MEMO^2: MEthane goes MObile – MEasurements and MOdelling

Forward modelling simulations of CH_4 and isotopologues

Barbara Szénási
Philippe Bousquet
Université de Versailles St-Quentin-en-Yvelines (UVSQ)

point courrier 129
F-91191 GIF-SUR-YVETTE CEDEX
France

Telephone: (+33) 1-6908-1982
Email: barbara.szenasi@lsce.ipsl.fr

Deliverable D3.3			
Delivery month Annex I	30		
Actual delivery month	30		
Lead participant: UVSQ	Work package: 3	Nature: Report	Dissemination level: PU
Version: 01			

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 722479.

Table of contents

Acronyms and Abbreviations

CHIMERE	name of a multi-scale area-limited Eulerian chemistry-transport model
COSMO	Consortium for Small-scale Modelling
ECMWF	European Centre for Medium-Range Weather Forecasts
ECPL	Environmental Chemical Process Laboratory
EDGAR	Emission Database for Global Atmospheric Research
Empa	Swiss Federal Laboratories for Materials Science and Technology
FLEXPART	FLEXible PARTicle dispersion model
FMI	Finnish Meteorological Institute
LMDz	Laboratoire de Météorologie Dynamique, zoom
MACC	Monitoring Atmospheric Composition and Climate
MicroHH	name of a computational fluid dynamics code made for Direct Numerical Simulation (DNS) and Large-Eddy Simulation (LES) of turbulent flows in the atmospheric boundary layer
NILU	Norwegian Institute for Air Research
OSU	Observatoire des Sciences de l'Univers
OVSQ	Observatoire de Versailles Saint-Quentin-en-Yvelines
PYVAR	PYthon based VARiational data assimilation framework
RMSE	Root Mean Square Error
TNO	Netherlands Organisation for Applied Scientific Research
UHEI	University of Heidelberg
UU	Utrecht University
UVSQ	Université de Versailles Saint-Quentin-en-Yvelines

1. Executive Summary

The aim of this task is to study how the various CH_4 sources, with different isotopic signatures, in different areas and environments in Europe, such as the regional or city scale, blend into larger-scale concentration fields. Forward simulations of atmospheric CH_4 mixing ratios and CH_4 isotopes have been carried out for 2015 at the European scale and at the city-scale. Simulated CH_4 total mixing ratios and isotopic ratios of $\delta^{13}C$ and δD have been compared to measurements at various locations in Europe.

The simulations were carried out at UVSQ and Empa using two meso-scale models. Regional-scale CH_4 simulations were made using yearly natural wetland emissions and yearly emissions from two anthropogenic inventories. The isotopic composition of CH_4 was computed from the forward simulated sectoral CH_4 mixing ratios combined with source signatures from the literature.

The comparison to measurements results in a good agreement between simulated and measured data, both for CH_4 mixing ratio and the isotopic composition.

These simulations are the basis for the estimation of errors in transport models and emission fluxes that are required to derive top-down estimates of emissions from atmospheric measurements of CH_4 for the deliverable D3.4 (Top-down estimates of EU-scale CH_4 emissions, due project month 42).

2. Introduction

2.1 Background

Simulations allow a broad investigation of the magnitude, the sectoral and spatial distribution of atmospheric CH_4 mixing ratios, and how the simulated mixing ratios depend on emissions. Isotopologues are useful to discriminate sector contributions of CH_4 emissions as the isotopic composition varies highly depending on the source type. For instance, the signature is different depending on whether CH_4 is produced by thermogenic (e.g. natural gas), biogenic (e.g. domestic animals) or pyrogenic (combustion) sources.

The comparison between measured and simulated CH_4 mixing ratios and isotopic composition can be used for evaluating flux measurement methods and other data gained from measurements, such as isotopic source signatures or emissions estimated from measurements.

In the MEMO^2 project, forward simulations of atmospheric CH_4 mixing ratio and isotopic composition have been made with the regional models CHIMERE (Menut et al., 2013, Mailler et al., 2017) and FLEXPART-COSMO (Henne et al., 2016). Given their horizontal resolutions of 1-50 km, these models are suitable to interpret measurements that are taken at some distance from main emission sources, i.e. after these emissions have been mixed in the atmosphere. Interpretation of local measurements within MEMO^2 relies on small scale dispersion modelling, like the Gaussian Plume model Polyphemus for simple cases and the fluid dynamic code MicroHH for more complex terrains. The small-scale models were introduced during several training events (1st MEMO^2 school, Workshop on Gaussian Plume Modeling) and are discussed in more detail in the deliverable D3.1 (New tools to estimate CH_4 source strengths from point sources, including mobile measurements) and the milestone report MS10 (Large Eddy simulation tools ready for campaign and workshop).

2.2 Scope of the deliverable

As mentioned above, numerical models have been used for performing forward simulations of CH_4 and isotopic compositions of $\delta^{13}C$ ($^{13}C/^{12}C$ ratio) and δD (D/H ratio) at the European scale. The simulations have been carried out with the aim to characterize the various CH_4 sources in different areas and environments in Europe, as well as at different spatial scales, i.e. from city to regional scales. Another objective is to compare the simulated mixing ratios to measured mixing ratios to assess the representation errors in the modelling approach (due to the resolution of the models' grids as compared to point measurements).

3. Content

As part of the MEMO^2 project, UVSQ and Empa performed forward simulations of atmospheric CH_4 mixing ratio with regional scale models over Europe.

3.1 Data and model description

Measurements

We use hourly data obtained from measurement sites that have hourly CH_4 measurements available for at least six months in our analysis period of 2015. This resulted in 31 measurement sites in Europe that are described in Table 4 and shown in Figure 1. We chose 2015 for the analysis as this was the most recent year at the time of the work with the most available measurements. Regarding measurements of isotopologues, we obtained semi-hourly measurements of nearly 5 months, started in November 2016, made in Lutjewad (NL) and Heidelberg (DE) by the partner universities Utrecht University (UU) and Heidelberg University (UHEI). These measurements are of good quality and very valuable as isotopic measurements of this length and frequency in time are scarce in Europe.

Regional scale models

CHIMERE is a Eulerian chemistry-transport model designed for regional atmospheric composition. At UVSQ, it is driven by the PYVAR-CHIMERE modelling and data assimilation framework (Chevallier et al. 2005, Pison et al., 2007). FLEXPART-COSMO is a Lagrangian particle dispersion model. Both models are driven by meteorological fields from high-resolution numerical weather prediction. We carried out forward simulations on a horizontal resolution of 0.5°x0.5° (~50 x 50 km^2), 0.1° x 0.1° (~10 x 10 km^2) (CHIMERE) and 7x7 km^2 (FLEXPART-COSMO).

These two models need inputs in the form of meteorological data, boundary and initial conditions, as well as emissions from anthropogenic and/or natural sources. The model specifications, including their set-ups and input data, are listed in Table 1.

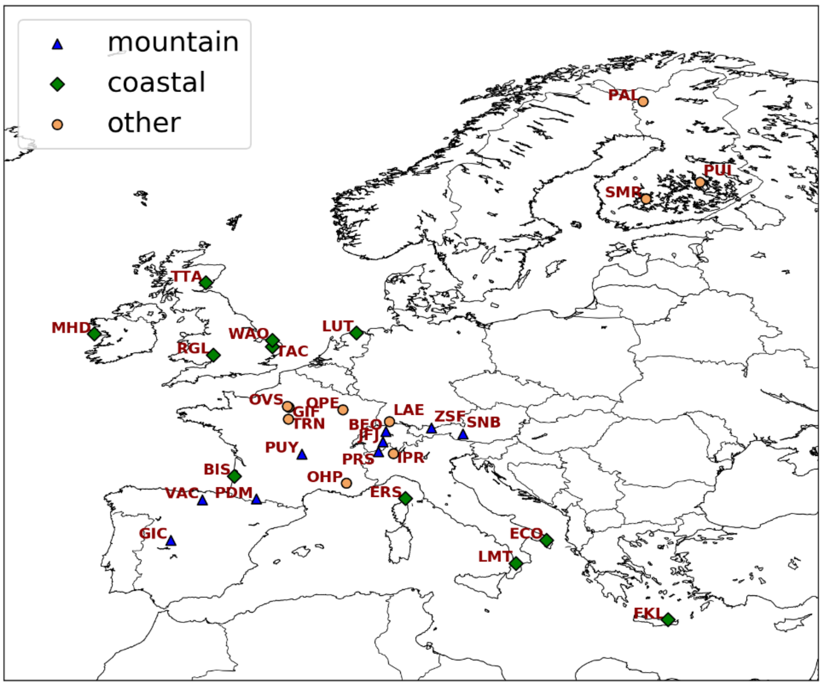

Figure 1: Measurement sites used for analysis in 2015.

Meteorological data

The meteorological data used to drive the CHIMERE model are obtained from the ECMWF (European Centre for Medium-Range Weather Forecasts) model which provides short-range meteorological forecasts (0-12 hours). The meteorological data used for FLEXPART-COSMO are obtained from the COSMO (Consortium for Small-scale Modelling) model (Baldauf et al., 2011).

Boundary mixing ratios and initial mixing ratios

In case of CHIMERE, the boundary mixing ratios, i.e. the background values that enter the model domain at the boundaries, and initial mixing ratios of CH_4 are taken from the analysis and forecasting system developed in the MACC (Monitoring Atmospheric Composition and Climate) projects (Marécal et al. 2015). In case of FLEXPART-COSMO, they are taken from the measurement time series of the measurement stations of interest.

Regarding the background values of the isotopes, simulations of $\delta^{13}C$ and δD made by the LMDz (Laboratoire de Météorologie Dynamique, zoom mode) model (Hourdin et al., 2006) were used. The average value over the year 2015 of the LMDz simulations for $\delta^{13}C$ is -47.5‰, for δD -85.7‰.

Emissions

The prior anthropogenic emissions are taken from the TNO-MACC_III (Kuenen et al., 2014), the EDGARv4.3.2 (Janssens-Maenhout et al., 2017) and the TNO GHGco (Denier van der Gon et al., 2019) emission inventories as shown in Table 2. These inventories were chosen because they are available over Europe at a resolution finer than 0.5°x0.5°, the lowest model resolution we used for carrying out the simulations.

The simulation of atmospheric CH_4 mixing ratio and isotopologues has been carried out for total CH_4 but also for each of the main emission sectors of CH_4 for 2015 using yearly emissions from 2011. This year was the latest available year of the TNO-MACC_III emission inventory at the time of the study. Therefore, we used this year for extracting the emissions from both the TNO-MACC_III and EDGARv4.3.2 emissions inventories.

In Europe, for anthropogenic emissions, agriculture is the main emitting sector, followed by the waste sector. Other relevant emission sources for CH_4 are non-industrial combustion plants and the production, extraction and distribution of fossil fuels. The latter two sectors were grouped into one category and named extraction and distribution of fossil fuels and non-industrial combustion hereafter.

Table 1: *Configurations of the CHIMERE and FLEXPART-COSMO models for carrying out the forward simulations of CH_4 mixing ratio (see text and list of acronyms for abbreviations)*

	CHIMERE	FLEXPART-COSMO
Type	Eulerian	Lagrangian
Species	Total + sectoral CH_4	Total + sectoral CH_4
Period simulated	2015	2015
Type of emissions	Anthropogenic + Natural wetland	Anthropogenic
Horizontal resolution	0.5° x 0.5°, 0.1° x 0.1°	7 km x 7 km
Anthropogenic emissions	TNO-MACC_III & EDGARv4.3.2.	TNO-MACC_III & TNO GHGco
Wetland emissions	ORCHIDEE	None
Meteorology	ECMWF	COSMO
Boundary and initial concentrations	MACC	Background from the measurement time series of the desired station

Table 2*: Description of the anthropogenic emission inventories used in this study (see text and list of acronyms for abbreviations)*

Inventory/Model	EDGAR version 4.3.2	TNO-MACC_III	TNO GHGco
Emission	Anthropogenic	Anthropogenic	Anthropogenic
Coverage	Global	Europe	Europe
Spatial resolution	0.1° x 0.1°	0.125° x 0.0625°	0.1° x 0.05°
Temporal resolution	Monthly and yearly	Yearly	Yearly
Available years	1970-2012	2000-2011	2015
Years used	2011	2011	2015

3.2 Methodology

Isotopic signatures

As none of the regional models is set up to simulate isotopic composition, UVSQ and Empa computed the ^{13}C and ^{12}C, as well as the atmospheric isotopic ratios of $\delta^{13}C$ and δD, from the forward simulations of CH_4. Sectoral simulated CH_4 mixing ratios and signatures of $\delta^{13}C$ and δD obtained from various literature sources (Table 3) were used to determine the "simulated" $\delta^{13}C$ and δD ratios through the following steps (shown for $\delta^{13}C$):

1) Obtain sectoral ^{13}C and ^{12}C: $\frac{13C}{12C} = \left(\frac{\delta^{13}C}{1000‰} + 1\right) * PDB_{std}$
2) Sum the sectoral ^{13}C and ^{12}C to get the totals
3) Compute modelled $\delta^{13}C$: $\delta^{13}C = \left(\frac{13C/12C}{PDB_{std}} - 1\right) * 1000\ ‰$

   with PDB_{std}=0.0112372 being the Pee Dee Belemnite reference standard.

Table 3: *Initial $\delta^{13}C$ and δD values from literature used for the different emission sectors. As not all studies provide error ranges, we only used the averages: the error ranges are therefore not reported here.*

Emission sector	Isotope ratio $\delta^{13}C$ (‰)	Isotope ratio δD (‰)	Literature source
Agriculture	-68	-319	Levin et al., 1993, Bréas et al., 2001, Bilek et al., 2001, Klevenhusen et al., 2010, Uzaki et al., 1991, Tyler and Bilek, 1997, Röckmann et al., 2016
Waste	-55	-293	Bergamaschi et al., 1998, Levin et al., 1993, Zazzeri et al., 2015, Games and Hayes, 1976, Röckmann et al., 2016
Extraction and distribution of fossil fuels & non-industrial combustion	-47	-175	Levin et al., 1999, Lowry et al., 2001, Thielemann et al., 2004, Zazzeri et al., 2016, Röckmann et al., 2016
Other anthropogenic sources	-35	-175	Levin et al., 1999, Chanton et al., 2000, Nakagawa et al., 2005, Röckmann et al., 2016
Natural wetlands	-69	-330	Tyler et al., 1987, Smith et al., 2000, Galand et al., 2010, Happell et al., 1995, Martens et al., 1992, Bilek et al., 2001, Sugimoto and Fujita, 2006
Background	Simulations of isotope ratios by the LMDz model (~-47.5)	Simulations of isotope ratios by the LMDz model (~-85.7)	Thanwerdas et al., (in prep)

3.3 Results and conclusion

The total CH_4 mixing ratios simulated by CHIMERE are illustrated in Figure 2 a) showing their average over 2015. As expected, the mixing ratios are highest above emission hot-spot areas, such as over the Po Valley in Italy (red and purple colours with values > 2050 ppb) or the area over Belgium, the Netherlands and North-western Germany (mainly red and some purple colours with values > 2000 ppb), which are areas of intensive agriculture. Furthermore, the Silesian Coal Basin in Poland, at the border to the Czech Republic and Slovakia (purple colours with values >2100 ppb) and some areas of Romania, including Bucharest, show elevated mixing ratios (red and purple colours with values > 2020 ppb); activities connected to fossil fuels (e.g. coal mining, oil refineries) are the reason for that.

Figure 2 b) shows CH_4 mixing ratios made by FLEXPART-COSMO at the location of one specific measurement site, Lutjewad, for one specific day, 01.11.2016. Most of the area in Figure 2 b) is empty as the CH_4 in the FLEXPART-COSMO model, taken from the emission inventory, was released from the Lutjewad measurement site and the modelled weather conditions on that day carried the released CH_4 to the coloured areas, mainly the Netherlands, Belgium and the UK.

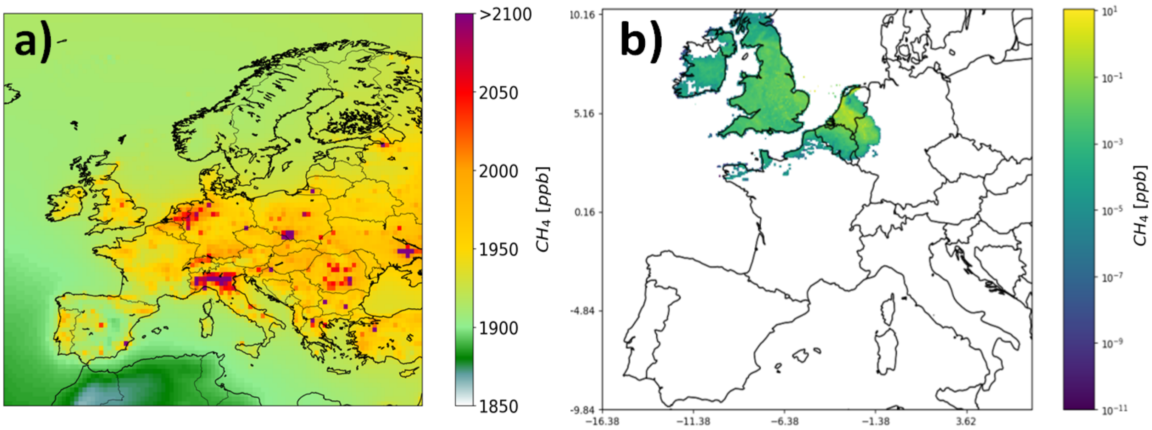

Figure 2: Simulated total CH4 at the surface level made by CHIMERE (**a)**) over Europe and by FLEXPART-COSMO (**b)**) at the location of Lutjewad for one specific day (01.11.2016). For both simulations, the TNO-MACC_III emission inventory was used.

The simulated isotopic composition has been compared to the measurements provided by the MEMO^2 partners, at Lutjewad (Figure 3) and Heidelberg. The models are able to represent the average and to capture the temporal variability of the measured ratios. The performances of the models have been evaluated with the aid of the Pearson correlation (Pearson, 1895) and the RMSE (root mean square error) (Armstrong and Collopy, 1992) in Figure 4. Generally, the simulated isotopic compositions by both models are well correlated, i.e. $R^2 \geq 0.55$, to the measurements. The correlation between the FLEXPART-COSMO simulations and the measurements is about 14% higher than the correlation between the CHIMERE simulations and the measurements, meaning that the FLEXPART-COSMO simulations represent the measurements' variability better. The RMSEs are similar for both models showing that both models' simulated values are, in absolute terms, similarly close to the measured values.

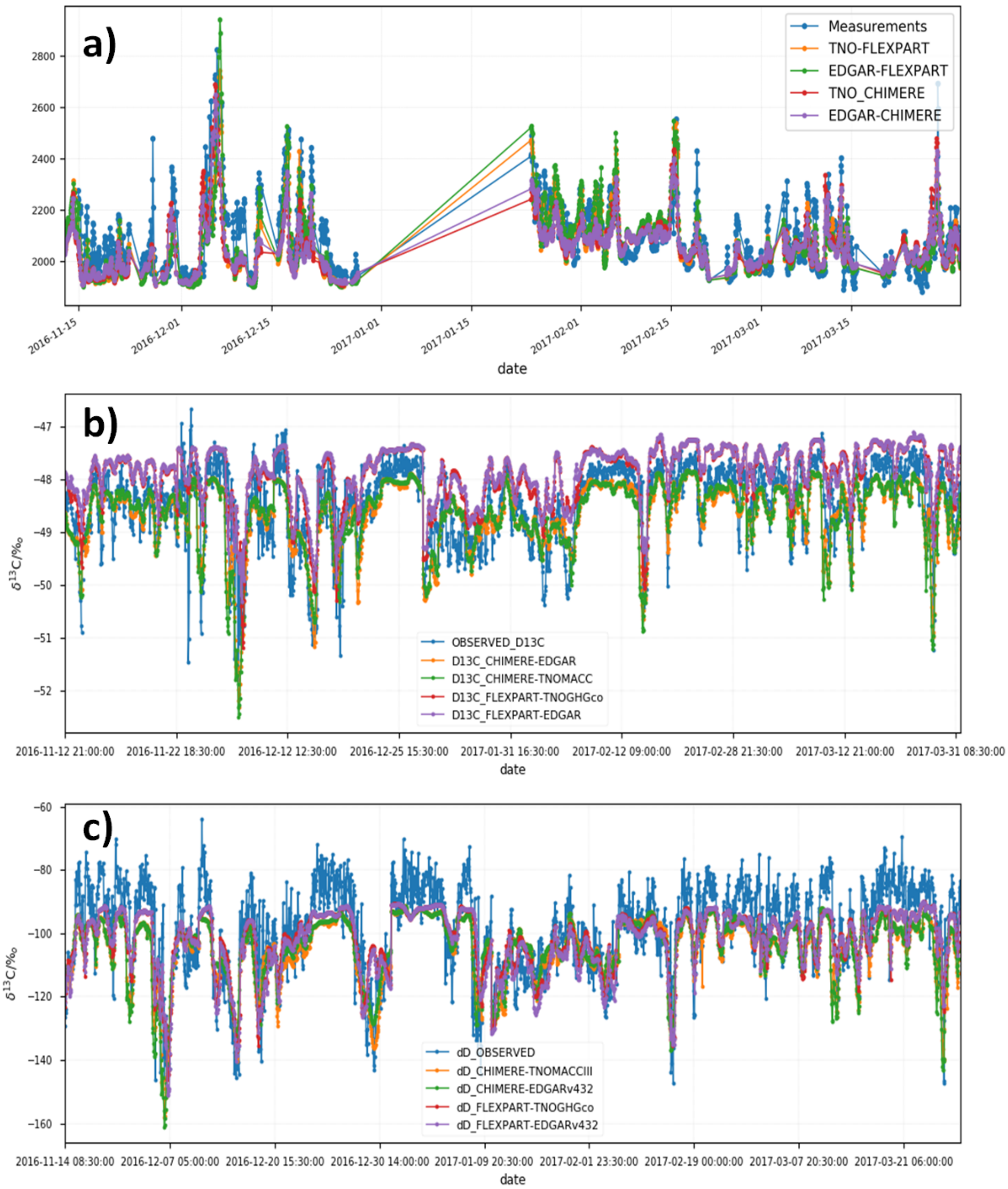

Figure 3: *Comparison of the simulated CH_4 (a)), $\delta^{13}C$ (b)) and δD (c)) to the measured ones (blue lines) at the measurement site Lujtewad (Netherlands) in the period of 12.11.2016-31.03.2017*

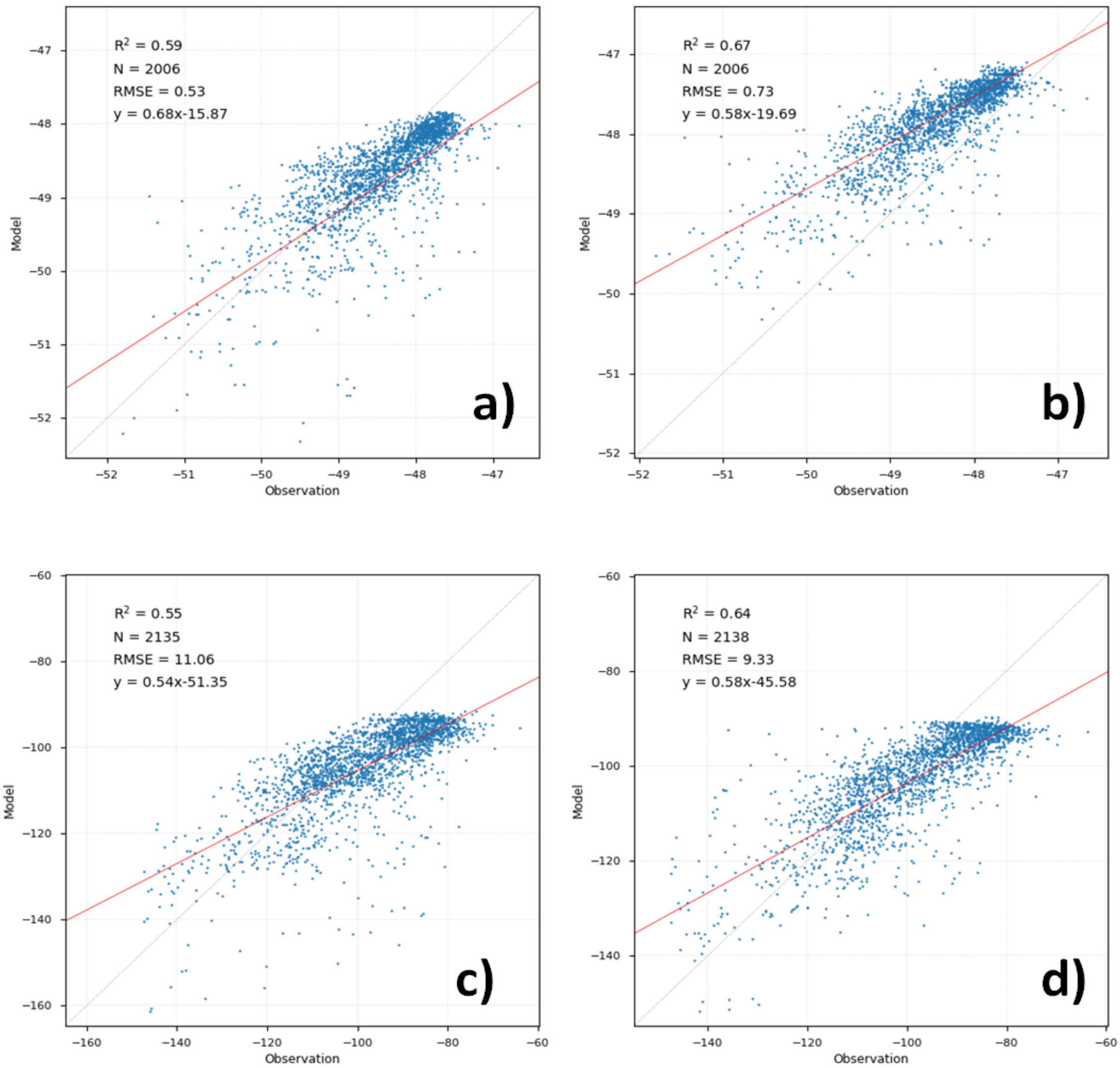

Figure 4: *Correlation between simulated and observed δ13C (a + b) and δD (c + d) at the measurement site Lujtewad. Simulated values were made by FLEXPART-COSMO (b + d) and CHIMERE (a + c) using the TNO-MACC_III inventory.*

The simulations enable us to explore the sectoral contributions: Figure 5 shows the results of the sectoral discrimination at Lutjewad. For this figure, we took the simulated CH_4 from the anthropogenic and wetland emission sources, as well as the total CH_4 without the background into account. The background here is neglected as we are interested in the sectoral contributions above the background. We compared the contribution of each emission sector to the total contribution in relative terms, which showed that 40-60% of the simulated mixing ratio above the background is due to the agriculture sector.

The simulated mixing ratios of total CH_4 have been compared to the measurement sites listed in Table 4. Figure 6 shows the correlation of simulated CH_4 mixing ratios to measured ones in the form of a so-called hexbin plot. The colours indicate how often one data point, a comparison of one measured and one simulated value, occurs. The values with light blue colour are outliers. Most of the data (orange and red) are close to the “perfect” line (black line) that indicates where a data point should be if the simulation matched the measurement perfectly. The correlation between measurements and simulations is r=0.73, a good agreement, for both the TNO-MACC_III and EDGARv4.3.2 inventories, which means that these inventories lead to similar (i.e. not significantly different) simulated mixing ratios on the annual scale. This indicates that the inventories were built in a similar way.

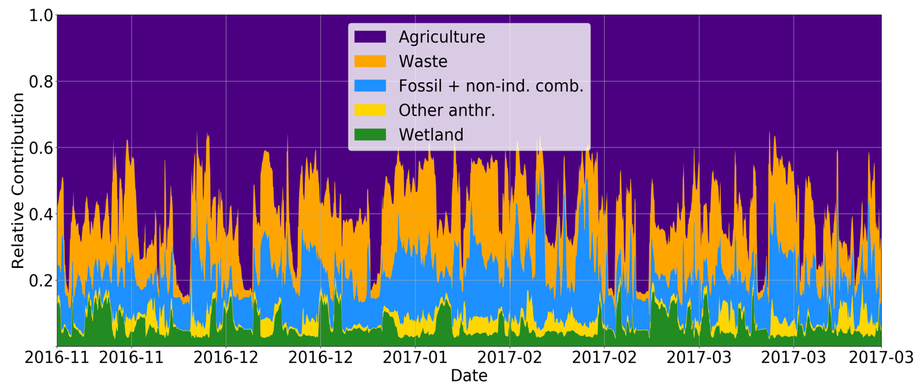

Figure 5: *Sectoral discrimination of CH_4 mixing ratios above background at Lutjewad. The emissions from TNO-MACC_III were used to simulate the sectoral contributions of CH_4 by CHIMERE that are shown in this figure. Only the results for TNO-MACC are shown as the other inventories contain very similar amounts of emissions at this location. Moreover, the sectoral contributions are similar with FLEXPART-COSMO.*

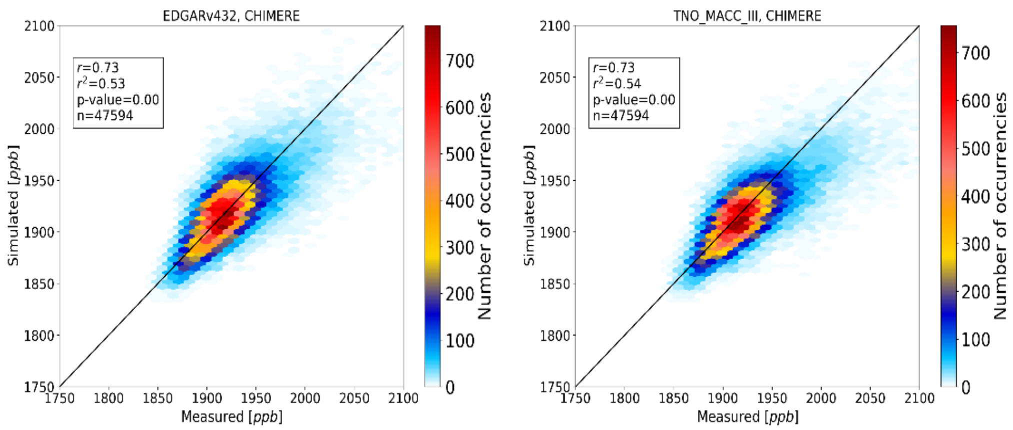

Figure 6*: Correlation between simulated and measured CH_4 mixing ratios for 2015. The hourly simulations were carried out with CHIMERE using the EDGARv4.3.2 (left) and TNO-MACC_III (right) emission inventories. For the comparison, hourly measurements were used.*

Table 4: *List of measurement sites measuring CH_4 and available for the simulation year 2015*

Trigram	Name of site	Contributor	Country	Coordinates (latitude, longitude)	Altitude above sea level [m]
BEO	Beromuenster	UBERN	Switzerland	47.19, 8.18	1009
BIS	Biscarrosse	LSCE	France	44.38, -1.23	120
CBW	Cabauw	InGOS	the Netherlands	51.9703, 4.9264	0
CGR	Capo Granitola	WDCGG	Italy	37.6667, 12.65	5
DEC	Deltadel'Ebre	WDCGG/IC3	Spain	40.74, 0.79	15
ECO	Lecce Environmental-Climate Observatory	WDCGG	Italy	40.3358, 18.1245	36
ERS	Ersa	LSCE	France	42.9692, 9.3801	533
FKL	Finokalia	ECPL[a]	Greece	35.3378, 25.6694	150
GIC	Gredos	WDCGG/IC3	Spain	40.35, -5.18	1456*
GLH	Giordan Lighthouse	WDCGG	Malta	36.07, 14.22	160
HEI[M]	Heidelberg	UHEI	Germany	49.25, 8.41	146
IPR	Ispra	InGOS/JRC	Italy	45.8147, 8.636	210
LAE	LaegernHochwacht	UBERN	Switzerland	47.82, 8.4	872
LMT	Lamezia Terme	WDCGG	Italy	38.8763, 16.2322	6
LUT[M]	Lutjewad	InGOS	The Netherlands	53.4036, 6.3528	1
OHP	Observatoire de Haute Provence	OSU[b]	France	43.931, 5.712	650
OPE	Observatoire pérenne de l'environnement	LSCE	France	48.5619, 5.5036	390
OVS	OVSQ	LSCE	France	48.7779, 2.0486	150
PDM	Pic du Midi	LSCE	France	42.9372, 0.1411	2877*

PUI	Puijo	FMI[c]	Finland	62.9096, 27.6549	232
PUY	Puy de Dôme	InGOS/LSCE	France	45.7719, 2.9658	1465*
RGL	Ridge Hill	University of Bristol	UK	51.9974, -2.5398	199
SAC	Saclay	CEA[d]	France	48.7227, 2.142	160
SMR	Hyytiälä	University of Helsinki[e]	Finland	61.8474, 24.2947	181
SNB	Sonnblick	WDCGG/UBA	Austria	47.05, 12.95	3106*
TAC	Tacolneston	University of Bristol	UK	52.5177, 1.1388	56
TRN	Trainou	InGOS/LSCE	France	47.9647, 2.1125	131
TTA	Angus	University of Bristol	UK	56.555, -2.9864	313
VAC	Valderejo	WDCGG/IC3	Spain	42.88, -3.21	1122*
WAO	Weybourne	NILU[f]	Norway	52.95, 1.121	31

* mountain sites
[M]: Isotopic data obtained through MEMO²
[a] ECPL: Environmental Chemical Process Laboratory
[b] OSU: Observatoire des Sciences de l'Univers
[c] OVSQ: Observatoire de Versailles Saint-Quentin-en-Yvelines
[d] FMI: Finnish Meteorological Institute
[e] NILU: Norwegian Institute for Air Research

4. Possible impact

UVSQ and Empa successfully established the modelling framework necessary for performing forward simulations of CH_4 and isotopologues, which is a crucial step in the modelling work within MEMO². The simulations of CH_4 have been thoroughly analysed but with only two available long-term measurement time series of isotopologues, our knowledge about them is still limited. The modelling and analysis of isotope ratios will be continued in more detail as the number of available measurements is expected to increase, due to the measurement work within MEMO² (especially on the isotopic signatures of the different sources). This will make it feasible to investigate possible improvements from using isotopes to separate sector contribution.

The forward simulations and the knowledge gained through them are currently used for estimating the errors in emission fluxes and transport models required for deriving top-down estimates of CH_4 emissions, as well as build the basis of the inverse modelling work necessary for the deliverable D3.4. Even though we found that the emission inventories used here lead to similar forward simulated mixing ratios, their impact on the top-down derived emission estimates will be analysed.

5. Dissemination & Exploitation

This report will be available via the MEMO^2 website and the associated simulations will be available on the ICOS repository. Furthermore, the results from forward simulations are being used for on-going publications that will be open to the public.

6. References

Armstrong and Collopy, 1992: J. Scott Armstrong and Fred Collopy: Error Measures For Generalizing About Forecasting Methods: Empirical Comparisons, International Journal of Forecasting, 8, 69-80, 1992

Baldauf et al., 2011: Baldauf, M., Seifert, A., Förstner, J., Majewski, D., Raschendor-fer, M., and Reinhardt, T.: Operational Convective-Scale Nu-merical Weather Prediction with the COSMO Model: de-scrip-tion and Sensitivities, Mon. Weather Rev., 139, 3887–3905, doi:10.1175/MWR-D-10-05013.1, 2011

Bergamaschi et al., 1998: P. Bergamaschi, C. Lubina, H. Fisher, A.C. Veltkamp, and O. Zwaagstra: Stable isotopic signatures ($\delta^{13}C$, δD) of methane. Journal of Geophysical Research, 103(D7):8251-8265, 1998.

Bilek et al., 2001: R.S. Bilek, S.C. Tyler, M. Kurihara and K. Yagi: Investigation of cattle methane production and emission over a 24-hour period using measurements of ^{13}C and D of emitted CH_4 and rumen water. Journal of Geophysical Research, 106(D14):15405-15413, 2001.

Bréas et al., 2001: Bréas, O., C. Guillo, F. Reneiro, E. Wada: The global methane cycle: isotopes and mixing ratios, sources and sinks. Isotopes in environmental and health studies, 37(4):257-379. IssN 1025-6016. Doi:10.1080/10256010108033302, January 2001

Chanton et al., 2000: Chanton, Jeffrey & Rutkowski, Christine & Schwartz, Candace & Ward, D. & Boring, Lindsay. Factors influencing the stable carbon isotopic signature of methane from combustion and biomass burning. Journal of Geophysical Research. 105. 1867-1877. 10.1029/1999JD900909. 2000.

Chevallier et al. 2005: Chevallier, F., M. Fisher, P. Peylin, S. Serrar, P. Bousquet, F.-M. Bréon, A. Chédin, and P. Ciais: Inferring CO2 sources and sinks from satellite observations: method and application to TOVS data, *J. Geophys. Res*., 110, D24309, doi:10.1029/2005JD006390, 2005.

Denier van der Gon et al., 2019: Hugo Denier van der Gon, Jeroen Kuenen, Eirini Boleti, Marilena Muntean, Greet Maenhout, Julia Marshall, Jean-Matthieu Haussaire: Emissions and natural fluxes Dataset. 2019

Galand et al., 2010: Galand, P. E., Yrjälä, K., and Conrad, R.: Stable carbon isotope fractionation during methanogenesis in three boreal peatland ecosystems, Biogeosciences, 7, 3893–3900, https://doi.org/10.5194/bg-7-3893-2010, 2010.

Games and Hayes, 1976: Games, L. M., and Games, J. M: On the mechanisms of CO2 and CH4 production in natural anaerobic environments. Environmental Biogeochemistry, 1. Carbon, Nitrogen, Phosphorus, Sulfur and Selenium Cycles. pp. 51-73. 1976.

Happell et al., 1995: James D. Happell, Jeffrey P. Chanton, William J. Showers: Methane transfer across the water-air interface in stagnant wooded swamps of Florida: Evaluation of mass-transfer coefficients and isotropic fractionation. https://doi.org/10.4319/lo.1995.40.2.0290. Limnology and Oceanography. 1995.

Henne et al., 2016: Stephan Henne, Dominik Brunner, Brian Oney, Markus Leuenberger, Werner Eugster, Ines Bamberger, Frank Meinhardt, Martin Steinbacher, and Lukas Emmenegger: Validation of the Swiss methane emission inventory by atmosphericobservations and inverse modelling, Atmos. Chem. Phys., 16, 3683–3710, doi:10.5194/acp-16-3683-2016, 2016

Hourdin et al., 2006: Hourdin, F., I. Musat, S. Bony, P. Braconnot, F. Codron, J.-L. Dufresne, L. Fairhead, M.-A. Filiberti,P. Friedlingstein, J.-Y. Grandpeix, G. Krinner, P. Levan, Z.-X. Li, and F. Lott,2006 : The LMDZ4general circulation model : climate performance and sensitivity to parametrizedphysics with emphasison tropical convection,Climate Dynamics,27, 787–813

Janssens-Maenhout et al., 2017: Greet Janssens-Maenhout, Monica Crippa, Diego Guizzardi, Marilena Muntean, Edwin Schaaf, Frank Dentener, Peter Bergamaschi, Valerio Pagliari, Jos G.J Olivier, Jeroen A.H.W. Peters, John A. van Aardenne, Suvi Monni, Ulrike Doering, A.M. Roxana Petrescu, Earth Syst. Sci. Data Discuss., https://doi.org/10.5194/essd-2017-79, 2017

Klevenhusen et al., 2010: F. Klevenhusen, S. M. Bernasconi, M. Kreuzer and C.R. Soliva: Experimental validation of the Intergovernmental Panel on Climate Change default values for ruminant-derived methane and its carbon-isotop signature. Animal Production Science, 50(3):159, 2010.

Kuenen et al., 2014: J. J. P. Kuenen, A. J. H. Visschedijk, M. Jozwicka, and H. A. C. Denier van der Gon: TNO-MACC_II emission inventory; a multi-year (2003–2009) consistent high-resolution European emission inventory for air quality modelling, Atmos. Chem. Phys., 14, 10963–10976, doi:10.5194/acp-14-10963-2014, 2014

Levin et al., 1993: Levin I., P. Bergamaschi, H. Doerr, D. Trapp : Stable isotopic signature of methane from major sources in Germany, Chromosphere, 26, 161-177,1993

Levin et al., 1999: Levin, Ingeborg & Glatzel-Mattheier, Holger & Marik, Thomas & Cuntz, Matthias & Schmidt, Martina & Worthy, Douglas. Verification of German Methane emissions inventories and their recent changes based on atmospheric observations. Journal of Geophysical Research - Atmospheres. 104. 10.1029/1998JD100064. 1999.

Lowry et al., 2001: Lowry, David & Holmes, C.W. & Rata, N.D. & O'Brien, P. & Nisbet, E.G.: London methane emissions: Use of diurnal changes in concentration and δ13C to identify urban sources and verify inventories. Journal of Geophysical Research: Atmospheres. 106. 7427-7448. 2001.

Martens et al., 1992: Christopher S. Martens, Cheryl A. Kelley, Jeffrey P. Chanton, William J. Showers: Carbon and hydrogen isotopic characterization of methane from wetlands and lakes of the Yukon-Kuskokwim delta, western Alaska. Journal of Geophysical Research, https://doi.org/10.1029/91JD02885. 1992.

Mailler at al., 2017: Mailler S., L. Menut, D. Khvorostyanov, M. Valari, F. Couvidat, G. Siour, S. Turquety, R. Briant, P. Tuccella, B. Bessagnet, A. Colette, L. Letinois, and F. Meleux, CHIMERE-2017: from urban to hemispheric chemistry-transport modelling, *Geosci. Model Dev.*, 10, 2397-2423, https://doi.org/10.5194/gmd-10-2397-2017, 2017

Menut et al., 2012: Menut, L., Bessagnet, B., Khvorostyanov, D., Beekmann, M., Blond, N., Colette, A., Coll, I., Curci, G., Foret, G., Hodzic, A., Mailler, S., Meleux, F., Monge, J.-L., Pison, I., Siour, G.,Turquety, S., Valari, M., Vautard, R., and Vivanco, M. G.: CHIMERE 2013: a model for regional atmospheric composition modelling, Geosci. Model Dev., 6, 981–1028, doi:10.5194/gmd-6-981-2013, 2013

Nakagawa et al., 2005: Nakagawa, Fumiko, Tsunogai, Urumu, Komatsu, Daisuke, Yamada, Keita, Yoshida, Naohiro, Moriizumi, Jun, Nagamine, Koichiro, Iida, Takao, Ikebe, Yukimasa: Automobile exhaust as a source of 13C- and D-enriched atmospheric methane in urban areas. Organic Geochemistry - ORG GEOCHEM. 36. 727-738. 10.1016/j.orggeochem.2005.01.003. 2005.

Pearson, 1895: Karl Pearson: "Notes on regression and inheritance in the case of two parents," Proceedings of the Royal Society of London, 1895.

Pison et al., 2007: Pison, I., Menut, L., and Bergametti, G.: Inverse modelling of surface NOx anthropogenic emission fluxes in the Paris area during the ESQUIF campaign, *J. Geophys. Res. Atmos.*, 112, D24302, doi:10,1029/2007JD008871, 2007

Röckmann et al., 2016: Thomas Röckmann, Simon Eyer, Carina van der Veen, Maria E. Popa, Béla Tuzson, Guillaume Monteil, Sander Houweling, Eliza Harris, Dominik Brunner, Hubertus Fischer, Giulia Zazzeri, David Lowry, Euan G. Nisbet, Willi A. Brand, Jaroslav M. Necki, Lukas Emmenegger, and Joachim Mohn: In situ observations of the isotopic composition of methane at the Cabauw tall tower site. Atmos. Chem. Phys., 16, 10469–10487, 2016.

Smith et al., 2000: Smith, L.K., Lewis, W.M., Chanton, J.P., Cronin, G., & Hamilton, S.K.: Methane emissions from the Orinoco River floodplain, Venezuela. Biogeochemistry, 51, 113-140. 2000.

Sugimoto and Fujita, 2006: Sugimoto, Atsuko & Fujita, Noboru: Hydrogen Concentration and Stable Isotopic Composition of Methane in Bubble Gas Observed in a Natural Wetland. Biogeochemistry. 81. 33-44. 10.1007/s10533-006-9028-4. 2006

Thanwerdas et al., (in prep): Joël Thanwerdas, Marielle Saunois, Antoine Berchet, Isabelle Pison, Philippe Bousquet, Didier Hauglustaine, Michel Ramonet, Cyril Crevoisier, Bianca Baier: Impact of stratospheric atomic chlorine on the modelling of total methane and its isotopic ratios at the global scale. In preparation.

Thielemann et al., 2004: Thielemann, Thomas & Cramer, Bernhard & Schippers, Axel: Coalbed methane in the Ruhr Basin, Germany: A renewable energy resource? Organic Geochemistry. 35. 1537-1549. 10.1016/j.orggeochem.2004.05.004. 2004

Tyler et al., 1987: Stanley C. Tyler, Donald R. Blake, F. Sherwood Rowland: $^{13}C/^{12}C$ ratio in methane from the flooded Amazon forest. Journal of Geophysical research, https://doi.org/10.1029/JD092iD01p01044. 1987.

Tyler and Bilek, 1997: S.C. Tyler and R.S. Bilek: Methane oxidation and pathways of production in a Texas paddy field deduced from measurements of flux, $\delta^{13}C$, and δD of CH_4. Global Biogeochmical Cycles, 11(3):323-348, 1997.

Uzaki et al., 1991: Minoru Uzaki, Hiroshi Mizutani, and Eitaro Wada: Carbon isotope composition of CH_4, from rice paddies in Japan. Biogeochemistry, 13:159-75, 1991.

Zazzeri et al., 2015: Zazzeri, G., Lowry, David, Fisher, R.E., France, J., Lanoisellé, Mathias, Nisbet, E.G. Plume mapping and isotopic characterisation of anthropogenic methane sources. Atmospheric Environment. 110. 10.1016/j.atmosenv.2015.03.029. 2015

Zazzeri et al., 2016: Zazzeri, G., Lowry, D., Fisher, R. E., France, J. L., Lanoisellé, M., Kelly, B. F. J., Necki, J. M., Iverach, C. P., Ginty, E., Zimnoch, M., Jasek, A., and Nisbet, E. G.: Carbon isotopic signature of coal-derived methane emissions to the atmosphere: from coalification to alteration, Atmos. Chem. Phys., 16, 13669–13680, https://doi.org/10.5194/acp-16-13669-2016, 2016

7. History of the document

7.1 Document history

Version	Author(s)	Date	Changes
1.0	Barbara Szénási	09/08/2019	
	Randulph Morales		
	Maarten Krol		
	Philippe Bousquet		
	Isabelle Pison		