

# Singly and doubly substituted isotopocules of nitrous oxide and their application in environmental studies

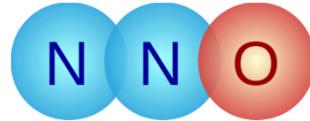
Kristýna Kantnerová

# Overview

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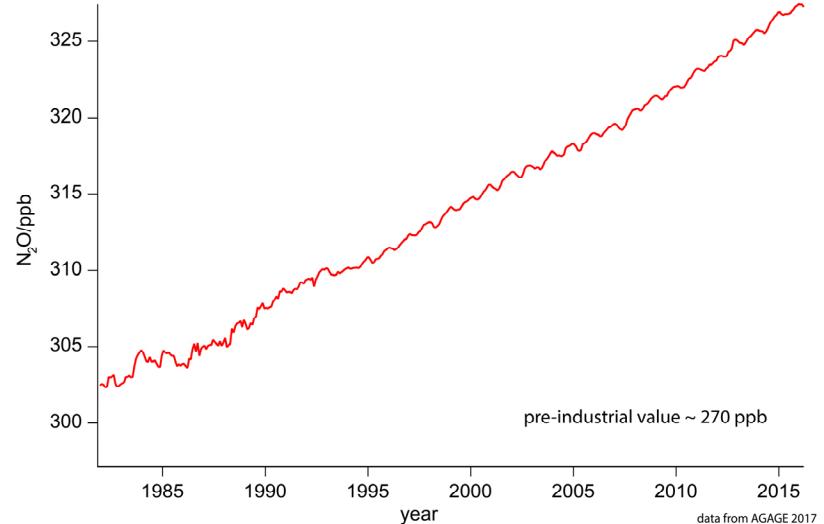
- ▶ introduction about N<sub>2</sub>O
- ▶ QCLAS method
- ▶ applications in our lab with singly substituted isotopologues
- ▶ development for doubly substituted isotopologues





# Introduction

- ▶ important trace gas
  - ▶ contribution by 6 % to global warming
  - ▶ depletion of stratospheric ozone
- ▶ increasing atmospheric concentration, 328 ppb (2015)

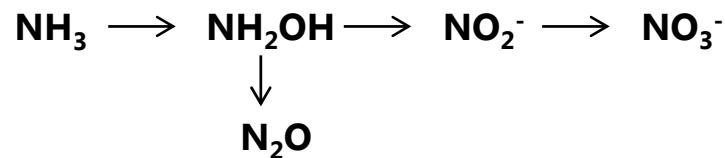
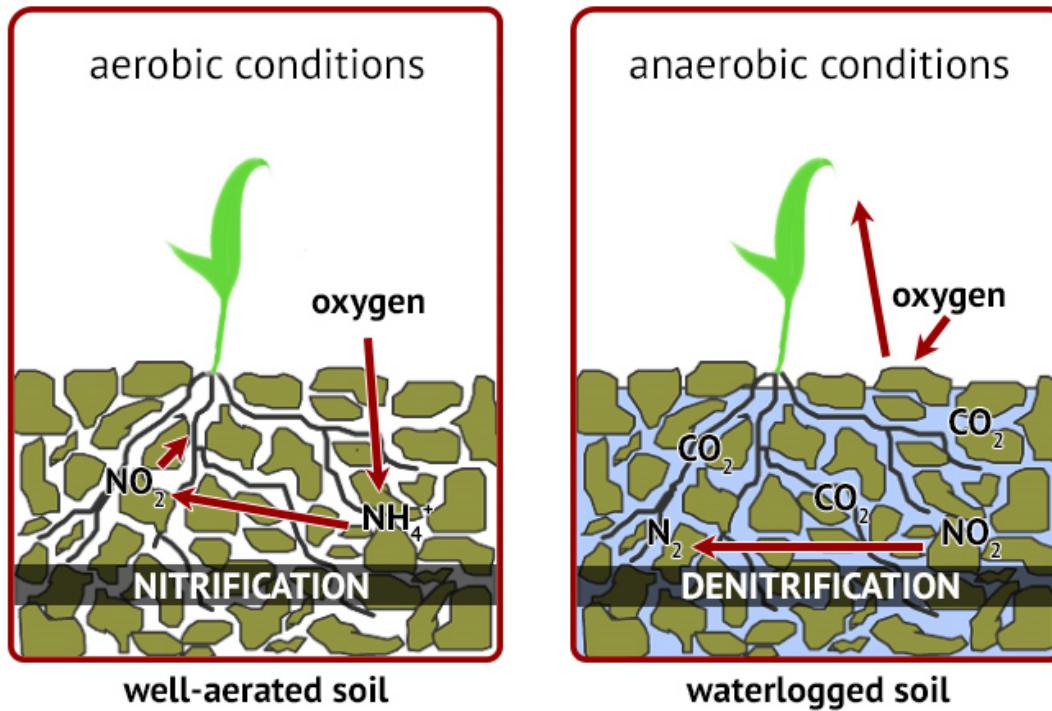


anthropogenic sources



natural sources



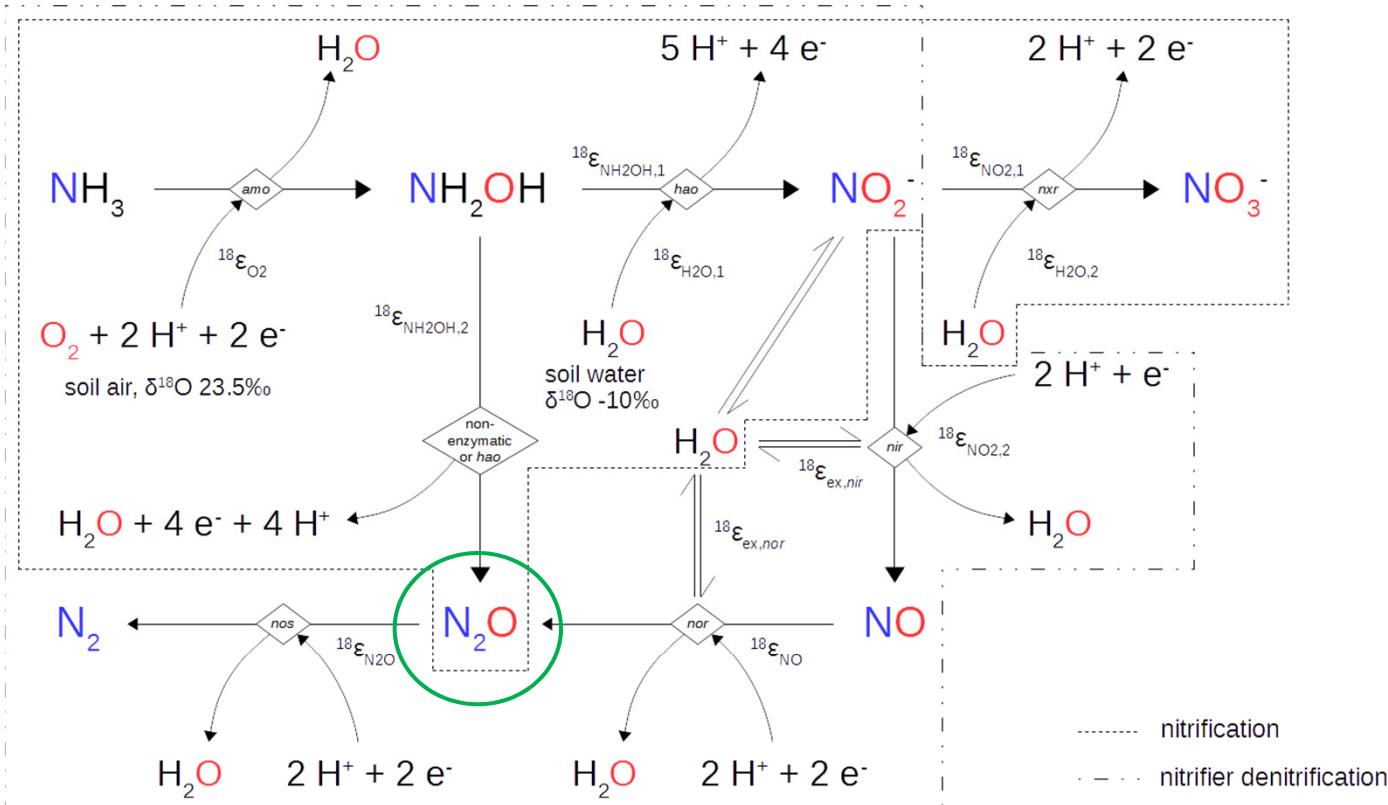
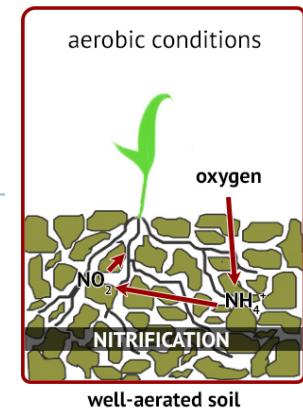


ammonia-oxidizing bacteria (AOB)  
ammonia-oxidizing archaea (AOA)



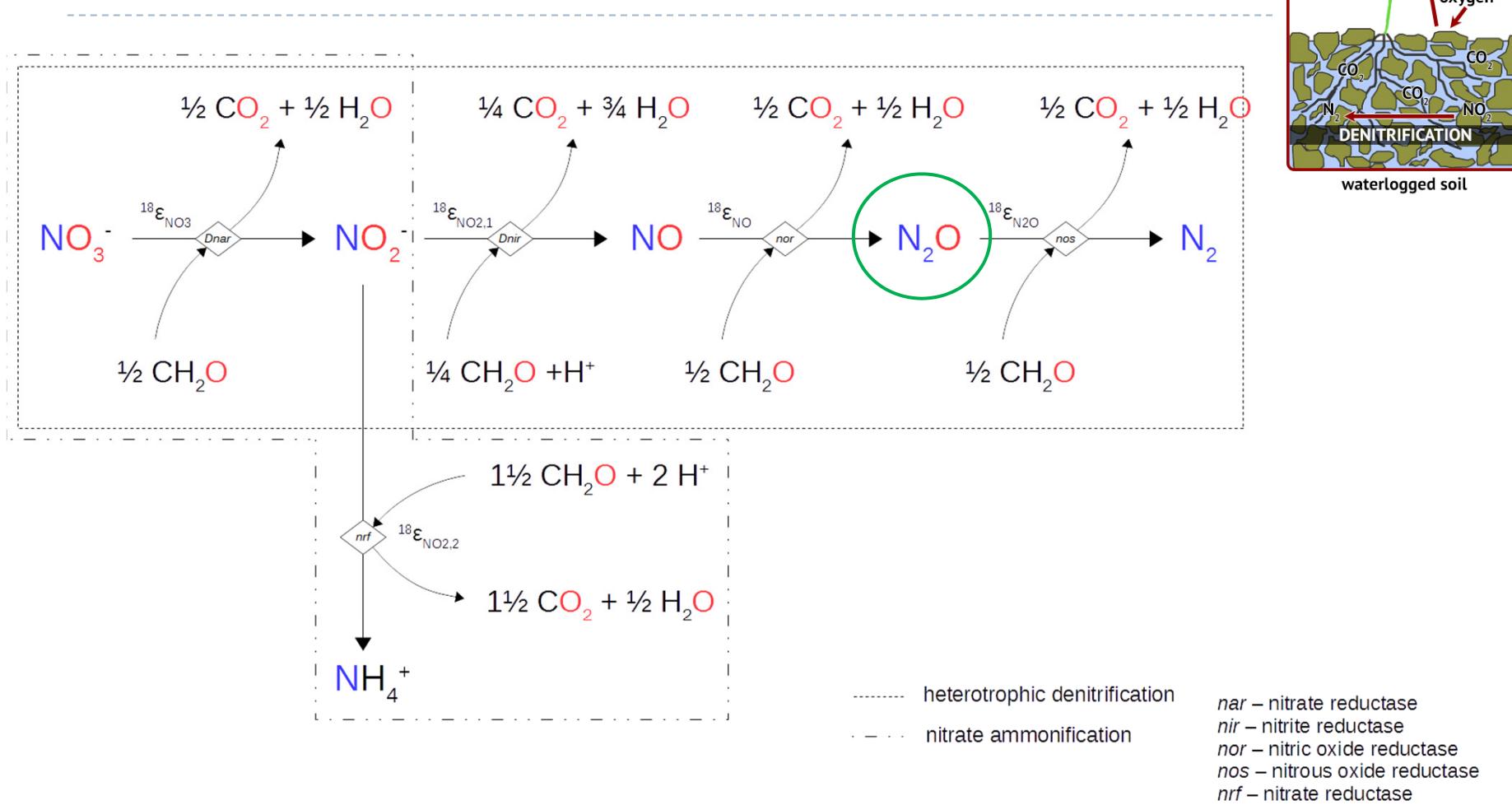
denitrifying bacteria

# Aerobic environment



Snider et al. 2012, Casciotti et al. 2010, Baggs 2008

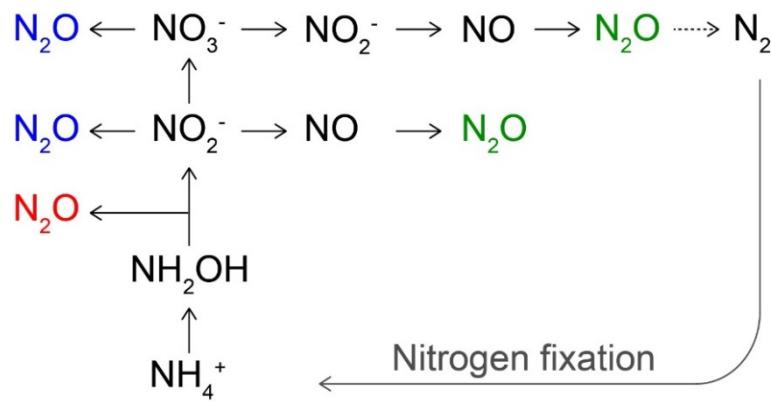
# Anaerobic environment



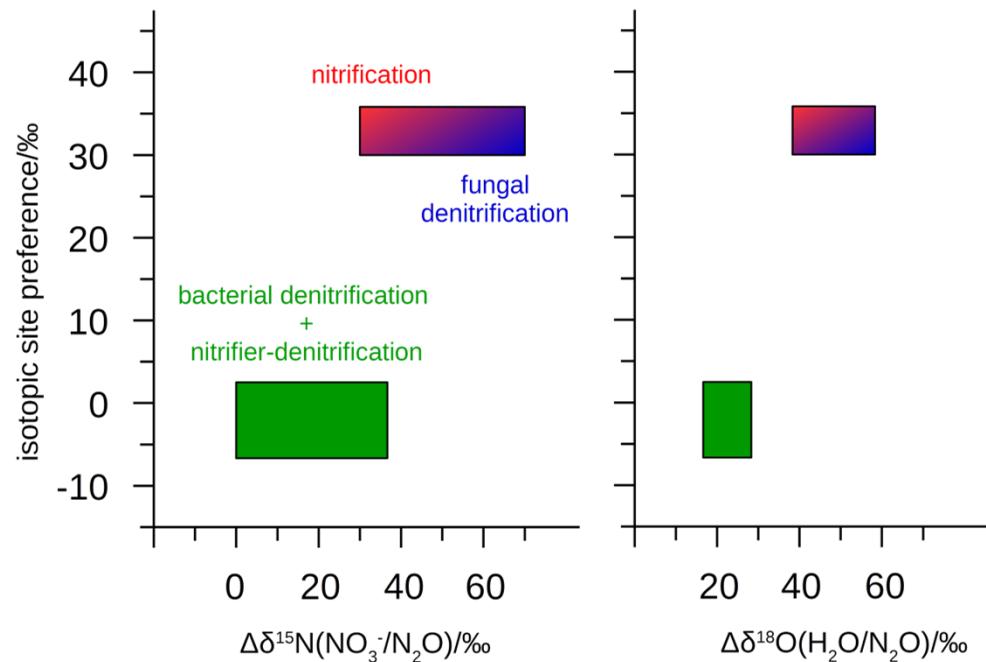
van de Leemput et al. 2011



# Isotopic studies of N<sub>2</sub>O



Keeling plots



# IRMS tradition

*Anal. Chem.* 1999, 71, 4711–4718

## Determination of Nitrogen Isotopomers of Nitrous Oxide on a Modified Isotope Ratio Mass Spectrometer



Sakae Toyoda<sup>\*,†,§</sup> and Naohiro Yoshida<sup>†,‡</sup>

Department of Environmental Science and Technology, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan, and CREST, Japan Science and Technology Corporation (JST), Kawaguchi, Saitama, Japan

RAPID COMMUNICATIONS IN MASS SPECTROMETRY  
*Rapid Commun. Mass Spectrom.* 13, 2028–2033 (1999)

## Mass Spectrometry of the Intramolecular Nitrogen Isotope Distribution of Environmental Nitrous Oxide Using Fragment-ion Analysis

C. A. M. Brenninkmeijer\* and T. Röckmann

Max Planck Institute for Chemistry, Atmospheric Chemistry Division, Mainz, Germany

RAPID COMMUNICATIONS IN MASS SPECTROMETRY  
*Rapid Commun. Mass Spectrom.* 2003; 17: 1897–1908  
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/rcm.1132

RCM

## Gas chromatography/isotope-ratio mass spectrometry method for high-precision position-dependent $^{15}\text{N}$ and $^{18}\text{O}$ measurements of atmospheric nitrous oxide

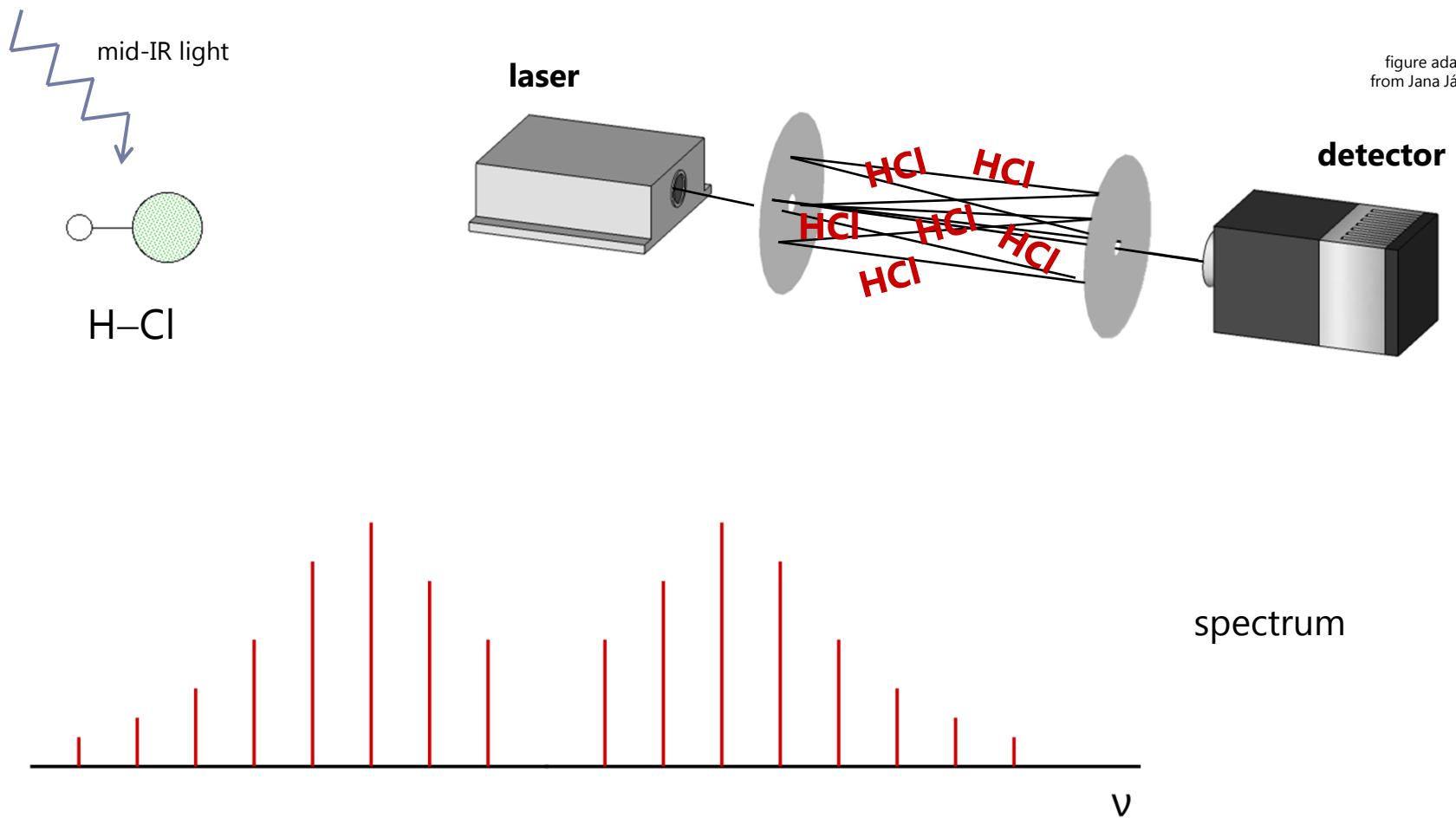
Thomas Röckmann<sup>1\*</sup>, Jan Kaiser<sup>1†</sup>, Carl A. M. Brenninkmeijer<sup>2</sup> and Willi A. Brand<sup>3</sup>

<sup>1</sup>Max-Planck-Institut für Kernphysik, Bereich Atmosphärenphysik, Heidelberg, Germany

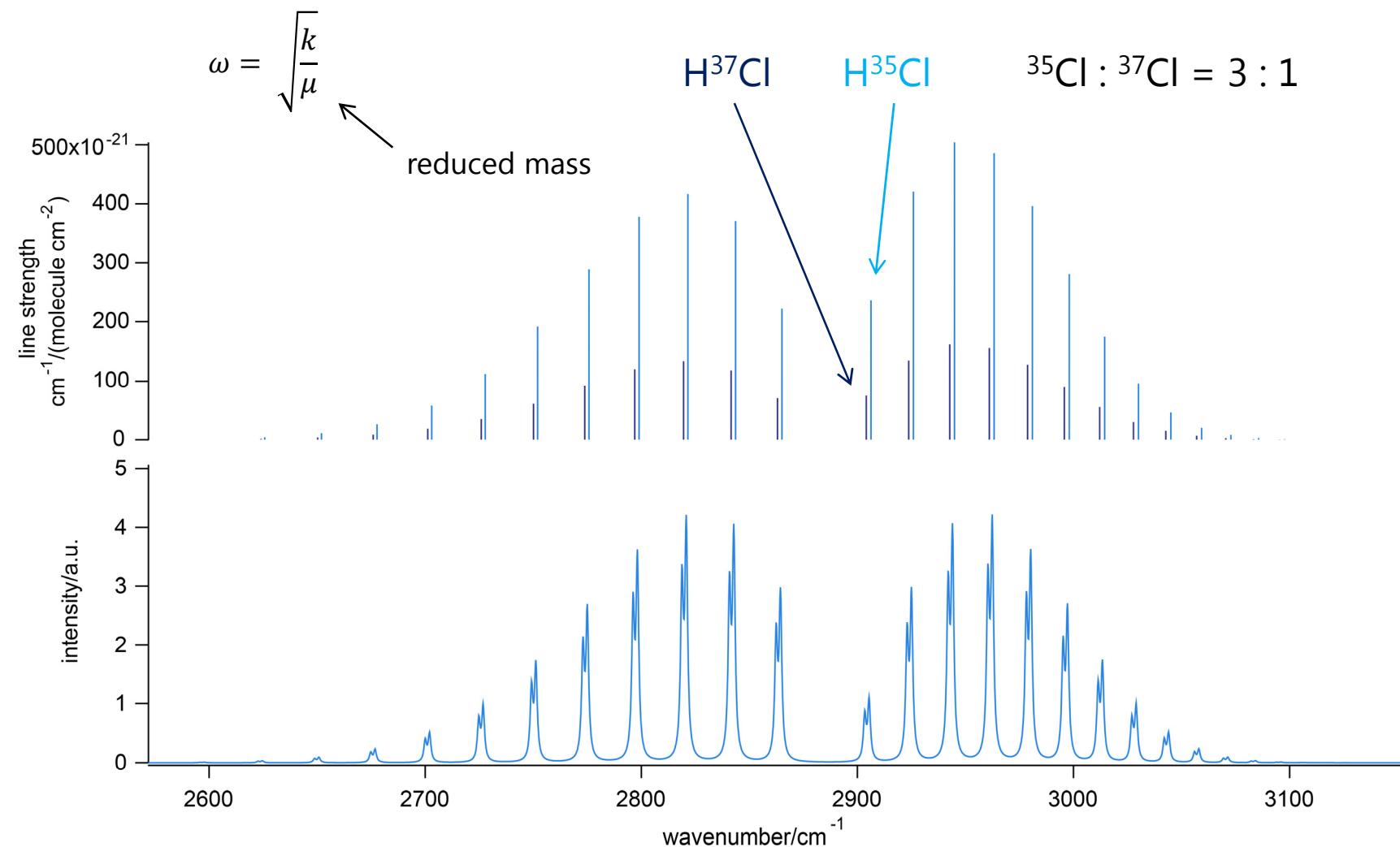
<sup>2</sup>Max-Planck-Institut für Chemie, Abteilung Chemie der Atmosphäre, Mainz, Germany

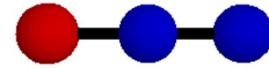
<sup>3</sup>Max-Planck-Institut für Biogeochemie, Jena, Germany

# Molecular spectroscopy

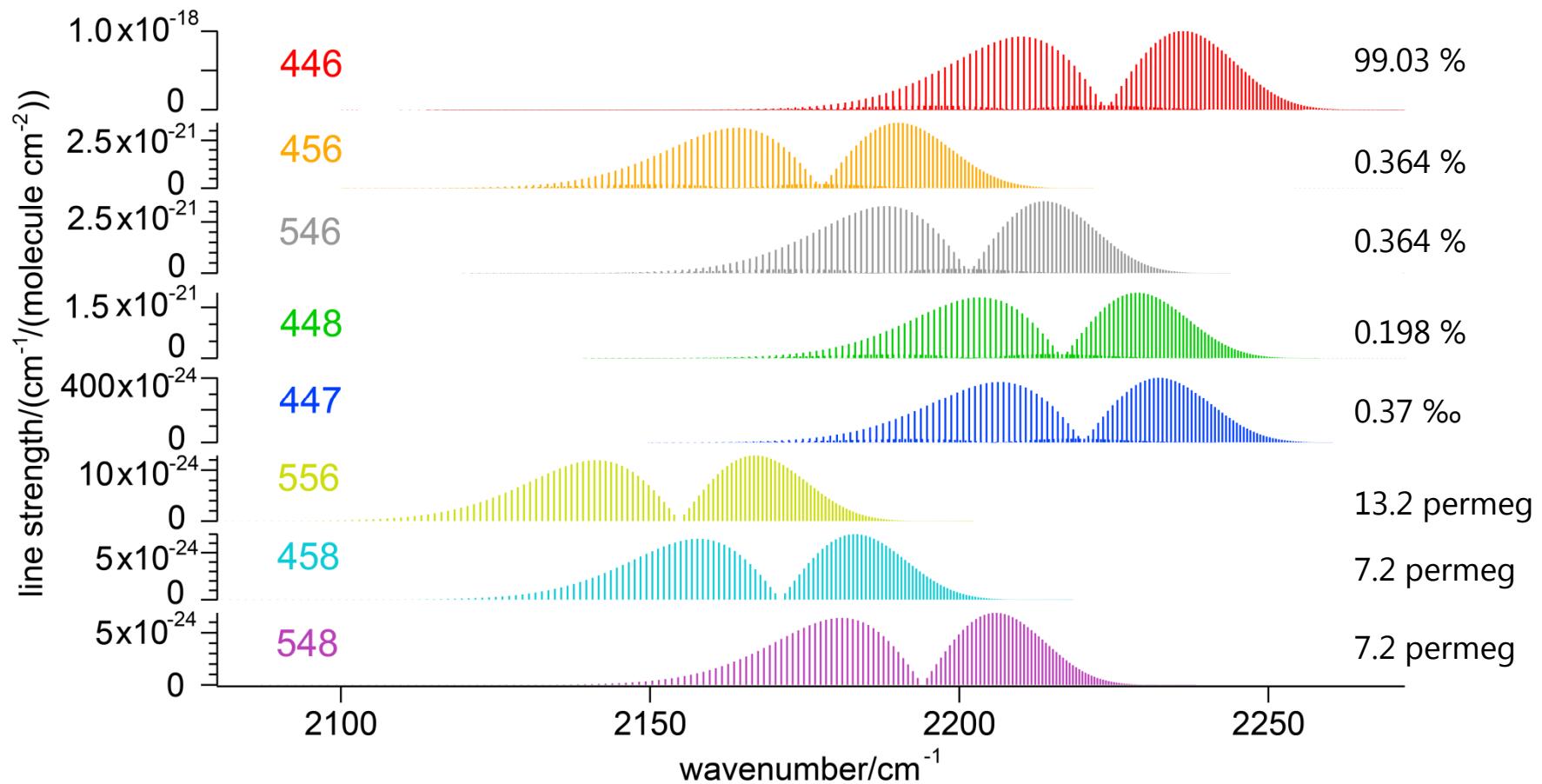


# Isotopes in molecular spectroscopy

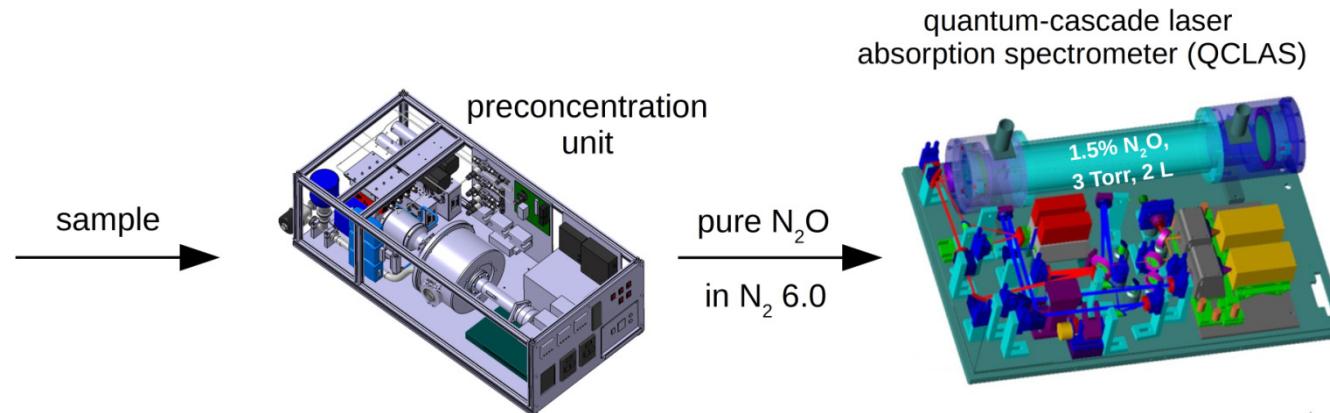




# N<sub>2</sub>O ro-vibrational spectra

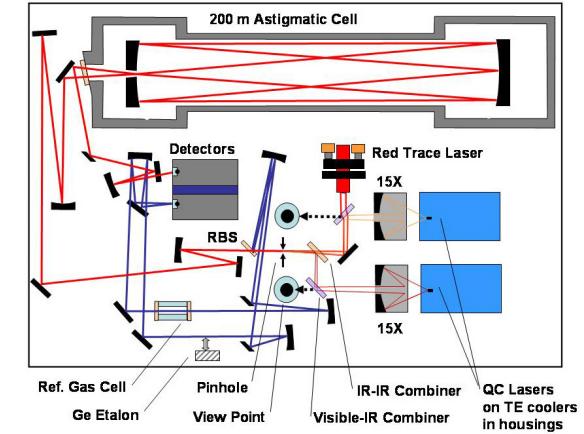


# Analytical technique (TREX-QCLAS)

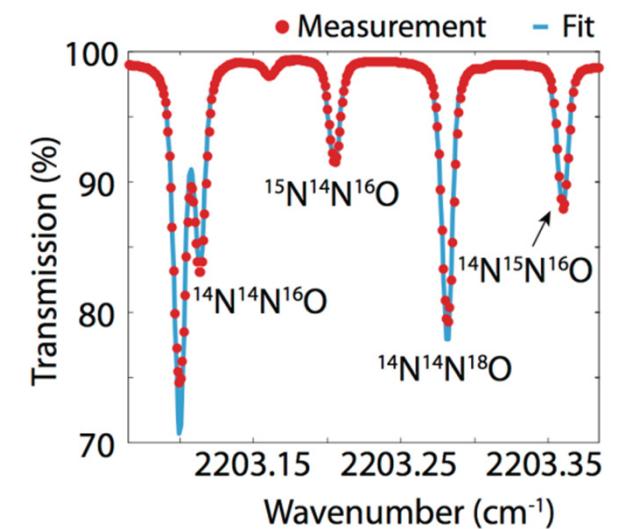
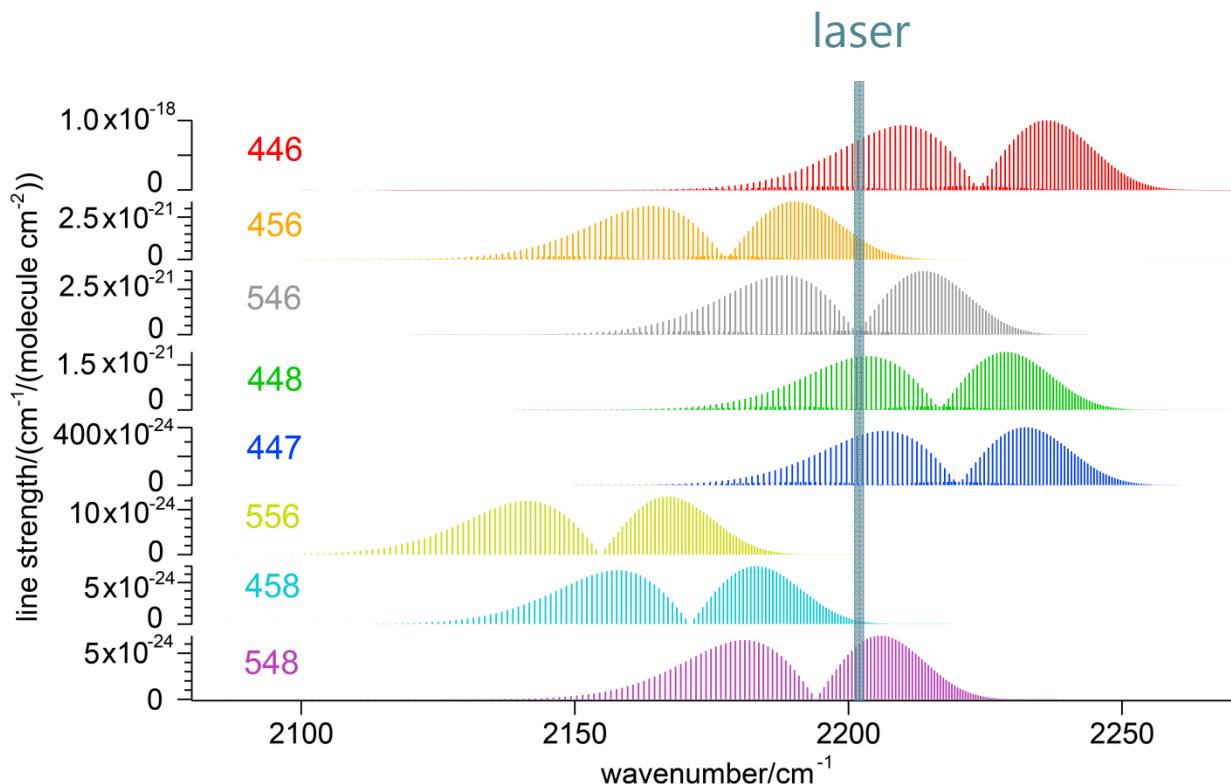
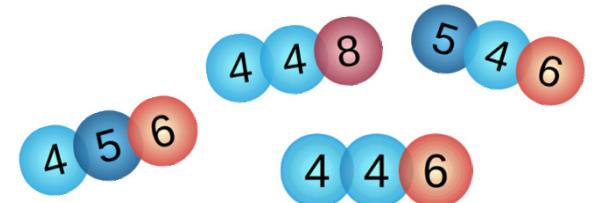


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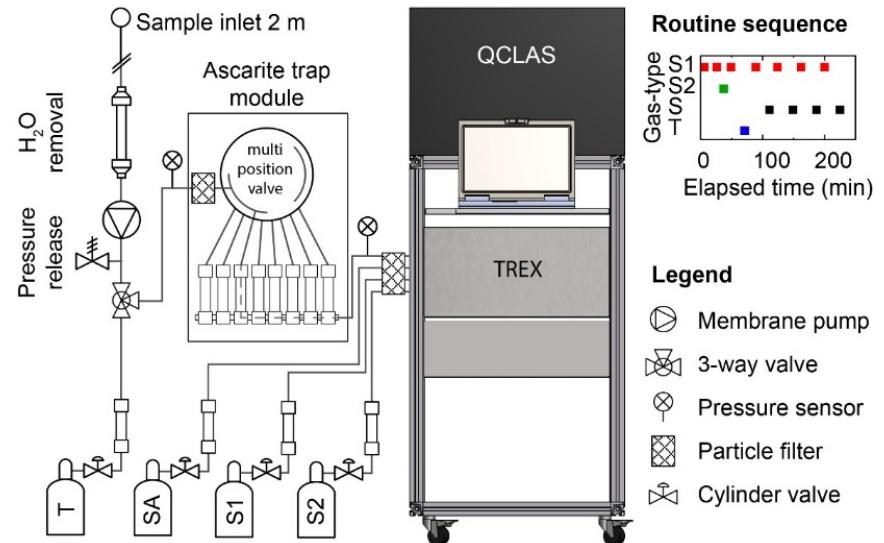
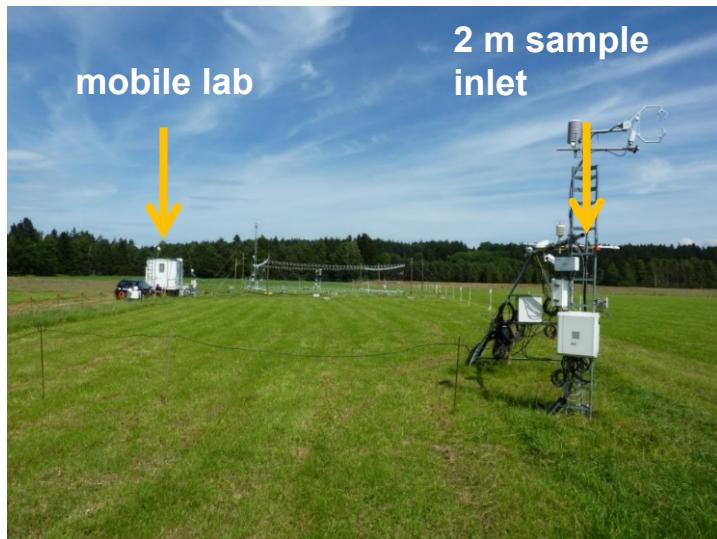
# Singly substituted isotopocules



# Field study #1 – southern Germany



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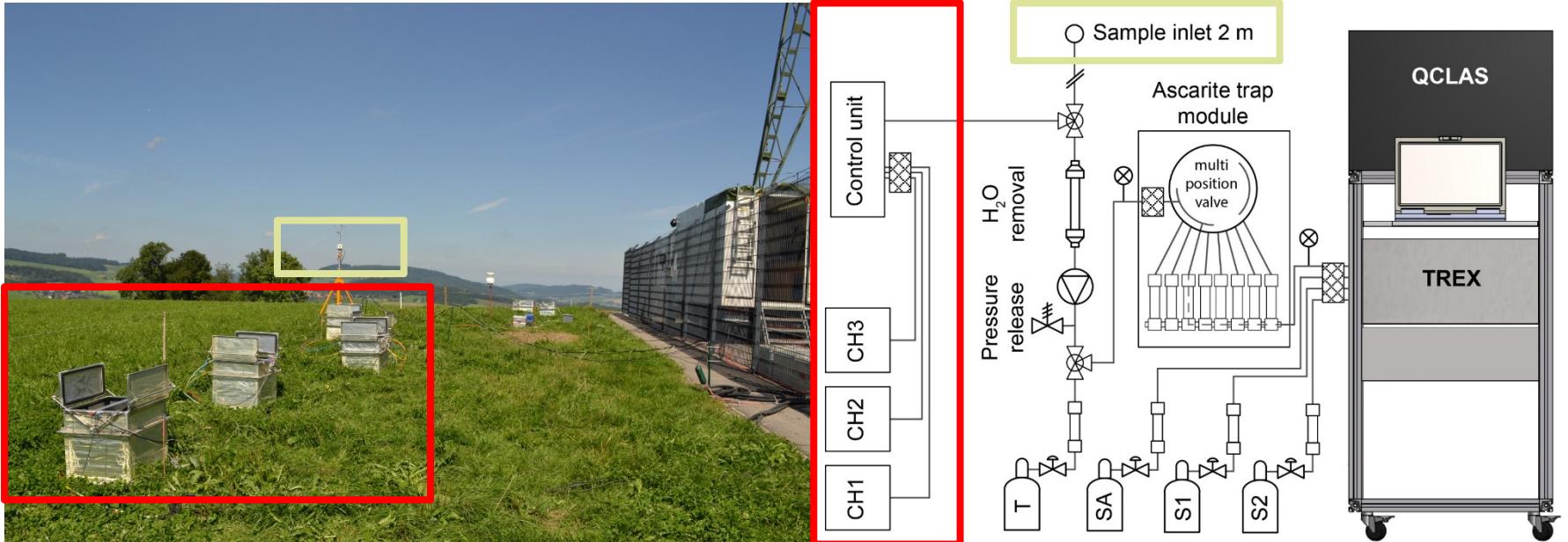


- ▶ June – August 2016
- ▶ intensively managed grassland research site
- ▶ local N<sub>2</sub>O fluxes, meteo and wind observation

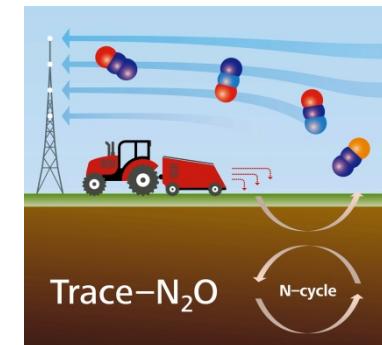
# Field study #2 – central Switzerland



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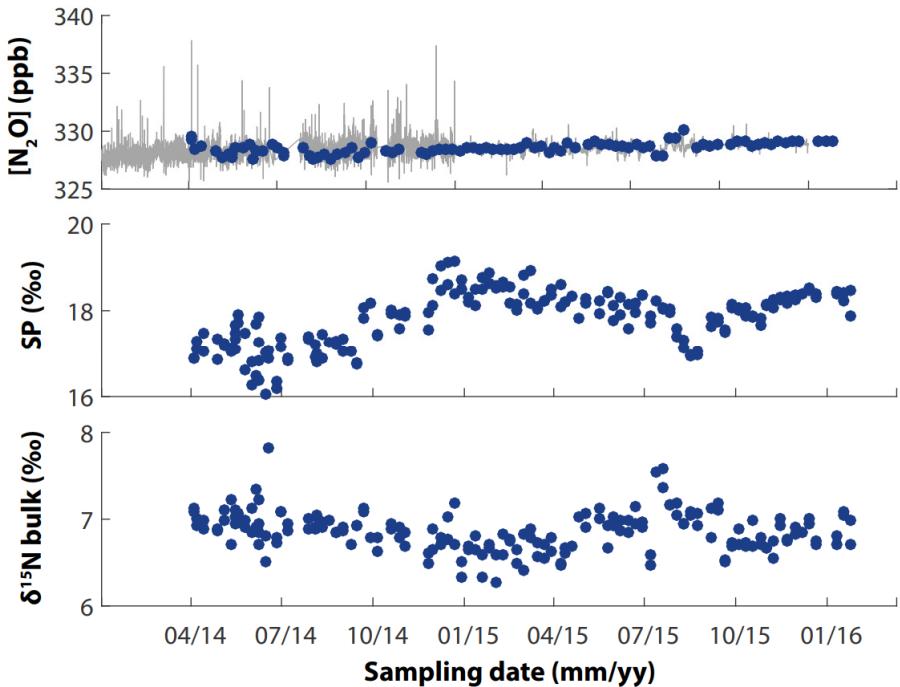
- ▶ September – December 2017 in central Switzerland
- ▶ intensively managed grassland research site
- ▶ TREX-QCLAS using flux chambers



# Study #3 – high-altitude station Jungfraujoch



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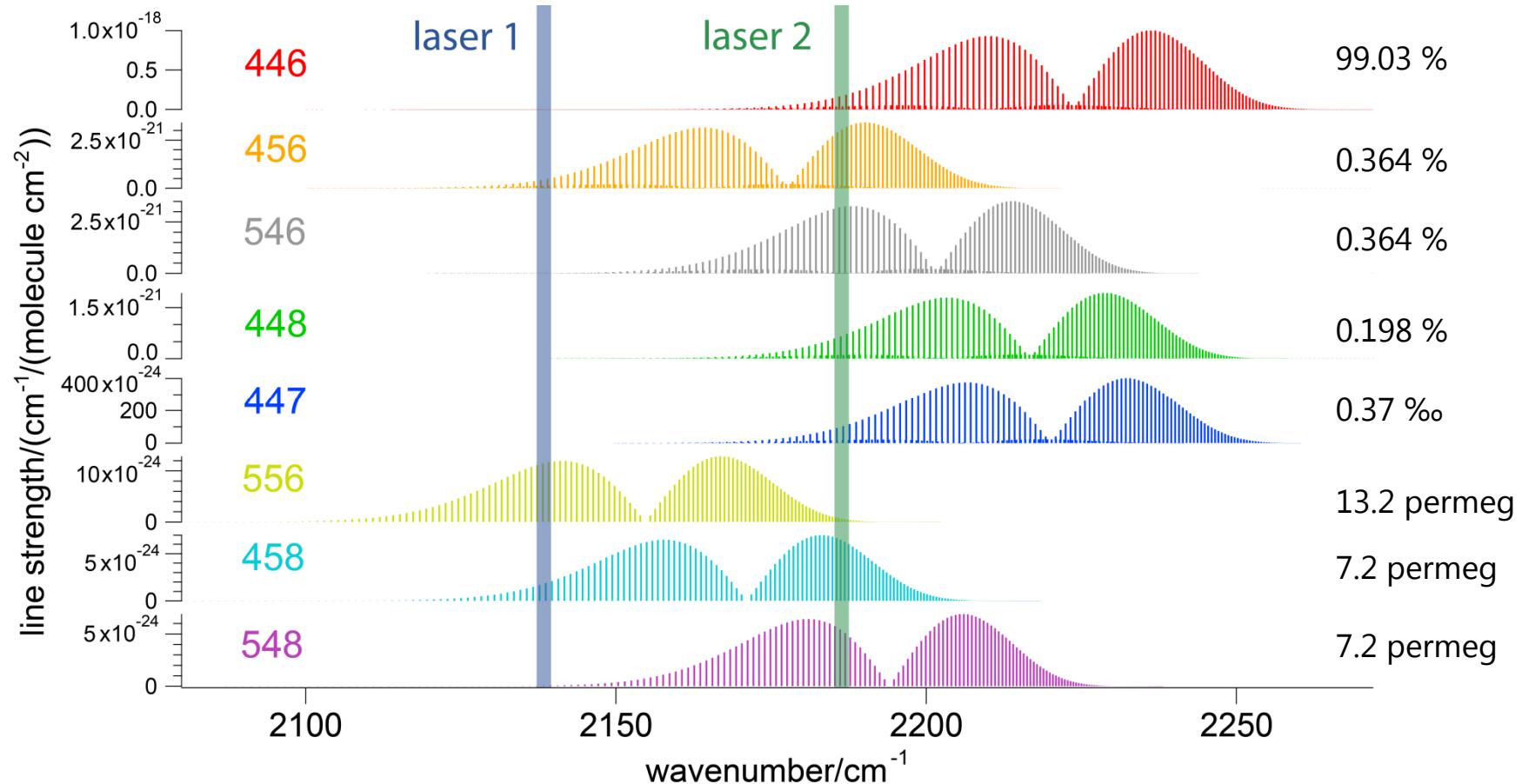
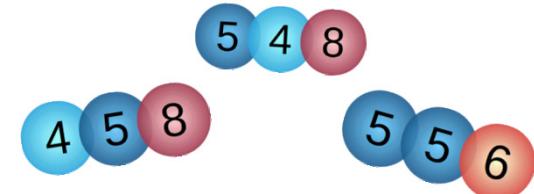


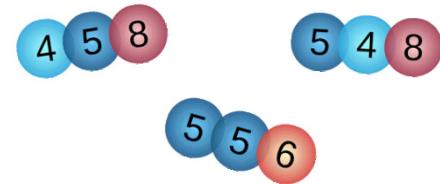
- ▶ identification of seasonal variability since April 2014, ongoing
- ▶ stratosphere-troposphere exchange observable





# Clumped isotopes in N<sub>2</sub>O





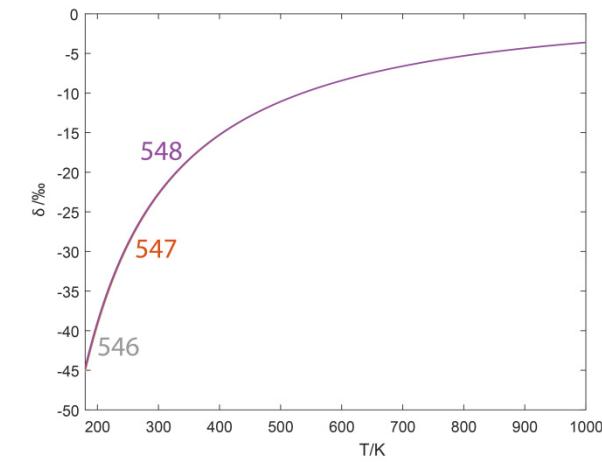
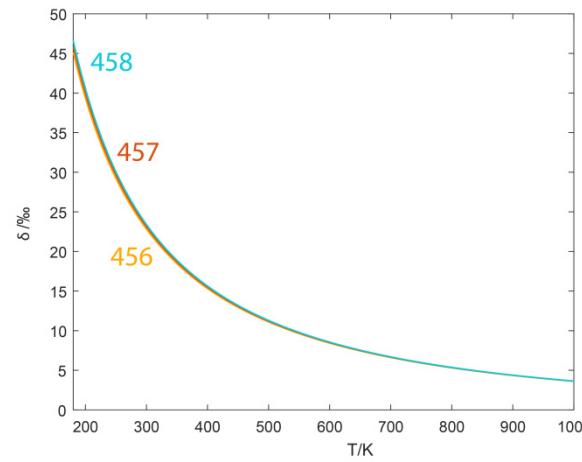
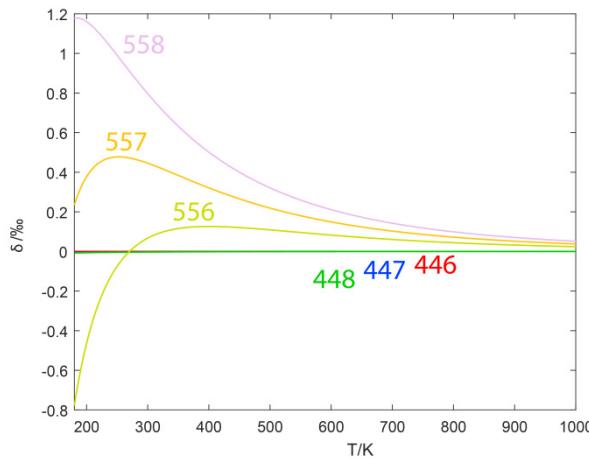
# New reference scale for clumped N<sub>2</sub>O

- equilibration of N<sub>2</sub>O – driving into stochastic (random) distribution

$$\delta_i = \left( \frac{\left( \frac{[i]}{[446]} \right)_{sample}}{\left( \frac{[i]}{[446]} \right)_{reference}} - 1 \right) \cdot 1000 (\text{‰})$$

reference – stochastic (random) distribution

- different temperatures – different equilibrium composition, calculated using statistical thermodynamics predictions



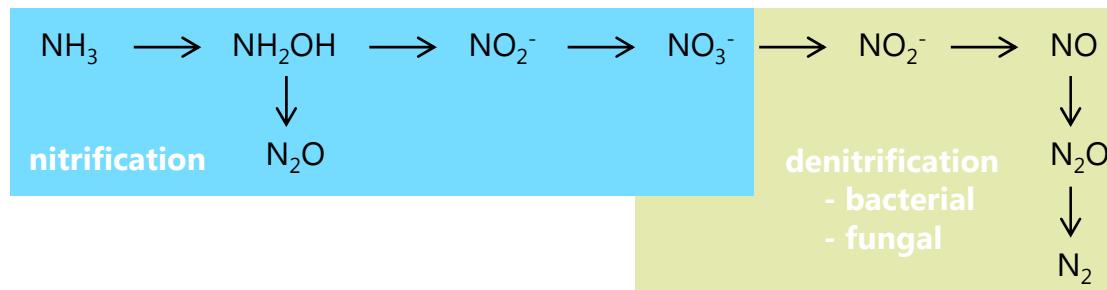
# Summary

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- ▶ TREX-QCLAS for singly substituted isotopologues
- ▶ selective and precise analysis of clumped isotopes
- ▶ a new reference isotopic scale has been developed

## Outlook

- ▶ applications for clumped N<sub>2</sub>O isotopic signatures from pure microbial cultures



# Acknowledgement

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- ▶ Joachim Mohn – supervisor at Empa Dübendorf
- ▶ Stefano Bernasconi – supervisor at ETH Zürich
- ▶ lab people – Kerstin Zeyer, Sarah Eggleston, Erkan Ibraim, Longfei Yu, Béla Tuzson, Lukas Emmenegger



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SWISS NATIONAL SCIENCE FOUNDATION



Thank you for the attention!



# Used figures

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- ▶ <https://www.roboticsbusinessreview.com/wp-content/uploads/2014/05/agriculture-robot.jpg>
- ▶ <http://www.motherearthnews.com/-/media/Images/MEN/Editorial/Articles/Magazine-Articles/2016/04-01/The-Benefits-of-Earthworms-and-How-to-Attract-Them/soil-and-worm-jpg.jpg>
- ▶ <https://images.designtrends.com/wp-content/uploads/2016/02/24090853/Ocean-Wave-Dolphins-Wallpaper.jpg>
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