Real-time analysis of $\delta^{13}$C- and $\delta$D-CH$_4$ in ambient air with laser spectroscopy: Method development, validation and applications

vorgelegt von
Simon Eyer

Leiter der Arbeit:
Prof. Hubertus Fischer

Abteilung für Umwelttechnik und Luftfremdstoffe
Empa

3. Februar 2016
Inauguraldissertation

der Philosophisch-naturwissenschaftlichen Fakultät
der Universität Bern

Real-time analysis of $\delta^{13}$C- and $\delta$D-CH$_4$ in ambient air with laser spectroscopy: Method development, validation and applications

vorgelegt von
Simon Eyer
aus Termen (VS)

Leiter der Arbeit:
Prof. Hubertus Fischer
Abteilung für Klima- und Umweltphysik
Physikalisches Institut der Universität Bern

Co-Leiter:
Dr. Joachim Mohn
Dr. Lukas Emmenegger
Abteilung für Umwelttechnik und Luftfremdstoffe
Empa

Von der Philosophisch-naturwissenschaftlichen Fakultät angenommen

Bern, 3. Februar 2016

Dekan:
Prof. Dr. G. Colangelo

Vorsitz:
Prof. Dr. Fortunat Joost

Examinator:
Prof. Dr. Thomas Röckmann
“The pessimist complains about the wind; 
the optimist expects it to change; 
the realist adjusts the sails.”

William Arthur Ward
About 20% of the increase in radiative forcing due to human emitted greenhouse gases is attributed to CH₄, and thus, reducing CH₄ emissions offers a great short-term target in mitigating global warming. However, understanding what controls the global CH₄ cycle remains a challenge, as many CH₄ sources vary strongly on spatial and temporal scales. Therefore, measuring the isotopic composition of CH₄ can provide valuable information to reduce uncertainties in the CH₄ emission budget. Up till now, however, high precision measurements of CH₄ isotopologues are scarcely available as they are limited to isotope ratio mass spectrometry (IRMS), which is generally a laboratory based technique.

This PhD thesis is about the development, validation and application of a field-deployable, fully automated, liquid nitrogen free measurement platform, called TREX-QCLAS, capable of performing real-time, high precision analysis of ambient air ¹²CH₄, ¹³CH₄ and ¹²CH₃D mole fractions and their relative isotope ratios δ¹³C- and δD-CH₄.

Chapter 1 provides an introduction to the topic, presenting the relevance of CH₄ as a greenhouse gas, the value of isotopic information to pinpoint CH₄ emission sources and the basic principles of mid infrared laser spectroscopy for high precision atmospheric trace gas and isotope measurements.

Chapter 2 is an in-depth study comparing six different adsorbent materials with respect to their effectiveness for CH₄ preconcentration from ambient air. After an investigation of adsorption/desorption isotherms, HayeSep D was found to exhibit an outstanding selectivity for CH₄ over N₂.

Chapter 3 describes the TREX-QCLAS technique, which consists of two components: a fully automated preconcentration unit, called TRace gas EXtractor (TREX) and a high-precision dual-quantum cascade laser absorption spectrometer (QCLAS). The TREX system enhances the mole fraction of the target gas CH₄ by a factor of up to 500 while simultaneously removing other trace gases such as carbon dioxide, nitrous oxide and water, which would otherwise interfere during spectral analysis. The QCLAS is capable of analyzing δ¹³C- and δD-CH₄ values with a precision of 0.1‰ and 0.5‰, respectively, at 10 min averaging time. Chapter 3 also presents a two-week measurement campaign at the Empa Campus in Dübendorf, Switzerland, during which the newly developed TREX-QCLAS system was validated against flask samples analyzed by IRMS.

Chapter 4 presents results of a 5-month measurement campaign on CH₄ isotopologues at the CESAR-tower in Cabauw, the Netherlands, where the TREX-QCLAS system was operated along with a dual-IRMS system of the University of Utrecht. Based on replicate measurements of compressed air, the repeatability of the TREX-QCLAS was determined to be 0.17‰ and 0.85‰ for δ¹³C- and δD-CH₄, respectively, making it competitive with IRMS technique. Despite the dominant contribution of isotopically depleted ruminant emissions, events with elevated fossil or landfill contributions were distinguishable, demonstrating the value of in situ and high temporal resolution isotope ratio measurements. Comparison with atmospheric transport model simulations confirmed the temporal trends of different source contributions, but also indicated a possible overestimation of fossil fuel emissions by the EDGAR inventory. In summary, the measurement campaign demonstrates the feasibility of high precision long-term measurements of CH₄ isotopologues and their capability in constraining emission inventories as well as verifying transport model predictions.
## Contents

Abstract v

1 Introduction 1

1.1 Atmospheric Methane .............................. 1

1.1.1 Methane as a greenhouse gas ......................... 1

1.1.2 The global CH$_4$ budget .......................... 1

1.1.3 CH$_4$ sources and sinks ............................ 3

1.1.4 Global network for CH$_4$ observation ................. 4

1.1.5 Natural abundance of CH$_4$ isotopologues and fractionation processes 7

1.1.6 Isotopic signatures of CH$_4$ sources ................... 8

1.1.7 Clumped CH$_4$ isotopes ............................ 11

1.2 Laser absorption spectroscopy ....................... 13

1.2.1 QCLAS for high precision atmospheric trace gas measurements 13

1.2.2 Performance requirements for analysis of ambient CH$_4$ isotopologues 14

2 Methane preconcentration by adsorption: a methodology for materials and conditions selection 15

2.1 Introduction ........................................... 16

2.2 Materials and methods ............................... 17

2.3 Analysis ............................................. 17

2.3.1 Adsorption models ................................. 17

2.4 Results and discussion ............................... 18

2.4.1 Adsorption of CH$_4$ and N$_2$ in the Temperature Range of 196 to 296 K 18

2.4.2 Isosteric enthalpy of adsorption ...................... 20

2.4.3 Surface area ........................................ 20

2.4.4 Selectivity ......................................... 20

2.4.5 Temperature behavior .............................. 22

2.4.6 Co-adsorption .................................... 24

2.4.7 Limits of the approach ............................. 24

2.5 Conclusion ........................................... 25

2.6 Acknowledgments ..................................... 26

3 Real-time analysis of $\delta^{13}$C- and $\delta^D$-CH$_4$ in ambient air with laser spectroscopy: method development and first intercomparison results 27

3.1 Introduction ........................................... 28

3.2 Experimental ......................................... 29

3.2.1 Preconcentration and analysis of CH$_4$ isotopologues by TREX-QCLAS 29

Requirements for the preconcentration system ....................... 29
4.4.4 Evaluation of emission databases with high temporal resolution CH₄ isotope data .......................... 67
4.5 Conclusions and outlook ....................................... 68

5 Conclusion & Outlook ........................................... 71
5.1 Analytical developments & achievements ...................... 71
5.2 Potential for optimization ...................................... 71
5.3 Accomplished field studies and interpretation of isotopic source signatures ... 72
5.4 Future research applications ................................... 73

6 Appendix A ........................................................ 75

Acknowledgements .................................................. 77

Bibliography .......................................................... 79
List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>GHG</td>
<td>Green House Gas</td>
</tr>
<tr>
<td>Gt</td>
<td>Giga tonnes, $1 \times 10^9$ t</td>
</tr>
<tr>
<td>Tg</td>
<td>Terra gram, $1 \times 10^{12}$ grams</td>
</tr>
<tr>
<td>ppm</td>
<td>parts-per-million, $1 \text{ ppm} = 10^{-6}$ mole/mole</td>
</tr>
<tr>
<td>ppb</td>
<td>parts-per-billion, $1 \text{ ppb} = 10^{-9}$ mole/mole</td>
</tr>
<tr>
<td>ppt</td>
<td>parts-per-trillion, $1 \text{ ppt} = 10^{-12}$ mole/mole</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>Methane</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>Nitrous Oxide</td>
</tr>
<tr>
<td>QCL</td>
<td>Quantum Cascade Laser</td>
</tr>
<tr>
<td>QCLAS</td>
<td>Quantum Cascade Laser Absorption Spectroscopy</td>
</tr>
<tr>
<td>IRMS</td>
<td>Isotope Ratio Mass Spectrometry</td>
</tr>
<tr>
<td>SCIAMACHY</td>
<td>SCanning Imaging Absorption Spectrometer for Atmospheric Cartography</td>
</tr>
<tr>
<td>GOSAT</td>
<td>Greenhouse Observing Satellite</td>
</tr>
<tr>
<td>TCCON</td>
<td>Total Carbon Column Observing Network</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>UNFCCC</td>
<td>United Nations Framework Convention on Climate Change</td>
</tr>
<tr>
<td>AGAGE</td>
<td>Advanced Global Atmospheric Gases Experiment</td>
</tr>
<tr>
<td>NOAA</td>
<td>National Ocean and Atmospheric Administration</td>
</tr>
<tr>
<td>WMO</td>
<td>World Meteorologic Organization</td>
</tr>
<tr>
<td>GAW</td>
<td>Global Atmospheric Watch</td>
</tr>
<tr>
<td>ESA</td>
<td>European Space Association</td>
</tr>
<tr>
<td>ICOS</td>
<td>Integrated Carbon Observation System</td>
</tr>
<tr>
<td>InGOS</td>
<td>Integrated non-CO$_2$ Greenhouse gas Observing System</td>
</tr>
<tr>
<td>IAEA</td>
<td>International Atomic Energy Agency</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Atmospheric Methane

1.1.1 Methane as a greenhouse gas

The anthropogenic increase in atmospheric CH\textsubscript{4} contributes about 20\% to the global warming induced by human activities, which makes it the second most important long living greenhouse gas after CO\textsubscript{2} and before N\textsubscript{2}O (WMO/GAW, 2015). The global warming potential per molecule CH\textsubscript{4} is 28 – 34 times larger compared to CO\textsubscript{2} on a 100 year time scale (Myhre et al., 2013). Since the start of industrialization around 2 centuries ago, the global annual mean abundances of atmospheric CH\textsubscript{4} increased by a factor of 2.54 to 1833 ± 1 ppb in the year 2014, mainly due to anthropogenic emissions (MacFarling Meure et al., 2006; WMO/GAW, 2015). Unlike CO\textsubscript{2}, CH\textsubscript{4} emissions are not directly related to energy consumption. Governments and industry are interested in reducing CH\textsubscript{4} emissions, as it is economically favorable and cost-effective (Dlugokencky et al., 2011). This is because CH\textsubscript{4} is the main component of natural gas and thus a source of energy, making it an attractive short-term target in mitigating global warming. Examples for cost-effective CH\textsubscript{4} emission reductions are finding and fixing leaks in oil and gas pipelines, optimizing waste management and minimizing the number of CH\textsubscript{4} producing microbes in ruminants. For instance the Global Methane Initiative partnership (www.globalmethane.org) provides expert knowledge to the oil and gas industry in preventing CH\textsubscript{4} loss. Gas emitted from landfills consists mainly of CH\textsubscript{4}, which can be collected and sold. Alternatively organic matter can be sorted out from waste providing a valuable soil-supplement when composting it. Studies have shown, that cows producing less methane are more efficient in generating weight (Soliva and Hess, 2007).

Since the Kyoto Protocol and the United Nation Framework Convention on Climate Change (UNFCCC) entered into force in the years 2005 and 1994, respectively, CH\textsubscript{4} attracted the attention of policymakers and industries. Both are contracts with universal membership, obliging industrially developed countries to limit their GHG-emissions. In parallel, the Intergovernmental Panel on Climate Change (IPCC) stands as the leading international body for the assessment of climate change. The renowned IPCC-reports inform governments in a neutral, policy-relevant way about possible consequences and global warming mitigation scenarios. In the context of the subsequent inventory estimations and emission trading schemes, the development of a global CH\textsubscript{4} observation system is of urgent importance (Nisbet et al., 2014).

1.1.2 The global CH\textsubscript{4} budget

After a steady increase for almost 20 years and plateauing in the years 1999 to 2006, the global atmospheric CH\textsubscript{4} mole fraction is on the rise again (Rigby et al., 2008; Nisbet et al., 2014). The peaks in the growth rate in 1991, 1997 and 2002/2003 shown in Figure 1.1 b) can be explained by the eruption of Mt. Pinatubo, the El Niño, event and cumulation of biomass burning mainly in South Asia and the boreal regions in the respective years (Bousquet et al., 2006; Chen and Prinn, 2007).
2006; Dlugokencky, 2003; Werf et al., 2004). The two drastic changes in CH$_4$ trends in the years
1999 and 2006 have generated large debates upon their causes (Figure 1.1 a)). CH$_4$ growth rates
already declined in the beginning of the 1990s which was the time when the Soviet Union
broke apart. One theory is that this led to a decrease in the production of coal, oil and natural
gas and thus to a reduction of fossil emissions, causing finally the increase in the atmospheric
CH$_4$ mole fractions to halt after 1999 (Bousquet et al., 2011; Kirschke et al., 2013). However,
increasing atmospheric $\delta^{13}$C-CH$_4$ values after the year 2000 show that isotopically light wetland
emissions must have decreased during this time (Monteil et al., 2011). Additionally, they state,
that emissions from fossil fuel exploitation and/or biomass burning have decreased as well and
that a shorter atmospheric CH$_4$ lifetime due to a positive trend in OH is reasonable.

The CH$_4$ rise since 2006 remains a mystery in the global CH$_4$ growth rate leading to different
evolving theories, which is mainly due to insufficient understanding of the main drivers in the
global CH$_4$ cycle. Kirschke et al., 2013, assumed that natural emissions are overestimated and
the increase in CH$_4$ could be due to raising fossil emissions mainly in China, Russia and the
USA or due to natural wetland emissions. In contrast, $\delta^{13}$C data suggest that precipitation
events in the tropics and warmer temperatures in the Arctic have caused wetland emissions to
increase (Dlugokencky et al., 2009; Dlugokencky et al., 2011). Additionally, as temperatures in
the Arctic remain below zero a strong climate feedback from permafrost and CH$_4$ hydrates has
not yet been activated. Variable relevance is attributed to the role of the OH-sink in increasing
atmospheric CH$_4$ mole fractions since 2006 (Bousquet et al., 2011; Rigby et al., 2008).

Figure 1.1 a) and b) also illustrates the distinctive inter-annual variability, which is well
pronounced in the globally averaged CH$_4$ mole fraction. Wetlands are the main driver of the
inter-annual variability, as they are very sensitive to temperature changes at high altitudes and
precipitation events in the tropics (Ciais et al., 2014). In addition, biomass burning and the OH
sink exhibit great influence on the inter-annual variability (Dlugokencky et al., 1996).
1.1.3 \( \text{CH}_4 \) sources and sinks

Figure 1.2: Illustration taken from the IPCC report 2013, chapter 6 (Ciais et al., 2014), showing the global \( \text{CH}_4 \) cycle and its reservoirs estimated for the years 2000 to 2009. The black arrows indicate \( \text{CH}_4 \) fluxes from or to natural sources or sinks. Red arrows represent emissions from anthropogenic sources and the light brown one denotes a mixture of both (biomass burning). The atmosphere is one of four big reservoirs with the black numbers indicating the pre-industrial inventory value. The sizes of the other three reservoirs are difficult to estimate, but ocean hydrates exceed the others by far.

Figure 1.2 illustrates the atmospheric \( \text{CH}_4 \) cycle with the main sources and sinks estimated in Tg/y. Methane can be formed either by biogenic, thermogenic or pyrogenic transformation of organic matter. Biogenic \( \text{CH}_4 \) is generated by microbes when degrading organic matter under anaerobic conditions. Water covered soils rich in organic matter such as natural wetlands, flood plains, marshes, bogs, tundra, swamps, marine or freshwater sediments, as well as rice paddies provide such anaerobic conditions. There, the balance between methanogenic and methanotrophic archaea (methanogens and methanotrophs) regulates methane emissions, causing them to be very susceptible to temperature changes and precipitation events (Guo et al., 2011). Also acidic environments in the gastrointestinal tract of ruminants (mostly cows) or termites can provide anaerobic conditions with wide availability of organic matter, ideal for methanogens to produce \( \text{CH}_4 \). The same accounts for other extreme conditions, like marine sediments or...
Chapter 1. Introduction

lagoons and open sewers of developing countries without appropriate waste water treatment. Thermogenic CH\(_4\) is one byproduct when organic matter degenerates at high temperature and pressure over geological time scales. Its sources are thus mainly fossil (i.e. gas, coal and oil), which are emitted either naturally or anthropogenically through their extraction, refining and distribution systems.

Incomplete combustion of organic matter leads to pyrogenic CH\(_4\), with biomass and biofuel burning being typical examples. Besides, CH\(_4\) can also be produced by abiotic degradation of coal under specific geological circumstances (Abrajano et al., 1988; Schoell and Wellmer, 1981; Etiope and Ionescu, 2015) and (interestingly but also controversial) by plants under temperature and H\(_2\)O stress (Kepler et al., 2006; Qaderi and Reid, 2009). But significant emissions from the two source categories regarding the global budget are very unlikely (Ciais et al., 2014).

Roughly 90% of total CH\(_4\) emissions are decomposed by photochemical reaction with OH radicals in the stratosphere and troposphere (Voulgarakis et al., 2013). The strength of this main CH\(_4\) sink has high uncertainties of 20%, as the concentration of OH is very difficult to determine due to its short lifetime of \(\approx 1 s\). Thus, the atmospheric OH mole fraction can barely be measured and only estimated with sophisticated models, such as chemical transport and chemistry climate models (Young et al., 2013). This also leads to interesting discussions and contradictory results when it comes to the role of OH in changing the atmospheric methane growth rate during the years 1999 and 2007 (Rigby et al., 2008; Bousquet et al., 2011; Monteil et al., 2011). Besides the OH radicals there are a few additional minor CH\(_4\) sinks such as oxidation in aerated soils by methanotrophic bacteria (5%) and the reaction with Cl radicals and O(1D) in the stratosphere (7%). Similar to the OH sink their strengths have high uncertainties, leading to a relatively uncertain present atmospheric lifetime of 9.8 ± 1.6 years (Voulgarakis et al., 2013).

Figure 1.3 gives an overview of the most important source categories in 13 different regions of the world, including the ocean. According to the figure, wetland emissions are mainly dominant in tropical areas, such as Africa, South America and southeast Asia, as well as in temperate South America and the boreal regions of North America and Eurasia (Kirschke et al., 2013). Emissions from wild fires (biomass burning) and termites are largest in Africa, tropical South America and southeast Asia. Anthropogenic emissions dominate in Europe, North America, China and central Asia due to fossil fuel, agricultural and waste emissions. In terms of rice agriculture and livestock industries India, southeast Asia and South America have a strong contribution to anthropogenic emissions as well. However, in terms of CH\(_4\) emissions per capita India and China are still below the average OECD countries (Kirschke et al., 2013). Figure 1.3 also gives information on the agreement of bottom-up (BU) and top-down (TD) approaches and the uncertainty of estimations. Fossil CH\(_4\) emissions in China, estimated with a TD approach, exhibit a high uncertainty, possibly because atmospheric measurement data are limited and due to biases in the inventory. In North America and Europe, anthropogenic emission estimates have large uncertainty bars, possibly due to uncertainties in emission factors. Tropical wetland and biomass burning emissions show generally large discrepancy between TD and BU approaches, as there are only few in situ measurements available for these regions and BU estimates of biomass burning are likely too conservative due to undetected small fires. CH\(_4\) loss due to reaction with OH is strongest in the tropical atmosphere over both, land and ocean, as the OH-production is highest in this region.

1.1.4 Global network for CH\(_4\) observation

Since 1979, CH\(_4\) mole fractions are measured across the globe by large stationary measurement networks and mobile as well as remote sensing techniques, including satellite, aircraft, ship and balloon measurements (Bergamaschi et al., 2009). Temporal trends in atmospheric CH\(_4\) mole fractions before 1979 are only accessible by analyzing firn air and ice core samples, reaching up
Chapter 1. Introduction

Figure 1.3: Reproduced from Kirschke et al., 2013. Data were collected from bottom-up (BU) and top-down (TD) CH$_4$ budgets from the years 2000 to 2009 of 13 world regions, including the ocean. The error bars show the minimum and maximum estimated values.
Chapter 1. Introduction

to 800'000 years back in time (Loulergue et al., 2008). Stationary, mobile and remote sensing measurement techniques are often combined to improve the spatio-temporal coverage, reduce uncertainties in CH$_4$ emission estimations and to compensate for their weaknesses (Bergamaschi et al., 2009). The data is then accumulated and used together with inverse modeling technique in a TD approach to estimate CH$_4$ emissions and the global atmospheric budget. Large measurement networks, which usually operate at remote locations, such as NOAA, AGAGE, GAW, ICOS and TCCON have the advantage to measure on the regional to national scale with high accuracy and partially high temporal resolution. Figure 1.4 shows a world map with the locations of all the measurement sites from the GAW network (WMO/GAW, 2015). Unfortunately, such networks are irregularly distributed over the surface of the globe and especially sparse in some remote regions with high CH$_4$ emissions such as Siberia or the tropics in the Amazon region and Indonesia (Bergamaschi et al., 2009; Bergamaschi et al., 2013; Dlugokencky et al., 2009). Thus, for the top-down approach it is necessary to upgrade spatio-temporal resolution of the global measurement networks and possibly even with isotopic resolution in order to better quantify source emission strengths (Dlugokencky et al., 2009). A helpful supplement are aircraft and ship measurements (e.g. from NOAA) or even train and air core sampling with balloon flights, as they have relatively good precisions and flexible, although limited, spacial coverage. Spaceborn measurement systems such as the Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) on board ESA's environmental satellite ENVISAT or Greenhouse Gases Observing Satellite (GOSAT) have a quasi-global coverage and provide data also from remote regions such as the tropical wetlands, where currently not many measurement stations exist. However CH$_4$ satellite retrievals have rather low relative precision of 1 – 2% due to the limited available independent measurement data for validation and the large complexity of the retrieval algorithms (Frankenberg et al., 2005; Frankenberg et al., 2006; Schneising et al., 2011). Additionally, measurements are not possible under cloudy conditions.

A completely different, but complementary strategy in estimating global budgets and emissions is the “bottom-up” (BU) approach, in which either global (i.e. EDGAR, 4DVAR) or regional (i.e. TNO-MACC, which is European) emission inventories are assembled. With process-based forward modeling techniques, emissions as well as sink processes can be simulated. The BU approach can overestimate emissions easily, as uncertainties in emission factors and inventories scale up quickly (Ciais et al., 2014; Nisbet et al., 2014).

Conclusively both strategies, TD and BU approach, have their strengths and weaknesses. The top-down approach gives a good constraint and estimate for the global CH$_4$ budget, but the bottom up approach has major advantages in terms of source distinction due to the detailed inventories. Measuring the mole fraction of the three most common CH$_4$ isotopologues can help in reconciling these two different approaches. This is because the relative abundance of the heavy isotopologues can give additional information about the source processes, providing “bottom-up information” when applying a top-down approach (Rigby et al., 2012; Monteil et al., 2011; Dlugokencky et al., 2009).
1.1.5 Natural abundance of CH₄ isotopologues and fractionation processes

The three most abundant isotopologues of CH₄ are ¹²CH₄, ¹³CH₄ and ¹²CH₃D with a relative abundance of 98.9%, 1.1% and 0.06%. To enable compatibility of different techniques and laboratories, isotopic measurements are referenced to international isotope ratio scales (Werner and Brand, 2001). Relative isotope ratios, i.e. delta values, are defined by the quotient of the isotope ratio in the sample material to the isotope ratio in the standard material:

\[
\delta^{13}C - CH_4 = \frac{(^{13}CH_4/^{12}CH_4)_{Sample}}{(^{13}CH_4/^{12}CH_4)_{VPDB}} - 1 \quad \text{and} \quad \delta D - CH_4 = \frac{(DCH_3/CH_4)_{Sample}}{(DCH_3/CH_4)_{VSMOW}} - 1
\] (1.1)

VPDB stands for Vienna-Pee Dee Belemnite, the international isotopic ratio scale for the \(^{13}C/^{12}C\)-ratio and VSMOW stands for Vienna Standard Mean Ocean Water, the primary scale for the D/H-ratio. As the deviations in the isotope ratios between sample and standard are of the order of \(10^{-3}\), the \(\delta\)-values are expressed in ‰.

To understand the importance of isotopes when measuring the isotopic fraction of CH₄ in the atmosphere, one has to understand the principle of fractionation. In contrast to unstable radioactive isotopes (such as \(^{14}\)C), the absolute natural abundance of any stable isotope (e.g. \(^{13}\)C with respect to the total amount of carbon atoms) is constant. When chemical, physio-chemical or biochemical reactions break a chemical bond, the probability for the reaction to occur is
higher the lower the strength of the bond. Because of their higher masses, bonds involving heavy isotopes are generally stronger as there is more energy stored in their oscillatory movement. The kinetic reaction rate coefficient \( k \) of a particular process \( i \) quantitatively describes this phenomena and isotopic fractionation happens, when the fractionation factor

\[
\alpha_i = \frac{13k_i}{12k_i} \tag{1.2}
\]

for a heavy isotope (e.g. \(^{13}\text{C}\)) and a light (e.g. \(^{12}\text{C}\)) differs from 1. Usually the term kinetic isotope effect, parametrized as \( \varepsilon \), is used to quantify the isotopic fractionation. It is defined as

\[
\varepsilon_i = (1 - \alpha_i) \tag{1.3}
\]

and is expressed, similar as the \( \delta \)-values, in \( \%e \) due to the very low deviations in the \( \alpha_i \)'s from 1. As a consequence of fractionation processes, \( \text{CH}_4 \) formed by a source process with a non-zero \( \varepsilon_i \) may develop unique isotopic compositions, which can be characterized by performing near-source measurements or laboratory experiments. Fractionation effects are also influenced by a variety of parameters such as the reaction rate, the temperature and the availability of the substrate, i.e. source depletion effects. In addition, the delta values of the product \( \text{CH}_4 \) depends on the isotopic composition of the substrate and during equilibrium conditions of bidirectional processes, the heavy isotopes generally accumulate where bonding is strongest.

In the following section the isotopic signature of different sources is discussed with respect to the fractionation processes and their influencing parameters.

### 1.1.6 Isotopic signatures of \( \text{CH}_4 \) sources

In Figure 1.5 the \( \text{CH}_4 \) isotopic signatures of the most important source categories are presented: microbial (biogenic), fossil (thermogenic), and biomass burning (pyrogenic). In addition, subcategories are given, e.g. ruminants, rice paddies, wetlands and waste for the microbial-derived \( \text{CH}_4 \), and the influences of different substrates (e.g. \( \text{C}_3 \) versus \( \text{C}_4 \) plants) and processes (e.g. oxidation) are indicated.

In general \( \delta\text{D-CH}_4 \) values exhibit a larger variation as compared to \( \delta^{13}\text{C-CH}_4 \) because isotopic fractionation effects are considerably larger due to the high relative mass difference of the hydrogen isotopes with respect to carbon isotopes (Whiticar, 1996).

While \( \delta^{13}\text{C-CH}_4 \) values of most sub-categories center around \(-60\%e\) to \(-40\%e\), and exhibit a strong overlap, the source category biomass burning displays a characteristic enrichment in \(^{13}\text{C}\) (with \( \delta^{13}\text{C-CH}_4 \) values between \(-30\%e\) to \(-10\%e\)). \( \delta\text{D-CH}_4 \) values vary largely between \(-400\%e\) and \(-100\%e\) reflecting the different \( \text{CH}_4 \) pathways involved and the dependence on the hydrogen substrate (Whiticar and Schaefer, 2007). A gap in \( \delta\text{D-CH}_4 \) values exists at \(-270\%e\) to \(-250\%e\) between thermogenic \( \text{CH}_4 \) displaying the highest delta values (\(-220\%e\) to \(-100\%e\)) as well as \( \text{CH}_4 \) from pyrogenic processes (\(-250\%e\) to \(-220\%e\)), on one side, and \( \delta\text{D-CH}_4 \) values of biogenic \( \text{CH}_4 \) with delta values between \(-380\%e\) and \(-270\%e\). Combining information on the stable isotopic composition of carbon and hydrogen (\( \delta^{13}\text{C-} \) and \( \delta\text{D-CH}_4 \)) offers great potential to partition \( \text{CH}_4 \) emissions into source categories (microbial, fossil, biomass burning) or even sub-categories and to estimate individual contributions. This approach requires detailed knowledge on the isotopic signatures of individual processes and a precise analytical technique to determine the isotopic signature of atmospheric emissions.

In the following, the three main source processes as well as the atmospheric sink processes are described in more detail. Table 1.1 gives an overview of all the source signatures (including references) used in Figure 1.5.
Microbial

As discussed in section 1.1.3, microbial CH$_4$ production is very diverse with respect to the involved pathways and substrates, which is also reflected in the wide range of the isotopic source signature (Figure 1.5). This is especially pronounced for wetland emissions, where the two main microbial CH$_4$ production processes are present: acetate fermentation (AF) and carbon (i.e. CO$_2$) reduction with H$_2$ (CR). CR generally dominates in marine systems (e.g. marine sediments), while in freshwater systems (e.g. rice paddies) the preferential pathway is AF (Whiticar et al., 1986). This is related to the availability of different substrates, i.e. marine sediments are generally sulphate enriched and, therefore, methanogenic archaea are outcompeted for carbon substrates by sulphate-reducing bacteria. Isotopically, AF is more enriched in $^{13}$CH$_4$ and more depleted in CH$_3$D compared to CR due to its lower fractionation factor for $^{13}$C and higher fractionation factor for D (Levin et al., 1993; Whiticar, 1999; Chanton et al., 2006). In Figure 1.5 the systematic variation in $\delta^{13}$C and $\delta$D associated with CR and AF is indicated by the black double arrow in the bottom left, suggesting that a shift to CR leads to increased $\delta$D-CH$_4$ values and a shift to AF an enrichment in $^{13}$CH$_4$. 

**Figure 1.5**: $\delta^{13}$C- and $\delta$D-CH$_4$ signatures of the three major source categories as well as sub-categories, which can be distinguished by isotopic measurements. C3 and C4 represent the plant substrate (e.g. forests or grass) for biomass burning or fodder plant (e.g. maize or grass) in the case of ruminants. The black circle represent the mean isotopic values of atmospheric CH$_4$ and the black square the average isotopic source signature of atmospheric CH$_4$ emissions. The dashed line connecting these to points represents the fractionation effect responsible for this shift as discussed in the of this section. Additionally the following isotopic fractionation effects of processes or other parameters are indicated with black arrows: The shift in isotopic signature when the relative proportion between the processes of CR (CO$_2$ reduction) and AF (acetate fermentation) changes (bottom left). The depletion in CH$_3$D due to the depletion of DHO in meteoric H$_2$O with “Altitude”, e.g. for alpine regions, and with “Latitude” towards the northern pole. The enrichment of $^{13}$C in pyrogenic source signatures with increasing “burning efficiency”. The fractionation processes related to CH$_4$ oxidation causing $\delta^{13}$C- and $\delta$D-CH$_4$ values to increase with oxidation rate. Additionally the dashed line indicates fractionation processes related to atmospheric sink processes causing $\delta^{13}$C- and $\delta$D-CH$_4$ values to increase in the atmosphere relative to the estimated isotopic signature of the combined sources.
The isotopic signature of CH$_4$ that is produced in wetlands, rice paddies and landfills is often modified by secondary isotopic fractionation processes. Aerobic CH$_4$ oxidation by methanotrophic bacteria is the most important of these processes and can have significant effects on the source strength and isotopic signature (Levin et al., 1993; Bergamaschi et al., 1998b; Chanton, 2005). This effect occurs when CH$_4$, formed under anaerobic conditions, passes oxic soil layers before it is emitted into the atmosphere, causing a strong enrichment in $\delta^{13}$C- and $\delta^{19}$D-CH$_4$ (Coleman et al., 1981). Figure 1.5 indicates the fractionation processes related to CH$_4$ oxidation by the arrow in the top right corner pointing towards the direction of the shift in $\delta^{13}$C- and $\delta^{19}$D-CH$_4$. Emissions from landfills have been significantly reduced in several countries, such as the UK, due to the implementation of gas extraction systems. This could have possibly also affected the isotopic signature of CH$_4$ landfill emissions (Zazzeri et al., 2015).

In the rumen of cows, CR is assumed to be the dominant methanogenic pathway while AF is expected to be low (Morgavi et al., 2010). Additionally, the contribution of a third pathway, by which methanogens use C$_1$ compounds such as methanol as a substrate, might contribute to CH$_4$ production depending on substrate availability. The importance of this methylotrophic pathway, however, is still under debate (Morgavi, Forano et al. 2010), but its fractionation factor was found to be large compared to AF and CR (Penger et al., 2012). Microbial production of CH$_4$ in the rumen is largely influenced by the availability and the isotopic signature of the substrate. Ruminant CH$_4$ emissions, for example, are more depleted in $^{13}$C when feeding isotopically lighter C4 plants (grass, hay, barley) compared to C3 plants (e.g. maize) (Klevenhusen et al., 2010). In addition, $\delta^{19}$D-CH$_4$ reflects the isotopic signature of the hydrogen source, mainly H$_2$O, which in turn varies with latitude, altitude, and region (Levin et al., 1993; Whiticar, 1999; Chanton et al., 2006; Kawagucci et al., 2014. A global data base for isotopic values ($\delta^{15}$O-H$_2$O) of precipitation from the International Atomic Energy Agency (IAEA) (www.iaea.org/water) indicates, that the natural abundance of DHO is lower especially towards the northern pole and with altitude, e.g. for alpine regions.

**Thermogenic**

The substrate for thermogenic CH$_4$ is organic matter stored in sedimentary rocks, called kerogen. Depending on the chemical and isotopic composition of the original living matter (e.g. plankton, spores and pollen) as well as the ground or ocean water at the time and region the plants were growing, kerogen can have different isotopic compositions. Coal, oil, oil shales and natural gas are formed through thermocatalytic reorganization of the kerogen during various stages, which measured in terms of maturity. While the isotopic signature of coal, oil and heavy petroleum remains more or less unchanged with age, fractionation occurs during formation of CH$_4$ and other natural gases, associated with the thermal cracking of kerogen or oil. CH$_4$ is isotopically lighter, but the magnitude of this effect is strongly dependent on various parameters, such as temperature, pressure, and type or maturity of the kerogen Whiticar, 1996. Because of this, the isotopic signature of fossil CH$_4$ is highly variable and can be characteristic for a specific region. Recently, Zazzeri et al., 2015, found $\delta^{13}$C-CH$_4$ of natural gas from leaks in the supply-system in the UK to be quite stable around $-36 \pm 2\%$, while signatures for CH$_4$ emitted from coal mines in New England and Wales varied strongly in the range of $-30.9\%$ to $-51.2\%$. In Germany, the isotopic signature of natural gas from the Heidelberg distribution network has been found to vary in the range of $-50\%$ to $-30\%$ (Levin et al., 1999). The variations were seasonal, with $\delta^{13}$C-CH$_4$ depleted during summer, when supply came mostly from Russia, and more enriched during winter, when gas was mostly imported from northern Europe. Quay et al., 1999, suggested a value of $-43 \pm 7\%$ for $\delta^{13}$C-CH$_4$ of natural gas ($\delta^{18}$D: $-185 \pm 20\%$) and $-36 \pm 7\%$ for coal ($\delta^{18}$D: $-140 \pm 20\%$). Snover et al., 2000 assumed a fossil fuel mix of 35% coal and 65% natural gas (80% thermogenic and 20% microbial origin), resulting in an average
signature of $-40 \pm 7\%e$ and $-175 \pm 10\%e$ for $\delta^{13}C$- and $\delta D$-CH$_4$, respectively. In some cases, microbial generation of CH$_4$ in coal beds was found to exceed thermogenic methane by a factor of 2-5 with led to a decrease in delta values to a minimum of $-72\%e$ and $-209\%e$ for $\delta^{13}C$- and $\delta D$-CH$_4$, respectively (Kotarba and Lewan, 2004).

**Pyrogenic**

Pyrogenic CH$_4$ sources exhibit a very distinctive $^{13}C$ enriched source signature, making CH$_4$ emissions from incomplete combustion identifiable (Mikaloff Fletcher et al., 2004). The $^{13}C$ isotopic signature is influenced by the photosynthetic pathway of the combustible, i.e. plant substrate being either C3, e.g. most trees, or C4, e.g. some grass, and the efficiency of the combustion. Higher combustion temperatures generally lead to higher efficiency and produce less, but more $^{13}C$ enriched CH$_4$. In Figure 1.5, this is illustrated by the biomass burning box divided into a C3 and a C4 part indicating the respective isotopic source signatures. Additionally, the arrow displays the influence of the “burning efficiency” on the isotopic ratio. In the Figure, the pyrogenic source signature expands towards more enriched $^{13}C$ values accounting for stove fires or fuel burning, where the efficiency is much higher than in wild fires. Nakagawa et al., 2005, suggest that the isotopic source signature of CH$_4$ emitted by cars is significantly enriched in $^{13}C$ and D (Table 1.1).

**Atmospheric sink processes**

The main atmospheric sink processes are OH reduction, soil uptake, stratospheric removal and Cl, as discussed in section 1.1.3. The globally averaged isotopic background signature of atmospheric CH$_4$ depends on the isotopic signature of the combined sources and the kinetic fractionation effect associated with the atmospheric sinks (mainly reduction by OH). For instance the $\delta^{13}C$ value of the combined source is estimated to be $-54.2\%e$. Due to the non-zero KIEs of the atmospheric sink processes, fraction effects cause the atmospheric $\delta^{13}C$-CH$_4$ value to increase to $-47.1\%e$. Similarly $\delta D$ of atmospheric CH$_4$ is $-86\%e$, which is significantly more enriched in CH$_4$D than the mean source ($-295\%e$). The dashed line combining the isotopic signature of the atmospheric mean (black circle) and the combined source (black square) in Figure 1.5 illustrates this dependence of the CH$_4$ isotopic composition on fractionation effects associated with removal processes. The fractionation factors of individual sinks are summarized in Table 1.1.

**1.1.7 Clumped CH$_4$ isotopes**

In recent years a new research direction was established, analyzing doubly-substituted, so-called "clumped" isotopic species. Research was facilitated by the increased sensitivity and precision of both mass spectrometry and laser spectroscopy based instruments (Eiler, 2007; Ono et al., 2014). The abundance of the doubly-substituted isotopic species, in relation to the equilibrium isotopic composition, contains information on the formation temperature of CH$_4$ (Eiler, 2007; Ono et al., 2014; Wang et al., 2015). For CH$_4$ generated in shale and sedimentary basins this method apparently leads to realistic formation temperatures in contrast to CH$_4$ produced in lakes, swamps and cow rumens. This discrepancy was explained by a kinetic effect and thus a disequilibrium of hydrogen isotopic composition between the hydrogen source water and the produced CH$_4$. Thereby, the CH$_4$ clumped isotopic composition holds information on the reversibility of the CH$_4$ formation reaction.
Table 1.1: Isotopic source signatures and fractionation factors of the most common CH₄ emissions and atmospheric sinks.

<table>
<thead>
<tr>
<th>Category</th>
<th>Isotopic signature</th>
<th>Literature Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Microbial</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wetlands</td>
<td>-70 ± 20</td>
<td>-336 ± 44 Quay et al., 1999; Chanton, 2005</td>
</tr>
<tr>
<td>Ruminants</td>
<td>-60 ± 8</td>
<td>-310 ± 20 Quay et al., 1999; Klevenhusen et al., 2010</td>
</tr>
<tr>
<td>Rice paddies</td>
<td>-60 ± 12</td>
<td>-324 ± 34 Bergamaschi, 1997; Quay et al., 1999</td>
</tr>
<tr>
<td>Landfills</td>
<td>-56 ± 8</td>
<td>-301 ± 19 Bergamaschi et al., 1998a; Quay et al., 1999</td>
</tr>
<tr>
<td>Termites</td>
<td>-63</td>
<td>-390 Whiticar and Schaefer, 2007</td>
</tr>
<tr>
<td><strong>Thermogenic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural gas</td>
<td>-42 ± 11</td>
<td>-185 ± 20 Levin et al., 1999; Quay et al., 1999; Zazzeri et al., 2015</td>
</tr>
<tr>
<td>Coal</td>
<td>-52 ± 23</td>
<td>-165 ± 45 Kotarba and Pluta, 2009; Quay et al., 1999</td>
</tr>
<tr>
<td>Geological</td>
<td>-42</td>
<td>-200 Whiticar and Schaefer, 2007</td>
</tr>
<tr>
<td><strong>Pyrogenic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass burning</td>
<td>-23 ± 7</td>
<td>-225 ± 30 Chanton et al., 2000; Snover et al., 2000</td>
</tr>
<tr>
<td>Fuel burning</td>
<td>-15 ± 7</td>
<td>-134 ± 44 Nakagawa et al., 2005</td>
</tr>
<tr>
<td>Total sources</td>
<td>-53.3 ± 2.6</td>
<td>-283 ± 13 Snover et al., 2000 and therein</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>-53.5 ± 2.6</td>
<td>-283 ± 13 Snover et al., 2000 and therein</td>
</tr>
<tr>
<td>OH loss</td>
<td>-5.4,-9.9</td>
<td>-163,-231,-255 Snover et al., 2000 and therein</td>
</tr>
<tr>
<td>Stratospheric loss</td>
<td>-12.4,-0.6</td>
<td>-160 ± 14 Snover et al., 2000 and therein</td>
</tr>
<tr>
<td>Soil sinks</td>
<td>-22.1 ± 3.8</td>
<td>-81 ± 17 Snover et al., 2000 and therein</td>
</tr>
<tr>
<td>Total sinks</td>
<td>-6.8,-10.7</td>
<td>-158,-218,-239 Snover et al., 2000 and therein</td>
</tr>
</tbody>
</table>
1.2 Laser absorption spectroscopy

Laser spectroscopic techniques are widely used in a broad range of applications such as monitoring of air quality, atmospheric trace gas measurements, process control and surveillance in industrial applications, as well as in medical diagnostics. Recent developments on mid-infrared (MIR) laser sources and detectors triggered significant progress in instrumental performance making the optical measurement techniques a complementary analytical tool to the traditional techniques like gas chromatography and mass spectrometry (MS), with the advantage of better field applicability and higher high temporal resolution.

\[
\begin{array}{cccccc}
10^{-24} & 10^{-23} & 10^{-22} & 10^{-21} & 10^{-20} & 10^{-19} \\
\end{array}
\]

\[
\text{Linestrength \ [cm}^{-1}/\text{molecule*cm}^{-2}]
\]

\[
\begin{array}{cccccc}
6000 & 5000 & 4000 & 3000 & 2000 & 1000 & 0 \\
\end{array}
\]

\[
\text{Wavenumber \ [cm}^{-1}]
\]

\[
\begin{array}{cccccc}
700 & 600 & 500 & 400 & 300 & 200 & 100 & 0 \\
\end{array}
\]

\[
\text{meV}
\]

\[
\begin{array}{cccccc}
50 & 40 & 30 & 20 & 10 & 0 \\
\end{array}
\]

\[
\text{Absorption \ [%]}
\]

\[
\begin{array}{cccc}
\text{CH}_4 & \text{CH}_3D & \text{N}_2O & \text{CO}_2 & \text{H}_2O \\
\end{array}
\]

\[
\text{Restrahlen Window}
\]

\[
\text{THz-Range}
\]

\[
\text{Near-IR} \quad \text{Mid-IR}
\]

\[
\times 200
\]

\[
\text{Figure 1.6: Top: Overview of the spectra for the most abundant GHGs (including H}_2\text{O) at 100 mbar pressure and ambient mole fractions in the MIR and NIR range. On the bottom x - axis the wavenumber is given in cm}^{-1}, \text{while the top x - axis shows meV. Bottom: The linestrengths for CH}_4\text{ is up to 200 times larger in the MIR range, than in the NIR.}
\]

The absorption spectra of CO\textsubscript{2}, N\textsubscript{2}O, H\textsubscript{2}O and the three most abundant isotopologues of CH\textsubscript{4} are shown for the NIR and MIR in Figure 1.6. CH\textsubscript{4} has up to 200 times stronger absorption lines in the MIR range than in the NIR.

1.2.1 QCLAS for high precision atmospheric trace gas measurements

Since its invention, the advancements in QCL technology revolutionized MIR laser spectroscopy and both high-sensitivity and high-precision measurements of trace gases have been demonstrated (Curl et al., 2010; McManus et al., 2015).

Given their broad gain profiles, relatively high power, robust and stable operation at room temperature, and narrow line widths, QCLs represent a very attractive light source solution for the mid-infrared range, also known as molecular fingerprint region. QCLs are manufactured from material systems (InGaAs/AlInAs) that are commonly used for optoelectronic and high speed electronics applications, and are epitaxially grown on InP using commercial molecular beam epitaxy or metal-organic vapor phase epitaxy technology. Using a distributed feedback (DFB) grating grown into the active region of the laser, a monolithic device with single mode and narrow linewidth operation is achieved that is mandatory for high resolution laser spectroscopy.
Chapter 1. Introduction

The high output power (tens of mW) of the QCLs is the key factor for recent improvements in absorption spectroscopy as it allows deploying long path absorption cells with increased number of reflections. Several hundred of reflections can be implemented without being detector noise limited, even though the initial laser power is attenuated by more than 80%. In addition, the recent availability of thermoelectrically (TE) cooled mid-infrared detectors greatly facilitates the field applications of QCL-based instruments. Recently, both high-sensitivity and high-precision measurements of trace gases have been demonstrated. Relevant atmospheric trace gas mole fractions were measured with precisions in the parts-per-trillion (ppt) range, while isotope ratio measurement precisions on the order of one part in $10^4$ were demonstrated in field setups (Mohn et al., 2010; Mohn et al., 2012; Wolf et al., 2015). This capacity for continuous field measurement of isotopic ratios of atmospheric gases opens up new possibilities in atmospheric research.

1.2.2 Performance requirements for analysis of ambient CH$_4$ isotopologues

As a benchmark for the precision and accuracy requirements of ambient air isotopic CH$_4$-measurements, the WMO has released compatibility goals for background air and regionally focused studies (WMO/GAW, 2015). The goals are meant as a requirement for data quality and compatibility between laboratories. The WMO compatibility goals for background studies are 0.02‰ and 1‰ for $\delta^{13}$C- and $\delta^{2}$D-CH$_4$, respectively. Additionally, the WMO extended compatibility goals of 0.2‰ and 5‰ are intended for regionally focused studies with large local fluxes (WMO/GAW, 2015). Compatibility between two measurement techniques or laboratories in a meteorological sense means that “the absolute value of the difference between any pair of measured values from two different measurement results is within a chosen value which does not have to be the same as the total combined uncertainty” (WMO/GAW, 2015).

At present, the performance of leading IRMS laboratories is close to the range, where the WMO compatibility goals for background air are achievable, but only by repeated analysis of flask samples (Bock et al., 2014; Sperlich et al., 2012; Brass and Röckmann, 2010; Fisher et al., 2006). In addition, the WMO compatibility requirements for regionally focused studies can be fulfilled by IRMS on singular gas samples. However, as IRMS is basically a laboratory based technique, there is a need for a field-deployable high-precision analytical technique with the capability for simultaneous $\delta^{13}$C- and $\delta^{2}$D-CH$_4$ analysis.
Chapter 2

Methane preconcentration by adsorption: a methodology for materials and conditions selection

S. Eyer¹, B. Tuzson¹, N. P. Stadie², A. Borgschulte², L. Emmenegger¹, J. Mohn¹

¹Empa, Laboratory for Air Pollution & Environmental Technology, Dübendorf, Switzerland
²Empa, Laboratory Hydrogen & Energy, Dübendorf, Switzerland

Methane (CH₄) adsorption has been widely studied, mainly in the context of natural gas purification. A much less prominent, but highly relevant application is the preconcentration of CH₄ from ambient air. In this study, we compare six different commercial adsorbent materials with respect to their effectiveness for methane preconcentration: a macroporous polymeric resin (HayeSep D), multi-walled carbon nanotubes (MWCNT), two microporous metal-organic frameworks (HKUST-1 and ZIF-8), and two zeolites (5A and 13X). The most relevant properties, such as isosteric enthalpy of adsorption, specific surface area and the selectivity for CH₄ adsorption over N₂ were characterized by analyzing adsorption/desorption isotherms. Using these parameters, we discuss the tested adsorbents with respect to the most important properties and identify the most promising candidates. Furthermore we identify the experimental conditions that are expected to give the best results with respect to practical applications.

2.1 Introduction

Global warming resulting from anthropogenically emitted greenhouse gases (GHGs) is an important environmental issue. After CO$_2$, methane (CH$_4$) has the highest contribution to the greenhouse effect and on a per-molecule basis, its global warming potential is 25 times higher compared to CO$_2$ on a 100-year timescale (Ciais et al., 2014). Global CH$_4$ emissions are relatively well quantified, but the strength of the individual source components and their trends are not (Ciais et al., 2014). By measuring the stable isotopic composition of CH$_4$ in ambient air with high accuracy ($\approx 1$ ppt $= 10^{-12}$ mol/mol), the major source processes can be identified. The standard way to achieve such measurements is isotope-ratio mass-spectrometry, which is generally laboratory-based (Werner and Brand, 2001). However, recently developed infrared laser-based measuring systems are an attractive alternative, especially for field measurements. Such field measurements based on laser spectroscopy have been shown to yield reliable results at high temporal resolution for the stable isotopes of CO$_2$ (Tuzson et al., 2011; Tuzson et al., 2008). However, for the less abundant GHGs, such as N$_2$O and CH$_4$, preconcentration of the target species is required (Mohn et al., 2012; Mohn et al., 2010) to reach a precision of 0.1‰ for the ratio of the isotopologues. Otherwise analysis is limited to source studies at high mixing ratios (Wunderlin et al., 2013; Wunderlin et al., 2012; Köster et al., 2013). An efficient way for methane preconcentration is achieved by performing temperature cycles on suitable adsorbent materials (Bock et al., 2010). For continuous monitoring of CH$_4$ isotopologues in ambient air under field conditions, temperatures that do not require the use of liquid nitrogen are preferred.

High-precision laser spectroscopy by mid-infrared absorption comprises the usage of multipass absorption cells with a volume of up to one liter, generally at 1 - 10kPa (Mohn et al., 2012). The best spectroscopic precision is typically obtained at CH$_4$ mixing ratios of several hundred ppm. This implies the preconcentration by a factor $> 100$, given typical ambient mixing ratios of 1.8 ppm. For adsorptive preconcentration, it is necessary to use an adsorbent material with high CH$_4$ adsorption capacity, i.e., high specific surface area, and a high selectivity for CH$_4$ over N$_2$. Selectivity for CO$_2$ and H$_2$O is less important because these components can be quantitatively removed with a typical pretreatment (Mohn et al., 2012; Bock et al., 2010). Additionally, quantitative adsorption/desorption of the analyte is required to avoid kinetic isotopic fractionation effects due to subtle but characteristic differences in the enthalpy of adsorption of individual CH$_4$ isotopologues (Fayet et al., 1990; Phillips and Van Hook, 1967). The most frequently used preconcentration adsorbents for CH$_4$, N$_2$O and volatile organic compounds (VOC) are HayeSep polymers (Mohn et al., 2010; Bock et al., 2010; Reimann et al., 2008) and carbon-based materials (Thammakhet et al., 2005; Saridara et al., 2010; Wu et al., 2003; Wong et al., 2013; Dettmer and Engewald, 2002; Falkovich and Rudich, 2001). Recently, multi-walled carbon nanotubes (MWCNT) were reported to yield the highest uptake of a selection of carbon-based adsorbents (Saridara et al., 2010). Porous zeolites may also be a valuable alternative, because of their high surface area and high potential selectivity due to the molecular sieve effect (Yaremov et al., 2013; Delgado et al., 2013; Wang et al., 1998). For example, molecular sieves have been shown to be appealing for the application of CO$_2$/CH$_4$ separation (Lu et al., 2013). More recently, a different class of adsorbent materials known as metal-organic frameworks (MOFs), which exhibits exceptionally large specific surface areas, has shown to be highly promising for applications in gas storage and gas separation (Li et al., 1999; Li et al., 2009; Mendoza-Cortés et al., 2010; Düren et al., 2004; Wu et al., 2010; Möllmer et al., 2011). Using adsorbents under material-specific optimal conditions for selective CH$_4$ adsorption may greatly increase the performance of applications such as preconcentration of CH$_4$ from ambient air for laser spectroscopic analysis.

In this study, a selection of six promising commercially available adsorbents are compared regarding CH$_4$ adsorption amount, CH$_4$/N$_2$ selectivity and isosteric enthalpy: a macroporous polymeric resin (HayeSep D), MWCNT, two microporous metal-organic frameworks (HKUST-1 and ZIF-8), and two zeolites (5A and 13X). Adsorption measurements of CH$_4$ and N$_2$ at four temperatures between 77K and 296K were performed. The specific surface area was determined using N$_2$ and CH$_4$ adsorption isotherms at 77K, and the isosteric enthalpy was calculated using a model-independent method. This is to our knowledge the first systematic investigation of such a variety of different adsorbent materials for CH$_4$ with the aim of finding a material that is suitable for analytical applications.
2.2 Materials and methods

The investigated materials were obtained from the following sources: HayeSep D (100/120 mesh), the MOFs HKUST-1 (D50 15.96 μm) and ZIF-8 (D50 4.9 μm), as well as the zeolites Z5A and Z13X (both 100/120 mesh) from Sigma Aldrich (Switzerland). The MWCNT (> 95%, < 8 nm) were purchased from Cheap Tubes Inc (USA). All adsorption measurements were performed with a Belsorp Max (BEL Inc., Japan) volumetric Sieverts apparatus. Methane and nitrogen gas were obtained from Messer AG (Switzerland), with purities of 99.995% and 99.9999%, respectively.

During experiments, approximately 500 mg samples were held in a stable cold bath at temperatures of 296, 273, 196 and 77K (±0.2 K), corresponding to room temperature, ice water, dry ice and liquid nitrogen, respectively. Adsorption measurements were performed between 0 - 100 kPa and followed by desorption measurement at each temperature. For methane adsorption measurements at 77 K the pressure range was set to 0 - 1.8 kPa and desorption measurements were not possible, probably because the methane froze on the surface of the adsorbents. The accuracy of the volumetric Sieverts apparatus is determined by the resolution of the pressure gauge, among other factors. The overall uncertainty of an individual data point is approximately ±0.015 mmol/g upon repeated measurements.

2.3 Analysis

To determine the most suitable material for CH₄ preconcentration, specific uptake, selectivity and isosteric enthalpy of adsorption should ideally be investigated in a wide range of temperature and pressure. The relevant parameters may then be extracted from the measured isotherms and estimated for practical working conditions in the scheduled application. For this analysis, a fitting equation and/or model is necessary to interpolate the data. In the following sections, we briefly outline the methods used.

2.3.1 Adsorption models

The Langmuir model is the simplest model of physical adsorption of gas on a surface, beyond Henry’s law. It is useful for adsorption systems where the mechanism is monolayer-like and the adsorption sites are relatively homogeneous since only one binding energy is used. At low temperatures and on specific adsorbents where multiple layers cannot easily exist, it provides a good quality of fit to adsorption data and the isosteric enthalpy and specific surface area can be readily obtained (Gregg and Sing, 1991).

The Brunauer-Emmett-Teller (BET) model is an extension of the Langmuir model which allows for multilayer formation where the binding energy of sites in the second layer and higher is set equal to the heat of liquefaction. Beyond the initial point of multilayer formation (referred to as Point B), adsorption proceeds nearly linearly with respect to pressure, and the specific surface area of the adsorbent can thus readily be determined. This model is useful for characterizing a wide variety of sorbents at low temperature (usually with N₂ at 77 K) and although the limitations of this method have been widely discussed, it remains in common use due to its simplicity (Sing, 2001). For the purpose of this study, the low temperature adsorption measurements (77 K) were analyzed with both the Langmuir and the BET model to deduce adsorption surface areas. The quality of fit of both models is evaluated based on the residual of the fit given in the Online Resource.

However, adsorption models which can account for phenomena at higher temperatures and pressures are more complicated, as has been previously discussed in great detail (e.g. Bimbo et al., 2011). The data in this study were fitted, for example, with a generalized Langmuir type equation which can account for adsorption on heterogeneous surfaces. Though fits with even larger numbers of fitting parameters were attempted, the range of temperatures and pressures measured in this study were not conducive to its practical use. A common method for fitting adsorption data over a large range of temperature is to use a virial-type equation (2.1) (Czepirski and Jagieła, 1989; Stadie, 2013). This model-less approach is beneficial in that it relies on relatively few fitting parameters and retains a very simple expression for the isosteric enthalpy of adsorption.

\[
\ln \left( \frac{P}{n} \right) = \frac{1}{T} \sum_i a_i n_i + \sum_i b_i n_i^2
\]
where \( n \) is the molar amount of gas adsorbed per unit weight, \( p \) is the equilibrium pressure, \( T \) the temperature and \( a_i \) and \( b_i \) are the Virial coefficients of order \( i \). From this formula, the isosteric enthalpy is found by employing the Clausius-Clapeyron relation (2.2) (Stadie et al., 2013).

\[
-\Delta H_{\text{ads}} = R \left( \frac{\partial \ln p}{\partial (1/T)} \right) \approx R \sum_i a_i n_i
\]  

(2.2)

The temperature dependence of the isosteric enthalpy is not accessible in this method, and the pressure dependence is known to be susceptible to various pitfalls. For this reason, we focus on the value in the Henry’s law limit (\( p \rightarrow 0 \)) (2.3).

\[
-\Delta H_0 = R \lim_{n \to 0} \sum_i a_i n_i = Ra_0
\]  

(2.3)

The simplest approach, for comparison purposes, is to fit the adsorption data using a linear interpolation method and applying the simplified Clausius-Clapeyron equation (2.4).

\[
\ln(p) = -\frac{-\Delta H_{\text{ads}}}{RT} + \varepsilon
\]  

(2.4)

where \( R \) is the molar gas constant and \( \varepsilon \) is a constant. This is often unreliable for obtaining anything except an approximation of the isosteric enthalpy of adsorption (the Henry’s law value) via the Clausius-Clapeyron equation and relies on large numbers of data points to be successful (Stadie, 2013).

Once a fitting equation has been selected, the adsorptive selectivity between two gas species can also be estimated using gas uptake data. In this study, we focus on estimating the selectivity in two ways defined by the parameters \( X \) and \( Y \).

\[
X = \frac{n_{\text{CH}_4}(p,T)}{n_{\text{N}_2}(p,T)}
\]  

(2.5)

\[
Y = \frac{\Delta H_{\text{ads}}^{\text{CH}_4}}{\Delta H_{\text{ads}}^{\text{N}_2}} (p = 0, T)
\]  

(2.6)

Parameter \( X \) is the ratio of adsorption uptake of \( \text{CH}_4 \) and \( \text{N}_2 \) under identical conditions and \( Y \) is the ratio of the \( \Delta H_{\text{ads}} \) for \( \text{CH}_4 \) and \( \text{N}_2 \). The interpretation of these coefficients will be discussed in detail in section 2.4.4.

### 2.4 Results and discussion

From a phenomenological point of view, there is a considerable difference between the adsorption of gases at near ambient temperatures (above 196 K) and cryogenic temperature (77 K), where effects due to a nearly fully covered surface have to be taken into account. Therefore, we have chosen to focus on the temperature range of 196 - 296 K to determine isosteric enthalpy and selectivity, while the specific surface area was determined from the data measured at 77 K. With these important parameters, we discuss the possible application of the evaluated materials for preconcentration.

#### 2.4.1 Adsorption of \( \text{CH}_4 \) and \( \text{N}_2 \) in the Temperature Range of 196 to 296 K

At temperatures 196 K, 273 K and 296 K, all of the adsorbents exhibit Type I behavior with respect to \( \text{N}_2 \) and \( \text{CH}_4 \) adsorption (Gregg and Sing, 1991). In this temperature region the best global fit of adsorption data was obtained using the model-less virial approach in second order. Information on the model selection and the residual of the fits are given in the Online Resource. In Figures 2.1 - 2.6 the measured \( \text{CH}_4 \) and \( \text{N}_2 \) adsorption (closed symbols) and desorption isotherms (open symbols) are given. Based on the excellent agreement of adsorption and desorption measurements significant hysteresis effects can be excluded. The highest adsorption capacity for \( \text{CH}_4 \) and \( \text{N}_2 \) in the temperature range of 196 to 296 K was observed for HKUST-1. The zeolites exhibit a high adsorption capacity of \( \text{CH}_4 \) especially at low pressures (< 10kPa), but the difference in adsorption capacity of \( \text{CH}_4 \) and \( \text{N}_2 \) is significantly smaller than for the other candidate materials in this study.
Chapter 2. Methane preconcentration by adsorption

Figure 2.1: Adsorption isotherms of CH$_4$ and N$_2$ by HayeSep D at 196K, 273K and 296K. Filled symbols indicate adsorption and empty symbols indicate desorption measurement points.

Figure 2.2: Adsorption isotherms of CH$_4$ and N$_2$ by multi-walled carbon nanotubes (MWCNT) at 196K, 273K and 296K. Filled symbols indicate adsorption and empty symbols indicate desorption measurement points.

Figure 2.3: Adsorption isotherms of CH$_4$ and N$_2$ by HKUST-1 at 196K, 273K and 296K. Filled symbols indicate adsorption and empty symbols indicate desorption measurement points.

Figure 2.4: Adsorption isotherms of CH$_4$ and N$_2$ by ZIF-8 at 196K, 273K and 296K. Filled symbols indicate adsorption and empty symbols indicate desorption measurement points.
2.4.2 Isotherm enthalpy of adsorption

From the extracted fit coefficients, the isotherm enthalpy at zero adsorption amount ($\Delta H_0$) was determined using (2.3). Additionally, the isotherm enthalpy was calculated by a linear interpolation method at low adsorption amount and using (2.4). The results are presented in Table 2.1 and show that Zeolite 5A and HayeSep D have the highest enthalpy of methane adsorption while ZIF-8 exhibits the lowest (Figure 2.7). For $N_2$ the molecular sieves showed the highest enthalpy of adsorption and ZIF-8 the lowest. This will be discussed in more detail in section 2.4.4. In Table 2.1, the $\Delta H_0$ values calculated by the linear interpolation method are compared with those from the virial method.

2.4.3 Surface area

Figures 2.8 and 2.9 show the $N_2$ and $CH_4$ adsorption isotherms of the candidate materials at 77K. The data were fitted with both the Langmuir and the BET model, and the surface area was calculated according to convention (Gregg and Sing, 1991). The shape of the $CH_4$ isotherms are very similar to those of $N_2$, except that the saturation pressure is lower for $CH_4$. For $N_2$, the occupied surface area per molecule was taken to be 0.162 nm$^2$ (Gregg and Sing, 1991) and 0.1918 nm$^2$ for $CH_4$ (Chaix et al., 1996). The Langmuir model has a better agreement with the $N_2$ adsorption isotherms for the MOFs and the zeolites, presumably because of their monolayer-like adsorption behavior due to very narrow pores. For HayeSep D and MWCNT the $N_2$ and $CH_4$ adsorption curves show a multilayer behavior with a linear uptake according to Henry’s law above $\approx 2$ kPa; thus the BET-model is more suitable. This behavior can be rationalized by the macroporous structure of these materials. Table 2.1 shows the surface areas of materials calculated using the BET and the Langmuir method for both adsorbates. To indicate limited agreement between the experimental data and the model fit, some values are given in parentheses (see Online Resource for more information). The MOFs exhibit by far the highest surface of 1450 to 1700 m$^2$/g. MWCNT, on the other hand, show a relatively low surface area of 350 to 500 m$^2$/g.

2.4.4 Selectivity

Mixing ratios of $CH_4$ in background air are less than 2 ppm, compared to around 78% for $N_2$. In order to efficiently preconcentrate $CH_4$ to levels suitable for analysis, it is important that the adsorptive properties of the chosen adsorbent are largely superior for $CH_4$ over $N_2$. Thus, the adsorptive selectivity of $CH_4$ is perhaps the most important criterion for selection of an adsorbent for this purpose. This selectivity can be determined in several ways. A simplified and conventional approach is to compare $CH_4$ and
Chapter 2. Methane preconcentration by adsorption

**Figure 2.7:** Isosteric enthalpy as a function of CH$_4$ adsorption amount in mmol/g estimated by a linear interpolation method and applying the Clausius-Clapeyron equation (2.4).

**Figure 2.8:** Adsorption isotherms of N$_2$ at 77K for all candidate materials. Experimental data is fitted with the Langmuir and the BET model in order to extract the surface area.

**Figure 2.9:** Adsorption isotherms of CH$_4$ at 77K for all candidate materials. Experimental data is fitted with the Langmuir and the BET model in order to extract the surface area.
N\textsubscript{2} adsorption capacity, determined in separate experiments but under identical conditions (Wiersum et al., 2013). For example selectivities of various MOFs and other materials for different gas compounds have been investigated by comparing the equilibrium adsorption capacity at specific conditions (Li et al., 2009; Pawar et al., 2009). In cation-exchanged zeolite mordenite and MOFs, selective properties have been quantified by taking the ratio of the Henry’s constants or comparing the isosteric enthalpy of adsorption of each gas (Peter et al., 2005; Liu et al., 2008; Möllmer et al., 2011). More sophisticated methods of measuring the selectivity of CH\textsubscript{4} adsorption over N\textsubscript{2} adsorption are also reported, for example breakthrough measurements, however these experiments are tailored to specific process conditions and require elaborate experimental apparatus beyond the scope of this study.

In this study, we focus on estimating the selectivity in two ways defined by the parameters X and Y, which are given by Eq. (2.5) and (2.6). As mentioned before, both values are mainly discussed for a comparative assessment of candidate adsorbents. Variable X gives the ratio of the binding energy of a distinct adsorbent for CH\textsubscript{4} in relation to N\textsubscript{2} gas. Variable Y stands for the ratio of capacity at 196K and 100kPa for CH\textsubscript{4} relative to N\textsubscript{2}. This value is particularly interesting, as it represents the selectivity near the saturation point, where Henry’s law is less dominant. The respective ratios X and Y are given in Table 2.1, which reveals that both approaches are in good agreement. HayeSep D and ZIF-8 show the most promising properties in terms of selectivity. Due to its weaker $\Delta H_{ads}$, one must consider, however, that ZIF-8 is not saturated at 100kPa for either gas component and thus the ratio of adsorption of CH\textsubscript{4} and N\textsubscript{2} in this pressure range is not fully comparable to the other materials. This means that the value of Y is more significant for ZIF-8 in terms of selectivity and, thus, HayeSep D shows the best selectivity of all materials, followed by ZIF-8, HKUST-1 and MWCNT. A similar conclusion can be drawn from Figure 2.11, where the adsorption ratio have been calculated continuously in the range of 0-100kPa and 200-300K using the virial equation fits. While one must exercise caution when interpolating the data taken from only three isotherms, Figure 2.11 is meant to show a qualitative comparison of the effects of temperature and pressure on the selectivity of each material. There are two main conclusions drawn from this plot. First, HayeSep D offers the most promising selective properties under most conditions while the molecular sieves show the least, which is consistent with the information derived from the isosteric enthalpy of adsorption for CH\textsubscript{4} and N\textsubscript{2}. Secondly, the selective behavior of the adsorbents studied is more or less constant in the analyzed temperature and pressure regime, with one exception: namely, HayeSep D at low pressures and temperatures. In this region, HayeSep D exhibits an enhanced selectivity compared to the other candidate materials which can be directly evidenced in the measured isotherms at 196K. Zeolites 5A and 13X exhibit a low selectivity, with $\Delta H_{ads}$ being higher for N\textsubscript{2} than for CH\textsubscript{4}, which excludes them from being suitable candidates for this application.

### 2.4.5 Temperature behavior

To optimize the effectiveness of a preconcentration unit, it is important to find the ideal regime where selectivity and adsorption capacity are optimized for both adsorption, and desorption conditions. Such optimization processes have been useful in other reported applications (Wurzbacher et al., 2011; Harpalani et al., 2006). For example, thermogravimetric measurements on functionalized silica-gel were fitted to isotherm models and the results successfully applied to predict desorption capacities and optimize a temperature-vacuum swing process to capture CO\textsubscript{2} (Wurzbacher et al., 2011). Using the fitted isotherm data, it is possible to construct new isotherms within the regime measured to identify the best temperature ranges for obtaining maximum adsorption capacity and rapid desorption. Figure 2.10 shows the CH\textsubscript{4} adsorption isotherms of all adsorbent materials as a function of pressure and temperature; temperatures below 200K are found to be most promising because the adsorption capacity increases considerably with decreasing temperature, while the CH\textsubscript{4}/N\textsubscript{2} selectivity increases or stays more or less constant (Figure 2.11). This is particularly noticeable in the low pressure regime, while at atmospheric pressures CH\textsubscript{4} adsorption may saturate.

The practicality of lowering the adsorption temperature, however, is limited by cooling power of the system and the possibility of affecting other components. The two MOF candidates show a similar CH\textsubscript{4} adsorption behavior at 77K (Figure 2.9), but HKUST-1 has a much higher adsorption capacity at 196K (Figure 2.10). This is attributed to the low isosteric enthalpy of adsorption of ZIF-8 for CH\textsubscript{4} (Table 2.1). Therefore, ZIF-8 may be a promising adsorbent for methane preconcentration when the necessary cooling conditions are available.
Table 2.1: Physical properties of the tested adsorbents for CH\textsubscript{4} and N\textsubscript{2}

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm\textsuperscript{3})</th>
<th>BET surface (m\textsuperscript{2}/g)</th>
<th>Langmuir surface (m\textsuperscript{2}/g)</th>
<th>(\Delta H_0^{\text{CH}_4}) (virial) (kJ/mol)</th>
<th>(\Delta H_0^{\text{CH}_4}) (interpolation) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HayeSep D</td>
<td>0.33\textsuperscript{a}</td>
<td>850 - 900 (1200 - 1400)</td>
<td>19.9</td>
<td>21.0</td>
<td></td>
</tr>
<tr>
<td>MWCNT</td>
<td>0.21\textsuperscript{b}</td>
<td>500 (550)</td>
<td>15.8</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td>HKUST-1</td>
<td>0.35\textsuperscript{a}</td>
<td>1500 - 2200 (5000+)</td>
<td>15.7</td>
<td>15.1</td>
<td></td>
</tr>
<tr>
<td>ZIF-8</td>
<td>0.35\textsuperscript{a}</td>
<td>1250 - 1750 (2000)</td>
<td>14.0</td>
<td>12.5 - 13.5</td>
<td></td>
</tr>
<tr>
<td>Z5A</td>
<td>0.72\textsuperscript{a}</td>
<td>(552)</td>
<td>21.2</td>
<td>21.0</td>
<td></td>
</tr>
<tr>
<td>Z13X</td>
<td>0.65\textsuperscript{a}</td>
<td>(510)</td>
<td>18.3</td>
<td>17.6</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm\textsuperscript{3})</th>
<th>BET surface (m\textsuperscript{2}/g)</th>
<th>Langmuir surface (m\textsuperscript{2}/g)</th>
<th>(\Delta H_0^{\text{N}_2}) (virial) (kJ/mol)</th>
<th>(\Delta H_0^{\text{N}_2}) (interpolation) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HayeSep D</td>
<td>600 - 700 (640)</td>
<td>12.6</td>
<td>13.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MWCNT</td>
<td>350 - 400 (350 - 400)</td>
<td>14.1</td>
<td>16.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HKUST-1</td>
<td>(1450 - 1550)</td>
<td>14.1</td>
<td>14.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZIF-8</td>
<td>(1450 - 1600)</td>
<td>1700</td>
<td>11.4</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td>Z5A</td>
<td>(462)</td>
<td>537</td>
<td>26.1</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>Z13X</td>
<td>(540)</td>
<td>628</td>
<td>18.3</td>
<td>18.9</td>
<td></td>
</tr>
</tbody>
</table>

Selectivity

<table>
<thead>
<tr>
<th></th>
<th>CH\textsubscript{4} adsorption\textsuperscript{c} (mmol/g)</th>
<th>N\textsubscript{2} adsorption\textsuperscript{c} (mmol/g)</th>
<th>Selectivity (X) (n_{\text{CH}<em>4}/n</em>{\text{N}_2})</th>
<th>(\Delta H_0^{\text{CH}_4}) (kJ/mol)</th>
<th>(\Delta H_0^{\text{N}_2}) (kJ/mol)</th>
<th>Selectivity (Y) (\Delta H_0^{\text{CH}_4}/\Delta H_0^{\text{N}_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HayeSep D</td>
<td>1.78</td>
<td>0.49</td>
<td>3.7</td>
<td>19.9</td>
<td>12.6</td>
<td>1.6</td>
</tr>
<tr>
<td>MWCNT</td>
<td>1.45</td>
<td>0.51</td>
<td>2.9</td>
<td>15.8</td>
<td>14.1</td>
<td>1.1</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>10.71</td>
<td>3.80</td>
<td>2.8</td>
<td>15.7</td>
<td>14.1</td>
<td>1.1</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>4.02</td>
<td>0.77</td>
<td>5.2</td>
<td>14.0</td>
<td>11.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Z5A</td>
<td>3.42</td>
<td>2.63</td>
<td>1.3</td>
<td>21.2</td>
<td>26.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Z13X</td>
<td>3.14</td>
<td>2.10</td>
<td>1.5</td>
<td>18.3</td>
<td>18.3</td>
<td>1.0</td>
</tr>
</tbody>
</table>

\*Values in parentheses indicate limited agreement between the experimental data and the model.

\textsuperscript{a}Sigma Aldrich, \textsuperscript{b}Cheap tubes Inc.

\*Values in parentheses indicate limited agreement between the experimental data and the model.

\textsuperscript{c}: Excess adsorption amount at 100 kPa at 196K for CH\textsubscript{4} and N\textsubscript{2} respectively.
Practically, the desorption temperature can be as high as necessary. A temperature of $\approx 273 \, \text{K}$ should be sufficient to desorb 99.99% of the captured $\text{CH}_4$, as it has showed to be an ideal regime for the desorption of $\text{N}_2\text{O}$ from HayeSep D (Mohn et al., 2010). The optimal desorption temperature is likely to follow with the isosteric enthalpy of adsorption for $\text{CH}_4$, so that for example ZIF-8 would retain even less $\text{CH}_4$ than HayeSep D at $\approx 273 \, \text{K}$.

### 2.4.6 Co-adsorption

Methane adsorption from ambient air represents a big challenge as a very small volumetric mixing ratio around $2 \times 10^{-6}$ has to be separated from many other gases, such as $\text{N}_2$ (78%), oxygen (20.9%), argon (0.9%), water vapor (variable content), carbon dioxide ($400 \times 10^{-6}$) and nitrous oxide ($0.3 \times 10^{-6}$). The focus of the presented study was on the separation of $\text{CH}_4$ from $\text{N}_2$, which is by far the dominating component in ambient air. With respect to our target application it is not necessary to address possible co-adsorption differences between the materials with respect to oxygen ($\text{O}_2$), argon (Ar) and other noble gases, assuming that in a first approximation, the effects will be similar for the materials studied. Nonetheless, additional experiments on the separation of $\text{O}_2$ and Ar may be needed for other applications. Similarly, the adsorption of carbon dioxide ($\text{CO}_2$) and water vapor ($\text{H}_2\text{O}$) is of minor importance because both are routinely removed prior to $\text{CH}_4$ adsorption in the envisaged analytical applications (Mohn et al., 2010; Bock et al., 2010). Nitrous oxide ($\text{N}_2\text{O}$) has much lower ambient air mixing ratios and a higher boiling point than $\text{CH}_4$. Therefore, it is of lower importance and could be separated by selective desorption.

### 2.4.7 Limits of the approach

Additionally to the limits mentioned in section 2.4.4 and 2.4.6 there are also other considerations to make for this approach. The proposed material selection methodology focuses entirely on adsorptive selectivity, but does not consider any other properties which may be relevant, such as dispersion coefficients or...
Figure 2.11: Three-dimensional plot of the CH$_4$/N$_2$-Selectivity as a function of pressure and temperature for all materials generated from virial modeling of isotherms.

thermal conductivity (Wiersum et al., 2013; Saridara et al., 2010). The former is due to the kinetic behavior of gases inside the pores and is thus related to the pore-size distribution of the adsorbent. The kinetic behavior of gases inside the pores of zeolites is well known, and also investigated for MOFs (Yaremov et al., 2013; Li et al., 2009). Thermal conductivity is important in order to remove the large amount of heat being added to the system by the adsorbed gas. While these general material properties may be known, the behavior of a specific setup is difficult to predict. Therefore, these properties are best determined in breakthrough experiments which reflect the conditions that are expected for the target preconcentration setup. Our approach is based on the approximation of the selectivity of CH$_4$ over N$_2$. While this is a valuable first approximation, it may not reflect the full complexity of the kinetic effects that are present during methane preconcentration of ambient air.

2.5 Conclusion

In this study we have systematically evaluated six adsorbent materials for the application of high volume preconcentration of ambient air, with the aim of categorizing each material in adsorption capacity and CH$_4$/N$_2$-selectivity. For effective high volume preconcentration, the overall adsorption capacity becomes a critical parameter in addition to CH$_4$/N$_2$-selectivity. Thus, HKUST-1 is highly promising due to its good selectivity and exceptional total adsorption capacity compared to HayeSep D. ZIF-8 also exhibits a high surface area, which is similar to HKUST-1, and even better selective properties. However, due to the weak binding interaction of ZIF-8 with CH$_4$, its adsorption capacity is lower compared to HayeSep D in the low pressure and high temperature regime. MWCNT exhibits a good selectivity, but the overall adsorption capacity is much lower then HayeSep D or HKUST-1. Carbon nanotubes with higher surface areas could therefore also be promising materials, especially because of their high thermal conductivity (Saridara et al., 2010; Han and Fina, 2011). The zeolites have a low adsorption capacity and the lowest selectivity making them the least suitable candidates according to this study.

In conclusion, our data confirms that HayeSep D, a frequently used adsorbent for analytical preconcentration applications, is a suitable choice. It has a respectable adsorption capacity and the highest overall selectivity. The optimal adsorbent, however, would have a higher surface area combined with the isosteric enthalpy and selectivity of HayeSep D. We therefore suggest that a microporous equivalent of
HayeSep D would be an ideal future material for this purpose. The approach used in this study is suitable for identifying candidate materials for high volume preconcentration of CH$_4$ from ambient air, and can easily be extended by additional gas compounds such as O$_2$, Ar and N$_2$O, as well as to other applications.

2.6 Acknowledgments

Funding from the Swiss National Foundation for Scientific Research (SNF) and the EU funded INGOS is gratefully acknowledged. We thank Prof. Ulrich Müller from BASF and Prof. Hubertus Fischer from University of Bern for helpful discussions.
Chapter 3

Real-time analysis of $\delta^{13}$C- and $\delta$D-CH$_4$ in ambient air with laser spectroscopy: method development and first intercomparison results

S. Eyer$^1$, B. Tuzson$^1$, M. E. Popa$^2$, C. van der Veen$^2$, T. Röckmann$^2$, M. Rothe$^3$, W. A. Brand$^3$, R. Fisher$^4$, D. Lowry$^5$, E. G. Nisbet$^4$, M. S. Brennwald$^5$, E. Harris$^1$, C. Zellweger$^1$, L. Emmenegger$^1$, H. Fischer$^6$, J. Mohn$^1$

$^1$Empa, Laboratory for Air Pollution & Environmental Technology, Dübendorf, Switzerland; $^2$Utrecht University (UU), Institute for Marine and Atmospheric research Utrecht (IMAU), Utrecht, the Netherlands; $^3$Max-Planck-Institute (MPI) for Biogeochemistry, Jena, Germany; $^4$Royal Holloway University of London (RHUL), Department of Earth Sciences, Egham, UK; $^5$Eawag, Water Resources and Drinking Water, Dübendorf, Switzerland; $^6$University of Bern, Climate and Environmental Physics, Bern, Switzerland

In situ and simultaneous measurement of the three most abundant isotopologues of methane using mid-infrared laser absorption spectroscopy is demonstrated. A field-deployable, autonomous platform is realized by coupling a compact quantum cascade laser absorption spectrometer (QCLAS) to a preconcentration unit, called TRace gas EXtractor (TREX). This unit enhances CH$_4$ mole fractions by a factor of up to 500 above ambient levels and quantitatively separates interfering trace gases such as N$_2$O and CO$_2$. The analytical precision of the QCLAS isotope measurement on the preconcentrated (750ppm, parts-per-million, $\mu$mole/mole) methane is $0.1\%e$ and $0.5\%e$ for $\delta^{13}$C- and $\delta$D-CH$_4$ at 10 min averaging time.

Based on repeated measurements of compressed air during a two-week intercomparison campaign, the repeatability of the TREX-QCLAS was determined to be $0.19\%e$ and $1.9\%e$ for $\delta^{13}$C and $\delta$D-CH$_4$, respectively. In this intercomparison campaign the new in situ technique is compared to isotope-ratio mass-spectrometry (IRMS) based on glass flask and bag sampling and real time CH$_4$ isotope analysis by two commercially available laser spectrometers. Both laser-based analyzers were limited to methane mole fraction and $\delta^{13}$C-CH$_4$ analysis, and only one of them, a cavity ring down spectrometer, was capable to deliver meaningful data for the isotopic composition. After correcting for scale offsets, the average difference between TREX-QCLAS data and bag/flask sampling-IRMS values are within the extended WMO compatibility goals of $0.2\%e$ and $5\%e$ for $\delta^{13}$C- and $\delta$D-CH$_4$, respectively. This also displays the potential to improve the interlaboratory compatibility based on the analysis of a reference air sample with accurately determined isotopic composition.

Accepted for publication in Atmospheric Measurement Techniques
3.1 Introduction

Methane (CH₄) is the second most important anthropogenically emitted greenhouse gas after carbon dioxide (CO₂). Its globally averaged mole fraction has increased from around 722 ppb (parts-per-billion, nmole/mole) in pre-industrial times to 1824 ppb in 2013 and the anthropogenic fraction is estimated to be 60% of the total emissions (MacFarling Meure et al., 2006; WMO/GAW, 2015). While the tropospheric methane mole fraction and the most important sources, such as wetlands, ruminants, rice agriculture, fossil fuel production, landfills, and biomass burning, are relatively well known, considerable uncertainty remains regarding the strength and spatio-temporal variability of individual sources (Dlugokencky et al., 2011; Ciais et al., 2014; Manning et al., 2011; Rigby et al., 2012). A promising approach to improve the understanding of the CH₄ budget is the use of isotopologues to distinguish between various CH₄ source processes (Beck et al., 2012; Bergamaschi et al., 1998b; Fischer et al., 2008; Fisher et al., 2006; Nisbet et al., 2014). The isotopic composition is reported in the δ-notation, representing the relative difference in the amount of heavy vs. light isotope of a sample in relation to an international measurement standard (Brand2012,Coplen2011,Urey1948):

$$\delta^{13}C = \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1,$$

where $R$ represents the ratio $[^{13}\text{CH}_4]/[^{12}\text{CH}_4]$ in the case of $\delta^{13}C$, and analogously $[\text{CH}_4D]/[\text{CH}_4]$ for $\deltaD$. The international isotopic standards are Vienna Pee Dee Belemnite (VPDB) for $\delta^{13}C$ and Vienna Standard Mean Ocean Water (VSMOW) for $\deltaD$ (Werner and Brand, 2001 et al.). Measuring $\delta^{13}C$- and $\deltaD$-CH₄ is a great challenge, as the heavy isotopologues have low natural abundance, i.e. 1.1% for $^{13}\text{CH}_4$ and 0.06% for CH₄D of total CH₄ in the atmosphere. Nevertheless, combining the analysis of the CH₄ mole fraction and its isotopic composition with inverse modeling techniques and chemical transport models has the potential to validate emission scenarios (Monteil et al., 2011). Current modeling efforts, however, are restricted by the limited continuity and temporal resolution of $\delta^{13}C$-CH₄ measurements and the limited availability of $\deltaD$-CH₄ data (Monteil et al., 2011). This was confirmed by an observing system simulation experiment, showing significant reduction in the uncertainty of emission estimates from major national and global CH₄ source categories in the case of model-generated availability of real-time high-precision measurements for $\delta^{13}C$- and $\deltaD$-CH₄ data (Rigby et al., 2012). A critical requirement for such an observing system is the availability of a suitable high-precision measurement technique. Currently, IRMS is the standard technique to perform high-precision analysis of $\delta^{13}C$- and $\deltaD$-CH₄ in ambient air (Bock et al., 2014; Brass and Röckmann, 2010; Fischer et al., 2008; Sapart et al., 2012; Schmitt et al., 2014; Bock et al., 2010). Being a laboratory based technique, it relies on flask sampling, which severely limits its temporal and spatial resolution capability. Furthermore, the analysis of both isotope ratios requires two separate instruments with corresponding sample preparation.

Laser spectroscopy in the mid-infrared (MIR) spectral range has emerged as a powerful alternative for the analysis of stable isotopes of CO₂ (Sturm et al., 2013), N₂O (Köster et al., 2013; Mohn et al., 2012) and CH₄ (Bergamaschi et al., 1994; Bergamaschi et al., 1998b; Bergamaschi et al., 1998a; Santoni et al., 2012). This development has been triggered by the invention and availability of quantum cascade lasers (QCL), which offer high optical power in continuous wave operation at room temperature (Faist, 2006; Faist et al., 2002). This enables the realization of compact, field-deployable instruments for real-time analysis at ppt (parts-per-trillion, pmole/mole) level precision (Curl et al., 2010; McManus et al., 2010). However, high-precision measurements of low abundance isotopic species of trace gases (such as $\deltaD$-CH₄) at ambient mole fractions require preconcentration when using direct absorption techniques (Bergamaschi et al., 1998b). The strategy of trace gas preconcentration prior to isotopic analysis by quantum cascade laser spectroscopy (QCLAS) has been demonstrated for nitrous oxide (N₂O) isotopologues (Mohn et al., 2010; Mohn et al., 2012) and was applied in an extended field campaign (Wolf et al., 2015a).

In this paper, we present further improvements of coupling a preconcentration unit (TRace gas EXtractor, TREX) to QCLAS to achieve real-time, high-precision measurements of methane isotopic composition ($\delta^{13}C$-CH₄, $\deltaD$-CH₄) in ambient air. We provide details on the preconcentration with TREX and present results of CH₄ isotopologues analysis with QCLAS. The potential of the TREX-QCLAS technique to trace changes in ambient CH₄ isotopic composition was further demonstrated in an interlaboratory comparison campaign. Results are discussed with respect to the scientifically desirable level of compatibility between laboratories for future applications on both near-source studies and measurements.

$$\delta^{13}C = \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1,$$
of unpolluted air (WMO/GAW, 2013). Additionally, the need for whole air isotopologue reference gases with well calibrated CH$_4$ mole fraction and isotopic composition to improve compatibility of measurements performed in different laboratories is discussed.

3.2 Experimental

3.2.1 Preconcentration and analysis of CH$_4$ isotopologues by TREX-QCLAS

Requirements for the preconcentration system

The main analytical challenge in the present work is the quantification of the CH$_4$D isotopologue considering its very low natural abundance. A further constraint is given by the spectroscopic setup, as the same optical platform is used for simultaneous measurements of the $^{12}$CH$_4$, $^{13}$CH$_4$ and CH$_3$D isotopologues. This unavoidably involves compromises regarding the spectroscopic configuration, in particular the selected optical path length and the amount of trace gas needed to achieve the necessary measurement precision for both isotope ratios. Simulation of CH$_4$ absorption spectra in the target spectral regions indicated that optimal conditions are realized at a sample gas pressure in the range of 20 to 60hPa and for mole fractions ranging from 600 up to 1000ppm CH$_4$. Since the CH$_4$ mole fraction in ambient air is generally in the order of 1.8 ppm, the TREX system had to be designed to selectively extract CH$_4$ from several liter of ambient air and concentrate into a gas volume of around 20mL (e.g. equivalent to the amount of gas in the 0.5L absorption cell of the laser spectrometer at a pressure of 40hPa). In order to fulfill the above requirements, significant developments and innovative solutions for both TREX and QCLAS have been accomplished.

TREX: design

![Diagram of the preconcentration unit (TREX)](image)

**Figure 3.1:** Schematics of the preconcentration unit (TREX). The blue lines indicate the flow of sample air and TG, i.e. ambient air CH$_4$ mole fractions, while red lines represent the flow of calibration gases and desorbed air, i.e. high CH$_4$ mole fraction. MFC 1-4 and V1-4 stand for mass flow controllers and 2-position valves, respectively.
The basic technology of the TREX (Fig. 3.1) is based on the “Medusa” system (Miller et al., 2008), which was later adopted for the preconcentration of N\textsubscript{2}O and its subsequent isotope analysis by QCLAS (Mohn et al., 2010; Mohn et al., 2012; Mohn et al., 2013; Mohn et al., 2014; Waechter et al., 2008; Wolf et al., 2015a). The main advantages over previously developed systems (Brand, et al. 1995) are the low trapping temperatures in combination with its independence from liquid nitrogen. Preconcentration is achieved by temperature swing adsorption on a cold trap, filled with a specific adsorbent material. The trap is first cooled down to a temperature at which its dynamic adsorbing capacity for the target substance (here CH\textsubscript{4}) is sufficiently large, while the majority of the remaining bulk gases (e.g. N\textsubscript{2}, O\textsubscript{2}, Ar) pass through. During desorption, the trap is heated stepwise to separate the target substance from co-adsorbed interfering compounds. To minimize kinetic fractionation effects, it is important to adsorb and desorb the target substance quantitatively, i.e. with nearly 100% recovery and with a high degree of reproducibility, as discussed below.

Given the low boiling point temperature of CH\textsubscript{4} (112K) as an indication for its volatility, the original design of the preconcentration system required major revisions in terms of cooling power to enhance its CH\textsubscript{4} adsorption capacity. In addition, the layout was designed to fit in a compact and field-deployable 19” rack system. These two requirements led to a novel approach for the trap assembly.

Empirical investigations on the previous preconcentration unit (Mohn et al., 2010) with various trap models adsorbing CH\textsubscript{4} at different temperatures showed that for a complete and reliable CH\textsubscript{4} recovery, the amount of adsorbent material (HayeSep D, Sigma Aldrich, Switzerland) had to be increased by ten-fold. This resulted in 1.8g of HayeSep D filled in a stainless steel tubing (length 90cm, OD 4mm, wall thickness 0.5mm, volume 6.4cm\textsuperscript{3}) and bracketed with glass wool (BGB Analytics AG, Switzerland) and wired mesh. HayeSep D has previously been identified as an excellent high capacity adsorbent material for CH\textsubscript{4} (Eyer et al., 2014). The tubing is curled around a custom-made cylindrical aluminum standoff (outer diameter 70mm, height 28mm) with an optimized wall thickness of 0.5mm. A thermal conductance paste (340 HSC, Dow Corning Inc., USA) is applied at the contact region between trap and standoff to improve heat dissipation. To further increase the adsorption capacity of the trap, the trap temperature had to be decreased to 100K, which was not achievable with the previous preconcentration unit. Therefore, we decided for a compact Stirling cryo-cooler with a cooling capacity of > 20W at 100K (CryoTel GT, Sunpower Inc., USA) gaining in terms of size, weight and cooling performance, with respect to the standard refrigeration unit (PCC: Polycold Compact Cooler, Brooks Automation, USA) employed in the Medusa preconcentration device (Miller et al., 2008). A copper plate disk (diameter 14cm, weight 1.4kg) was mounted on the cold-tip of the cooler, serving as a cold-plate with large heat capacity. Furthermore, we minimized the thermal cycle time of the trap for repeated adsorption/desorption processes through a design in which the trap is movable by a linear actuator (ZLD225MM, VG Scienta Ltd, UK). During cooling, the actuator pushes the aluminum standoff against the cold-plate. The contact pressure is adjusted to 100N using a chromium-steel corrugated spring (WF-8941-SS, Durovis AG, Switzerland) placed centrically between actuator and standoff. The flat bottom surface of the aluminum standoff and the copper cold-plate were polished and coated with a thin layer of heat conductance paste (340 HSC, Dow Corning Inc., USA) to improve thermal contact. Before heating, the standoff is decoupled from the cold-plate. This approach is overall faster and yields lower trap temperatures compared to the previous preconcentration unit, because the cold plate and the Stirling cooler is completely undisturbed during the heating process.

For thermal isolation of the system, the core parts of the unit, i.e., the cold-tip of the Stirling cooler, the cold-plate, and the trap are housed in a custom-made vacuum chamber evacuated to < 10\textsuperscript{-4} mbar with a compact turbomolecular pump station (HiCube 80 Eco, Pfeiffer Vacuum GmbH, Switzerland). The TREX unit is controlled and monitored by a custom-developed LabVIEW program (National Instruments Corp., USA) with a graphical user interface. All peripherals are connected through a 16-port serial-to-ethernet connector (Etherlite 160, Digi International Inc., USA).
Chapter 3. Real-time analysis of $\delta^{13}$C- and $\delta$D-CH$_4$ in ambient air with laser spectroscopy

TREX: preconcentration procedure

![Diagram of the preconcentration unit (TREX) showing the flow of sample air and calibration gases.]

The overall CH$_4$ preconcentration cycle can be divided into three main phases, as illustrated by Fig. 3.2: CH$_4$ adsorption (phase I, 25 min), CH$_4$ desorption (phase II, 15 min) and trap conditioning (phase III, 5 min). At the onset of phase I, the trap is brought in contact with the cold-plate by the actuator. It takes about 15 min for the trap to cool down to a temperature of 101 K. CH$_4$ adsorption is initiated by switching the 6-port multi-position rotary valve (Valco Instruments Inc., Switzerland) to the adsorption position as shown in Fig. 3.1. Dehumidified (nafion drier with dew point <230 K, PD-50T-72MSS, Perma Pure, USA), particle-filtered (2-micron filter, SS-4FW-2, Swagelok, Switzerland) sample gas is pushed through the cooled trap with a membrane pump (PM 25012-022, KNF, Switzerland) at a pressure of 4000 hPa. The sample gas flow is adjusted downstream of the trap to a flow rate of 900 mL min$^{-1}$ using a mass flow controller (MFC 1, Vögtlin Instruments, Switzerland). After 500 s, corresponding to preconcentration of 7.5 L sample gas, the 6-port rotary valve is switched to the desorption position.

In phase II (CH$_4$ desorption), the linear actuator decouples the trap from the copper cold-plate with the 6-port rotary valve set to the desorption position (Fig. 3.1). Step-wise desorption enables quantitative separation of the target substance CH$_4$ from more volatile gases (e.g. traces of N$_2$, O$_2$) and less volatile trace gases, e.g. CO$_2$ and N$_2$O. To avoid that the latter gases, which are mainly adsorbed on the front part of the trap, are released when the ends of the trap heat up, the flow direction in the desorption step is forward. The trap temperature during phase II is stepwise increased. Immediately after decoupling, its temperature increases from around 106 to 113 K without heating. Then, the trap temperature is raised first to 145 K and then to 175 K by heating with a round flexible polyimide heat foil (diameter 62.2 mm, 100 W, HK5549, Minco Products Inc., USA) placed centrically at the bottom of the aluminum standoff and controlled by a PID temperature controller (cTron, Jumo Mess- und Regeltechnik AG, Switzerland). During this period, mainly volatile bulk gases (e.g. N$_2$, O$_2$, Ar) with low boiling points (77 to 90 K) are desorbed from the trap and vented through the QCLAS multipass cell. The CH$_4$ desorption is initiated by increasing the trap temperature to 258 K and purging with 2 mL min$^{-1}$ high-purity synthetic air (20.5% O$_2$ in N$_2$, purity 99.999%, Messer Schweiz AG). In parallel, a two-way solenoid valve (series 9, Parker Hannifin Corp., USA) at the outlet of the evacuated QCLAS gas cell is closed; the desorbed methane is thus accumulated in the cell. When the pressure in the QCLAS absorption cell reaches 39.64 ± 0.04 hPa...
(Baratron 700B, MKS Instruments, USA), the solenoid valve at the inlet of the cell is closed, isolating the desorbed CH$_4$ in the cell for subsequent analysis.

After CH$_4$ desorption, phase III (conditioning) is initiated, in which the residual, less volatile trace gases are removed from the HayeSep D trap to assure reproducible starting conditions for each pre-concentration cycle. This is achieved by heating the trap to 323K and purging it for 5 min at reduced pressure (via V3, N920APE, KNF, Switzerland) with 25 mL min$^{-1}$ high-purity synthetic air in backward flow direction. Thereby, residual gas compounds such as H$_2$O, N$_2$O, CO$_2$, and VOCs are removed. The preconcentration cycle is completed by turning the 6-port rotary valve to isolate the HayeSep D trap.

### QCLAS

![Figure 3.3: Measured absorption spectra for the determination of $\delta^{13}$C- (left) and $\delta$D-CH$_4$ (right) along with the spectral fit using Voigt-profiles and the corresponding line-strengths from the HITRAN database. Potential interferences are expected mainly from N$_2$O and H$_2$O. The spectral line of N$_2$O is divided by a factor of 1000 to fit in the graph, evidencing that even N$_2$O-mole fraction of around 300 ppb can cause severe interference.](image)

The laser spectrometer is a modified version of a previous dual-QCL instrument (QCL-76-D, Aerodyne Research Inc., USA) with a multi-pass cell of 76 m optical path length and a volume of 0.5 L, originally developed for CH$_4$, N$_2$O, and NO$_2$ eddy flux measurements (Tuzson et al., 2010). To comply with the demanding requirements of high-precision isotope ratio measurements, critical elements of the hardware electronics were upgraded as described in the following.

Because laser operation stability is of utmost importance, ultra-low noise laser drivers (QCL1000, Wavelength Electronics Inc., USA) were installed to minimize laser intensity variations and frequency jitter. The long-term performance was improved by tighter and more precise control of the laser heat-sink temperature by deploying high-precision controllers (PTC5K-CH, Wavelength Electronics Inc., USA).

A new pair of continuous wave DFB-QCL laser (Alpes Lasers SA, Switzerland) was installed. Figure 3.3 shows the covered spectral range at wavenumbers of 1295:7 and 1307:0 cm$^{-1}$ selected for $\delta^{13}$C- and $\delta$D-CH$_4$, respectively. The spectral regions were chosen to offer maximum sensitivity for the less abundant CH$_3$D isotopologues ($\approx 10^{-22}$ cm/mol cm$^{-2}$), comparable line-strength for $^{13}$CH$_4$ and $^{12}$CH$_4$ to avoid saturation and are relatively free from spectral interferences by other molecular species. The susceptibility to spectral interferences could be further reduced by decreasing the pressure in the laser spectrometer gas cell. These conditions could not be fulfilled within the tuning capabilities of a single DFB-QCL, therefore, the simultaneous measurement of $\delta^{13}$C- and $\delta$D-CH$_4$ required a dual-laser configuration (McManus et al., 2011). The measured absorption spectra were analyzed using commercially available software (TDLWintel, Aerodyne Research Inc., USA). In terms of precision and long-term stability, the instrument performance was characterized using the Allan variance technique (Werle, 2010).
In combination with the TREX technique the laser spectrometer is operated in a batch mode, i.e. the multipass cell is either filled with preconcentrated sample or with calibration gas. Before each preconcentrated sample (ambient or pressurized air), the cell is purged for two min with high-purity synthetic air at 25 mL min\(^{-1}\) flow rate and reduced pressure (8 hPa) and then evacuated to a pressure of 0.5 hPa. Similarly for the calibration gas measurements, the cell is first purged and then flushed with calibration gas dynamically diluted with high-purity synthetic air to the desired CH\(_4\) concentration at a total gas flow of 25 mL min\(^{-1}\). The cell pressure is set to around 40 hPa (±0.04 hPa).

### 3.2.2 Interlaboratory comparison campaign

![Diagram](image)

**Figure 3.4**: Schematics of the sampling setup used in the interlaboratory comparison campaign. Ambient air was continuously sampled from the rooftop of the building, and split from the main line to the batch sampling unit (bags and flasks), to the TREX-QCLAS system and to the continuous flow CRDS and OA-ICOS spectrometers. The laser spectrometers were additionally supplied with the calibration gases CG 1, CG 2 and the target gas to determine calibration factors and repeatability.
34 Chapter 3. Real-time analysis of $\delta^{13}$C- and $\delta$D-$\text{CH}_4$ in ambient air with laser spectroscopy

### Table 3.1: List of CH$_4$ mole fractions and isotopic composition ($\delta^{13}$C and $\delta$D-CH$_4$) of laboratory standards used in the intercomparison campaign. The indicated uncertainty is the 1σ standard deviation for repeated analysis of the respective measurement system.

<table>
<thead>
<tr>
<th>composition</th>
<th>CH$_4$ [ppm]</th>
<th>$\delta^{13}$C-CH$_4$ [‰]</th>
<th>$\delta$D-CH$_4$ [‰]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG 1</td>
<td>938.8 ± 3.5$^a$</td>
<td>−46.60 ± 0.10</td>
<td>−250.46 ± 1.05</td>
</tr>
<tr>
<td>CG 2</td>
<td>1103.8 ± 3.5$^a$</td>
<td>−36.13 ± 0.10</td>
<td>−180.58 ± 1.05</td>
</tr>
<tr>
<td>TG</td>
<td>2.3523 ± 0.0002$^b$</td>
<td>−48.07 ± 0.10</td>
<td>−120.00 ± 1.05</td>
</tr>
</tbody>
</table>

CH$_4$ mole fractions were measured by CRDS$^a$ after dilution by a factor of 1 : 500 or$^b$ by direct measurement.

$^c$ Isotopic values were analyzed by IRMS at MPI.

The intercomparison campaign took place from 6 to 22 June 2014 at the Empa campus, located in the densely populated area of Dübendorf, Switzerland (47° 24' 11" N/8° 36' 48" E, elevation 432 m a.s.l.). A main road passes 100 m south and a highway around 750 m north of the sampling site. Air was continuously sampled from the rooftop of a five-story building at a flow rate of 25 L min$^{-1}$ through a 25 m long unheated polyethylene-coated aluminum tubing (ID 9 mm, Synflex-1300) using a piston pump (Gardner Denver Thomas GmbH). At the inlet of the sampling pump the air was branched off to the different analyzers, as indicated in Fig. 3.4. The purpose of the campaign is to validate the TREX-QCLAS system under unattended operation conditions comparable to a “field campaign”. Flask and bag sampling as well as calibration of the commercial available laser spectrometers, however, were operated manually.

#### 3.2.3 Calibration gases and target gas

The calibration gases CG 1 and CG 2 were prepared at Empa based on gravimetric and dynamic dilution methods from pure fossil (99.9995%, Messer, Switzerland) and biogenic CH$_4$ (> 96%, biogas plant Volketswil, Switzerland), diluted with high-purity synthetic air. The exact amounts of added CH$_4$ were determined using a high precision flow measurement device (molbox1, DH Instruments Inc., USA), and the dilution with synthetic air was controlled gravimetrically (ID 3, Mettler Toledo GmbH, Switzerland). Before use, the biogenic CH$_4$ was purified from major contaminants, mainly CO$_2$ and H$_2$O, by flushing it through an Ascarite/Mg(ClO$_4$)$_2$ trap. The $\delta^{13}$C and $\delta$D-CH$_4$ values of the reference gases CG 1 and CG 2, as well as of a cylinder with pressurized ambient air used as the target gas were calibrated against the calibration scales of the Stable Isotope Laboratory of the Max-Planck-Institute (MPI) for Biogeochemistry in Jena, Germany (Sperlich et al., 2012; Sperlich et al., 2013; Sperlich et al., in preparation). It should be noted that the isotopic composition of the measuring gas is outside the range covered by the calibration gases CG 1 and CG 2 for $\delta^{13}$C- and $\delta$D-CH$_4$, which may create problems for analytical techniques with a non-linear response to isotope ratios. This, however, is assumed to be compensated by a correction of results of all analytical techniques/laboratories for the offset in the target gas between assigned value determined by MPI and respective measured values. Results of all analytical techniques/laboratories were corrected for the offset in the target gas between assigned value determined by MPI and respective measured values.

The CH$_4$ mole fractions of CG 1 and CG 2 were analyzed with QCLAS against commercial standards for CH$_4$ mole fractions (1000±20 ppm CH$_4$ in synthetic air, Messer, Switzerland), while the target gas was analyzed by WCC-Empa against the NOAA/GMD scale by CRDS (G1301, Picarro Inc., USA). Table summarizes the CH$_4$ mole fractions and δ-values of TG, CG 1 and CG 2.
TREX-QCLAS

![Diagram](image)

**Figure 3.5:** A complete measurement cycle consists of three main sequences: (A) three consecutive measurements of preconcentrated ambient air samples, (B) one measurement of preconcentrated pressurized air (target gas), followed by the calibration phase (C). The latter is used for the determination of calibration factors for $\delta^{13}$C-CH$_4$ and $\delta^D$-CH$_4$ and the dependence of isotope ratios on elevated CH$_4$ mole fractions. The calibration gases are dynamically diluted to the indicated CH$_4$ mole fractions as described in Section 3.2.3. All measurements are bracketed by the analysis of CG 1 (anchor) at 635 ppm CH$_4$ to drift-correct the measurements.

During the intercomparison campaign a measurement cycle of 220 min duration was applied (Fig. 3.5), including the measurement of three different types of calibration gases (CG 1 at 635 and 745 ppm, CG 2 at 635 ppm) as well as repeatability measurements with preconcentrated target gas (TG). This sequence allowed the measurement of up to 20 ambient air samples per day.

Raw isotope ratio measurements were at first corrected for their dependence on the laser frequency position followed by a drift correction based on regular measurements of CG 1 at 635 ppm. Calibration factors for referencing isotope ratios to the international standard scales as well as correction factors to account for the dependence of isotope ratios on CH$_4$ mole fractions were determined by taking the mean of the calibration gas measurements in intervals of 16 to 48 h and applying a linear regression analysis. Note that the calibration gases were not preconcentrated, thus, violating the identical treatment principle. This was compensated, however, by referencing the results to pressurized ambient air (TG) measurements.

The $\delta^{13}$C values of preconcentrated samples were corrected for a 2.3‰ offset, which was caused by an increase in O$_2$ mole fractions to 40 ± 2% during preconcentration as discussed in Section 3.3.1. The $\delta^{13}$C-offset value was shown to be constant for a large range of CH$_4$ mole fractions and the full range of $\delta$-values covered by this study. For $\delta^D$-CH$_4$ no significant effect could be observed; most likely, its magnitude was within the uncertainty of the system.

CH$_4$ mole fractions in both ambient air and target gas were determined based on the analysis of preconcentrated CH$_4$ mole fractions (12CH$_4$), divided by the preconcentration factor. This factor was computed for each cycle from the gas volume in the multipass cell and the volume of preconcentrated air. The latter is derived from the sample gas flow and the adsorption time. As the trap additionally adsorbs small amounts of N$_2$ and O$_2$ (up to 4% of the preconcentrated sample volume, depending on the trap temperature), variations in the trap temperature also need to be considered. Finally, the CH$_4$ mole
fraction measurements were linked to the WMO-X2004 calibration scale (Dlugokencky et al., 2005) through calibration of the target gas against NOAA reference standards at Empa.

Commercial laser spectrometers

During the campaign, an off-axis integrated cavity output spectrometer (OA-ICOS, δ13C-CH4 and CH4 mole fraction, MCIA-24e-EP, Los Gatos Research, USA) provided by Utrecht University (UU), and a cavity ring-down spectrometer (CRDS, δ13C-CH4, δ13C-CO2, CH4 and CO2 mole fraction, G2201-I, Picarro Inc., USA) provided by Eawag, were deployed. The OA-ICOS analyzer operated in the MIR spectral region, while the CRDS instrument comprises a NIR laser source. OA-ICOS and the CRDS isotope analyzers were calibrated twice per day using the calibration gases CG 1 and CG 2 (Table 3) for 30 min each. These standards were diluted with high-purity synthetic air by a factor of 1 : 500, to 1955.3 ± 6.8 ppb CH4, which is close to the ambient mole fraction. The dependencies of δ-values on CH4 mole fraction were linear up to a concentration of around 2500 ppb and determined to be −6.35 and 1.18 ‰ ppm⁻¹ for OA-ICOS and CRDS, respectively. Variations over the duration of the campaign were not significant and therefore a constant factor was applied. Thereafter, for both analyzers a drift and a two-point calibration correction for δ13C-CH4 was performed based on the measurements of CG 1 and CG 2. Finally, 30 min averages of sample data were calculated, resulting in 550 measurement points for the CRDS over the two-week period of the intercomparison campaign. The repeatability of OA-ICOS and CRDS for δ13C-CH4 was assessed based on repeated analysis of the target gas (pressurized air) every six hours for 30 min.

Bag and flask sampling

In addition to the in situ optical analyzers, manual sampling in glass flasks and Tedlar bags for subsequent IRMS laboratory analysis was performed. Glass flasks were purged for 10 min with dehumidified (Mg(ClO4)2, Sigma-Aldrich, Switzerland) sample gas at 2 L min⁻¹ using a membrane pump (KNF, Netherlands) and then filled to 2000 hPa. Air samples collected in glass flasks were analyzed for δ18O by continuous flow IRMS (ThermoFinnigan Delta plus XL) (Brass and Röckmann, 2010). First a 40 mL stainless steel (SS) sample loop is filled with sample or reference air at atmospheric pressure. The air is flushed by a flow of helium carrier gas (purity 99.9999% or better than 0‰) to the preconcentration unit (1/8” SS tube filled with 6 cm HayeSep D 80/100 mesh) cooled to 137 K, where the CH4 is retained and separated from the bulk air. The CH4 is released by heating the adsorbent trap to 238 K and focused in the cryo-focus unit (25 cm PoraPLOT Q, 0.32 mm ID, 117 K). For δD analysis the CH4 is injected (by heating the cryo-focus trap to 198 K) into a pyrolysis tube furnace (1620 K), where CH4 is converted to H2 and carbon. The H2 enters the IRMS, after passing a 2 m CarboPLOT column at room temperature (RT) and a nafion dryer, via the GasBench interface. No krypton interference could be determined in this setup. The repeatability for δD-CH4 is better than ±2‰, based on 10 consecutive analyses of standard air. A detailed inter-laboratory comparison between UU and MPI is presently ongoing and a preliminary scale offset of 4 ‰ has been used for the present evaluation.

IRMS analysis of δ13C-CH4 and δD-CH4 in flask samples at UU

Both δD and δ13C of CH4 were measured by continuous flow IRMS (ThermoFinnigan Delta plus XL) (Brass and Röckmann, 2010). First a 40 mL stainless steel (SS) sample loop is filled with sample or reference air at atmospheric pressure. The air is flushed by a flow of helium carrier gas (purity 99.9999% or better than 0‰) to the preconcentration unit (1/8” SS tube filled with 6 cm HayeSep D 80/100 mesh) cooled to 137 K, where the CH4 is retained and separated from the bulk air. The CH4 is released by heating the adsorbent trap to 238 K and focused in the cryo-focus unit (25 cm PoraPLOT Q, 0.32 mm ID, 117 K). For δD analysis the CH4 is injected (by heating the cryo-focus trap to 198 K) into a pyrolysis tube furnace (1620 K), where CH4 is converted to H2 and carbon. The H2 enters the IRMS, after passing a 2 m CarboPLOT column at room temperature (RT) and a nafion dryer, via the GasBench interface. No krypton interference could be determined in this setup. The repeatability for δD-CH4 is better than ±2‰, based on 10 consecutive analyses of standard air. A detailed inter-laboratory comparison between UU and MPI is presently ongoing and a preliminary scale offset of 4 ‰ has been used for the present evaluation.

For δ13C, the CH4 is injected from the cryo-focus unit into a combustion oven with nickel wire catalyst at 1100°C, where the CH4 is converted to CO2 and H2O. The resulting gas mixture passes a nafion dryer and a 5 m PoraPLOT Q column (RT) to eliminate an interference from co-trapped krypton (Schmitt et al., 2013) before entering the IRMS via the GasBench interface. The repeatability of δ13C is better than 0.07 ‰.
IRMS analysis of $\delta^{13}$C-$\text{CH}_4$ and $\delta^D$-$\text{CH}_4$ in flask samples at MPI

At the Stable Isotope Facility of MPI Jena (“BGC-IsoLab”) methane isotopes from air samples have been analyzed using a new custom made twin-mass spectrometer analysis system (Delta V+, Thermo-Fisher, Bremen, Germany) with cryogenic preconcentration and GC separation (Brand et al., in preparation). The system allows analyzing $\delta^{13}$C and $\delta^D$ simultaneously in an automated and fully calibrated fashion. For every air sample, a reference air sample is analyzed concurrently. Only the difference between the reference and sample air is used for calibration. While the ion currents are analyzed on the same mass spectrometers, reference and sample air pass through dedicated cryogenic acquisition lines. The isotopic relation between these lines is established daily using four complete analyses with reference air sent through the sample preconcentration duct.

Using small-volume flow controllers, cryogenic acquisition is made at 5 mL min$^{-1}$ over 20 min, thereby consuming 100 mL air for each isotope measurement. Prior to methane concentration, CO$_2$ is removed cryogenically using a permanent liquid nitrogen bath. The cryo traps for methane retention consist of 1/8” stainless steel tubes filled with HayeSeptember-D polymer for specific absorption of CH$_4$ at 143 K. The latter temperature is generated by compression coolers (Cryotiger, Brooks Automation, Jena, Germany), which can operate down to 123 K at a heat digestion capacity of around 30 W.

After acquisition, the acquired methane is transferred to a cryogenic focus trap of similar design, from where gas chromatographic separation is initiated by rapid heating. The methane peaks are heart cut (Deans, 1968) for combustion ($\delta^{13}$C) and pyrolysis ($\delta^D$), respectively. CH$_4$-derived CO$_2$ is separated from non-reacted CH$_4$ and from the co-trapped krypton with a post-reaction gas chromatographic separation before being introduced to the respective mass spectrometer via open split coupling. An entire sample carousel with 18 analyses (13 sample analyses net) takes about 27 h.

The system is in continuous operation since July 2012. The overall precision including all instrument failure times is ±0.15‰ ($\delta^{13}$C) and ±1.14‰ ($\delta^D$), as determined through daily measurement of a QA (quality assurance) sample air. Removing the times of instrumental malfunction improves the precision to ±0.10‰ ($\delta^{13}$C) and ±1.05‰ ($\delta^D$) over the entire period of operation (3 years). The precision for 10 repeated measurements of standard air is typically 0.07‰ ($\delta^{13}$C) and 0.7‰ ($\delta^D$).

IRMS analysis of $\delta^{13}$C-$\text{CH}_4$ in bag samples at RHUL

$\delta^{13}$C-$\text{CH}_4$ was measured using a modified GC-IRMS system (Trace Gas and Isoprime, Isoprime Ltd.). This system uses a modified Trace Gas preparation system in dynamic mode whereby the original catalyst is replaced by palladized quartz wool in a wider 4 mm ID ceramic furnace tube. Conversion of methane to CO$_2$ and H$_2$O is completed at 1063 K using oxygen in the air sample as the oxidant. A highly modified and automated inlet system (Fisher et al., 2006) was applied consisting of an auto-sampler including a 6-port rotary valve (Valco Instruments Inc.) with a 75 cm$^3$ Swagelok stainless steel sample volume and four samples, one standard gas and a vacuum line attached. The 75 cm$^3$ sample volume is evacuated up to the solenoid valve directly before the bag valve, then the air moves from the bag into the sample volume maintaining ambient atmospheric pressure. This air is then pushed through the preparation system with a flow of helium gas set to a pressure of 758 hPa. Individual sample analysis last approximately 19 min and all sample measurements were made in triplicate. Repeatability based on 10 consecutive analyzes of standard air is ±0.05‰ or better. $\delta^{13}$C-$\text{CH}_4$ values of RHUL are offset corrected by −0.3‰ based on intercomparison measurements with NIWA (Lowe et al., 2004).
3.3 Results and discussion

3.3.1 TREX-QCLAS

Performance characteristics of QCLAS

The QCLAS precision and stability were investigated using the Allan variance technique. Therefore, individual CH$_4$ isotopologues were measured with one second integration time over a period of a few hours, as shown in Fig. 3.6. From the associated Allan variance plots, an optimum averaging time of approximately 600s can be derived, corresponding to a root mean square noise of 0.1 and 0.5‰ for $\delta^{13}$C-CH$_4$ and $\delta^{D}$-CH$_4$, respectively. The one second noise performance was determined to be in the $4.0 \times 10^{-5}$, which corresponds to a noise equivalent absorbance per unit path length of $5.2 \times 10^{-9}$ cm$^{-1}$ when considering the 76m optical path.

Similar to earlier work on CO$_2$ and N$_2$O (Tuzson et al., 2008; Waechter et al., 2008), we found also in the case of methane a linear dependence of the spectroscopically retrieved isotope ratios on the mole fractions. In a series of experiments, the magnitude of this dependence was empirically determined and verified in the range of 600-1000ppm CH$_4$. The coefficients were 0.0145 and $-0.0521$‰ ppm$^{-1}$ for $\delta^{13}$C- and $\delta^{D}$-CH$_4$, respectively. At each calibration phase in the intercomparison campaign, these dependencies were determined repeatedly via two-point calibration and remained stable during the two-week period.

The influence of laser temperature variation on $\delta^{13}$C and $\delta^{D}$-values has been determined by systematically changing the laser heat-sink temperature over $\pm 20$ mK in steps of 3 mK, and measuring the changes observed in the retrieved isotope ratios. We found a rather strong linear dependence, i.e., 0.1 and $-0.2$‰ mK$^{-1}$ for $\delta^{13}$C- and $\delta^{D}$-CH$_4$, respectively. Thus, it was crucial not only to control the laser temperature at high-precision ($\approx 1$ mK), but also to record the laser temperature at high resolution and to apply a drift correction caused by this effect during data post-processing.
Optimization of TREX-QCLAS

The preconcentration procedure was optimized to reduce cycle time and reach the target sample volume of 7.5L of ambient air, but also to allow quantitative and reproducible CH$_4$ desorption (> 99.9%) with simultaneous separation of other trace gases, such as N$_2$, O$_2$, and CO$_2$. Various trap temperatures (108 to 93K) and gas flows (500 to 1000mL min$^{-1}$) have extensively been tested and the optimal conditions were found to be 900mL min$^{-1}$ with an initial trap temperature of 101K. Under standard operation conditions, the breakthrough volume was determined to be above 9L of air. During this period the CH$_4$ mole fraction downstream of the trap, at the outlet of MFC 1, was below 0.5ppb (G1301, Picarro Inc., USA). Tests with higher trap temperatures (111K) indicated considerable CH$_4$ breakthrough at much lower adsorption volumes of 6.1L, given the very high flow rates of 900mL min$^{-1}$ (data not shown).

Figure 3.7 displays the sequential desorption of the various compounds adsorbed on the trap. For the optimization of this procedure CH$_4$ and N$_2$O were quantified by QCLAS, while N$_2$, O$_2$, and CO$_2$ were measured by a quadrupole mass spectrometer (MKS, Switzerland). Quantitative (> 99.9%) CH$_4$...
desorption was verified by a subsequent second desorption and analysis of the resulting effluent gas for CH₄. This verifies that the tail in CH₄ mole fractions after the main desorption peak originates from a consecutive flushing of the QCLAS gas cell and not from CH₄ eluting from the trap. In parallel to CH₄, also bulk air components such as O₂ and N₂ are co-desorbed from the trap. Due to the much lower boiling point of O₂ (90 K) relative to N₂ (77 K), the O₂ mixing ratio in the absorption cell after preconcentration is increased to 40 ± 2 %. To investigate the effect of this gas matrix change on the δ-values and additional fractionation effects, calibration gases with δ¹³C- and δD-CH₄ values ranging from −36.1 to −58.5‰ and −181 to −331‰, respectively, were diluted with synthetic air to mole fractions of 2 and 2.2 ppm CH₄, then preconcentrated and measured against the respective undiluted calibration gas. We observed a constant offset of 2.3 ± 0.2 ‰ for δ¹³C compared to the undiluted calibration gas, independent of CH₄ mole fraction or δ value. For δD no detectable influence was observed. The most plausible explanation for this effect is a change in the pressure broadening of the line profiles caused by the increased O₂-mixing ratio after preconcentration. The HITRAN database contains the air pressure broadening coefficients only. Consequently, any deviation in the N₂/O₂ ratio leads to a bias due to this effect, as the fitting model uses improper coefficients for line profile estimation.

In order to verify this hypothesis, we deliberately changed the gas matrix composition by setting its O₂-mole fraction to 21, 37 and 53 %. For each O₂-mixing ratio the CH₄ mole fraction was increased stepwise from 600 to 1000 ppm and the δ¹³C dependence on CH₄ mole fraction was accounted for. Figure 3.8 shows the measured dependence of δ¹³C-CH₄ on changing O₂-mixing ratio. The gray bars indicate the ranges of the O₂-mixing ratio of sample gas after preconcentration as determined by mass spectrometry.
Chapter 3. Real-time analysis of δ\textsuperscript{13}C- and δD-CH\textsubscript{4} in ambient air with laser spectroscopy

and the resulting offset in the δ\textsuperscript{13}C values obtained for individual experiments. As mentioned before, the δD-CH\textsubscript{4} values showed no significant dependence on O\textsubscript{2}-mixing ratio.

This result confirms that the O\textsubscript{2} interference is the main source of systematic bias for δ\textsuperscript{13}C-CH\textsubscript{4}, whereas fractionation effects for both, δ\textsuperscript{13}C- and δD-CH\textsubscript{4} values, are insignificant. The gas matrix effect could be reduced or at least maintained stable by enhancing the temperature control of the trap to constrain the O\textsubscript{2}-mixing ratio in the gas matrix and thereby to improve the repeatability of δ\textsuperscript{13}C measurements. Another solution could be to substitute the HayeSep D adsorbent material by a candidate either exhibiting a superior selectivity for CH\textsubscript{4} over O\textsubscript{2} or having a larger capacity for CH\textsubscript{4}, so that the adsorption temperature can be increased. Higher adsorption temperatures would reduce the amount of O\textsubscript{2} trapped in the system.

3.3.2 Repeatability of analytical techniques and scale differences between laboratories

<table>
<thead>
<tr>
<th>CH\textsubscript{4} [ppb]</th>
<th>No. of counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>2340</td>
<td>0</td>
</tr>
<tr>
<td>2350</td>
<td>5</td>
</tr>
<tr>
<td>2360</td>
<td>7</td>
</tr>
<tr>
<td>2370</td>
<td>15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>δ\textsuperscript{13}C [%]</th>
<th>No. of counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>-48.4</td>
<td>2</td>
</tr>
<tr>
<td>-48.0</td>
<td>1</td>
</tr>
<tr>
<td>-47.6</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>δD [%]</th>
<th>No. of counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>-124</td>
<td>1</td>
</tr>
<tr>
<td>-120</td>
<td>1</td>
</tr>
<tr>
<td>-116</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 3.9: Repeated measurements of pressurized air (target gas) by TREX-QCLAS over two weeks throughout the interlaboratory comparison campaign. CH\textsubscript{4} mole fractions and relative differences of isotope ratios (δ\textsuperscript{13}C, δD) were plotted as a histogram with bin widths of 3 ppb (CH\textsubscript{4}), 0.1‰ (δ\textsuperscript{13}C) and 1‰ (δD), respectively. The uncertainty is given as the 1σ standard deviation.

Scale differences between different analytical techniques/laboratories and their repeatability were assessed based on repeated target gas measurements (Table ). Figure 3.9 shows the histograms of the target gas measurements obtained with the TREX-QCLAS: CH\textsubscript{4} mole fraction of 2352.0 ± 4.4 ppb, δ\textsuperscript{13}C-CH\textsubscript{4} = -47.99 ± 0.19‰ and δD-CH\textsubscript{4} = -120.9 ± 1.9‰. The repeatability of TREX-QCLAS was comparable to manual sampling with subsequent IRMS analysis for δD-CH\textsubscript{4}, but about a factor three worse for δ\textsuperscript{13}C-CH\textsubscript{4}. The CRDS exhibited a comparable repeatability (0.24‰) to TREX-QCLAS for δ\textsuperscript{13}C-CH\textsubscript{4}, while with 0.78‰ the performance of OA-ICOS was significantly worse. In summary, the repeatability of TREX-QCLAS, CRDS and all IRMS laboratories offer the capability to reach the extended WMO/GAW compatibility goals for δ\textsuperscript{13}C and δD-CH\textsubscript{4}, of 0.2 and 5‰, defined for regional scale studies (WMO/GAW, 2013), while the goals for background measuring stations of 0.02 and 1‰ for δ\textsuperscript{13}C and δD-CH\textsubscript{4} are beyond the performance of any of the applied techniques. A more detailed discussion is given in Section 3.3.4.

For assessing the compatibility between the instruments, IRMS measurements of MPI were chosen as the reference point, as MPI recently established a direct link to the international isotope standard scales. The data obtained from the laser spectroscopic techniques (TREX-QCLAS, CRDS and OA-ICOS) are referenced to the standards CG 1 and CG 2, analyzed by MPI, while the IRMS measurements of UU and RHUL are referenced to their respective laboratory standards. The agreement for δ\textsuperscript{13}C-CH\textsubscript{4} is within 0.1‰ for all techniques/laboratories, except the IRMS measurements of RHUL, which were 0.25‰ higher and the OA-ICOS results, which were offset by as much as −8.87‰. For δD-CH\textsubscript{4}, no significant differences were observed between TREX-QCLAS and the MPI IRMS, while the UU IRMS values were 2.3‰ higher.
Table 3.2: List of measured $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ values of the target gas (pressurized air) as reported by different analytical techniques/laboratories. The indicated uncertainty is the 1σ standard deviation. Results of laser spectroscopic techniques are referenced to standards CG 1 and CG 2, while IRMS results where referenced to their respective laboratory standards.

<table>
<thead>
<tr>
<th>number of measurements</th>
<th>$\delta^{13}$C-CH$_4$ [‰]</th>
<th>$\delta$D-CH$_4$ [‰]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass-flask/IRMS (MPI)</td>
<td>1 $-48.07 \pm 0.10$</td>
<td>$-120.0 \pm 1.05$</td>
</tr>
<tr>
<td>TREX-QCLAS (Empa)</td>
<td>62 $-47.99 \pm 0.19$</td>
<td>$-120.9 \pm 1.9$</td>
</tr>
<tr>
<td>Glass-flask/IRMS (UU)</td>
<td>4 $-47.96 \pm 0.08$</td>
<td>$-117.7 \pm 2.0$</td>
</tr>
<tr>
<td>CRDS (Eawag)</td>
<td>64 $-48.04 \pm 0.24$</td>
<td>n.a.</td>
</tr>
<tr>
<td>OA-ICOS (UU)</td>
<td>10 $-56.94 \pm 0.78$</td>
<td>n.a.</td>
</tr>
<tr>
<td>Bag/IRMS (RHUL)</td>
<td>3 $-47.82 \pm 0.05$</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

n.a.: not analyzed.

The ambient air measurements during the campaign were offset-corrected for differences in $\delta^{13}$C and $\delta$D-CH$_4$ measurements of TG by individual techniques/laboratories and MPI summarized in Table . Differences for IRMS laboratories include differences in scales and instrumental issues, while the laser spectroscopic techniques are all calibrated using CG 1 and CG 2. The OA-ICOS data are not considered further due to the limited performance with respect to repeatability and scale offset.

### 3.3.3 Real-time analysis of CH$_4$ isotopic composition in ambient air

![Graph showing CH$_4$ mole fractions and isotopic composition analyzed during the interlaboratory comparison campaign in real-time by the laser spectroscopic techniques: TREX-QCLAS (CH$_4$, $\delta ^{13}$C, $\delta$D), CRDS G2201-i (CH$_4$, $\delta ^{13}$C), and on glass flask/bag samples with IRMS by UU (CH$_4$, $\delta ^{13}$C, $\delta$D), MPI (CH$_4$, $\delta ^{13}$C, $\delta$D) and RHUL (CH$_4$, $\delta ^{13}$C).]
Chapter 3. Real-time analysis of $\delta^{13}$C- and $\delta$D-CH$_4$ in ambient air with laser spectroscopy

The CH$_4$ mole fraction and isotopic composition measurements in ambient air between 6 and 22 June 2014 of the various laser spectroscopic and mass spectrometric analytical techniques is shown in Fig. 3.10. Data of all laboratories have been offset corrected as discussed in the previous section. During the campaign, more than 250 air samples (199 samples of ambient air, 62 target gas samples) were analyzed in stand-alone operation by TREX-QCLAS and more than 120 manually taken samples were analyzed by IRMS. The CRDS data were averaged for 30 min, resulting in 550 mean values.

The CH$_4$ mole fractions exhibit a regular diurnal variation with night-time values increasing up to 2300 ppb, which is around 400 ppb higher than at daytime. When comparing the measurement data from the local weather station in Dübendorf with the measured CH$_4$ mole fractions, the nights with the highest CH$_4$ mole fractions also exhibit very low wind speed (0-7 m$^{-1}$s), indicating formation of night-time inversion in the atmospheric boundary layer. Stable boundary conditions reduce the mixing volume of emissions, which leads to a stronger CH$_4$ signal. Variations in the $\delta^{13}$C- and $\delta$D-CH$_4$ values display a clear anti-correlation with the mole fraction changes indicating emissions of CH$_4$ depleted in $^{13}$CH$_4$ and CH$_3$D. The compatibility of different techniques for CH$_4$ isotopic analysis in ambient air is discussed based on correlation diagrams in the next section.

3.3.4 Compatibility of analytical techniques for $\delta^{13}$C- and $\delta$D-CH$_4$ in ambient air

The compatibility of different analytical techniques for CH$_4$ isotope measurements was assessed on the ambient air measurements shown in Fig. 3.10. Measurements were done either on identical gas samples, i.e. for IRMS measurements of glass flask samples by UU and MPI, or on simultaneously collected ambient air samples, i.e. for all other techniques (laser spectrometers and bag samples/IRMS). The $\delta^{13}$C- and $\delta$D-CH$_4$ measurements on glass flasks by IRMS at UU were chosen as reference for this comparison, due to the much higher number of samples ($n = 67$) analyzed as compared to MPI ($n = 15$). Isotope data of all techniques were offset-corrected as described in Section 3.3.1 to account for systematic differences (scale differences and instrumental artifacts) between individual laboratory results.
Figure 3.11: Correlation diagrams for CH$_4$ isotope ($\delta^{13}$C, $\delta$D-CH$_4$) measurements in ambient air by different techniques and laboratories. The dashed black line is the 1:1 line, the red dashed lines indicate the WMO compatibility goals of $\pm 0.2\%$ for $\delta^{13}$C and $\pm 5\%$ for $\delta$D. Results of individual techniques are corrected to a common scale based on MPI results for a pressurized air target gas. For the middle and bottom graphs differences in CH$_4$ mole fractions in gas samples are represented by the shading (black: identical mole fractions, white: 30 ppb difference). Top: IRMS analysis on glass flasks by the Stable Isotope Laboratory of MPI vs. UU for $\delta^{13}$C-CH$_4$ (left) and $\delta$D-CH$_4$ (right); Middle: TREX-QCLAS analysis by Empa vs. IRMS analysis on glass flasks by UU for $\delta^{13}$C-CH$_4$ (left) and $\delta$D-CH$_4$ (right). The temporal difference between TREX-QCLAS analysis and glass flask sampling is indicated by the point size (big: $\pm$ 10 min, medium: $\pm$ 20 min, small: $\pm$ 30 min); Bottom: IRMS analysis on bag samples by RHUL (left) and CRDS analysis by Eawag (right) vs. IRMS analysis on glass flasks by UU for $\delta^{13}$C-CH$_4$.

Figure 3.11 displays correlation diagrams for the different analytical techniques and laboratories. They exhibit a generally good compatibility of individual techniques. The standard deviation of differences in $\delta^{13}$C-CH$_4$ values is lowest for the two IRMS techniques that also measured identical samples,
Chapter 3. Real-time analysis of \(\delta^{13}\text{C}\)- and \(\delta\text{D-CH}_4\) in ambient air with laser spectroscopy

intermediate for TREX-QCLAS vs. IRMS and highest for CRDS vs. IRMS, the same order as observed for the repeatability of techniques. Noticeable is also, that the CRDS seems to drift away during certain periods, i.e. on the 18 and 19 June, making the compatibility worse. For \(\delta\text{D-CH}_4\) the standard deviation of differences between TREX-QCLAS and the UU IRMS is comparable or smaller than the one corresponding to the two IRMS systems (UU and MPI), which is also in agreement with repeatability results.

Systematic differences in the \(\delta^{13}\text{C-CH}_4\) values of individual techniques are small (−0.13 to +0.2‰) within their extended uncertainties. For \(\delta\text{D-CH}_4\) a similar picture arises with a 2.1 to 2.6‰ difference between the applied analytical techniques. These differences in IRMS results of Utrecht University have been introduced by a −2.3‰ offset correction based on analysis of the target gas. In summary, the applied offset correction based on the pressurized air target gas led to a consistent dataset but also indicates limitations of this correction procedure based on a single gas. This underlines the need for a set of common \(\text{CH}_4\) isotope standard gases at ambient mole fraction to guarantee the compatibility among different analytical techniques and laboratories. The compatibility of individual techniques with separate sampling, is shown in Fig. 3.11. Deviations in \(\text{CH}_4\) mole fractions as well as temporal offsets are illustrated by different shades and symbol sizes, respectively.

### 3.3.5 Feasibility of TREX-QCLAS for \(\text{CH}_4\) source identification

Keeling plots (Keeling, 1958; Keeling, 1961) of selected data were used to assess the feasibility of the developed TREX-QCLAS technique for real-time analysis of \(\text{CH}_4\) isotopic composition in ambient air and subsequent source appointment (Fig. 3.12 and Table ). The data were split into noon-to-noon periods and evaluated when night-time \(\text{CH}_4\) mole fractions exceeded 2050ppb. By this approach, periods with minor diurnal changes in \(\text{CH}_4\) mole fractions were excluded because the derived isotope source signatures have larger uncertainties for small mole fraction elevations. The Keeling plot approach assumes mixing of unpolluted background air with \(\text{CH}_4\) from a single source process or a constant mixture of different source processes for one noon-to-noon period. This assumption is valid for most noon-to-noon periods, as indicated by the linear regression parameters \((R^2\)-values) being between 0.63 and 0.95 for \(\delta^{13}\text{C}\) and between 0.97 and 0.99 for \(\delta\text{D-CH}_4\). The period from 19 to 20 June exhibited a low correlation \((R^2\delta^{13}\text{C}: 0.02, \delta\text{D-CH}_4: 0.85)\), caused by the contribution of various \(\text{CH}_4\) sources as discussed in the next paragraph.
Chapter 3. Real-time analysis of $\delta^{13}$C- and $\delta D$-CH$_4$ in ambient air with laser spectroscopy

![Figure 3.13: $\delta D$-CH$_4$ vs. $\delta^{13}$C-CH$_4$ of different CH$_4$ sources. The symbols indicate CH$_4$ source signatures derived from Keeling plots. The error bars are uncertainties derived from the linear regression. The star-symbols are source signatures from 21 June noon till 22 June noon derived from different techniques. The shadings indicate typical values for different source categories from the literature.]

In Fig. 3.13, CH$_4$ isotopic source signatures for selected noon-to-noon periods are displayed. All source signatures indicate a major contribution of a microbial CH$_4$ source process, e.g. by ruminants (Rigby et al., 2012), except the data recorded between 19 to 20 June. During this period there was a singular and pronounced emission event, with CH$_4$ mole fractions up to 2599 ppb, suggesting significant contributions of CH$_4$ emissions from a local fossil gas source process. This short lasting (10-20 min) CH$_4$ emission event was also confirmed by measurements at the nearby monitoring station of the Swiss Air Pollution Monitoring Network (NABEL), showing a sudden increase in CH$_4$ mole fractions above 3000 ppb. Using a simple mass balance calculation and clean background air with 1900 ± 15 ppb CH$_4$ with isotopic composition of $-47.5\%$ for $\delta^{13}$C and $-81\%$ for $\delta D$-CH$_4$ as reported by Bergamaschi et al., 2000, it is rather straightforward to estimate the isotopic signature of this singular event. Thus, the measured values are best explained by an emission source enriched in $^{13}$CH$_4$ and CH$_3$D ($\approx -37.2 \pm 1.5\%$ for $\delta^{13}$C and $\approx -152 \pm 11\%$ for $\delta D$) contributing up to 60% to the observed increase in the CH$_4$ mole fraction. The remaining 40% is attributed to microbial sources with isotopic signatures repeatedly determined during the campaign, i.e. $-61.5\%$ for $\delta^{13}$C and $-372\%$ for $\delta D$-CH$_4$ (see also Table ??). Although, the estimated source signature values agree with fossil origin, it should be noted that the analysis relies only on a single data point. This result, however, is plausible, as no landfill site is situated in the vicinity of the sampling location. When ignoring this emission event, the source signature indicates a microbial source similar as in the other periods (Table ). Unfortunately, the CRDS analyzer was in calibration mode during this event, and no flask or bag sample was collected for IRMS analysis. This event also highlights the importance of real-time CH$_4$ isotope analysis. For the period between 21 and 22 June, source signatures obtained by TREX-QCLAS were compared to the IRMS results by UU and MPI of glass flask sampling and the agreement is within the expanded uncertainty of the linear regression (Table ). Source signatures derived from the CRDS data display a high temporal coverage, but only in four cases the Keeling plot regression analysis lead to reasonable correlations ($R^2 > 0.5$) and thus meaningful source estimates. For all other cases with $R^2$ below 0.5, the CRDS based signatures deviate significantly from the TREX-QCLAS and IRMS results. In the context of the present study, the increased temporal coverage alone does not provide any additional information, while the unavailability of $\delta D$ information...
is a serious limitation with respect to the interpretation of the data.

The measurements made during this campaign clearly demonstrate that the TREX-QCLAS technique is a valuable attractive alternative to the existing laboratory-based techniques that rely on flask sampling. Moreover, the TREX-QCLAS is capable to resolve temporal changes in ambient CH$_4$ isotopic composition. Finally, the preconcentration unit can be applied for the analysis of mole fraction and isotopic composition of other trace gases, e.g. N$_2$O and VOCs. The potential of this technique for N$_2$O isotopes was recently demonstrated in an extended field campaign (Wolf et al., 2015a).

### 3.4 Conclusion and outlook

This study presents the development and validation of a novel measurement technique, called TREX-QCLAS, for real-time analysis of the three main CH$_4$ isotopologues $^{12}$CH$_4$, $^{13}$CH$_4$, and $^{12}$CH$_3$D in ambient air. The fully automated instrument is based on cryogen-free CH$_4$ preconcentration, followed by selective and high-precision isotope analysis with mid-IR QCL absorption spectroscopy.

This is the first demonstration of analyzing $\delta^{13}$C and $\delta$D-CH$_4$ simultaneously with one instrument in ambient air, real-time and under field conditions. The TREX-QCLAS technique was deployed in an interlaboratory comparison campaign for a period of two weeks. Data of the TREX-QCLAS instrument was compared to commercial laser spectroscopic techniques (CRDS, OA-ICOS) as well as to the established IRMS technique using flask or bag sampling. During this period, the TREX-QCLAS performed more than 250 measurement cycles, while 120 air samples were manually collected for subsequent IRMS analysis. The repeatability of TREX-QCLAS based on target gas measurements was found to be 0.19% for $\delta^{13}$C-CH$_4$ and 1.9% for $\delta$D-CH$_4$, which is similar or slightly worse than the state of the art IRMS techniques. Selected noon-to-noon periods of the recorded time-series were analyzed using Keeling plots. During these intervals, the TREX-QCLAS method was able to successfully distinguish between CH$_4$ emissions with predominantly microbial origin and a case with significant influences from a fossil source.

The intercomparison campaign also exposed calibration scale issues and underlined the need for CH$_4$ isotope standard gases at ambient mole fractions to improve the compatibility among different analytical techniques and laboratories. With its compactness and ability to analyze simultaneously $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ in a stand-alone operation, the TREX-QCLAS is perfectly suited for field studies at ecosystem measurement sites in order to identify regional source processes.

### Table 3.3: Overview of all the $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ source signatures derived using the Keeling plot approach for the given time periods.

<table>
<thead>
<tr>
<th>System</th>
<th>Time period</th>
<th>#Points</th>
<th>CH$_4^{\text{Max}}$ [ppb]</th>
<th>$\delta^{13}$C-CH$_4$ [%]</th>
<th>$\delta$D-CH$_4$ [%]</th>
<th>$R^2$-$\delta^{13}$C</th>
<th>$R^2$-$\delta$D</th>
</tr>
</thead>
<tbody>
<tr>
<td>TREX-QCLAS</td>
<td>07–08 Jun 2014</td>
<td>18</td>
<td>2222</td>
<td>$-55.1 \pm 1.2$</td>
<td>$-368 \pm 13$</td>
<td>0.72</td>
<td>0.97</td>
</tr>
<tr>
<td>CRDS</td>
<td>07–08 Jun 2014</td>
<td>35</td>
<td>2228</td>
<td>$-50.2 \pm 0.9$</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TREX-QCLAS</td>
<td>08–09 Jun 2014</td>
<td>18</td>
<td>2308</td>
<td>$-57.9 \pm 0.6$</td>
<td>$-351 \pm 7$</td>
<td>0.95</td>
<td>0.99</td>
</tr>
<tr>
<td>CRDS</td>
<td>08–09 Jun 2014</td>
<td>35</td>
<td>2321</td>
<td>$-58.8 \pm 1.3$</td>
<td>0.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TREX-QCLAS</td>
<td>18–19 Jun 2014</td>
<td>18</td>
<td>2208</td>
<td>$-57.2 \pm 1.3$</td>
<td>$-344 \pm 12$</td>
<td>0.78</td>
<td>0.97</td>
</tr>
<tr>
<td>CRDS</td>
<td>18–19 Jun 2014</td>
<td>35</td>
<td>2147</td>
<td>$-58.7 \pm 1.0$</td>
<td>0.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TREX-QCLAS</td>
<td>19–20 Jun 2014$^a$</td>
<td>17</td>
<td>2599</td>
<td>$-49.7 \pm 2.1$</td>
<td>$-264 \pm 18$</td>
<td>0.02</td>
<td>0.85</td>
</tr>
<tr>
<td>TREX-QCLAS</td>
<td>19–20 Jun 2014$^b$</td>
<td>16</td>
<td>2176</td>
<td>$-61.5 \pm 1.3$</td>
<td>$-372 \pm 12$</td>
<td>0.89</td>
<td>0.97</td>
</tr>
<tr>
<td>CRDS</td>
<td>19–20 Jun 2014</td>
<td>35</td>
<td>2151</td>
<td>$-60.2 \pm 1.3$</td>
<td>0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TREX-QCLAS</td>
<td>21–22 Jun 2014</td>
<td>15</td>
<td>2067</td>
<td>$-55.4 \pm 1.7$</td>
<td>$-374 \pm 12$</td>
<td>0.63</td>
<td>0.98</td>
</tr>
<tr>
<td>IRMS UU</td>
<td>21–22 Jun 2014</td>
<td>10</td>
<td>2072</td>
<td>$-52.4 \pm 1.9$</td>
<td>$-351 \pm 19$</td>
<td>0.34</td>
<td>0.94</td>
</tr>
<tr>
<td>IRMS MPI</td>
<td>21–22 Jun 2014</td>
<td>6</td>
<td>2072</td>
<td>$-54.7 \pm 1.9$</td>
<td>$-356 \pm 20$</td>
<td>0.74</td>
<td>0.98</td>
</tr>
<tr>
<td>CRDS</td>
<td>22–23 Jun 2014</td>
<td>37</td>
<td>2092</td>
<td>$-55.5 \pm 0.8$</td>
<td>0.71</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$values from the period between 19 and 20 June were derived with$^a$and without$^b$consideration of the event data point.
3.5 Acknowledgments

Funding from the Swiss National Science Foundation (SNSF) within grant No. 200021_134611 and the European Community’s Seventh Framework Programme (FP7/2007-2013) within the InGOS project under grant agreement No. 284274 is gratefully acknowledged. We thank Biogas Volketswil for providing us with pure biogenic CH$_4$. S. Eyer is very thankful for the continuous support from the electronic (W. Knecht and A. Kunz) and mechanic (U. Hintermüller and E. Pieper) workshops at Empa. In addition we would like to thank Kerstin Zeyer, Antoine Roth and Marco Weber (Empa) for their support. M. E. Popa travel to Dübendorf was supported by the COST ACTION MP1204 TERA-MIR.
Chapter 4

In-situ observations of the isotopic composition of methane at the Cabauw tall tower site


1Utrecht University (UU), Institute for Marine and Atmospheric research Utrecht (IMAU), Utrecht, the Netherlands; 2Empa, Laboratory for Air Pollution & Environmental Technology, Dübendorf, Switzerland; ‡now at Department of Physical Geography and Ecosystem Science, Lund University, Lund, Sweden; ¶University of Bern, Climate and Environmental Physics, Bern, Switzerland; §Royal Holloway University of London (RHUL), Department of Earth Sciences, Egham, UK; ¶Max-Planck-Institute (MPI) for Biogeochemistry, Jena, Germany; ∥Environmental Physics Group, Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Krakow, Poland;

High precision analyzes of the isotopic composition of methane in ambient air can potentially be used to discriminate between different source categories. Due to the complexity of isotope ratio measurements, such analyzes have generally been performed in the laboratory on air samples collected in the field. This poses a limitation on the temporal resolution at which the isotopic composition can be monitored with reasonable logistical effort. Here we present the performance of a dual isotope ratio mass spectrometric system (IRMS) and a quantum cascade laser absorption spectroscopy (QCLAS) based technique for in-situ analysis of methane isotopic composition under field conditions. Both systems were deployed at the Cabauw experimental site for atmospheric research (CESAR) in the Netherlands and performed in-situ, high-frequency (approx. hourly) measurements for a period of more than 5 months. IRMS and QCLAS were in excellent agreement with the exception of a slight systematic offset of +0.05 ± 0.03‰ for $\delta^{13}C$-CH$_4$ and −3.6 ± 0.4‰ for $\deltaD$-CH$_4$. This was corrected for, yielding a combined dataset with more than 2500 measurements of both $\delta^{13}C$- and $\deltaD$. The high precision and temporal resolution dataset does not only reveal the overwhelming contribution of isotopically depleted agricultural CH$_4$ emissions from ruminants at the Cabauw site, but also allows the identification of specific events with elevated contributions from more enriched sources such as natural gas and landfills. Source assignment and evaluation of current inventories were performed using the global model TM5 and the mesoscale model FLEXPART-COSMO. The applied continuous high-resolution techniques present new possibilities to evaluate inventories in a top-down approach with respect to source contributions.

To be submitted for publication to Atmospheric Chemistry and Physics

*These authors contributed equally to this work
4.1 Introduction

The global increase of the important greenhouse gas methane in the atmosphere since the beginning of the industrial period is very well established (Dlugokencky et al., 2009; Dlugokencky et al., 1996; Dlugokencky et al., 1997; Etheridge et al., 1998; Khalil et al., 2007; Loulergue et al., 2008; MacFarling Meure et al., 2006; Rasmussen and Khalil, 1981; Spahni et al., 2005). The existing CH$_4$ mole fraction measurement data enable accurate assessment of the source-sink imbalance through time, and together with the estimated total sink strength, they allow for a top-down constraint on the global source of methane to the atmosphere (Bergamaschi et al., 2013; Houweling et al., 2014). Bottom-up estimates of the global methane budget carry much larger uncertainties, which are inherent to the assumptions made in the extrapolation of local scale measurements to larger scales (Bruhwiler et al., 2014; Kirschke et al., 2013; Nisbet et al., 2014). The advantage of bottom-up estimates is, however, the possibility to distinguish different sources and to link observations to process-level understanding of the emissions.

An alternative approach for distinguishing between source categories of CH$_4$ is the analysis of its isotopic composition, which is strongly linked to the source/sink processes. This is particularly true for methane from biogenic, thermogenic and pyrogenic sources (Quay et al., 1999). A more detailed differentiation within one source category, e.g. biogenic CH$_4$, for emissions from wetlands, ruminants, rice paddies or termites, however, is complicated because of the overlap of the respective isotopic source signatures. Further, complications arise because individual source signatures can show pronounced dependence on environmental parameters and metabolized substrates (Kawagucci et al., 2014; Klevenhusen et al., 2010). In addition to the source contributions, the sink processes (mainly chemical removal by the hydroxyl radical (OH), but also soil deposition and stratospheric loss) also affect the isotopic composition of atmospheric methane (Brenninkmeijer et al., 1995; Röckmann et al., 2011; Saueressig et al., 1996; Saueressig et al., 2001; Snoe et al., 2000). Over the past decades, numerous studies have shown the potential of isotope measurements to identify individual source categories from isotope observations (Beck et al., 2012; Lassey et al., 1993; Tarasova et al., 2006; Umezawa et al., 2012a; Zazzeri et al., 2015) and to constrain budgets (Ferretti et al., 2005; Fischer et al., 2008; Houweling et al., 2008; Lassey et al., 2000; Lowe et al., 1994; Sapart et al., 2012; Umezawa et al., 2012b). For interpretation of global or continental scale atmospheric data the expert group at the WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT) has set a scientifically desirable level of compatibility of 2 ppb, 0.02‰ and 1‰ for CH$_4$ mole fraction, δ$^{13}$C- and δD-CH$_4$, respectively (WMO/GAW, 2013). In addition, for regionally focused studies with large local fluxes, extended compatibility goals of 5 ppb, 0.2‰ and 5‰ for CH$_4$ mole fraction, δ$^{13}$C- and δD-CH$_4$ were defined.

Due to the complexity of the involved measurement techniques, CH$_4$ isotope measurements have been limited mostly to relatively low frequency sampling in the field followed by isotope analysis in the laboratory (Bock et al., 2010; Brass and Röckmann, 2010; Sapart et al., 2011; Sperlich et al., 2013; UMEZAWA et al., 2009; Yamada et al., 2003). For many decades, the dominant method for high precision isotope analysis of atmospheric methane was isotope ratio mass spectrometry. In particular, the development of continuous-flow IRMS in the past two decades (Merritt et al., 1994; Merritt et al., 1995) has greatly increased the throughput of IRMS methods, making this the technique of choice in most laboratories, also because of the small sample amounts required.

Recently, mid-infrared laser absorption spectroscopy has proven its potential for high precision isotope ratio analysis. First attempts of measuring the isotopic composition of methane (Bergamaschi et al., 1998b; Bergamaschi et al., 1998a; Bergamaschi et al., 1994) were restricted to enhanced CH$_4$ mole fractions (> 50 ppm for δ$^{13}$C-CH$_4$ and > 2000 ppm for δD-CH$_4$) and required cryogenic cooling for both the laser source and the detector, which impeded in-situ and long-term applications. The invention of room temperature, quantum cascade laser (QCL) sources has triggered the development of a novel generation of spectrometers suitable for in-situ analysis of the isotopic composition of greenhouse gases (Eyer et al., 2015; Tuzson et al., 2008; Waechter et al., 2008). Their capability of high-temporal resolution led to new applications aiming for source attribution (Moh et al., 2012; Tuzson et al., 2011; Wolf et al., 2015a). The advantages of in-situ measurements are particularly apparent in combination with atmospheric modeling techniques, which enables the identification of specific source regions (Rigby et al., 2012; Sturm et al., 2013). Similarly, high-frequency, high-precision CH$_4$ isotope data are expected to greatly reduce uncertainties of national and global source estimations, as demonstrated in an observing system simulation experiment (Rigby et al., 2012).
In this paper we present the analytical setup and results of a 5-month campaign at the Cabauw tall tower site in the Netherlands, where the isotopic composition ($\delta^{13}$C and $\delta^D$) of CH$_4$ was measured with two instruments, one IRMS system developed at Utrecht University and one QCLAS-instrument developed at Empa. In the Methods section (4.2) we describe the site, the experimental setup and the deployed isotope measurement techniques. In addition, descriptions of the modeling tools that were used to support interpretation of the dataset are given. In the Results section (4.3) we present the dataset, including evaluation of the calibration and the compatibility of the techniques. In the Discussion section (4.4) the results and new approaches for data evaluation of such high-resolution isotope datasets are discussed.

4.2 Methods

4.2.1 Site description

The 213m tall tower is the central construction of the Cabauw Experimental Site for Atmospheric Research (CESAR, www.cesar-observatory.nl, 51° 58’ N, 4° 55’ E, 2m a.s.l.). The CESAR site is dedicated to atmospheric research and hosts a wide variety of instruments for in situ and remote sensing measurements of meteorological parameters, trace gases, pollutants, aerosols, and clouds. The site is located in an agricultural landscape, with CH$_4$ emissions originating from ruminants and other agricultural activities, but also from the peaty soil and the drainage ditches between the surrounding fields (Peltola et al., 2014). The small town Lopik ($\approx$ 7500 inhabitants) is located 1km east of the tower. Population and road density increase steeply further away from the tower towards the country’s major cities: Utrecht (at about 20km distance), Rotterdam (30km), the Hague (40km) and Amsterdam (45km). An estimated seven million people inhabit these cities and their many neighboring settlements. The location and surroundings are described in more detail in (Peltola et al., 2014; Peltola et al., 2015; Vermeulen et al., 2011). The instruments were operated in a room on the ground floor of the CESAR building. Since this room is not commonly used as laboratory, it has a limited air-conditioning capacity and the temperature varied between 25°C and 30°C.

4.2.2 Air sampling at the Cabauw tall tower

Air was continuously drawn through $\frac{1}{8}$” o.d. Dekabon tubing from 20m height at a total flow of 161min$^{-1}$ provided by a scroll pump (Varian Inc.). The sample gas flow was adjusted by means of a flow restriction at the inlet of the pump, thereby the pressure in the sampling line was maintained above 950hPa. The sample gas flows for the methane isotope analyzers were branched off upstream of the scroll pump and the restriction, using $\frac{1}{4}$” o.d. Dekabon lines.
4.2.3 IRMS system

The new IRMS method for δ^{13}C and δD analysis of atmospheric CH₄, which was developed during the INGOS project by IMAU and used during the Cabauw campaign, is based on the ISAAC system as developed at the MPI for Biogeochemistry in Jena (W. Brand et al., manuscript in preparation). Importantly, the system does not require liquid nitrogen coolant for the preconcentration and focusing steps, but uses a massive copper block cooled down to about −145°C, to which the cold traps for preconcentration and cryo-focusing are connected via standoffs (see 2.3.1). This cold assembly is contained in an evacuated steel Dewar to prevent condensation of moisture. During the campaign, the extraction unit and two IRMS instruments (Thermo Delta Plus XL for hydrogen isotopes and Thermo Delta Plus XP for carbon isotopes) were operated at the CESAR site. The system is schematically shown in Fig. 4.1.

4.2.4 Cryogenic trapping

A Polycold compact cooler compressor (Brooks Automation Inc., USA), filled with coolant PT-30, cooled a cold end on which a copper cylinder (70mm diameter * 85mm height, 3kg) is mounted. In this configuration, the copper block reached a temperature of −145°C. The pre-concentration trap (Pre-Con) was a 10cm 1/8" SS tube filled with 4cm 60/80mesh HayeSep D in the center and 3cm 60/80mesh glass beads on each end. It was connected with Valco fittings and the packing material was retained in the trap using removable frits (CEF1F). The focus trap (Focus) was a 10cm 1/16" SS tube filled with 2cm HayeSep D and 4cm glass beads at both ends, connected with Valco fittings (ECF211.0F). The traps could be heated with 0.5m Thermsys heating wire wrapped around the tubes. The focus units were glued together with a PT-100 temperature sensor in heat-conducting two component epoxy on a brass standoff. The brass standoffs were mounted to the copper cylinder. In the “trapping” configuration the temperatures of the traps were usually kept at −135°C.

4.2.5 Measurement procedure

A 3-port 2-position Valco valve (3PV, Fig. 4.1) selected either ambient air drawn from the tower through a Mg(ClO₄)₂ dryer, or cylinder air that was injected via one port of a 8-port multiposition Valco valve.
(MPV). To check the system performance, a reference air cylinder (Ref) was measured alternately with ambient air, and three other target gas cylinders were measured occasionally. The inlet line connected to a 4-port 2-position Valco valve (4PV1), which directed either Helium (He Air Products, BIP quality) or the selected air flow to the PreCon unit, which was connected in the loop position of a 6-port 2-position Valco valve (6PV). All He and air flows were controlled by MKS mass flow controllers (MFC). The preconcentration and cryofocussing was done similarly to Brass and Röckmann, 2010. After flushing the inlet line with > 20 ml air, the 6PV was switched to the load position and air was admitted to the PreCon unit. The duration of the air sampling for the IRMS system was 10 min at a flow rate of 5 ml min$^{-1}$ for $\delta^{13}$C-CH$_4$ and 7 ml min$^{-1}$ for $\delta$D-CH$_4$. The flow was provided by a Xavitech mini pump (P200-GAS-12V). During this step, the temperature measured at the PreCon stayed below $-132$°C. At this temperature CH$_4$ and other trace species were retained on the HayeSep D, while the air matrix was efficiently flushed out.

After preconcentration, the PreCon unit was heated to $-30$°C and a He-flow of 3 ml min$^{-1}$ transported the CH$_4$ in 90 sec to the Focus unit, which was held at a temperature $< -137$°C. After transfer of the sample to the Focus, the 6PV was switched to the load position and the PreCon was heated to $-10$°C to release any remaining trapped gases such as CO$_2$. The Focus was then heated to release the CH$_4$, which was directed via 4PV2 and 4VP3 either to the combustion oven and the Delta plus XP IRMS for 13C analysis or to the pyrolysis oven and the Delta plus XL IRMS for D analysis.

The typical measurement order during the Cabauw campaign was Ref $\delta^{13}$C – Air $\delta^{13}$C –Ref $\delta$D – Air $\delta$D. A full measurement cycle took 84 min. On a regular base, pressurized air from a cylinder, applied as a target gas, was analyzed. The CH$_4$ mixing ratio and isotopic composition in ambient air and target gas were calculated using an interpolation of the reference air analyzed before and afterwards.

For $\delta$D analysis, the CH$_4$ was injected (by heating the cryofocus trap to $-45$°C) into a pyrolysis tube furnace (1400°C), where CH$_4$ was converted to H$_2$ and carbon. The H$_2$ entered the IRMS, after passing a 2 m CarboPLOT column at room temperature (RT) and a nafion dryer, via the GasBench interface. No krypton interference could be determined in this setup. The repeatability for $\delta$D-CH$_4$ was better than $\pm 2$%,$^e$, based on 10 consecutive analyses of standard air.

For $\delta^{13}$C, the CH$_4$ was injected from the cryofocus unit into a combustion oven containing a nickel / nickel oxide wire catalyst at 1100°C, where the CH$_4$ was converted to CO$_2$ and H$_2$O. The resulting gas mixture passed a nafion dryer and a 10 m PoraPLOT Q column (5°C) to eliminate an interference from co-trapped krypton (Schmitt et al., 2013) before entering the IRMS via the GasBench interface. The repeatability of $\delta^{13}$C was better than 0.07%,$^e$. A custom made LabVIEW software program was used to control and log the temperature of the traps, the valve switching and the flow setpoints of the MFCs.

4.2.6 IRMS system isotope calibration

The isotope calibration of the IRMS system was based on a reference air cylinder that contains ambient air collected at the IMAU in 2014, with 1888 ppb of CH$_4$ and isotope values of $\delta^{13}$C = -47.75% and $\delta$D = -88.6%,$^e$. The isotope calibration scale is based on the reference scale that was described in detail in Brass and Röckmann, 2010. We used the average of the reference air measurement before and after the sample air measurement to calculate the mole fraction and $\delta$ values. The system linearity was monitored by injecting various amounts of reference air. Occasionally, the long-term stability of the system was checked by measuring 3 target cylinders with different CH$_4$ mole fractions and isotopic compositions. A robust link of the isotopic composition to the international reference materials VPDB and VSMOW has been established in the framework of the INGOS project (Sperlich et al., Development and evaluation of a suite of reference gases for methane in air, manuscript in preparation).

4.2.7 QCLAS system

The analytical procedure of the laser based measurement system involves two steps: preconcentration of the CH$_4$ from 7.5 L of ambient air in a trace gas extractor (TREX) by adsorption on HayeSep D (Eyer et al., 2014; Mohn et al., 2010) and analysis of methane isotopologues with a modified commercial QCLAS (QCL-76-D, Aerodyne Inc, USA). Details on the development, optimization and validation of the TREX-QCLAS system are given by Eyer et al., 2015.

The present manuscript comprises the first application of the TREX-QCLAS system for in-situ analysis of CH$_4$ isotopologues at a field site for an extended period of time. In comparison to the original
setup, the heating power of the polyimide foil on the cold trap was reduced to 60 W to increase its lifetime. Due to the lower heating power the duration of the desorption step had to be extended, which led to an improved separation from residual bulk gases (e.g. N\textsubscript{2} and O\textsubscript{2}) and thus a lower offset in $\delta^{13}\text{C}$ of 1.58‰ with respect to the MPI-scale, as compared to previously published results (Eyer et al., 2015). The offset has been found to be related to a higher O\textsubscript{2} mixing ratio in the gas matrix after CH\textsubscript{4} preconcentration. One measurement cycle consisted of four consecutive measurements of ambient air samples and one sample of pressurized air used as a target gas, followed by a calibration phase and took around 4:30h.

A calibration gas (CG1, 1200 ± 50 ppm CH\textsubscript{4}), $\delta^{13}\text{C}$-CH\textsubscript{4} = −44.24 ± 0.10‰, δD-CH\textsubscript{4} = −104.7 ± 1.1‰ was diluted to 688 ppm and analyzed between every preconcentrated sample as an anchor to correct the measurements for instrumental drifts. A second calibration gas (CG2, 1103.8 ± 3.5 ppm CH\textsubscript{4}), $\delta^{13}\text{C}$-CH\textsubscript{4} = −36.13 ± 0.10‰, δD-CH\textsubscript{4} = −180.6 ± 1.1‰, diluted to a similar CH\textsubscript{4} mole fraction of 681 ppm was used to calculate calibration factors for $\delta^{13}\text{C}$-CH\textsubscript{4} and δD-CH\textsubscript{4} values. Furthermore, gas cylinders of pressurized ambient air, referred to as target gas (TG1, TG2), were frequently measured over the entire campaign to determine and verify the repeatability of the measurement system, which was found to be 0.28‰ and 1.7‰ for $\delta^{13}\text{C}$ and δD-CH\textsubscript{4} (1σ), respectively. Additional adjustments in the preconcentration procedure and in the analytical routine for isotope analysis improved the repeatability to 0.18‰ and 0.85‰ for $\delta^{13}\text{C}$ and δD-CH\textsubscript{4} in the last month of the campaign.

The CH\textsubscript{4} isotopic composition of the calibration gases, as well as the target gases (TG1, 2639.5 ± 0.6 ppb CH\textsubscript{4}), $\delta^{13}\text{C}$-CH\textsubscript{4} = −46.48 ± 0.10‰, δD-CH\textsubscript{4} = −119.0 ± 1.1‰, TG2, 2659.8 ± 0.6 ppb CH\textsubscript{4}, $\delta^{13}\text{C}$-CH\textsubscript{4} = −45.87 ± 0.10‰, δD-CH\textsubscript{4} = −114.1 ± 1.1‰) were determined by the Stable Isotope Laboratory at the Max-Planck-Institute for Biogeochemistry. CH\textsubscript{4} mole fraction measurements were linked to the WMO-X2004 calibration scale (Dlugokencky et al., 2005) through calibration of the target gases against NOAA reference standards at Empa.

4.2.8 Modeling

Two complementary atmospheric transport models (TM5, FLEXPART-COSMO), both in combination with two different emissions inventories (TNO-MACC_2, EDGAR/LPJ-WhyMe), were applied to support interpretation of the measurements. The Eulerian tracer model TM5 simulated the distribution of CH\textsubscript{4} and $^{13}$CH\textsubscript{4} at global scale with a zoom on Europe at 1° x 1° resolution and considered both the isotopic signatures of different sources and the fractionation by different oxidation pathways of CH\textsubscript{4} in the atmosphere. The Lagrangian particle dispersion model FLEXPART-COSMO, conversely, was run in backward mode at a higher resolution of 0.06° x 0.06° but only over Europe. This model is better able to represent the spatial variability of methane sources in the near field of Cabauw but it only simulated the contributions from the last 4 days of emissions within Europe and not the large-scale background. Oxidation of CH\textsubscript{4} was not considered due to the short transport times between the sources and the receptor point at Cabauw. δD-CH\textsubscript{4} was only simulated with FLEXPART-COSMO.

TM5 modeling

Simulations of atmospheric CH\textsubscript{4} and $\delta^{13}$C-CH\textsubscript{4} were performed using the global tracer model TM5 (Krol et al., 2005). The Eulerian off-line model was driven by meteorological fields from the European Centre for Medium Range Weather Forecast (ECMWF) reanalysis project Era-Interim (Dee et al., 2011), pre-processed for use in TM5. For vertical transport due to moist convection we made use of Era Interim archived convective mass fluxes, replacing the use of the Tiedke scheme in Krol et al., 2005. The model was run at a horizontal resolution of 6° x 4° globally and 1° x 1° inside a zoom domain covering Western Europe. The model uses 25 hybrid sigma-pressure levels from the surface to top of atmosphere.

Two parallel (forward) TM5 simulations were performed with CH\textsubscript{4} and $^{13}$CH\textsubscript{4} as transported tracers. In the standard configuration, anthropogenic CH\textsubscript{4} emissions were taken from EDGAR4.2 FT2010 (European Commission and (PBL), 2009), extrapolated to 2014 and 2015 using annual statistics from the Food and Agriculture Organization of the United Nations (FAO) and the British Petroleum Company (BP), as described in Houweling et al., 2014. For natural wetland emissions, an average of the emission estimates derived by Spahni et al., 2011 for the period 2003-2008 was taken, using the LPJ-WhyMe model. For a complete description of the CH\textsubscript{4} emissions, see Monteil et al., 2013 and references therein. $^{13}$CH\textsubscript{4} emissions were derived from the CH\textsubscript{4} emissions using prescribed $\delta^{13}$C-CH\textsubscript{4} source signatures (see Table...
Chapter 4. In-situ observations of $\delta^{13}$C- and $\delta$D-CH$_4$ at the Cabauw tall tower site

Table 4.1: European CH$_4$ emissions and $\delta$ values for the different source categories used in TM5.

<table>
<thead>
<tr>
<th>Process</th>
<th>Yearly emissions (Europe)</th>
<th>$\delta^{13}$C-CH$_4$ source signature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural emissions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural wetlands (1)</td>
<td>22.1</td>
<td>$-59.2%e$</td>
</tr>
<tr>
<td>Peatland</td>
<td>9.3</td>
<td>$-68 \pm 3%e$</td>
</tr>
<tr>
<td>Wet mineral soils</td>
<td>4.6</td>
<td>$-65 \pm 3%e$</td>
</tr>
<tr>
<td>Inundated wetlands</td>
<td>1.3</td>
<td>$-60 \pm 3%e$</td>
</tr>
<tr>
<td>Geological emissions (2)</td>
<td>6.5</td>
<td>$-42 \pm 5%e$</td>
</tr>
<tr>
<td>Termites (3)</td>
<td>0.4</td>
<td>$-63 \pm 5%e$</td>
</tr>
<tr>
<td>Anthropogenic emissions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass burning (4)</td>
<td>45.3</td>
<td>$-52.4%e$</td>
</tr>
<tr>
<td>Agriculture (5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Domestic ruminants</td>
<td>11</td>
<td>$-64 \pm 3%e$</td>
</tr>
<tr>
<td>Manure</td>
<td>3</td>
<td>$-54 \pm 3%e$</td>
</tr>
<tr>
<td>Rice paddies</td>
<td>0.17</td>
<td>$-65 \pm 5%e$</td>
</tr>
<tr>
<td>Energy sector (5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal mining</td>
<td>3.4</td>
<td>$-47 \pm 13%e$</td>
</tr>
<tr>
<td>Oil production</td>
<td>3</td>
<td>$-42 \pm 5%e$</td>
</tr>
<tr>
<td>Oil combustion</td>
<td>0.41</td>
<td>$-32 \pm 5%e$</td>
</tr>
<tr>
<td>Residential sector (5)</td>
<td>1.6</td>
<td>$-32 \pm 3%e$</td>
</tr>
<tr>
<td>Waste treatment (5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Landfills</td>
<td>9</td>
<td>$-54 \pm 8%e$</td>
</tr>
<tr>
<td>Waste waters</td>
<td>3</td>
<td>$-50 \pm 4%e$</td>
</tr>
<tr>
<td>Total</td>
<td>67.4</td>
<td>$-54.6%e$</td>
</tr>
</tbody>
</table>

(1) Spahni et al., 2011; (2) Etiote et al., 2008; (3) Sanderson, 1996; (4) GFED3/4 (www.globalfiredata.org); (5) EDGAR4.2FT (2014).

4.1). The source signature confidence intervals were taken from existing literature. The actual source signatures were adjusted within these ranges to bring the background $\delta^{13}$C-CH$_4$ level in good agreement with observations (Monteil et al., 2011). In a second set of simulations, anthropogenic emissions in a regional domain centered on Cabauw were replaced by emissions from the European TNO-MACC_2 inventory used as the standard inventory in the FLEXPART-COSMO simulations (see below). Outside the regional domain covered by TNO-MACC_2, the EDGAR emissions were used.

Atmospheric oxidation of CH$_4$ was modeled as described in Monteil et al., 2013, using kinetic isotope effects of 1.0055, 1.066 and 1.013 for the reactions between CH$_4$ and OH, Cl (Saueressig et al., 1995) and O(1D) (Saueressig et al., 2001), respectively. Simulations of the period 2005-2015 were used to calculate a realistic state of the atmosphere at the start of the measurement campaigns. Time series were extracted from model-simulated mixing ratio fields after interpolation to the horizontal coordinate and height of the Cabauw tower air inlet.

FLEXPART-COSMO modeling

The Lagrangian Particle Dispersion Model (LPDM) FLEXPART (Stohl et al., 2005) was used in a modified version coupled to the mesoscale numerical weather forecast model COSMO (Baldauf et al., 2011) to simulate the regional contribution of different source categories to the concentrations and isotopic
Chapter 4. In-situ observations of $\delta^{13}$C- and $\delta^{D}$-CH$_4$ at the Cabauw tall tower site

Table 4.2: SNAP (Standardized Nomenclature for Air Pollutants) source categories and corresponding signatures from the TNO-MACC_2 inventory as used in FLEXPART-COSMO.

<table>
<thead>
<tr>
<th>SNAP Category</th>
<th>Description</th>
<th>$\delta^{13}$C-CH$_4$ source signature</th>
<th>$\delta^{D}$-CH$_4$ source signature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Energy industries, oil or gas production</td>
<td>$-42$‰</td>
<td>$-175$‰</td>
</tr>
<tr>
<td>2</td>
<td>Residential combustion</td>
<td>$-32$‰</td>
<td>$-175$‰</td>
</tr>
<tr>
<td>3+4</td>
<td>Industrial combustion and non-combustion processes</td>
<td>$-60$‰</td>
<td>$-175$‰</td>
</tr>
<tr>
<td>5</td>
<td>Extraction and distribution of fossil fuels including distribution of natural gas</td>
<td>$-42$‰</td>
<td>$-175$‰</td>
</tr>
<tr>
<td>7</td>
<td>Road transport</td>
<td>$-20$‰</td>
<td>$-175$‰</td>
</tr>
<tr>
<td>9</td>
<td>Waste including emissions from landfills</td>
<td>$-54$‰</td>
<td>$-293$‰</td>
</tr>
<tr>
<td>10</td>
<td>Agriculture including emissions from ruminants and manure management</td>
<td>$-64$‰</td>
<td>$-319$‰</td>
</tr>
<tr>
<td>6+8</td>
<td>Other emissions (negligible)</td>
<td>$-42$‰</td>
<td>$-175$‰</td>
</tr>
</tbody>
</table>

Signatures of CH$_4$ at Cabauw. FLEXPART–COSMO was driven by hourly operational analysis fields generated by the Swiss national weather service MeteoSwiss for a domain covering entire western and central Europe from Ireland, Denmark, Poland in the north to Portugal and southern Italy in the south with a horizontal resolution of approximately 7 km x 7 km and 60 vertical levels. Every 3 h, 50,000 particles (air parcels) were released from the position of the inlet 20 m above surface and traced backward in time for 4 days to compute the sensitivity of each 3-hourly measurement to upwind sources. The corresponding source sensitivity maps or footprints (Seibert and Frank, 2004) were multiplied with gridded CH$_4$ emissions to compute the mixing ratio enhancement above background expected from different sources. Emissions were taken from the TNO-MACC_2 inventory for Europe representative of the year 2009 and available at 0° x 0.0625° resolution (Kuenen et al., 2014) or, alternatively, from the same version of EDGAR/LPJ-WhyMe inventory driving TM5 at a resolution of 1° x 1°. This was done separately for a number of SNAP (Standardized Nomenclature for Air Pollutants) source categories with specific isotopic signatures as summarized in Table 4.2.

Source specific emissions were combined with isotopic signatures of the various categories from Table 4.2 to derive $\delta^{13}$C and $\delta^{D}$ isotope source signatures for the CH$_4$ that was picked up by the air parcel along the trajectory.

4.2.9 Interpretation of CH$_4$ isotope data by a Keeling plot technique

The isotopic source signatures of CH$_4$ emissions were estimated using the Keeling plot technique (Keeling, 1961; Pataki et al., 2003). This method allows determining the isotopic composition of a source that mixes into a background reservoir from the observed ambient isotopic composition and mole fraction. An implicit assumption of the Keeling plot approach is that the isotopic composition and mole fraction of the background reservoir and the isotopic composition of the source stay constant over the time range of the analysis. This may not always apply as CH$_4$ may originate from different sources and their relative contribution may change over time.

To exploit the high temporal resolution of our data, we applied a novel approach of a moving Keeling plot (MKP) method. Data within a moving window of 12 h were used to calculate the source isotopic composition. This window was moved in 1-h time steps over the data series. In addition, values for background conditions within a 48-h period, centered on the respective 12-h window, were included in the analysis. These background values were chosen between 10:00 and 18:00 local time, because during this period a convective boundary layer usually develops and hence local influence is weak; pollution events with CH$_4$ mole fractions above 2100 ppb were filtered out additionally. For each time window, an orthogonal least square fit was applied to the $\delta$ values vs. the inverse CH$_4$ mole fractions and $R^2$ values were calculated. A Keeling plot analysis only returns meaningful values for the source isotopic
composition if the variations in CH₄ mole fraction are significant and if the emissions are from a source with a well-defined isotopic composition. Therefore, two additional filters were applied: i) the mole fraction had to vary by more than 200 ppb within each time window and ii) the $R^2$ of the fit had to be larger than 0.8. If $R^2 < 0.8$, the 12-h interval was reduced consecutively by one hour to a minimum of six hours until either the $R^2$ of the fit was > 0.8 or the number of data points was lower than five. On average this technique accumulated 22 data points per 12-h time window.

4.3 Results

![Figure 4.2: CH₄ mole fractions and isotopic composition (δ¹³C-CH₄, δD-CH₄) measured at the Cabauw tall tower from 17 October 2014 until 29 March 2015. Real-time measurements by IRMS (Utrecht University) are indicated in yellow, TREX-QCLAS (Empa) data in blue. In addition, bag-samples were collected on March 17-18 2015 and analyzed with IRMS in the RHUL laboratory (red circles).](image)

4.3.1 Overview of the field measurements at the Cabauw site

The full record of the methane mole fraction and isotopic composition obtained with the two measurement techniques at the CESAR site is shown in Fig. 4.2. The IRMS system started with δD measurements first, and after 3 weeks delivered both δ¹³C and δD data. The TREX-QCLAS system started later and ran continuously from mid-December to mid-January, and from mid-February to the end of the campaign. Despite a number of interruptions mainly due to various kinds of instrument malfunction, the combined time series of both techniques shows a high temporal coverage with more than 2500 measurements performed for both δ¹³C and δD-CH₄.

A qualitative inspection of the time series already conveys the obvious features that will be discussed below in more detail: the methane mole fraction shows a large number of substantial increases above background level, and these positive methane excursions are accompanied by negative excursions in the δ values from the background level. Thus the additional methane is generally depleted in both δ¹³C and δD.
Chapter 4. In-situ observations of $\delta^{13}$C- and $\delta$D-$\text{CH}_4$ at the Cabauw tall tower site

4.3.2 Intercomparison of the two analytical techniques

4.3.3 The global CH$_4$ budget

Before presenting a detailed analysis of the CH$_4$ isotopic composition in ambient air, we compare the results obtained with the IRMS and QCLAS techniques in order to evaluate their performance and to combine the results into one final dataset. Although both systems measured air from the same intake line, the sampling intervals could not be synchronized since both instruments operated in different measurement cycles. A full measurement cycle (including measurement of the reference gas) took 84 min for the IRMS system and 54 min for the TREX-QCLAS system. The actual duration of the air sampling was 10 min for the IRMS system and 15 min for the QCLAS system. So even if the systems coincidentally started sampling at the same time, they never actually analyzed exactly the same air mass. Consequently, differences between the systems contain contributions from natural variability, random fluctuations due to limited measurement precision, and system offsets. Fig. 4.3 shows a comparison of the CH$_4$ mole fraction, as well as $\delta^{13}$C and $\delta$D-$\text{CH}_4$ values that were obtained with the TREX-QCLAS and the IRMS technique. To visualize the possible effect of time shifts, the size of the points corresponds to the proximity of the sampling intervals. A total of 727, 333 and 277 measurement pairs for CH$_4$ mole fractions, $\delta^{13}$C and $\delta$D, respectively, analyzed by both techniques were combined in this way.
The mole fraction intercomparison shows good agreement along the 1:1 line but with a large scatter, which has two contributions: i) instrumental noise, as the isotope systems have a relatively large uncertainty for measurement of the mole fraction compared to existing high-precision CH$_4$ analyzers, and ii) natural variability associated with the sampling of different air masses as described above. The second point is supported by the fact that the average difference in CH$_4$ mole fractions between the two analytical techniques was larger for larger temporal differences in the sampling intervals.

For the isotope intercomparison plots, the grey-black shading of the circles indicates the difference in methane mole fractions of the respective measurement pair analyzed by both techniques. The overall difference between the measurements conducted with the two systems (QCLAS-IRMS) is $+0.05 \pm 0.03 \%$ for $\delta^{13}C$ and $-3.6 \pm 0.4 \%$ for $\delta^D$-CH$_4$ (the stated errors are standard errors of the mean). The mean offsets of $0.05 \%$ for $\delta^{13}C$ and $3.6 \%$ for $\delta^D$ are well within the WMO extended compatibility goals of $0.2 \%$ for $\delta^{13}C$ and $5 \%$ for $\delta^D$, as indicated by the red dashed lines (WMO/GAW, 2013). Individual measurement pairs, however, can show significantly larger deviations for aforementioned reasons. In addition, we note that the $\delta^D$ comparison indicates a deviation from the linear dependence that becomes larger at lower $\delta^D$ values.

The mean offset values determined above were applied to the QCLAS data to create one combined dataset with 2610 data points for $\delta^{13}C$ and 2673 data points for $\delta^D$.

### 4.3.4 FLEXPART-COSMO source attribution

![Figure 4.4](image_url)

**Figure 4.4:** Absolute (top) and relative (bottom) contributions of methane emissions that are picked up along the 4-day FLEXPART-COSMO trajectories during the campaign. The results shown are from the FLEXPART-COSMO simulations with the TNO-MACC inventory. They indicate major contributions of the following source categories: “agriculture” (mainly ruminants), “waste” (mainly landfills) and “fossil” (fugitive losses from coal, oil and natural gas production and from gas transportation and distribution) to the increase in CH$_4$ mixing ratios at Cabauw. The category “rest” primarily represents residential CH$_4$ emissions.
In FLEXPART-COSMO, the contributions of the individual source types are simulated separately and added up to obtain the cumulative CH$_4$ mole fraction. Figure 4.4 shows these contributions in absolute (top) and relative terms (bottom). According to the model, the relative contributions at the Cabauw site are quite uniform, with agricultural sources accounting for more than 60%, waste (mostly landfills) around 20–40%, and fossil sources between 0 and 40%. We note that significant contributions from fossil sources are only detected episodically, during several events that usually last a few days. Contributions from other source categories are generally negligible at the Cabauw site.
4.3.5 TM5 and FLEXPART-COSMO modeling including isotopes

Figure 4.5: Comparison of the modeled and measured time series of CH$_4$ mole fraction and isotopic composition ($\delta^{13}$C- and $\delta$D-CH$_4$). Measurements are shown as circles and model results as lines. Top graph: two selected model configurations for the entire campaign: FLEXPART-COSMO using the TNO-MACC inventory (blue) and TM5 using the Edgar/Why-Me inventory (red). Bottom graph: Time series for March 2015 with all four model – inventory combinations. For $\delta$D, only the synthetic FLEXPART-COSMO results are available for comparison since TM5 does not simulate $\delta$D.
Chapter 4. In-situ observations of $\delta^{13}$C- and $\delta^D$-CH$_4$ at the Cabauw tall tower site

The TM5 model calculates the combined influence of the global methane sources and sinks on CH$_4$ and $\delta^{13}$C-CH$_4$ at the Cabauw tower, and therefore the TM5 results can be compared directly to the measured time series. For FLEXPART-COSMO, a representative background mole fraction and isotopic signature needs to be added for comparison with the observations. For simplicity we assumed a constant background similar to the observed values for background conditions: 1930 ppb CH$_4$ with $\delta^{13}$C = $-47.1\%$ and $\delta^D = -86\%$.

Figure 4.5 shows a comparison of these model-generated time series with the measured data for the entire campaign. Both models capture the amplitude and the temporal variability of the CH$_4$ mole fraction well. Most of the methane pollution events observed at the CESAR site are also present in the modeled time series and the increase in CH$_4$ mole fractions is of a comparable size. In addition, the results of the TM5 and the FLEXPART-COSMO model for CH$_4$ mole fractions agree relatively well with each other ($R^2 = 0.69$), in particular when both models are run with the same inventory at the same coarse spatial resolution, i.e. with EDGAR/LPJ-WhyMe.

A few pronounced methane events in Figure 4.5 show larger differences between the models. On 2 November, FLEXPART-COSMO simulates an emission signal that is not captured by TM5. Unfortunately no measurements are available for this event to decide on which model performs better. On 30 November TM5 simulates a CH$_4$ plume, which is absent in FLEXPART-COSMO, and this event is also not supported by the measurements. Nevertheless, the overall performance of the TM5 global model is quite remarkable given its coarse spatial resolution. The global model has the advantage that it includes the influence of long-range transport. As expected, however, the observed variability is predominantly influenced by local and regional emissions.

Regarding the time series of the $\delta$ values, both TM5 and FLEXPART-COSMO qualitatively display the expected anti-correlations between CH$_4$ and $\delta^{13}$C-CH$_4$. However, the amplitude of the $\delta^{13}$C-CH$_4$ variability is generally underestimated in the model runs, especially when using the EDGAR inventory. In addition, the modeled background level of $\delta^{13}$C-CH$_4$ in TM5 is offset by up to 1%, but this is consistent with data-model comparisons at clean background sites at mid latitudes (not shown). Using the TNO-MACC inventory in FLEXPART-COSMO results in better agreement with the observed variability of $\delta^{13}$C-CH$_4$. In TM5, the TNO-MACC emissions reduce the amplitude of the CH$_4$ variability, which is explained by the 13% lower emissions in TNO-MACC compared with EDGAR. Furthermore, the results of both models are consistent with the emissions being more depleted in $\delta^{13}$C in TNO-MACC than in EDGAR. The measurements indicate emissions that are even more depleted in $\delta^{13}$C than TNO-MACC values. These results suggest that the fractional contribution of isotopically heavy fossil emissions is overestimated in EDGAR, at least in the area sampled by Cabauw, although the uncertainty in the assumed $\delta^{13}$C source signatures could also contribute. For instance, recent literature showed, that landfill emissions from the UK are more depleted in $^{13}$CH$_4$ due to the implementation of gas extraction systems (Zazzeri et al., 2015).

The $\delta^D$-CH$_4$ time series simulated with FLEXPART-COSMO using the TNO-MACC inventory is in good agreement with the measurements. This further indicates that TNO-MACC has a realistic source mixture though the uncertainties in the $\delta^D$ source signatures are too large to draw firm conclusions. Despite these uncertainties, Figure 4.5 clearly demonstrates how isotopic measurements highlight differences between emission inventories, which would go unnoticed looking only at CH$_4$ mole fractions. Differences between measurement and model results will be investigated in more detail in Section 4.4.4.

4.4 Discussion

4.4.1 Diurnal and synoptic variability

A prominent feature of the high-resolution dataset is the pronounced diurnal variability, with large increases in CH$_4$ mole fraction that occur often during the night, due to the shallow planetary boundary layer. In addition, there are also several synoptic (but much smaller) pollution events, where CH$_4$ mole fractions stay above the unpolluted background level for several days. These elevations are likely caused by synoptic scale advection of CH$_4$ plumes from other source regions with a different source mix.
4.4.2 Isotope identification of the cumulative source

In Fig. 4.6, the Keeling plot technique is applied to identify the isotopic signature ($\delta^{13}C$, $\delta D$-$\text{CH}_4$) of the combined $\text{CH}_4$ emissions detected at the Cabauw site. An orthogonal regression method was applied to determine the fit parameters. This analysis yields well-defined isotopic signatures of the cumulative source (the y-intercept of the regression analysis) of $\delta^{13}C = -60.9 \pm 0.2 \%e$ and $\delta D = -295 \pm 1 \%e$. The...
inferred isotopic signature agrees well with emission from ruminants, which are expected to be the main source of methane in this rural area. This is plausible, because the cumulative source signature is largely determined by the pronounced nighttime methane elevations, which represent the local emissions close to the tower. Also the source contributions modeled by FLEXPART-COSMO suggest the dominant influence of agricultural emissions in this rural area (Fig. 4.4). Interestingly, the source signature for the much smaller synoptic CH$_4$ variations of the background (red points in Fig. 4.6) is not significantly different from the one for the complete dataset.

### 4.4.3 Short-term variability

**Figure 4.7**: MKP intercepts of $\delta^{13}$C vs. $\delta$D. The colored areas indicate typical isotope signatures for different source categories. Circles show the 6h-averaged source signatures. Large colored symbols indicate data from the three events that are highlighted in detail in Fig. 4.9. $\delta^{13}$C values are taken from Table 4.2 and $\delta$D values from recent literature (Rigby et al., 2012)
Chapter 4. In-situ observations of $\delta^{13}$C- and $\delta^{2}D$-CH$_4$ at the Cabauw tall tower site

Figure 4.8: Keeling plots for the period between 16 and 18 March, illustrating a rapid change in $\delta$ values over the course of hours, which is most probably related to a change from mainly ruminant derived CH$_4$ to a significant contribution of fossil and/or waste CH$_4$. The dashed lines indicate the regression line, the shaded areas the uncertainty (one standard deviation) of the regression line. Left panels show the region near the y-axis intercept.
Given the high temporal resolution of the dataset presented here, the isotope variations can be interpreted in much more detail than the overall analysis performed above. This allows identifying varying contributions of CH₄ sources during different periods of the campaign. To do so, we applied a 12-h MKP method to the data, as described in Section 4.2.9.

Fig. 4.7 summarizes the results of the MKP method in the form of a δD vs. δ¹³C plot. To combine δ¹³C and δD measurements at different times, MKP intercepts were averaged over 6h intervals. δ¹³C-CH₄ source signatures range between −68‰ and −55‰ and δD-CH₄ source signatures cover a wide range between −350‰ and −230‰, indicating emissions mainly from microbial sources as derived from the cumulative Keeling plot analysis. During some periods, however, elevated δ¹³C and δD source signatures indicate significant additional contributions from waste and/or fossil emissions.

The colored symbols in Fig. 4.7 highlight the source signatures of three 48h events (March 10-12, 16-18 and 22-24) that are discussed in more detail in the following. For one event (March 16-18), the results of the 12h MKP method are displayed in Fig. 4.8 demonstrating the advantage of the high temporal resolution data. It is possible to distinguish between two individual events within this period and even identify their isotopic source signatures. The increase by about 6‰ for δ¹³C and about 50‰ for δD, in the source isotopic signature clearly indicates the gradually increasing contribution of CH₄ from isotopically enriched sources, e.g. fossil fuel- or waste-related CH₄.

The temporal evolution of the observed source mixture is investigated in further detail in Fig. 4.9, where the March 16-18 period (labeled as 2) is compared to two other 48h-periods (March 10-12; label 1, and March 22-24; label 3), each with significant diurnal methane elevations. For event 1, the isotope source signatures stayed rather constant at values around δ¹³C = −62‰ and δD = −320‰. These
Chapter 4. In-situ observations of \( \delta^{13}\text{C} \) and \( \delta\text{D-CH}_4 \) at the Cabauw tall tower site

Figure 4.10: Histograms of \( \text{CH}_4 \) isotope source signatures at the CESAR site between October 2014 and March 2015. Bin widths are 1‰ for \( \delta^{13}\text{C-CH}_4 \) and 10‰ for \( \delta\text{D-CH}_4 \). Source signatures are derived from measured data (grey bins), FLEXPART-COSMO modeling (squares) as well as TM5 modeling (circles) using the 12h MKP method. Two different inventories, TNO-MACC (blue) and Edgar/LPJ-Why-Me (red), were used. The shaded areas show histograms for the “direct” source signatures that were picked up along the FLEXPART-COSMO trajectory (right axis).

values are typical for microbial emissions from an agricultural source and agree well with the source contributions predicted for this period by the FLEXPART-COSMO model.

Period 2 is characterized by much stronger isotopic change within the 48h period. The \( \delta^{13}\text{C} \) source signature increases to above \(-60\%e\) and the \( \delta\text{D} \) source signature increases to \(-240\%e\) by the end of the period (see Fig. 4.9). As shown in the double-isotope plot in Fig. 4.7, the change in \( \delta\text{D} \) during event 2\( b \) clearly points towards fossil fuel sources, which is further supported by the FLEXPART-COSMO simulations, where the contributions from fossil-fuel- derived emissions are higher for the second day. This also underlines the importance of \( \delta\text{D-CH}_4 \) measurements in distinguishing between microbial and fossil (thermogenic) emissions.

For period 3, the \( \delta^{13}\text{C} \) source signatures increased during the 48h by about \(-2\%e\), whereas the \( \delta\text{D} \) signatures remained constant around \(-300\%e\). For this period, the double isotope plot of Fig. 4.7 indeed shows a shift towards the waste category. Also this observation is independently confirmed (at least qualitatively) by the FLEXPART-COSMO model derived source attribution, which indicates the largest fraction of waste-derived \( \text{CH}_4 \) for the first day and a small addition of fossil \( \text{CH}_4 \) for the second day of event 3. These examples show that even at a location like Cabauw, where one source category strongly dominates, contributions from isotopically different sources can be identified if sufficiently high-resolution isotope ratio data are available.

4.4.4 Evaluation of emission databases with high temporal resolution \( \text{CH}_4 \) isotope data

As described in Section 4.3.5, both the TM5 and the FLEXPART-COSMO model-generated time series of \( \text{CH}_4 \) mole fractions show an adequate agreement with the \( \text{CH}_4 \) measurements at the Cabauw site. Therefore, the comparison between measurement data and the models can be used to evaluate the methane budget in more detail. In this context, the isotopic source signatures can be employed to assess the validity of emission inventories, EDGAR and TNO-MACC, with respect to the magnitude and spatial distribution of source categories. To compare the measured isotopic source signatures to the model results, the simulated isotope time series were linearly interpolated and evaluated in the same way as the observations using the 12h MKP method. This analysis was performed for both models (TM5 and FLEXPART-COSMO), each using both the EDGAR/LPJ-Why-Me and the TNO-MACC inventories. Additionally, isotopic source signature time series were calculated directly from FLEXPART-COSMO data, without using of the MKP method. This direct method allowed an independent estimation of the source signatures and, thus, also provided an opportunity to evaluate the MKP method.
Chapter 4. In-situ observations of $\delta^{13}$C- and $\delta$D-$\text{CH}_4$ at the Cabauw tall tower site

Table 4.3: Mean value and standard deviation of the histograms of the source isotopic composition shown in Fig. 4.10.

<table>
<thead>
<tr>
<th>Model + inventory</th>
<th>Method</th>
<th>$\delta^{13}$C value</th>
<th>$\delta$D value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement data</td>
<td>MKP</td>
<td>$-60.9 \pm 3.1$</td>
<td>$-301 \pm 24$</td>
</tr>
<tr>
<td>TM5 + Edgar</td>
<td>MKP</td>
<td>$-53.3 \pm 1.1$</td>
<td></td>
</tr>
<tr>
<td>FLEXPART-COSMO + Edgar</td>
<td>MKP</td>
<td>$-54.5 \pm 1.6$</td>
<td>$-277 \pm 10$</td>
</tr>
<tr>
<td>FLEXPART-COSMO + Edgar</td>
<td>direct</td>
<td>$-53.4 \pm 1.7$</td>
<td>$-269 \pm 10$</td>
</tr>
<tr>
<td>TM5 + TNO-MACC</td>
<td>MKP</td>
<td>$-56.7 \pm 0.8$</td>
<td></td>
</tr>
<tr>
<td>FLEXPART-COSMO + TNO-MACC</td>
<td>MKP</td>
<td>$-57.6 \pm 1.9$</td>
<td>$-294 \pm 12$</td>
</tr>
<tr>
<td>FLEXPART-COSMO + TNO-MACC</td>
<td>direct</td>
<td>$-57.2 \pm 1.7$</td>
<td>$-289 \pm 11$</td>
</tr>
</tbody>
</table>

The statistics of the isotope source signatures from all four model-inventory combinations are shown as histograms in Fig. 4.10, together with the measurement-derived source signatures and the directly derived source signatures from FLEXPART-COSMO modeling. Table 4.3 gives a summary of the mean values and the standard deviations of the histograms. A clear difference can be observed between the source signatures derived with the two different emission inventories. Model runs with the EDGAR/LPJ-WhyMe emission inventory (red in Fig. 4.10) tend to produce $\text{CH}_4$ isotope source signature distributions that are more enriched in $\delta^{13}$C and $\delta$D than the model runs with TNO-MACC emissions. These differences are very similar for the time series modeled with TM5 and FLEXPART-COSMO, suggesting that differences originate from the emission inventories, rather than from differences between the models themselves. The $\delta^{13}$C source signatures derived from the measurements at the Cabauw tower are even significantly more depleted than any of the model-generated datasets. For $\delta$D, the source signatures using TNO-MACC emissions are relatively close to the measurements at Cabauw, whereas the values using EDGAR emissions are much more enriched in CH$_4$D.

The high temporal resolution isotope data that are described in this paper thus provide relevant information to further constrain models and/or emission inventories, because the isotope source signatures do change rapidly. The comparison of our first high-resolution isotope measurements at Cabauw to model calculations clearly identify differences between the modeled inventories, where the EDGAR inventory produced too enriched source signatures due to a higher contribution from fossil fuel sources. Similar differences in terms of source contributions between EDGAR and TNO-MACC_2 were also reported by Hiller et al., 2014, for Switzerland and (Henne et al., in preparation), concluded that natural gas emissions in Switzerland are likely overestimated in EDGAR. Given the many degrees of freedom (transport, source signatures used in the models, emission inventories), one single dataset is not sufficient to make a final decision on the quality of the emission dataset, because it reflects only one region. High frequency isotope observations at several locations would allow better constraints on isotope source signatures and emissions in atmospheric models.

4.5 Conclusions and outlook

The dual isotopic composition of CH$_4$ has been monitored for the first time with high temporal resolution in an extended (5 months) field deployment with two different instruments, an IRMS system and a QCLAS system, at the tall tower site Cabauw, the Netherlands. The measurements of both instruments compare well and can be combined to a time series of more than 2500 measurements for both $\delta^{13}$C and $\delta$D. Using a moving Keeling plot technique, the isotopic source signatures of periods with significant methane elevations can be derived with high temporal resolution. Overall, methane emissions at the Cabauw tall tower are dominated by agricultural sources, but variations in the source signatures allow identification of events with increased contributions from fossil fuel and waste sources, which can be used to validate variations in the source mix calculated using the FLEXPART-COSMO model. While the $\delta^{13}$C-$\text{CH}_4$ isotopic signatures of different source processes strongly overlap, $\delta$D-$\text{CH}_4$ measurements provided valuable complementary information, which allows to disentangle microbial and fossil emissions.
Chapter 4. In-situ observations of $\delta^{13}$C- and $\delta^{D}$-CH$_4$ at the Cabauw tall tower site

The high-resolution isotope ratio measurements at Cabauw were compared to model calculations that used two different emission inventories. When two very different models (TM5 and FLEXPART-COSMO) used emissions from the EDGAR inventory, they produced clearly too enriched source signatures. The modeled source signatures were systematically more depleted and closer to the measured ones when the TNO-MACC inventory was used. The differences in the source signatures appear to originate from differences in the inventories and not from differences in the models, which supports indications in the recent literature that fossil fuel related emissions might be overestimated in EDGAR. We note that measurements at Cabauw reflect only one limited region of the European domain, and given the many degrees of freedom (transport, source signatures used in the models, emission inventories), one single dataset is not sufficient to make a final decision on the quality of the emission dataset. High frequency analysis of $\delta^{13}$C- and $\delta^{D}$-CH$_4$ at several locations would allow better constraints on isotope source signatures and emissions in atmospheric models. Our proof-of-concept study presented here using continuous high-resolution techniques shows that this will be feasible in the future.

Acknowledgements

This project was funded by the European Community’s Seventh Framework Program (FP7/2007-2013) within the InGOS project under grant agreement No. 284274. Additional funding from the Swiss National Science Foundation (SNSF) within grant No. 200021_134611 and TNA grants within INGOS is gratefully acknowledged. The campaign at the Cabauw tall tower was made possible with strong support from Marcel Brinkenberg (KNMI), Michel Bolder and Henk Snellen (IMAU). We also thank Marco Weber (Empa) for assistance during transport and setup of the TREX-QCLAS system at the CESAR site.

Author contributions

Chapter 5

Conclusion & Outlook

5.1 Analytical developments & achievements

This PhD thesis is about the development, validation and application of a field-deployable fully automated liquid nitrogen free measurement platform, called TREX-QCLAS for real-time high precision analysis of methane isotopologues in ambient air, i.e. CH₄ mole fractions and their ratios quantified as δ¹³C- and δD-CH₄. The measurement system comprises a preconcentration unit (TREX) and a quantum-cascade laser absorption spectrometer (QCLAS). As part of this PhD thesis, the TREX was fully developed at Empa including the design of the vacuum chamber and the integration of a linear drive to couple/decouple the adsorbent trap to the cold end of a novel Stirling cooler. In addition, an automated gas handling module was developed to provide purge, sample and calibration gases at the required flow rates and concentrations. The TREX was tailored for the target gas CH₄ by prior investigation of several commercially available and novel research-grade adsorbents, which were evaluated with respect to their effectiveness for CH₄ preconcentration from ambient air. HayeSep D, a macroporous polymeric resin, was selected for its outstanding selective properties and high isosteric enthalpy of adsorption. Major upgrades of the QCLAS with respect to the previous system involved the installation of a new set of DFB-QC lasers, and improving driving and controlling electronics. The complete system was assembled in a 19” compatible housing and automatized by a custom-tailored LabVIEW program.

Major achievements of the TREX-QCLAS technique include:

- High precision analysis of δ¹³C- and δD-CH₄ isotopic composition in ambient air achieved through enhancement of CH₄ mole fractions by a factor of up to 500 during preconcentration.
- Removal of potential spectral interferences from N₂O, CO₂ and H₂O by sequential desorption of the target gas.
- Achieving the WMO compatibility goals for regional studies under field conditions, with a repeatability better than 0.18‰ and 0.85‰ for δ¹³C- and δD-CH₄, respectively. The repeatability for CH₄ mole fractions is 10ppb.
- Fully autonomous analysis of δ¹³C-, δD-CH₄ and CH₄ in ambient air for extended periods of time.

5.2 Potential for optimization

Despite the outstanding performance of the TREX-QCLAS technique for CH₄ isotopic analysis a number of technical and methodological improvements might be implemented for future applications:

- Better temperature control of the cold trap during CH₄ adsorption (< 0.5 K) would be beneficial. This requires either a regulation of the stirling cooling power or slightly heating the trap. Thereby the variability of the preconcentration factor and the O₂ mixing ratio in the analyte gas could be reduced resulting in an improved repeatability for ¹²CH₄ and δ¹³C-CH₄ measurements.
- Better temperature control during CH₄ adsorption and desorption. This is feasible by repositioning the heat foil from the bottom of the stand-off to the inner side of the standoff cylinder walls. This would reduce the distance between heating foil and temperature sensor and thereby reduce delays in the heating control cycle. Such modification, however, would require major modifications in the trap design.
Further improvement in separating CH$_4$ from O$_2$ would be advantageous to keep the O$_2$-mixing ratio in the measurement cell at $\approx 21\%$. This could be accomplished by novel research-grade adsorbents, such as a metal organic framework (i.e. HKUST-1). Initial test with HKUST-1 displayed promising results, but also problems with high back pressure, as the adsorbent was only available at very small particle sizes.

5.3 Accomplished field studies and interpretation of isotopic source signatures

Immediately after its development, the TREX-QCLAS system was successfully applied in two measurement campaigns. First, a feasibility study was conducted during two weeks in Dübendorf, Switzerland. The study demonstrated the capabilities of the TREX-QCLAS technique to measure the isotope ratios of CH$_4$ in ambient air and validated the system against the standard flask sampling/IRMS technique. The measurements agreed with the leading IRMS laboratories within the WMO compatibility goals for regional studies. The second extended five month field campaign at the Cabauw tall tower near Utrecht in the Netherlands was aimed to record long-term CH$_4$ isotopic composition data with about one hour temporal resolution. Even though CH$_4$ emissions were dominated by the agricultural source, the unique time-series measured by TREX-QCLAS could be applied to identify and resolve even small changes in the contribution of individual CH$_4$ source processes. The comparison of atmospheric transport model simulations and measurements revealed potential differences in emission inventories. Thereby fossil emissions in the EDGAR inventory were found to be possibly overestimated.

![Figure 5.1](image)

**FIGURE 5.1:** Isotopic source signatures derived from the two measurement campaigns on CH$_4$ isotopes at the tall tower in Cabauw, the Netherlands (NL, blue, Chapter 4) and at the Empa in Dübendorf, Switzerland (CH, red, Chapter 3) for comparison.

In Figure 5.1 results of both measurement campaigns, Dübendorf, Switzerland (CH, red, Chapter 3) and Cabauw, the Netherlands (NL, blue, Chapter 4) are combined with best estimates of isotopic signatures for different source categories (Chapter 1). The most dominant contribution from ruminant emissions (mainly cows) in both countries (estimated as 60\% for NL and $>85\%$ for CH; Hiller et al., 2014) is very well represented by the measurement data. While the derived source signatures from the Cabauw-site agree relatively well with the ruminant source, the source signatures from the campaign in Dübendorf are more depleted in CH$_3$D and on average slightly more enriched in $^{13}$CH$_4$. Differences in $\delta^{13}$C-$\text{CH}_4$ source signatures could be rationalized by a general tendency towards a higher fodder contribution of C3 plants in the Netherlands as compared to Switzerland. The significantly lower $\delta^D$ source signature of CH$_4$ emissions from cows in Switzerland may be explained by a lower $\delta^D$ value of the meteoric
water. In fact, measurements from IAEA (International Atomic Energy Agency; www.iaea.org/water) show a difference of up to 60% in the $\delta D$ isotopic signature of precipitations between the Netherlands and Switzerland. The above argumentation displays the potential of future research activities, but also reveals the need for additional source studies to further consolidate data interpretation.

### 5.4 Future research applications

The pilot studies described above demonstrate the potential of the developed analytical technique, but also reflect the complexity and the still limited insight in the interpretation of $CH_4$ isotopic source signatures. In the following, a number of research opportunities are mentioned, which might be envisaged for future applications of the TREX-QCLAS technique:

- **Assimilation of background information for $\delta^{13}C$- and $\delta D$-$CH_4$, and $CH_4$ mole fraction.** This turned out to be a problem in the Netherlands, as $CH_4$ concentrations sometimes remained elevated for several days. Extraction of source signatures from the isotopic measurement data (i.e. via Keeling plot technique or a mixing model) is more robust when the composition of unpolluted background is known. Such background information could be attained by frequently analyzing samples from remote measurement stations i.e. at the high alpine research station Jungfraujoch. In tall tower campaigns (i.e. > 150m) background information on trace gas mole fractions and isotopic composition could alternatively be obtained from air samples collected at maximum height, during sufficiently stable meteorological conditions, i.e. when the atmospheric boundary layer is lower than the sampling height.

- **Refinement of emission inventories by a combination of real-time high-precision $CH_4$ isotopic analysis and inverse atmospheric modeling.** Due to their higher footprint area, tall tower measurements (e.g. Beromünster in Central Switzerland) are especially attractive for such studies. Different sampling heights offer the potential to focus on local (lower height), regional (intermediate height) or larger scale emission sources (top height) or collect information on background conditions. Whether large scale studies are feasible depends on the sensitivity of the instrument in relation to the magnitude of variations in the isotopic signatures. The latter depends on the strength of the total emissions, the variations in terms of relative contribution of each source and the relative difference of the distinct isotopic source signatures on the $\delta^{13}C$ vs $\delta D$ scale.

- **Improved process-level understanding of individual sources by real-time analysis of $CH_4$ isotopologues could be accomplished by the TREX-QCLAS technique in near-source measurement studies.** Thereby, variations in the isotopic source signature could be resolved at high temporal resolution (i.e. < 1h), which would provide a more detailed understanding of the interplay between different parameters.

- **The developed TREX design can be extended to the analysis of mixing ratios and isotopic composition of other trace gases.** Thus, a powerful approach would be the simultaneous preconcentration of multiple gases with one TREX system and the subsequent analysis by several analyzers. The desorption experiment in chapter 3 expresses the feasibility of this idea for $CH_4$ and $N_2O$. Ongoing developments in multi-component QCLAS may further facilitate relatively simple TREX-QCLAS systems for several GHG isotopes.

- **An obvious application of TREX-QCLAS is the analysis of rare singly or doubly substituted isotopic species of $CH_4$ and other greenhouse gases, such as $N_2O$ and $CO_2$.** For $CH_4$ clumped isotope analysis, the capacity of the current TREX system would have to be further optimized as the required precision is currently only accessible in pure $CH_4$.

- **Integration of the TREX-QCLAS system into existing atmospheric monitoring networks, such as WMO GAW, NOAA, or ICOS is a feasible and promising possibility, given its high precision and capability for continuous unattended operation at remote locations.** For instance, TREX-QCLAS could replace existing manual flask sampling as performed within NOAA on a weekly base for $\delta^{13}C$-$CH_4$ at 16 measurement stations around the globe. This would enable a better understanding of global and regional $CH_4$ budgets as displayed by Rigby et al., 2012, and reduce the effort for flask collection and transportation. The availability of additional $\delta D$-$CH_4$ data would facilitate the disentanglement of fossil and microbial emissions. However, the required expenditure of
work and financial resources has to be taken into consideration. The complexity and investment for the present TREX-QCLAS system is in the range of the MEDUSA GC-MS system applied within the AGAGE network for the analysis of the halogenated hydrocarbons. The effort for setup and operation of a similar, possibly joined, network should therefore be in a comparable range. However, technological progress in both preconcentration and laser spectroscopy may significantly reduce this effort in the future.
Chapter 6

Appendix A
Figure 6.1: Overview of the TREX unit showing the most important components and the manufacturer, where the parts were purchased.
For more information contact: joachim.mohn@empa.ch.
Acknowledgements

During my time at the Empa, my visits at the University of Bern and the campaign in Utrecht I have been able to meet so many interesting and wonderful people who supported me, laughed with me and generally who made my time as a PhD student unforgettable. These people I owe so much and I would like to thank them in the following:

Many THANKS to....

• Joachim Mohn, Lukas Emmenegger and Béla Tuzson, my three supervisors at Empa, which I hold in high esteem. Joachim, you supported me during my whole thesis, in good as in bad times and even when you were supposed to be on holidays :). I always appreciated the constructive comments you gave me, the wonderful discussions we had and when you helped me to solve complex analytical problems, such as the annoying second peak during my first methane desorption tests. Your inputs kept me going throughout my thesis! Lukas, even though very busy, you were always there to give me the right input at the right time - and the kick I sometimes needed. Béla, the expert in laser spectroscopy and IGOR, you taught me so many things and I always enjoyed laughing with you :). Without the three of you this thesis wouldn’t be as it is now! :)

• my Prof. Hubertus Fischer for always being there when I needed your help. I admire your kind, uncomplicated way, with which you supported me during my thesis whenever you could and I always enjoyed the interesting discussions with you.

• Prof. Thomas Röckmann, Carina v. d. Veen, Elena Popa and Henk Snellen as well as the rest of the atmospheric physics and chemistry group at IMAU for offering me hospitality during my stay in Utrecht and for successfully organizing the whole measurement campaign at Cabauw. I also enjoyed the interesting discussions in Tuesday mornings group seminars as well as the familiar and collegial atmosphere at the IMAU.

• the people that reviewed my thesis, especially Prof. Thomas Röckmann and Prof. Hubertus Fischer, which did the reviewing during their Christmas holidays. I am really sorry and thank you so much! I really appreciated your effort and your constructive inputs! I also special thank to Thomas for coming the long way from Utrecht to Bern in order to be an examiner at my defense. And special thanks to Prof. Fortunat Joos, who accepted my request to be the chairman during my defense.

• my fellow sufferers, Brian and Pascal, who are also finishing their PhD theses. I really enjoyed the time with you guys and the interesting philosophical discussions we had. Especially on weekends at Empa it was good to have some company. The barbecues at Brian’s place were always a highlight – we should proceed with this “tradition” in the future!

• Dorota, Alexis, Sudhanshu, Lisa, Fernando, Ljuba, Abdel, Markella and Mauro for the unforgettable time I had in Utrecht. Besides Utrechts countless bars I was able to visit concerts, learn a little bit salsa, watch your favorite Southpark series or exchange cooking skills with you guys. It was certainly never boring with you, not even in HOORN! :)

• the Swiss/German connection in Utrecht: Marion, Magdalena and Christian! Thanks to you guys I didn’t lose my Swiss-German tongue. :)

• my cool Empa office mates Willi G., Erkan and Fabian for the nice time we had and for cheering me up when experiments or thesis writing didn’t go so well.

• the “Zivis” Marco Weber and Antoine Roth for their support during the preparation of the measurement campaign in Utrecht or in assembling the TREX unit.

• Angelina Wenger, Matz Hill, Martin Vollmer and Stefan Reimann for showing me how to build cold traps and giving them names, and generally teaching me all the basics needed to understand the functionality of a preconcentration unit.

• Eliza Harris, Dominik Brunner and Stefan Henne for the interesting research we did together. It was a pleasure working with you and I always appreciated your competent input!
• Andreas Borgschulte and Nick Stadie from the laboratory of hydrogen and energy at Empa. The collaboration with you gave me a fascinating, complementary point of view on the topic of adsorption and we found our ideal candidate :). I enjoyed the time with you and wish we could have done even more together!

• Urs Hintermüller, Erwin Pieper and his group from the workshop for drafting and constructing the components for the TREX unit. I also thank Willy Knecht for supporting me with all the installations and the electronics. It was a pleasure to working with so many competent experts.

• Herbert Looser for your support in writing the LabVIEW software and for providing me your LabVIEW documentations.

• Christoph Zellweger, Martin Steinbacher and Beat Schwarzenbach for your support. Discussions with you were always helpful and of course lending me a Picarro every once in a while was incredible convenient, thank you! :)

• Willi Brand for the interesting discussions we had when Joachim and I visited you in Jena or at the many conferences we met!

• all my co-authors for the various constructive inputs you gave me!

• the Empa running team for letting me chase you guys. :)

• the whole Laboratory for Air Pollution & Environmental Technology! I have spent an unforgettable time there and I will certainly miss it!

• Bea, my “Dutch mother”, for taking good care of me in Utrecht and for showing me how to cook Surinam food.

• my cousin Tatjana and her friends Elena and Melanie for letting me stay at their WG in Zürich. It is a pleasure to be there and enjoy your company. I owe you! :)

• Daniela for the great time we had together and for reminding me from time to time that there is a world besides research :). I will never forget you!

• my family and friends, especially my parents, Ludmilla and Martin, who supported me and always believed in me! :)


Faist, Jerome (2006). “Continuous-Wave, Room-Temperature Quantum Cascade Lasers”. In: 
*Optics and Photonics News* 17.5, p. 32. ISSN: 1047-6938. DOI: 10.1364/OPN.17.5.000032.

for high duty cycle, high-temperature operation”. In: *IEEE Journal of Quantum Electronics* 
38.6, pp. 533–546. ISSN: 0018-9197. DOI: 10.1109/JQE.2002.1005404.

in Atmospheric Aerosols by Direct Sample Introduction Thermal Desorption GC/MS”. In: 
*Environmental Science & Technology* 35.11, pp. 2326–2333. ISSN: 0013-936X. DOI: 10.1021/es000280i.

Fayet, P., A. Kaldor, and D. M. Cox (1990). “Palladium clusters: H2, D2, N2, CH4, CD4, C2H4, 
and C2H6 reactivity and D2 saturation studies”. In: *The Journal of Chemical Physics* 92.1, 
p. 254. ISSN: 0021-9606. DOI: 10.1063/1.458472.

Ferretti, D F et al. (2005). “Unexpected changes to the global methane budget over the past 

Fischer, Hubertus et al. (2008). “Changing boreal methane sources and constant biomass burning 
during the last termination”. In: *Nature* 452.7189, pp. 864–867. ISSN: 0028-0836. DOI: 10.1038/nature06825.

methane and carbon dioxide using continuous-flow isotope-ratio mass spectrometry”. In: 


Houweling, Sander et al. (2008). “Early anthropogenic CH4 emissions and the variation of CH4 
and 13CH4 over the last millennium”. In: *Global Biogeochemical Cycles* 22.1, n/a–n/a. ISSN: 08866236. DOI: 10.1029/2007GB002961.

Houweling, Sander et al. (2014). “A multi-year methane inversion using SCIAMACHY, 


McManus, J. Barry et al. (2010). “Application of quantum cascade lasers to high-precision atmospheric trace gas measurements”. In: Optical Engineering 49.11, p. 111124. ISSN: 00913286. DOI: 10.1117/1.3498782.

McManus, J. Barry, Mark S Zahniser, and David D Nelson (2011). “Dual quantum cascade laser trace gas instrument with astigmatic Herriott cell at high pass number”. In: Applied optics 50.4, A74–A85. ISSN: 0003-6935. DOI: 10.1364/AO.50.000A74.


84
In: Journal of Geophysical Research 100.D1, p. 1317. ISSN: 0148-0227. DOI: 10.1029/94JD02689.

Mikaloff Fletcher, Sara E. et al. (2004). “CH4 sources estimated from atmospheric observations of CH4 and its 13C/12C isotopic ratios: 1. Inverse modeling of source processes”. In: Global Biogeochemical Cycles 18.4. ISSN: 08866236. DOI: 10.1029/2004GB002223.


Santoni, Gregory W. et al. (2012). “Mass fluxes and isofluxes of methane (CH4) at a New Hampshire fen measured by a continuous wave quantum cascade laser spectrometer”. In:


Wunderlin, Pascal et al. (2013). “Isotope signatures of N2O in a mixed microbial population system: Constraints on N2O producing pathways in wastewater treatment”. In: *Environmental Science and Technology* 47.3, pp. 1339–1348.


List of Figures

1.1 Globally averaged atmospheric mole fraction of CH$_4$ (a) and the global growth (b) from 1984 to 2014. ................................. 2
1.2 Illustration taken from the IPCC report 2013, chapter 6 (Ciais et al., 2014), showing the global CH$_4$ cycle and its reservoirs estimated for the years 2000 to 2009. The black arrows indicate CH$_4$ fluxes from or to natural sources or sinks. Red arrows represent emissions from anthropogenic sources and the light brown one denotes a mixture of both (biomass burning). The atmosphere is one of four big reservoirs with the black numbers indicating the pre-industrial inventory value. The sizes of the other three reservoirs are difficult to estimate, but ocean hydrates exceed the others by far. ............................. 3
1.3 Reproduced from Kirschke et al., 2013. Data were collected from bottom-up (BU) and top-down (TD) CH$_4$ budgets from the years 2000 to 2009 of 13 world regions, including the ocean. The error bars show the minimum and maximum estimated values. ............................... 5
1.4 Map of all the GAW measurement stations for CO$_2$, including surface, ship and aircraft analysis sites. The network is for CH$_4$ similar (WMO/GAW, 2015). ................................. 7
1.5 $\delta^{13}$C- and $\delta$D-CH$_4$ signatures of the three major source categories as well as sub-categories, which can be distinguished by isotopic measurements. C3 and C4 represent the plant substrate (e.g. forests or grass) for biomass burning or fodder plant (e.g. maize or grass) in the case of ruminants. The black circle represent the mean isotopic values of atmospheric CH$_4$ and the black square the average isotopic source signature of atmospheric CH$_4$ emissions. The dashed line connecting these to points represents the fractionation effect responsible for this shift as discussed in the of this section. Additionally the following isotopic fractionation effects of processes or other parameters are indicated with black arrows: The shift in isotopic signature when the relative proportion between the processes of CR (CO$_2$ reduction) and AF (acetate fermentation) changes (bottom left). The depletion in CH$_3$D due to the depletion of DHO in meteoric H$_2$O with “Altitude”, e.g. for alpine regions, and with “Latitude” towards the northern pole. The enrichment of $^{13}$C in pyrogenic source signatures with increasing “burning efficiency”. The fractionation processes related to CH$_4$ oxidation causing $\delta^{13}$C- and $\delta$D-CH$_4$ values to increase with oxidation rate. Additionally the dashed line indicates fractionation processes related to atmospheric sink processes causing $\delta^{13}$C- and $\delta$D-CH$_4$ values to increase in the atmosphere relative to the estimated isotopic signature of the combined sources. 9
1.6 Top: Overview of the spectra for the most abundant GHGs (including H$_2$O) at 100mbar pressure and ambient mole fractions in the MIR and NIR range. On the bottom x-axis the wavenumber is given in cm$^{-1}$, while the top x-axis shows meV. Bottom: The linestrengths for CH$_4$ is up to 200 times larger in the MIR range, than in the NIR. 13
2.1 Adsorption isotherms of CH$_4$ and N$_2$ by HayeSep D at 196K, 273K and 296K. Filled symbols indicate adsorption and empty symbols indicate desorption measurement points. 19
2.2 Adsorption isotherms of CH$_4$ and N$_2$ by multi-walled carbon nanotubes (MWCNT) at 196K, 273K and 296K. Filled symbols indicate adsorption and empty symbols indicate desorption measurement points. ......................................................... 19
2.3 Adsorption isotherms of CH$_4$ and N$_2$ by HKUST-1 at 196K, 273K and 296K. Filled symbols indicate adsorption and empty symbols indicate desorption measurement points. 19
2.4 Adsorption isotherms of CH$_4$ and N$_2$ by ZIF-8 at 196K, 273K and 296K. Filled symbols indicate adsorption and empty symbols indicate desorption measurement points. 19
2.5 Adsorption isotherms of CH$_4$ and N$_2$ by zeolite 5A at 196K, 273K and 296K. Filled symbols indicate adsorption and empty symbols indicate desorption measurement points. 20
2.6 Adsorption isotherms of CH₄ and N₂ by zeolite 13X at 196K, 273K and 296K. Filled symbols indicate adsorption and empty symbols indicate desorption measurement points. 20

2.7 Isosteric enthalpy as a function of CH₄ adsorption amount in mmol/g estimated by a linear interpolation method and applying the Clausius-Clapeyron equation (2.4). 21

2.8 Adsorption isotherms of N₂ at 77K for all candidate materials. Experimental data is fitted with the Langmuir and the BET model in order to extract the surface area. 21

2.9 Adsorption isotherms of CH₄ at 77K for all candidate materials. Experimental data is fitted with the Langmuir and the BET model in order to extract the surface area. 21

2.10 Methane adsorption capacity for all materials as a function of pressure and temperature. Data is interpolated by the virial-model. 24

2.11 Three-dimensional plot of the CH₄/N₂-Selectivity as a function of pressure and temperature for all materials generated from virial modeling of isotherms. 25

3.1 Schematics of the preconcentration unit (TREX). The blue lines indicate the flow of sample air and TG, i.e. ambient air CH₄ mole fractions, while red lines represent the flow of calibration gases and desorbed air, i.e. high CH₄ mole fraction. MFC 1-4 and V1-4 stand for mass flow controllers and 2-position valves, respectively. 29

3.2 Schematics of the preconcentration unit (TREX). The blue lines indicate the flow of sample air and TG, i.e. ambient air CH₄ mole fractions, while red lines represent the flow of calibration gases and desorbed air, i.e. high CH₄ mole fraction. MFC 1-4 and V1-4 stand for mass flow controllers and 2-position valves, respectively. 31

3.3 Measured absorption spectra for the determination of δ¹³C- (left) and δD-CH₄ (right) along with the spectral fit using Voigt-profiles and the corresponding line-strengths from the HITRAN database. Potential interferences are expected mainly from N₂O and H₂O. The spectral line of N₂O is divided by a factor of 1000 to fit in the graph, evidencing that even N₂O-mole fraction of around 300ppb can cause severe interference. 32

3.4 Schematics of the sampling setup used in the interlaboratory comparison campaign. Ambient air was continuously sampled from the rooftop of the building, and split from the main line to the batch sampling unit (bags and flasks), to the TREX-QCLAS system and to the continuous flow CRDS and OA-ICOS spectrometers. The laser spectrometers were additionally supplied with the calibration gases CG 1, CG 2 and the target gas to determine calibration factors and repeatability. 33

3.5 A complete measurement cycle consist of three main sequences: (A) three consecutive measurements of preconcentrated ambient air samples, (B) one measurement of preconcentrated pressurized air (target gas), followed by the calibration phase (C). The latter is used for the determination of calibration factors for δ¹³C-CH₄ and δD-CH₄ and the dependence of isotope ratios on elevated CH₄ mole fractions. The calibration gases are dynamically diluted to the indicated CH₄ mole fractions as described in Section 3.2.3. All measurements are bracketed by the analysis of CG 1 (anchor) at 635ppm CH₄ to drift-correct the measurements. 35

3.6 Allan variance plots for δ¹³C-CH₄ (left) and for δD-CH₄ (right) using 750ppm CH₄. The upper plot shows the corresponding time series of δ-values recorded at one second temporal resolution. At 600s spectral averaging, the square root of the Allan variance indicates a precision of 0.1‰ for δ¹³C-CH₄ and 0.5‰ for δD-CH₄. 38

3.7 Phase II (desorption) and phase III (conditioning) of the CH₄ preconcentration cycle by TREX. Mass spectrometer results (upper graph) indicate that the bulk gases N₂ and O₂ leave the trap shortly after decoupling the trap from the cold-plate and heating successively to 145K (1min) and 175K (3min), but a small reminder is also released in the main CH₄ desorption step (see text for details). QCLAS measurements (middle graph) display that CH₄ desorption is initiated by heating the trap to 258K (8min) and purging it with 2 mLmin⁻¹ synthetic air in forward flow direction; the gray shaded area indicates the period, during which the desorbed methane is filled into the gas cell of the laser spectrometer. In phase III (conditioning) the trap is heated up to 323K and purged with 25 mLmin⁻¹ of high-purity synthetic air. The bottom graph exhibits the trap temperatures and flows of synthetic air in the preconcentration device (TREX). 39
List of Figures

3.8 $\delta^{13}$C-offset as a function of $O_2$ mole fraction determined from measurements of calibration gases without preconcentration with the QCLAS. This effect was found to be constant for CH$_4$ mole fractions from 600 to 1000ppm. The grayed region shows the ranges of the $O_2$-mole fractions in the QCLAS-cell after preconcentration and the resulting offset in the $\delta^{13}$C values for typical TREX operation as determined from a series of experiments. The dashed horizontal line represents the offset in $\delta^{13}$C values of 2.3‰ used as a correction throughout the measurement campaign. ................................................................. 40

3.9 Repeated measurements of pressurized air (target gas) by TREX-QCLAS over two weeks throughout the interlaboratory comparison campaign. CH$_4$ mole fractions and relative differences of isotope ratios ($\delta^{13}$C, $\delta^D$) were plotted as a histogram with bin widths of 3 ppb (CH$_4$), 0.1‰ ($\delta^{13}$C) and 1‰ ($\delta^D$), respectively. The uncertainty is given as the 1σ standard deviation. .................................................................................. 41

3.10 CH$_4$ mole fractions and isotopic composition analyzed during the interlaboratory comparison campaign in real-time by the laser spectroscopic techniques: TREX-QCLAS (CH$_4$, $\delta^{13}$C, $\delta^D$), CRDS G2201-i (CH$_4$, $\delta^{13}$C), and on glass flask/bag samples with IRMS by UU (CH$_4$, $\delta^{13}$C, $\delta^D$), MPI (CH$_4$, $\delta^{13}$C, $\delta^D$) and RHUL (CH$_4$, $\delta^{13}$C). ................................................................. 42

3.11 Correlation diagrams for CH$_4$ isotope ($\delta^{13}$C, $\delta^D$-CH$_4$) measurements in ambient air by different techniques and laboratories. The dashed line is the 1 : 1 line, the red dashed lines indicate the WMO compatibility goals of ±0.2‰ for $\delta^{13}$C and ±5‰ for $\delta^D$. Results of individual techniques are corrected to a common scale based on MPI results for a pressurized air target gas. For the middle and bottom graphs differences in CH$_4$ mole fractions in gas samples are represented by the shading (black: identical mole fractions, white: 30 ppb difference). Top: IRMS analysis on glass flasks by the Stable Isotope Laboratory of MPI vs. UU for $\delta^{13}$C-CH$_4$ (left) and $\delta^D$-CH$_4$ (right); Middle: TREX-QCLAS analysis by Empa vs. IRMS analysis on glass flasks by UU for $\delta^{13}$C-CH$_4$ (left) and $\delta^D$-CH$_4$ (right). The temporal difference between TREX-QCLAS analysis and glass flask sampling is indicated by the point size (big: ±10min, medium: ±20min, small: ±30min); Bottom: IRMS analysis on bag samples by RHUL (left) and CRDS analysis by Eawag (right) vs. IRMS analysis on glass flasks by UU for $\delta^{13}$C-CH$_4$. ................................................................. 44

3.12 Representative Keeling plots for $\delta^{13}$C-CH$_4$ and $\delta^D$-CH$_4$ for the period 8 June noon till 9 June 2014 noon. The isotopic source signature indicates a microbial origin, possibly referring to CH$_4$ emissions from ruminants. ................................................................. 45

3.13 $\delta^D$-CH$_4$ vs. $\delta^{13}$C-CH$_4$ of different CH$_4$ sources. The symbols indicate CH$_4$ source signatures derived from Keeling plots. The error bars are uncertainties derived from the linear regression. The star-symbols are source signatures from 21 June noon till 22 June noon derived from different techniques. The shadings indicate typical values for different source categories from the literature. .................................................................................. 46

4.1 Schematics of the preconcentration and extraction system developed for the IRMS technique. MFC denotes mass flow controller. The 8-port valve through which the Ref air bottle was connected to the first selection valve is not shown to reduce complexity. For further description see the main text. .................................................................................. 52

4.2 Overview measurement data Cabauw ........................................................................ 57

4.3 Compatibility TREX-QCLAS vs IRMS in Cabauw .......................................................... 58

4.4 FLEXPART: source contribution from Cabauw ................................................................. 59

4.5 TM5-FLEXPART comparison with isotopic measurements of Cabauw ......................... 61

4.6 Cumulative isotopic signature derived by Keeling plot method ........................................ 63

4.7 SourcePlot to pinpoint the isotopic signatures derived by the moving Keeling plot method on to different source categories. .................................................................................. 64

4.8 Keeling plots for the period between 16 and 18 March, illustrating a rapid change in $\delta$ values over the course of hours. .................................................................................. 65
4.9 Detailed analysis of three 2-day periods with large CH₄ elevations in March 2015. The top panel exhibits CH₄ mole fraction (grey) with background values in red (10:00-18:00, >2100 ppb). The middle panels show the isotopic source signatures ($\delta^{13}$C-CH₄, $\delta^{2}$D-CH₄) derived with the 12-h MKP method. The color coding in the middle panels (red, light blue, purple) indicates characteristic contributions from different sources; red-microbial, light blue-fossil, purple-waste. For consistency, the same color-coding was chosen in Figure 4.7. The bottom graph presents CH₄ source contributions as computed with the FLEXPART-COSMO model using the TNO-MACC inventory, averaged over 24h.

66

4.10 Histograms of CH₄ isotope source signatures at the CESAR site between October 2014 and March 2015. Bin widths are 1‰ for $\delta^{13}$C-CH₄ and 10‰ for $\delta^{2}$D-CH₄. Source signatures are derived from measured data (grey bins), FLEXPART-COSMO modeling (squares) as well as TM5 modeling (circles) using the 12h MKP method. Two different inventories, TNO-MACC (blue) and Edgar/LPJ-Why-Me (red), were used. The shaded areas show histograms for the “direct” source signatures that were picked up along the FLEXPART-COSMO trajectory (right axis).

67

5.1 Isotopic source signatures derived from the two measurement campaigns on CH₄ isotopes at the tall tower in Cabauw, the Netherlands (NL, blue, Chapter 4) and at the Empa in Dübendorf, Switzerland (CH, red, Chapter 3) for comparison.

72

6.1 Overview of the TREX unit showing the most important components and the manufacturer, where the parts were purchased. For more information contact: joachim.mohn@empa.ch.

76
## List of Tables

1.1 Isotopic source signatures and fractionation factors of the most common CH$_4$ emissions and atmospheric sinks. .......................................................... 12

2.1 Physical properties of the tested adsorbents for CH$_4$ and N$_2$ ................................. 23

3.1 List of CH$_4$ mole fractions and isotopic composition ($\delta^{13}$C and $\delta$D-CH$_4$) of laboratory standards used in the intercomparison campaign. The indicated uncertainty is the 1σ standard deviation for repeated analysis of the respective measurement system. ................. 34

3.2 List of measured $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ values of the target gas (pressurized air) as reported by different analytical techniques/laboratories. The indicated uncertainty is the 1σ standard deviation. Results of laser spectroscopic techniques are referenced to standards CG 1 and CG 2, while IRMS results were referenced to their respective laboratory standards. ................................................................. 42

3.3 Overview of all the $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ source signatures derived using the Keeling plot approach for the given time periods. ................................................................. 47

4.1 European CH$_4$ emissions and $\delta$ values for the different source categories used in TM5. 55

4.2 SNAP (Standardized Nomenclature for Air Pollutants) source categories and corresponding signatures from the TNO-MACC_2 inventory as used in FLEXPART-COSMO. ........ 56

4.3 Mean value and standard deviation of the histograms of the source isotopic composition shown in Fig. 4.10. ................................................................. 68
Erklärung

gemäß Art. 28 Abs. 2 RSL 05

Name/Vorname: Eyer Simon
Matrikelnummer: 05-920-566
Studiengang: Physik
Bachelor ☐ Master ☐ Dissertation ☑
Titel der Arbeit: Real-time analysis of d13C- and dD-CH4 in ambient air with laser spectroscopy: Method development, validation and applications
LeiterIn der Arbeit: Hubertus Fischer


30.09.2015
Ort/Datum
Döbendorf, 21.11.2015
Unterschrift
PhD
> 01.2012 – 1.2016, Empa Dübendorf / University of Bern, Switzerland
> Titel: Real-time analysis of $\delta^{13}$C- and $\delta$D-CH$_4$ in ambient air with laser spectroscopy:
  Method development, validation and applications

Internship
> 9.2011 – 11.2011, Sapporo University, Japan
> Titel: Development of a dispersion technique for 3D-laser imaging

Bachelor and Master in physics
> 9.2005 – 1.2012, ETH Zürich, Switzerland
> With focus on experimental physics, solid state physics and electronics
> Master thesis at the „Nanophysics group“ of Prof. K. Ensslin
  Titel: „Aharonov-Bohm effect in p-GaAs quantum-rings“
> Semester thesis at CERN
  Titel: “Investigation of the scintillation properties of lead-tungstate crystals”

Simon Alexander Eyer

Born on: 17.12.1984
Hometown: Termen (VS, CH)

simon.eyer@gmail.com
Peer reviewed publications


Oral presentations

> NAREP Seminar, Empa (07.12.2015)
> InGOS-Meeting, Utrecht (23.09.2015)
> Naturforschende Gesellschaft Oberwallis, Brig (20.05.2015)
> International Symposium on Non-CO$_2$ Greenhouse Gases (NCGG7), Amsterdam (07.11.2014)
> European Geoscience Union (EGU), Wien (02.05.2014)
> Seminar for climate and environmental physics, Uni Bern, Bern (21.10.2013)
> Jahrestagung der Arbeitsgemeinschaft Stabile Isotope (ASI), Braunschweig (30.09.2013)
> NAREP Seminar, Empa (01.07.2013)

Awards

> Best oral presentation at Jahrestagung der ASI in Braunschweig (09.2013)

Simon Alexander Eyer

Born on: 17.12.1984
Hometown: Termen (VS, CH)

simon.eyer@gmail.com