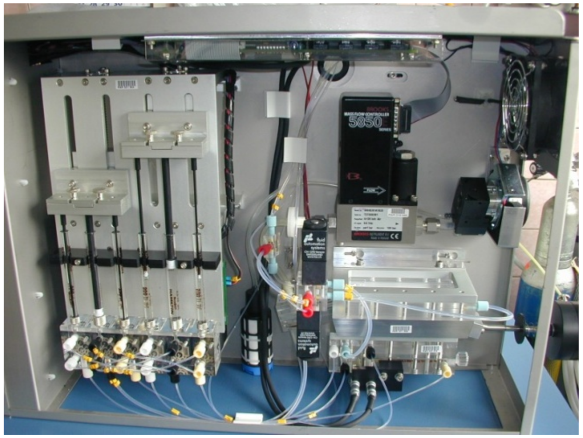
# Different Ammonia Measurements at IfT and Experiences with a Photo-Acoustic Device (TGA 310)

G. Spindler, E. Brüggemann, T. Gnauk, A. Gruener, E. Renner, H. Herrmann



LEIBNIZ-INSTITUT FÜR
TROPOSPHÄRENFORSCHUNG

Workshop - Symposium
Air Monitoring Instrumentation
10-12 december, 2007

Schagen, The Netherlands

ECN

applikon®

RR mechatronics

# CONTENT

- Different Results of $NH_3$-Measurements with **AMMANDA, AiRRmonia®** and **passive Wind-Vane-Samplers** at Melpitz site (Examples)
- $NH_3$-Measurements with an **Photo-acoustic Device** TGA-310 (Fa. Omnisens, CH)
    - Photo-acoustic Detection of $NH_3$ – Principle of Function
    - Laboratory tests and Calibration
    - Long-term Measurements at different places and comparison with AiRRmonia® and a modified chemiluminescence detection
- **Summary** and **Outlook**

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**Location of the Melpitz site in the German low lands**

(in operation since 1992)

Trace gases $SO_2$, $NO_x$, $O_3$
$HNO_3$, $HNO_2$, $NH_3$,
wet and dry deposition,
size segregated physical and chemical characterization of particles $PM_1$, $PM_{2.5}$ and $PM_{10}$

Now integrated also in:

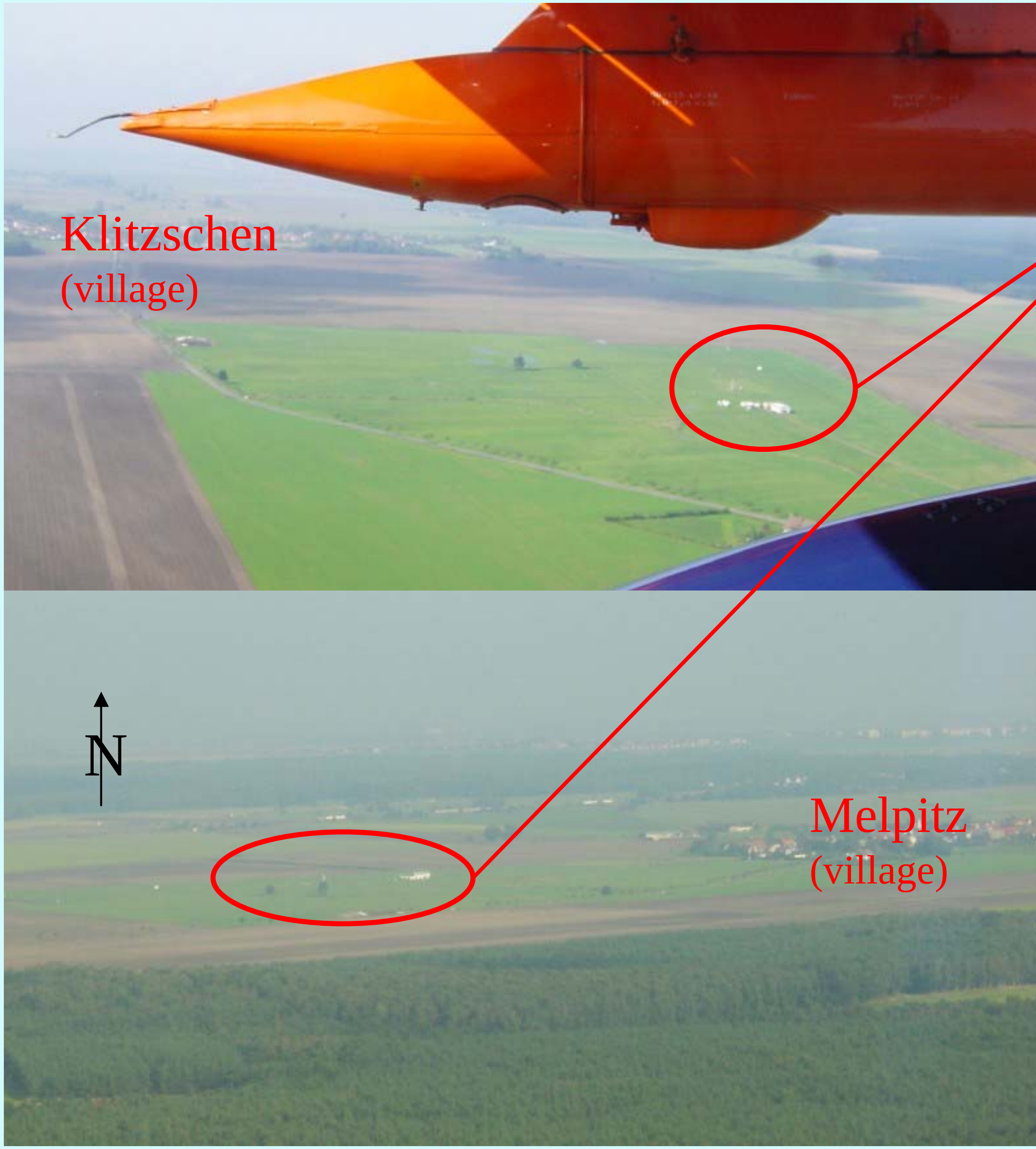
EUSAAR

ACCENT
ATMOSPHERIC COMPOSITION CHANGE
THE EUROPEAN NETWORK OF EXCELLENCE

emep

Co–operative programme for monitoring and evaluation of the long–range transmissions of air pollutants in Europe

ift



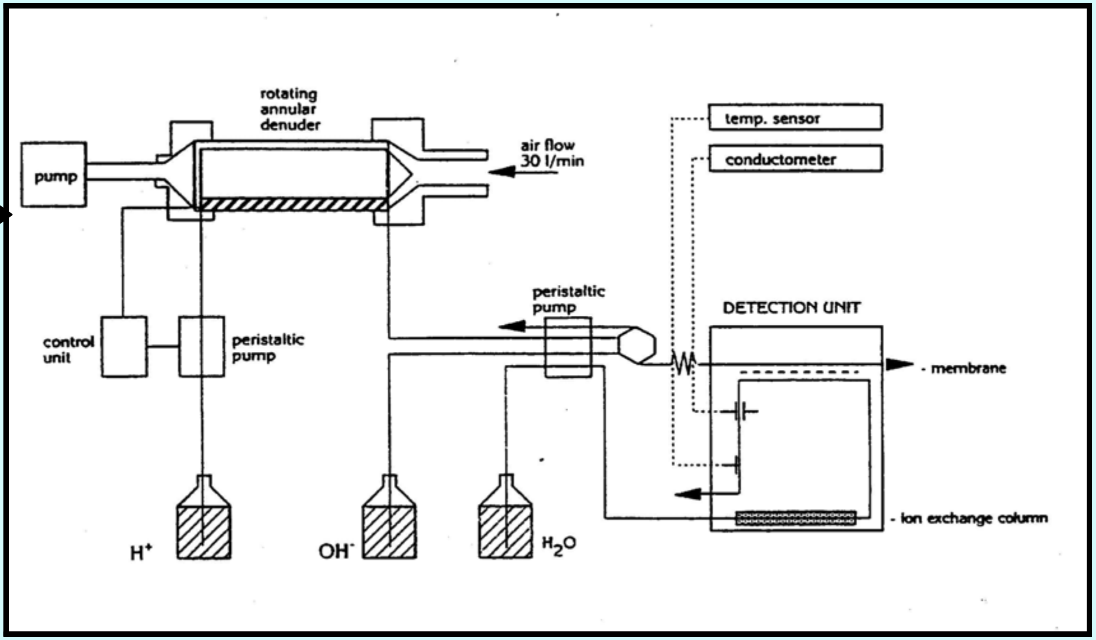

**measuring field**

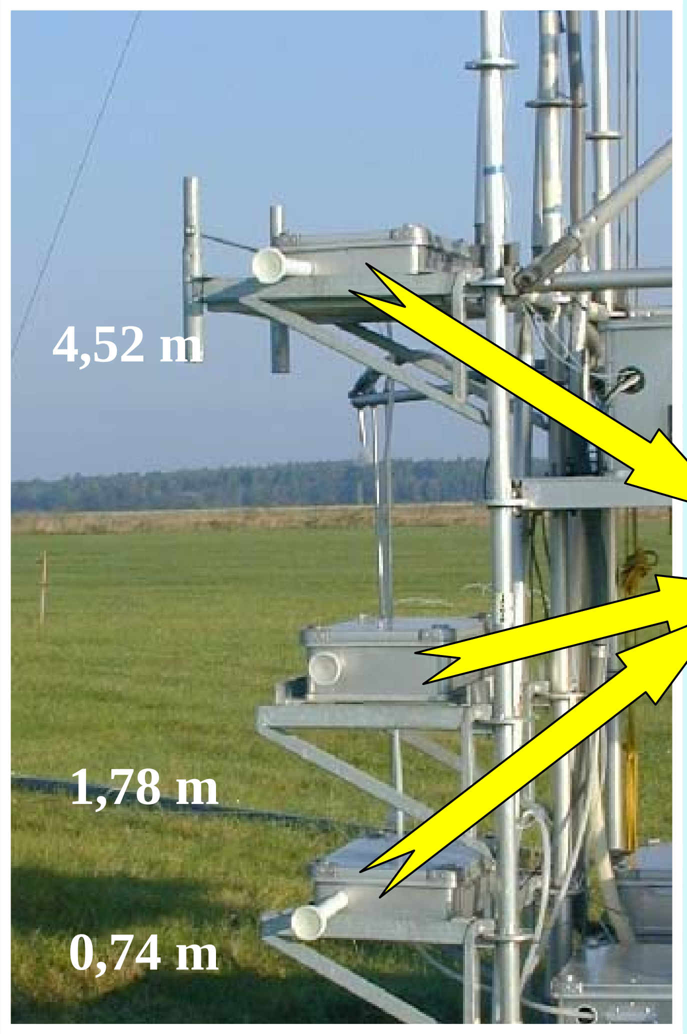
**Location**
(12°56‘ E, 51°32‘ N,
Altitude 86 m
above see level)

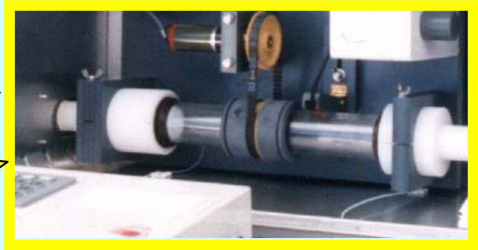
Fotos: Bange
September 2001
TU-Braunschweig

## View from air craft to the rural Melpitz site in the state of Saxony (Germany)

# $NH_3$-Gradient-System AMANDA 1995 (functional principle)



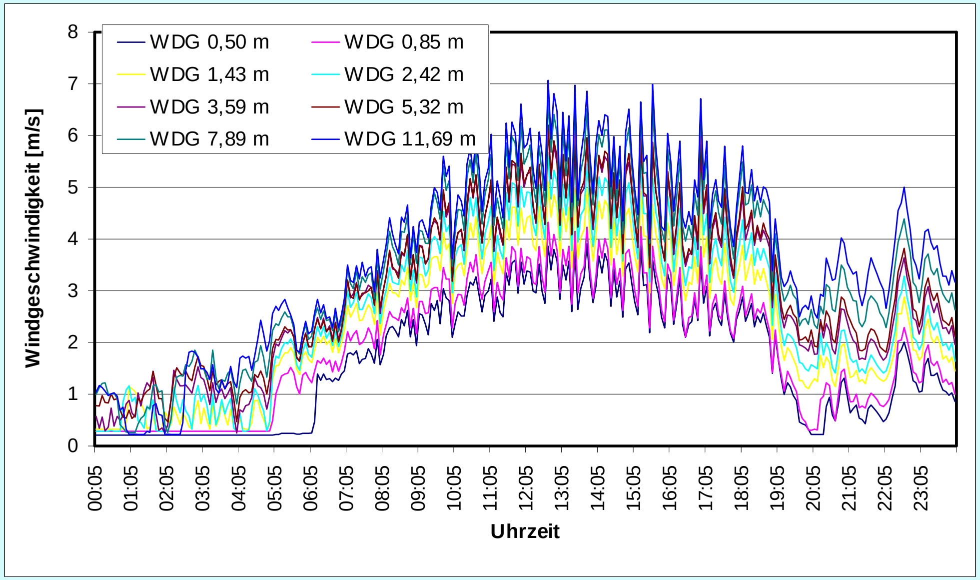
**rotating wet annular denuder**

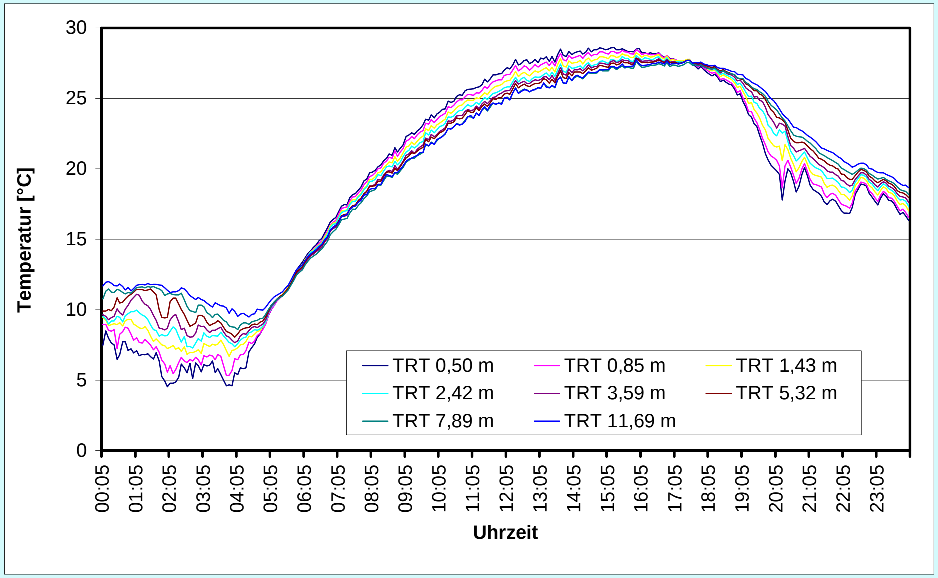
**detector box**

AMANDA was the predecessor of GRAHAM (**GR**adient-**A**mmonia-**H**igh **A**ccuracy – **M**onitor)

# Micrometeorological gradient measurements at Melpitz for horizontal wind velocity and temperature

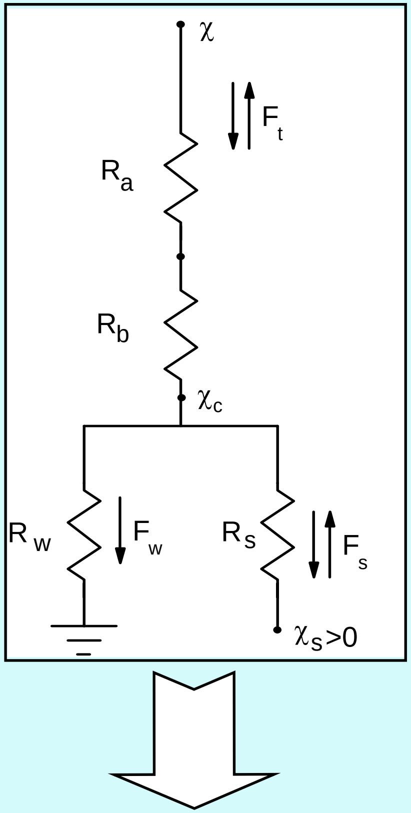
**gradient of wind velocity (2000-06-09) (5-minute-means)**

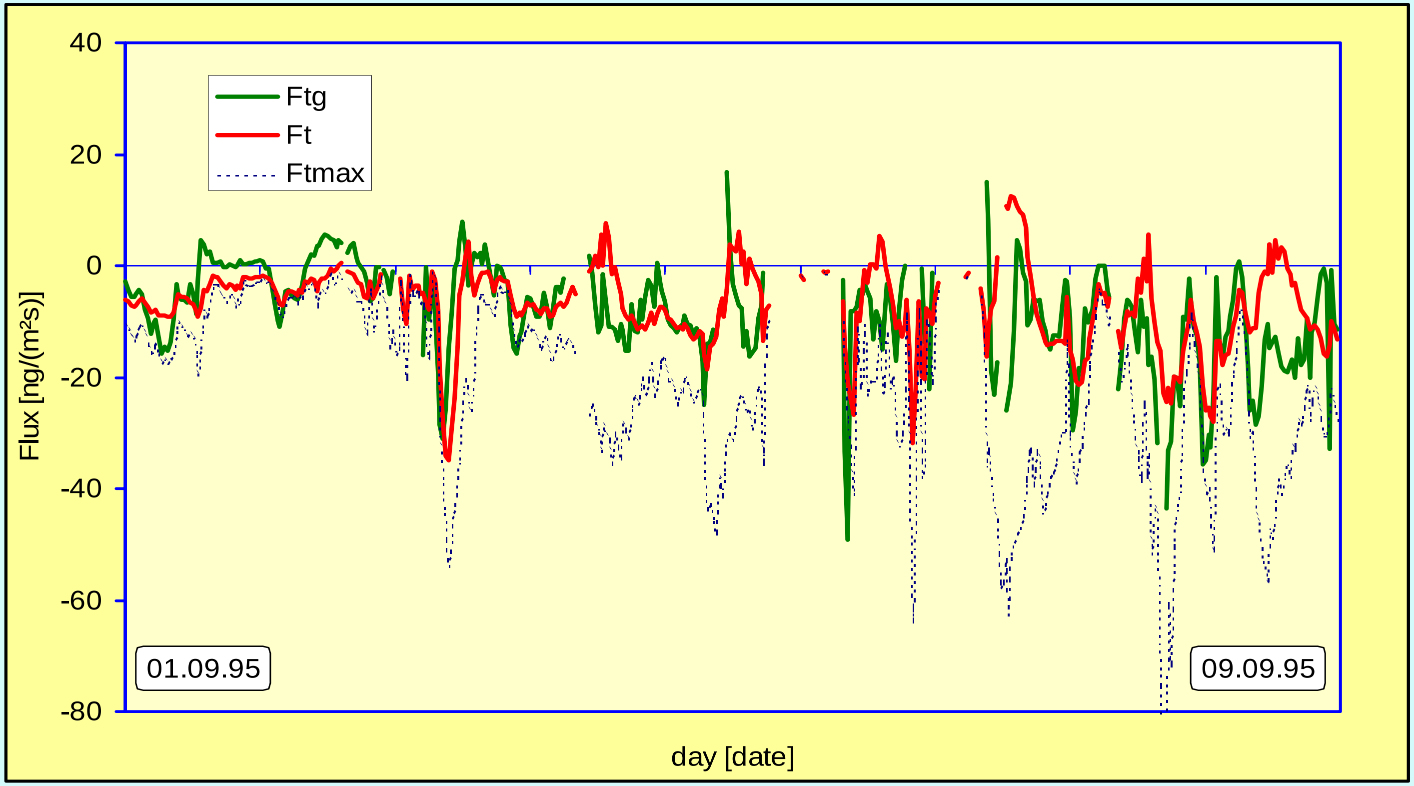



**gradient of temperature (2000-06-09) (5-minute-means)**

# Measured flux ($F_{tg}$), maximal possible flux ($F_{tmax}$) und modeled ($F_t$) $NH_3$-flux at Melpitz site




**Single layer canopy-compensation-point-cuticula-resistance-model for bidirectional $NH_3$-Flux (M.A. Sutton, 1995)**

*Spindler, et al. 2001: Ammonia dry deposition over grassland – micrometeorological flux-gradient Measurements and bidirectional flux calculation using an inferential model. Q.J.R.Meteorol. Soc., 127, 795-814.*

# Comparison of two AMANDA-systems (from FAL and IfT) during the GRAMINE-Experiment at a meadow in in Braunschweig-Völkenrode,  Summer 2000

FAL
Bundesforschungsanstalt für Landwirtschaft

ift

# Result of two days parallel measurements with two AMMANDA-Systems, Melpitz 2000-10-12 and 13


**4.52 m above ground, concentration in µg/m³**

Bundesforschungsanstalt für Landwirtschaft

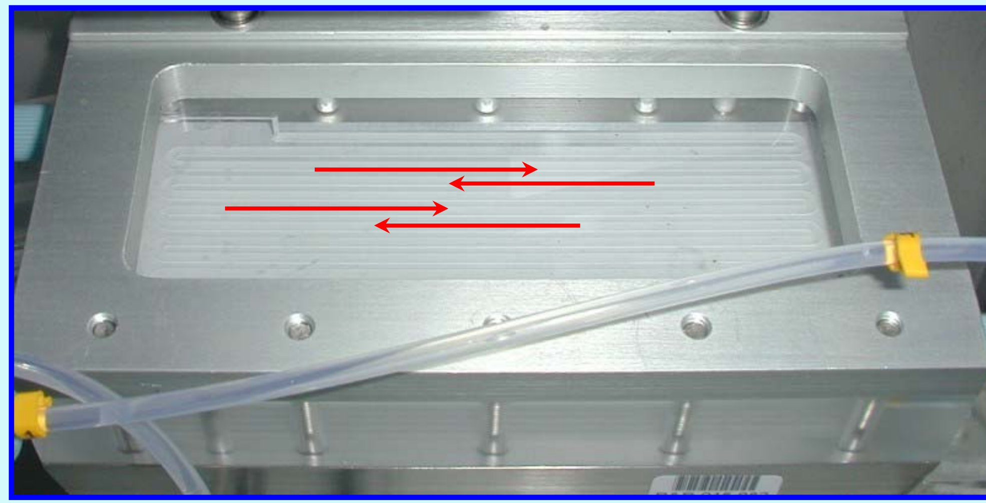
Examples for $NH_3$-measurements with

# AiRRmonia®

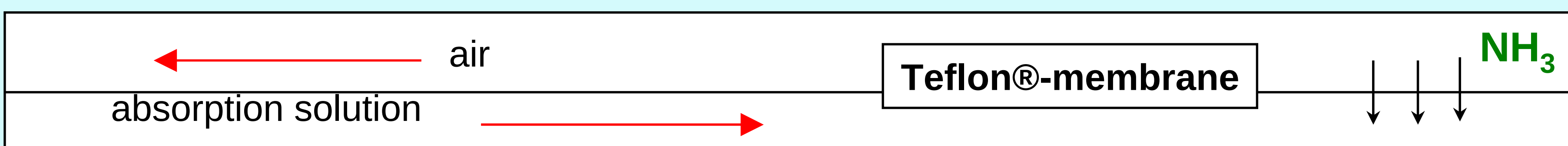
**2001**

RR mechatronics ISO 9001

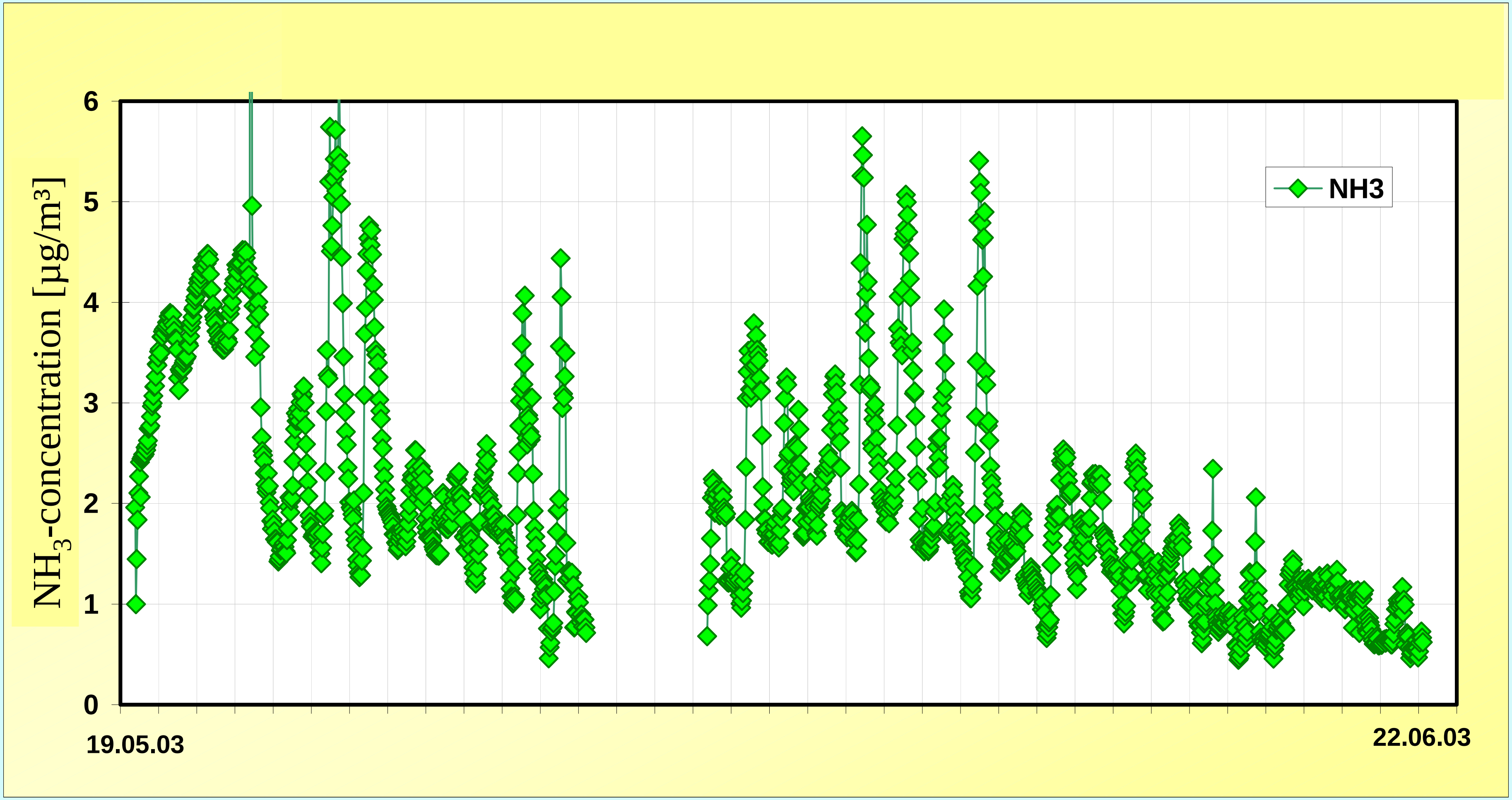
**detector membrane**



**functional principle**

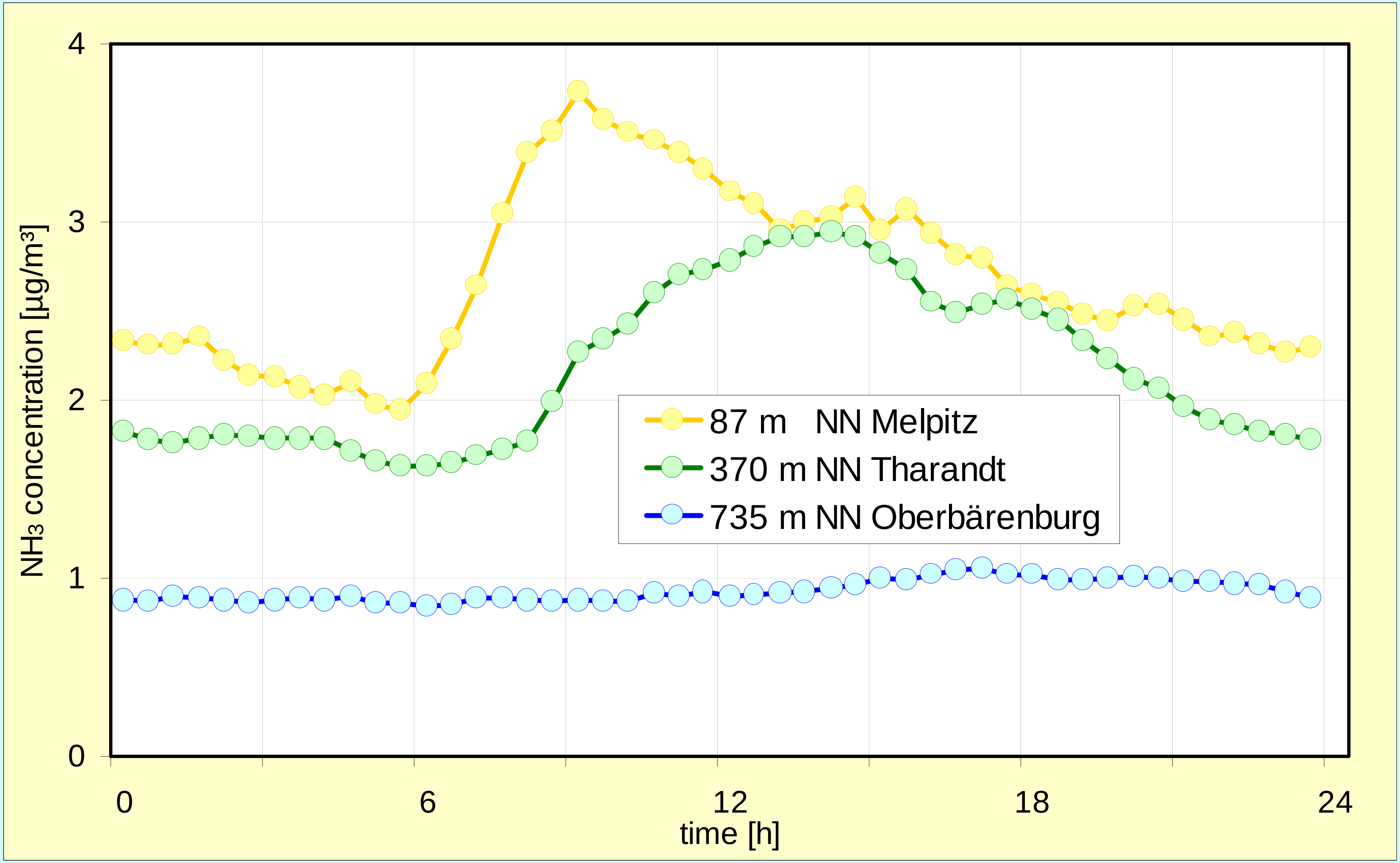


# $NH_3$-concentration measurements, Tharandt Forest




half hourly means

# Average daily course of $NH_3$-concentration 2003 at Melpitz (29 days in July), Tharandt (32 days in May and June) and Oberbärenburg (15 days in October)

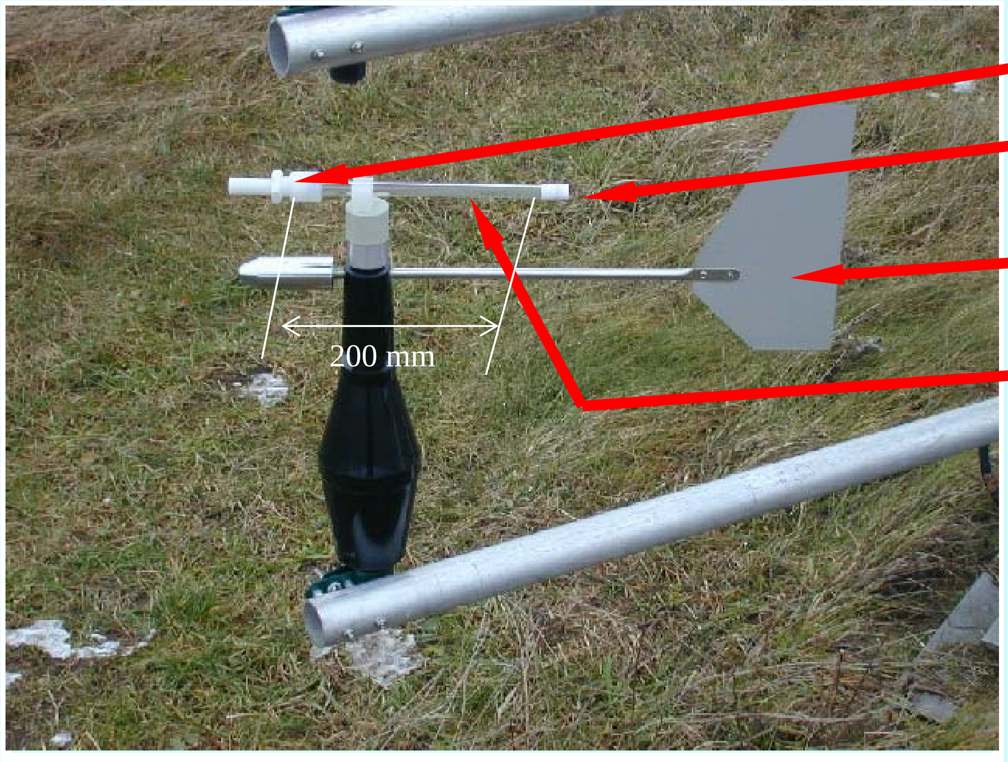


# Passive Wind-Vane Samplers

## Determination of the dry deposition of $NH_3$ using passive samplers

Project: VASKO (**V**erfahren **A**mmoniak **s**ammelnder Windfahnen im Vergleich zu einer **ko**nventionellen Gradiententechnik

UBA Grant number 298 42 290




drainage

pinhole

wind-vane

diffusion tube (impregnated inside with citric acid)

**experimental buildup for determination of $NH_3$-concentration**

# Calculation of $NH_3$-concentration using a diffusion tube fastened at a wind-vane

amount of sampled $NH_3$

horizontal $NH_3$-Flux

$$c_{NH_3} = \frac{F_{hz}}{u} = \frac{M}{\pi r^2 \cdot \Delta t \cdot u \cdot K}$$

sampling time

horizontal wind-velocity

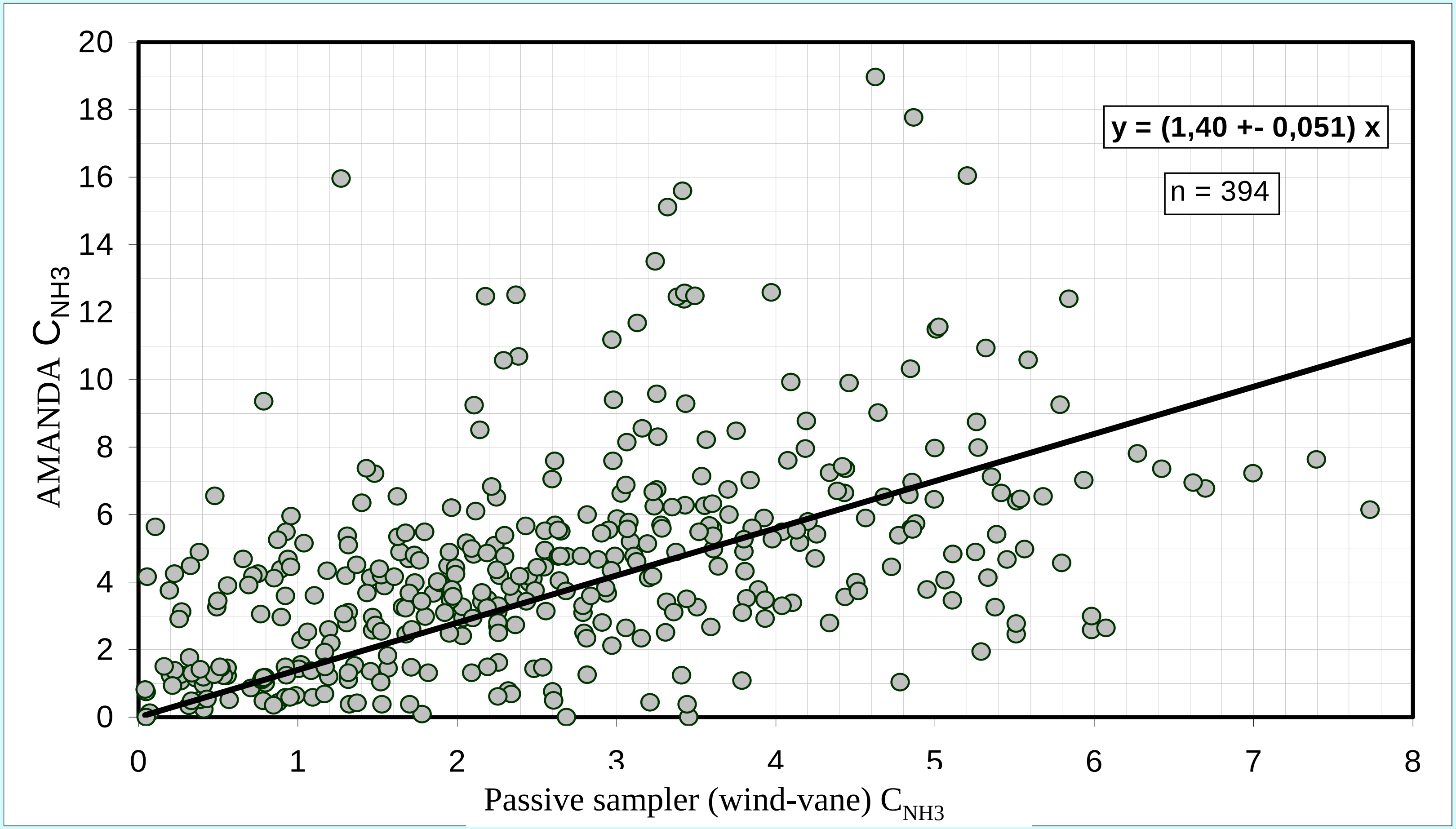
correction for pinhole (critical orifice) (0,69 for 1mm hole diameter)


B. Hansen, P. N∅rnberg, K.R. Rasmussen (1998) *Atmosperic Ammonia Exchange on a Heathland in Denmark.* Atmos. Environ., **32**, 461-464

B. Hansen (1997) Nitrogen inputs to semi-natural ecosystems: atmospheric deposition and weathering. Dissertation Universität Aarhus, Dänemark

B. Hansen,G.P. Wyers, P. N∅rnberg, E. Nemitz, M.A. Sutton (1999) *Intercalibration of a passiv wind-vane flux sampler against a continuous-flow denuder for the measurements of atmospheric ammonia concentrations and surface exchange fluxes*. Atmos. Environ. **33**, 4379-4388

# Comparison of results of the $NH_3$ concentration measurements using passive samplers fastened at wind-vane and a rotating wet annular denuder (AMANDA)




**time slot 1999-05-25 till 2000-12-18 r = 0,42**

(correlation only Sumer 99-05-25 till 99-09-13 and 00-05-15 till 00-09-14, n = 152, r = 0,12
correlation only winter 99-10-11 till 00-03-27 and 00-10-12 till 00-12-18, n = 159, r = 0,60)

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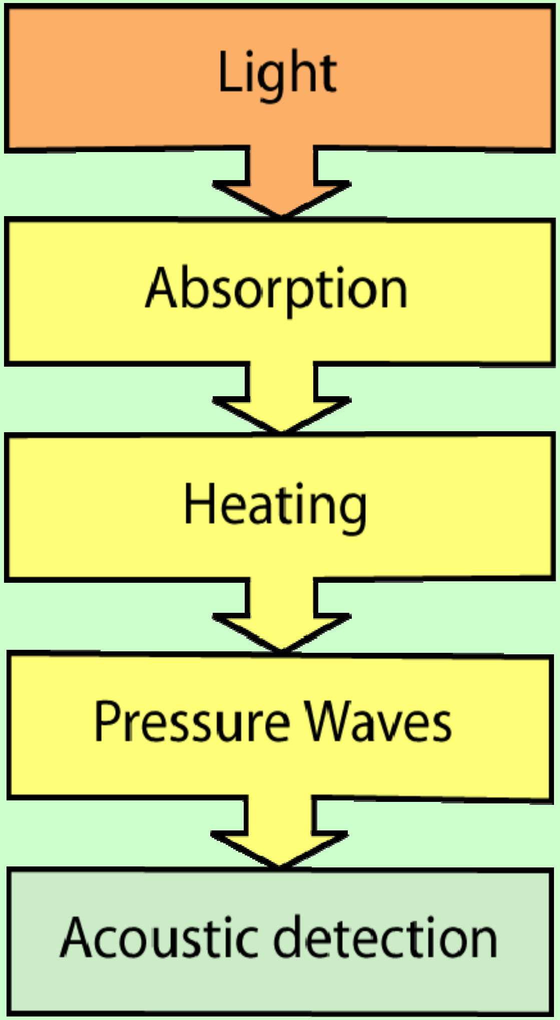
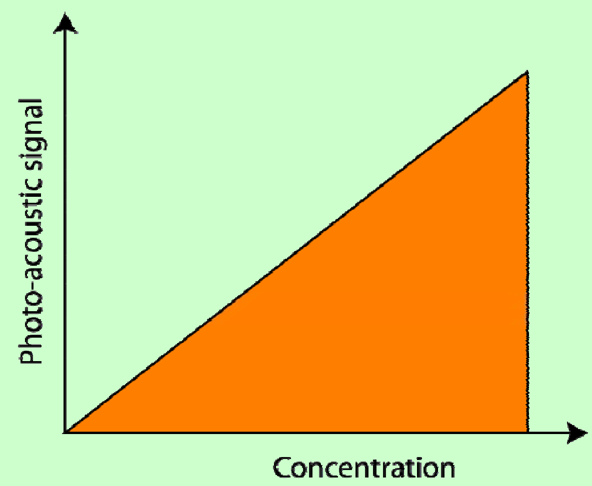
# Photo-acoustic Spectroscopy

## Principle of Function




## Advantages

**Zero baseline**:
zero concentration = zero signal
**Linearity**:
directly proportional to the concentration
**Large dynamic range**:
high accuracy (e.g. $NH_3$: 0.1 ppb to 6ppm)

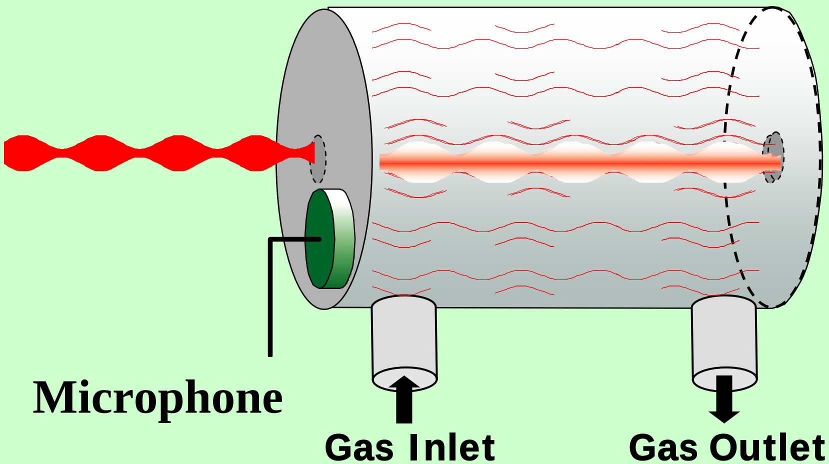



omnisens

# Resonant Photo-acoustic Spectroscopy

Acoustic waves are reflected on the cell walls

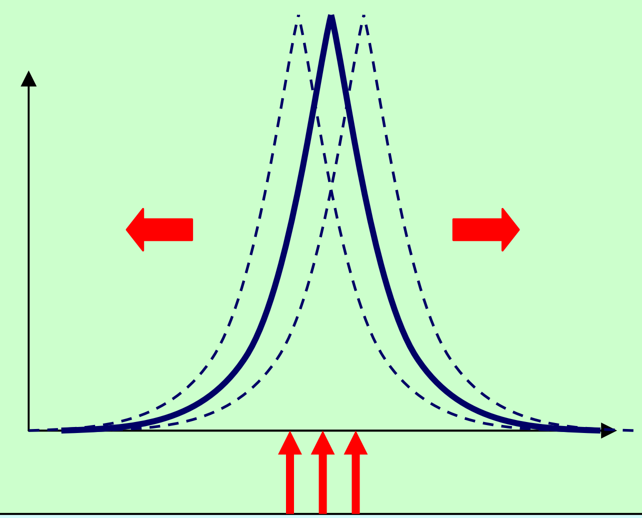
Waves constructive addition and signal increase




PAS = $\alpha$ $C_{cell}$ x $P_{laser}$ x $C_{NH3}$

**Resonance function of sound velocity; varies with temperature and gas density.**

- Continuous resonance tracking
- Feed back loop on Laser modulation frequency
- Digital Signal Processing



# Interference management for $NH_3$

**Single wavelength laser guarantees high measurement selectivity.**

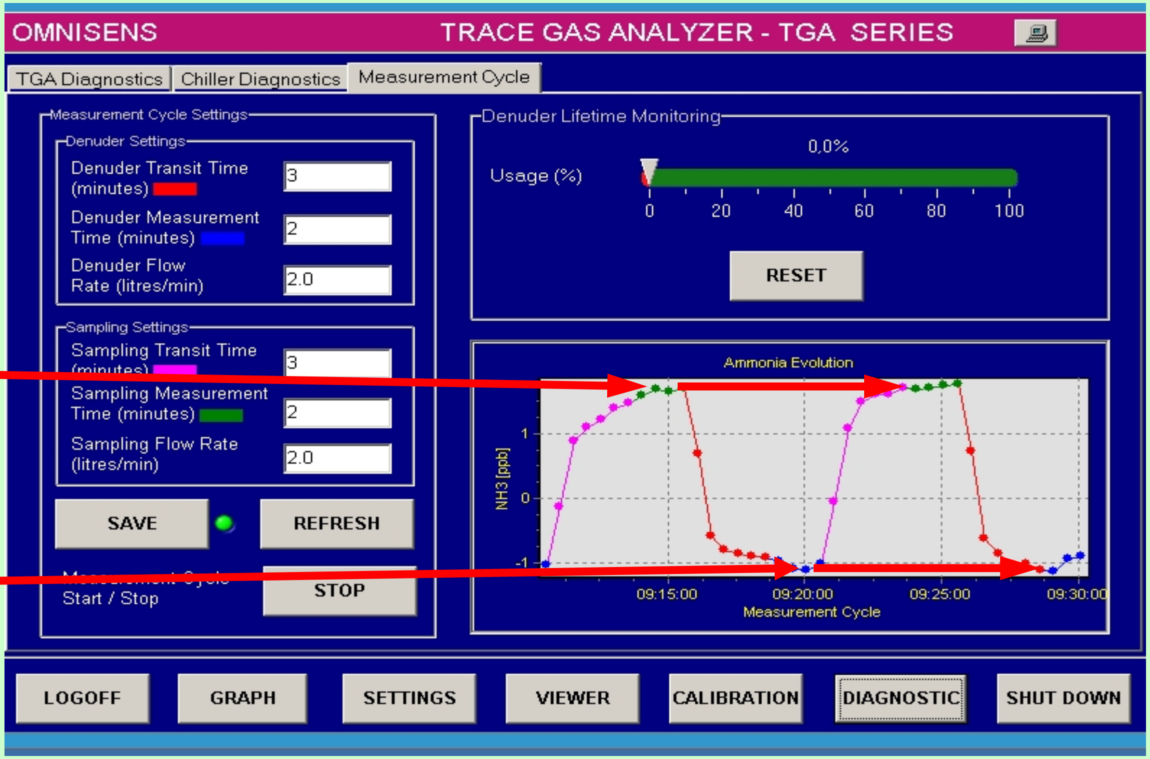
- Small contribution from atmospheric gases (HITRAN 2002)
- Isotopic $CO_2$ laser for $CO_2$ interference removal

**Water interference measured by hygrometer, corrected by calibration**

**Residual interference eliminated by differential measurement scheme**

Sampling Channel direct measurement

Reference Channel using annular denuder coated with citric acid



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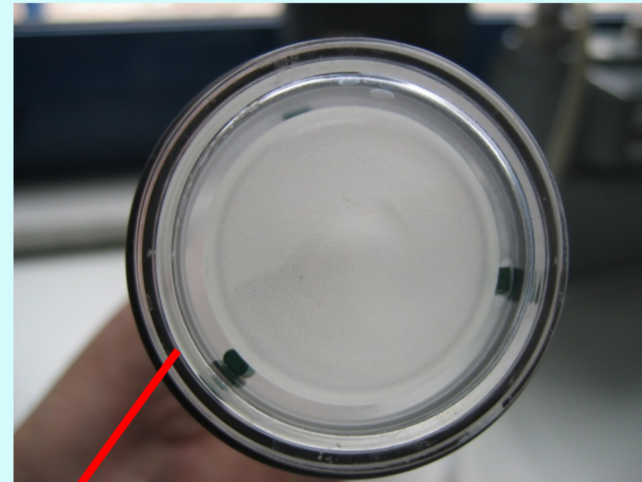
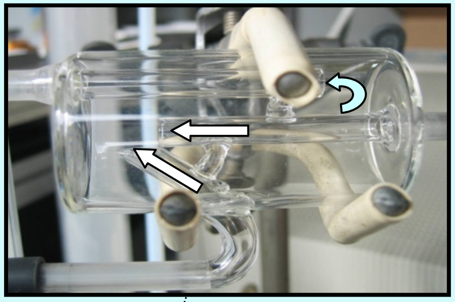
## The Omnisens TGA 310 with water cooling system and denuder during the laboratory tests

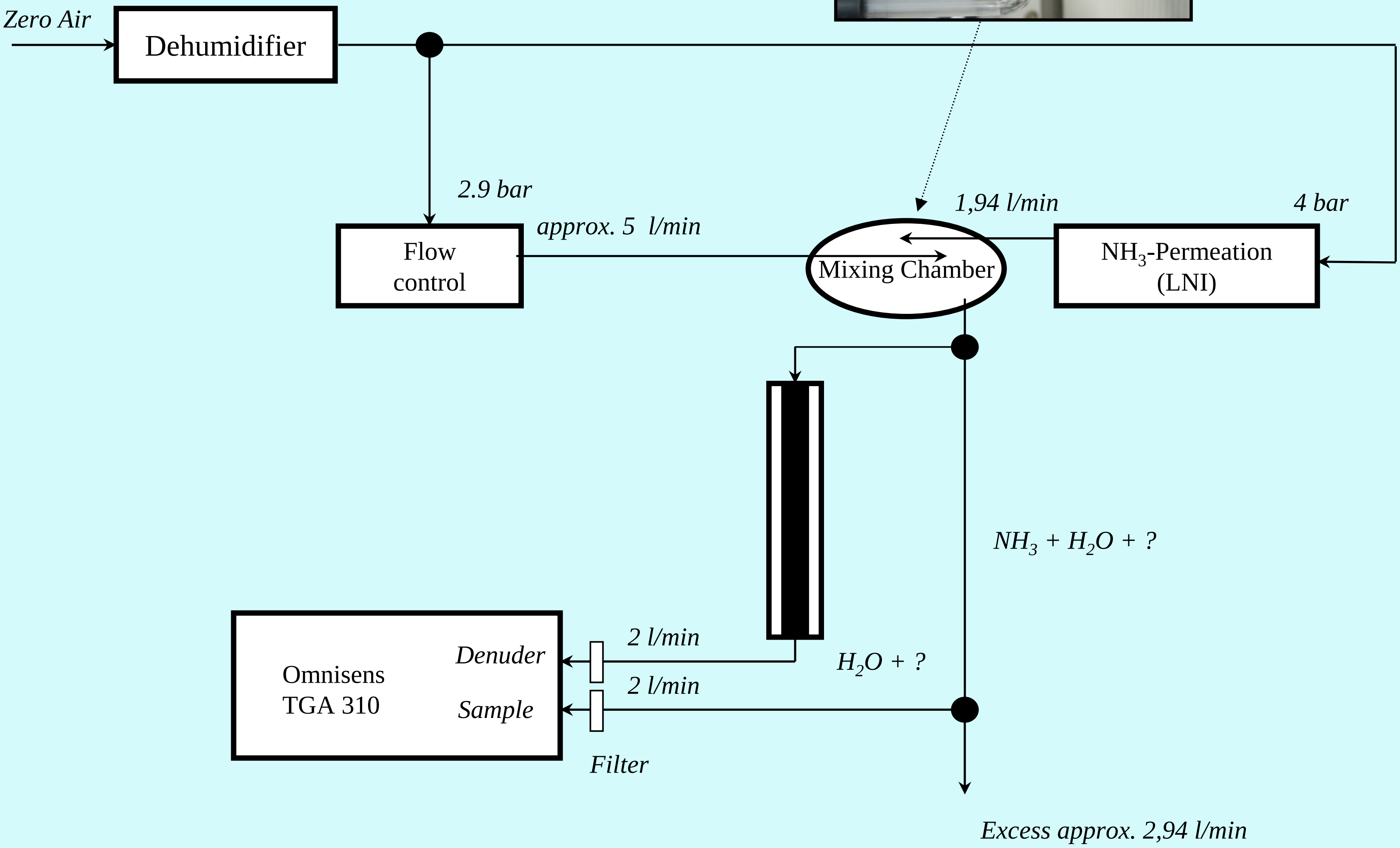



Filter fastener backward of the device

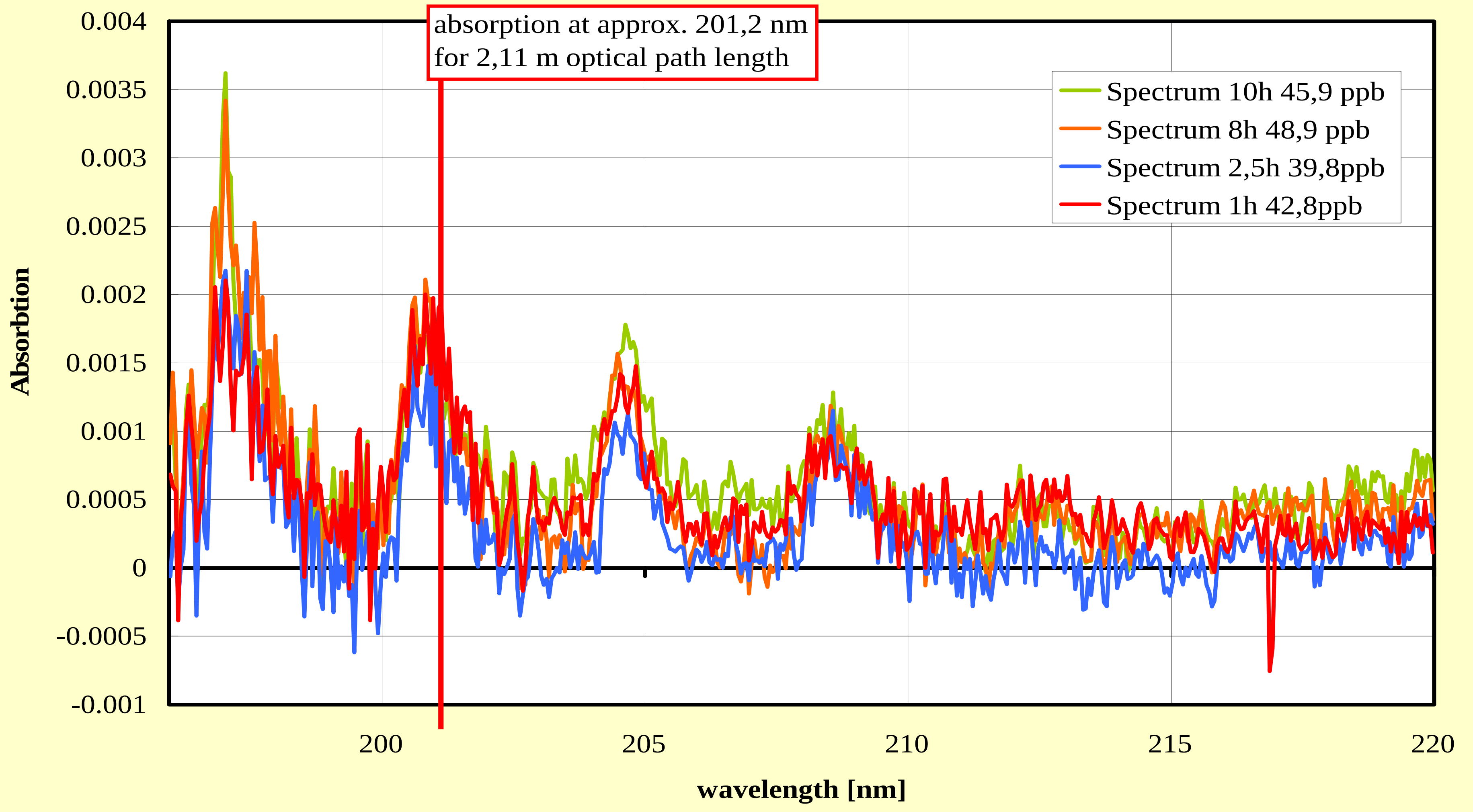
water cooling system

# Laboratory Test with different $NH_3$ concentrations (Permeation)



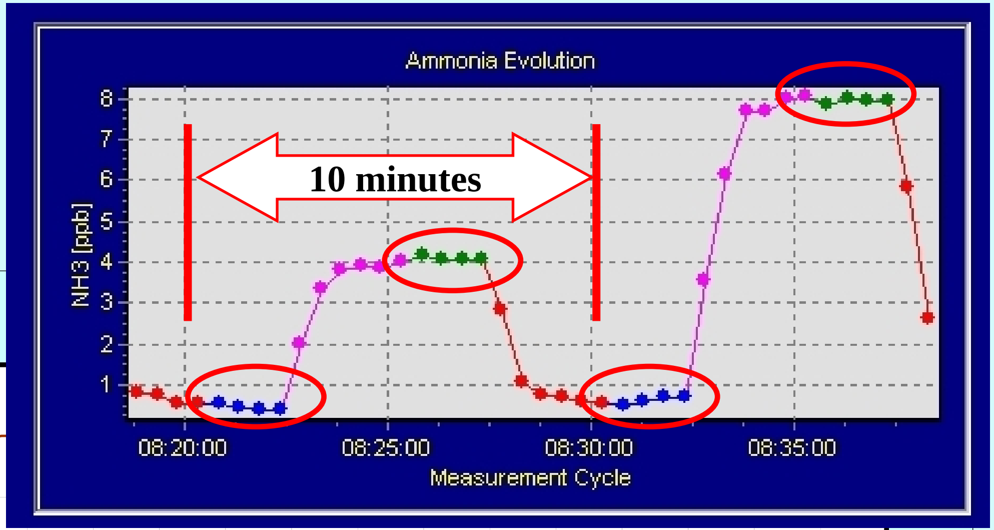


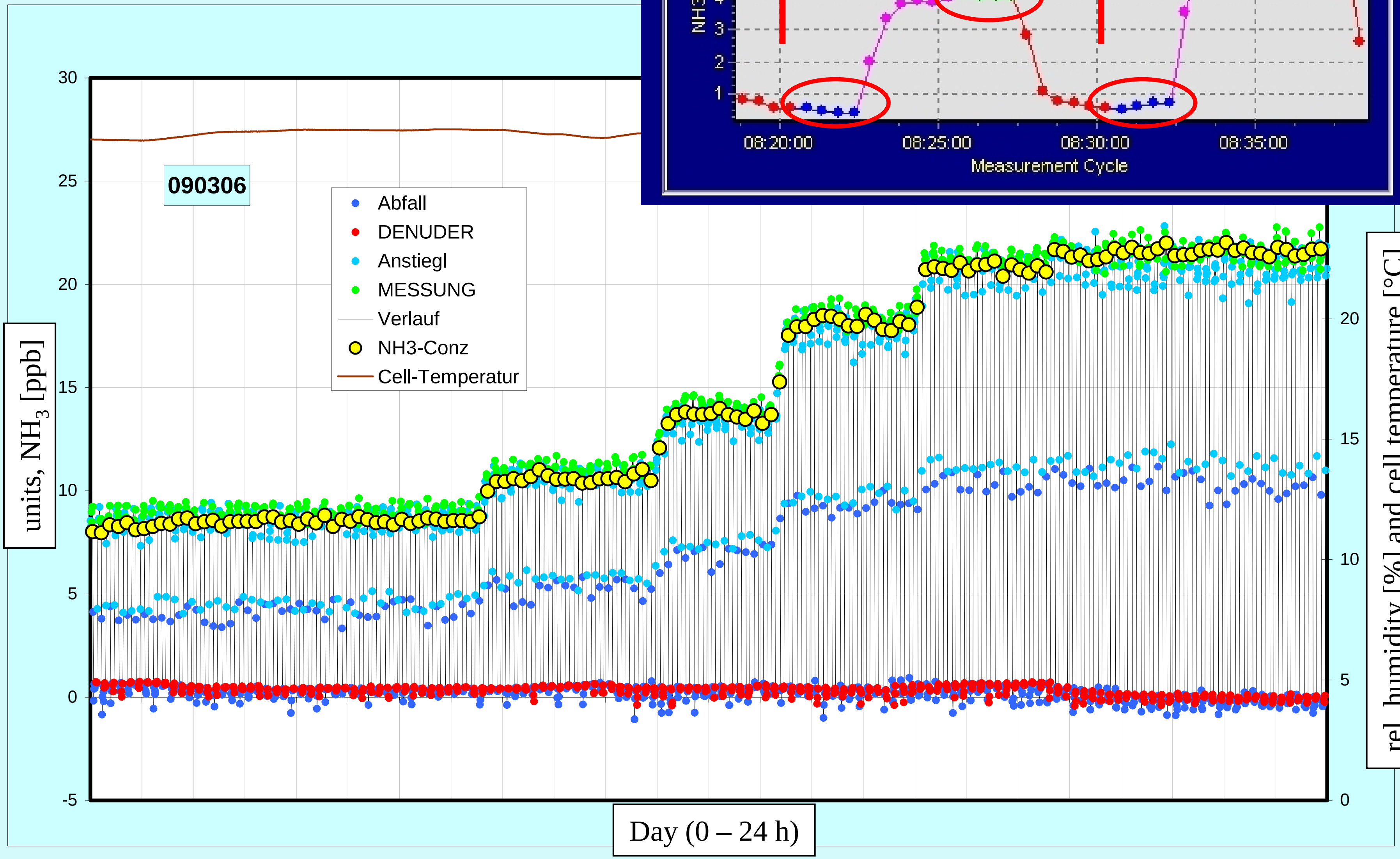
# Test of the $NH_3$ permeation standard by UV-Spectroscopy



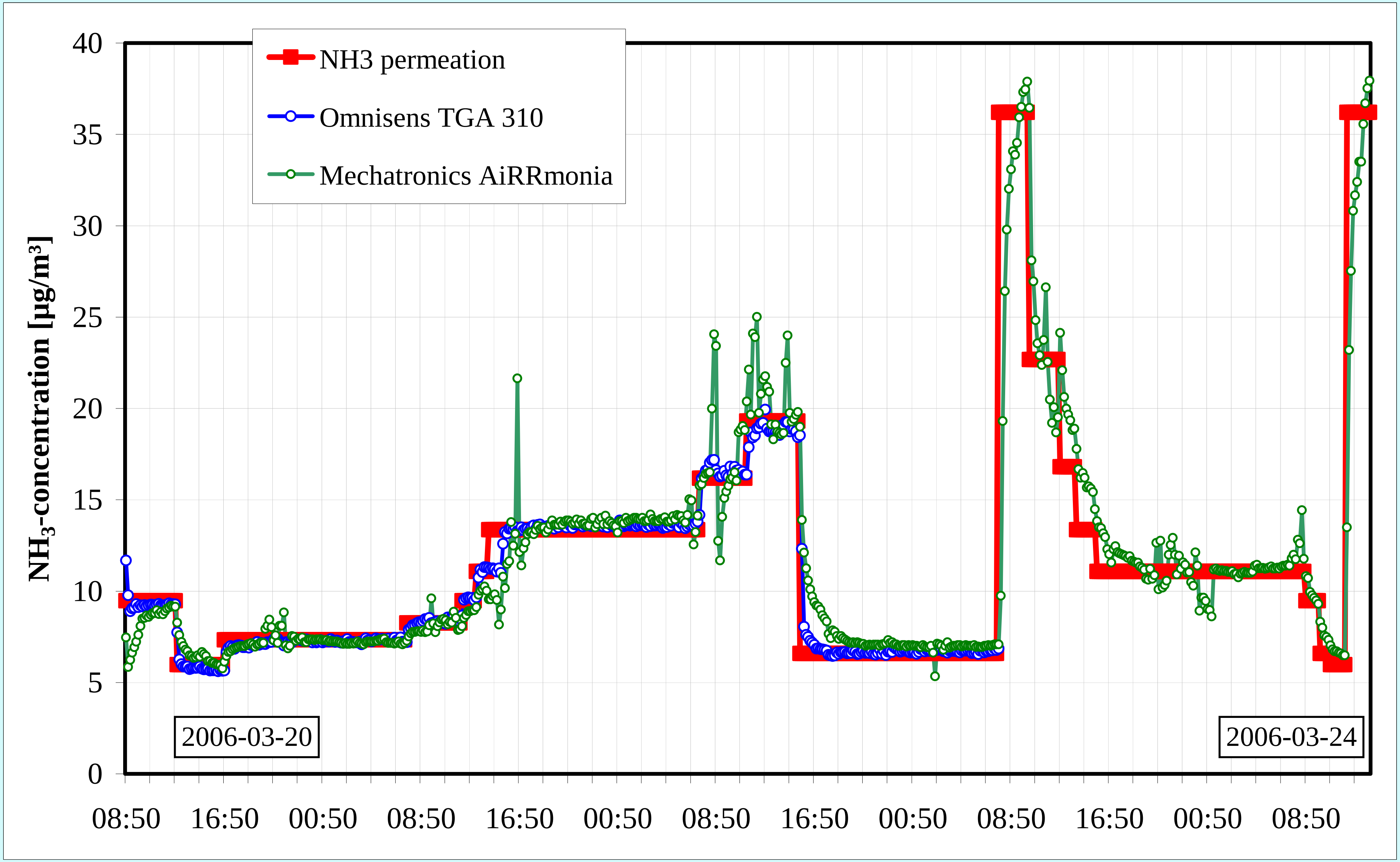

**$NH_3$-Permeation tube waver type DYNACAL® Typ 40F3,**
**permeation rate 82 ng/min at 40 °C (± 25 %)**
201.2 nm cross section = $6.3 \times 10^{-18}$ $cm^2$ , Suto, M.,Lee, L.C. (1983) Photodissociation of $NH_3$ at 106-200 nm, J.Chem.Phys., 78, 4515-4522.

# Example for the Measuring of different constant $NH_3$-concentrations in the laboratory with Omnisens TGA 310

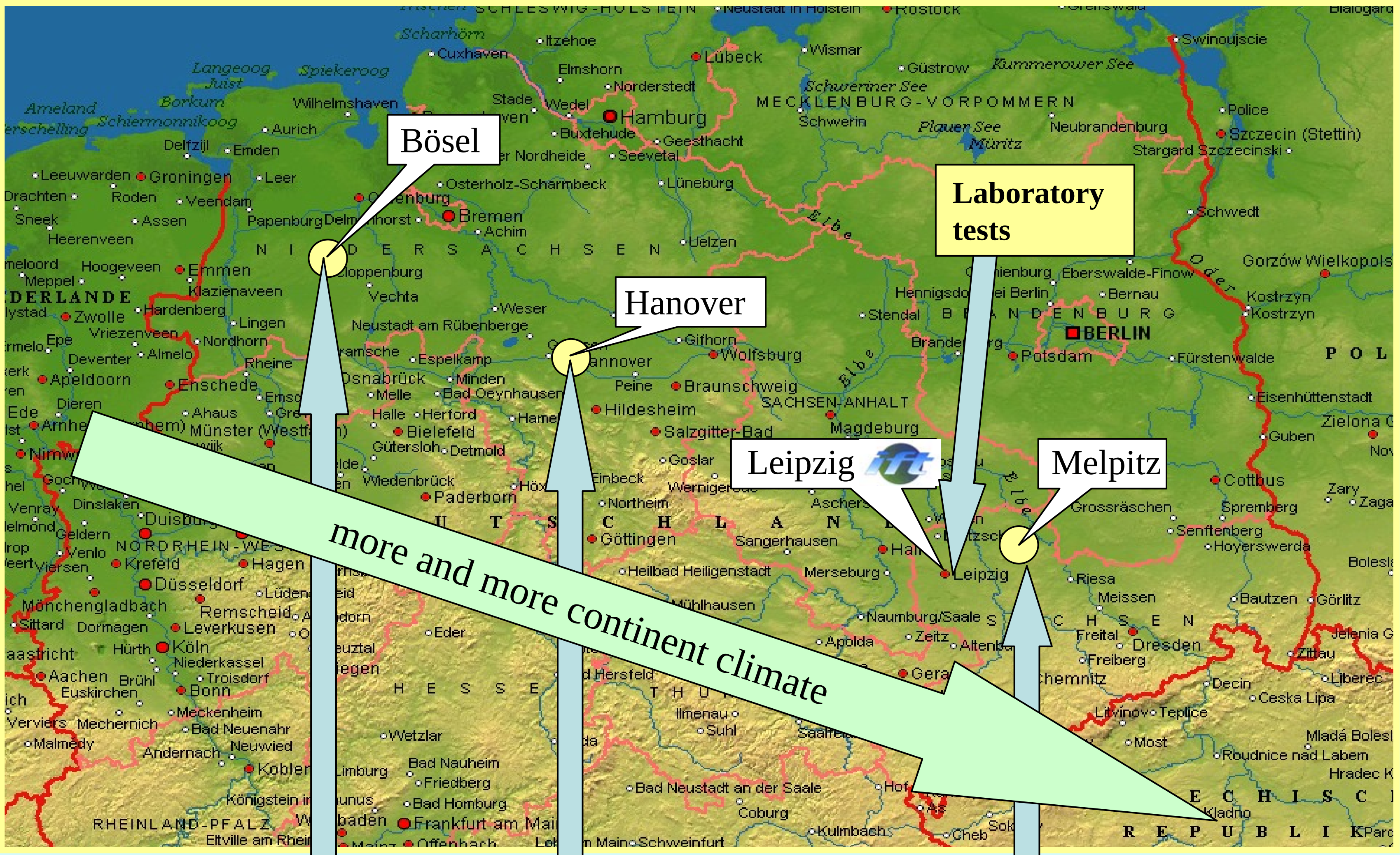


# Comparison of Omnisens TGA 310 and Mechatronics AiRRmonia® for different $NH_3$-concentrations



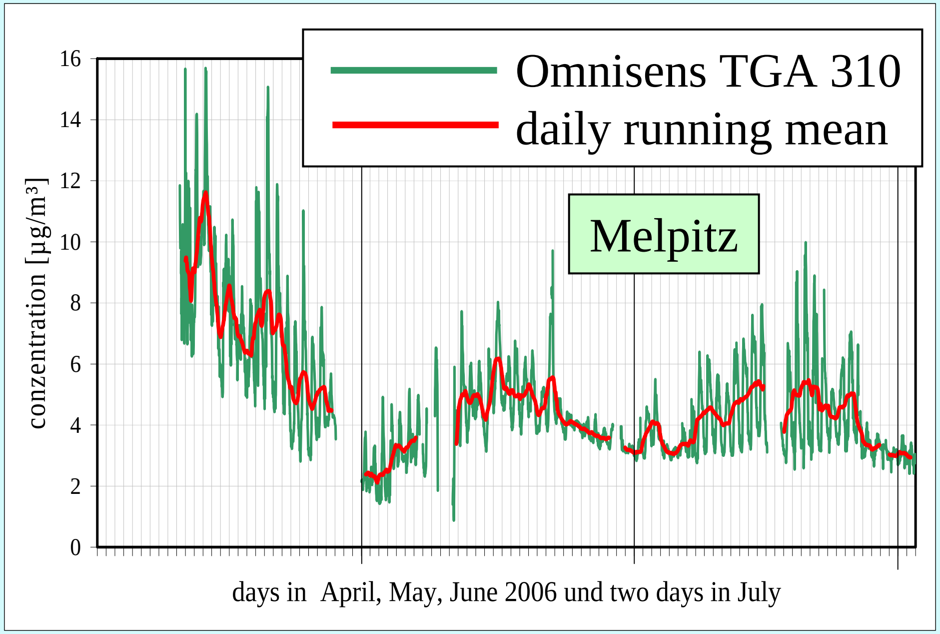
# Geographic position of three places for $NH_3$-measurements (project AMMONISAX)

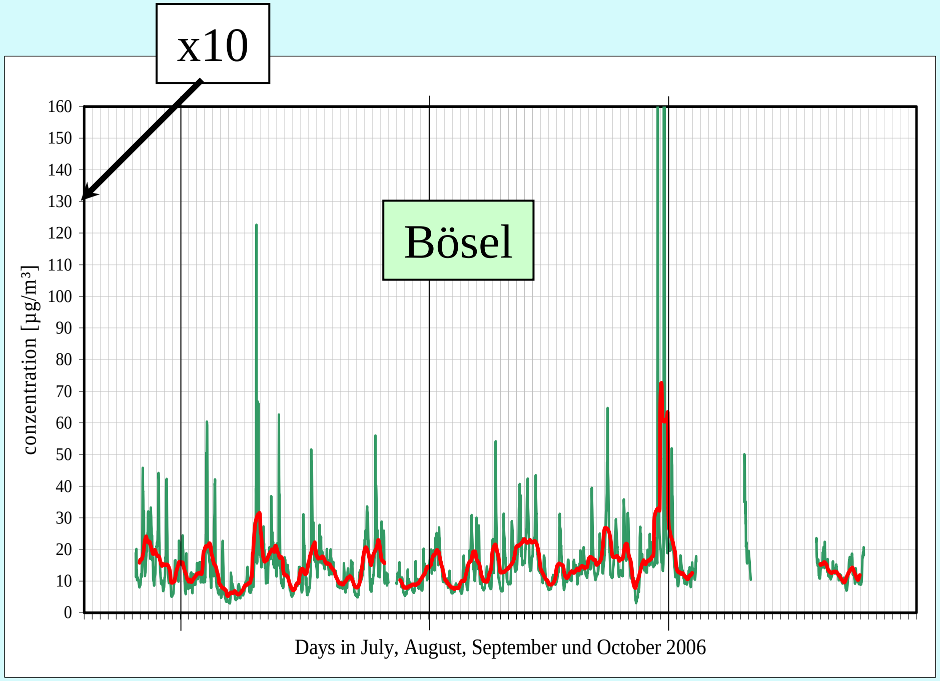


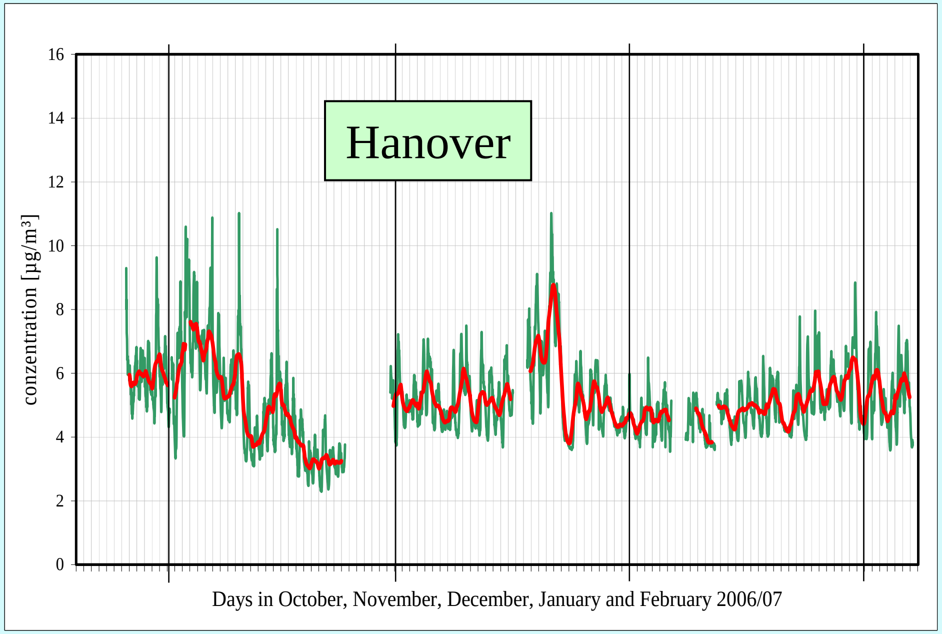

**Intensive agriculture**
**(period 06-07 till 06-10-25)**
**15.4 µg/m³ $NH_3$**

**Göttinger Straße 5.1 µg/m³ $NH_3$**
**Downtown, traffic**
**(period 06-10-26 till 07-02-07)**

**Rural site**
**(period 06-04-10 till 06-07-02)**
**4.8 µg/m³ $NH_3$**

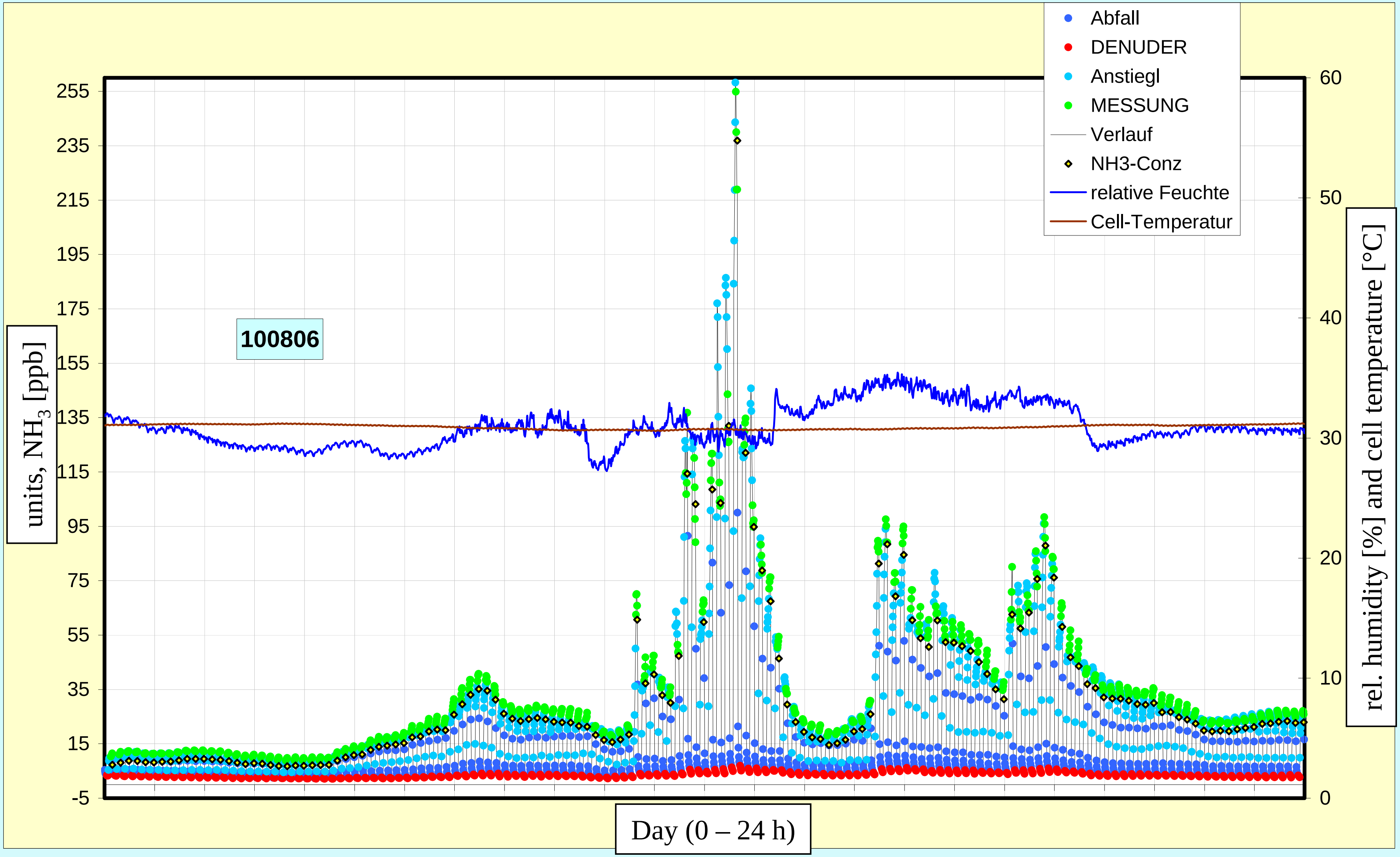


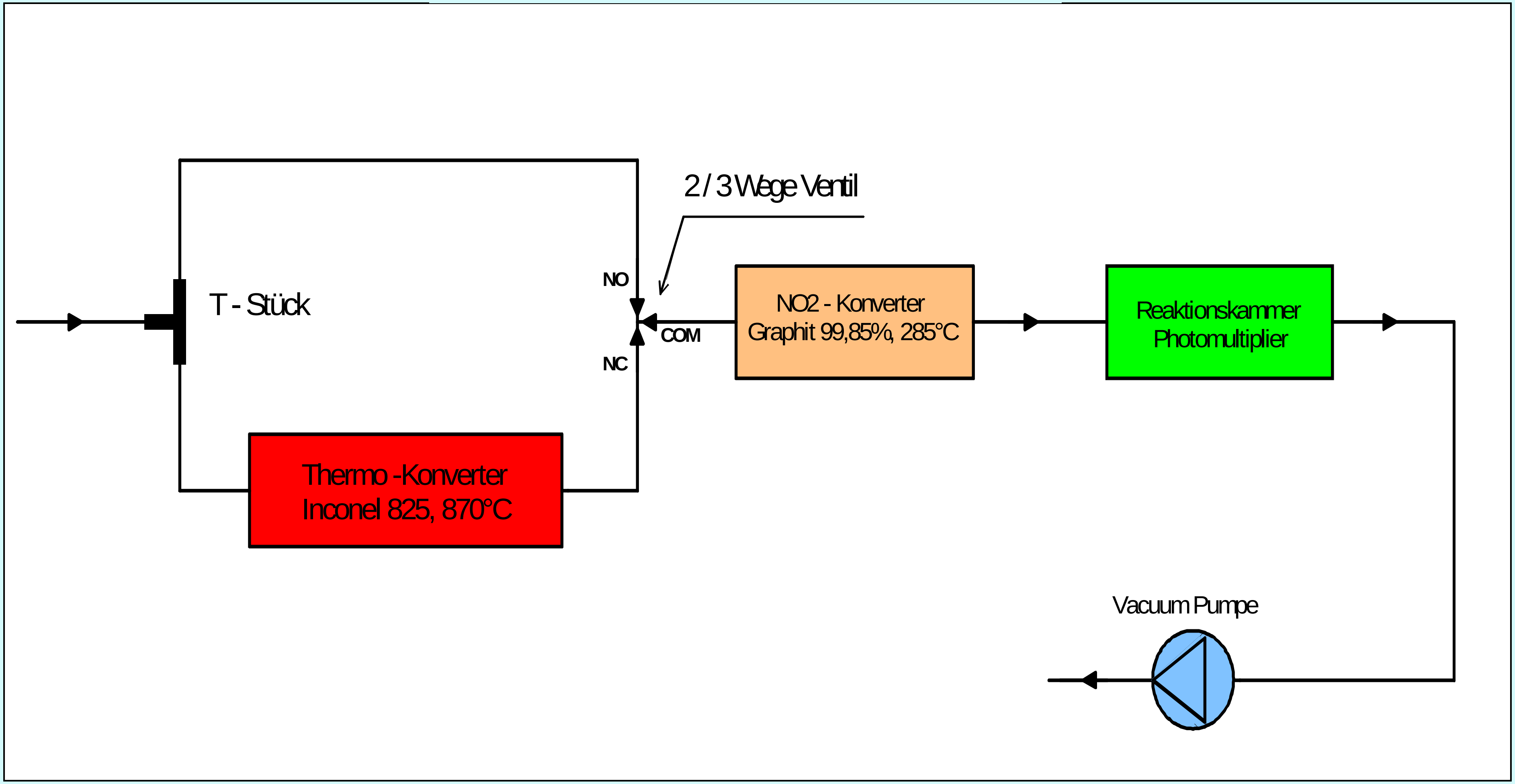

**Results of one year $NH_3$ field measurements with Omnisens TGA 310 at three different places**

**(project AMMONISAX)**

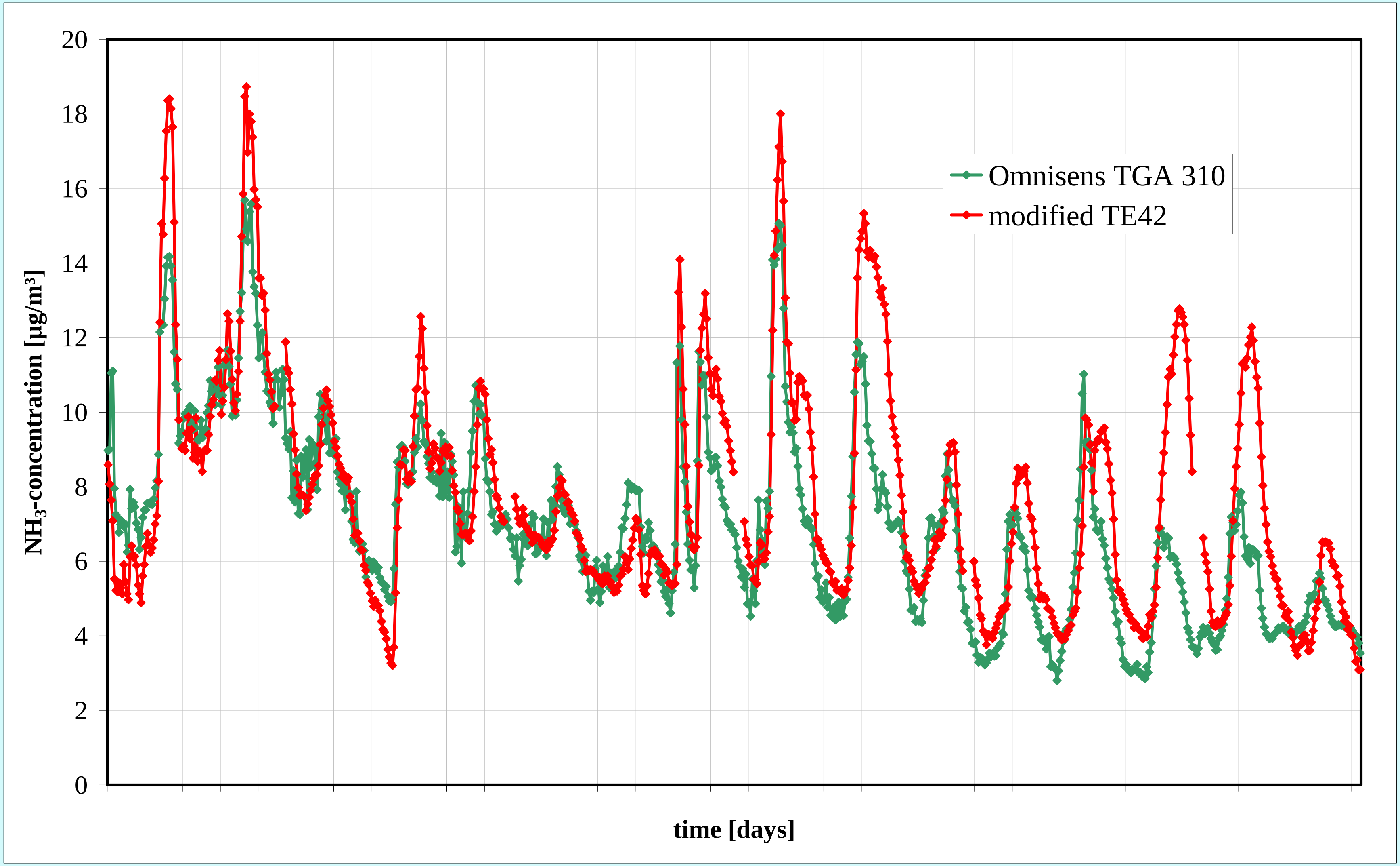



One day of measurement with Omnisens TGA 310 at Bösel site during extremly high $NH_3$-concentrations (2006-08-10)

# $NH_3$ measurement using an oxidation converter and chemiluminescence detection of NO

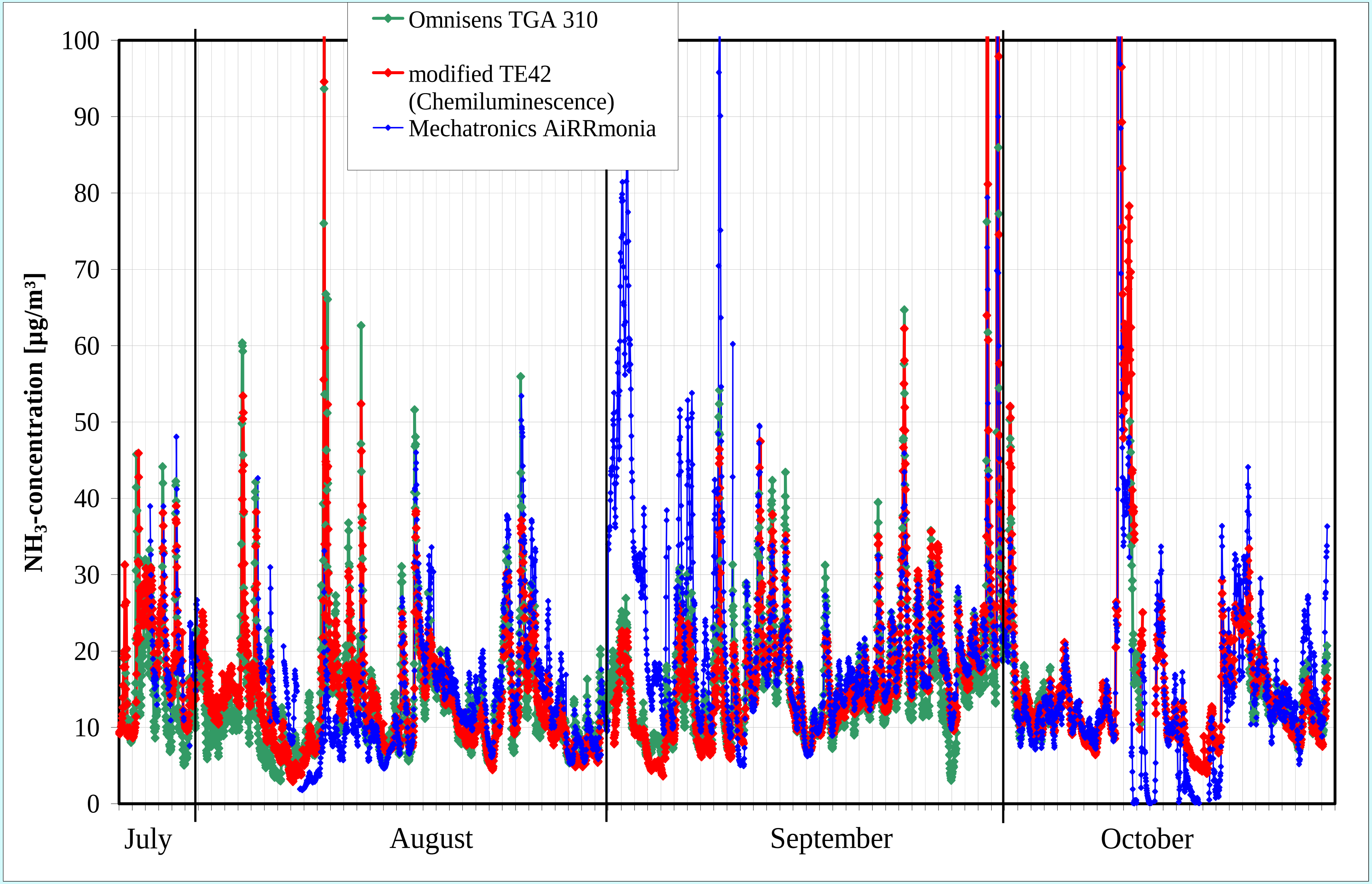


# Comparison of Omnisens TGA 310 and a modified TE-42 (Chemiluninescence) at Melpitz site

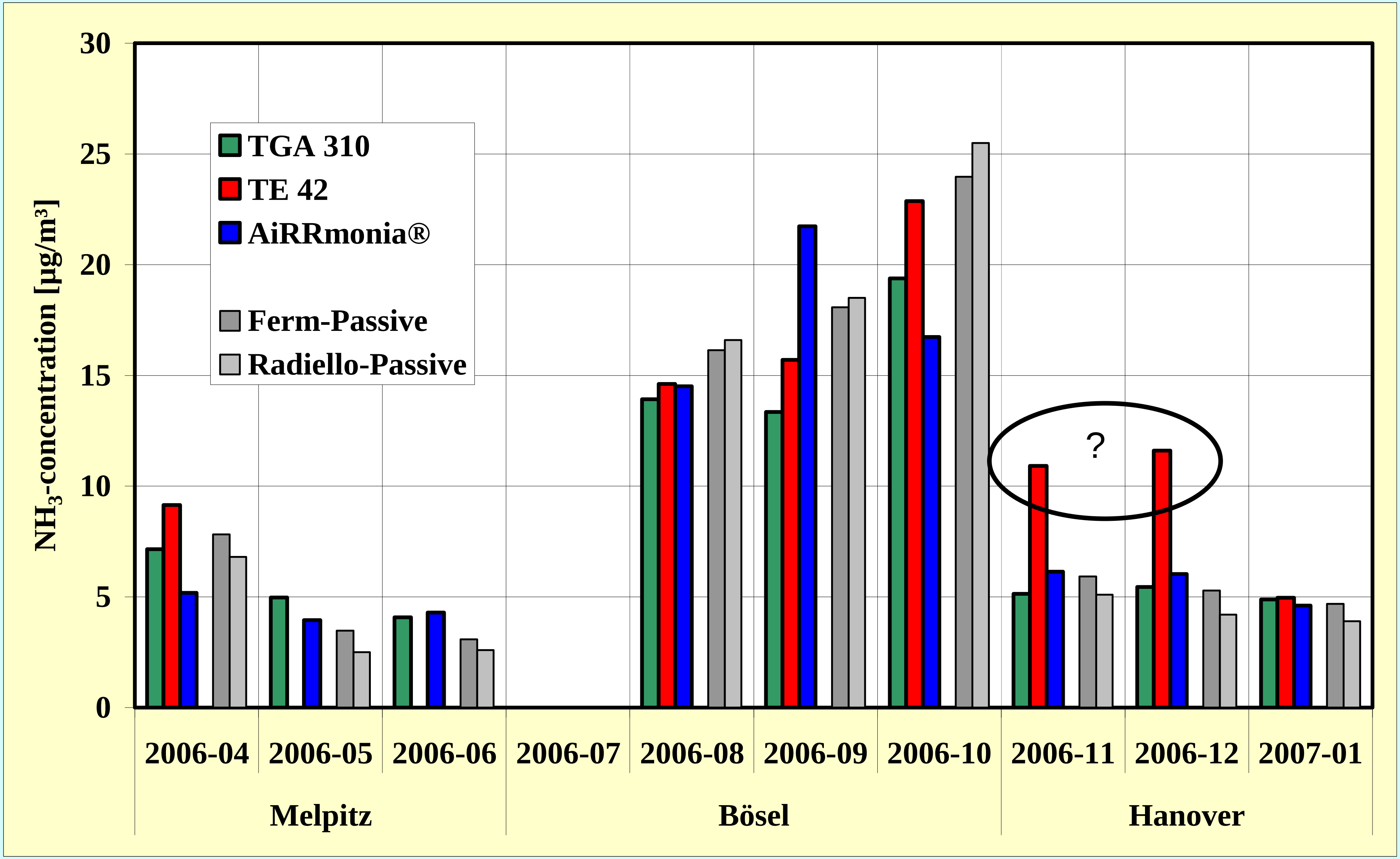



2006-04-11 till 2006-04-28

# Comparison of Omnisens TGA 310, modified TE-42 (Chemiluninescence) and Mechatronics AiRRmonia ® during continuous measurements at Bösel site



# Comparison of Omnisens TGA 310, modified TE-42 (Chemiluninescence) and Mechatronics AiRRmonia ® with passive samplers at Melpitz, Bösel and Hanover site (monthly means)



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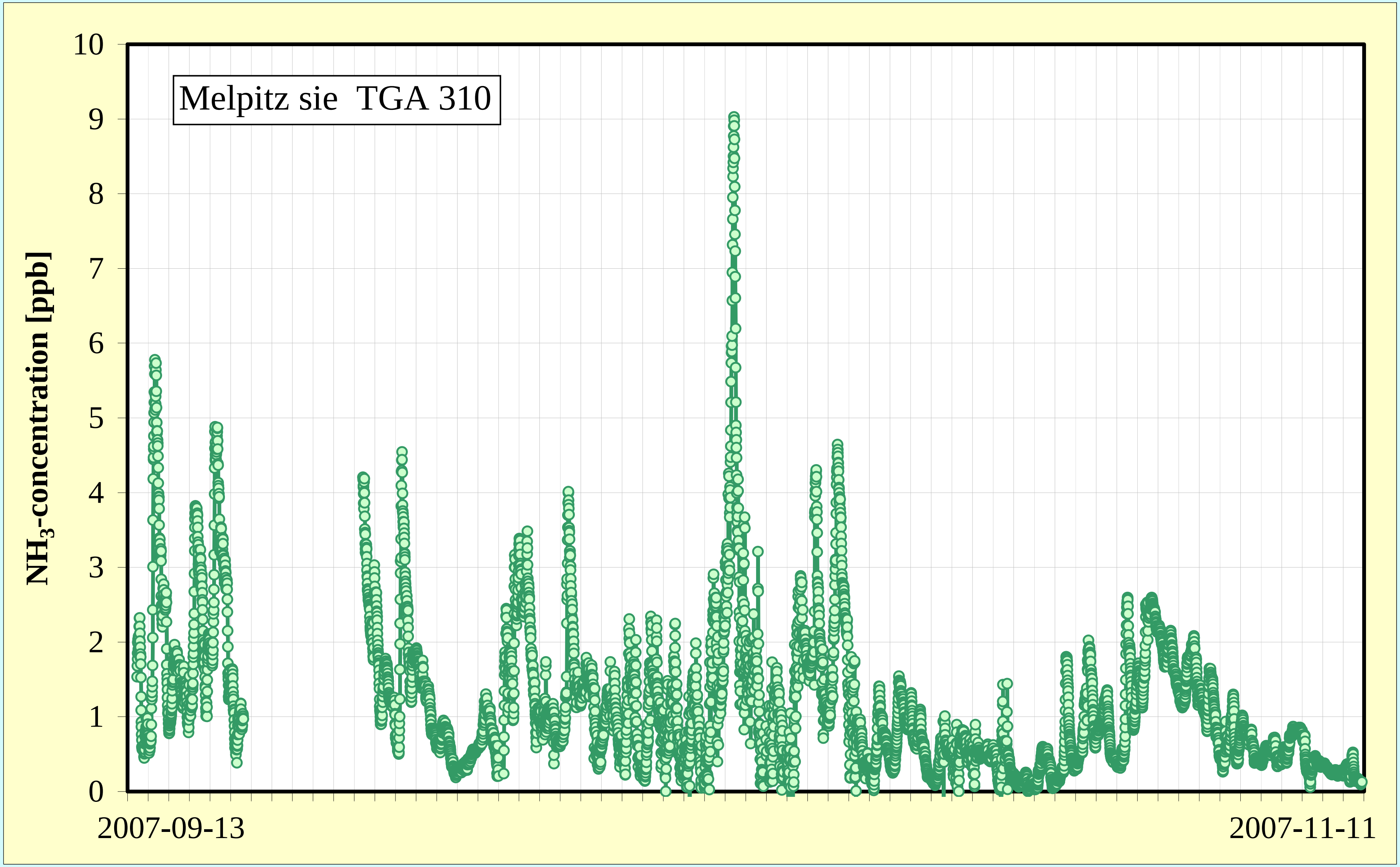
# Measurement of $NH_3$-concentration at the research site of IfT in Melpitz (now with a TGA 310 by our own)



# Summary

**Wet chemical detection of $NH_3$ is possible with high accuracy, often the devices needs in the past a lot of assistance and can’t use during frozen days.**

**The ammonia detection in the troposphere is possible with resonant Photo-acoustic Spectroscopy if ammonia was separated from water. The commercial device TGA 310 from Omnisens can measure $NH_3$ permanent with a constant calibration in a brought concentration range.**

**The indirect $NH_3$ detection using chemiluminescence can be influenced from the oxidation of nitrogen and other nitrogen compounds, especially in high polluted city areas (positive artifact).**

**$NH_3$-detection with passive samplers can alternatively used for large-area characterizations with long-time-means.**

In the AMMONISAX project a lot of tests and comparisons were done with the OMNISENS TGA-310 and also results of the model calculations with the chemical-transport-model LM-MUSCAT for PM are integrated.

# You can find the report for the AMMONISAX project

http://www.umwelt.niedersachsen.de/master/C23004085_N21119655_L20_DO_1598.html


Position 13.
report "Einfluss erhöhter NH3-Konzentrationen auf die Partikelmassebildung PM10" (17,4 MB)

Abschlussbericht zum Forschungs- und Entwicklungsvertrag AMMONISAX
Laufzeit: Oktober 2005 bis April 2007

**Einfluss erhöhter $NH_3$-Konzentrationen auf die Partikelmassebildung $PM_{10}$ – Vergleich von $NH_3$-Messverfahren an drei Standorten mit unterschiedlichen Spurengaskonzentrationen in Niedersachsen und Sachsen (AMMONISAX)**

von

*G. Spindler, E. Brüggemann, T. Gnauk, A. Grüner, E. Renner, R. Wolke und H. Herrmann*

Auftraggeber: Land Niedersachsen, vertreten durch das Staatliche Gewerbeaufsichtsamt Hildesheim, Hindenburgplatz 20, 31134 Hildesheim (GAA)

Leibniz-Institut für Troposphärenforschung e.V. (IfT), Permoserstr. 15, 04318 Leipzig

Leipzig, den 18. Juli 2007

Results of new laboratory intercomparisons and hints for problems using the chemiluminescence technique in combination with an $NH_3$-converter are in:
***J.J. Schwab et al. 2007, Environ.Sci.Technol. online first since 2007-11-03***


?

For future investigations at Melpitz site ?

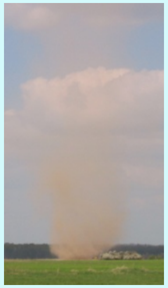
We acknowledge the support of the European Union, the Umweltbundesamt for support in different contracts.
The German state of Lower Saxony we acknowledge for supporting the project AMMONISAX

Assistance and support from M. Köster, H. Rienecker and E. Helmholz from the Gewerbeaufsichtsamt Hildesheim is gratefully acknowledged.

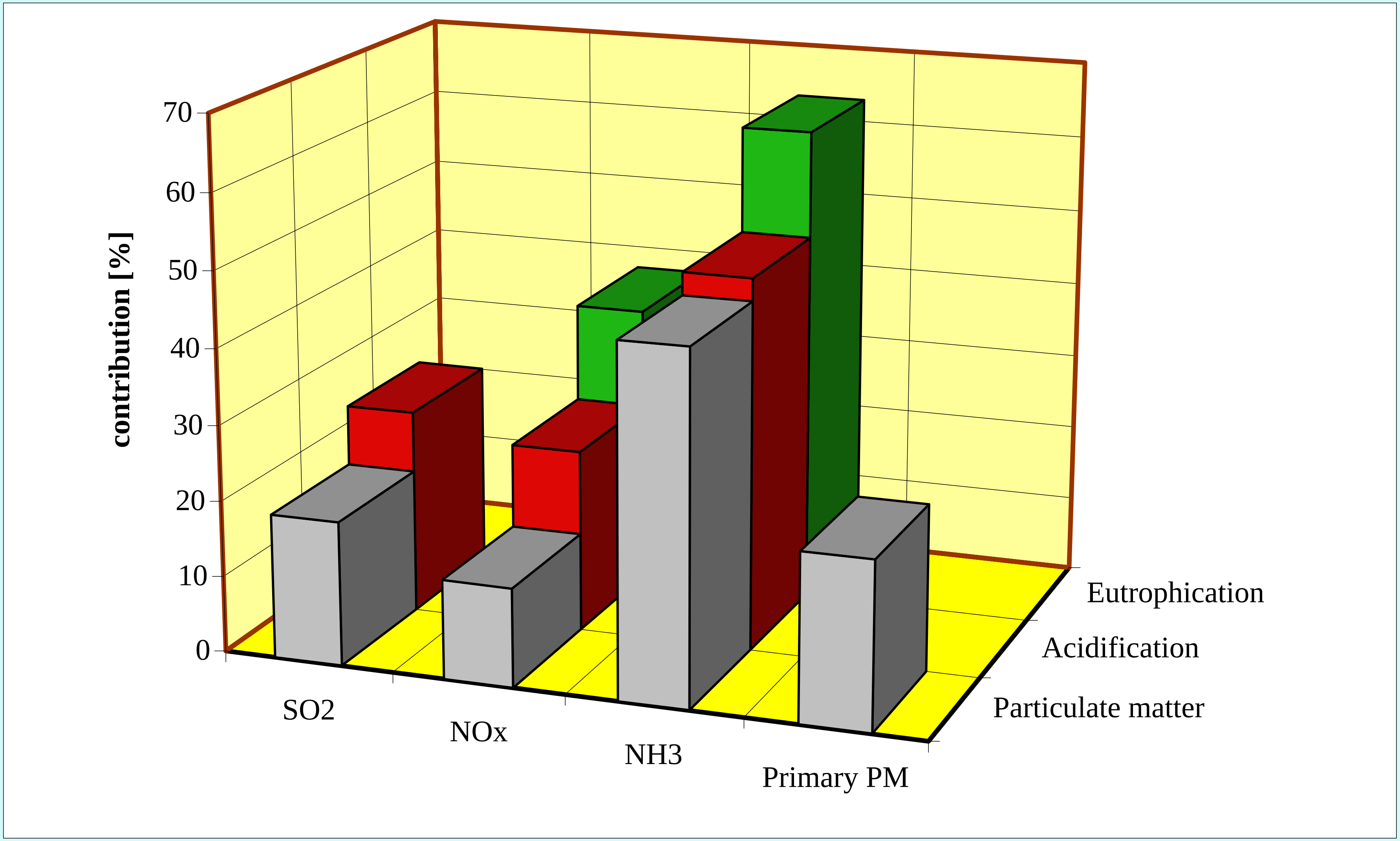
We are grateful to T. Berndt from IfT for the spectroscopic $NH_3$-Detection and quantification.

Thank's to the Pollution-emitters for $NH_3$ and PM in the atmosphere.



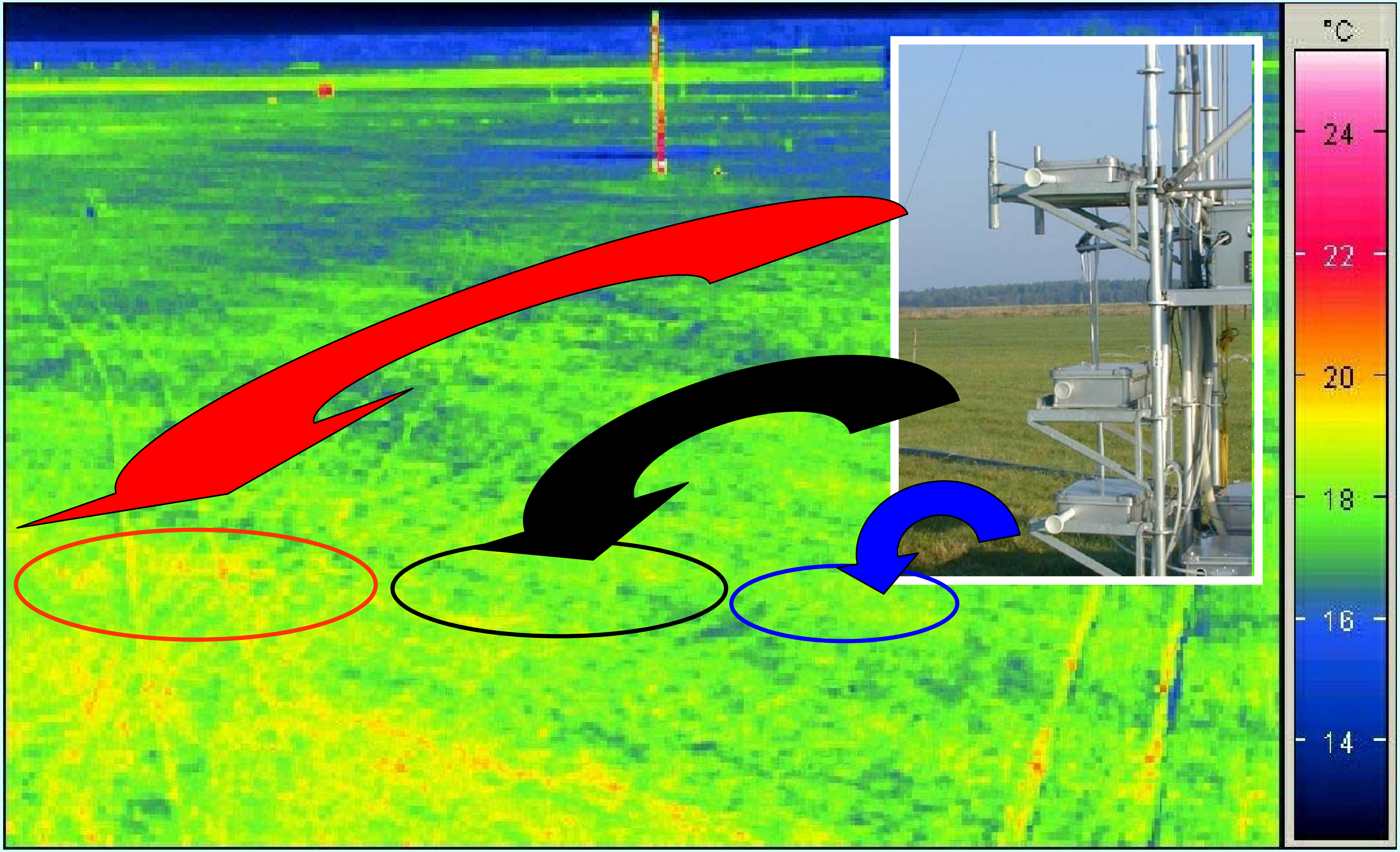



# Supplement




**The estimated contribution of $NH_3$, $SO_2$, $NO_x$ and PM to environmental problems in 2020. (CAFÉ programme)**

# „Footprints“ - micrometeorological gradient method




surface temperature

# Micrometeorological flux-gradient calculation

$$F_{NH_3(neutral)} = k^2 \cdot (z-d)^2 \cdot \frac{du}{d(z-d)} \cdot \frac{dc}{d(z-d)}$$

Correction of Stability

$$F_{NH_3(stable)} = F_{NH_3(neutral)} (1-5R_i)^2$$

$$F_{NH_3(unstable)} = F_{NH_3(neutral)} (1-16R_i)^{3/4}$$

Gradient-Richardson-Number

$$R_i = \frac{g}{T} * \frac{(T_2-T_1)(z_2-z_1)}{(u_2-u_1)^2}$$

Calculation of deposition velocity

$$V_{d(z)} = \frac{F_{NH_3}}{c_{(z)}}$$