that around 74% of the change in tropospheric methane burden two years after the volcanic eruption is related to the decrease in wetland emissions. Using the CTM TM5, Bândã et al., (2016) [7] found a less pronounced impact of decreasing wetland emissions, although their applied wetland emissions data set reported a similar emission decline in 1992. Their results are similar to the the study of Bekki and Law (1997) [9], who used a two-dimensional CTM, but this study finds a dominant effect of decreasing wetland emissions in the Northern Hemisphere but not in the tropics, only by investigating the effect of temperature after the volcanic eruption. Moreover, both studies indicate the strongest impact of decreasing wetland emissions before mid-1992 and a recovery afterwards. The influence of wetlands strongly depends on the chosen database: Bândã et al., (2016) [7] found a much stronger impact, when applying the ORCHIDEE database. Nevertheless, the lifetime of the wetland effect is again shorter and almost fully recovered after two years, where in our simulations the effect is still present in May 1993.

Figure 5.5 describes the tropospheric methane burden of the different regions based on the tracer diagnostics. Eight regions show a decline in tropospheric methane burden two years after the volcanic eruption and are listed from the highest to the lowest absolute change (taken from the difference between NOPIN and WET): tropical South America, South Africa, tropical Asia, boreal North America, boreal Eurasia, India, East Asia temperate, and Europe. Four tracers show an increase in tropospheric methane burden: temperate South America, North Africa, temperate North America, and Middle East. Figure 5.6 summarizes the difference between NOPIN and WET for the sum of all the tracers and each tracer two years following the volcanic eruption.
Figure 5.5: Global tropospheric methane burden (in Tg, left y axis) up to 500 hPa for nine methane tracers as well as total methane for REF simulations (red), NOPIN simulations (blue), and WET simulations (green). For each simulation the line represents the average over the 5 ensemble members, and the area covers the maximum and minimum values. Black lines represent the accumulated CH$_4$ emissions from wetlands (in Tg/yr) only when 1990 is kept constant (dashed lines) or when emissions are varying (thick lines) for the different regions or in global average in the plot for total methane.
The strongest impact is given to tropical South America, with a decrease of roughly 4 Tg in tropospheric methane burden (43% of the total change between NOPIN and REF). As discussed in the previous section, this is due to a negative anomaly in precipitation after the volcanic eruption. Tropical South America is also the region where LPJ-WSL simulates the highest CH$_4$ emissions from wetlands: 35% of the total emissions in 1990.

The tracers showing an increase in tropospheric methane burden compared to NOPIN are mainly South America temperate and North Africa (Fig. 5.6). Based on previous section, this change is also driven by precipitation anomalies starting before the volcanic eruption, especially for the Northern Africa tracer. Using 1990 as a baseline takes into account changes occurring before the volcanic eruption. As shown in Figure 5.3, North Africa shows slight negative anomalies in CH$_4$ emissions from wetland after
the volcanic eruption. Figure 5.5 shows that CH$_4$ emissions from wetlands in this region are low compared to tropical South America and represent 7% of the emissions simulated by LPJ-WSL in 1990. Therefore, the discrepancy obtained by taking 1990 as a baseline, having an effect mainly over this region, does not change the global decrease in tropospheric methane burden due to the CH$_4$ emissions from wetlands two years after the volcanic eruption.

5.3.4 Change in tropospheric methane due to OH

In this section we investigate the effects of the post eruptive tropospheric cooling and stratospheric ozone decline on the main CH$_4$ sink, the reaction with the OH radical. The decreased surface temperatures induce a slowdown of the chemical reaction between CH$_4$ and OH as well as a reduced tropospheric water vapor abundance, both affecting OH formation. These effects are analyzed by the model experiment SST. With the simulation AER, we investigate the stratospheric ozone effect on tropospheric UV levels, photochemical OH formation and tropospheric methane burden.

As obvious from Figure 5.7, tropospheric cooling leads to an enhanced tropospheric methane burden compared to the simulations NOPIN, while stratospheric ozone depletion results in less tropospheric methane. Both effects become significant in late 1992. Two years after the volcanic eruption the two effects compensate each other: the difference in methane burden between AER and NOPIN amount of -4.1 Tg, while SST and NOPIN differ by 4.4 Tg. Absolute values are smaller than the effect of wetlands, which remain the main driver of methane variations after the Pinatubo eruption. Figure 5.7 also describes the variations in temperature, O$_3$ photolysis rate as well as water vapor mixing ratio in the troposphere, the main actors of OH variations impacted by the volcanic eruption. Temperature and water vapor concentration decrease (by respectively 0.2 K and 1.5% on average over the second year after the volcanic eruption) due to the general cooling, which becomes sensitively more important after the second half of 1992. The combination of these two factors contribute to the higher global methane burden in the SST simulation compared to the NOPIN simulation. By choosing to keep the SSTs constant to the 1990 values, other factors are then implied which can contribute to the simulated difference between SST and NOPIN. Bândă et al. (2016) [7] mentioned that changing the SSTs could affect cloudiness as well as large scale tropospheric transport, potentially affecting tropospheric methane as well. 1992-93 is also marked by an ENSO event which counteracts the volcanic cooling. Therefore, in our process, ENSO is also considered and not only the cooling due to the volcanic eruption. On the other hand, Figure 5.7 reveals an increase in tropospheric ozone photolysis rate by about 5% the second year after the volcanic eruption with the AER simulation (again compared to NOPIN), leading then to an increase in OH production and therefore the shown lower methane burden in AER compared to NOPIN. As already discussed, the change in photolysis rates might be overestimated in our simulations considered stratospheric ozone depletion (Fig. 5.1).

The compensating effect between tropospheric cooling and stratospheric ozone deple-
tion is similar to the CTM study from Bândă et al. (2016) [7]. However, a larger impact is given to the stratospheric ozone depletion compared to the tropospheric cooling (about -3.5 ppbv/yr compared to 3 ppbv/yr two years after the volcanic eruption). As their CTM is driven by ERA-Interim reanalysis data, the tropospheric cooling is expected to be the same as our simulations (Fig. 5.2). They also take into account a decrease in stratospheric O\textsubscript{3} column between 1991 to early 1993, close to our values (Figure 5.1). In their study, other effects are considered and having an impact on tropospheric OH, such as variations in CO and NOx emissions, which both show an increase until mid-1992 and a decrease afterwards. However, the inter annual variations in NOx and CO emissions are mainly driven by other factors than the volcanic eruption, like ENSO events and anthropogenic emissions, and therefore not included in this study. Furthermore, Telford et al. (2010) Telford et al. [136] simulated a decrease in isoprene emissions of 40 Tg(C)/yr (corresponding to about 7% of total isoprene emissions) in the late 1992 and early 1993, leading to an intensified methane loss up to 5 Tg (CH\textsubscript{4})/yr. Bândă et al. (2016) [7] found the strongest contribution two years following the volcanic eruption from non-wetland emissions, about -4 ppbv/yr, however without making the distinction between anthropogenic, CO, NOx, or isoprene emissions.

As discussed before our simulations do not capture the observed short-term ozone increase right after the volcanic eruption (Fig. 5.1). However, based on Bândă et al. (2016) [7], it does not appear to have an impact on tropospheric methane and this effect does not change our conclusions on stratospheric ozone impact on tropospheric methane. Furthermore, Dlugokencky et al. (1996) [33] reported a positive, but rather small effect
of the enhanced stratospheric scattering, which leads to a reduction of surface UV by 12% immediately after the volcanic eruption. The scattering effect amounts to about 10% of the negative effect of stratospheric ozone depletion two years after the volcanic eruption (Bândă et al., 2016 [7]), and therefore is not expected to significantly change our conclusions that tropospheric methane is essentially driven by its wetlands emissions at this period. This effect has not been included in SOCOLv3 and needs to be developed in order to get a correct impact of stratospheric ozone on methane variability.

Finally the sum of the three effects (WET, AER, and SST) is not equivalent to the difference between REF and NOPIN, highlighting the nonlinear nature of there effects. By taking the sum of the differences between the sensitivity runs and NOPIN, 2.8 Tg are missing to match the difference between REF and NOPIN.

5.4 CONCLUSIONS

This study analyzed and quantified the impact of the volcanic eruption of Mount Pinatubo on tropospheric methane by various model simulations with the CCM SOCOL, distinguishing different drivers as stratospheric ozone depletion, tropospheric cooling and changes in wetland emissions. An implemented tracer diagnostic tracking methane emissions from different source categories and emission regions allows to diagnose the main regions responsible for the change in tropospheric methane due to changing wetland emissions in an unique manner.

The decrease in wetlands emissions, mainly over tropical South America, is found to be the main driver of the tropospheric methane decrease after the volcanic eruption. Tropical South America accounts for more than 70% of the change caused by the wetlands. A negative anomaly in precipitation over that area after the volcanic eruption is found to be responsible for the reduced CH$_4$ emissions from wetlands. Two years after the volcanic eruption, about 70% of the change is due to decreasing CH$_4$ emissions from wetlands.

Besides changing wetland emissions, the post-eruptive tropospheric cooling and stratospheric ozone decline both affect the hydroxy radical, the main CH$_4$ sink, in a compensating manner.

Because of nonlinear effects, the sum of the individual effects does not match the overall change. Furthermore, some effects are not considered in this study, mainly the decrease in isoprene emissions leading to increasing OH and a reduced CH$_4$ lifetime as well as the enhanced scattering of UV radiation by stratospheric aerosols, leading to the opposite effects on OH. If the impact of the decrease in isoprene emissions remains unknown, taking into account the scattering of UV radiation by the volcanic aerosols would have a maximum effect in early 1992, compensating 40% the impact of stratospheric ozone depletion on tropospheric methane. However, this effect becomes less important after the first year and accounts for less than 10% of the stratospheric ozone depletion after two years. New studies including these effects would help to ob-
tain a more detailed picture of the influence of the volcanic eruption on tropospheric methane.
After a period of zero growth between 2000 and 2006, atmospheric methane concentrations are on the rise again since 2007. The role of natural and anthropogenic emissions in this renewed increase is heavily discussed. In this study we present model simulations performed with the global chemistry-climate model SOCOL, in which regionally and source-wise disaggregated methane tracers as well as the carbon isotopologues of methane have been implemented in order to disentangle the role of different source categories and emissions regions to the observed methane increase after 2007. Our model results indicate that the observed rise of global methane concentrations is driven by anthropogenic sources from Africa, Middle East, India, China, and South America, which are partly compensated by reduced emissions from Eurasia and North America. Our simulations further indicate that the EDGAR4.2 inventory strongly overestimates anthropogenic methane emissions from coal in China. Re-evaluating the methane trend using a reduced emission rate for Chinese fossil fuel emissions leads to a better agreement with the observed decreasing trend in $\delta^{13}C$ after 2008, and puts stronger weight on agricultural emissions from India and South America.
Atmospheric methane (CH$_4$) concentrations have increased by a factor of 2.5 since pre-industrial times (Ciais et al., 2013 [23]), making CH$_4$ the second most important greenhouse gas after carbon dioxide in terms of anthropogenic radiative forcing (Myhre et al., 2013 [93]). After a period of continuous increase, methane levels remained almost constant from 1999 to 2006. Since 2007, atmospheric methane abundances are increasing again (Rigby et al., 2008 [112], Dlugokencky et al., 2009 [30]. Different scenarios have been investigated to explain this rise: the Emission Database for Global Atmospheric Research version 4.2 (EDGAR4.2) reports a significant increase in anthropogenic emissions, mainly in China, albeit overestimated (Bergamaschi et al., 2013 [12]). At the same time, increase in natural emissions (from tropical wetlands) were also found as a possible contributor for the increase after 2007 (Bousquet et al., 2011 [16]). The relative contribution of the changes in anthropogenic and natural emissions remain unknown (Kirschke et al., 2013 [73]). The impact of the main sink of methane, the reaction with tropospheric OH, also remains uncertain. Because of its very short lifetime, proxies of OH, such as methyl chloroform (MCF), are used. Variations in MCF, combined with box model study, showed a substantial impact of OH on methane growth rate before 2006 (Rigby et al., 2008 [112]). However, a small inter-annual variability in OH between 1998 and 2007 was found when using only variations in observed MCF (Montzka et al., 2011 [91]). A small decrease in globally averaged OH (4 ± 14%) was simulated between 2006 and 2007 but was not considered as significant to explain the rise in atmospheric methane (Rigby et al., 2008 [112]). Observations of the stable carbon isotope of methane, $^{13}$CH$_4$, provide useful information on the relative importance of methane sources. Biogenic sources (e.g. wetlands, agriculture, waste management), deplete the atmospheric ratio $^{13}$C/$^{12}$C, while thermogenic (e.g. fossil fuel, mud volcanoes), pyrogenic (biomass burning), as well as methane sinks induce an atmosphere enriched in $^{13}$CH$_4$. Observations in $\delta^{13}$C (relative ratio in $^{13}$C/$^{12}$C) show a global decrease after 2008 leading to an enrichment in lighter carbon isotopes impacted to increasing natural (both wetlands and ruminant) emissions (Nisbet et al., 2014 [96]). This study presents model simulations performed with the global chemistry-climate model SOCOLv3 for the period 2001-2010 in order to compare the state of near-surface methane before and after 2007 with available isotope observations. To disentangle the impact of various methane source categories and emissions regions, we have implemented a suite of diagnostic methane tracers into SOCOLv3. This tracer tracking, in combination with the implemented methane carbon isotope tracers, enables us to understand and quantify the contribution of individual methane sources from different geographical regions to the observed methane variations during the last decade. The model set up including emissions as lower boundary conditions and interactive OH chemistry allows for a consistent treatment of the atmospheric methane cycle. A detailed description of the model and its set up is given in Section 6.2. Section 6.3 presents an analysis of the simulated methane trends including an assessment of the different categories and emission regions. The model results are evaluated by com-
paring the simulated isotope ratio to observations. Conclusions are drawn in Section 6.4.

6.2 METHODOLOGY

Table 6.1: Summary of applied methane emission fluxes by source type.

<table>
<thead>
<tr>
<th>Source category</th>
<th>Available emissions</th>
<th>Inventory</th>
<th>2001-2010 Global average (Tg/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthropogenic</td>
<td>2001 – 2010</td>
<td>EDGAR 4.2 database</td>
<td>289</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EC-JRC/PBL. EDGAR version 4.2.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>“SCHWIETZKE” database</td>
<td>305</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Schwietzke et al., (2014) [124]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Schwietzke et al., (2014b) [123]</td>
<td></td>
</tr>
<tr>
<td>Wetlands</td>
<td>2001 – 2010</td>
<td>LPJ-WSL</td>
<td>172</td>
</tr>
<tr>
<td></td>
<td>2010: extension of 2009</td>
<td>SDGVM</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hopcroft et al., (2011) [66]</td>
<td></td>
</tr>
<tr>
<td>Rice</td>
<td>2001-2007</td>
<td>Hodson et al., (2011) [64]</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Climatology otherwise</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2010: Extension of 2009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wild animals</td>
<td>Climatology</td>
<td>Houweling et al., (1999) [68]</td>
<td>5</td>
</tr>
<tr>
<td>Mud volcanoes</td>
<td>Climatology</td>
<td>Patra et al., (2011) [97]</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Etiopie and Milkov, (2004) [47]</td>
<td></td>
</tr>
<tr>
<td>Ocean hydrates</td>
<td>Climatology</td>
<td>Patra et al., (2011) [97]</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lambert and Schmidt, (1993) [79]</td>
<td></td>
</tr>
<tr>
<td>Termites</td>
<td>Climatology</td>
<td>Patra et al., (2011) [97]</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fung et al., 1991 [54]</td>
<td></td>
</tr>
<tr>
<td>Uptake by soils</td>
<td>Climatology</td>
<td>Spahni et al., 2011 [130]</td>
<td>-25*</td>
</tr>
</tbody>
</table>

*Representative for a global average CH₄ mixing ratio of 1800 ppb. Scaled to the actual simulated methane values during the model simulations.
6.2.1 Chemistry-climate model SOCOLv3

The study of atmospheric methane variability had been performed using the global chemistry-climate model SOCOLv3 (Stenke et al., 2013 [134]). It consists of the middle atmosphere version of the general circulation model (GCM) ECHAM5 (Roeckner et al., 2003 [114]) and the chemistry transport model MEZON (Egorova et al., 2003 [41]). The coupling between GCM and chemistry scheme is done via temperature and the distribution of the radiatively active species. Water vapor, cloud water and the chemical constituents are advected by a flux-form semi Lagrangian scheme (Lin and Rood, 1996 [82]). The chemical mechanism takes into account 41 chemical species, 140 gas-phase reactions, 46 photolysis reactions, and 16 (stratospheric) heterogeneous reactions in/on aqueous sulfuric acid aerosols as well as three types of polar stratospheric clouds (PSCs). Isoprene oxidation is accounted for following the Mainz Isoprene Mechanism (MIM-1, Poeschl et al., 2000 [104]), with 16 species and 44 additional chemical reactions. The time step for dynamical processes and physical parameterizations is 15 min, while the radiation and chemistry scheme are called every two hours. A detailed description of the model version, used in the present study, can be found in Revell et al. (2015) [110]. To ensure best compatibility with observational data SOCOLv3 was run in nudged mode, meaning that the prognostic model variables temperature, vorticity, divergence, as well as the logarithm of the surface pressure were forced towards prescribed meteorological fields from ERA-Interim re-analysis data (Dee et al., 2011 [28]). Nudging fields are called every six hours. All simulations were run with T42 spectral resolution, which corresponds to a horizontal grid of about 2.8° x 2.8°. In the vertical a hybrid-sigma pressure coordinate system is used, with 39 vertical levels from Earth’s surface up to 0.01 hPa. (≈ 80 km).

In contrast to the operational model version and most other chemistry-climate models, which prescribe global mixing ratios as lower boundary condition for methane, we apply here a so-called flux boundary condition for methane. Eight different source categories of methane emissions have been taken into account and are summarized in Table 6.1. In addition, the uptake of methane by soils is taken into account using a climatology from Spahni et al. (2011) [130]: it is implemented as a negative emission scaled with atmospheric methane concentrations (Table 6.1).

To allow for tracking of methane from various sources and different geographical regions we have implemented 48 diagnostic tracers, split into 11 of anthropogenic origin, 13 wetland, 13 biomass burning, 7 rice, and 1 each of volcanoes, termites, oceans, and wild animals. The emission regions follow the recommendations of the TransCom-CH4 project (Gurney et al., 2000 [60]) and differ between the source categories. A detailed description of the applied method can be found in Chapter 4.

In order to further constrain the simulated methane budget, we have implemented two methane carbon isotope tracers into SOCOLv3, namely $^{12}$CH$_4$ and $^{13}$CH$_4$. The atmospheric abundance of $^{14}$C is negligible. Each source category is characterized by a specific isotopic ratio (Table 6.2). It should be mentioned that there are substantial uncertainties related to the isotopic source ratios, which might lead to uncertainties in trend in the $\delta^{13}$C. A definition of $\delta^{13}$C is given in Appendix B. The chosen val-
Table 6.2: Isotopic signature of methane sources as well as the sink fractionation of $^{13}$CH$_4$.

<table>
<thead>
<tr>
<th>Source</th>
<th>$\delta^{13}$C (‰)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetlands</td>
<td>-59</td>
<td>Monteil et al. (2011) [90]</td>
</tr>
<tr>
<td>Oceans</td>
<td>-59</td>
<td>Monteil et al. (2011) [90]</td>
</tr>
<tr>
<td>Volcanoes</td>
<td>-40</td>
<td>Monteil et al. (2011) [90]</td>
</tr>
<tr>
<td>Termites</td>
<td>-57</td>
<td>Monteil et al. (2011) [90]</td>
</tr>
<tr>
<td>Wild Animals</td>
<td>-62</td>
<td>Monteil et al. (2011) [90]</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>-21.8</td>
<td>Monteil et al. (2011) [90]</td>
</tr>
<tr>
<td>Landfills and Waste</td>
<td>-55</td>
<td>Monteil et al. (2011) [90]</td>
</tr>
<tr>
<td>Rice</td>
<td>-63</td>
<td>Monteil et al. (2011) [90]</td>
</tr>
<tr>
<td>Coal</td>
<td>-65</td>
<td>Monteil et al. (2011) [90]</td>
</tr>
<tr>
<td>Oil and Gas</td>
<td>-40</td>
<td>Monteil et al. (2011) [90]</td>
</tr>
<tr>
<td>Sink</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha^{13}$C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>0.9961</td>
<td>Saueressig et al. (2001) [118]</td>
</tr>
<tr>
<td>O($^1$D)</td>
<td>0.9872</td>
<td>Saueressig et al. (2001) [118]</td>
</tr>
</tbody>
</table>

Chemical destruction rates of the heavy isotope tracers were calculated by dividing the corresponding $^{12}$CH$_4$ reaction rates by the fractionation factor in Table 6.2.

### 6.2.2 Performed simulations

Four different transient simulations were performed for the time period 1980-2010, using a combination of two different datasets for anthropogenic, EDGAR4.2 (referred to EDGAR in this study) and Schwietzke et al. (2014a) [124] (referred to SCHWIEtZKE), and wetlands, LPJ-WSL (WSL) and SDGVM, emissions (Table 6.1). The two emissions inventories SCHWIEtZKE and EDGAR differ mainly in the evaluation of methane emissions in Eurasia and China: a stronger decrease is reported in Eurasia after the fall of the Soviet Union in SCHWIEtZKE (from 74 Tg/yr in 1991 to 52 Tg/yr in 2000), compared to EDGAR 4.2 (from 61 Tg in 1991 to 46 Tg in 2000). Both values are consistent with the range of values inferred from simulations using ethane observations (10-21 Tg of global decrease fossil fuel emissions between 1984 and 2010, Simpson et al., 2012 [128]), while Worthy et al. (2009) [152] simulated a drop twice as large as then reported from EDGAR in Europe and Siberia in order to be consistent with the decrease of methane concentrations observed in Alert, Canada. Furthermore, SCHWIEtZKE reports a lower increase in coal emissions in China after 2002: a linear trend of 2.84 Tg/yr per year of increasing anthropogenic emissions in China in EDGAR from 2002 to 2008 and 2.17 Tg/yr per year for SCHWIEtZKE. Both values are higher than the simulated 1.1 Tg/yr per year increase given in Bergamaschi et al. (2013) [12]
from 2003 and 2008. This will be discussed in the next section. Moreover, the wetlands datasets, WSL and SDGVM, mainly differ in higher emissions simulated by SDGVM, especially in northern hemisphere high latitudes regions during summer time as well tropical wetlands in South America during northern hemisphere winter time.

As shown in previous studies, tropospheric OH concentration in SOCOLv3 are slightly high biased (Chapter 4). Global mean tropospheric (air mass weighted) OH concentration in 2000 from SOCOLv3 is $12.5 \times 10^5$ molec.cm$^{-3}$, higher than the averaged value reported in the Atmospheric Chemistry and Climate Inter-comparison Project (ACCMIP; Naik et al., 2013 [94]): $11.1 \times 10^5$ molec.cm$^{-3}$. However, the range of values from the 16 different CCMs is large (from $6.5$ to $13.4 \times 10^5$ molec.cm$^{-3}$) and SOCOLv3 belongs to the upper limit of this range. In order to stabilize the simulated atmospheric methane concentrations, we had to apply a scaling factor on the total methane emissions. The scaling factor has been determined by a spin-up simulation for the year 1980. The representative factors for our four model simulations are: 1.23 for EDGAR-WSL, 1.12 for EDGAR-SDGVM, 1.16 for SCHWIETZKE-WSL, and 1.06 for SCHWIETZKE-SDGVM. Therefore, the total annual emissions averaged over the years 2000 and 2009 used as model input range between 634 Tg/yr and 665 Tg/yr, which is close to the bottom-up estimate of 678 Tg/yr provided by Kirschke et al. (2013) [73], and well within the range of provided bottom-up estimates from 542 Tg/yr to 852 Tg/yr. The simulated isotope ratio as well as the change in methane concentration between the time periods 2008-2010 and 2001-2003 have been compared to observational data from eight sites of the NOAA-ESRL global network (Dlugokencky et al., 2015 [31]). The locations of the measurement sites have different characteristics and are described in Table ??.

6.3 RESULTS AND DISCUSSION

Figure 6.1 shows the relative change in near-surface methane concentrations between the late (average over 2008 to 2010) and early (average over 2001 to 2003) 2000s for the four different SOCOLv3 simulations, highlighting substantial differences among the different emission inventories. The methane change in simulations using EDGAR for anthropogenic emissions is approximatively twice as large as in the SCHWIETZKE based simulations, and clearly overestimates the observations. This is in agreement with previous studies, which indicated that EDGAR strongly overestimates anthropogenic emissions (Bruhwiler et al., 2014 [18]) and mainly in China (Bergamaschi et al., 2013 [12]). Using the SCHWIETZKE database as model input leads to a better agreement with the measurements. Between the late and the early 2000s, anthropogenic emissions over this region increase by 2 Tg/yr per year in EDGAR, but still decrease by 4 Tg/yr per year in SCHWIETZKE. This difference remains difficult to explain (Schwietzke et al., 2014b [123]), e.g. technological development, decrease in energy consumption. However, the simulated increase in China is still overestimated:
Figure 6.1: Relative change in methane concentration (in %) between the average over the years 2008-2010 and 2001-2003 for the various SOCOLv3 simulations using different inventories for anthropogenic and wetlands emissions: (a) EDGAR and WSL; (b) EDGAR and SDGVM; (c) SCHWIEITZKE and WSL; (d) SCHWIEITZKE and SDGVM. The circles indicate the observed CH$_4$ change at the NOAA-ESRL measurement sites. The triangles are the selected locations: AZR, BRW, CGO, MLO, NWR, SMO, SPO, and TAP.

The measurement sites in the Chinese region indicate an increase of about 1% over the analyzed period, while the SCHWIEITZKE simulations show a methane increase of 5% and more. The choice of the wetlands database affects mainly the methane change over South America, leading to a more pronounced increase in SDGVM. However, as obvious from Fig. 6.1, the impact of the different wetland data sets is less important as the impact of the anthropogenic emission inventories.

Figure 6.2 disentangles the contribution of the most important source categories and emission regions to the methane changes between the late and early 2000s at the selected locations. As seen in Figure 6.1, the four simulations overestimate the observed increase in methane at all the sites. The simulated methane increase is dominated by anthropogenic sources rather than wetlands. Strong negative contributions from anthropogenic emissions in Europe and North America, as well as Siberia in case of SCHWIEITZKE, are overcompensated by other regions, mainly China, India and South America. Enhanced anthropogenic emissions agree with former studies attributing the increase in methane to an increase of this source, mainly coal exploitation in China.
Figure 6.2: Differences in the dominating main methane tracers (in ppbv) at the eight chosen locations between the average over the years 2008-2010 and 2001-2003. For each plot, the thick bars represent the four performed simulations EDGAR-WSL (E-W), EDGAR-SDGVM (E-S), SCHWIETZKE-WSL (SC-W), and SCHWIETZKE-SDGVM (SC-S). The thin bars show the respective result using the trend estimate for anthropogenic emissions over China from Bergamaschi et al. (2013) [12], see text for details.
The negative contribution from anthropogenic emissions in North America shown here is mainly related to decreasing oil and gas emissions. This might change in the future with increasing emissions from gas extraction by fracking (Wang et al., 2014 [146]).

The minor role of wetlands emissions differ from previous studies, which highlight the role of increasing wetland emissions between 2006 and 2008 due to strong La Niña conditions (Bousquet et al., 2011 [16]). Only wetland emissions from tropical Southern America (defined as wet_SA_Tropical) make a substantial contribution to the methane increase in the SDGVM simulations (Figure 6.2). However, maps of the changes on methane concentrations between the late and early 2000s show an increase mainly over the tropical Pacific in the Southern hemisphere, a region which will be the most influenced by a strong increase from the wetland emissions in South America. However, this is not supported by the measurement sites in this region (Figure 6.1). Therefore, SDGVM might overestimate the increase in CH₄ emissions from wetlands between late and early 2000s. Moreover, taking an average of 3 years decreases the impact of wetlands on methane’s year-to-year variability.

Fossil fuel emissions in China increased rapidly after 2004, as described in the previous section. In the late 2000s anthropogenic emissions in China as reported in EDGAR and SCHWIEZKKE are 19 Tg/yr and 15 Tg/yr higher than the early 2000s. The change in emissions for both inventories is larger than the estimate by Bergamaschi et al. (2013) [12], who calculated a trend of 1.1 Tg/yr per year between 2003 and 2008 using inverse modeling based on satellite measurements and surface observations. We estimated then the impact of the reduced increase of anthropogenic emissions of Chinese emissions via the following approach:

\[ C_B = C_A \cdot \frac{B}{A} \]  

where \( C_B \) represents the change in atmospheric concentrations of the tracer following anthropogenic emissions in China between two consecutive years induced by using the trend in anthropogenic emissions over China from Bergamaschi et al. (2013) [12]; \( C_A \) is the simulated change in atmospheric concentration of the same tracer; \( A \) the change in anthropogenic emissions over China between two consecutive years; and \( B \) the change in anthropogenic emissions over China given by Bergamaschi et al. (2013) [12]. This approach gives a linear approximation of the methane tracer following the anthropogenic emissions in China, assuming constant OH concentrations. In fact, all our model runs simulate on average a 1.5% decrease in tropospheric OH between 2001 and 2010, which might be associated with the overly strong increase in methane burdens due to the high emissions in China. Previous studies found a decrease in OH after 2007: a small decrease of 1% in 2007 compared to 2006 (Bousquet et al., 2011 [16]) or of 4% but not considered as significant because of its large uncertainty range (14%) (Rigby et al., 2008 [112]). It is consistent with the small OH variability inferred from MCF observations up to 2007 (Montzka et al., 2011 [91]). However, if OH does not vary strongly during the 2000 decade, a less pronounced increase of methane emissions in China would lead to lower decrease in global OH and the removal of methane will
be then higher: this estimation of methane tracer concentration using Bergamaschi et al. (2013) [12] is therefore high biased, because of assumed decreasing OH concentrations. The thin bars in Fig. 6.2 represent the results applying the emission trend estimate provided by Bergamaschi et al. (2013) [12]. The contribution of the tracer “ant _China” decreases by about 50% for all the sites, leading to a better agreement with the observed increase. From the four different simulations SCHWIETZKE-WSL is the closest to the observed methane increase. Using the trend estimate from Bergamaschi et al. (2013) [12], the relative contribution from anthropogenic emissions in China (dominated by coal mining, Fig. 6.5) is now comparable to other anthropogenic sources, mainly to those from India and South America (both dominated by farming - ruminants, Fig. 6.5).

Due to the different isotopic ratios of the source categories, a change in the relative contribution of methane sources is expected to change the atmospheric isotope ratio. Therefore, methane isotopes can be used to constrain the changes in simulated methane concentrations discussed above. Figure 6.3 compares the simulated time series of δ¹³C from our simulations with measurements at the eight selected locations. It should be noted that for each site the simulations were offset to the starting value.
of observations. As obvious from Fig. 6.3 the SCHWIETZKE dataset shows the best agreement with the observed $\delta^{13}$C trend and is within the observational uncertainty range. Simulations with the EDGAR inventory lead to an increase in $\delta^{13}$C after 2004. This is related to the overly high fossil fuel emissions, a heavy source in terms of carbon isotopes. Using the SDGVM dataset for wetlands emissions also leads to a decrease in $\delta^{13}$C. This is related to pronounced increase wetland emissions mainly in the tropical wetlands, but also in Europe and Siberia (Figure 6.2).

Figure 6.4: Calculated $\delta^{13}$C of the sources for different simulations. It is evaluated based on the isotopic signature of the different emissions and the relative contribution of the tracer tracking this source depending on the location. The values are scaled to 2002 in order to highlight the differences in trend between 2002 and 2010. The BERGAMASCHI-WSL as well as BERGAMASCHI-SDGVM calculations are performed using the trend of anthropogenic emissions over China from Bergamaschi et al. (2013) \cite{12}, assuming that the change occurs only for the coal emissions (the other anthropogenic categories remain constant). This re-evaluation is performed for the SCHWIETZKE database.
A transient isotopic source signature can be calculated given the atmospheric methane concentration of the different tracers as well as the different isotopic signature of the specific sources. It can therefore also be re-calculated using the Bergamaschi et al. (2013) \[12\] trend for coal emissions over China. Figure 6.4 shows the change in the isotopic source ratio for the various emissions data sets taking into account the temporal development of the composition of methane tracers. Applying the “Bergamaschi” approximation to the SCHWETZKE simulations lowers the trend by roughly 0.01-0.015 %/yr, with the highest impact at the TAP measurement site (0.02 %/yr), where the difference between model simulations after 2008 is the largest. As the calculation of the isotopic source signature gives a high estimate of atmospheric $\delta^{13}$C (because no sink effect is taken into account), the found difference is the upper limit of the change that can be assumed for $\delta^{13}$C, and therefore the simulated isotopic ratio would still be in the uncertainty range of the observations.

Figure 6.5 shows the composition of anthropogenic methane emissions for the different geographical regions applied for the tracer tracking in SOCOLv3. In India and

![Figure 6.5: Sum of emissions (in Tg) for the 2001-2003 period (left bars) and the 2008-2010 period (right bars) for EDGAR4.2 (two left bars) and SCHWETZKE (two right bars) for nine regions defined from the methane tracking: Africa, China, Eurasia Boreal (EB), Europe, India, Middle East (ME), North America (NA), South America (SA) and tropical Asia (TA). The signs below the regions represent if the regions are lighter or richer than the global average anthropogenic $\delta^{13}$C over the 2001-2010 period: - means lighter, + means richer, and = similar to the averaged value.](image)
South America, most of the anthropogenic emissions are related to ruminants (50% and 68% for both inventories, respectively). Only emissions from China and the Middle East are dominated by thermogenic emissions and therefore heavier in terms of carbon, even if the contribution of farming is not negligible in China for both inventories (22% for EDGAR and 23% for SCHWIETZKE), but on average the Chinese region is richer in terms of $^{13}$C than the anthropogenic $\delta^{13}$C (Fig. 6.5). The other regions (except boreal Eurasia and Northern America) do not have a main source or are dominated by lighter sources, mainly enteric fermentation. Therefore, the assumed increase in anthropogenic emissions in India and South America mainly caused by more intense agriculture and the assumed decrease in fossil fuel emissions in North America and Eurasia is consistent with the increase in methane concentrations after 2007 and a simultaneous decrease in $\delta^{13}$C. The impact of CH$_4$ emissions from rice paddies, another biogenic source of methane, can not be seen in this study, because a climatology is used after 2007. However, data provided by the LPJ-Bern dynamic global vegetation model (Spahni et al., 2013 [131]), shows an increase in global CH$_4$ emissions from rice paddies of 1.3 Tg/yr per year, or 3.7%, between late and early 2000. This increase is about half than enhanced anthropogenic emissions in India, and four times lower than anthropogenic emissions over South America, for the same period. Therefore, if its influence is underestimated in our study, it can not be considered as a main driver of methane increase since 2007. Nisbet et al. (2014) [96] attributed global $\delta^{13}$C decrease after 2008 to increasing natural emissions (wetlands and/or agriculture) However in our study methane increase since 2007 is impacted by emissions from South America and India mainly, but also tropical Asia, consistent with measurements showing a pronounced increase in the tropics (Houweling et al., 2014 [67]). Schaefer et al. (2016) [119] also found a main contribution from tropical agricultural emissions, using a combination of isotopes measurements and one-box model study. Decreasing fossil fuel emissions in the Eurasian region were known to have an impact on global methane levels after the fall of Soviet Union (Dlugokencky et al., 2003 [37], Bousquet et al., 2006 [15], Aydin et al., 2011 [5]), but its impact after 2007 is new. This development is responsible for the decrease in methane growth rate from 1991 to 2006, while increasing emissions mainly from Africa, China, India, and South America compensate and become larger than this decrease on a global scale.

6.4 CONCLUSIONS

We have presented four model simulations with the CCM SOCOLv3 for the time period 2001 to 2010, using two different emission data sets for anthropogenic (EDGAR4.2 and SCHWIETZKE) and wetlands (LPJ-WSL and SDGVM) methane emissions, respectively. The role of different methane source categories from various geographical regions for the reinforced methane increase after 2007 has been disentangled by a tracer tracking method and methane carbon isotopes implemented into SOCOLv3. Our model results show that the increase after 2007 is driven by anthropogenic activities. Negative contributions in Europe, Eurasia, and Northern America, mainly
due to reduced fossil fuels, are overcompensated by increasing emissions in Africa (dominated by cow farming), China (increasing coal emissions), India (cow farming), South America (cow farming), Middle East (oil and gas production), and Tropical Asia (dominated by coal farming and waste management). Observations of isotopes show a decreasing trend in $\delta^{13}C$ after 2008, especially in Asia. This seems to be in agreement with increasing anthropogenic emissions from agriculture over India and South America, increasing coal mining emissions in China as well as decreasing emissions over Eurasia. However, our simulations further indicate that the EDGAR4.2 inventory strongly overestimates anthropogenic methane emissions from coal over China. In terms of OH sink, a detailed study had been performed in Chapter 4 and did not show any significant trend in OH that could explain the increase since 2007. It should be mentioned that there are significant uncertainties in the isotope source signatures and sink fractionation. For example, available values for the isotopic signature from coal emissions range between $-66.4\%$ and $-30.9\%$ (Zazzeri et al., 2016 [153]). Here we used a value of $-35\%$. Lighter coal emissions, an important source category in China, would further decrease the simulated $\delta^{13}C$. The sensitivity of the model results to these uncertainties was not investigated in this study, but will be subject of a companion paper.
Appendix A: Selection of the 8 measurement sites

Table 6.3 describes the 8 locations chosen for comparison between simulations and observations. These locations represent different geographical situations (e.g. background sites, remote from strong emissions regions) and therefore represent different methane regimes. TAP is strongly influenced by emissions in China (mainly anthropogenic), while BRW is more affected by boreal wetland emissions.

Appendix B: Isotopic notation

Since the deviations of isotopic ratios from the standard ratio are usually small, they are often reported in permille notation:

$$\delta^{H_X} = \left( \frac{^{H_R}_{^{H_R}_{\text{sample}}}}{^{H_R}_{^{H_R}_{\text{std}}}} - 1 \right) \times 1000 \, ^{\circ}_{oo}$$

$$^{H_R}_{^{H_R}} = \frac{^{H_X}}{^{L_X}}$$

where X is an element, H is the heavier isotope, L is the lighter isotope, and $R_{\text{sample}}$ and $R_{\text{std}}$ are the isotope ratios of the sample and standard, respectively. $R_{\text{std}}^{13}$ is taken from Vienna Pee Dee Belemnite (VPDB), equal to 0.0112372. For chemical reactions, differences in the rate constants (k) between the heavier and lighter isotopologues can be described with the fractionation factor, $\alpha^{H_X}$ (Allegre et al.,2008 [2]):

$$\alpha^{H_X} = \frac{^{H_k}}{^{L_k}}$$
Appendix C: Harmonic regression

While the model tracers are outputted continuously, observations of CH₄ and its isotopologues suffer from irregular sampling periods and prolonged data gaps. We employed a harmonic regression approach on the observations to reduce the influence of these irregularities on the comparison. Harmonic regression has often been applied to measurements of atmospheric trace gases (Nakazawa et al., 1997 [95]; Levin et al., 2012 [81]).

The procedure for harmonic regression begins with fitting the data points to the following curve:

\[ y(t) = ay_0 + bt + ct^2 + dt^3 + \sum (e_i \sin Wt + f_i \cos Wt) \]

where \( t \) is time, \( a, \ldots, f_i \) are fitting coefficients, \( W = \frac{2\pi}{p} \), and \( p \) is a time period from 1 month to 12 years. Any points that fall outside the 3\( \sigma \) margin from the fitting curve are removed from the data pool. The curve fitting is repeated with the new data pool until no outliers remain (Nakazawa et al., 1997 [95]). This procedure yielded a smoothed, continuous approximation of the data points, while retaining seasonal and interannual variability. The fitted curve could be deseasonalized by removing the cosine and sine terms with periods between 1 month and 24 months. Smoothing of simulated quantities was performed using a 12 month running average.

The harmonic regression fitting was performed using forward stepwise regression. In this method, the terms that are least likely to have a coefficient of zero (having smallest p-value) are sequentially added to the model. When no more terms can be added then the term with the largest p value is removed and the previous step is repeated. This is performed until no terms in the regression model have a p-value larger than 0.1 (Draper et al., 1998 [39]).
Methane is the second most important greenhouse gas after carbon dioxide. Since pre-industrial times, atmospheric methane concentrations have more than doubled to reach 1840 ppbv nowadays. Even if methane sources and sinks are well known, their relative contribution to the observed methane variations are still heavily discussed. The aim of this thesis was to investigate atmospheric methane fluctuations over the last three decades. Understanding its variability is crucial to reduce its impact on future climate.

The following research questions were addressed:

• Which processes are responsible for the observed CH$_4$ variations over the last three decades?

• A specific event from the last three decades was the volcanic eruption of the Mount Pinatubo in June 1991. How did this strong eruption affect tropospheric methane?

• Observations of methane isotopes have become nowadays a standard tool to study methane fluctuations. How do simulated methane isotopes compare with observations? Moreover, can it be used to retrieve the driving factors of increasing methane after 2007 where isotopic studies show a global enrichment in methane from natural sources?

Four transient simulations were performed using the chemistry-climate SOCOLv3 to disentangle the impact of various sources and sinks during the last three decades. A specific set-up had been implemented for this purpose. The runs were performed with specified dynamics, i.e. the prognostic variables, namely temperature, vorticity, divergence, as well as the logarithm of surface pressure are forced every 6 hours by means of reanalysis data. The full methane cycle was simulated by using CH$_4$ emissions fluxes as lower boundary conditions. To allow for a tracking from different sources and different geographical regions, 48 tracers had been implemented into SOCOLv3 to quantify the impact of a specific source (anthropogenic, wetland, biomass burning, rice, mud volcanoes, ocean hydrates, termites, and wild animals) from a specific region (mainly covering Europe, China, India, South America, and North America, etc.). Two different inventories were used for anthropogenic emissions (EDGAR4.2 and SCHWIEITZKE) as well as two databases based on dynamical vegetation models for wetlands sources (SDGVM and LPJ-WSL). These 2 × 2 inventories are combined in the four performed simulations. To compensate for high levels of OH in the troposphere simulated by SOCOLv3, emission factors were applied to methane fluxes in
order to equilibrate tropospheric methane during the model spin-up for the starting year of the simulations, 1980, in order to reach an equilibrium between CH$_4$ and OH. This procedure is not expected to affect however simulated methane fluctuations. Furthermore, the enhanced methane emissions are still within the uncertainty range of total methane emissions provided in the literature.

An implemented methyl chloroform tracer was used in order to both evaluate the model in simulating tropospheric OH and study its variations. Before 1998, continuously decreasing emissions of MCF influence its atmospheric decay rate and make MCF as proxy for OH variability less reliable. After 1998 the simulated methyl chloroform indicates small interannual variability of modeled OH levels, comparable to the observations. Simulated absolute decay rate are stronger than the observations, confirming high levels of OH in SOCOLv3 already analyzed in previous studies as well as compared to a CCM inter-comparison. Still after 1998, OH anomalies inferred from the simulated MCF are comparable to the observations, but remain however higher than direct anomalies inferred from simulated OH, highlighting the uncertainties behind this proxy suggested in previous studies.

Between 1984 and 1990, the four simulations manage to reasonably reproduce the observed methane growth rate. They all agree that the major contribution, namely 60% of the total growth rate, stems from increasing emissions over Europe, China, and India for this period. However, the contribution from natural emissions differ from the chosen database. In terms of wetland emissions, SDGVM reports a stronger year-to-year variability and a higher impact from Northern Hemisphere high latitudes than LPJ-WSL, which are both not supported by the observations for this period.

The beginning of the 1990s is marked by a strong decrease in methane growth rate, well captured by simulations using LPJ-WSL but strongly overestimated with SDGVM. Two factors are responsible for this abrupt decrease. First, the fall of the Soviet Union implied a large reduction of fossil fuel production in Europe and Siberia, responsible for half of the simulated decrease. Moreover, the volcanic eruption in June 1991 played a significant role in tropospheric methane variability via different processes. Simulations with LPJ-WSL show a decrease in wetland emissions, responsible for 40% of the decrease in methane growth rate. The main contribution is for the first time attributed to tropical South America, driven by negative anomalies in precipitation after the volcanic eruption. While the change induced by the volcanic eruption comes essentially from the reduced wetland emissions, other effects influenced tropospheric methane. Sensitivity simulations show an increase in tropospheric ozone photolysis by 4% two years after the volcanic eruption, because of an enhanced stratospheric ozone depletion due to the heterogeneous reactions induced by the volcanic aerosols leading to more chlorine-induced ozone depletion. This effect, leading to more tropospheric OH production, is shown to be compensated two years after the volcanic eruption by the tropospheric cooling, leading to both a reduced water vapor concentration by about 3% and a slow down of the reaction between CH$_4$ and OH by 0.5%. Further investigations are needed as the scattering of UV by SO$_2$, which decreases tropospheric UV levels, is currently missing. This effect is expected to be significant within the first year following the eruption.
Furthermore, and complicating the attribution, the 1997-98 period is influenced by a strong ENSO event. Results from the present tracer diagnostics show the largest contribution from the tracer following the biomass burning emissions over tropical Asia. Dry conditions in this region led to an increase of 26.4 Tg/yr in biomass burning emissions in this region.

The simulations using anthropogenic emissions from SCHWIEITZKE underestimate the years between 1993 and 2004. The decrease in fossil fuel emissions from the Eurasian region after the collapse of the Soviet Union is better represented with EDGAR 4.2.

The observed plateau in methane levels between 1999 and 2006 is modeled as a compensation between negative contributions from anthropogenic emissions over Europe and Siberia and positive increasing emissions mainly from India, China, and South America. The contribution of wetlands to the methane variability is again dependent of the chosen data set: SDGVM shows large regional year-to-year variability for this period. However, these regional differences cancel each other out on a global scale, and does not affect the conclusion, that the attribution to this plateau is discovered as opposing regional trends in anthropogenic emissions.

The four simulations overestimate the increase in methane growth rate after 2004, due to an overestimation of the methane emissions from coal mining emissions in China in both inventories, corroborating previous studies. The use of a reduced growth rate of coal mining emissions from this region based on inverse modeling from satellite measurements helps to reduce the overestimation. The tracer diagnostics shows then that the contribution of Chinese anthropogenic emissions over China becomes roughly equals to the contribution of anthropogenic emissions in India or South America. Furthermore, using the stable carbon isotope of methane, $^{13}\text{CH}_4$, helps to understand the drivers of methane increase in this period. A decrease in the relative isotopic ratio, $^{13}\text{CH}_4/^{12}\text{CH}_4$, is both observed and simulated after 2007. As anthropogenic emissions over India and South America are largely dominated by ruminants, a biogenic, and therefore isotopically lighter, source of methane, it explains the decrease in the isotopic ratio. In addition, decreasing fossil fuel production in Siberia contribute to the isotopic decrease and are overcompensated by increasing anthropogenic emissions in other regions, namely India, South America, China, tropical Asia and Middle East. At the same time, OH levels stayed roughly constant and can not be the main explanation of the methane increase since 2007. The two wetland databases, SDGVM and LPJ-WSL, show for this period different contributions to the methane trend during this period. However, a strong contribution of wetlands in tropical South America, as indicated by SDGVM, does not seem to be consistent with observations. From our simulations, the increase since 2007 is mainly explained by anthropogenic sources from ruminants and to a lesser extent by increasing coal mining emissions over China.

This thesis was a unique approach to understand past methane fluctuations. A strong contribution is given to anthropogenic emissions. The tracer diagnostics help to disentangle the effects of various sources from different regions. Applying this approach to different models as well as more emission inventories will narrow the uncertainties
behind past methane variations, and would help to understand the potential main
drivers in the future.

7.2 OUTLOOK

Previous studies performed with SOCOLv3 revealed an overestimation of tropospheric
ozone in the northern hemisphere by 50% as well as a low bias in simulated CO con-
centrations (Revell et al., 2015 [110]). These model deficiencies are consistent with
the high tropospheric OH bias reported in this thesis. Enhanced ozone levels are ex-
pected to cause a large amount of OH production from ozone photolysis. Although
the high tropospheric OH concentrations are not expected to affect the presented con-
cclusions concerning methane trends, especially after 1998 where OH variations are
shown to be small. One step in reducing tropospheric ozone levels has been made
during this thesis by implementing a new parameterization of the nitric acid washout.
As photochemistry involving nitrogen oxides (NOx) is crucial for tropospheric ozone
production, one possibility of this model biases comes from high NOx concentration
because of a too weak NOx removal via HNO$_3$ washout (as nitric acid recycles NOx
via reaction with OH or photolysis). While this new parameterization leads to an im-
proved representation of tropospheric HNO$_3$ levels compared to observations, as well
as a more robust parameterization based on physical processes, the effect of ozone
stays small.

So far the chemical mechanism of SOCOL does not include the oxidation of NMVOCs
from anthropogenic sources. In parallel of this thesis, a master thesis was completed by
Fabio Vivian to study the impact of a new oxidation mechanism based on NMVOCs
from anthropogenic sources. A simplified lumped reaction mechanism was imple-
mented into a chemical box model version derived from SOCOLv3 to reproduce this
effect. Even if it was not implemented on the full 3D model, this new oxidation mech-
nism led to a decrease in ozone production in the polluted regions (therefore with
high NOx mixing ratios) but the overall effect remains small.

If the NOx/VOC regime of SOCOLv3 is important for ozone production, its photol-
ysis in the troposphere is a main factor and needs to be further investigated. Could
effects are unlikely to have large impacts on global tropospheric ozone (Voulgarakis
et al., 2009 [30]). However, other factors such as the overhead ozone column, cross
sections and quantum yields used in the photolysis scheme could have a significant
on tropospheric ozone levels.

The combination of different data sets for anthropogenic and wetland emissions high-
lighted the sensitivity of modeled methane to the choice of the data set to the ap-
plied boundary conditions. However, large uncertainties remain in the modeling wet-
lands emissions from the past. The Wetland CH$_4$ Inter-Comparison of Models Project
(WETCHIMP) (Wania et al., 2013 [147]; Melton et al., 2013 [89]) revealed large dis-
crepancies in methane emissions from wetlands among the ten participating models,
both in terms of total amount and spatial distribution, but also year-to-year variability
between 1993 and 2007. In general, reducing uncertainties in emission data sets, either
process-based estimates or estimates derived from top-down approaches, is highly desirable, and will help to narrow the sensitivity to our modeled simulations and give stronger confidence in methane variations from the past and therefore help to predict its future variations and their role in climate change.

One way of reducing uncertainties in methane emissions from data sets is to use emissions based from inverse modeling. This thesis belongs to the MAIOLICA-2 project, which aims to gather three different modeling techniques to investigate methane variability. The process-based emission model LPJ-WSL provides CH$_4$ emissions from wetlands to two models: the CCM SOCOLv3, and also the Lagrangian chemistry-transport model FLEXPART (Henne et al., 2010 [63]). Inverse modeling, based on a fixed-lag Kalman filter (Bruhwiler et al., 2005 [19]), can be performed by this model, and results in an improved emission data set of emissions for the different methane source categories. Figure 7.1 shows preliminary results from the FLEXPART simulation performed within MAIOLICA-2. The inversion does not only provide improved information about the absolute emissions from a certain source category, but also that emissions from inverse modeling indicate the annual cycle for anthropogenic emissions, a missing piece of information in the two chosen applied emission inventories. Once the final results from the inversion will be available, it is intended to perform a SOCOL simulation applying the new emissions data sets and to investigate the impact of emissions including an annual cycle on the overall agreement between model simulations and observations. Model simulations provided by the FLEXPART model will also help to disentangle the contributions from the sources and the sinks (as OH is prescribed in FLEXPART). Chapter 4 showed an observed decrease in 2004 in methane growth rate not simulated by the four performed runs. The new simulations with this new emission data set could help to understand the drivers of this decrease. Moreover, since both models were forced with identical methane emission data sets and meteorological reanalysis data, simulations with prescribed OH from FLEXPART and with interactive OH from SOCOLv3 would help to understand the impact of OH during different time periods of the last three decades. This is a new information that will reduce the remaining uncertainties from the current simulations and will clarify the picture of methane fluctuations over the last three decades.

From a general perspective, pursuing the tracer diagnostics developed in this thesis, using more chemistry-climate models with the same boundary conditions, could help to strengthen the results found here and put more weight on our conclusions in order to address a clearer message to the policy makers in order to take actual decisions to reduce methane emissions in the near future.
Figure 7.1: The top plots represent the prior simulation (blue line) performed with FLEXPART model. The black line represents the observed methane mixing ratio at the measurement site (Ascension in the NH Atlantic) and the red line represents the a posteriori simulation done to match the observations. The bottom plot represents the anthropogenic emissions over North America given from the previous inventory (red line) and from the inverse modeling (blue line).
The description of the model includes the implementation of a new Mechanism for Iso-
prene oxidation (MIM-1, Poeschl et al., 2000). It is a NMVOC responsible for ozone for-
mation and therefore OH concentration in the troposphere. Including such a scheme
allows the model to get a more detailed tropospheric chemistry scheme. The appendix
focuses on the impact of this oxidation mechanism on tropospheric OH and then
methane lifetime. It should be noted that the simulations presented in this appendix
were not performed in the frame of this thesis and are presented here to highlight the
impact of the isoprene mechanism.

A.1 IMPACT ON TROPOSPHERIC OH

Figure A.1 shows that the implementation of the isoprene oxidation scheme improves
OH levels in comparison to the averaged value from the Atmospheric Chemistry and
Climate Model Intercomparison Project (ACCMIP, Nail et al., 2013 [94]), but remains
slightly lower. However, there is a large spread of values simulating OH levels high-
lighting the difficulty to get an agreement in terms of OH among the different current
CCMs.

A.2 IMPACT ON METHANE LIFETIME

Figure A.2 shows the impact of the isoprene oxidation scheme on tropospheric methane
lifetime. There is a direct correlation between the decrease in tropospheric OH levels
and an increasing methane lifetime, as OH is the main sink of methane in the tropo-
sphere. However, methane lifetime remains lower than the averaged value and in the
lowest values of the different ACCMIP models. The fact that the methane lifetime is
lower than the value evaluated with SOCOLv2 (PhD thesis of Patricia Kenzelmann,
2009) is an indication but will not be further investigated.

A.3 IMPACT ON OH INTER-HEMISPHERIC RATIO

The inter-hemispheric ratio of OH decreased with the implementation of the MIM iso-
prene scheme. However, the northern hemisphere remains higher than the southern
hemisphere. Although this is a common feature seen in most of the CCMs (Figure
A.3), it is not supported via methyl chloroform studies (used as proxy for OH concen-
trations) which estimate a more balanced inter hemispheric ratio for OH (Patra et al.,
2011 [97]).
Figure A.1: Airmass-weighted average tropospheric OH (up to 250 hPa independent of the latitudes) averaged over 1980 (1980, 1981, 1982, and 1983) and over 2000 (1999, 2000, 2001, 2002) for 4 different SOCOLv3 simulations: without Isoprene scheme in a T31 resolution (pink points) and T42 (green point); with the Isoprene oxidation mechanism in T31 (blue point) and with the EDGAR4 methane emissions as boundary conditions (black point). The blue points represent the values for the different CCMs involved in ACCMIP. The red lines represent the averaged ACCMIP value for 1980 and 2000.

Figure A.2: Same as A.1 but for tropospheric methane lifetime
Figure A.3: Same as A.1 but for OH inter-hemispheric (Northern hemisphere versus southern hemisphere) ratio
This appendix shows the zonal mean temperature and zonal wind for the nudged as well as free simulations averaged over different seasons than presented in section 2.

**B.1 DJF, MAM, AND SON FOR THE TEMPERATURE**

Figure B.1: Zonal mean temperature (in K) averaged over the DJF season for the 1980-1989 period from ERA-Interim (top plot). Absolute difference (in K) between the nudged simulation and ERA-Interim (bottom left plot) and the free simulation and ERA-Interim (bottom right plot). The black lines represent the tropopause height for the nudged (thick line) and the free (dashed line) simulation.

**B.2 DJF, MAM, AND SON FOR THE ZONAL WIND**
Figure B.2: Same as Figure B.1 for MAM.

Figure B.3: Same as Figure B.1 for SON.
Figure B.4: Zonal wind (in m/s) averaged over the DJF season for the 1980-1989 period from ERA-Interim (top plot). Absolute difference (in m/s) between the nudged simulation and ERA-Interim (bottom left plot) and the free simulation and ERA-Interim (bottom right plot).

Figure B.5: Same as B.4 for MAM.
Figure B.6: Same as B.4 for SON.
This appendix shows 3 methane tracers as well as the total methane concentrations averaged over the 2000-2009 decade (Fig. C.1). It allows to have a visualization of the tracer diagnostics implemented into SOCOLv3.

Figure C.1: Total methane concentration at the surface (in ppbv) averaged over 2000-2009 (top left plot), as well as for three tracers: anthropogenic China (top right plot); boreal North America wetlands (bottom left plot) and tropical South America wetlands (bottom right plot). The tracers are taken from the EDGAR-WSL simulation (see Chapter 4 for an description of this simulation).

Fig. C.2 shows that the concentration of the sum of the tracers is equal of the concentration of methane. Therefore, the tracer diagnostics can be used in order to quantify the impact of CH₄ emissions on its past variability.
Figure C.2: Global total methane concentration at the surface (red line, in ppbv), as well as the sum of all the methane tracers (blue line). Note that the two lines overlap on this plot. The results are based on the EDGAR-WSL simulation (see Chapter 4 for more details on this simulation).


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