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Consideration of methane emissions in the modelling of ozone concentrations in chemical transport models

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by

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Abstract: Consideration of methane emissions in the modelling of ozone concentrations in chemical transport models

Methane is a powerful greenhouse gas as well as a precursor of ground-level ozone, a pollutant which is damaging to the health of both humans and ecosystems. Methane concentrations are currently about 3 times higher than in pre-industrial times, and are still rising. Accurate assessment of the consequences requires high quality modelling tools along with good emission data. We systematically examine the treatment of methane in a representative selection of widely-used models: three regional-scale models and one global-scale model, with a special focus on how this treatment of methane influences the production of ozone. There is still considerable uncertainty about global methane emissions, especially from natural sources. None of the models studied here rely exclusively on methane emission data, but rather adjust their modelled methane concentrations to be consistent with observations. Due to the relatively long lifetime of ozone in the troposphere, all models must include information about ozone production from methane at the global scale. Based on existing model datasets, we quantify the contribution of methane to annual-average surface ozone in Germany at 20 µg/m^3, with only 3.2 µg/m^3 of this due to oxidation of methane in the European region. Future work should focus on intercomparison of alternative methods for source attribution of ozone, including the contribution of different ozone precursors to policy-relevant exposure metrics. Large inter-model differences remain in the simulation of ground-level ozone. A better understanding of these differences is still required for more accurate simulation of ground-level ozone.

Kurzbeschreibung: Berücksichtigung von Methanemissionen bei der Modellierung von Ozonkonzentrationen in Chemie-Transport-Modellen

Methan ist ein besonders wirksames Treibhausgas sowie ein Vorläufer von bodennahem Ozon, einem Schadstoff, der die menschliche Gesundheit und Ökosysteme belastet. Die Methankonzentrationen sind derzeit etwa dreimal höher als in vorindustriellen Zeiten und steigen weiter an. Eine genaue Abschätzung der Folgen erfordert hochwertige Modellierungswerkzeuge und gute Emissionsdaten. Wir haben die Behandlung von Methan in einer Auswahl von repräsentativen und verbreitet benutzten Modellen untersucht. Drei Modellen im regionalen Maßstab und einem Modell im globalen Maßstab wurden ausgewählt, mit einem besonderen Fokus darauf, wie die Behandlung von Methan die Ozonproduktion beeinflusst. Die weltweiten Methanemissionen, insbesondere aus natürlichen Quellen, sind nach wie vor mit erheblichen Unsicherheiten behaftet. Die hier untersuchten Modelle stützen sich nur begrenzt auf Methanemissionsdaten, sondern passen die modellierten Methankonzentrationen so an, dass sie mit den Beobachtungen übereinstimmen. Aufgrund der relativ langen Lebensdauer von Ozon in der Troposphäre müssen alle Modelle Informationen über die Ozonproduktion aus Methan im globalen Maßstab enthalten. Basierend auf vorhandenen Modelldatensätzen haben wir den Beitrag von Methan zum jährlichen durchschnittlichen bodennahen Ozon in Deutschland auf 20 µg/m^3 quantifiziert, wobei nur 3,2 µg/m^3 davon auf die Oxidation von Methan im europäischen Raum zurückzuführen sind. Zukünftige Arbeiten sollten sich auf den Vergleich alternativer Methoden zur Quellenzuordnung von Ozon konzentrieren, einschließlich des Beitrags verschiedener Ozonvorläufer zu politisch relevanten Expositionsmetriken. Bei der Simulation von bodennahem Ozon bestehen weiterhin große Unterschiede zwischen den Modellen. Ein besseres Verständnis dieser Unterschiede ist für eine genauere Simulation von bodennahem Ozon weiterhin erforderlich.

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List of abbreviations

ACCMIP	Atmospheric Chemistry and Climate Model Intercomparison Project
CBM	Carbon Bond Mechanism
CH_4	Methane
CO_2	Carbon dioxide
CAMS	Copernicus Atmosphere Monitoring Service
CLRTAP	Convention on Long-range Transboundary Air Pollution
CTM	Chemical Transport Model
EMEP	European Monitoring and Evaluation Programme
GADM	Database of Global Administrative Areas
GHG	Greenhouse Gas
GNFR	Gridded Nomenclature for Reporting
HTAP	Task Force on Hemispheric Transport of Air Pollution
IPCC	Intergovernmental Panel on Climate Change
IUPAC	International Union of Pure and Applied Chemistry
JPL	Jet Propulsion Laboratory, National Aeronautics and Space Administration
MDA8	Maximum Daily 8-hour Average
MOZART	Model for Ozone And Related Tracers
MSC-W	Meteorological Synthesizing Centre – West
NMVOC	Non-Methane Volatile Organic Compound
NOx	Oxides of nitrogen
OH	Hydroxyl radical
RCP	Representative Concentration Pathway
UNFCCC	United Nations Framework Convention on Climate Change
VOC	Volatile Organic Compound

Summary

This project aims to analyze and compare a selection of CTMs with respect to their ability to simulate the link between emissions of methane and ambient concentrations of ground-level ozone. The current ability of models to perform attribution of ground-level ozone to methane emissions is also assessed, and recommendations are given for future work to improve the ability of CTMs to perform this attribution.

Four CTMs were chosen in order to represent the current state of the art in simulation of atmospheric chemistry. Three regional CTMs were chosen to represent a range of different approaches to modelling surface ozone within Europe. The WRF-Chem model includes highly detailed representations of processes of relevance for atmospheric chemistry, along with feedbacks between these processes. The LOTOS-EUROS model on the other hand represents a very different approach to atmospheric chemistry simulation, with a focus on computational efficiency at the expense of detailed process representation. The EMEP MSC-W model represents an intermediate level of complexity, and is also chosen due to its role in the development of air quality policy in the European Union. The CAM-chem global model is also included in this analysis due to the large spatial scales inherent in modelling tropospheric ozone, and for its unique ability to perform attribution of ground-level ozone to methane oxidation.

Methane has a lifetime in the troposphere of approximately one decade, and is thus well-mixed. Methane sources anywhere in the world all contribute to locally observed methane concentrations in approximate proportion to the relative magnitude of their emission strength compared with total global emissions of methane. Methane emissions in CTMs must be specified at the global scale. There is currently a high level of uncertainty in understanding of methane emissions. Methane emissions from bottom-up emission inventories are currently inconsistent with observed global background concentrations of methane, and must be adjusted through top-down inverse modelling. Natural emissions of methane, which make up about half of the global emissions, are more uncertain than anthropogenic emissions.

As a result of these uncertainties in global methane emissions, none of the CTMs studied here are exclusively forced with datasets representing methane emissions. Instead, the concentrations of methane in these models are obtained either in whole or in part from ambient concentration measurements. Regional models must necessarily specify methane concentration somehow, since by construction they only represent a subset of the globe. A typical approach is to specify concentration at the lateral model boundaries based on the output of a global model. Common practice in global modelling studies is to specify methane concentration at the surface of the model domain based on measurements from global sampling networks. The CAM-chem model simply specifies a uniform background methane concentration at its lowest layer. The CAMS system provides an inverse product designed for use as lateral boundary conditions for the regional models in the CAMS European ensemble, which is used by the version of LOTOS-EUROS analyzed here. The EMEP MSC-W CTM simply specifies a uniform concentration of methane throughout its entire model domain when run in its default configuration. CAMS also provides an inventory of anthropogenic methane emissions for Europe for us in regional modelling, but these emissions are only 8% of the global total methane emissions.

The four CTMs analyzed here show differences in their treatment of processes relevant for methane oxidation and the resultant production of ozone. As a global model, CAM-chem must include a larger number of reactions to represent all possible chemical regimes encountered in the troposphere (the polluted and remote boundary layer, as well as the upper troposphere). Its chemical mechanism has 206 thermal, photolytic, and heterogeneous reactions. WRF-Chem shares a highly related version of this chemical mechanism (and can also be run with other

mechanisms which are not described in this report). LOTOS-EUROS in contrast only has 89 such reactions, since its primary purpose is simulation of the polluted boundary layer. The EMEP MSC-W CTM is designed to be run at both regional and global scales, so the complexity of its chemical mechanism, at 187 reactions, is closer to that of CAM-chem. The number of reactions required to describe the production of ozone from methane in CAM-chem, EMEP MSC-W, and LOTOS-EUROS are 47, 40, and 16 respectively. In each case this represents approximately 20% of the total number of reactions in each mechanism. The CBM-IV mechanism used in LOTOS-EUROS primarily achieves its small size through a simplified representation of organic molecules. In particular it represents almost all organic peroxy radicals with a single chemical species, and neglects all of the decomposition products of these peroxy radicals formed under low-NOx conditions. This simplification is appropriate for simulation of the polluted boundary layer, but not for the simulation of methane chemistry on the global scale.

The rates of photolysis reactions are also calculated using very different approaches in the four CTMs analyzed here. WRF-Chem includes the most detailed and physically realistic approach of all four models, in which the spectrally-resolved flux of solar radiation is calculated at each model level, including interactions with modelled clouds and aerosols, and used to calculate photolysis rates based on temperature- and pressure-dependent absorption cross sections and quantum yields from laboratory measurements. CAM-chem uses a similar approach, but makes simplifications for molecules which absorb radiation below 200 nm, and does not couple photolysis rates with modelled aerosol. LOTOS-EUROS uses the simplest approach. Radiative transfer is not explicitly calculated, but instead photolysis rates are parameterized based on solar zenith angle and cloudiness. Again, this simplification is appropriate for simulation of the polluted boundary layer, but not for simulation of methane chemistry on the global scale. The EMEP MSC-W model also doesn't calculate radiative transfer online. Instead, it uses an array of pre-calculated photolysis rates based on latitude, altitude, and solar zenith angle based on standard atmospheric conditions, which are adjusted online in the model based on cloudiness.

Attribution of modelled ozone to particular precursor emissions can be performed using either sensitivity studies or tagging. Prior work by HTAP has shown that the sensitivity of global annual average surface ozone to perturbations of methane abundance is approximately linear. Studies attributing surface ozone to methane using tagging are comparatively rare. In principle any model can be used to perform a sensitivity study, whereas adding tagging to a model requires significant model development effort.

The developers of LOTOS-EUROS have performed a sensitivity study in which the oxidation of methane was simply switched off. Compared with a base run in which methane oxidation was not switched off, the modelled annual average surface ozone over Germany was lowered by 3.2 $\mu g/m^3$. This represents the contribution of methane oxidation in the European domain to surface ozone over Germany.

CAM-chem has been modified at IASS Potsdam to include a tagging scheme for the attribution of ozone to its precursors (NOx and VOC). The contribution of methane to annual average surface ozone over Germany in a run of this system with VOC tagging enabled is 20 $\mu g/m^3$. This represents the contribution of methane oxidation over the entire globe to surface ozone in Germany. The total annual average surface ozone simulated by CAM-chem over Germany is 68 $\mu g/m^3$, so we estimate that methane is responsible for approximately 30% of annual average surface ozone in Germany.

Combining the results from CAM-chem and LOTOS-EUROS, we estimate that most (84%) of the ozone attributable to methane over Germany is not produced in Europe, but rather elsewhere over the globe, and arrives at Germany via long-range transport. This result is consistent with both the well-mixed nature of methane in the troposphere, and the lifetime of tropospheric ozone. A strong influence of methane on surface ozone in Europe is also consistent with a large body of prior work performed by HTAP using global models. The synthesis presented here affirms the importance of considering long-range hemispheric transport when modelling surface ozone.

The CAM-chem results presented here are not directly comparable to prior results from HTAP. The tagging approach used in CAM-chem calculates the total contribution of methane to ozone (30% over Germany as determined in this work), while the prior HTAP work calculates the sensitivity to a 20% change in global methane abundance (about 2 µg/m^3 of ozone based on HTAP publications). Future work should perform a more detailed comparison of these two complementary source attribution methods, and could also include models which have implemented alternative approaches for ozone tagging.

The same tagging approach used in the global CAM-chem model has also been implemented at IASS Potsdam into the regional WRF-Chem model, and has been used to perform global-to-regional downscaling in order to attribute ozone in Europe to regional and extra-regional NOx emissions, including assessment of the contribution of different source regions to more policy-relevant exposure metrics such as MDA8. Attribution of European ozone to VOC precursors (including methane) should be a high priority for future work. Global-to-regional downscaling with sensitivity studies is also possible given the availability of global model output from HTAP, which could be used as boundary conditions for regional models.

A large remaining uncertainty in ozone source attribution is the large spread of ozone simulated in different global CTMs, as well as the large spread of simulated responses to changes in emissions of ozone precursors, including methane. The reasons for these large inter-model differences remain unclear. Future work to understand these differences should include multi-model simulations with detailed chemical budget output. Implementation of a consistent ozone tagging methodology in a larger number of global models would also help to understand differences in simulated ozone and its response to changing precursor emissions. Global-to-regional downscaling using consistent source attribution methodologies would also allow for improved understanding of the ozone budget and its uncertainty in regional models.

Zusammenfassung

Ziel dieses Projekts ist es, eine Auswahl von CTMs auf ihre Fähigkeit hin zu analysieren und zu vergleichen, den Zusammenhang zwischen Methanemissionen und der Konzentration von bodennahem Ozon zu simulieren. Die derzeitige Fähigkeit von Modellen, eine Zuordnung von bodennahem Ozon zu Methanemissionen vorzunehmen, wird ebenfalls bewertet, und es werden Empfehlungen für künftige Arbeiten zur Verbesserung der Fähigkeit von CTMs zur Durchführung dieser Zuordnung gegeben.

Vier CTMs wurden ausgewählt, um den aktuellen Stand der Simulation der Atmosphärenchemie darzustellen. Drei regionale CTMs wurden ausgewählt, um verschiedene Ansätze zur Modellierung von bodennahem Ozon in Europa darzustellen. Das WRF-Chem-Modell enthält sehr detaillierte Darstellungen von Prozessen, die für die atmosphärische Chemie relevant sind, und berücksichtigt Rückkopplung zwischen diesen Prozessen. Das LOTOS-EUROS-Modell hingegen stellt einen ganz anderen Ansatz für die Simulation der atmosphärischen Chemie dar, wobei der Schwerpunkt auf der Recheneffizienz auf Kosten einer detaillierten Prozessdarstellung liegt. Das EMEP MSC-W-Modell stellt eine mittlere Komplexität dar und wurde auch aufgrund seiner Rolle bei der Entwicklung der Luftqualitätspolitik in der Europäischen Union ausgewählt. Das globale Modell von CAM-chem wird ebenfalls in diese Analyse einbezogen, da die Modellierung des Ozons in der Troposphäre große räumliche Skalen aufweist und die Möglichkeit besteht, Ozon in Bodennähe der Methanoxidation zuzuordnen.

Methan hat eine Lebensdauer in der Troposphäre von ungefähr einem Jahrzehnt und ist daher gut gemischt. Alle Methanquellen auf der ganzen Welt tragen zu lokal beobachteten Methankonzentrationen in einem ungefähren Verhältnis zur relativen Größe ihrer Emissionsstärke im Vergleich zu den globalen Gesamtemissionen von Methan bei. Methanemissionen in CTMs müssen global spezifiziert werden. Derzeit besteht ein hohes Maß an Unsicherheit hinsichtlich des Verständnisses der Methanemissionen. Methanemissionen aus Bottom-up-Emissionskatastern stimmen derzeit nicht mit den beobachteten globalen Hintergrundkonzentrationen von Methan überein und müssen durch inverse Top-down-Modellierung angepasst werden. Die natürlichen Methanemissionen, die etwa die Hälfte der weltweiten Emissionen ausmachen, sind unsicherer als die anthropogenen Emissionen.

Aufgrund dieser Unsicherheiten bei den globalen Methanemissionen nutzt keines der hier untersuchten CTMs ausschließlich Emissionsdatensätze für Methan. Stattdessen werden die Methankonzentrationen in diesen Modellen entweder ganz oder teilweise aus Messungen der Umgebungskonzentration erhalten. Regionale Modelle müssen die Methankonzentration notwendigerweise irgendwie spezifizieren, da sie konstruktionsbedingt nur eine Teilmenge der Erde darstellen. Ein typischer Ansatz besteht darin, die Konzentration an den lateralen Modellrändern basierend auf der Ausgabe eines globalen Modells anzugeben. In globalen Modellierungsstudien ist es gängige Praxis, die Methankonzentration an der Oberfläche der Modelldomäne auf der Grundlage von Messungen aus globalen Beobachtungs-Netzwerken zu bestimmen. Das CAM-chem-Modell spezifiziert einfach eine gleichmäßige Hintergrundmethankonzentration in seiner untersten Schicht. Das CAMS-System bietet ein inverses Produkt, das als seitliche Randbedingungen für die regionalen Modelle im europäischen CAMS-Ensemble vorgesehen ist und von der hier analysierten Version von LOTOS-EUROS verwendet wird. Das EMEP MSC-W CTM spezifiziert einfach eine einheitliche Methankonzentration in seiner gesamten Modelldomäne, wenn es in seiner Standardkonfiguration ausgeführt wird. CAMS liefert uns auch ein Kataster der anthropogenen Methanemissionen für Europa im Rahmen der regionalen Modellierung. Diese Emissionen machen jedoch nur 8% der weltweiten Methanemissionen aus.

Die vier hier analysierten CTMs zeigen Unterschiede in der Behandlung von Prozessen, die für die Methanoxidation und die daraus resultierende Ozonproduktion relevant sind. Als globales Modell muss CAM-chem eine größere Anzahl von Reaktionen umfassen, um alle möglichen Gebiete in der Troposphäre (verschmutzte und gering belastete Grenzschichtgebiete sowie die obere Troposphäre) abzubilden. Sein chemischer Mechanismus weist 206 thermische, photolytische und heterogene Reaktionen auf. WRF-Chem hat eine ähnliche Version dieses chemischen Mechanismus (und kann auch mit anderen Mechanismen betrieben werden, die in diesem Bericht nicht berücksichtigt werden). LOTOS-EUROS hingegen hat nur 89 solcher Reaktionen, da sein Hauptzweck die Simulation der Grenzschicht in verschmutzten Gebieten ist. Das EMEP MSC-W CTM kann sowohl auf regionaler als auch auf globaler Ebene eingesetzt werden, sodass die Komplexität seines chemischen Mechanismus bei 187 Reaktionen der von CAM-chem ähnelt. Die Anzahl der Reaktionen, die zur Beschreibung der Ozonproduktion aus Methan in CAM-chem, EMEP MSC-W und LOTOS-EUROS erforderlich sind, beträgt 47, 40 bzw. 16. In jedem Fall entspricht dies ungefähr 20% der Gesamtzahl der Reaktionen in jedem Mechanismus. Der in LOTOS-EUROS verwendete CBM-IV-Mechanismus erreicht seine geringe Größe hauptsächlich durch eine vereinfachte Darstellung organischer Moleküle. Insbesondere repräsentiert es fast alle organischen Peroxyradikale mit einer einzigen chemischen Spezies und vernachlässigt alle Zersetzungsprodukte dieser Peroxyradikale, die unter NOx-armen Bedingungen gebildet werden. Diese Vereinfachung eignet sich für die Simulation der verschmutzten Grenzschicht, nicht jedoch für die Simulation der Methanchemie im globalen Maßstab.

Die Geschwindigkeiten von Photolysereaktionen werden auch in den vier hier analysierten CTM nach sehr unterschiedlichen Ansätzen berechnet. WRF-Chem beinhaltet den detailliertesten und physikalisch realistischsten Ansatz aller vier Modelle, bei dem der spektral aufgelöste Fluss der Sonnenstrahlung auf jeder Modellebene berechnet wird, einschließlich Wechselwirkungen mit modellierten Wolken und Aerosolen. Photolyseraten werden auf der Grundlage der temperatur- und druckabhängige Absorptionsquerschnitte und Quantenausbeuten aus Labormessungen gerechnet. CAM-chem verwendet einen ähnlichen Ansatz, vereinfacht jedoch für Moleküle, die Strahlung unter 200 nm absorbieren, und koppelt die Photolyseraten nicht mit modelliertem Aerosol. LOTOS-EUROS verwendet den einfachsten Ansatz. Der Strahlungstransfer wird nicht explizit berechnet, sondern die Photolyseraten werden anhand des Sonnenzenitwinkels und der Bewölkung parametrisiert. Auch diese Vereinfachung eignet sich für die Simulation der verschmutzten Grenzschicht, nicht jedoch für die Simulation der Methanchemie im globalen Maßstab. Das EMEP MSC-W-Modell berechnet den Strahlungstransfer auch nicht online. Stattdessen werden eine Reihe von vorberechneten Photolyseraten je nach Breitengrad, Höhe und Sonnen-Zenit-Winkel basierend auf den atmosphärischen Standardbedingungen verwendet, die online im Modell entsprechend der Bewölkung angepasst werden.

Die Zuordnung von modelliertem Ozon zu bestimmten Vorläuferemissionen kann entweder mithilfe von Sensitivitätsstudien oder mithilfe von Markierungen erfolgen. Frühere Arbeiten von HTAP haben gezeigt, dass die Empfindlichkeit des globalen Jahresmittelwerts von bodennahem Ozon auf Änderungen der Methankonzentration annähernd linear ist. Studien, die bodennahes Ozon mithilfe von Markierungen auf Methan zurückführen, sind vergleichsweise selten. Grundsätzlich kann jedes Modell zur Durchführung einer Sensitivitätsstudie verwendet werden, wohingegen das Hinzufügen von Markierungen zu einem Modell einen erheblichen Aufwand für die Modellentwicklung erfordert.

Die Entwickler*innen von LOTOS-EUROS haben eine Sensitivitätsstudie durchgeführt, bei der die Oxidation von Methan einfach abgeschaltet wurde. Im Vergleich zu einem Basislauf, bei dem die Methanoxidation nicht abgeschaltet wurde, wurde das modellierte durchschnittliche jährliche bodennahe Ozon über Deutschland um 3,2 µg/m^3 gesenkt. Dies stellt den Beitrag der Methanoxidation im europäischen Raum zum bodennahen Ozon über Deutschland dar.

CAM-chem wurde am IASS Potsdam um ein Markierungsschema für die Zuordnung von Ozon zu seinen Vorläufern (NOx und VOC) erweitert. Der Beitrag von Methan zum jährlichen durchschnittlichen bodennahen Ozon über Deutschland in einem Lauf dieses Systems mit aktivierter VOC-Markierung beträgt 20 µg/m^3. Dies stellt den Beitrag der weltweiten Methanoxidation zum bodennahen Ozon in Deutschland dar. Das gesamte jährliche durchschnittliche bodennahe Ozon, das CAM-chem in Deutschland simuliert, beträgt 68 µg/m^3. Wir schätzen, dass Methan für ungefähr 30% des jährlichen durchschnittlichen bodennahen Ozons in Deutschland verantwortlich ist.

Wir kombinieren die Ergebnisse von CAM-chem und LOTOS-EUROS und schätzen, dass der größte Teil (84%) des auf Methan zurückzuführenden Ozons in Deutschland nicht in Europa, sondern weltweit erzeugt wird und über Ferntransporte nach Deutschland gelangt. Dieses Ergebnis passt sowohl zur gut gemischten Natur von Methan in der Troposphäre als auch zur Lebensdauer von troposphärischem Ozon. Ein starker Einfluss von Methan auf das bodennahe Ozon in Europa steht auch im Einklang mit zahlreichen früheren Arbeiten, die von HTAP unter Verwendung globaler Modelle durchgeführt wurden. Die hier vorgestellte Synthese bestätigt, wie wichtig es ist, den Hemisphärentransport über große Entfernungen bei der Modellierung von bodennahem Ozon zu berücksichtigen.

Die hier vorgestellten CAM-chem-Ergebnisse sind nicht direkt mit früheren Ergebnissen von HTAP vergleichbar. Der in CAM-chem verwendete Markierungsansatz berechnet den Gesamtbeitrag von Methan zu Ozon (30% über Deutschland, wie in dieser Arbeit ermittelt), während die vorherige HTAP-Arbeit die Empfindlichkeit für eine 20% ige Änderung der globalen Methankonzentration berechnet (etwa 2 µg/m^3 Ozon basierend auf HTAP-Publikationen). Zukünftige Arbeiten sollten einen detaillierteren Vergleich dieser beiden komplementären Quellenzuweisungsmethoden durchführen und könnten auch Modelle umfassen, die alternative Ansätze für die Ozonmarkierung implementiert haben.

Derselbe in CAM-chem verwendete Markierungsansatz wurde auch am IASS Potsdam in WRF-Chem implementiert, und zur Durchführung einer Herunterskalierung von global zu regional für Ozon in Europa verwendet. Ozon wurde zu regionalen und überregionalen NOx-Emissionen zugeordnet, einschließlich der Bewertung der Beiträge verschiedener Herkunftsregionen zu politisch relevanteren Expositionskennzahlen wie MDA8. Die Zuordnung von europäischem Ozon zu VOC-Vorläufern (einschließlich Methan) sollte für die künftige Arbeit eine hohe Priorität haben. Aufgrund der Verfügbarkeit von globalen Modellausgaben aus HTAP, die als Randbedingungen für regionale Modelle verwendet werden könnten, ist auch eine Herunterskalierung von global zu regional für Sensitivitätsstudien möglich.

Eine große verbleibende Unsicherheit bei der Zuordnung von Ozonquellen ist die große Verbreitung von Ozon, die in verschiedenen globalen CTMs simuliert wurde, sowie die große Bandbreite möglicher Auswirkungen von Änderungen der Emissionen von Ozonvorläufern, einschließlich Methan, auf die simulierten Reaktionen. Die Gründe für diese großen Unterschiede zwischen den Modellen bleiben unklar. Zukünftige Arbeiten zum Verständnis dieser Unterschiede sollten Multi-Modell-Simulationen mit detaillierten Ausgaben des Budgets aller enthaltenen Stoffspezies umfassen. Die Implementierung einer konsistenten Ozonmarkierungsmethode in einer größeren Anzahl globaler Modelle würde auch dazu beitragen, Unterschiede im simulierten Ozon und dessen Reaktion auf sich ändernde Vorläuferemissionen zu verstehen. Die Herunterskalierung von global zu regional unter

Verwendung einheitlicher Methoden zur Quellenzuordnung würde auch ein besseres Verständnis des Ozonbudgets und seiner Unsicherheit in regionalen Modellen ermöglichen.

1 Introduction

1.1 Background

Methane (CH_4) is recognised by the UNFCCC as a greenhouse gas. It was included along with CO_2 in the 1997 Kyoto Protocol as part of the "basket" of six greenhouse gases for which parties to the UNFCCC agreed to emission reductions. The importance of methane as a greenhouse gas was reaffirmed in the 2015 Paris Agreement. As well as being a greenhouse gas itself, methane also contributes to global warming through its role as a precursor to tropospheric ozone, which is also a greenhouse gas (Stevenson et al. 2006). More recently, it has been recognised that methane's role as an ozone precursor also has important implications for global background air quality, especially in Europe (eg. van Dingenen et al. (2018), HTAP (2010), and references therein).

Based on records from ice cores and a network of observing sites spread across the globe, present-day methane concentrations are approximately 3 times higher than during the pre-industrial period (Saunois et al. 2019). After a period of rapid growth in the late 20th century, the global average surface concentration stabilised briefly at a mixing ratio of about 1775 ppb between the years 2000 and 2007, but has since resumed growth, and currently stands at about 1865 ppb (https://esrl.noaa.gov/gmd/ccgg/trends_ch4/). Reasons for the brief stabilisation and resumption of growth in the global average methane concentration are currently unclear. The current state of global methane observations is not detailed enough to clearly and unambiguously attribute the observed changes in global methane concentration to any particular changes in the sources or sinks of methane (Turner et al. 2019).

Out of all of the future scenarios in the IPCC Fifth Assessment Report (AR5), the current growth rate in atmospheric methane most closely resembles the scenario RCP 8.5 (Riahi et al. 2011), the most pessimistic of all emission scenarios in AR5, in which methane concentration is expected to double by the end of the 21st century. Based on the methane increase in the RCP 8.5 scenario, the global CTM intercomparison exercise ACCMIP (Young et al. 2013) projects an increase in global average ground-level ozone by 2100 of approximately 10 $\mu g/m^3$, which would have significant consequences for the attainment of ozone target values under current EU air quality legislation. The ACCMIP model ensemble showed a wide range of estimates in their simulations of both present-day and future tropospheric ozone (Young et al. 2013). The ACCMIP ensemble also simulates a wide range of global OH concentrations, meaning that the magnitude of the global methane sink is not well constrained (Voulgarakis et al. 2013). Furthermore, Parrish et al. (2014) showed that current generation global models are not able to simulate the observed long-term changes in tropospheric ozone.

1.2 Emissions of methane

1.2.1 Emission inventories

Emission inventories are traditionally constructed in a "bottom-up" manner, by combining activity data (such as energy consumption) with appropriate emission factors. A prominent example of a global emission inventory including methane is EDGAR (Crippa et al. 2018). In the case of methane, parties to the UNFCCC are also required to report their own national emission estimates using a similar process.

1.2.2 Emission models

Process models are often used to simulate the physical mechanisms of methane production for natural source processes such as anaerobic decay processes in wetland ecosystems (eg. Bloom et al. 2017). These models can be used to produce emission inventories, and can be included in the land surface component of Earth System Models (ESMs).

1.2.3 Inverse models

Top-down methods (also known as inverse modelling) combine ambient concentration measurements with CTMs and an *a-priori* estimate of emission fluxes (usually from an emission inventory) to produce an optimised *a-posteriori* set of emission fluxes which are more consistent with the ambient concentration estimates (eg. Houweling et al. 2014). The recent review of the global methane budget by Saunois et al. (2019) found a significant mismatch between total global methane emission estimates for the period 2008-2017 calculated using bottom-up methods (including process-based models) and top-down methods, with no overlap in their respective global uncertainty ranges. Most of the mismatch is attributable to uncertainty in natural methane sources. When considering only anthropogenic sources, the bottom-up and top-down methods are in better agreement.

Inverse modelling of methane emissions at the European scale is possible using existing in-situ measurements of methane (Bergamaschi et al. 2018), and is also expected to benefit from a new generation of satellite measurements (Maasakkers et al. 2019).

1.2.4 Mass balance approaches

Due to the significant uncertainty in current estimates of methane emissions and large inter-model differences in the strength of the methane sink, many global CTMs do not use emission inventories as a source of methane emission data, but instead constrain modelled methane concentration to observed values. For example, the most recent HTAP multi-model experiment, in which the objectives included investigation of the sensitivity of global ozone budget to changes in methane, all participants were required to simply hold the surface mixing ratio of methane constant at 1798 ppb for the year 2010 for their base run (Galmarini et al. 2017). The models calculate the necessary emissions per time step required to maintain these fixed concentrations. Earlier studies such as Butler et al. (2005) have used this technique to implement a simple form of "mass balance" inverse modelling for methane by including these calculated emissions in the model output, but typically these emissions are not saved or written as model output.

1.3 Modelling the production of ozone from methane

Due to the relatively long atmospheric lifetimes of methane and ozone, most prior work has employed global scale CTMs (eg. Fiore et al. (2008), HTAP (2010), van Dingenen et al. (2018)). Regional CTMs have not typically treated the processes related to methane with a high priority. Typically, regional CTMs are employed over highly polluted regions, in which local and regional sources of NOx and NMVOC are expected to be the dominant precursors of ground-level ozone. For example, in the recent EURODELTA-III model intercomparison exercise (Bessagnet et al. 2016), methane is only acknowledged briefly as a component of the emission inventory, while in the related EURODELTA-Trends exercise (Colette et al. 2017), which aimed to quantify multi-decadal influences on European air quality, no methane emissions were specified. Instead, the modelling groups were instructed to specify methane lateral boundary conditions based on observed trends at the Mace Head observing site. Neither EURODELTA-III nor EURODELTA-Trends attempted to isolate the influence of methane on ozone air quality for Europe.

1.3.1 Chemical mechanisms

Tropospheric ozone is produced during the oxidation of VOCs in the presence of NOx (Atkinson 2000). The fundamental chemical process responsible for production of tropospheric ozone is the reaction of a peroxy radical (resulting from VOC oxidation) with a molecule of nitrogen monoxide (NO), producing a molecule of nitrogen dioxide (NO_2). The NO_2 thus-produced can then be photolysed, producing atomic oxygen (O), which reacts rapidly with molecular oxygen (O_2) to form ozone. For the specific case of ozone production from methane oxidation, there are only two relevant peroxy radicals: the methylperoxy radical (CH_3O_2), and the hydroperoxy radical (HO_2). The rate-limiting step for the production of ozone from methane is the initial step in which methane is oxidized. The relevant chemical reactions can be summarized and classified as follows:

- Initial oxidation of methane, subsequently producing CH_3O_2.
  - The predominant oxidant in the troposphere is the OH radical.
  - There are two other minor oxidation pathways:
    - Oxidation by excited oxygen atoms (O^1D), primarily in the stratosphere.
    - Oxidation by atomic chlorine (Cl), primarily in the remote marine boundary layer.
- Reaction of CH_3O_2 with NO, producing NO_2, HO_2, and formaldehyde (HCHO), an oxygenated VOC.
  - Under low NOx conditions, CH_3O_2 can also react with other peroxy radicals, forming minor products such as methanol (CH_3OH) and formic acid (CH_3OOH).
- Oxidation or photolysis of HCHO, producing HO_2, carbon monoxide (CO).
  - Hydrogen (H_2) can also be formed, but is relatively long lived, and therefore ignored in some mechanisms as a minor product.
  - Under low NOx conditions, $HOCH_2OO$ can be formed from HCHO as a minor product.
- Oxidation of CO, producing CO_2 and HO_2.
- Reaction of HO_2 with NO, producing NO_2, and regenerating OH.
  - A number of other organic and inorganic reactions compete with this process.
  - HO_2 can also be taken up on aerosols.
- Photolysis of NO_2, resulting in the regeneration of NO and production of O, which rapidly forms O_3.

Photolysis rates for each molecule depend on their temperature- and pressure-dependent absorption cross-sections and quantum yields, as well as the spectral actinic flux. Absorption cross-sections and quantum yields are measured in laboratory experiments. The actinic flux depends on absorption and scattering of solar radiation in the atmosphere.

1.3.2 Timescales for modelling methane and ozone

The rate constant for the OH oxidation of methane is much smaller than for OH oxidation of NMVOC (Saunders et al. 2003), meaning that the typical lifetime for methane in the troposphere is approximately 10 years (eg. van Dingenen et al. 2018). In contrast, NMVOC typically have lifetimes of minutes to weeks (eg. von Kuhlmann et al. 2003). The timescale for interhemispheric transport in the troposphere is approximately 1 year (Geller et al. 1997). Since the lifetime of methane is much longer than this important mixing timescale, this has the consequence that methane is spatially well-mixed in the troposphere (van Dingenen et al. 2018). Methane emissions anywhere in the world all contribute to locally observed methane concentrations in approximate proportion to their global emissions, and similarly the ozone produced from methane oxidation is approximately due proportionally to all global sources of methane, except in the immediate vicinity of very strong sources under highly unusual meteorological conditions (Schnell et al. 2016).

For continental-scale regional air quality modelling, this has the important consequence that methane emitted within the model domain is much more likely to simply be advected out of the domain than to be oxidised within the domain.

Similarly, most of the methane present within the model domain will be due to emission sources from outside the domain. For this reason, regional modelling studies for Europe and elsewhere have traditionally focused more on including methane via lateral boundary conditions than via emissions.

While not itself globally well-mixed in the atmosphere, ozone is still long lived enough such that it can be transported over hemispheric spatial scales (HTAP 2010). Ozone must also be accurately specified at the lateral boundaries of regional models in order to correctly represent the long-range transport of ozone into these models (eg. Galmarini et al. 2017). Some of the ozone transported into the model domain will be attributable to methane oxidation. Similarly, some of the ozone produced locally in the model domain will be attributable to methane oxidation. In both cases, the origin of the methane could be anywhere on Earth.

1.3.3 Methods for attribution of ozone to precursor emissions

Thunis et al. (2019) distinguishes between attribution and sensitivity studies. Attribution studies estimate the contribution of some type of emission source to some particular pollutant, while sensitivity studies estimate the change in the ambient amounts of some particular pollutant given some change in its emissions or those of its precursors.

At the global scale, attribution of ground-level ozone to methane and other precursors has been more commonly performed using sensitivity studies. HTAP has performed two sets of systematic, multi-model experiments (HTAP1 and HTAP2) in which emissions of ozone precursors (including methane abundance) were changed by 20%, and compared with base runs in which all emissions remained unperturbed (Wild et al. (2012), Turnock et al. (2018)). 14 models reported results for methane perturbations in HTAP1 (Wild et al. 2012) while only 2 models reported results in HTAP2 (Turnock et al. 2018). The responses of global annual mean surface ozone to a 20% reduction in global methane abundance were similar in HTAP1 (-1.80 ± 0.28 µg/m^3) and HTAP2 (-2.10 ± 0.24 µg/m^3) (Turnock et al. 2018). A similar change in annual average surface ozone in response to a change in methane abundance was seen over Europe (Jonson et al. 2018), which was comparable in magnitude to the combined effects of 20% emission perturbations of short-lived ozone precursors in all other regions of the world combined. A global-to-regional downscaling of the HTAP2 sensitivity studies was performed by Im et al. (2018). They performed sensitivity studies with regional models using boundary conditions based on the sensitivity studies performed by the HTAP2 global models to examine the sensitivity of ozone and other pollutants in Europe to emissions perturbations inside and outside of Europe. Unfortunately, Im et al. (2018) do not include the HTAP2 methane perturbation experiments.

A novel source attribution methodology for modelled ozone, including separate attribution to both NOx and VOC precursors via a “tagging” methodology, was developed recently by Butler et al. (2018) based on the global CAM-chem model (Tilmes et al., 2015). This work extended previous work, in which only tagging of NOx precursors was possible (Emmons et al. 2012). Using this method for attribution of ozone to VOC precursors in a model run following the most recent HTAP experiment protocol, Butler et al. (2018) recently quantified the contribution of methane to the global tropospheric background burden as approximately one third. The remainder of the ozone burden was attributed to oxidation of NMVOC and CO, and to transport of ozone from the stratosphere.

An alternative methodology for attribution of methane to its precursors was presented by Grewe et al. (2017). This method differs from that of Butler et al. (2018) in that it does not distinguish between the effects of NOx and VOC precursors, but rather attributes each molecule of ozone equally to its NOx and VOC precursor with 50% weight. Grewe et al. (2017) report a contribution of methane to tropospheric ozone of 15%. Butler et al. (2018) report a contribution of methane to ozone of 30% when performing VOC tagging. These results are consistent with each other, since ozone production requires both NOx and VOC precursors. Grewe et al. (2017) gives methane a 50% weighing to ozone production from methane (the other 50% coming from the source of the NOx required for this ozone production), while Butler et al. (2018) gives each VOC precursor a 100% weighting to the ozone it produces during VOC tagging, and gives each NOx precursor a 100% weighting to the ozone it produces during NOx tagging. Despite the seeming agreement between these two alternative tagging methodologies in the case of methane, it is however not clear exactly how comparable these two alternative approaches are with each other. For example, the approach of Grewe et al. (2017) also attributes CO in the atmosphere to lightning: a result for which there is no production pathway represented in their model. This appears to be an unphysical artefact of their source attribution methodology, which could potentially also lead to misattribution of modelled ozone. In order to better understand the differences between these two approaches, they should be systematically compared with each other.

Ozone source attribution modules are present in two regional CTMs: CAMx (Dunker et al. 2002); and CMAQ (Kwok et al. 2015)) We are not aware of any studies which have used these models to calculate the contribution of methane to ozone over Europe. It is also not clear how appropriate these techniques would be for application at the global scale, since they rely on classification of the chemical regime at the grid-cell level as either NOx-limited or VOC-limited in order to perform their attribution. The relatively large size of the grid cells in global models would likely result in almost the entire atmosphere being classified as NOx-limited, resulting in almost no attribution of ozone to methane. A thorough review of alternative methodologies for ozone source attribution in models is given by Butler et al. (2018).

Recently Lupascu and Butler (2019) implemented the ozone tagging scheme of Butler et al. (2018) into the regional CTM WRF-Chem. So far this scheme has only been used for attribution of European ozone to NOx emissions, and not to VOCs. A manuscript is currently in preparation which will extend this analysis to VOCs (including methane).

1.4 Choice of CTMs used in this study

WRF-Chem (Grell et al. 2005) is used extensively worldwide as well as in-house at IASS Potsdam (eg. Mar et al. (2016), Churkina et al. (2017), Kuik et al. (2018), Lupascu and Butler (2019)). Several other groups have used WRF-Chem for simulations over Europe and Germany (eg. Galmarini et al. (2017), Fallmann et al. (2016)). WRF-Chem is an online-coupled model with several different parameterisations of relevant processes available, as well as the ability to simulate feedbacks. We are familiar with the model source code and the various ways in which this highly flexible model can be configured. Here we analyse version 3.9.1 of WRF-Chem in the configuration in which it supports the ozone source attribution described in Lupascu and Butler (2019). This configuration uses a modified version of the MOZART chemical mechanism, and is described in more detail by Lupascu and Butler (2019).

The EMEP MSC-W CTM (Simpson et al. (2012), Simpson et al. (2019), hereafter referred to as the EMEP CTM) is used extensively in the development of air quality policy in the European Union. The model is used to perform simulations which form the basis of European status reports to CLRTAP, which describe concentration and deposition of a wide range of atmospheric pollutants, including ozone. The EMEP CTM can be run either as a regional model or a global model. The EMEP CTM is a member of the CAMS European regional model ensemble. The EMEP CTM is released as an open source model along with the EMEP emission inventory, which is based on officially reported emissions by EU member states. The model also ships with other ancillary input data, and a sample year of model output. The current version of the model is version rv4.33, was released in July 2019. This version of the model ships with input and output data for the year 2015. We have the full set of publically-available input and output data, the open source model code, and all other relevant documentation in-house at IASS Potsdam, downloaded in August 2019 from the official EMEP GitHub repository: https://github.com/metno/emep-ctm. We also have links with an expert collaborator (David Simpson, Norwegian Meteorological Institute), who has provided us with additional information about the EMEP CTM for this project.

LOTOS-EUROS (Manders et al. (2017), (Manders-Groot et al. 2016)) is one of the regional CTMs which make up the CAMS European regional ensemble (Copernicus Atmosphere Monitoring Service), an operational analysis and forecasting system for air pollution and greenhouse gases (Inness et al. 2019). A unique feature of LOTOS-EUROS compared with other models analyzed here is its treatment of vertical resolution, with two layers representing the surface and the planetary boundary layer, and three layers above this representing the free troposphere. This low vertical resolution compared with other models allows a high computational efficiency, enabling the simulation of longer periods in shorter times relative to other models. LOTOS-EUROS is maintained by TNO Netherlands and provided to the community as an open source model. Here we analyse version 2.1.002 of LOTOS-EUROS. We have links with an expert collaborator (Martijn Schaap, Freie Universität Berlin and TNO Netherlands), who has provided us with model output for 2015 for this project.

We also include results for 2015 from the widely-used CAM-chem global chemistry-climate model (Tilmes et al. 2015), version 1.2.2, as modified for ozone source attribution at IASS Potsdam as described by Butler et al. (2018).

2 Representation of methane emissions in CTMs

2.1 Methane emissions in WRF-Chem

By inspection of the WRF-Chem source code, we discovered that the code for adding the methane flux to the methane concentration in the model is commented out. Any methane emissions specified in input files for runs of the WRF-Chem model would simply have no effect on the model run.

The only source of methane in WRF-Chem, when run in its standard configuration, is advection through the lateral boundaries of the model. At IASS Potsdam, we have two data sources for specifying these lateral boundary conditions: the CAM-chem global CTM (Tilmes et al. 2015), which we run ourselves at IASS Potsdam; and the MOZART-4 CTM (Emmons et al. 2010), run by NCAR in the USA. Output from the MOZART-4 CTM is a popular source of boundary condition data within the WRF-Chem community, as data is freely available to the public specifically for use in WRF-Chem simulations (https://www.acom.ucar.edu/wrf-chem/mozart.shtml). Operational runs of MOZART-4 were ceased by NCAR on 26.01.2018, so boundary condition data from NCAR are no longer available after this date. NCAR now promotes their global models CAM-chem and WACCM as sources of data for the community.

Any methane concentrations from global models which are used as boundary conditions for regional models must have been ultimately due to emissions of methane in these global models. In all three of MOZART-4, CAM-chem, and WACCM, methane emissions are not explicitly specified as emission datasets, but are rather calculated online during model simulations based on specified surface concentrations. Thus, the global methane emissions which are typically used in studies with WRF-Chem are not available.

2.2 Methane emissions in the EMEP MSC-W CTM

By default, methane in the EMEP CTM is specified as a fixed background value throughout the entire model domain. Thus, emissions of methane at the global scale in the EMEP CTM are accounted for by “mass balance” in a way similar to WRF-Chem.

The standard European emission inventory used by the EMEP CTM is based on data reported by European countries to CLRTAP, which do not include methane. Inspection of the source code of version rv4.33 of the EMEP CTM shows that the model contains a software infrastructure for including methane emissions in the same way that emissions of other chemical species are included, but users of the EMEP CTM must provide their own datasets if they wish to do this.

2.3 Methane emissions in LOTOS-EUROS

Here we describe the methane emissions used in LOTOS-EUROS when run as a member of the CAMS European regional air quality model ensemble. The CAMS system provides global and regional emissions of reactive gases and greenhouse gases as described in Granier et al. (2019). In addition, CAMS also includes a set of global methane inverse model products as described by Segers and Houweling (2018). The LOTOS-EUROS configuration we describe here uses European methane emissions from the CAMS-REG-GHG product (Granier et al. 2019) and sets methane concentrations at the lateral model boundaries based on the “v17r1” global inverse product (Segers and Houweling 2018). We report on the model setup as used to simulate the year 2015.

2.3.1 Methane emissions for Europe from CAMS-REG-GHG

The CAMS-REG-GHG emissions are described by Granier et al. (2019). As a product of the Copernicus CAMS system, this dataset will eventually be released to the public. At the time of writing this dataset is not yet publically available, so has been obtained directly from TNO, who were contracted by CAMS to produce the dataset. These data should be considered preliminary until the dataset is publically released. This dataset can be considered the successor to the TNO-MACC emission data (Kuenen et al. 2014), of which the most recent version was TNO-MACC-III, which included emissions up to the year 2011. Granier et al. (2019) describe two versions of CAMS-REG-GHG: version 2.2 which includes emissions for 2000-2015; and version 3.1 which adds emissions for 2016. Given that these emission data are intended for use in an ongoing operational air quality forecasting system (CAMS), regular updates to these data can be expected. The frequency of the update cycle is currently unknown.

Here we describe the methane emissions from CAMS-REG-GHG version 2.2 for the year 2015. Methane emissions are based on information reported by countries to the UNFCCC in their reports for 2017. Only anthropogenic emission sources are reported. These reported emissions are remapped onto GNFR sectors by TNO for consistency with the emissions of reactive air pollutants, and shown in Table 1.

Table 1: Annual average methane emissions (kt/yr) in 2015 from CAMS-REG-GHG version 2.2 for the CAMS European domain, and for Germany

2015 methane emissions in kt/yr by sector	Full CAMS domain	Germany
Public Power	773	102
Industrial Combustion	3920	160
Other Stationary Combustion	1930	45
Fugitive	11400	204
Solvents	3.4	1.5
Road transport	101	5.5
Shipping	0.0	0.0
Aviation	0.5	0.1
Off road	10	0.8
Waste	9330	414
Livestock	4520	248
Agriculture	9240	1060
Total Emissions	**41300**	**2240**

The temporal profile of emissions (seasonal, weekly, and diurnal) for the CAMS-REG-GHG dataset is specified by the CAMS-TEMPO product (Granier et al. 2019). At the time of writing, this dataset has not been publically released. These data are currently undergoing quality checks and may be subject to change (Jeroen Kuenen, personal communication). Given the long atmospheric lifetime of methane (approximately a decade), we do not expect that these temporal profiles in methane emissions will have any significant influence on the ozone production from these emissions.

2.3.2 Methane emissions from the global CAMS inverse product

Lateral boundary conditions for methane concentration used in LOTOS-EUROS are taken from the global CAMS "v17r1" inverse product (Segers and Houweling 2018). This product uses a-priori emissions from a range of current methane emission inventories. These emissions are optimised using 4D variational data assimilation in the TM5 CTM for better agreement with observed methane mixing ratios from the NOAA surface monitoring network, and provided at monthly temporal resolution. The CAMS global inverse products are explicitly produced for the purpose of providing boundary conditions to the regional models in the CAMS ensemble (Arjo Segers, personal communication). CAMS global inverse emissions are calculated for four aggregated source categories: rice cultivation; wetlands; biomass burning; and "other" (which includes all anthropogenic sectors, as well as all remaining natural sources and sinks of methane). These emissions are produced on a grid of approximately 2x2 degrees. To extract emissions for Germany we used a raster resampling approach to re-grid these emissions onto a resolution of 0.01 degrees, which we then sampled using a mask of grid cells for Germany based on data obtained from GADM (https://gadm.org/, accessed September 2019). Methane emissions from this system for 2015 are summarised in Table 2, where they are compared with Saunois et al. (2019), who present an aggregated review of bottom-up and top-down emissions for the period 2008-2017.

Table 2: Methane emissions (German and Global) for 2015 by sector from the v17r1 CAMS inverse product compared with global estimates from Saunois et al. (2019) for 2008-2017

Annual methane emissions (kt/yr)	Wetlands	biomass burning	Rice	other	Total
Germany (v17r1)	38.3	0.22	0.07	4880	4920
Global (v17r1)	200000	21000	43600	291000	555000
Global (top-down Saunois et al., 2019)	178000 [155000-200000]	NA	NA	356000 [338000-366000]	534000 [493000-566000]
Global (bottom-up Saunois et al., 2019)	149000 [102000-182000]	17000 [14000-26000]	30000 [25000-38000]	541000 [452000-634000]	737000 [593000-880000]

The “other” emissions from v17r1 include the soil sink, so we have also included this sink (38000 kt/yr) in the comparison with top-down estimates from Saunois et al. (2019). The bottom-up estimates from Saunois et al. (2019) do not include the soil sink, so we have not considered this in the comparison with the “other” emissions from v17r1. Thus, the bottom-up estimates from Saunois et al. (2019) as presented here are expected to be systematically higher than the top-down estimates by approximately 38000 kt/yr.

The global methane emissions from the CAMS inverse product are generally consistent with the review of Saunois et al. (2019). The European anthropogenic emissions from CAMS_REG-GHG (41300 kt/yr) are approximately 8% of the total global top-down methane emissions from Saunois et al. (2019), indicating that methane transport through the lateral boundaries is a much more important source of methane for European regional models than emissions within the European domain.

The German methane emissions from the CAMS inverse product (4920 kt/yr) are significantly higher than the anthropogenic emissions reported by Germany to the UNFCCC (2240 kt/yr). This can only be partly explained by the inclusion of natural wetland emissions. It is possible that other natural emissions are being allocated by the inverse system to the “other” category, but it seems more likely that this discrepancy is due to the limits of the inverse system itself, which is designed primarily for the purpose of providing boundary conditions for the CAMS regional model ensemble, rather than determination of accurate regional emission totals, and thus only uses measurements of methane from stations representative of background conditions (Segers and Houweling 2018). Regional inverse modelling of European emissions is performed using models with high resolution over Europe and a denser network of stations covering the European domain (Bergamaschi et al. 2018), but such top-down European methane emissions are not used for the simulation of European air quality in any of the CTMs studied here.

3 Representation of relevant processes in CTMs

3.1 Chemical mechanisms

LOTOS-EUROS uses a chemical mechanism based on the CBM-IV (Carbon Bond Mechanism, version 4), which was originally described by Gery et al. (1989). The CBM-IV mechanism was designed to simulate ground-level ozone on urban and regional scales under polluted conditions, and so only includes the chemical species and reactions which are most important for these conditions. The CBM family of mechanisms has undergone several updates since 1989, but studies using the original CBM-IV mechanism are still published in the modern scientific literature, using a number of different regional CTMs (including LOTOS-EUROS). All of the reactions involved in ozone production from methane in LOTOS-EUROS are directly traceable to the original CBM-IV mechanism, along with their rate constants. None of these reactions in LOTOS-EUROS include any of the updates made to the original CBM-IV mechanism.

The tagged version of CAM-chem uses a modified version of the MOZART-4 chemical mechanism. The MOZART mechanism was originally developed at NCAR for use in the MOZART global CTM (Brasseur et al. 1998), and therefore is designed to include species and reactions which cover the full range of chemical regimes expected in the troposphere, as well as some basic stratospheric chemistry. The mechanism has been updated with new releases of the MOZART CTM to include updated rate constants from JPL, and to incorporate additional emitted VOC species, and updated understanding of atmospheric chemistry (Horowitz et al. (2003), Emmons et al. (2010)). Ozone source attribution using the MOZART-4 mechanism for NOx precursors was first described by Emmons et al. (2012). The version of the MOZART-4 mechanism used here (Butler et al. 2018) is based on Emmons et al. (2012), with modifications to facilitate tagging the mechanism for the attribution of ozone to both NOx and VOC precursors. These modifications do not substantially alter the results of simulations compared to simulations performed with the MOZART-4 mechanism as described by (Emmons et al. 2012). Subsequent minor updates to the MOZART-4 mechanism by NCAR for use in CAM-chem have not significantly affected the simulated ozone compared with the original MOZART-4 mechanism (Tilmes et al. 2015). These updates from NCAR have not been included in the tagged version of the MOZART mechanism analyzed here. The modified MOZART-4 mechanism used in CAM-chem at IASS Potsdam (Butler et al. 2018) does not differ substantially from the MOZART mechanism as used in WRF-Chem at IASS Potsdam (Lupascu and Butler 2019).

Chemical mechanisms in the EMEP CTM are updated periodically with new releases of the EMEP CTM. Simpson et al. (2012) describe version rv3.7 of the EMEP CTM, which used the EmChem09 chemical mechanism. Since then, the EMEP chemical mechanism has been updated twice. New versions of the EmChem mechanism include updated rate constants from IUPAC, and modified chemical reaction schemes to retain traceability to updates in the MCM (eg. Jenkin et al. 2015, and references therein), with a focus on keeping the mechanism small enough to be computationally viable for regional-scale modelling. Version rv4.15 of the EMEP CTM introduced the EmChem16 mechanism (Simpson et al. 2017), while the version of the EMEP CTM as analyzed here (version rv4.33) uses the EmChem19 chemical mechanism (Simpson et al. 2019). The list of reactions and rate constants in the EmChem19 mechanism is not included in the open source version of the EMEP CTM. These were obtained by personal communication with David Simpson, who provided us with an updated version of the EmChem19 mechanism, EmChem19a, which will be included in an upcoming release of the EMEP CTM.

Table 3: **Comparison of the complexity of chemical mechanisms by number of reactions per category**

Number of reactions per category in each mechanism	CBM-IV	EmChem19a	MOZART
Initial CH_4 oxidation	1	1	2
Reactions of CH_3O_2	4	5	3
Reactions of HCHO	4	4	5
Reactions of CO	1	1	2
Reactions of minor products	0	5	9
Additional reactions of HO_2 with organic species	2	12	14
Inorganic reactions of HO_2	4	10	11
Aerosol uptake of HO_2	0	1	1
Production of O_3 from NO_2	1	2	2
Total number of reactions	**16**	**40**	**47**

The three chemical mechanisms are compared in Table 3 by counting the number of reactions used in the mechanism to represent the different categories of chemical processes related to ozone production from methane oxidation. Clearly, CBM-IV (16 reactions related to methane oxidation) as used in LOTOS-EUROS is substantially simpler than either the EmChem19a (40 reactions related to methane oxidation) or MOZART (47 reactions related to methane oxidation) mechanisms. The number of methane-related reactions in each mechanism in each case is approximately 20% of the total number of reactions (thermal, photolytic and heterogeneous) in each model (LOTOS-EUROS: 89, EMEP: 187, CAM-chem: 206).

The relatively low number of reactions in the CBM-IV mechanism related to ozone formation from methane oxidation is primarily achieved through a simplified representation of the chemistry of intermediate organic products of methane oxidation, and the omission of a number of reactions which are only important under low-NOx conditions. It is worth noting here that these simplifications in CBM-IV also apply to ozone production from other VOC, to the extent that they also produce CH_3O_2 and HO_2 during their oxidation.

The relatively small size of the CBM-IV mechanism can be explained by its explicit focus on regional scales and relatively polluted conditions. This implies that the LOTOS-EUROS model with CBM-IV should also only be employed on regional scales with a focus on polluted regions.

The larger size of the MOZART mechanism results from the need to simulate atmospheric chemistry on a global scale, which includes pristine regions with relatively low levels of NOx. The EMEP model is capable of being run at global scales, which can justify the comparable number of methane-related reactions to the MOZART mechanism.

3.1.1 Thermal chemical reactions

Table 4: Comparison of some key processes for ozone formation from methane in the CBM-IV, EmChem19a, and MOZART mechanisms

Chemical process	Representation in CBM-IV	Rate constant in CBM-IV	Representation in EmChem19a	Rate constant in EmChem 19a	Representation in MOZART	Rate constant in MOZART
Initial oxidation of methane by OH	CH_4 + OH -> XO2 + HCHO + HO_2	6.21E-15	CH_4 + OH -> CH_3O_2	6.39E-15	CH_4 + OH -> CH_3O_2 + H_2O	6.36E-15
Conversion of NO to NO_2 by methylperoxy radical	XO2 + NO -> NO_2	8.10E-12	CH_3O_2 + NO -> HCHO + HO_2 + NO_2	7.69E-12	CH_3O_2 + NO -> HCHO + HO_2 + NO_2	7.66E-12
Conversion of NO to NO_2 by HO_2	HO_2 + NO -> OH + NO_2	8.28E-12	HO_2 + NO -> OH + NO_2	8.53E-12	HO_2 + NO -> OH + NO_2	8.10E-12
Radical termination: methylperoxy + HO_2	XO2 + HO_2 -> (no products)	5.95E-12	CH_3O_2 + HO_2 -> 0.9 CH_3OOH + 0.1 HCHO	5.20E-12	CH_3O_2 + HO_2 -> CH_3OOH + O_2	5.07E-12

Rate constants are standardized at 298 K and 1 atm. Species names have been harmonised between mechanisms for clarity.

A selection of the most important chemical reactions involved in the formation of ozone from oxidation of methane is shown in Table 4. Comparison of the representation of these processes in the three mechanisms, as well as their rate constants (standardized to 298 K and 1 atm) helps to illustrate some of the similarities and differences between the mechanisms.

- The rate constants for these key processes all agree within an order of magnitude, despite 30 years of progress in laboratory measurements of chemical kinetics between the development of CBM-IV and EmChem19a.
    - In particular, the rate constants for the initial oxidation step of methane by OH only differ by 3%.
    - The largest differences in rate constants are seen in peroxy radical termination (16% between CBM-IV and MOZART), reflecting ongoing uncertainty in the chemistry of organic peroxy radicals.

    - Product yields are a major part of the uncertainty in peroxy radical chemistry. This mostly applies to large organic peroxy radicals from oxidation of NMVOC, but is also of some relevance for methane chemistry, as seen here by the inclusion of formaldehyde as a minor product of CH_3O_2 + HO_2 in the EmChem19a mechanism.

- CBM-IV makes a number of simplifications to the chemistry, consistent with its intended purpose of simulating the polluted planetary boundary layer.
  - The production of HCHO and HO_2 from methane is included in the initial oxidation step.
  - CH_3O_2 is not represented explicitly, but rather as "XO2", which is a generic species representing all organic peroxy radicals formed in the oxidation of VOC.
    - The EmChem19a and MOZART mechanisms represent peroxy radicals from different VOC explicitly, allowing more detailed representation of their subsequent chemistry.
  - Minor products of peroxy radical termination reactions are ignored.
    - This results in non-conservation of mass under low-NOx conditions when these reactions are relatively fast.

The simplifications made by CBM-IV allow for a more computationally efficient simulation of ozone production under high NOx conditions, but are not suitable for the simulation of relatively clean background conditions, under which the production of ozone from methane oxidation over large spatial scales is still relevant.

3.1.2 Photolysis

Table 4 only includes thermal chemical reactions. Many of the processes important for the production of ozone from methane oxidation also involve photolysis, especially of formaldehyde and NO_2. As seen from Table 3, the treatment of formaldehyde in each mechanism is represented by a similar number of reactions. Direct comparison of the photolysis rate constants between the models is more difficult however, because these are calculated online from different input parameters in each model, and are not typically included in model output. Here we compare the photolysis schemes used in each CTM in terms of their complexity.

One of the most explicit models available for calculating photolysis rates is the TUV (Tropospheric Ultra-Violet Visible) model (Madronich 1987). This model explicitly calculates the vertical transfer of radiation on an arbitrary number of vertical levels including absorption and scattering based on the gaseous and particulate composition of each layer. The radiation spectrum is resolved in TUV using 140 wavelength bins between 121 nm and 750 nm, allowing direct calculation of any photolysis rate based on laboratory-measured data of absorption cross-sections and quantum yields, including their dependencies on temperature and pressure. The TUV model is available as an option in WRF-Chem, where it can be coupled with the simulated atmospheric composition, including clouds and aerosol. The composition of the atmosphere above the top level of the model must be specified using an input file in order to account for absorption of short-wave radiation. To reduce computational expense, an option is also available in WRF-Chem to lower the spectral resolution to 17 wavelength bins (F-TUV, or Fast TUV), which are chosen to resolve the attenuation of short-wave radiation in the troposphere due to absorption by ozone. This is the photolysis option used in WRF-Chem simulations performed at IASS Potsdam with the MOZART mechanism.

CAM-chem uses a hybrid approach for calculation of photolysis rates (Lamarque et al. 2012). Photolysis rates for molecules with strong absorption of radiation below 200 nm are calculated using an approach similar to the TUV model with a spectral resolution of 67 wavelength bins.

Photolysis rates for molecules absorbing radiation below 200 nm are calculated with a simplified approach using only 3 representative rates, to which all other photolysis rates are scaled. Photolysis rates in CAM-chem are coupled with modelled clouds, but not with modelled aerosol.

LOTOS-EUROS calculates photolysis rates at ground-level using a parameterized approach based only on the solar zenith angle and cloud fraction, together with 3 pre-computed constant parameters for each photolysis reaction (Manders-Groot et al. 2016). These ground-level photolysis rates are applied through the entire vertical domain of the model, and are not coupled to modelled aerosol. This design is consistent with the use of LOTOS-EUROS for simulation of ground-level pollution, as well as the general focus of LOTOS-EUROS on computational efficiency at the expense of detailed process representation.

The EMEP CTM also makes a trade-off between computational efficiency and detailed representation of processes in its calculation of photolysis rates. It does not resolve the spectral actinic flux for calculation of photolysis rates online, but instead reads in a set of pre-computed photolysis rates dependent on latitude, altitude, and solar zenith angle based on standard atmospheric conditions (Simpson et al. 2012). These rates are modified online in the EMEP CTM depending on the degree of cloudiness, but are not coupled to the simulated aerosol.

3.2 Biogenic emissions

WRF-Chem and LOTOS-EUROS both include the MEGAN model for foliar emissions of BVOCs (Guenther et al. 2012). The MEGAN model calculates emissions for over 100 different BVOC, of which methane is one. These emissions are however negligible compared with both total foliar BVOC emissions, and also compared with other sources of methane. WRF-Chem when run with MOZART chemistry simply ignores the methane emissions provided by MEGAN. LOTOS-EUROS includes these emissions in the modelled methane. The EMEP CTM uses a different algorithm for calculation of BVOC emissions, which only calculates emissions for isoprene and monoterpenes, with no emissions of methane (Simpson et al. 2012).

None of the CTMs analysed in this study include any other natural sources of methane such as wetlands.

3.3 Soil uptake

The sink of methane due to uptake by bacteria in soils is represented in CAM-chem and LOTOS-EUROS through their respective dry deposition schemes. In both cases, the deposition rates are dependent on land use type and soil moisture. The EMEP CTM, and WRF-Chem as run with the MOZART mechanism do not include this sink for methane.

4 Attribution of ozone to methane

4.1 Contribution of global methane oxidation to surface ozone

Based on a run of the CAM-chem global model for 2015, using the VOC tagging approach described in Butler et al. (2018), we calculate the methane contribution to annual average surface ozone for the globe and for Germany (Table 5). Note that at a resolution of approximately 2 degrees, Germany is covered by only 9 grid cells from this simulation.

Table 5: Contribution of global methane oxidation to surface ozone globally and in Germany calculated with CAM-chem

Annual average surface ozone	Global surface ozone	German surface ozone
Total ozone from all sources	58 µg/m³	68 µg/m³
Ozone due to methane oxidation	20 µg/m³	20 µg/m³

4.2 Sensitivity of surface ozone of methane oxidation in Europe

4.2.1 LOTOS-EUROS

We have access to two model runs of LOTOS-EUROS for 2015 provided by colleagues from TNO. One run (the “base run”) has been performed using the full set of methane emissions and lateral boundary conditions described in WP1, and the methane oxidation chemistry described in WP2. The other run (the “no methane oxidation” run) is identical in all other respects, except that the chemical reaction of methane with the OH radical has been disabled, thus also disabling the production of ozone from methane oxidation within the model domain. By taking the difference in surface ozone between these two runs, we estimate the sensitivity of surface ozone concentration in Europe to the oxidation of methane within the European domain.

Table 6: Change in surface ozone in Germany when methane oxidation is switched off in LOTOS-EUROS

Model run	Annual average surface ozone in Germany
LOTOS-EUROS “base” run	57.4 µg/m³
LOTOS-EUROS “no methane oxidation” run	54.2 µg/m³
Difference in annual average surface ozone	**3.2 µg/m³**

Assuming a linear relationship between the sensitivity of ozone in LOTOS-EUROS to methane oxidation, and the contribution of methane oxidation to ozone, we approximate the contribution of methane oxidation in the LOTOS-EUROS European model domain to annual average surface ozone in Germany as 3.2 µg/m³. This is approximately a factor of 6 smaller than the contribution of global methane oxidation to German surface ozone, given as 20 µg/m³ in Table 5. From this we draw the conclusion that approximately 80% of the ozone which can be attributed to methane in Europe is due to long-range transport from outside of Europe. A meaningful attribution of surface ozone in Germany to methane oxidation must therefore include information from larger spatial scales than are currently represented in European regional CTMs.

4.2.2 The EMEP CTM

We only have access to the standard output available with the open source version of the EMEP CTM. There is no ozone tagging system implemented in the EMEP CTM comparable to the tagging system in CAM-chem or WRF-Chem. We do not have access to any additional runs of the EMEP CTM performed with modified background methane concentration or with methane oxidation switched off. Since we identified (above) that information on ozone due to methane oxidation on the hemispheric scale must be included in regional CTMs for a meaningful attribution of surface ozone in Germany to methane oxidation, we do not attempt to derive the contribution of methane to surface ozone using available fields from the EMEP CTM.

Future work on attribution of ozone to methane oxidation using the EMEP CTM could be performed in a manner similar to that described here for LOTOS-EUROS without substantial modification to the EMEP CTM.

4.2.3 WRF-Chem

The ozone tagging used in CAM-chem has been implemented in WRF-Chem and applied by Lupascu and Butler (2019) for attribution of European surface ozone between April-September 2010 to NOx precursors emitted inside and outside of Europe. In principle, this implementation would also allow a complete global-to-regional attribution of annual average European surface ozone to all NOx and VOC precursors, including differentiation between methane oxidised inside and outside of the WRF-Chem model domain. This is planned for future work.

5 Conclusions and recommendations

Based on the model runs examined here, approximately one third of annual average surface ozone in Germany can be attributed to oxidation of methane. Approximately 80% of this amount is formed outside of Europe. The total contribution of methane to annual average surface ozone in Germany is estimated at 20 $\mu g/m^3$, while only 3.2 $\mu g/m^3$ of this is due to oxidation of methane in Europe. Each of these estimates is based on a single run of a global and a regional model respectively. This result is however consistent with prior knowledge of methane as a globally well-mixed gas, and the importance of hemispheric-scale transport of ozone due to its relatively long lifetime in the troposphere.

Global methane emissions remain poorly constrained, with poor agreement between bottom-up and top-down approaches. Better agreement between bottom-up and top-down approaches is seen for anthropogenic emissions, indicating a relatively high degree of confidence in the anthropogenic contribution to global methane, and thus potentially also to the ozone attributable to anthropogenic methane emissions.

Most CTMs avoid the problem of poorly-constrained methane emissions by specifying concentrations of methane at their boundaries (lateral or surface) rather than specifying methane emissions when used for simulating air quality. This is especially important for regional models over Europe, since most of the ambient methane over Europe is due to sources outside of Europe.

Verification of regional methane emission inventories for Europe is possible with inverse models using existing in-situ measurements, and will benefit further from the next generation of satellite-borne remote sensing instruments. Top-down regional methane emissions for Europe are not currently used for simulation of air quality.

Any assessment of the contribution of methane to ozone in Europe must include information on ozone production due to methane over at least the entire northern hemisphere, or ideally the entire globe. This could be achieved by using a global model, a hemispheric model, or a regional model taking boundary conditions from a global or hemispheric model. Some global models are also capable of using regionally refined grids, in which a part of the globe is simulated with a higher resolution than the rest of the globe.

Since methane is a well-mixed gas, and thus ubiquitous in all parts of the atmosphere, any model used to calculate ozone formation due to methane oxidation should be capable of representing all relevant chemical regimes present in the troposphere, from the highly-polluted PBL, to remote regions, also including the upper troposphere. Chemical mechanisms in such models should include processes relevant for both high- and low-NOx chemical regimes, and photolysis schemes should account for the vertical variability of photolysis rates.

It is less clear whether such a detailed representation of processes is necessary for simulation of the ozone due to methane in regional models when they are forced with boundary conditions from a sufficiently detailed global or hemispheric model. Model intercomparison exercises using models and chemical mechanisms of varying complexity would be useful here.

Information about the contribution of methane to ozone can be obtained through either sensitivity studies or using tagging approaches. Sensitivity studies are more common in the global modelling literature, where the response of ozone to perturbations of the methane concentration has been shown to be approximately linear.

HTAP have already performed a set of global sensitivity studies with global average methane concentrations reduced by 20%. Future sensitivity studies using regional models could take information from the HTAP simulations as boundary conditions. For any such regional sensitivity studies using information from the global scale through the lateral boundary conditions, it would not be necessary to switch off methane oxidation (as done in the LOTOS-EUROS runs examined here).

Tagging approaches have been more commonly used in regional models for source attribution of PM. Tagging of ozone in global models is also possible, and has the potential to deliver complementary information to sensitivity studies. The approach of Butler et al. (2018) in particular shows promise in being able to attribute ozone separately to both NOx and VOC precursors (including methane). Several alternative approaches for ozone source attribution also exist, and it would be instructive to compare these approaches.

So far, most work has focused on understanding the contribution of methane to ozone over relatively long time periods, such as annual or monthly averages. Future work should quantify the contribution of methane (and other precursors) to ozone over exposure-relevant timescales, for example exceedances of guideline values for MDA8 for human health, or flux-based metrics for ecosystem damage.

Unfortunately, the current generation of global chemistry-climate models shows a wide spread in their simulations of ground-level ozone as well as their simulated methane lifetimes. The reasons for these inter-model differences remain unclear. The common practice in the global modelling community of specifying methane as a concentration boundary condition rather than directly specifying methane emissions has the consequence that methane concentration is generally well simulated, but that the global oxidation rate of methane may vary substantially between models, potentially also leading to substantial differences in the amount of ozone produced during methane oxidation. These differences remain unquantified. Examination of the differences in ozone between model runs driven with methane emissions and methane concentrations would be informative.

The implementation of detailed chemical budget diagnostics in global models also would help to quantify the large differences in surface ozone simulated by these models. Ozone tagging schemes such as Butler et al. (2018) could also help to understand these inter-model differences if implemented in a larger number of models. Global-to-regional downscaling using consistent source attribution methodologies would also be useful for understanding the ozone budget and its uncertainties on scales of relevance for human and ecosystem health.

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