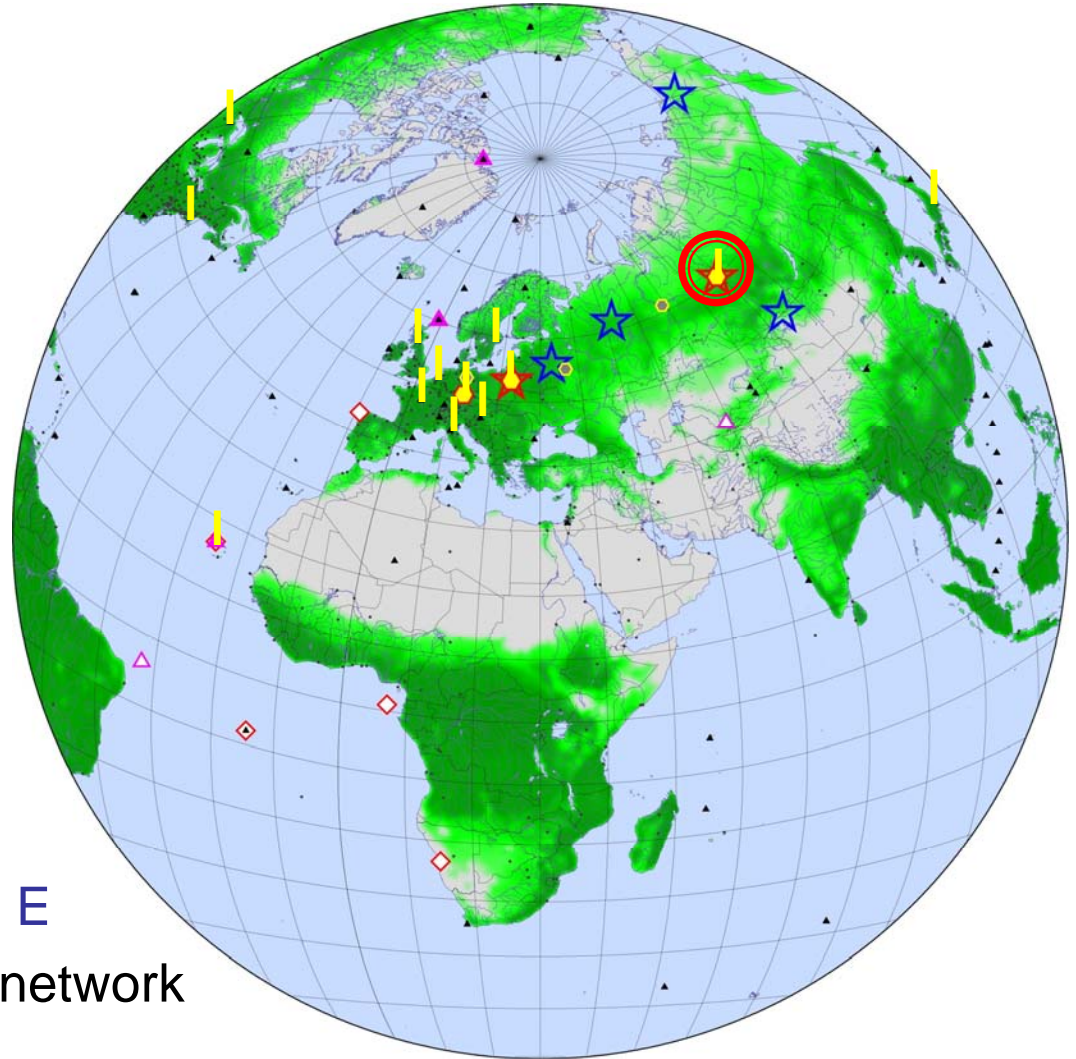


# Continuous CO<sub>2</sub>/CH<sub>4</sub> Measurement at Zotino Tall Tower Observatory (ZOTTO) in Central Siberia

Jan Winderlich  
PhD student

Huilin Chen, Annette Höfer, Christoph Gerbig, Martin Heimann





ZOTTO station: 60 °N, 90° E

- part of global tall tower network



## 1) Current Setup in ZOTTO

- Setup
- Data

## 2) CO<sub>2</sub> / CH<sub>4</sub> Analyzer

- Cavity Ring Down Spectroscopy
- Measurement performance

## 3) Water vapor

- Disturbances
- Corrections

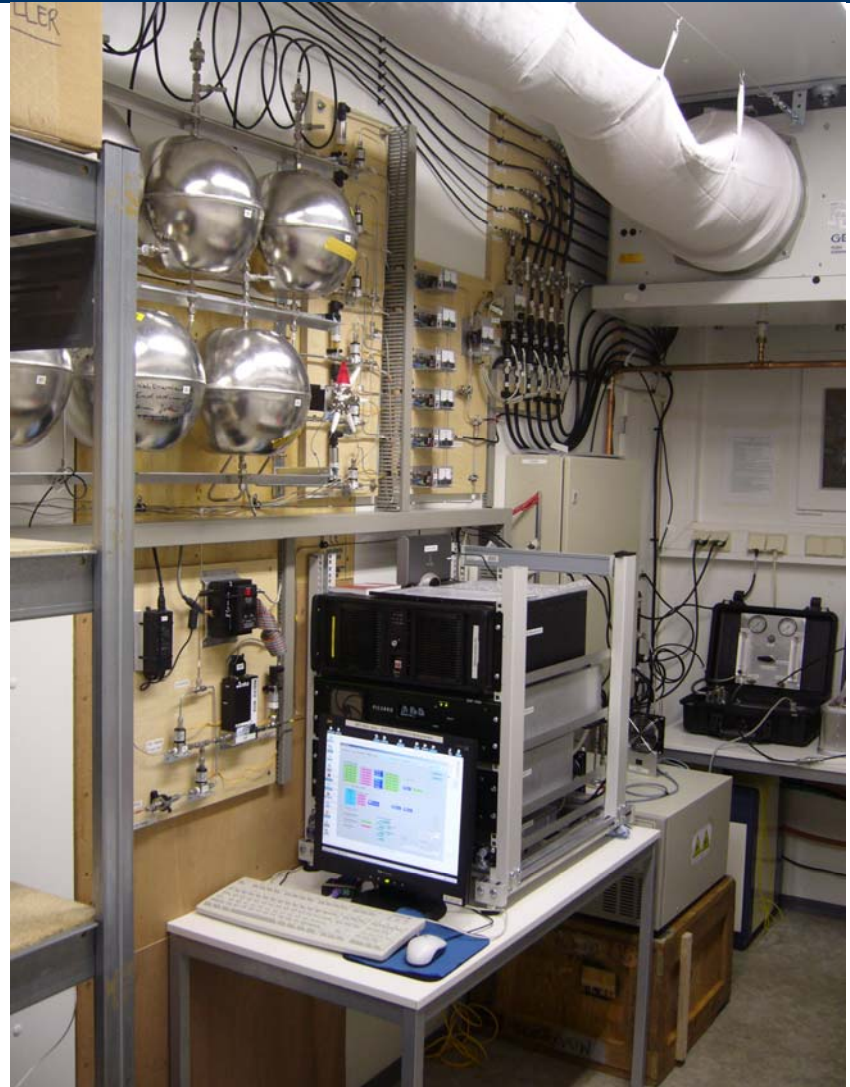


# 1) Current Setup in ZOTTO

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View into the Lab  
since April 2009

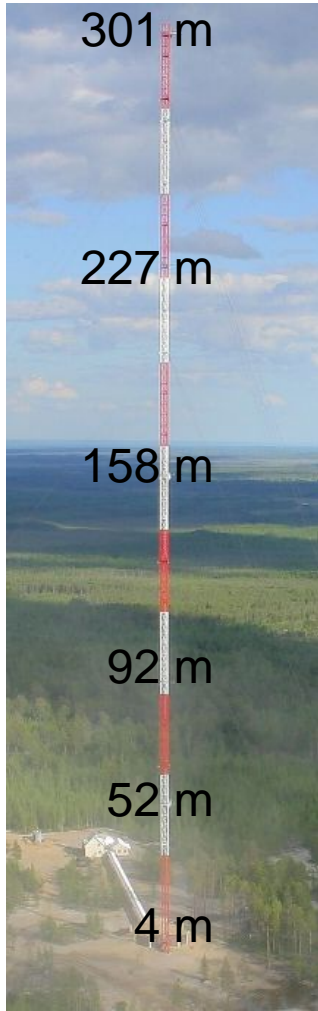


“CO<sub>2</sub>/CH<sub>4</sub> Measurement at ZOTTO” - Jan Winderlich - Jena, 10. Sept. 2009

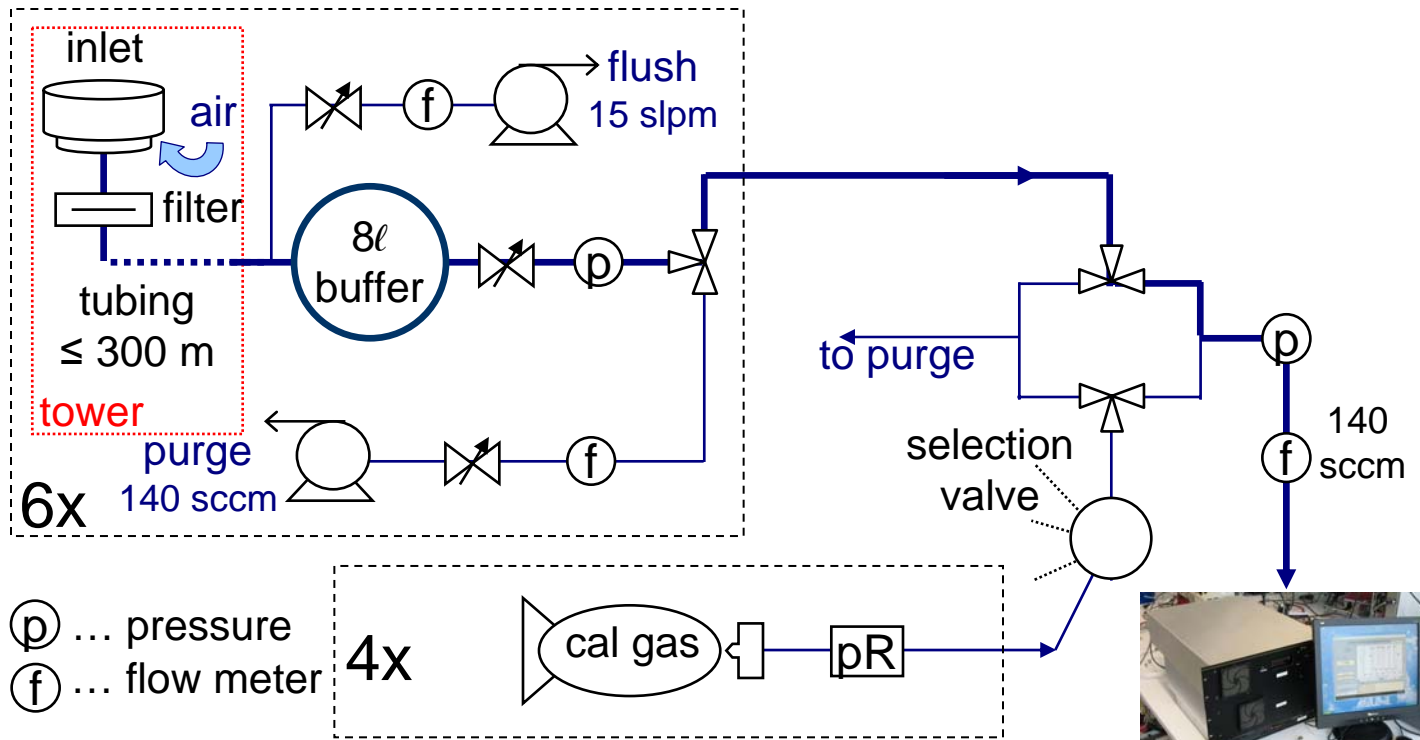
15th WMO/IAEA Meeting of Experts on Carbon Dioxide,  
Other Greenhouse Gases and Related Tracer Measurement Techniques



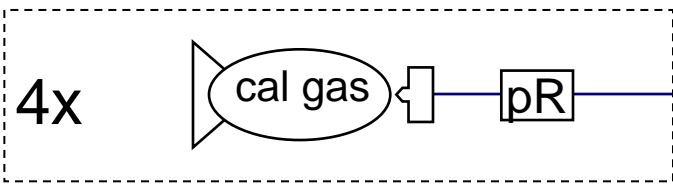
# 1) Current Setup in ZOTTO



- 6 tower levels to 1 instrument → Plumbing diagram:



(p) ... pressure  
(f) ... flow meter



calibration every 100 hrs



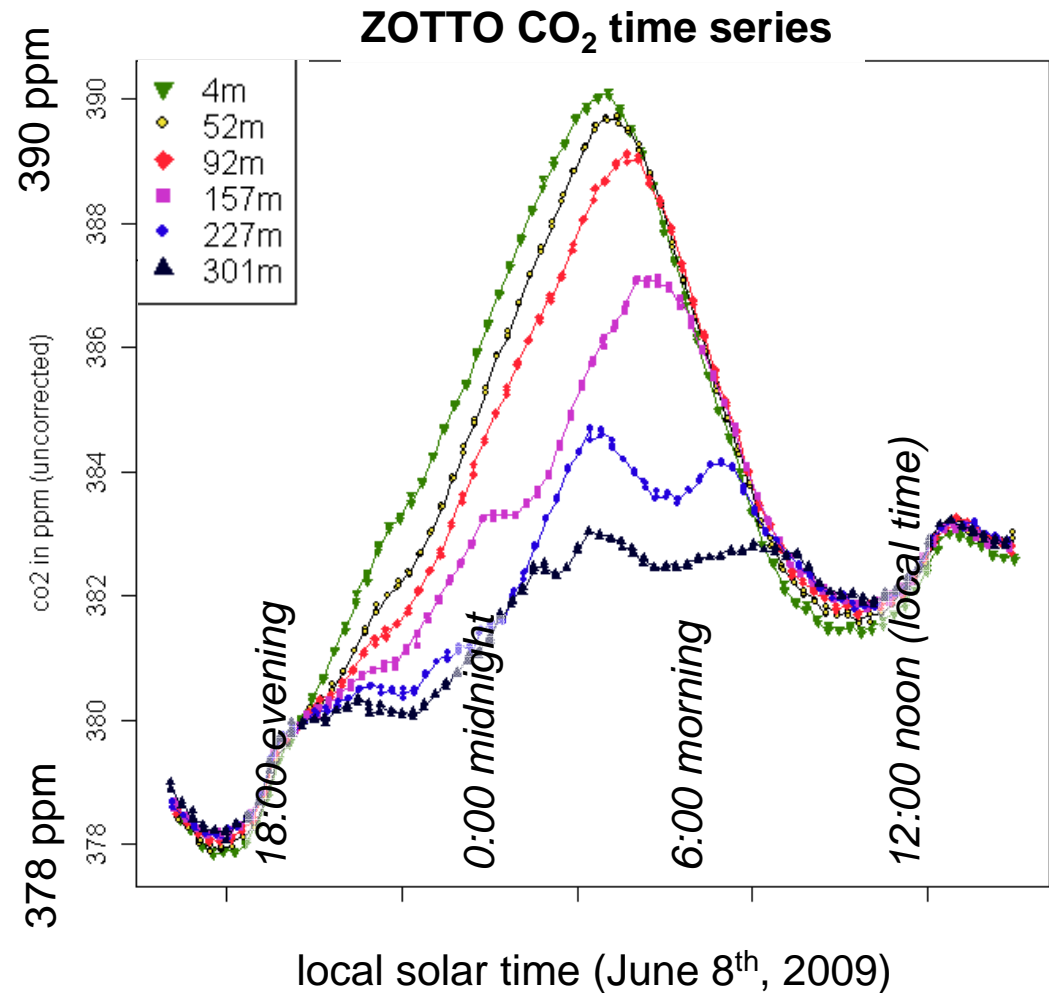
Picarro analyzer  
EnviroSense 3000i  
ESP-1000 platform

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# 1) Current Setup in ZOTTO



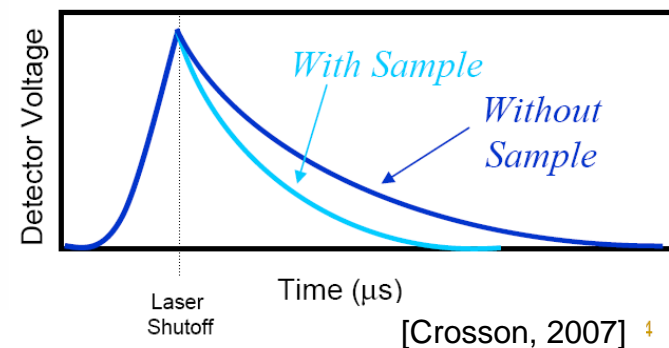
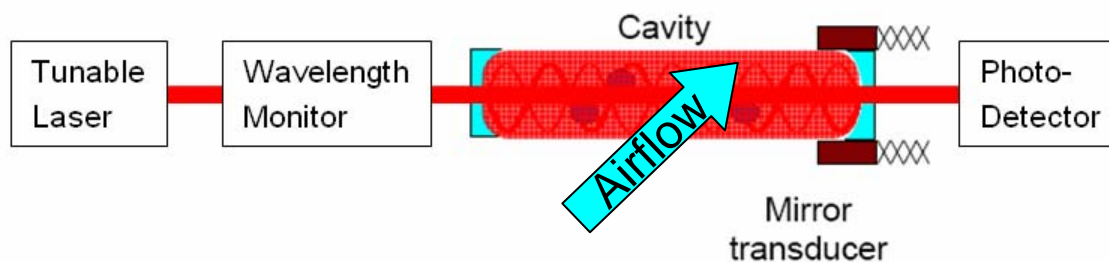
Early summer day



## 2) CO<sub>2</sub> / CH<sub>4</sub> Analyzer

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- CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O measurement system: Picarro, Inc.
  - EnviroSense 3000i, ESP-1000 platform
- Cavity Ring-Down Spectroscopy (CRDS):

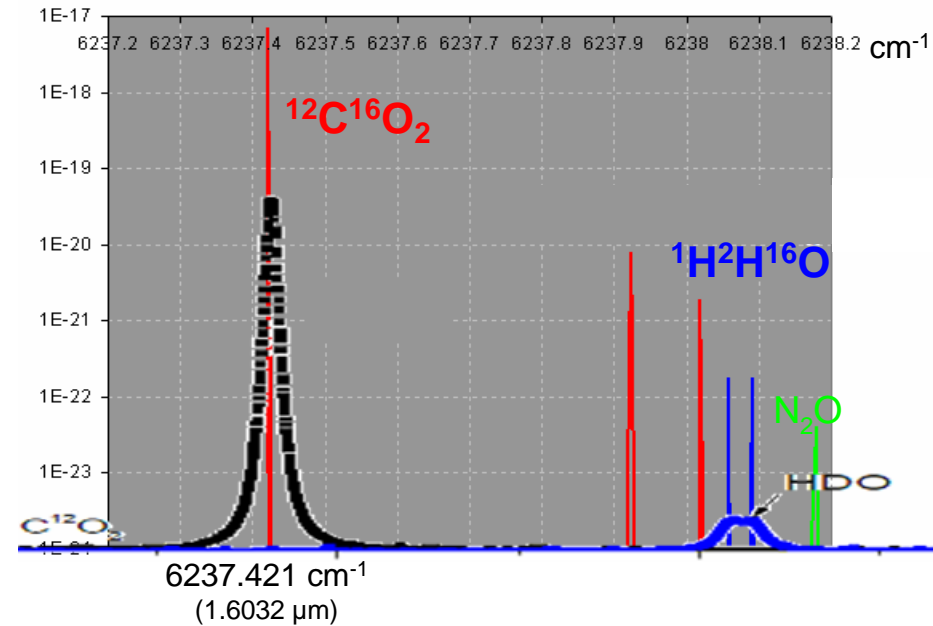
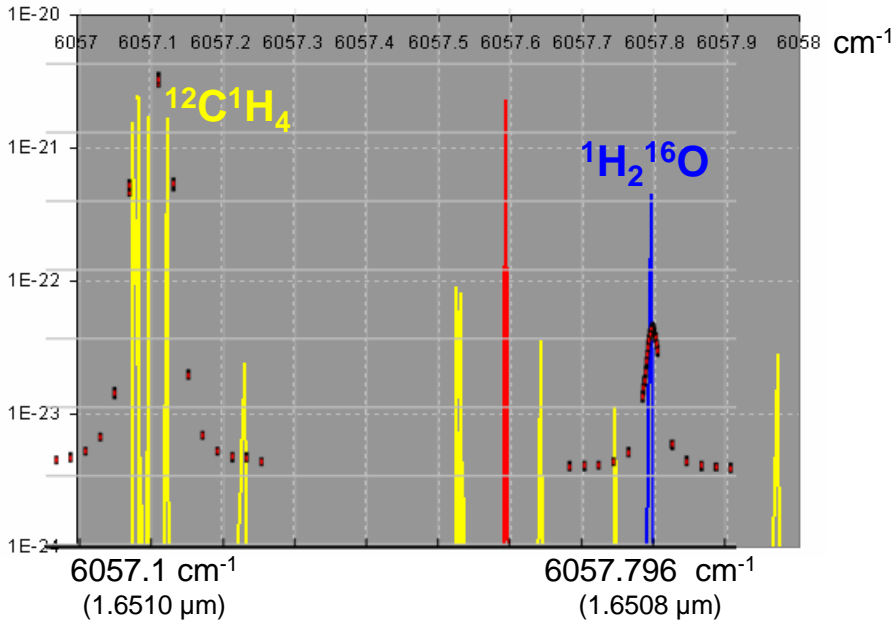


- Linear calibration
- Low noise:  $1\sigma$ SD < 0.06 ppm CO<sub>2</sub>  
< 0.4 ppb CH<sub>4</sub>
- Long-term stability: drift < 0.001 ppm / day CO<sub>2</sub>  
< 0.008 ppb / day CH<sub>4</sub>



# 2) CO<sub>2</sub> / CH<sub>4</sub> Analyzer

Zoom to spectral lines used by Picarro, Inc.  
(Overlaying spectra from HITRAN2004 database & Picarro)



- CRDS: <sup>12</sup>C<sup>16</sup>O<sub>2</sub>
- GC: all CO<sub>2</sub> isotopes
- NDIR: <sup>12</sup>C<sup>16</sup>O<sub>2</sub> (partly <sup>13</sup>C<sup>16</sup>O<sub>2</sub>,  
<sup>12</sup>C<sup>16</sup>O<sup>18</sup>O, <sup>12</sup>C<sup>16</sup>O<sup>17</sup>O)

CRDS detects only main isotops  
→ **δ<sup>13</sup>C & δ<sup>18</sup>O correction needed!** [Tohjima, JGR, 2009]  
up to 0.11+0.05 ppm for synthetic air CO<sub>2</sub>

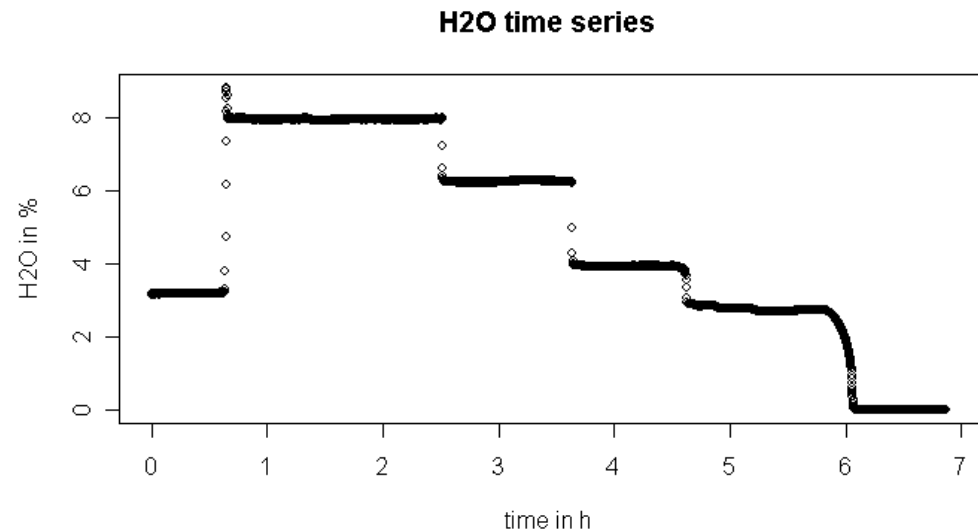




# 3) H<sub>2</sub>O Disturbance

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- Dilution correction  
(amount of H<sub>2</sub>O vapor influences relative CO<sub>2</sub> ratio)
- Pressure broadening  
(gas constitution influences absorption spectra)
  - Experiment: Humidify tank air in a water trap → wet air
    - H<sub>2</sub>O = f(droplet size, pressure, temperature)
    - CO<sub>2</sub> dry, CH<sub>4</sub> dry = const.



- Adsorption effects in tubes



# 3) H<sub>2</sub>O Correction

January 2009 with CFADS37:

- Quadratic fit (wet/dry ~ H<sub>2</sub>O)
- H<sub>2</sub>O calibrated for CFADS15

August 2009 with CFADS15:

- Empiric correction for wet CO<sub>2</sub>/CH<sub>4</sub>

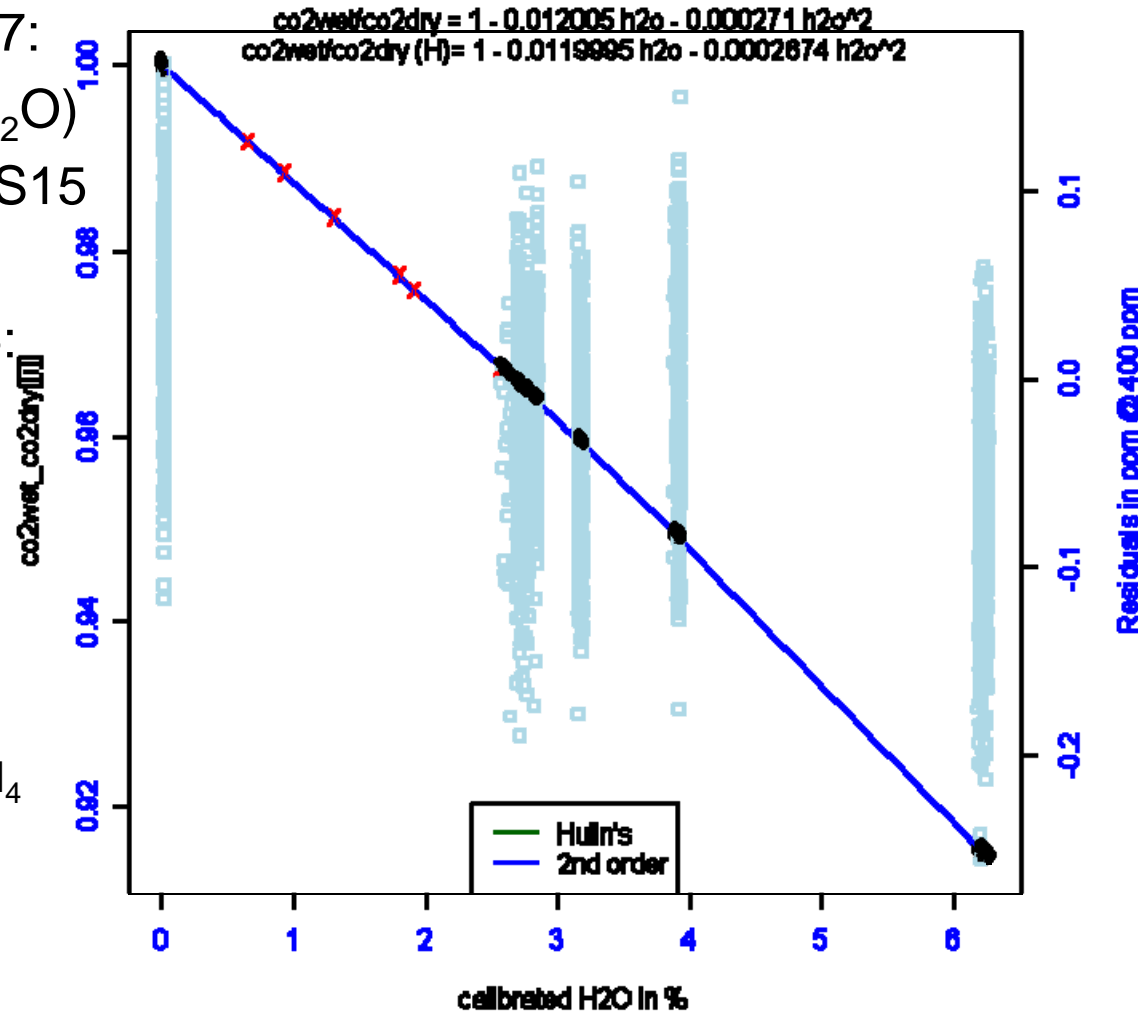
→ Residuals:

CO<sub>2</sub>  $0.005 \pm 0.053$  ppm

CH<sub>4</sub>  $0.001 \pm 0.530$  ppb

for air: 400 ppm CO<sub>2</sub>, 2000 ppb CH<sub>4</sub>

→ No drying of sample air

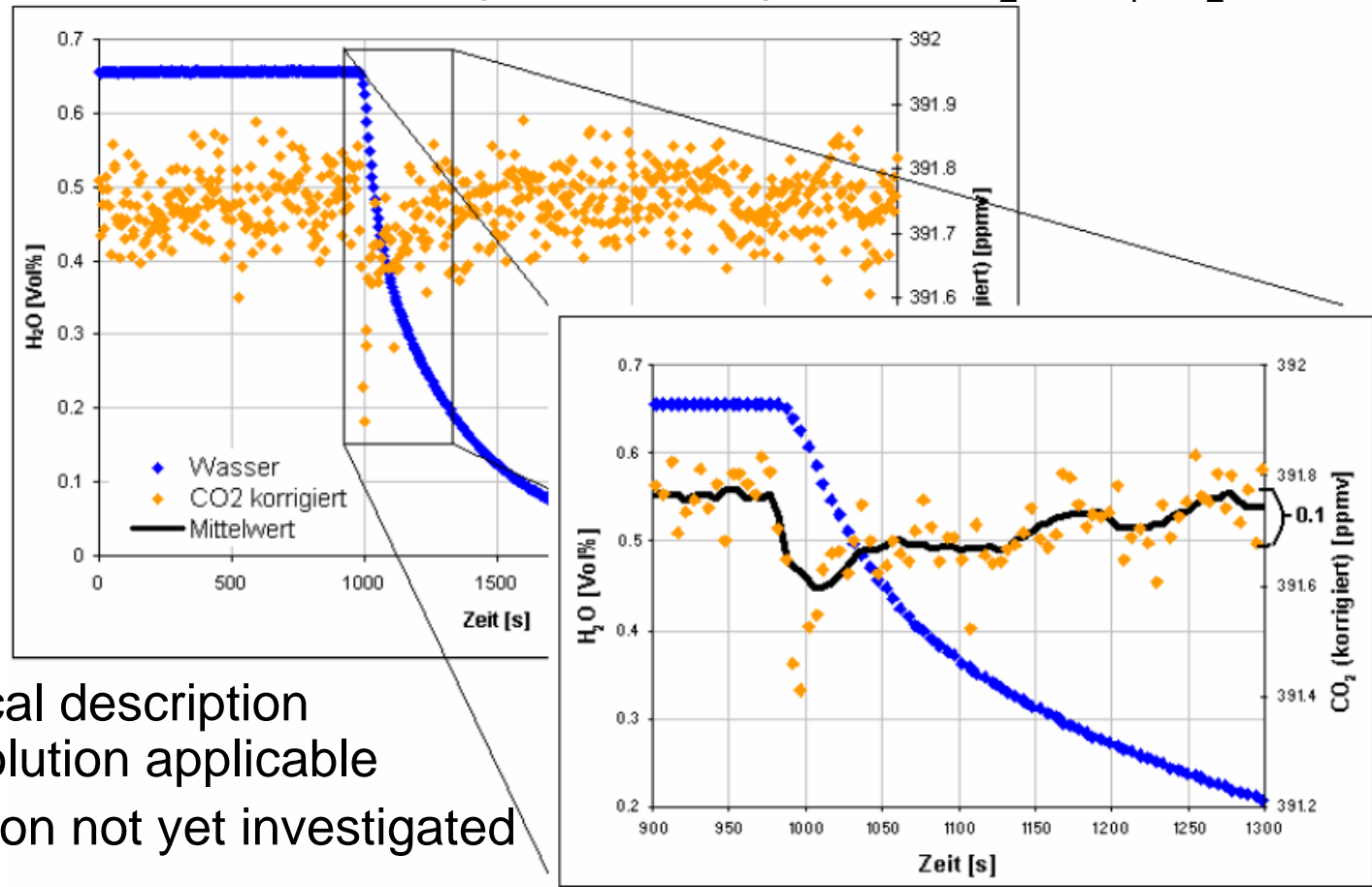


- High quality CO<sub>2</sub> & CH<sub>4</sub> measurement  
Cavity Ring Down Spectroscopy
- Quasi continuous measurement on 6 levels  
8 l Buffers
- No air drying  
Correction with H<sub>2</sub>O measurement



# Prospect: Influence of Wet Sampling Tube <sup>12/13</sup>

- H<sub>2</sub>O sticks to tube surface → Influence on measurement?
- Lab experiments done: Switching of several gases (CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O)



- Mathematical description
- Deconvolution applicable
- Condensation not yet investigated

[A. Höfer, 2009]

“CO<sub>2</sub>/CH<sub>4</sub> Measurement at ZOTTO” - Jan Winderlich - Jena, 10. Sept. 2009



# Acknowledgements

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... and more!

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## Thank you for you attention!

[view from 300 m level ZOTTO, Sept. 2008]

“CO<sub>2</sub>/CH<sub>4</sub> Measurement at ZOTTO” - Jan Winderlich - Jena, 10. Sept. 2009

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