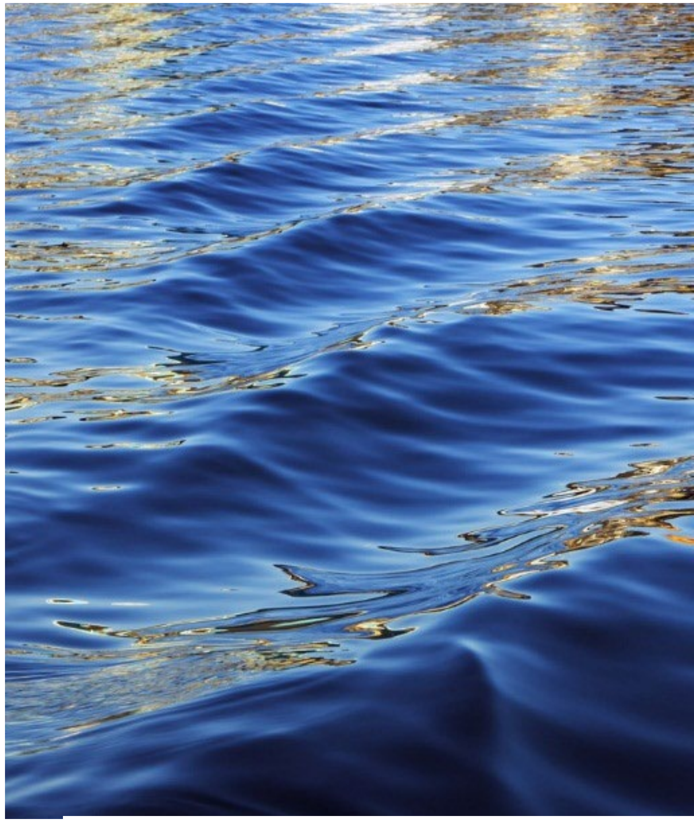
From Flow to Flux — chasing the wind

Contact: jun.zhang@tno.nl

Jun Zhang (TNO)

Yin Wang (Healthy Photon)



USCCC9 training
26th July, 2023, Nanjing

TNO innovation for life

National Institute for Public
and the Environment
Ministry of Health, Welfare and Sp

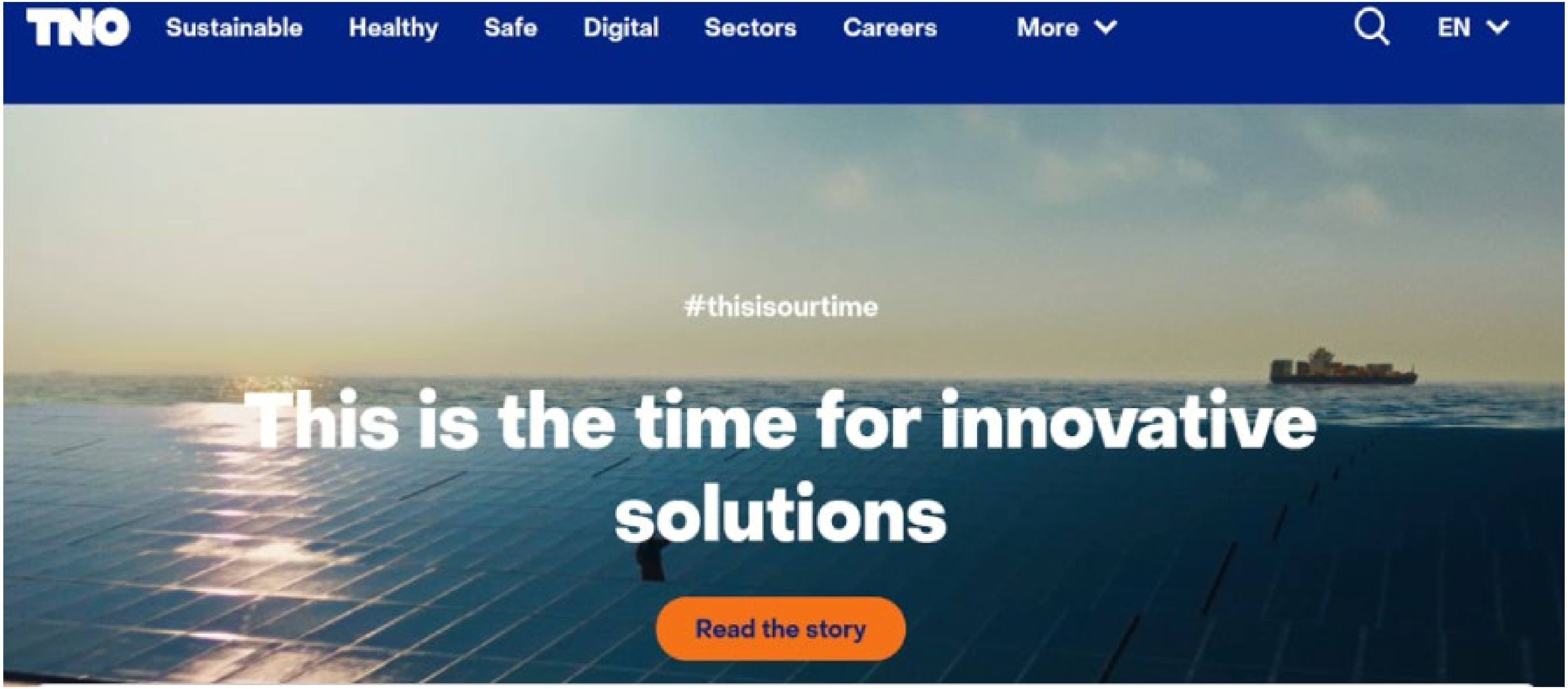
WAGENINGEN
UNIVERSITY & RESEARCH

HEALTHY PHOTON
海尔欣光电·昕甬智测

Paired-watershed monitoring in the Philippines (2013.06 – 2014. 06)

8 November 2013: super-TYPHOON HAIYAN strikes…

March 2019: joint TNO, Applied Science Research Institute of NL



The dual role of nature-based carbon sinks

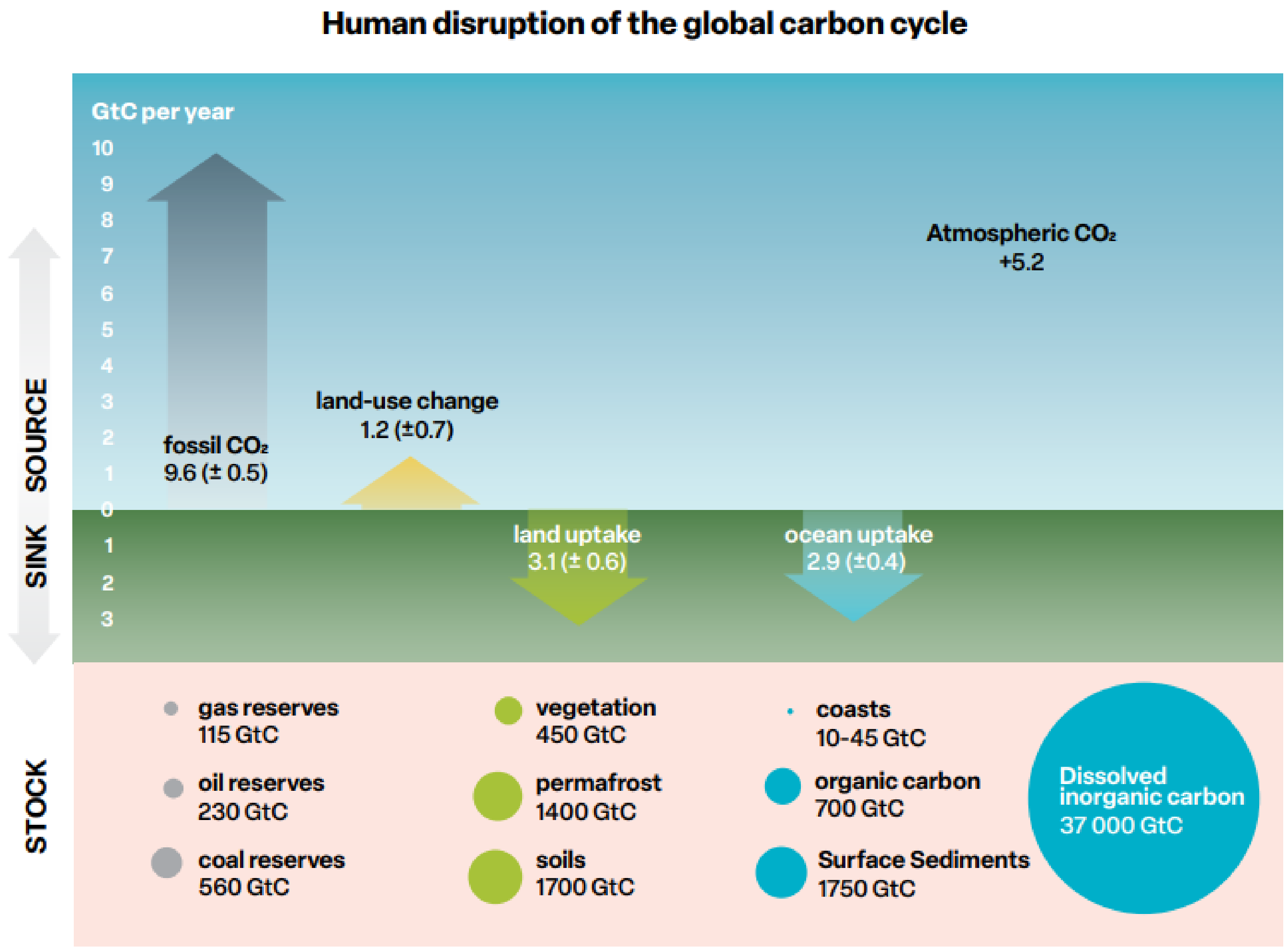
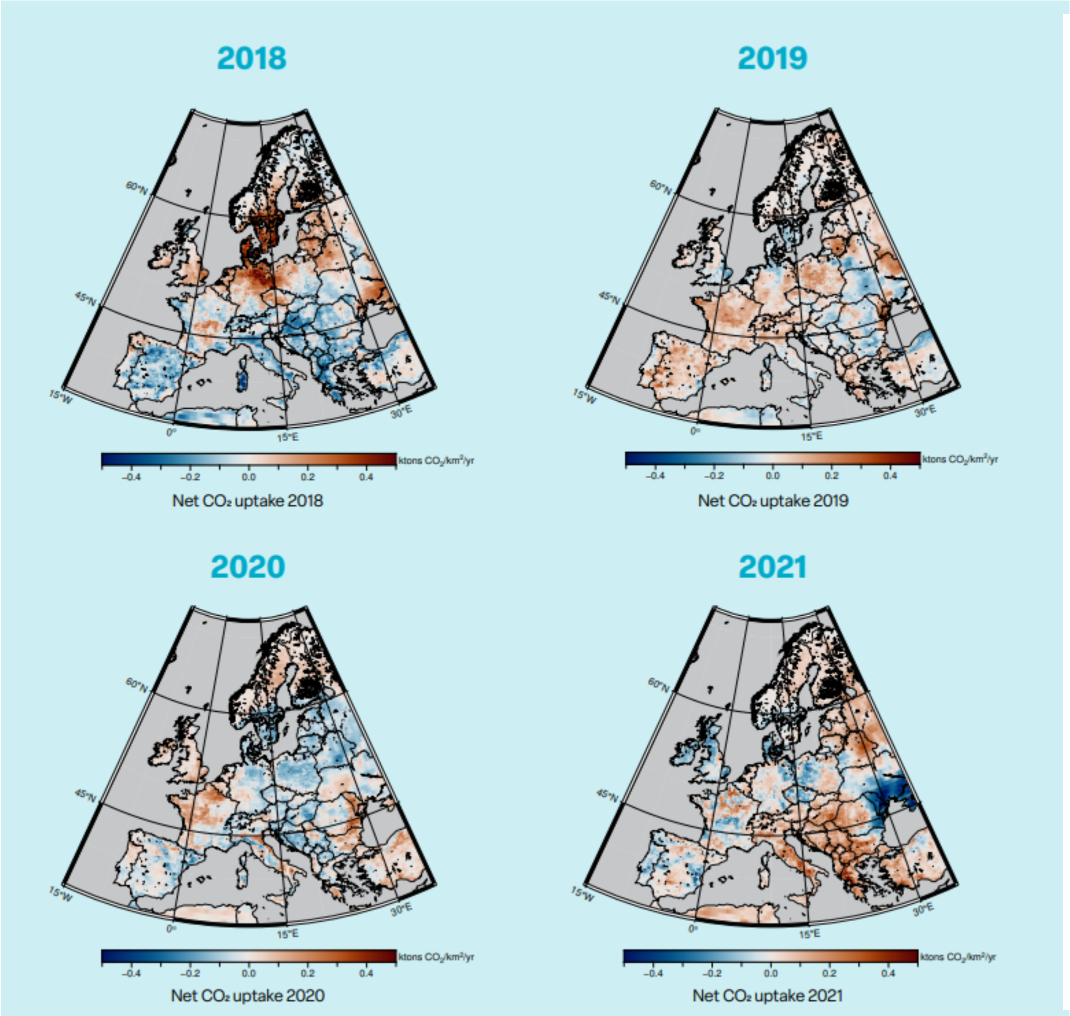
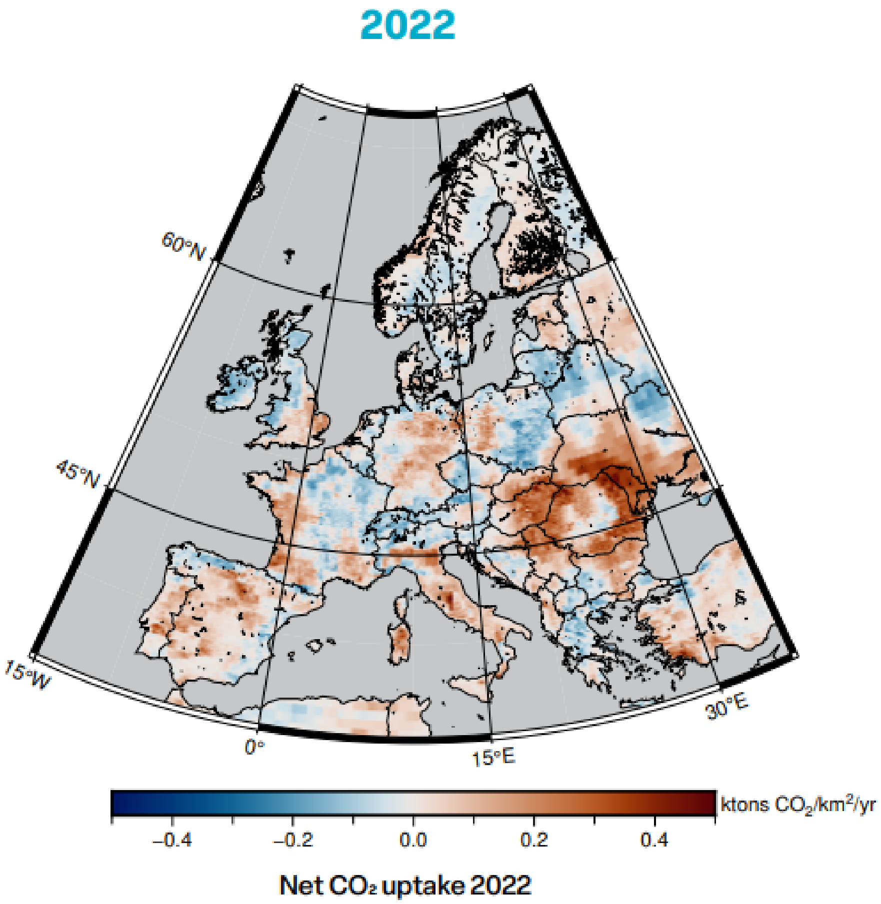


Figure 1. Average human influence in the global carbon cyclein GtC per year, gigatonnes of carbon, for the decade 2012-2021. adapted from Global Carbon Project 2022[1].

Source: FLUXES the European Greenhouse Gas Bulletin, Volume #2-2023

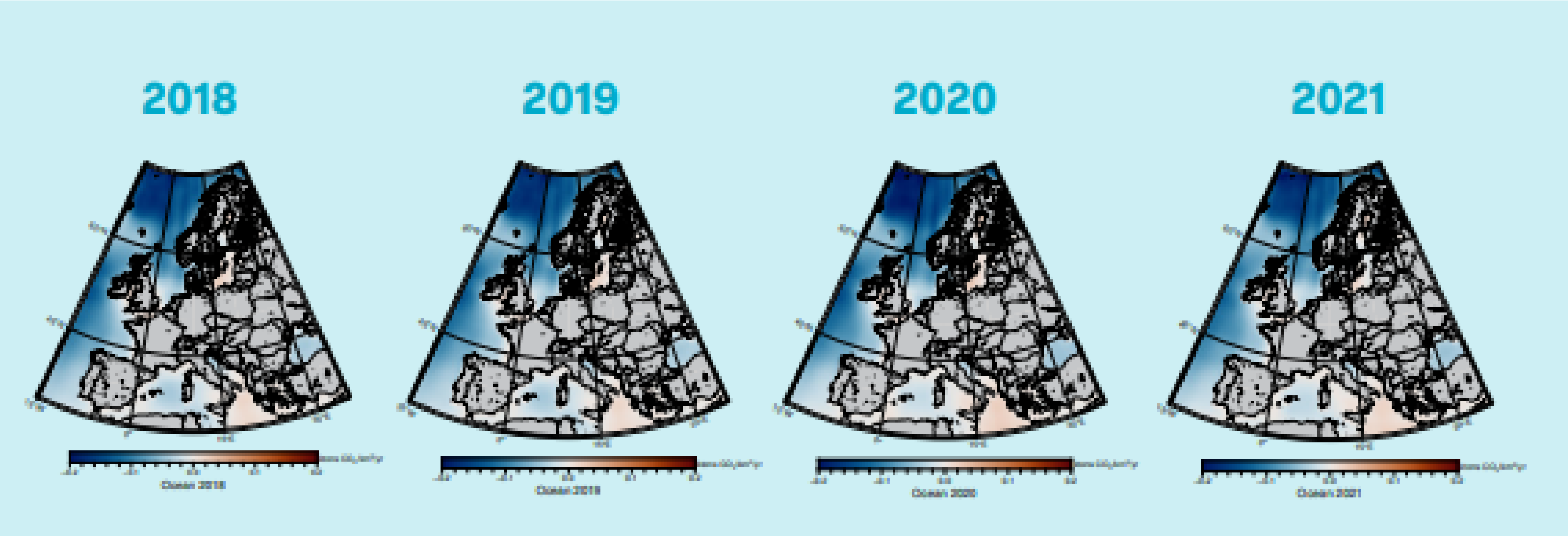
Net carbon dioxide uptake in the land ecosystems of Europe

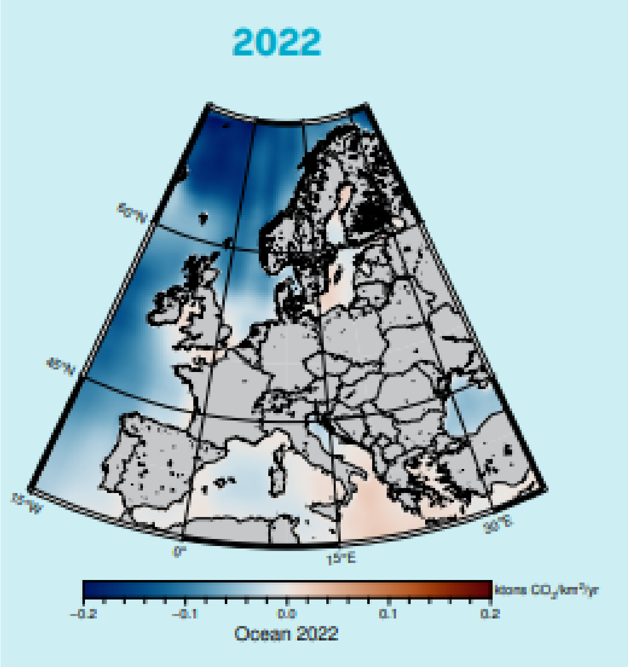




The maps use highly-integrated products based on observations, inventory data and models (hence are not the outcome of one kind of data alone). The colour scales in the maps are different to account for the different magnitude of the fluxes.

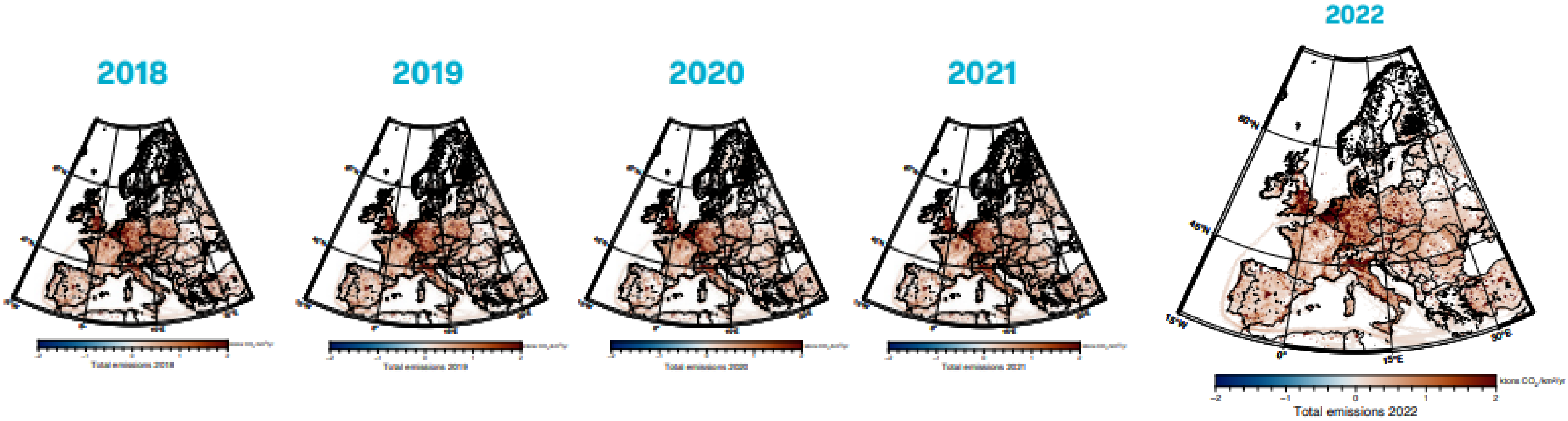
Net carbon dioxide uptake in the ocean of Europe





Strong CO2 uptake in the open ocean. Fluxes in the coastal areas, the Baltic Sea, the English Channel, and the Mediterranean Sea show a more complex pattern of sources and sinks. The inter-annual variation is small.

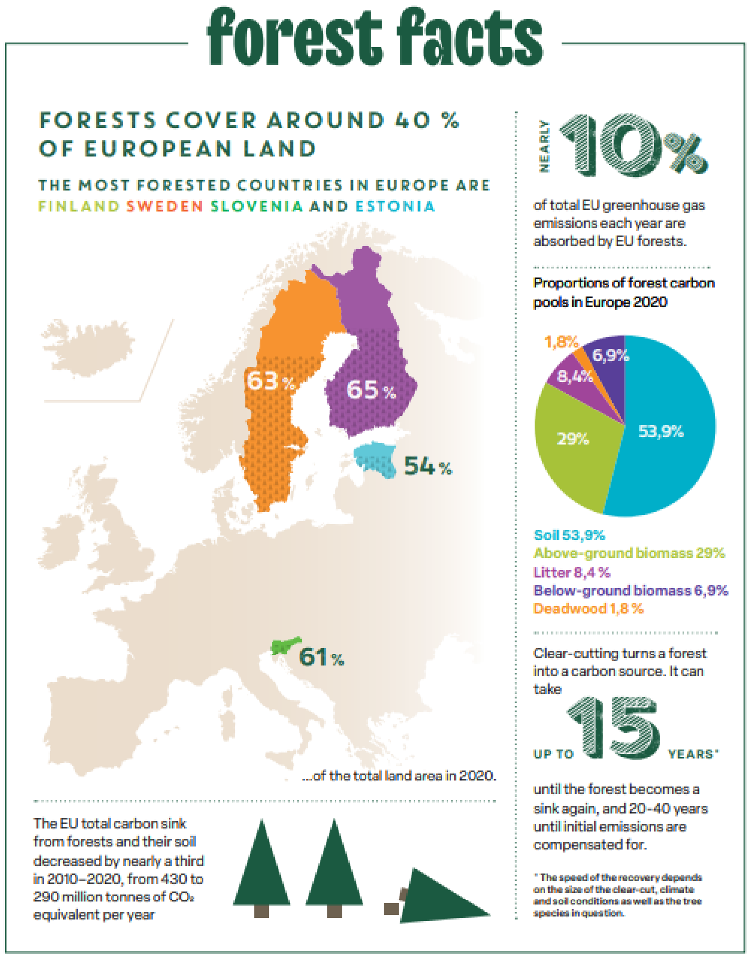
Carbon dioxide emissions from human activity



CO_2 emissions from human activity include contributions from electricity production, industry, households, ground transport, aviation, shipping and cement production. Highest emissions are seen in industrial areas and densely populated cities.

Forest carbon sink ?

The EU's total forest carbon sink decreased by nearly a third between 2010 and 2020. This decrease is attributed to increased harvests and natural ageing of the forests.



Modelling of the forest carbon sink under three different Finnish forest strategies

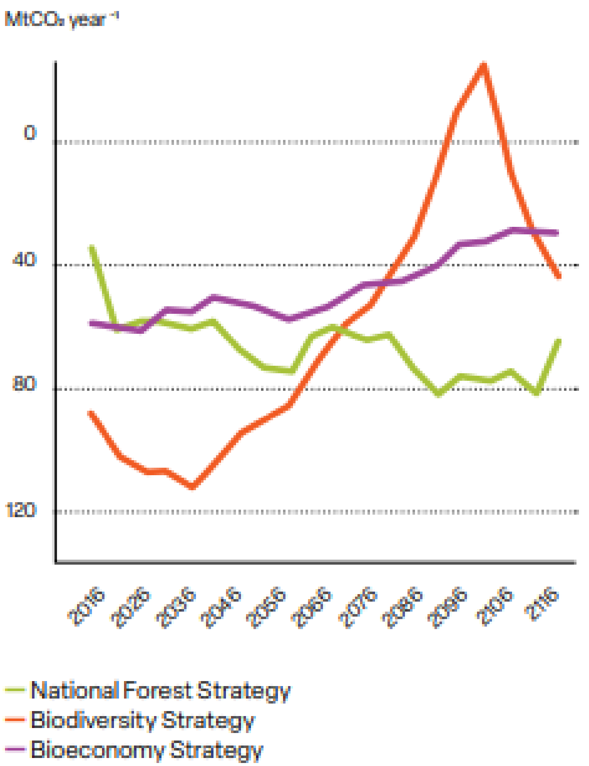


Figure 4. Graph showing the results of a modelling study done on the outcomes of three different Finnish forest strategies. The model did not include natural disturbances (i.e., insects, storms, or droughts).*

Ocean and agriculture carbon cycle

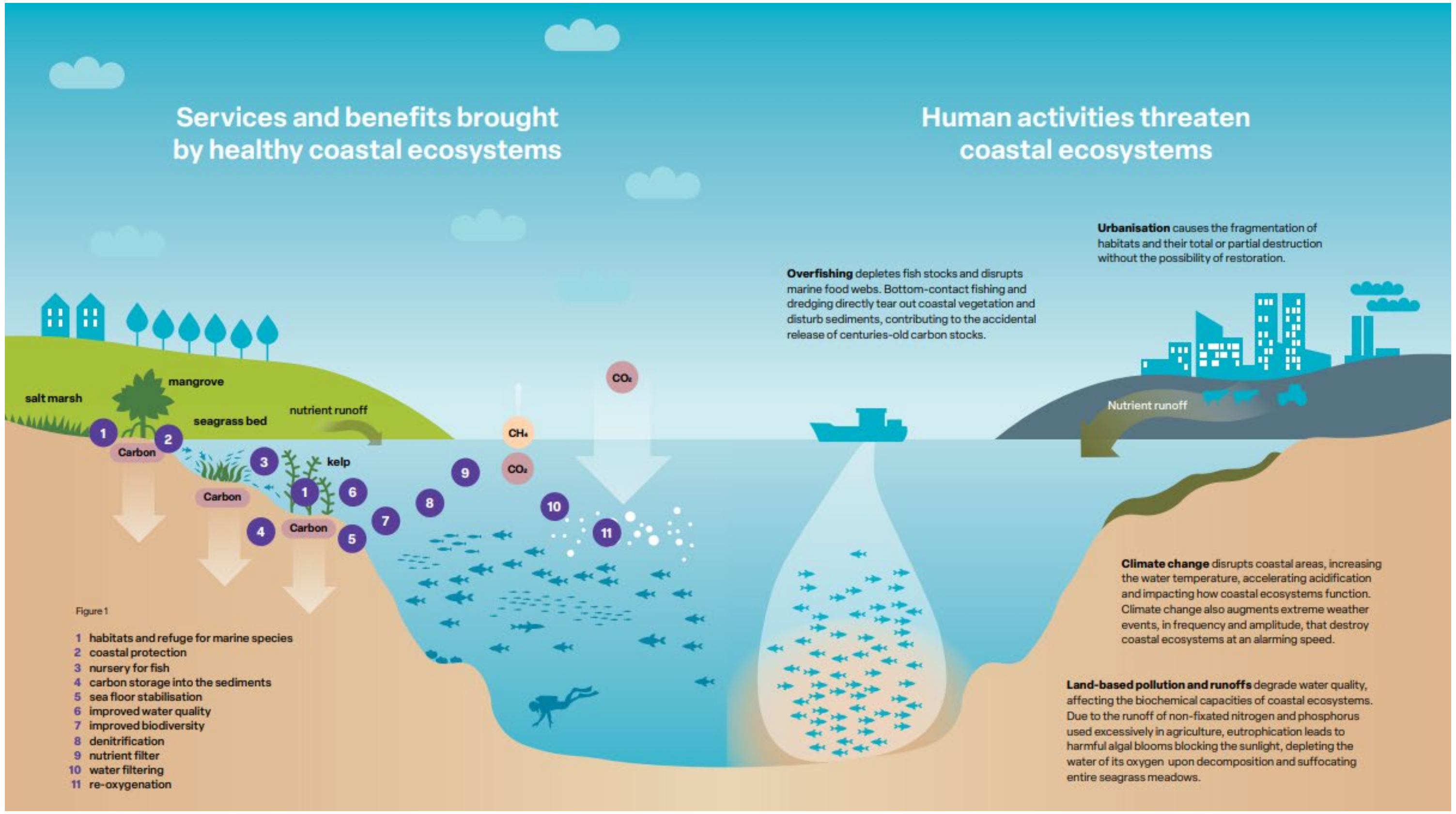


Figure 1

1 habitats and refuge for marine species
2 coastal protection
3 nursery for fish
4 carbon storage into the sediments
5 sea floor stabilisation
6 improved water quality
7 improved biodiversity
8 denitrification
9 nutrient filter
10 water filtering
11 re-oxygenation

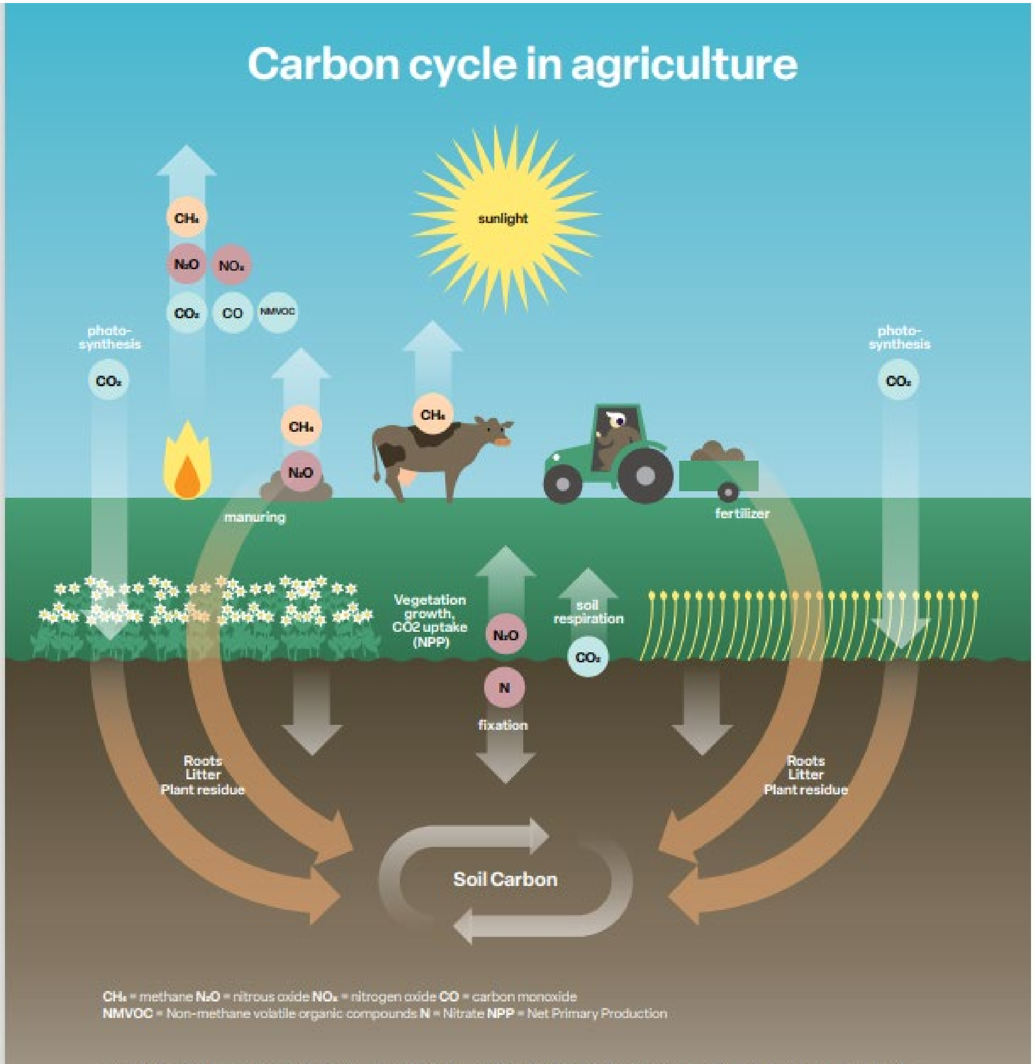


Figure 2. The carbon cycle between soil and atmosphere. Plants take up CO_2 from the atmosphere, but they also need sunlight, water and nutrients to grow. Since current cropland soils do not provide enough nutrients in a suitable format for the plants to use, nutrients are added to the soil to ensure profitable yields. (Source: IPCC, adapted)[7]

Currently, blue carbon observations around the world are almost all project-based. There are no long-term studies, and there are no standardized measuring processes.

Nitrogen emissions into the Environment

- Limited natural availability of reactive nitrogen (N_r) → great demand for synthetic fertilizer
- **N_r:** NH_3, NO, NO_2, HNO_3, HONO, pNO_3, pNH_4
- 1908: Haber-Bosch process → (**NH_3**): $N_2 + 3H_2 \rightarrow 2NH_3$
- Industrial revolution: increasing concentrations of nitrogen oxides (**NO_X**).

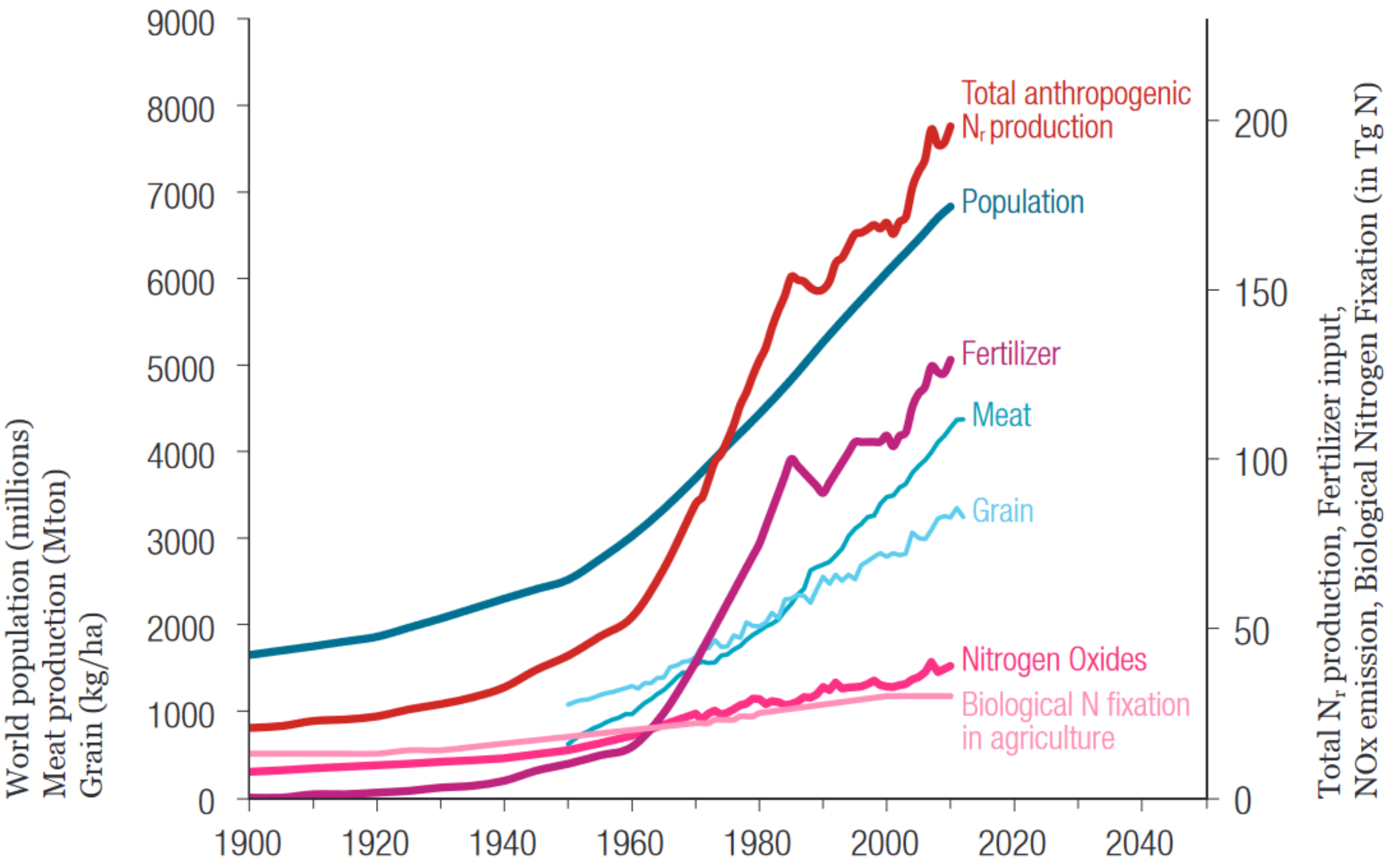
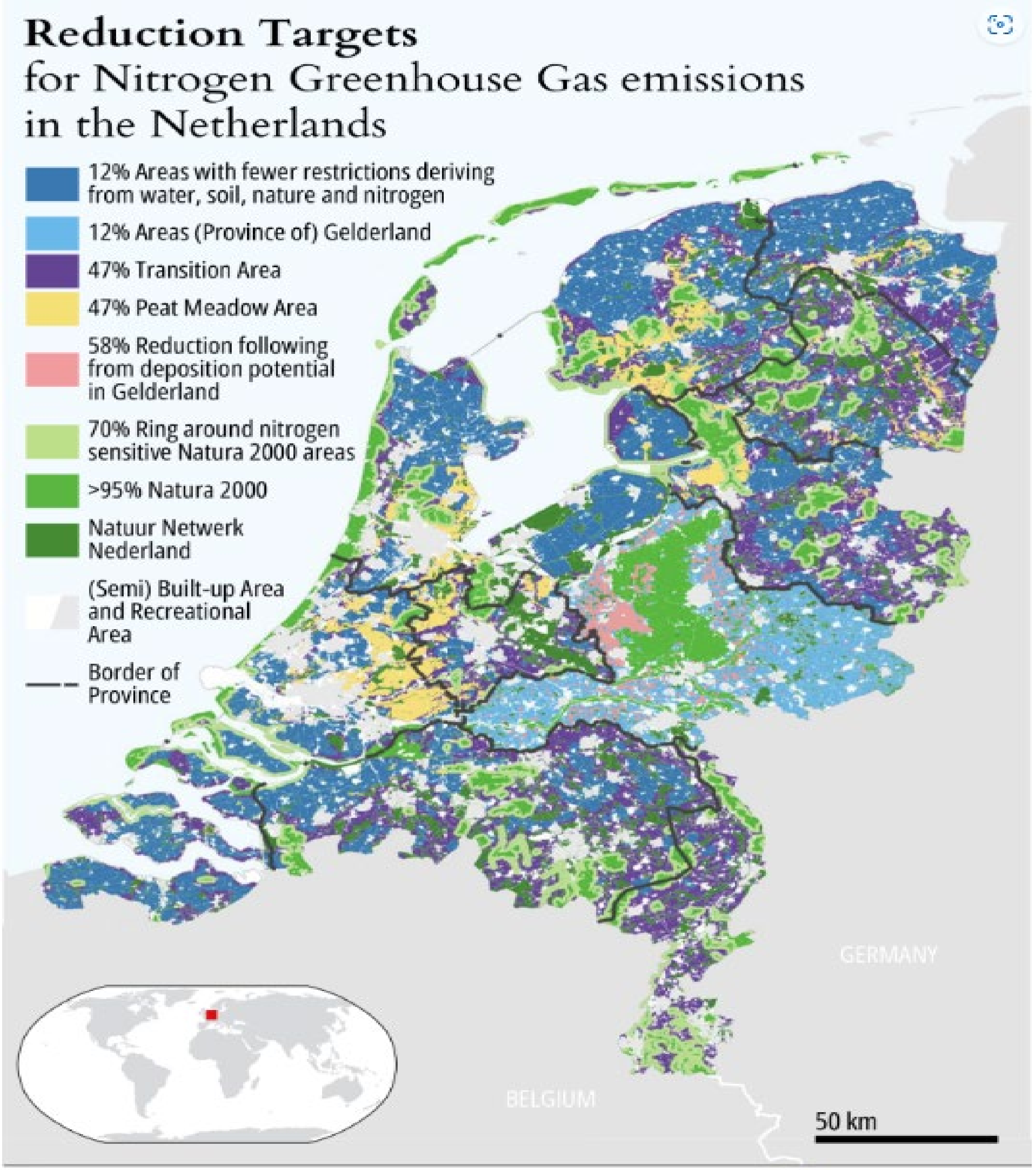


Image source: Erismann et al. (2015)



Source: USDA; Startnotitie Nationaal Programma Landelijk Gebied (2022)

MONGABAY

Reactive Nitrogen (N_r) – Environmental effects

- **Biodiversity loss: eutrophication** and **acidification** → e.g. grassing, leaching of minerals, algae blooms, fish death.
- **Health effects:** respiratory diseases due to particles and Ozone (O_3), lower drinking water quality.
- **Climate forcing effects:** formation N_2O and O_3 (warming) versus impacts on CH_4 depletion, carbon sequestration, and particle formation (cooling).



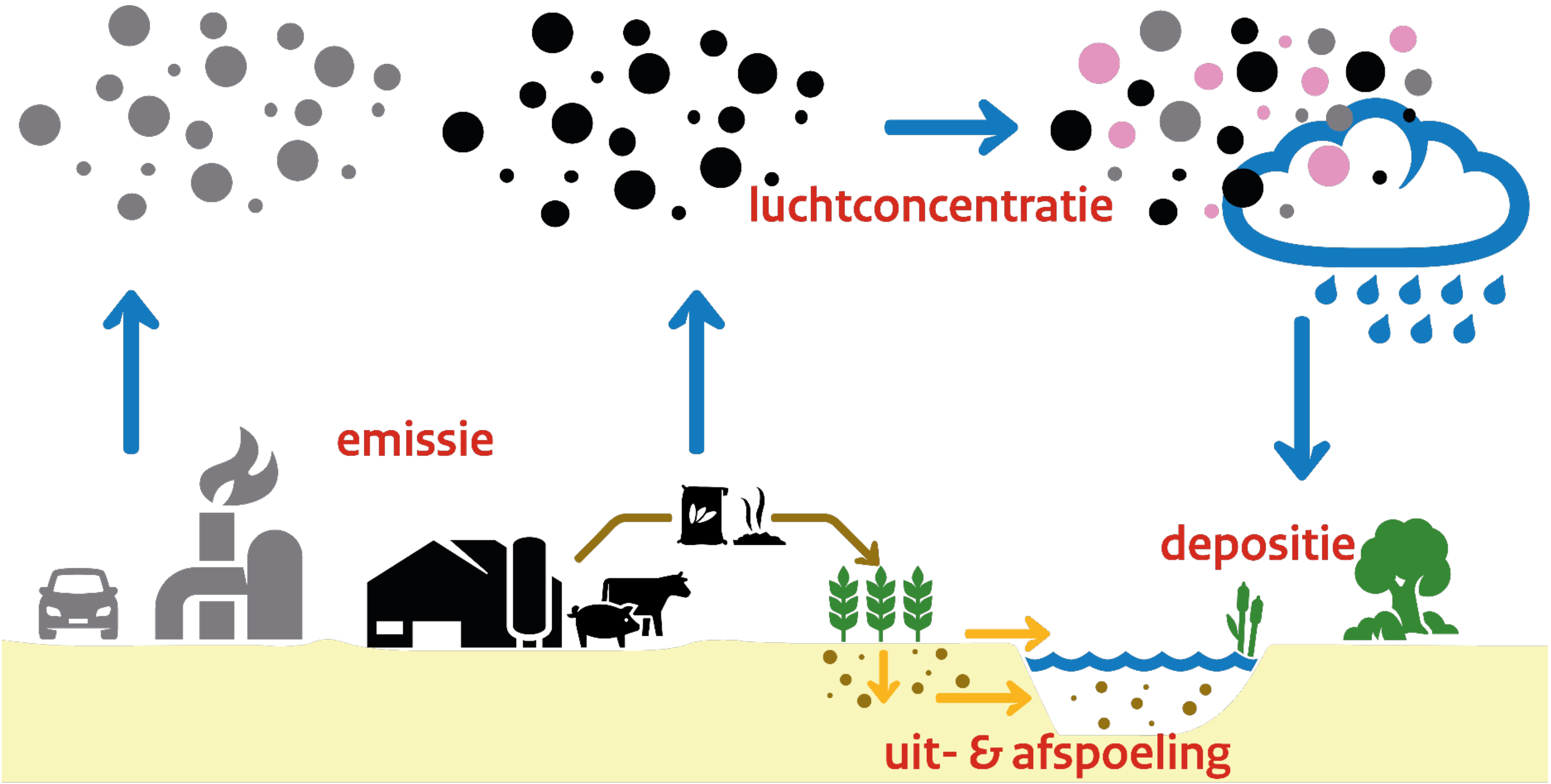



Images source: Sutton et al. (2011), wikimedia.org

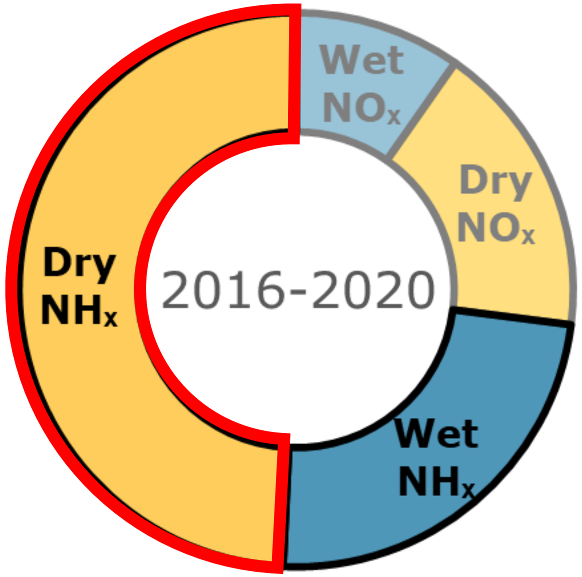
Nitrogen in the nature?

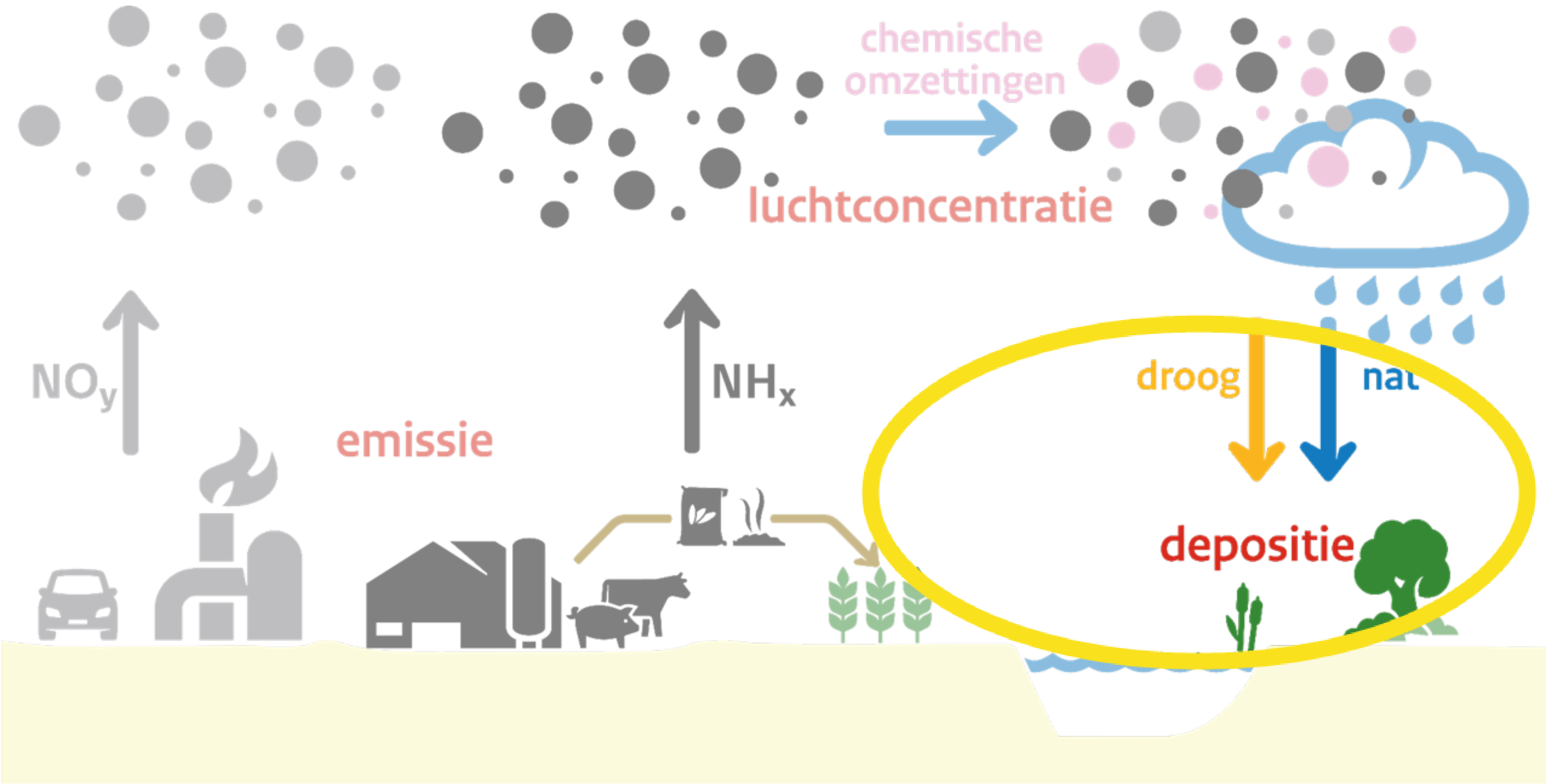
through the air

through soil and water



Path through the air

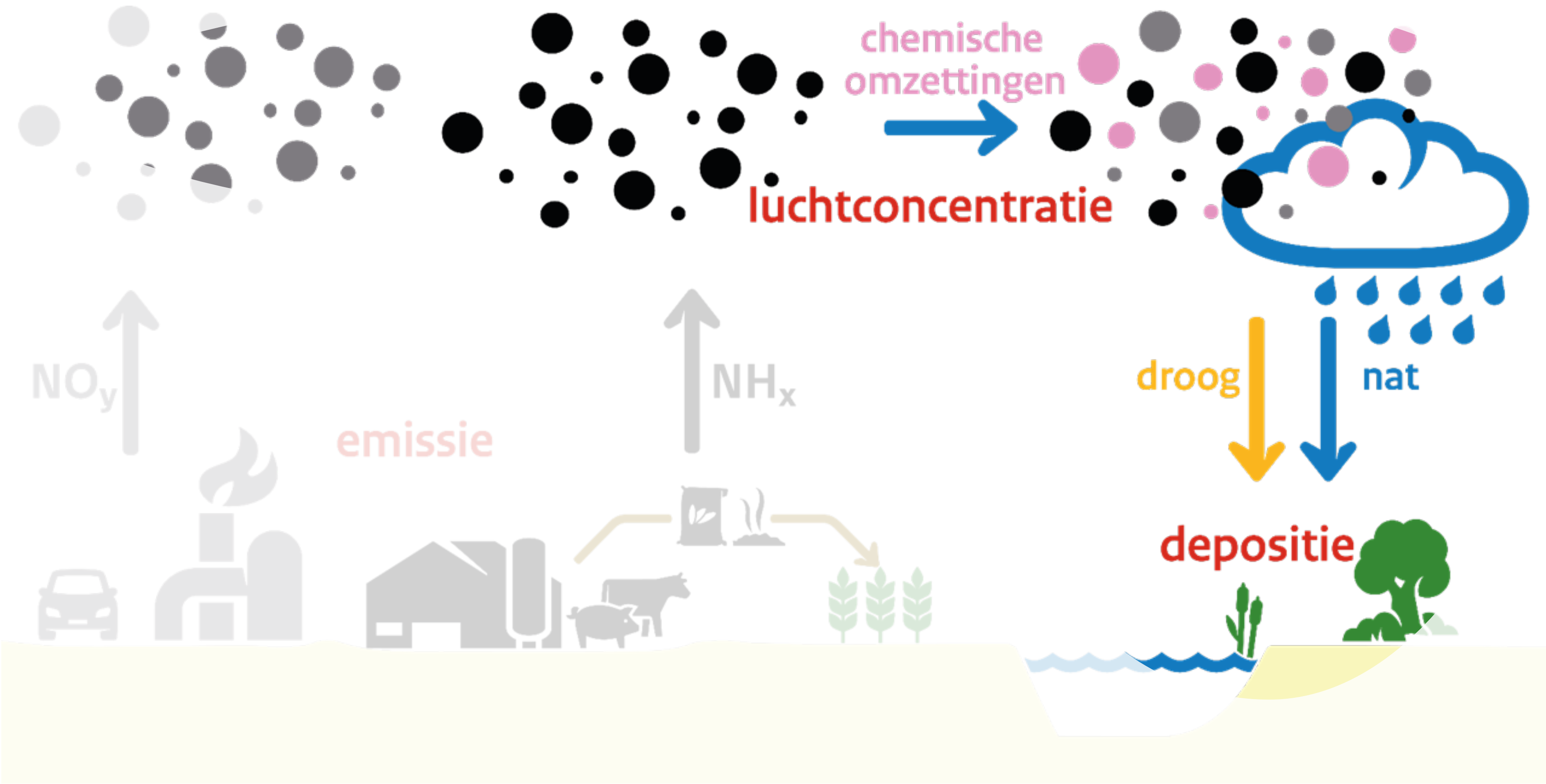




Total nitrogen depostion = NO_y(wet) + NO_y(dry) + NH_x(wet) + NH_x(drg)

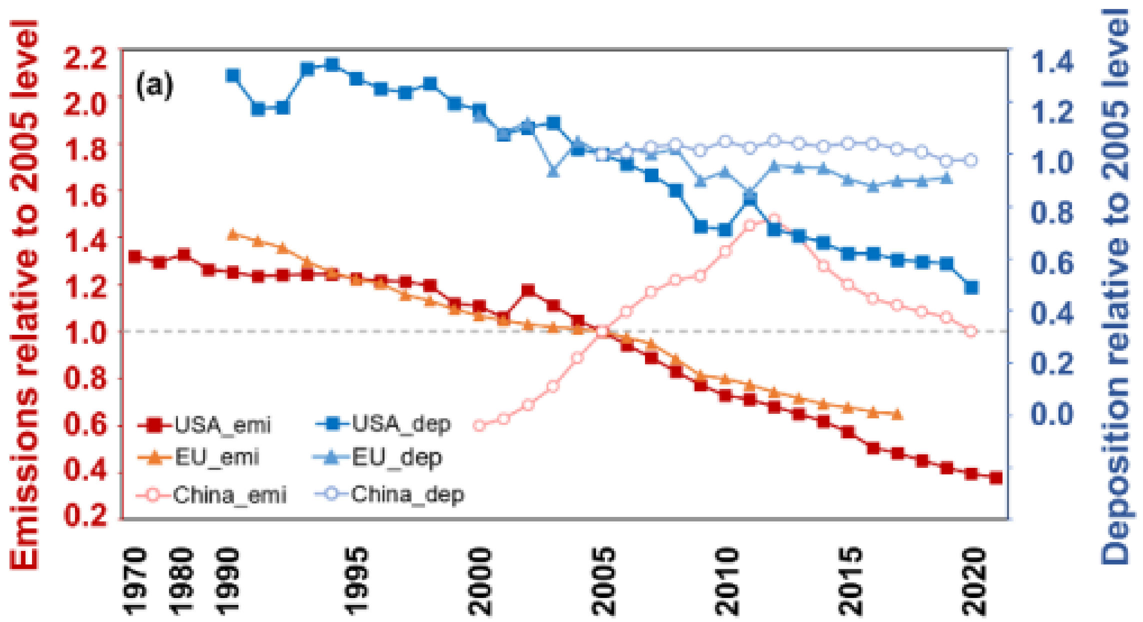
Measurement in the air

- NH_3 concentrations is difficult to measure
- because it dissolves easily in water
- suction problem

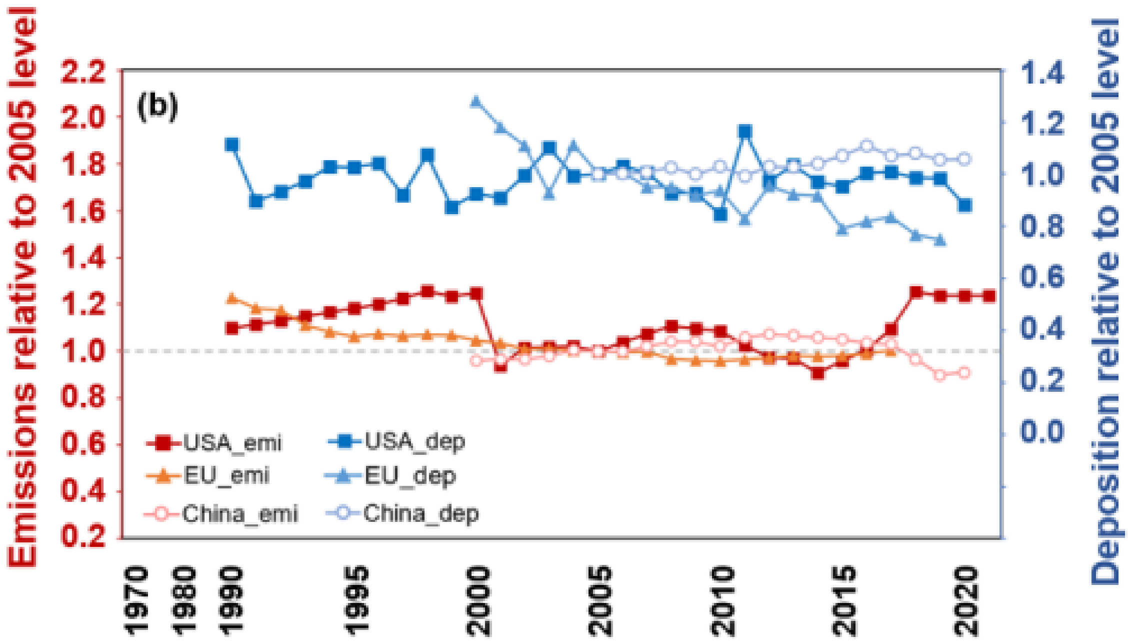


Comparison of N emissions and deposition in the process of pollution control in the USA, Europe, and China.

(a) NO_X emissions and **NOy** deposition



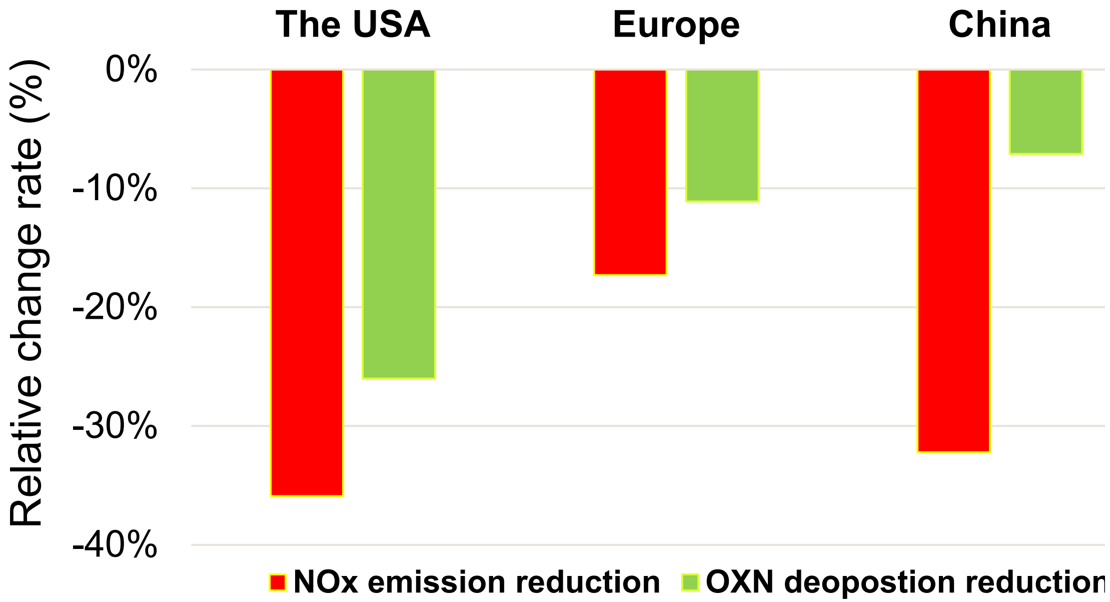
(b) NH3 emissions and **NHx** deposition

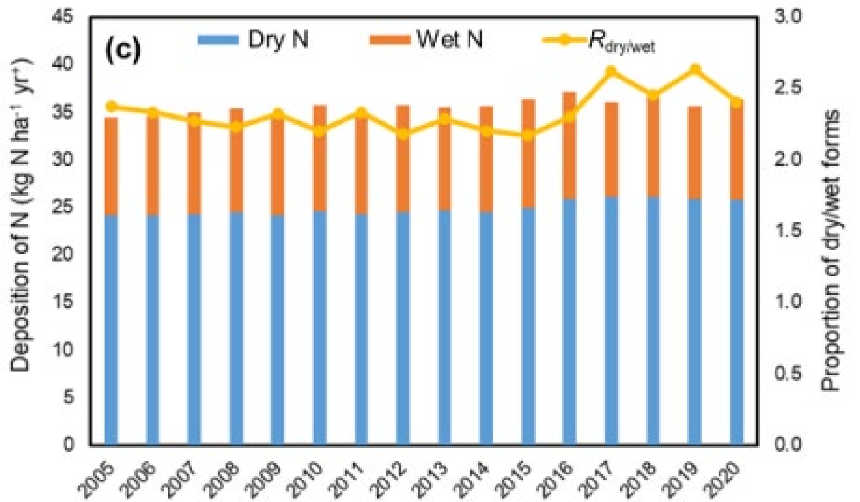


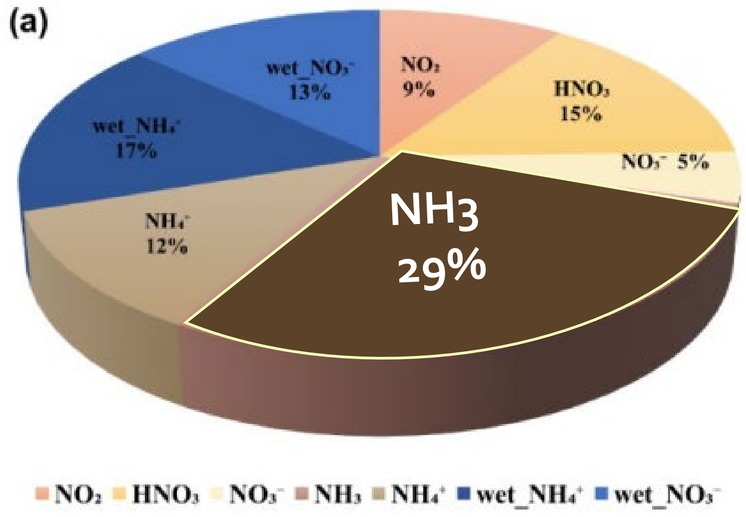
source: Zhou et al, Estimating nitrogen and sulfur deposition across China during 2005-2020 based on multiple statistical models (2023).

Current status of N deposition in China

- **Comparison of relative change rates of emissions and deposition in the process of pollution control in China, Europe, and the USA.**







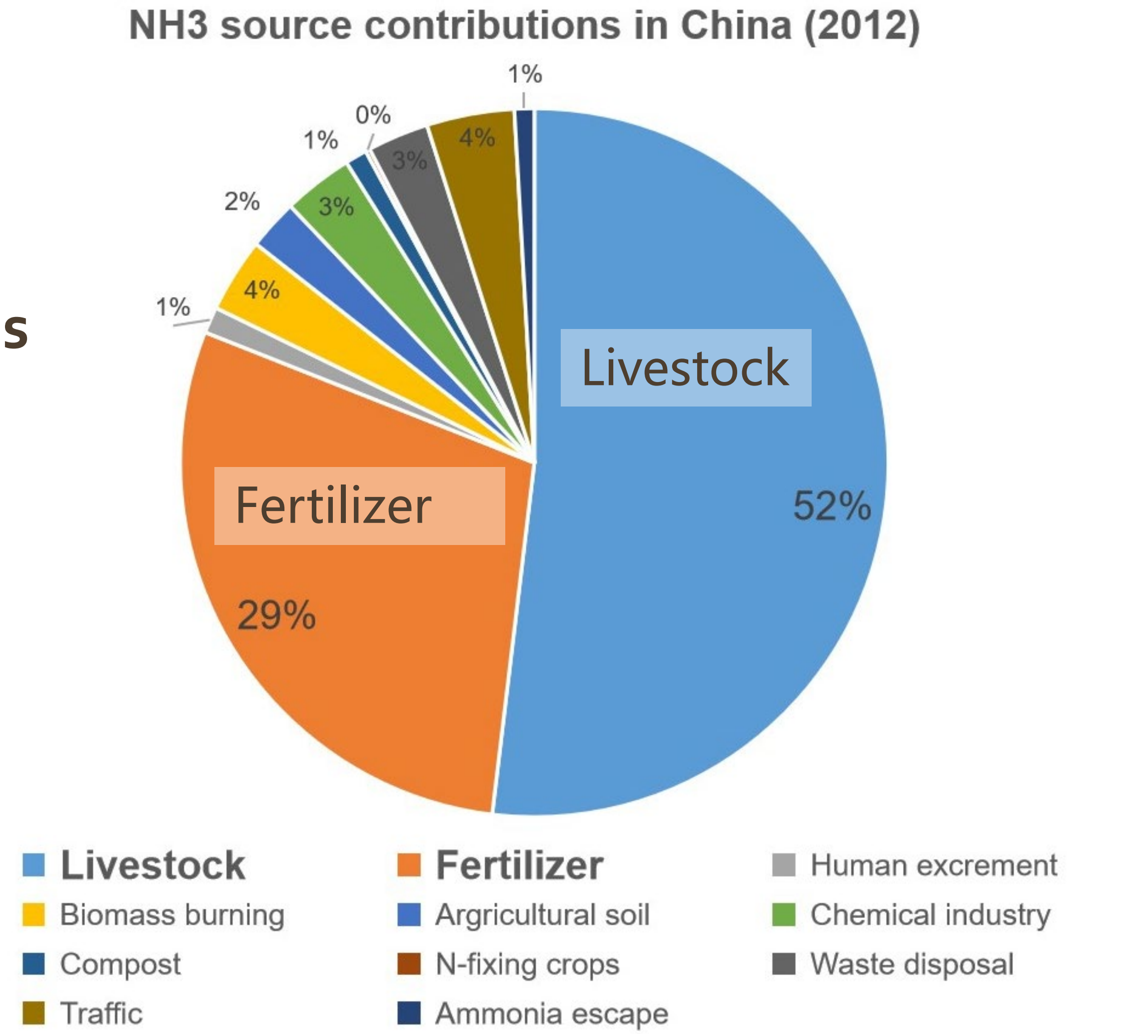
Wet N deposition: 30%
Dry N deposition: 70%
NH_3 dry deposition: 29%

Ammonia pollution in China

Ammonia (NH_3):

- **Important precursor of PM2.5**
- **Locatized emission/depostion**
- **Mainly from agricultural sources**

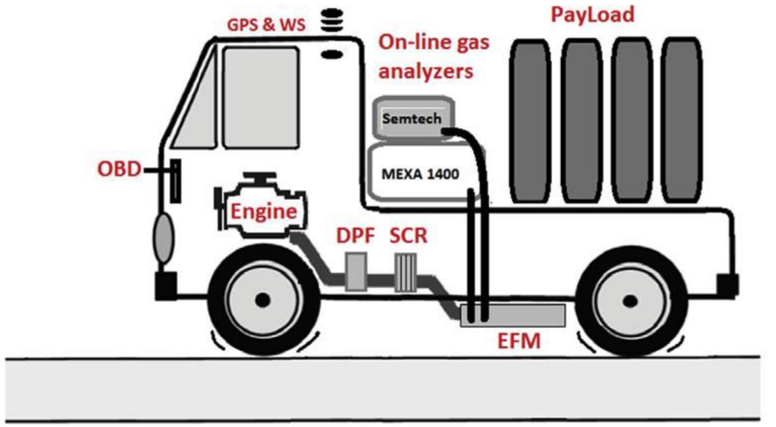
Clean day　　Polluted day



Kang, Y., Liu, M., Song, Y., Huang, X., Yao, H., Cai, X., Zhang, H., Kang, L., Liu, X., Yan, X., He, H., Zhang, Q., Shao, M., and Zhu, T.: High-resolution ammonia emissions inventories in China from 1980 to 2012, Atmos. Chem. Phys., 16, 2043–2058, https://doi.org/10.5194/acp-16-2043-2016, 2016.

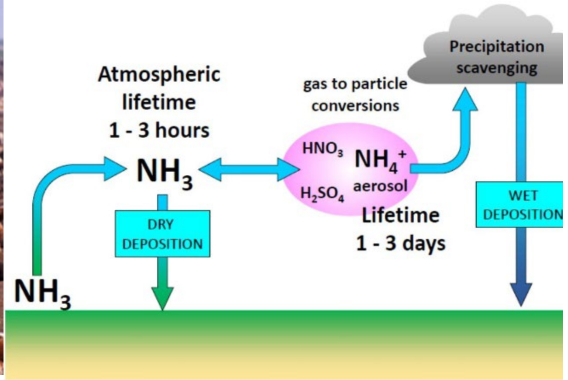
气态氨排放的观（监）测需求

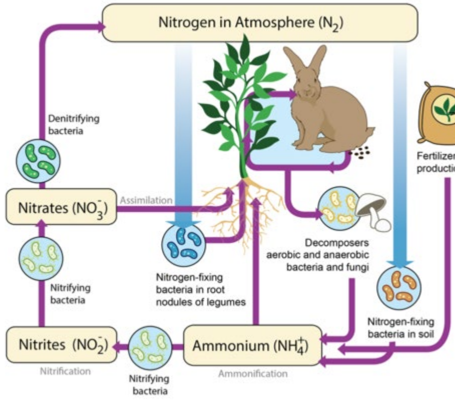
点源-浓度



锅炉烟气、化肥厂、合成氨厂（工业）小型封闭养殖场、池塘、堆肥点 汽车尾气氨排放

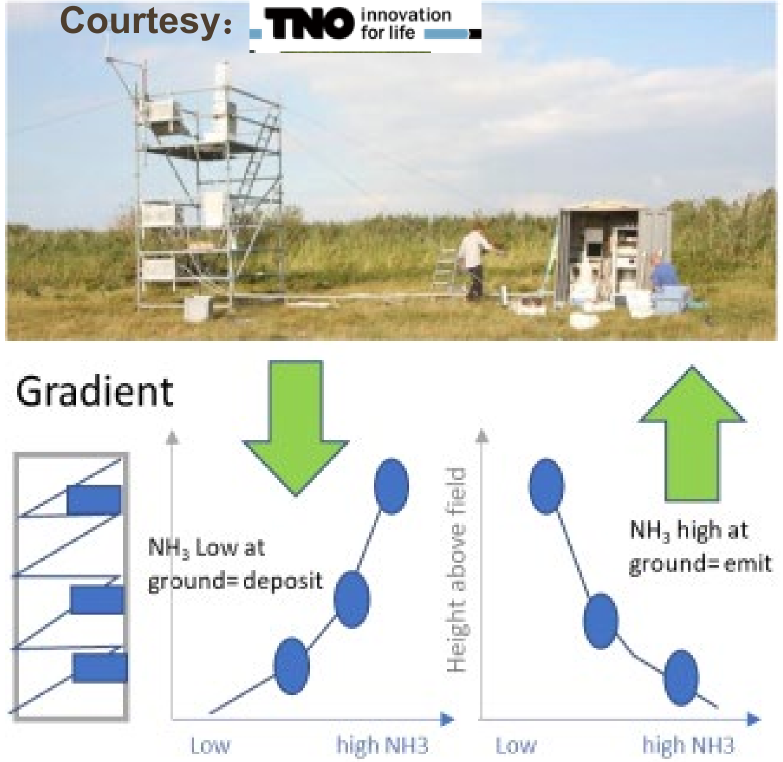
面源-通量

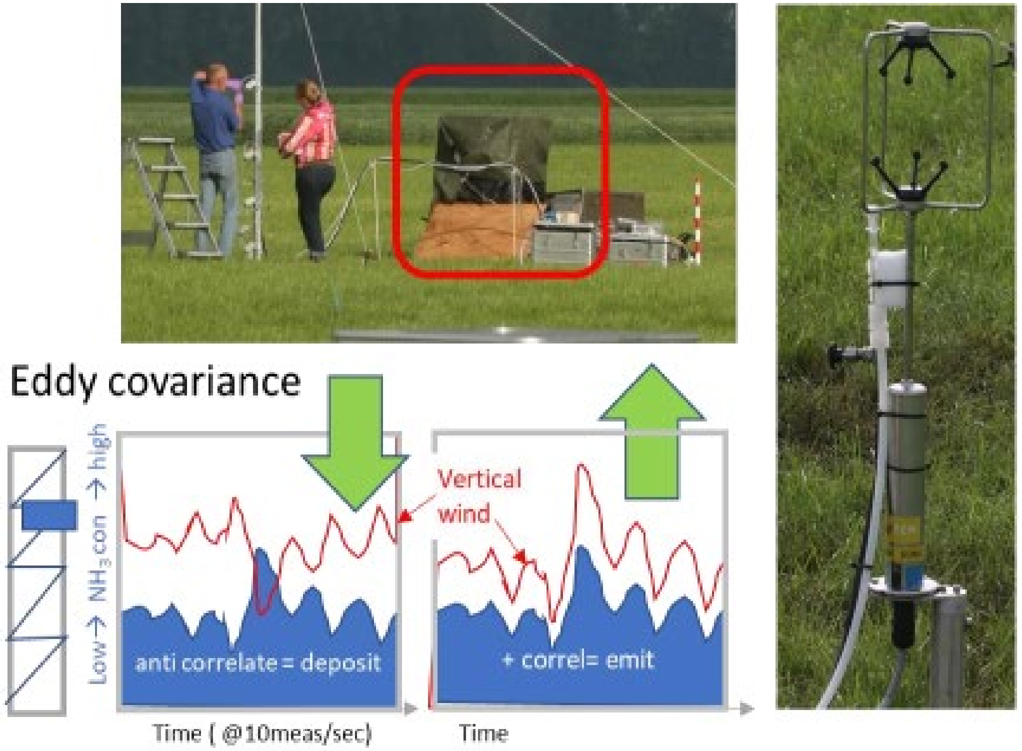




规模化施肥、农田草地 大型蓄牧区 大气环境化学 土壤微生物

氨通量测量：梯度法vs涡动法





- 在2-3个高度获取15分钟的平均浓度
- 根据不同高度的浓度差

+成熟技术，对气体分析仪速度要求不高

+上世纪80'和90'年代数据获取方法

-白天和黑夜数据，需做大量校正

在1个高度获取10 Hz的高频浓度数据

利用与浓度相关的垂直风速脉动的协方差

+新一代技术，理论上更优越

+现已成为H_2O，CO_2及其他温室气体通量测量标准

-需要快速、高精度NH_3分析仪器

The motivation of design A good NH_3 analyzer

- **Aim**: 探索农业施肥及畜牧养殖对不同生态系统中NH3排放/沉降通量的影响
- **METHOD**: Use **QCL光谱技术 open-path** (痕量) NH_3 analyzer

  Apply Eddy Converiance Method (涡动协方差技术)
- **Requirement**:
  - **Highly sensitive and high frequency sampling speed**
  - Large concentration range（ pre & post fertilizer)
  - Reduce NH_3 absorption loss
  - Low power
    - Apply at remote monitoring station without main power
    - Deploy rice field/wetland/coastal area without wet-issue

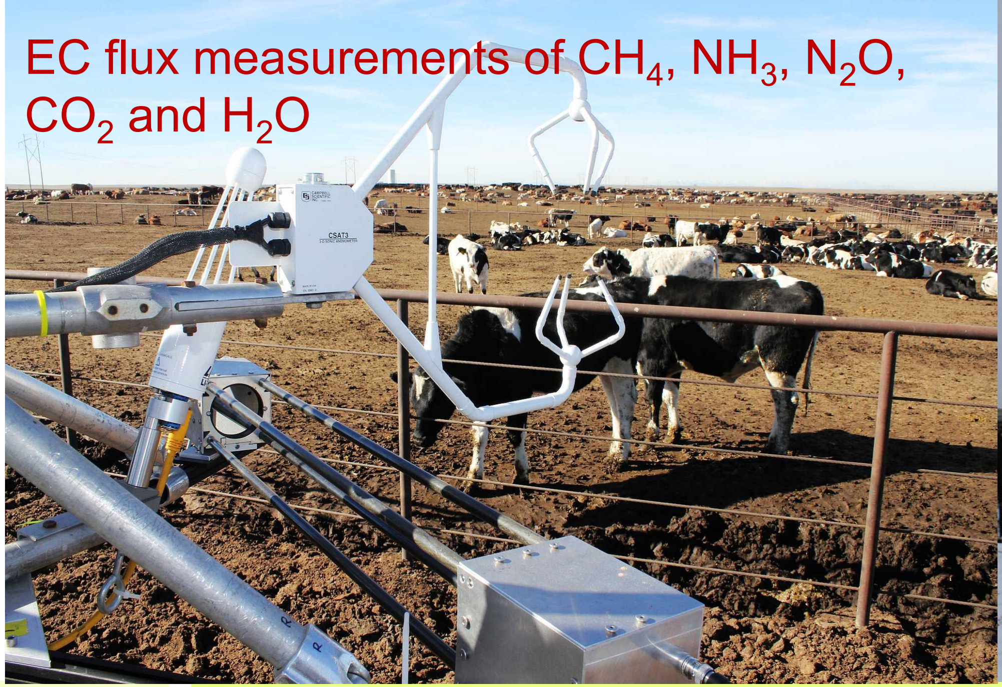
海尔欣光电——科研级气体分析仪器供应商

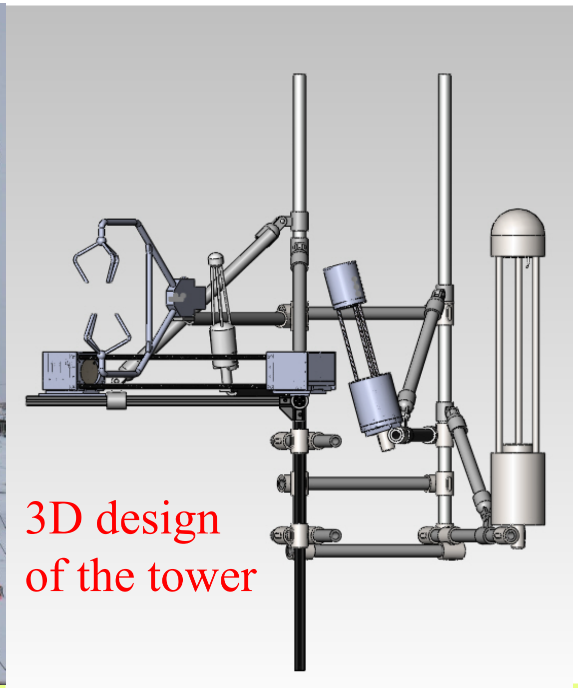
- 由美国普林斯顿大学校友创办，位于中国宁波
- 专注于中远红外激光光谱检测技术（QCL/ICL+TDLAS-可调谐激光吸收光谱技术）的高科技公司
- 产品主要包括：中高端气体分析仪器、工业过程监测、激光光谱研究等领域

开路氨分析仪科研原型机 @Princeton

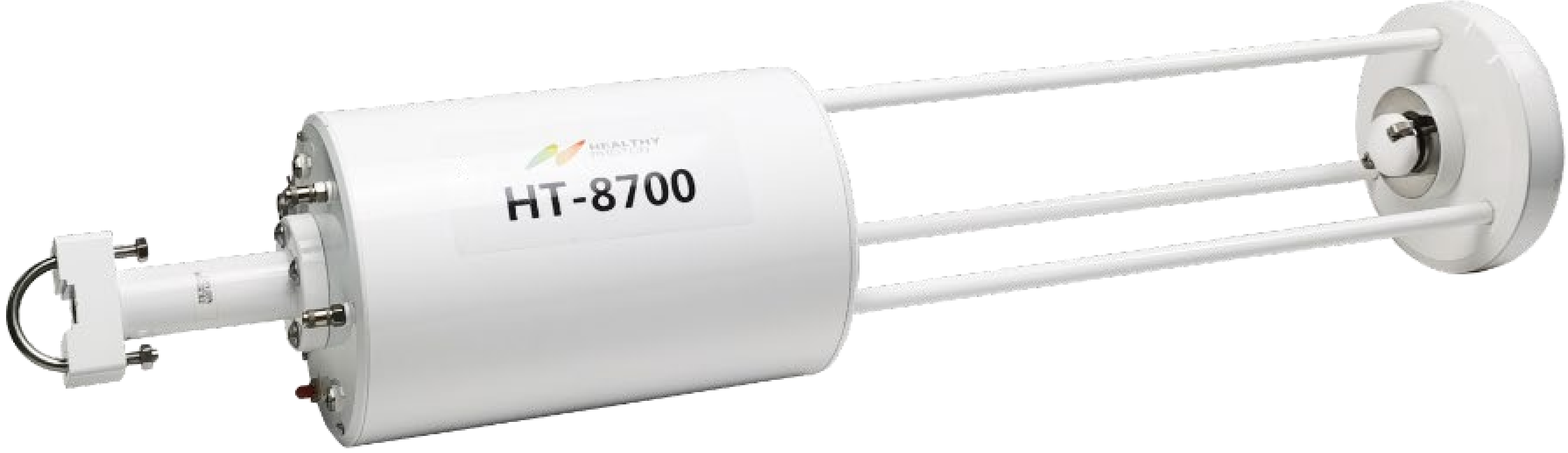
- Mid-InfraRed Technologies for Health and the Environment（主要以普林斯顿大学和莱斯大学为基地
- **开路氨分析仪科研原型机诞生于此**

（Courtesy：Prof. Mark Zondlo, Princeton University）

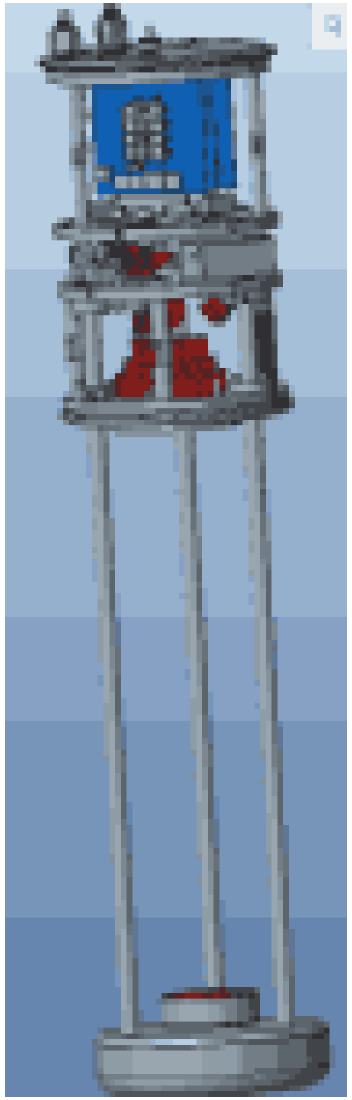




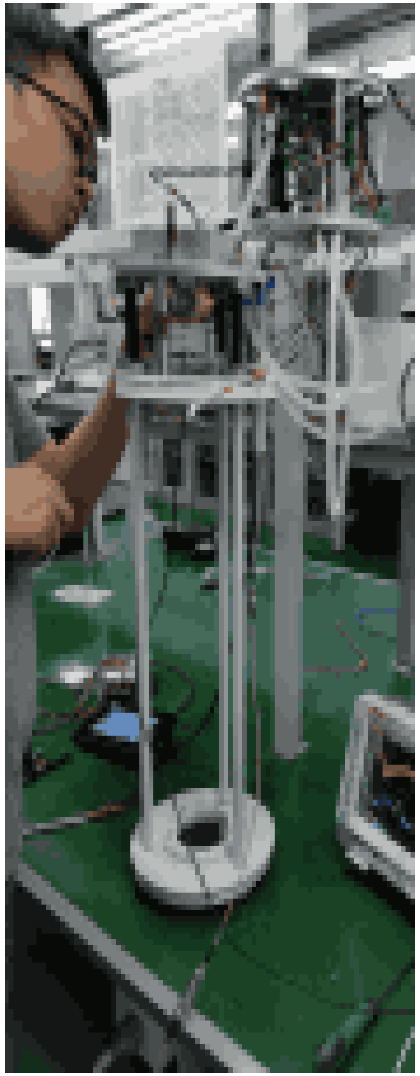
HT8700系列开路氨分析仪的特点



Product design → update → optimization



产品定义及设计

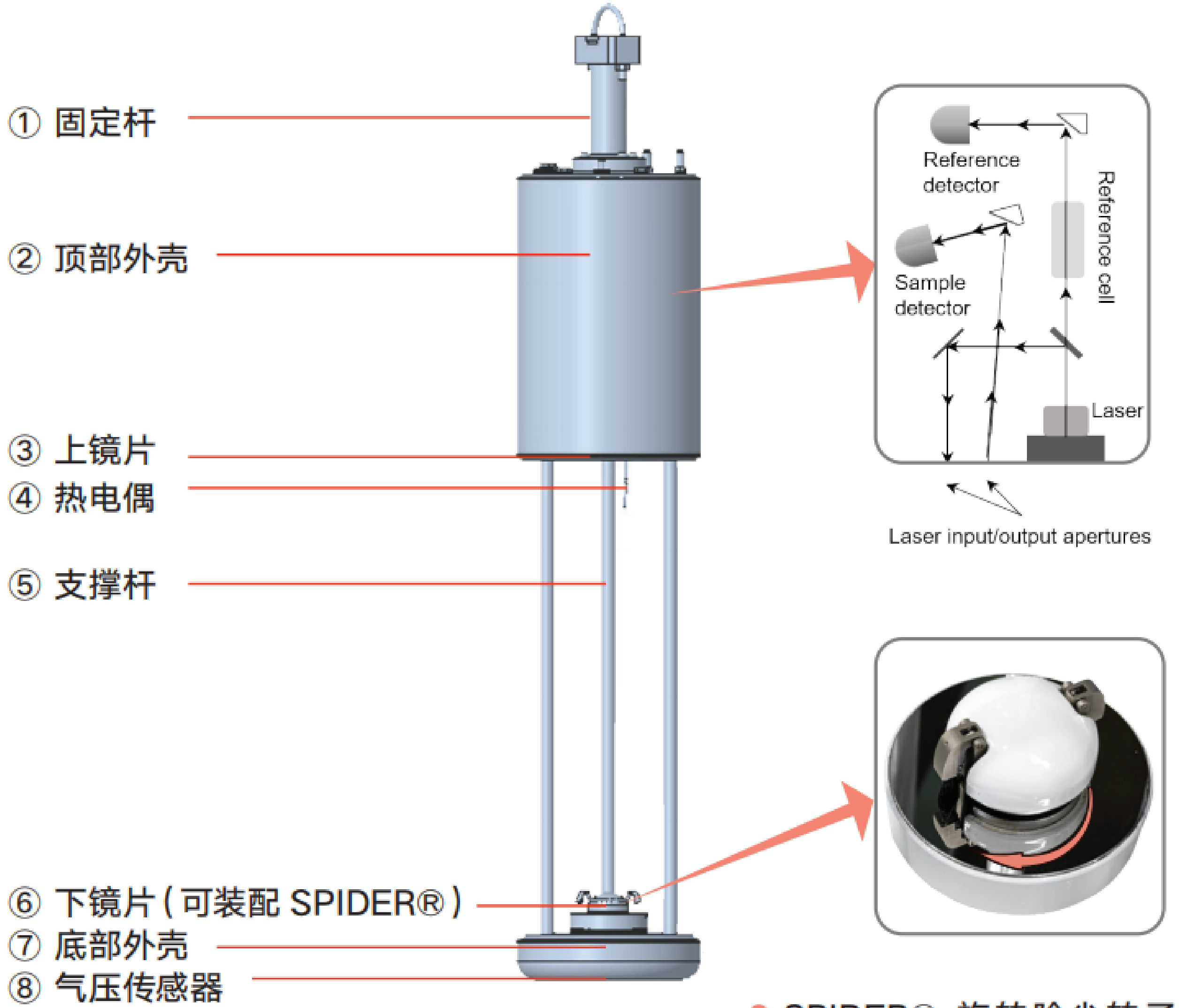


模块联调

室内测试

室外测试

Structure



- SPIDER® 旋转除尘转子是一项专利技术，利用刷子的自动旋转来清除下镜片上的灰尘，避免了常规的手动清洁维护。

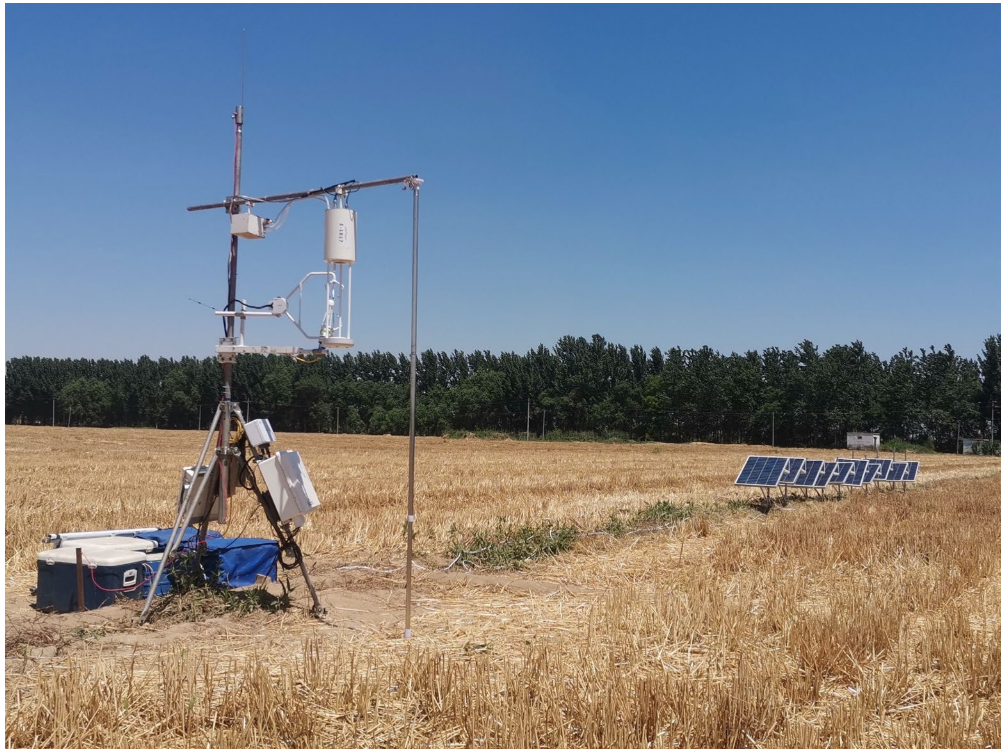
Appearence

检测技术	量子级联激光吸收光谱(QCLAS)
光学路径长度	物理长度:0.5m; 有效光程:50m
测量精度(1;0.1s/1s/10s)	0.5 ppb/ 0.15 ppb/ 0.05 ppb
量程范围	0 - 5 ppm（其他量程可选）
输出带宽	10Hz
大气压力范围	70 - 110 kPa
操作环境湿度	0-99%
操作环境温度	-10 ~ 45 ℃
存储方式	通过Campbell Scientific®采集器CF卡存储
操作方式	PC端UI界面
通讯接口	RS232串口（以太网可选）
电源	18 to 29 VDC
功率	50 W
尺寸	834mm×φ200mm
分析仪重量	5kg
环境适应性	IP67

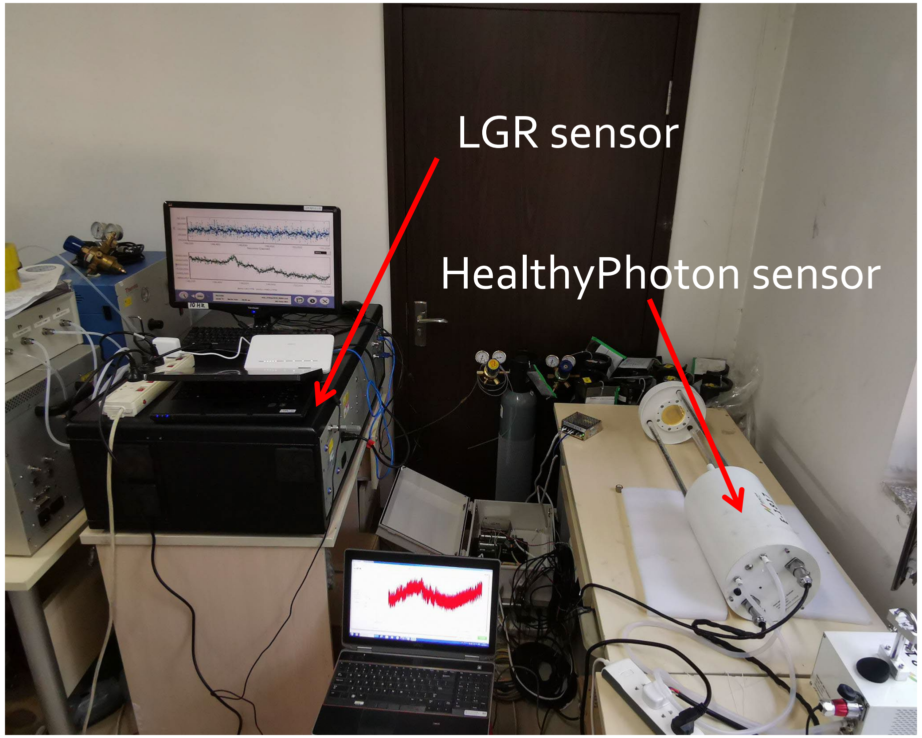
HT8700E	高精度大气氨激光开路式分析仪 包括:24VDC电源适配器,光学清洁套件,循环液态冷却系统,便携防震仪器包装箱
HT8700E-B120(可选)	24VDC,120 Ah便携式可充电蓄电池
HT8700E-DL(可选)	多通道数据记录系统:同步记录来自多个分析仪和其他设备(例如GPS,风速计)的串行(RS-232)输出
HT8700E-GPS(可选)	GPS模块,带RS-232输出

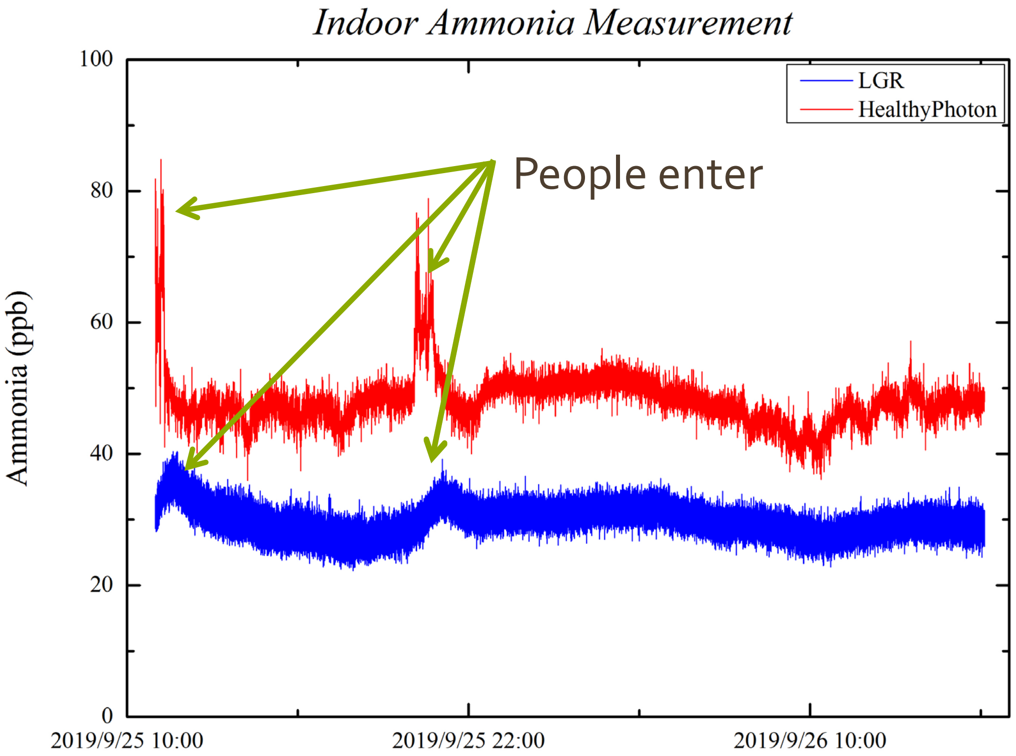
Advantages of HT-8700 NH_3 open-path analyzer

- **中红外独立强吸收谱线**：实现高灵敏度（亚ppb）、**高选择性**分析
- **开放光路设计**：避免氨的吸附效应造成的迟滞，保证**10Hz高速测量**；高频衰减小
- **避免大流量真空泵**：仪器便携，功耗低（50W），**部署灵活**



Indoor comparison

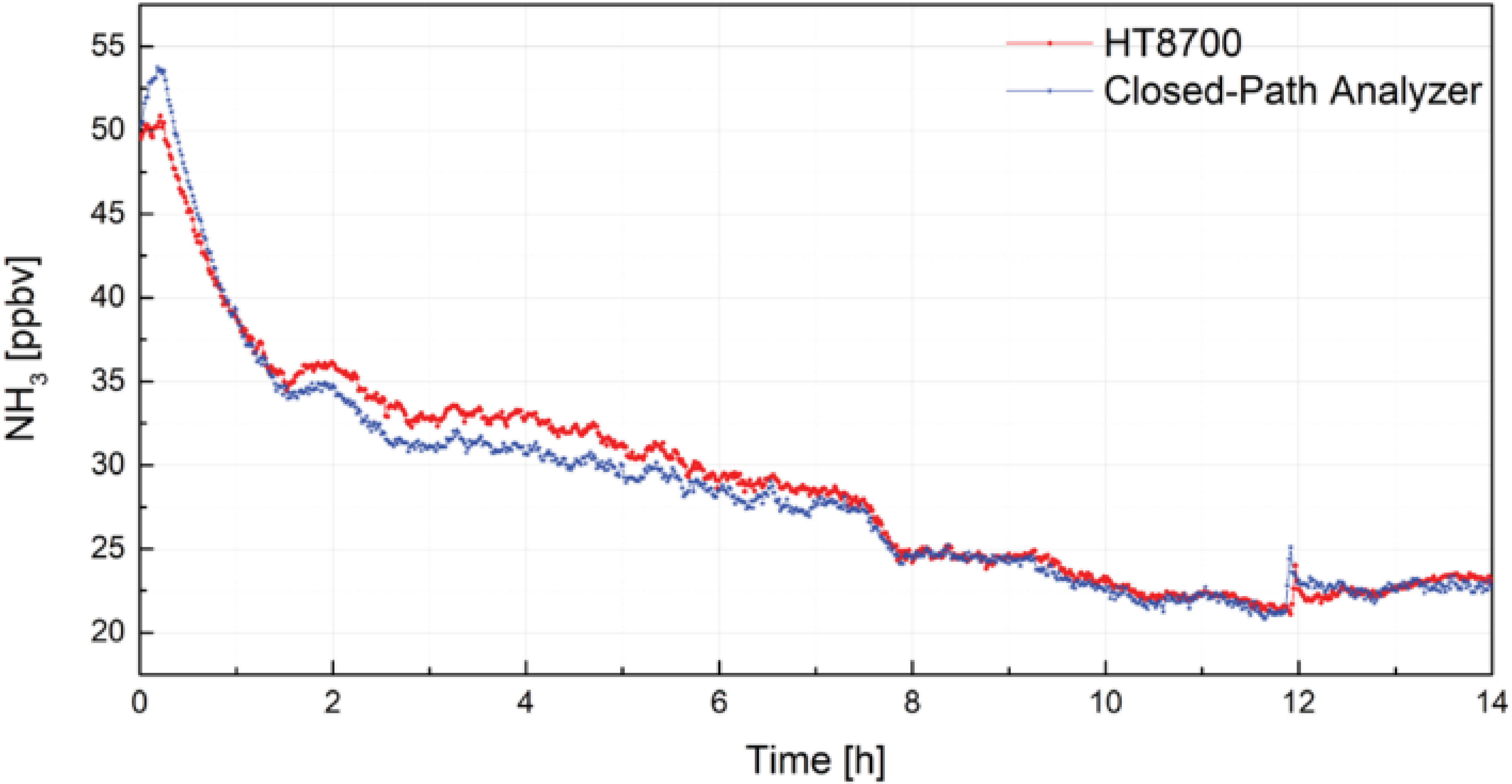




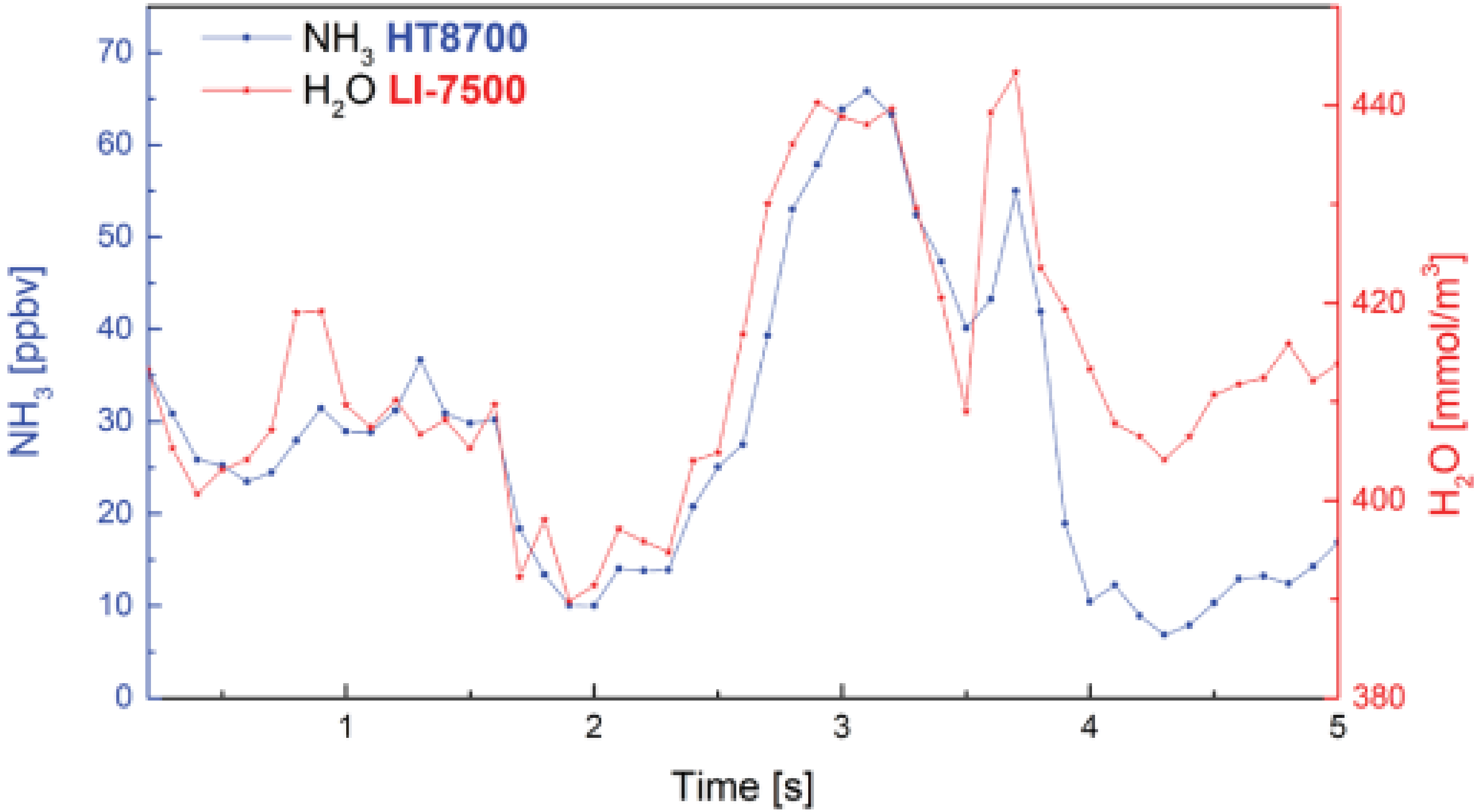
- The open-path sensor shows better response to NH_3 concentration change due to personnel entery of the room
- ~30% discrepancy due to calibration or sampling loss

** In collaboration with State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China*

Measurement accuracy



Respons speed



- 与LICOR®的LI-7500的开路水汽测量相比，HT8700的NH_3测量没有明显的延迟
- HT8700的速度与其他开路分析仪处于同一水平，这对于涡动测量至关重要

Case study in the Netherlands

- HT's first long journey from CN to Cabauw, the Netherlands…

Motivation and Aim of the Cabauw RITA-campaign

- NH_3 dry deposition is the largest fraction of nitrogen deposition
- Very difficult to measure (close-path *versus* open-path)
- Until recently only monthly averaged measurements
- Ruisdael campaign aim: at least *half-hourly* measurements to see the deposition and emission PROCESSES.

Four main goals to measure Nitrogen

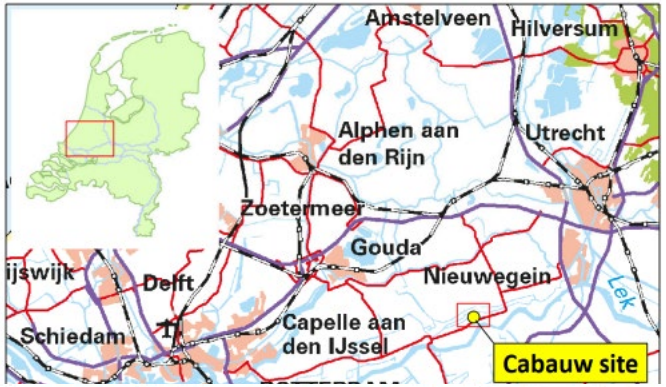
- validataion and calibration for the models

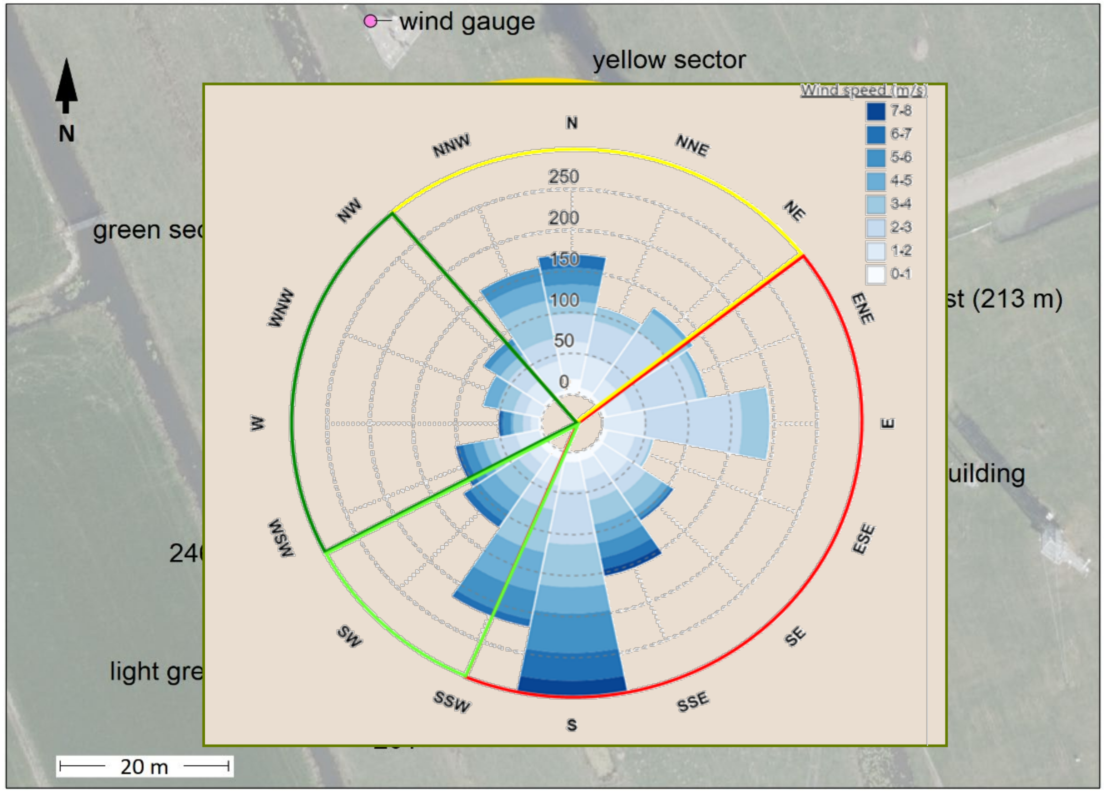
- studying nitrogen processes

- Follow N development in real-time

- assessing the quality of other measurements

Cabauw - ICOS station



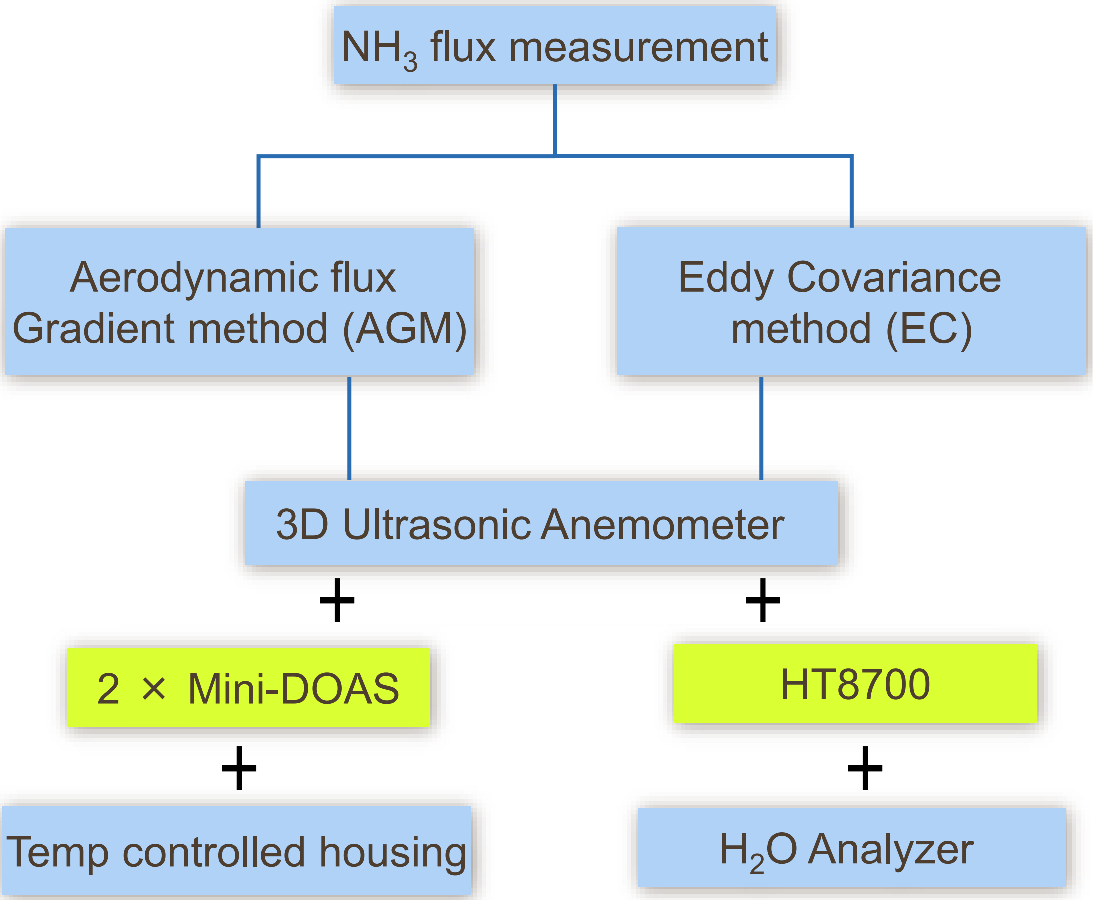


Soil: Peatland, covered by heavy clay
Land use: grassland
Occasionally grazing animals on the north side.

Campaigen period:Aug. 27 – Oct. 11, 2022
Average T_{air} : 14.8℃
Precipitation: 84 mm
Dominant wind direction: South

TNO innovation for life

NH_3 dry deposition measurement in Cabauw



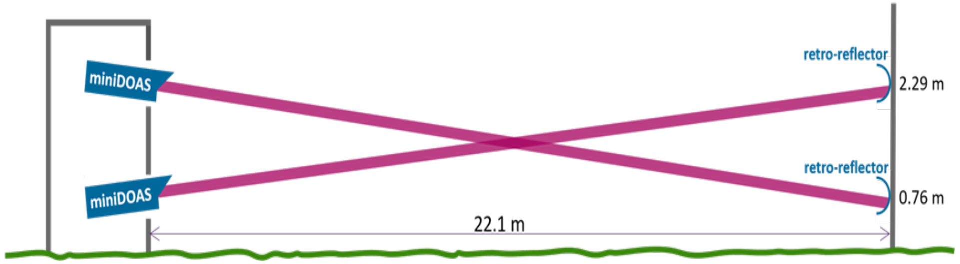
2021 RITA CAMPAIGN: OPEN-PATH INSTRUMENTS

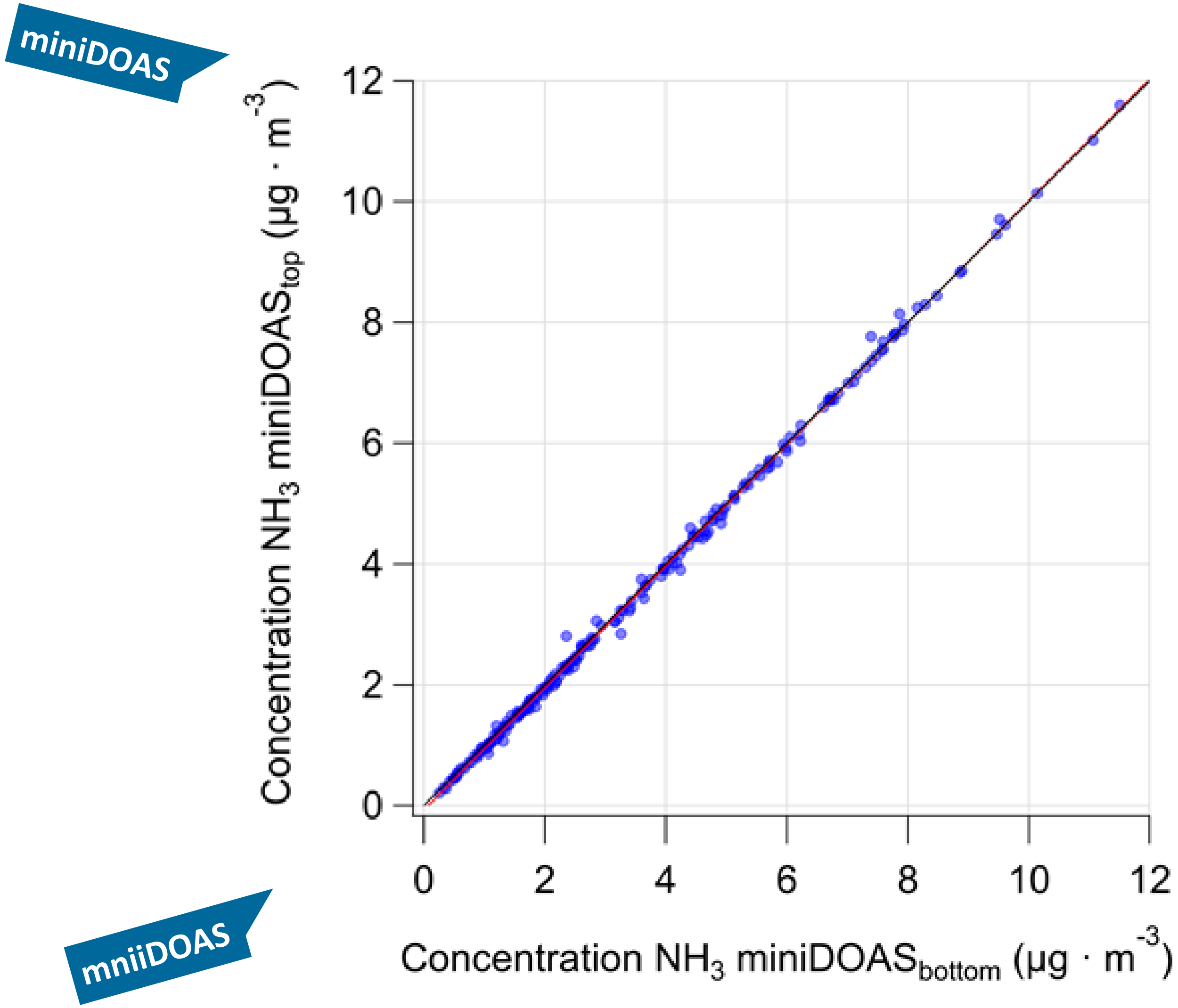
BROADBAND UV-BASED MINI-DOAS2.2d (RIVM, nl)

QCL INFRARED-BASED HT8700 (HEALTHY PHOTON LTD., CN)

miniDOAS – cross measurement

quantify and correct the bias





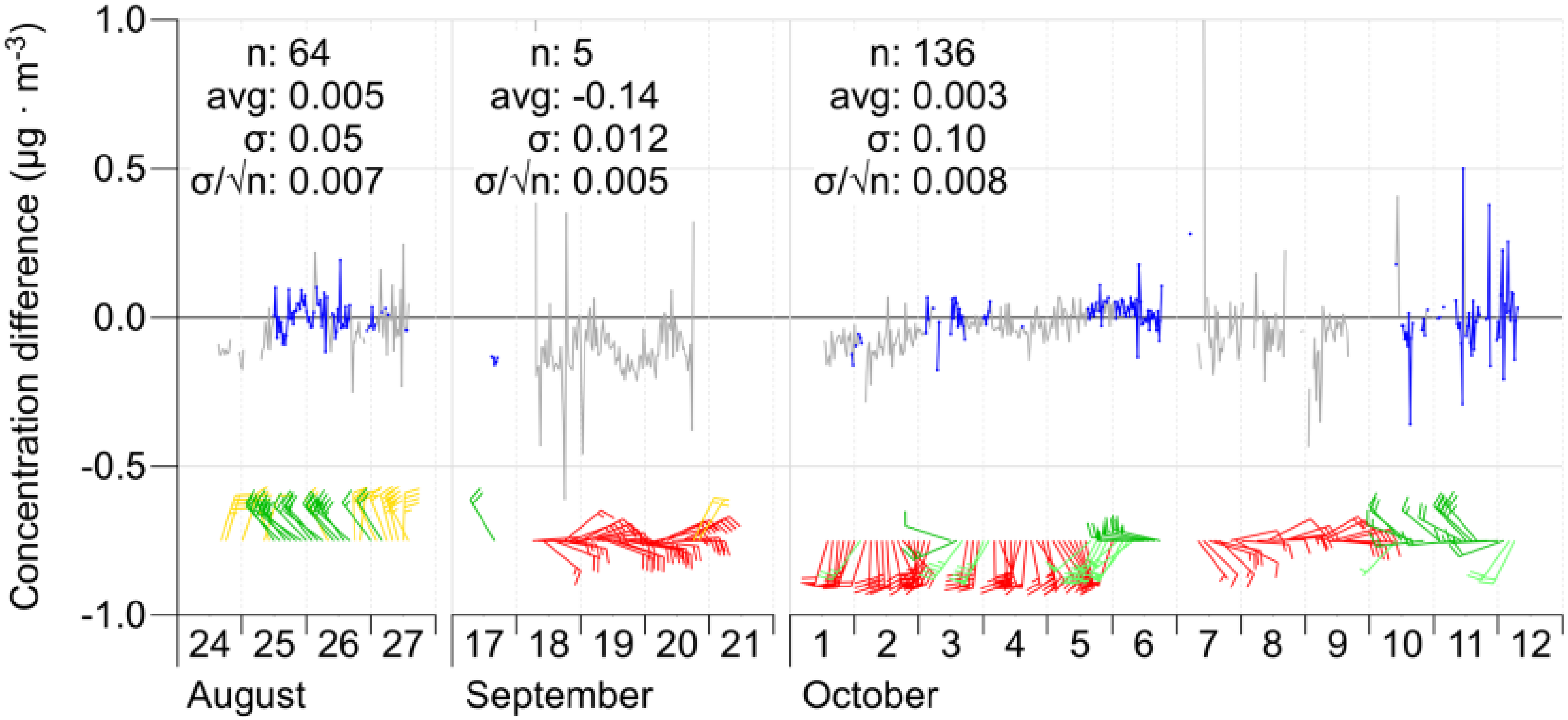


Figure 6. Top trace: Time series of de observed NH_3 concentration difference between the two miniDOAS instruments during the three cross periods, after correction of the top miniDOAS values based on the intercalibration as described in the text. Only data during well-mixed conditions ($u_* > 0.1\ ms^{-1}$) are shown. Measurements from obstacle-free wind directions are blue, other directions are grey. The sets of statistics given in the plots apply to the blue measurements only. Bottom trace: 30-minute wind vectors colour-coded with the wind sectors described earlier. Wind speed is indicated as barbs, as used on meteorological maps. To reduce clutter, only 1 in 4 wind vectors are shown.

HT: Eddy Covariance method

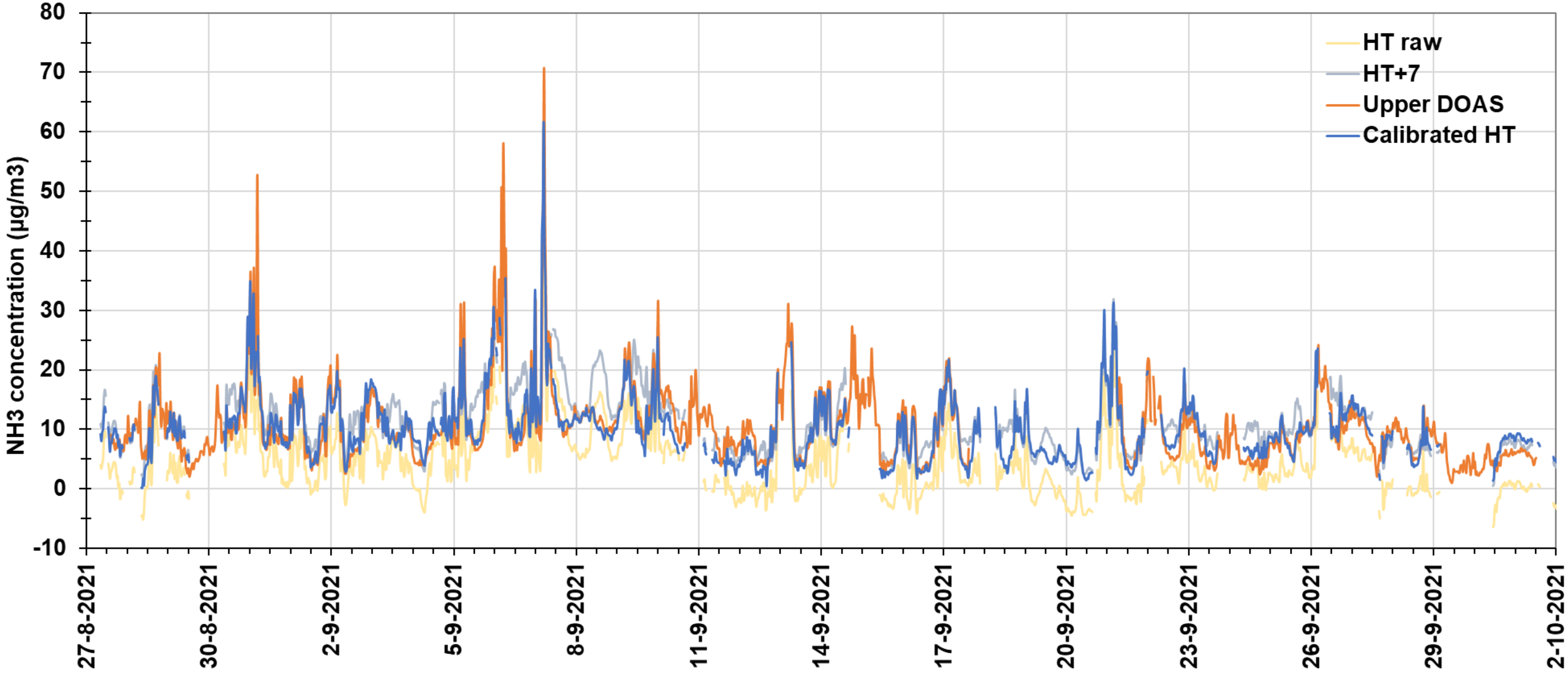
- Direct measure fluxes
- Quick response (10 Hz)

$$F_{NH_3} = -\overline{w'NH_3'}$$

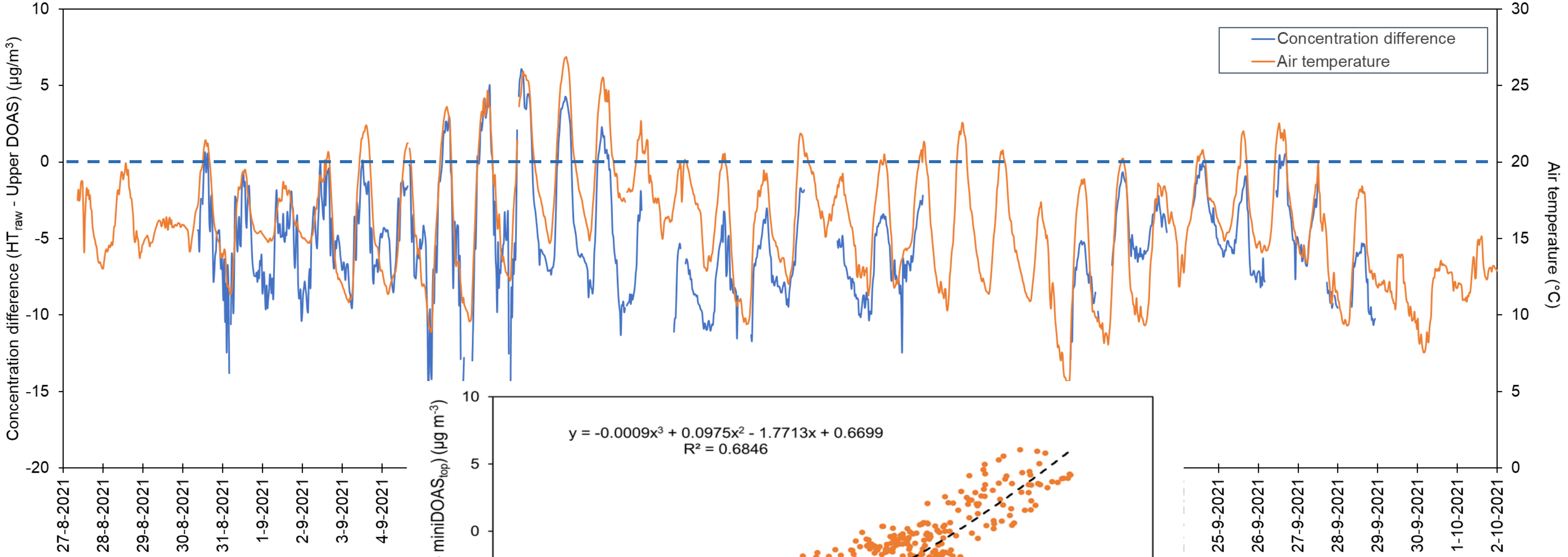
- Corrections needed:
  - Concentration offset
  - Density changes (WPL)
  - Missed flux due to not measuring small eddies (dampening)
- Instrument in the testing phase at Dutch field

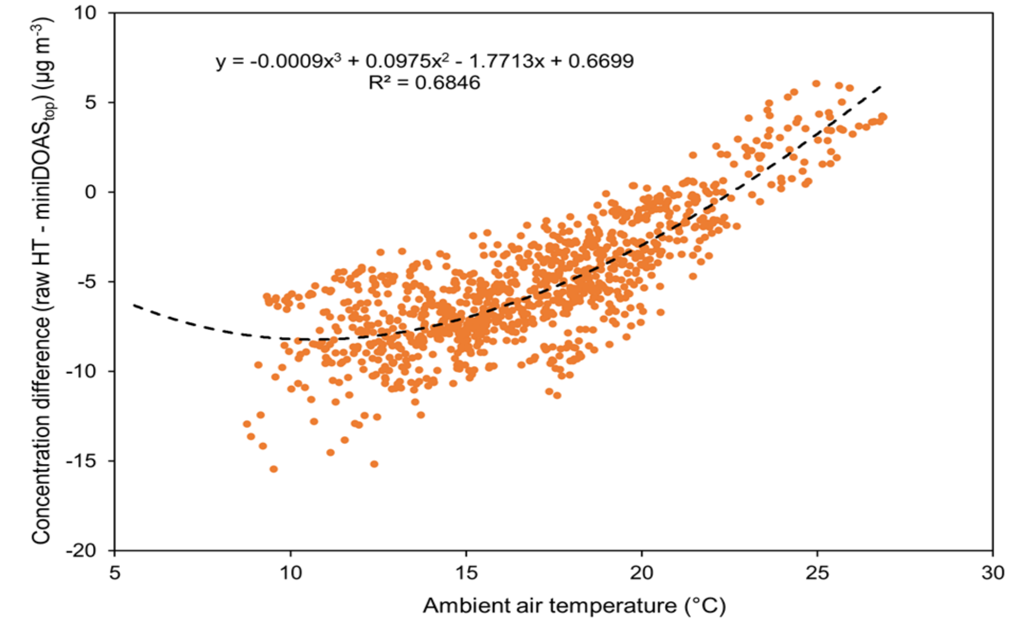
Measured concentrations

HT MEASURED CONCENTRATION SLOWLY CHANGES WITH AIR TEMPERATURE



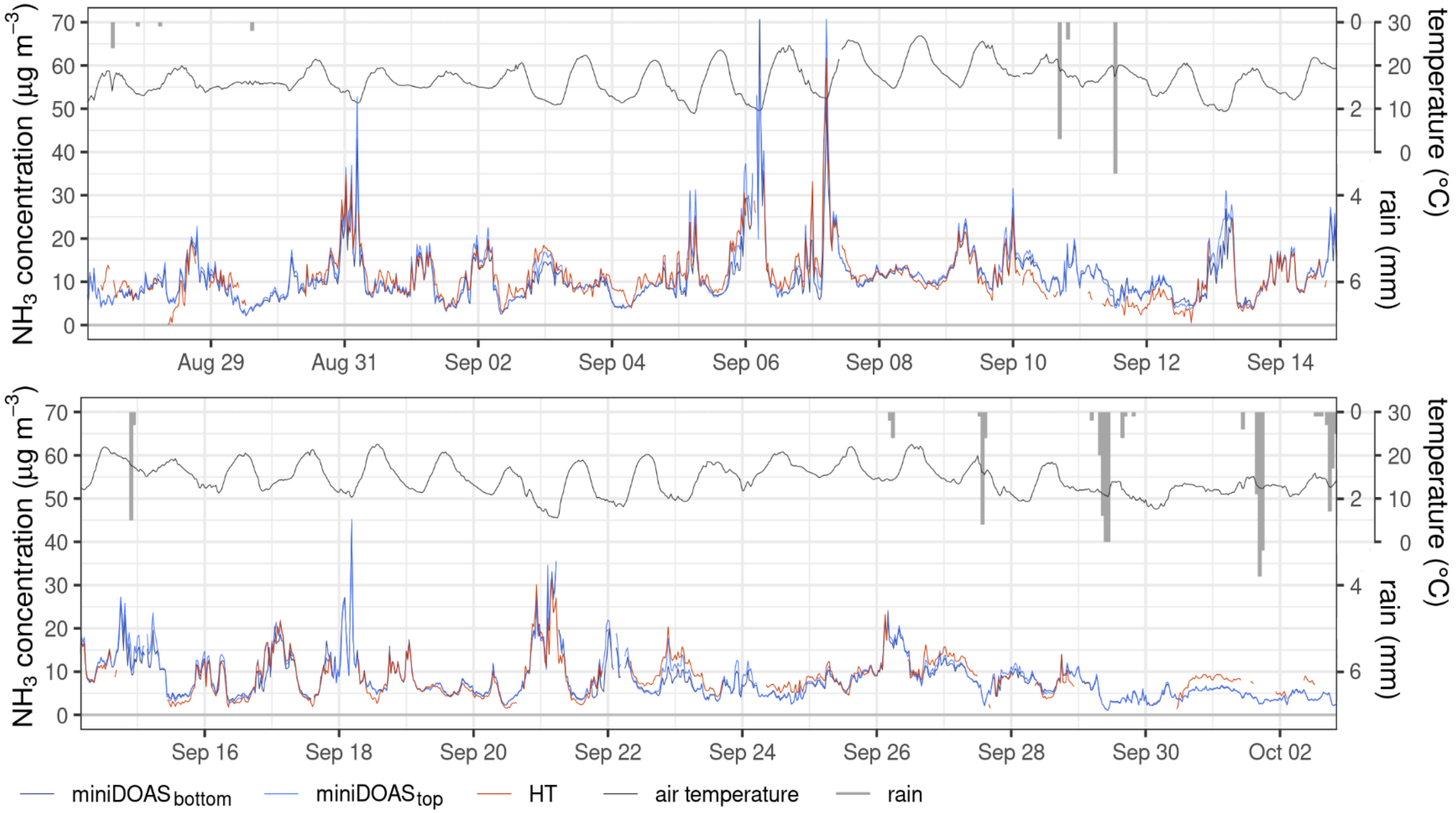
HT MEASURED CONCENTRATION SLOWLY CHANGES WITH AIR TEMPERATURE

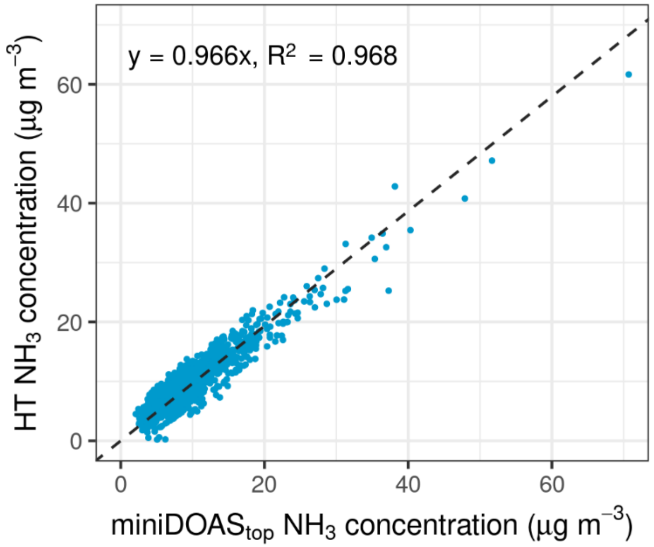




Measured concentration comparison

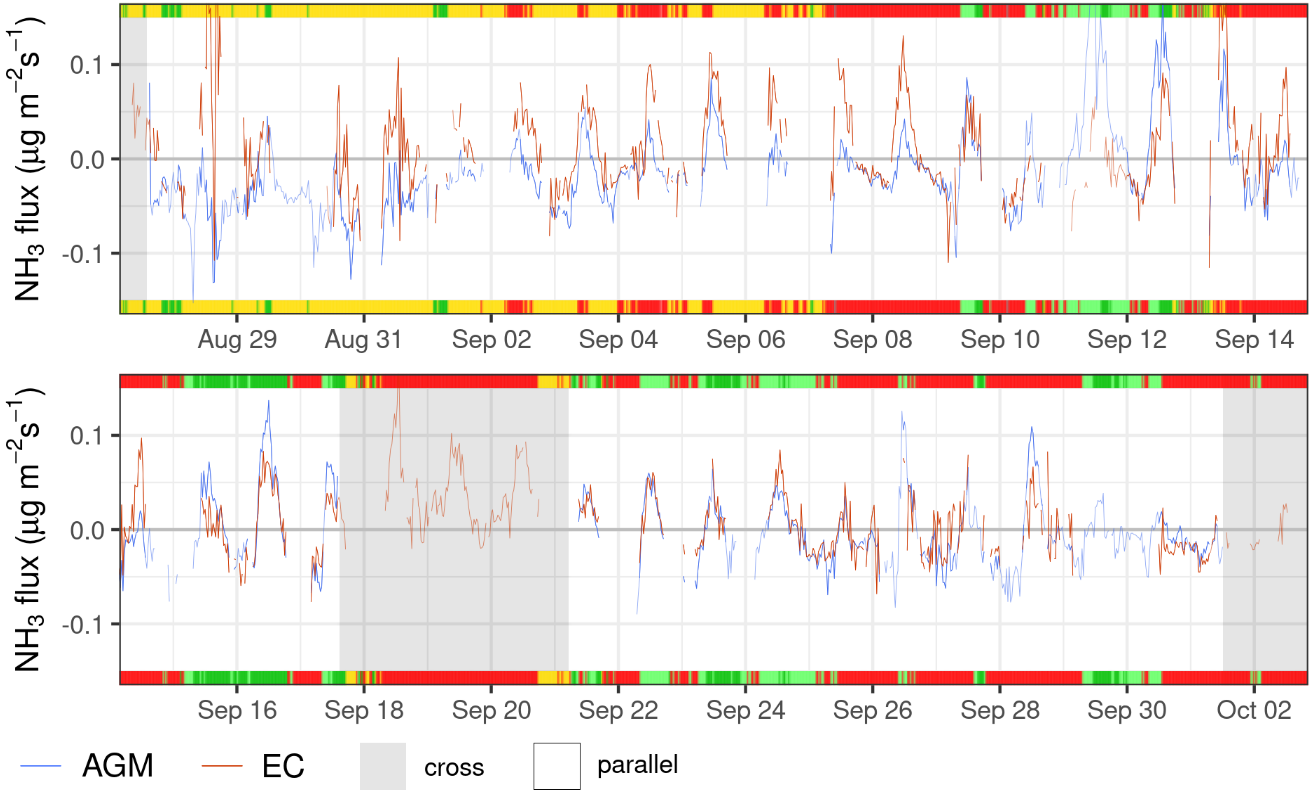
AFTER HT-TEMPERATURE CORRECTION: HIGHLY COMPARABLE

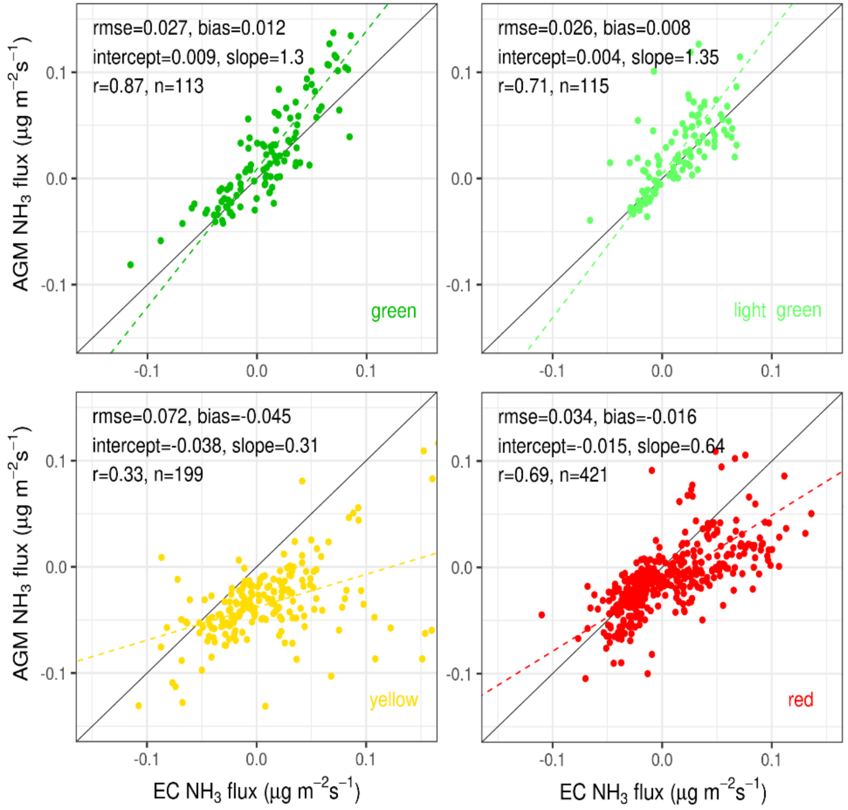




Measured NH_3 fluxes comparison

OBSTACLE-FREE AREA: HIGHLY COMPARABLE





$$F_{AGM} = -\frac{k u_*}{\ln\left(\frac{z_2}{z_1}\right) - \Psi_H\left(\frac{z_2}{L}\right) + \Psi_H\left(\frac{z_1}{L}\right)} \times \left[c_{NH_3}(z_2) - c_{NH_3}(z_1)\right] \quad \text{(Eq. 1)}$$

$$F_{EC} = A\left[\overline{w'\rho'_A} + B\mu\frac{\rho_A}{\rho_d}\overline{w'\rho'_v} + C\left(1 + \mu\frac{\rho_v}{\rho_d}\right)\frac{\rho_A}{T_a}\overline{w'T'_a}\right] \quad \text{(Eq. 2)}$$

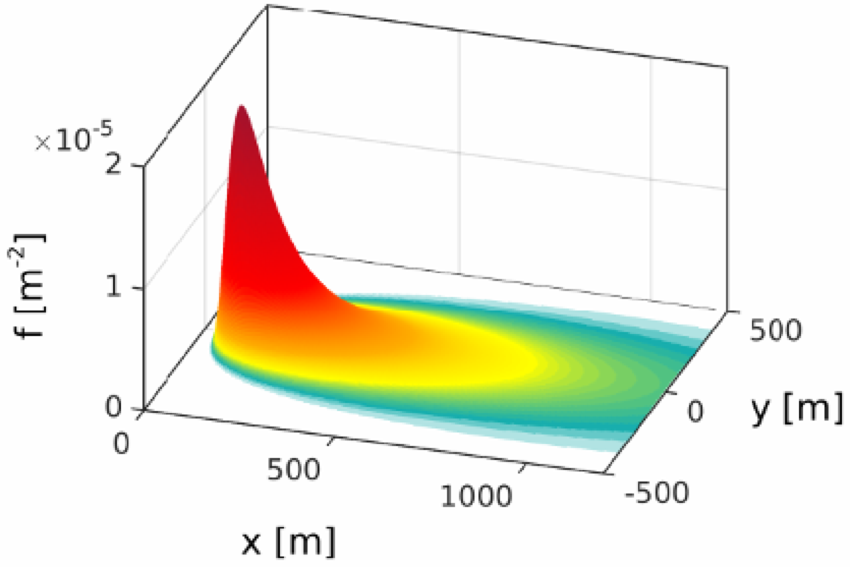
Potential cause of flux difference

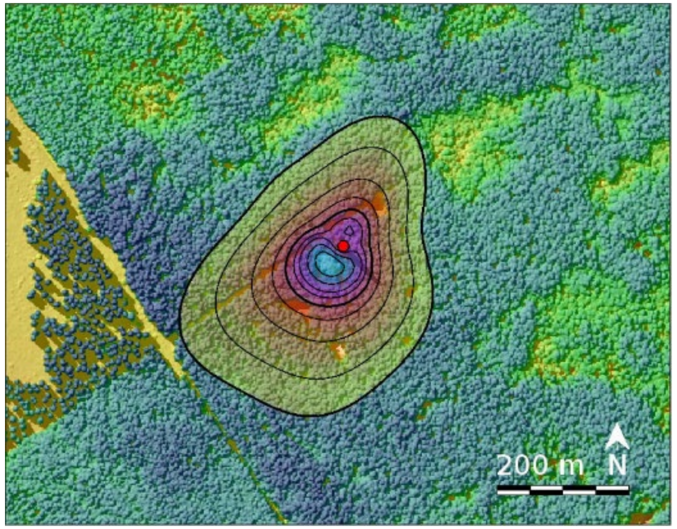
FLUX FOOTPRINT ANALYSIS

Flux footprint is the upwind area where the atmospheric flux measured by an instrument is generated. Specifically, the term flux footprint describes an upwind area "seen" by the instruments measuring vertical turbulent fluxes.

Three main factors affecting the size and shape of flux footprint:

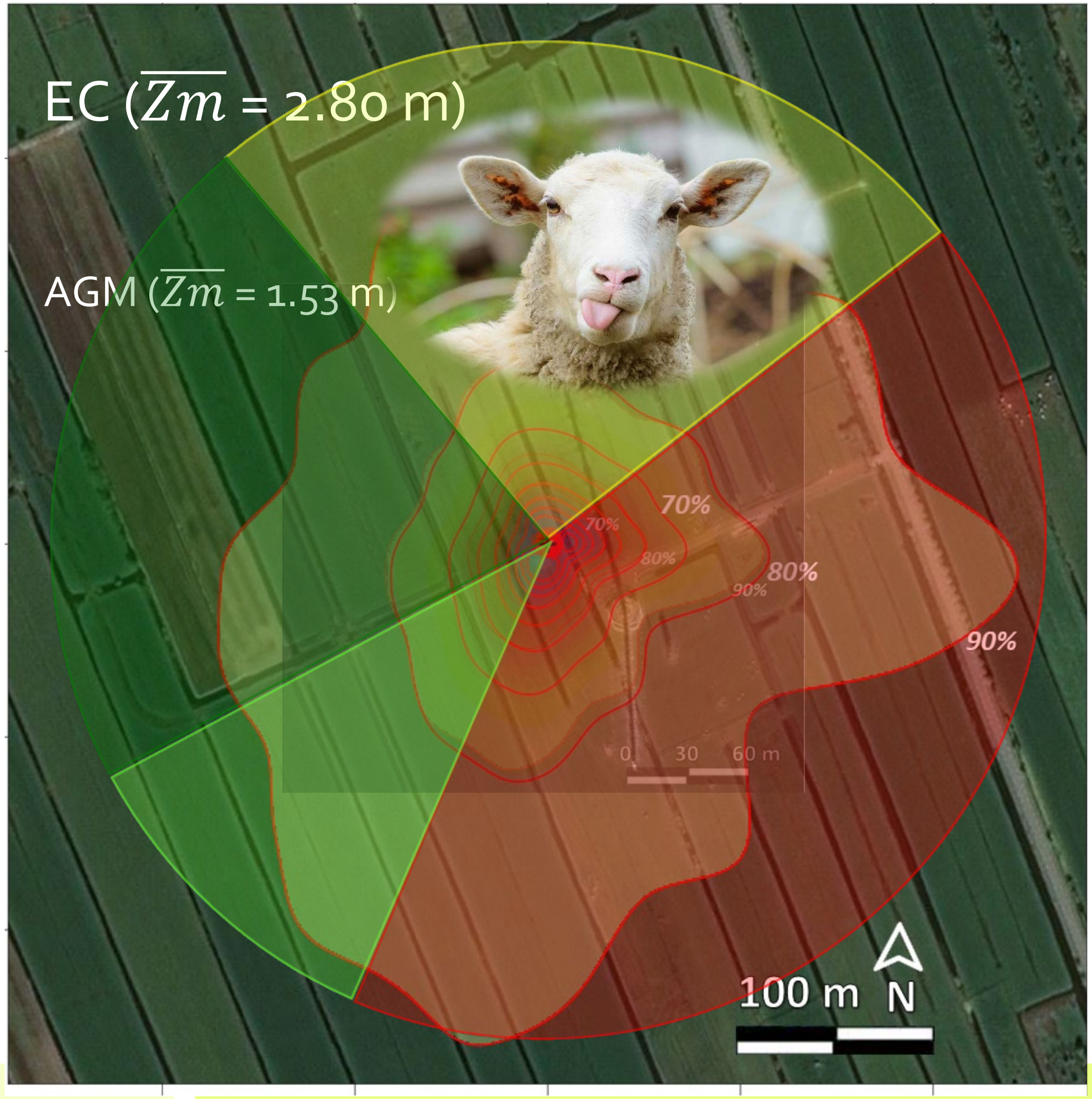
- measurement height
- surface roughness
- atmospheric thermal stability

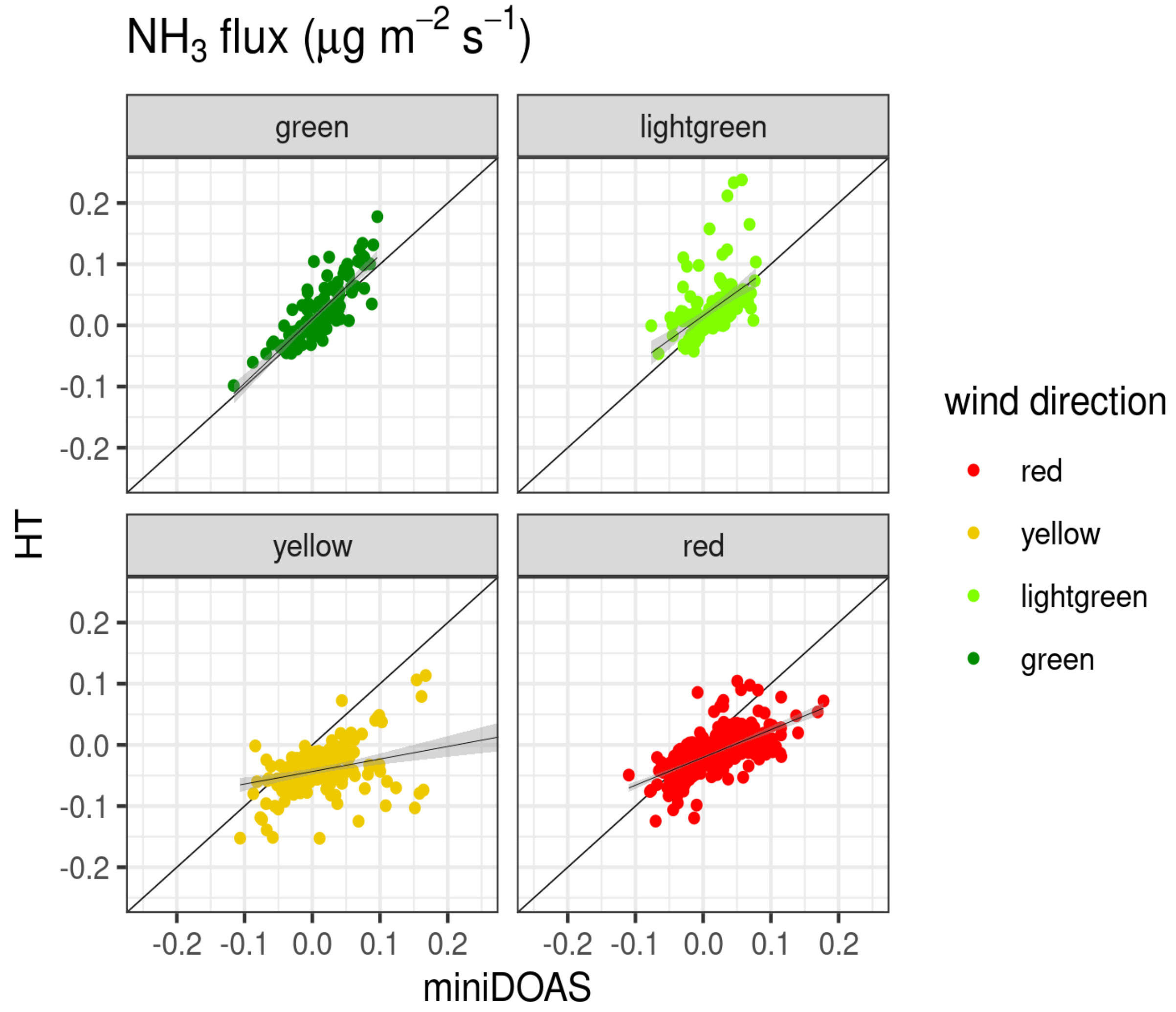




(Figure from https://footprint.kljun.net/)

Footprint and homogeneity: key factors influencing flux comparison

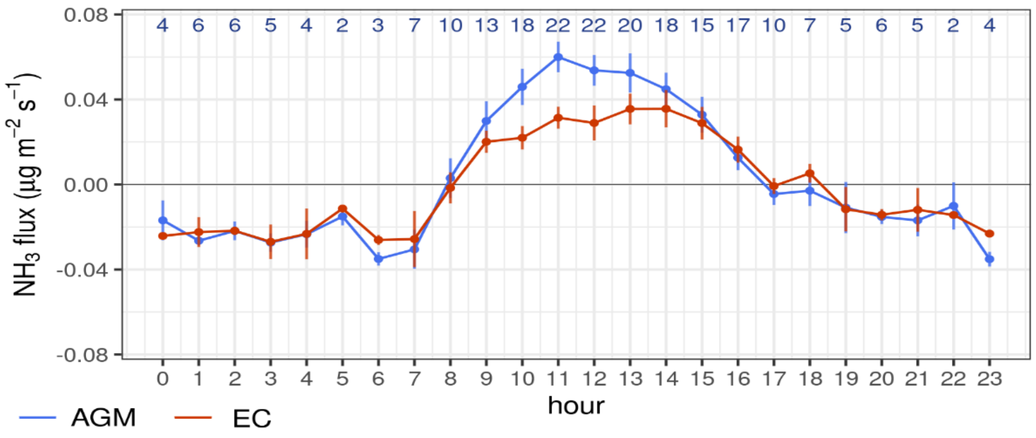




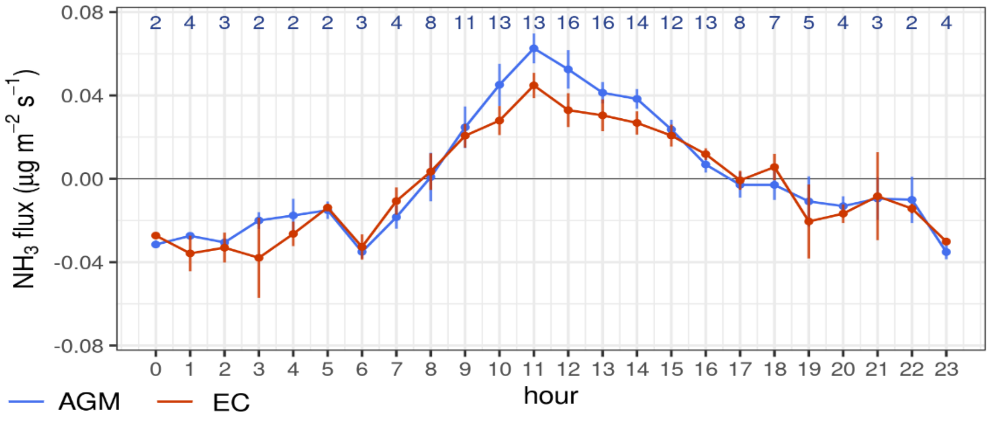
Measured NH_3 fluxes comparison

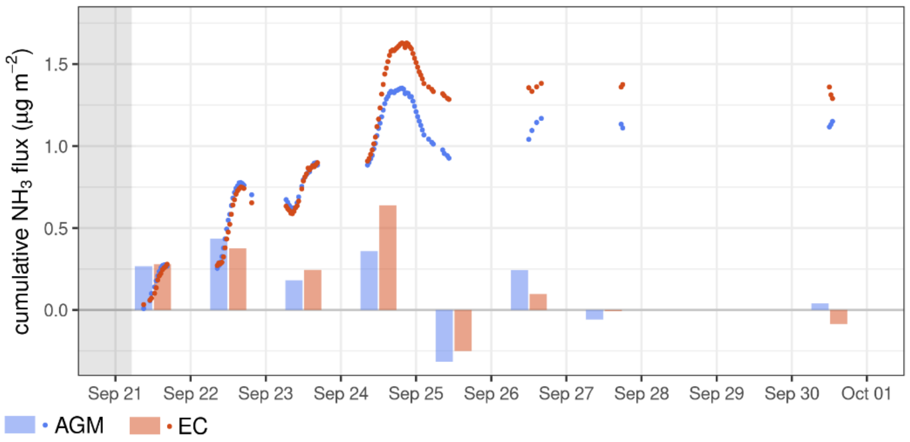
DIURNAL CYCLE OF AGM AND EC NH_3 FLUX: COMPARABLE

Whole period



Only after Sep. 15: farm manuring stopped



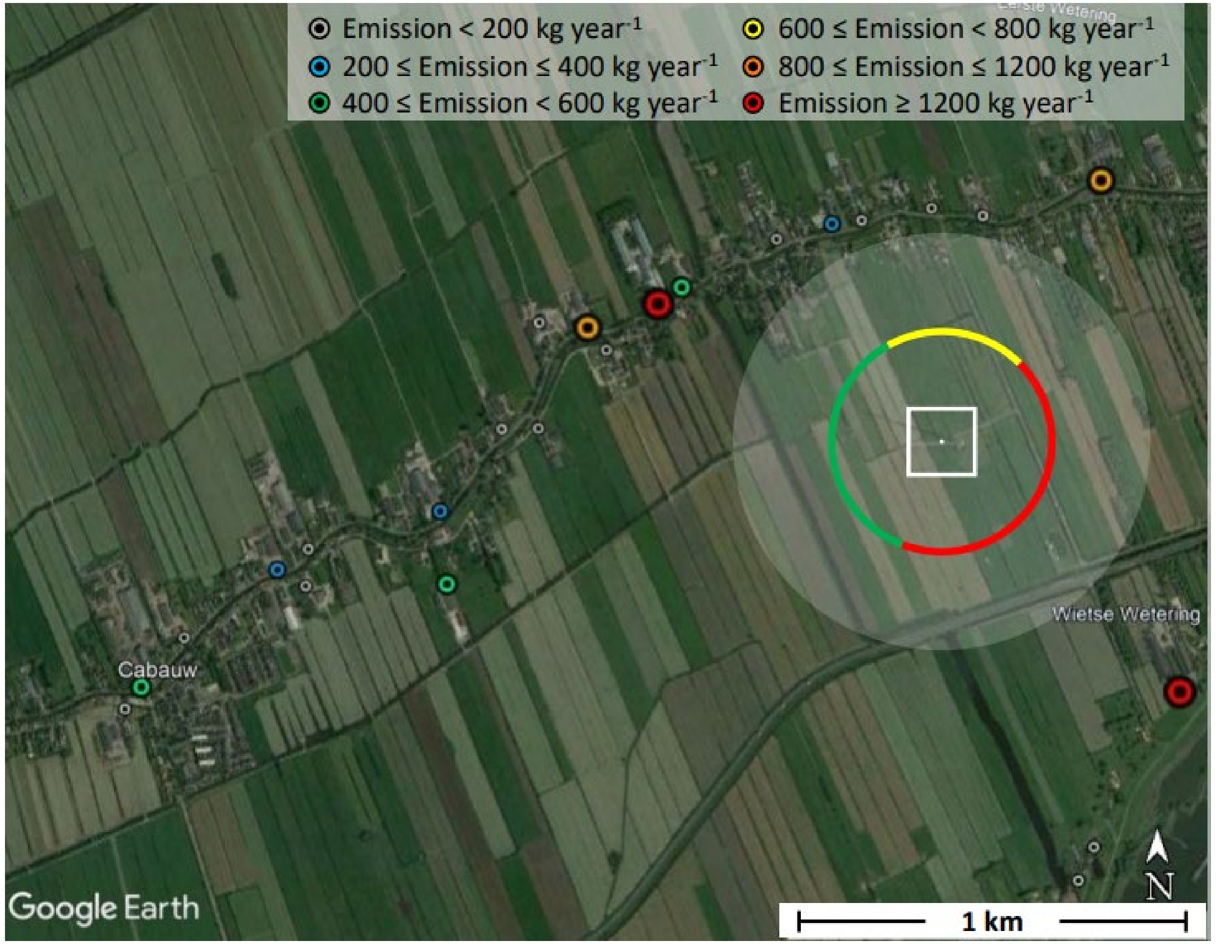


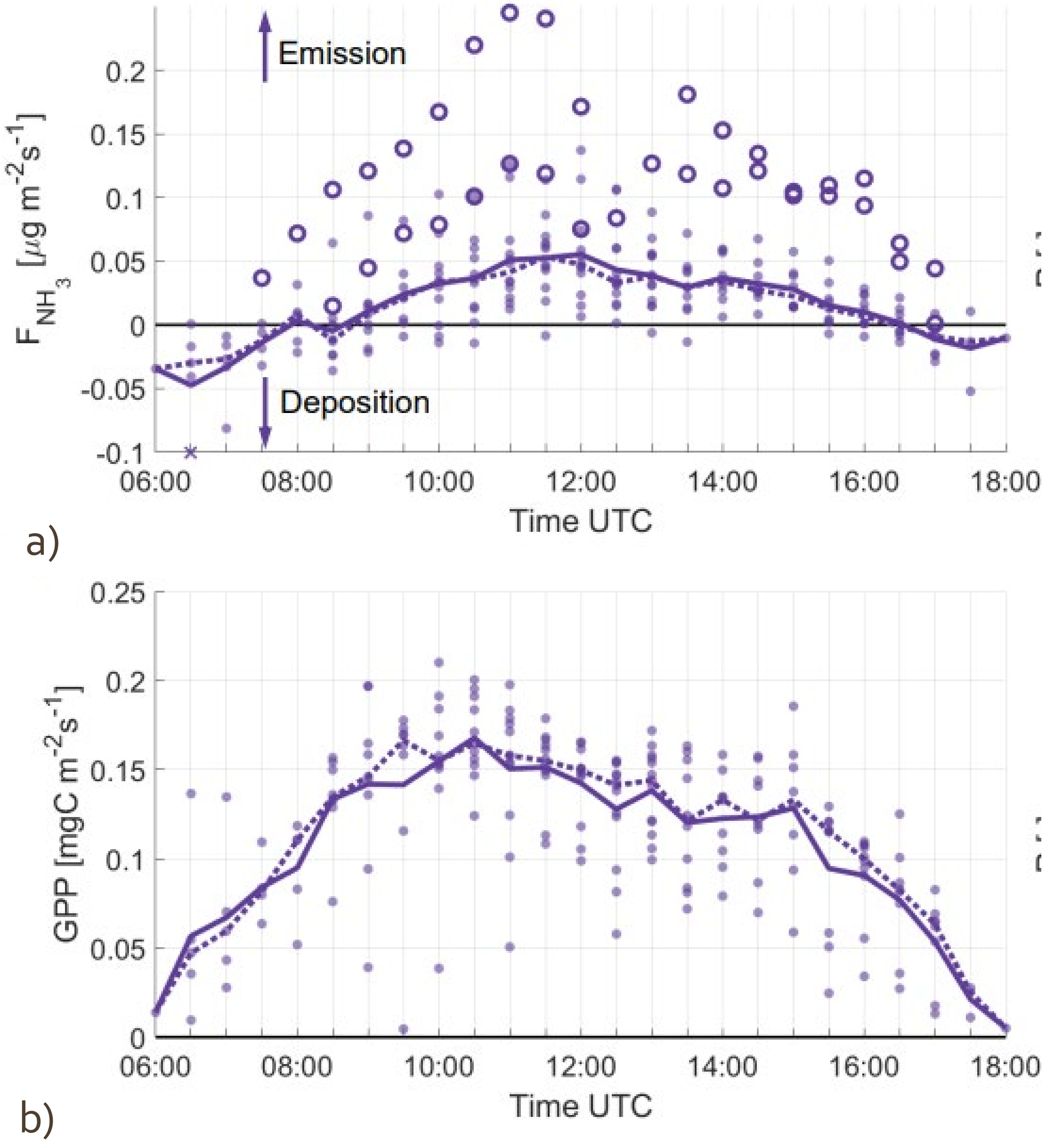
innovation for life

Lessons learned from this Campaigen

- Half-hourly measurements proved feasible.
- Both instruments show:
  - Comparable deposition values
  - Similar structures of time series and diurnal cycles
- MiniDOAS had ~100% uptime outside calibration periods (~35% of the total period).
- HT data loss during rain (~21% of the total period), and mirror deterioration
- Although HT measured concentration is sensitive to air temperature, it almost had no impact on its fluxes.

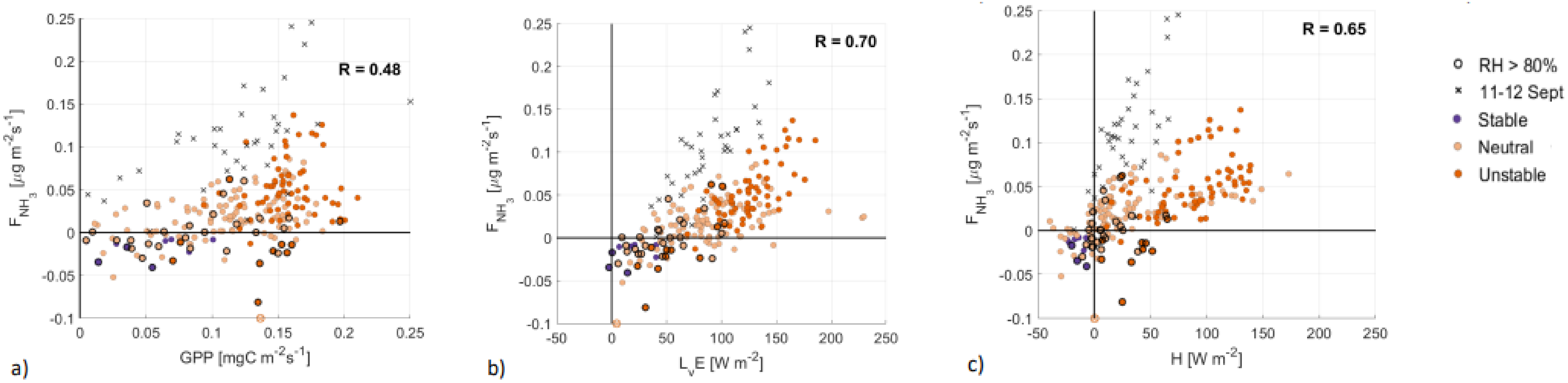
Observational relationships between NH_3 and GPP





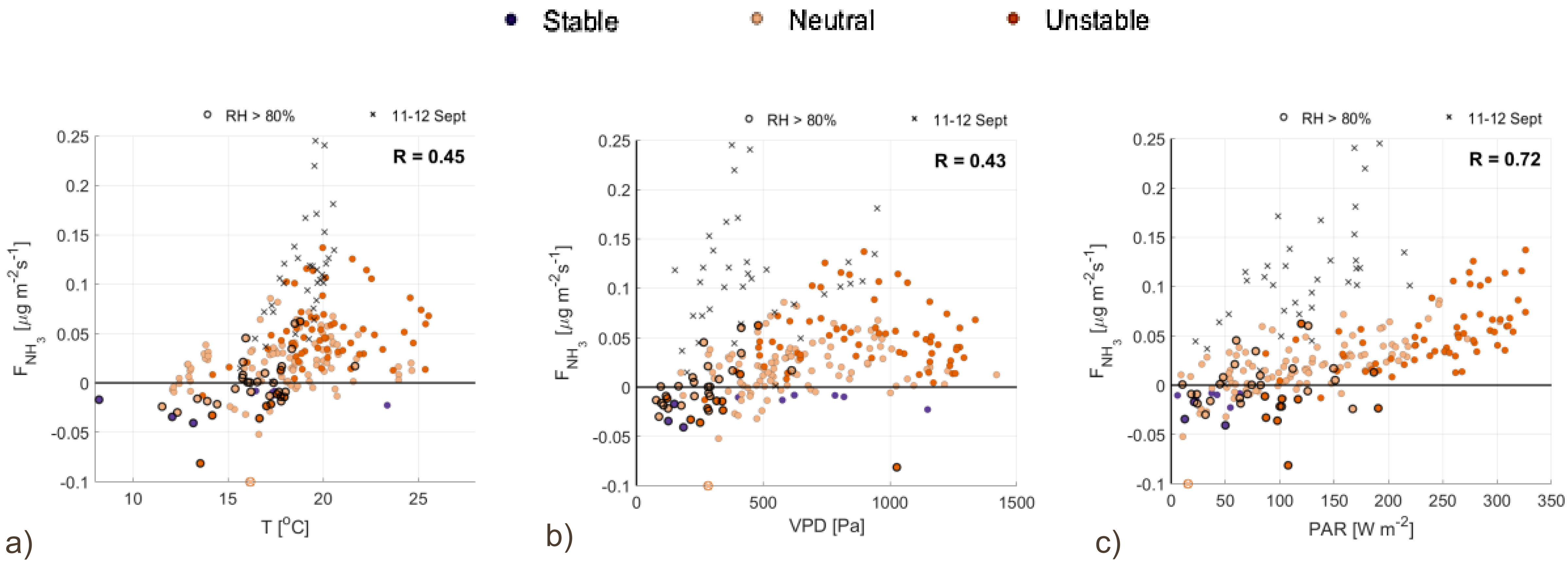
Schulte et al, 2023. Observational relationships between NH3, CO2 and evapotranspiration https://doi.org/10.5194/egusphere-2023-1526

Observational relationships between NH_3 ,CO_2 and ET



- There are relationships between the observed NH_3 flux and the other turbulent surface fluxes such as sensible heat flux and photosynthesis, i.e. the stomatal exchange of CO_2 and water vapor (plant transpiration).
- The process of photosynthesis has been more widely studied and such observations can be used to advance our understanding of NH_3 *surface-atmosphere exchange through the individual exchange pathways, e.g. stomatal exchange*.

Schulte et al, 2023. Observational relationships between NH3, CO2 and evapotranspiration. https://doi.org/10.5194/egusphere-2023-1526

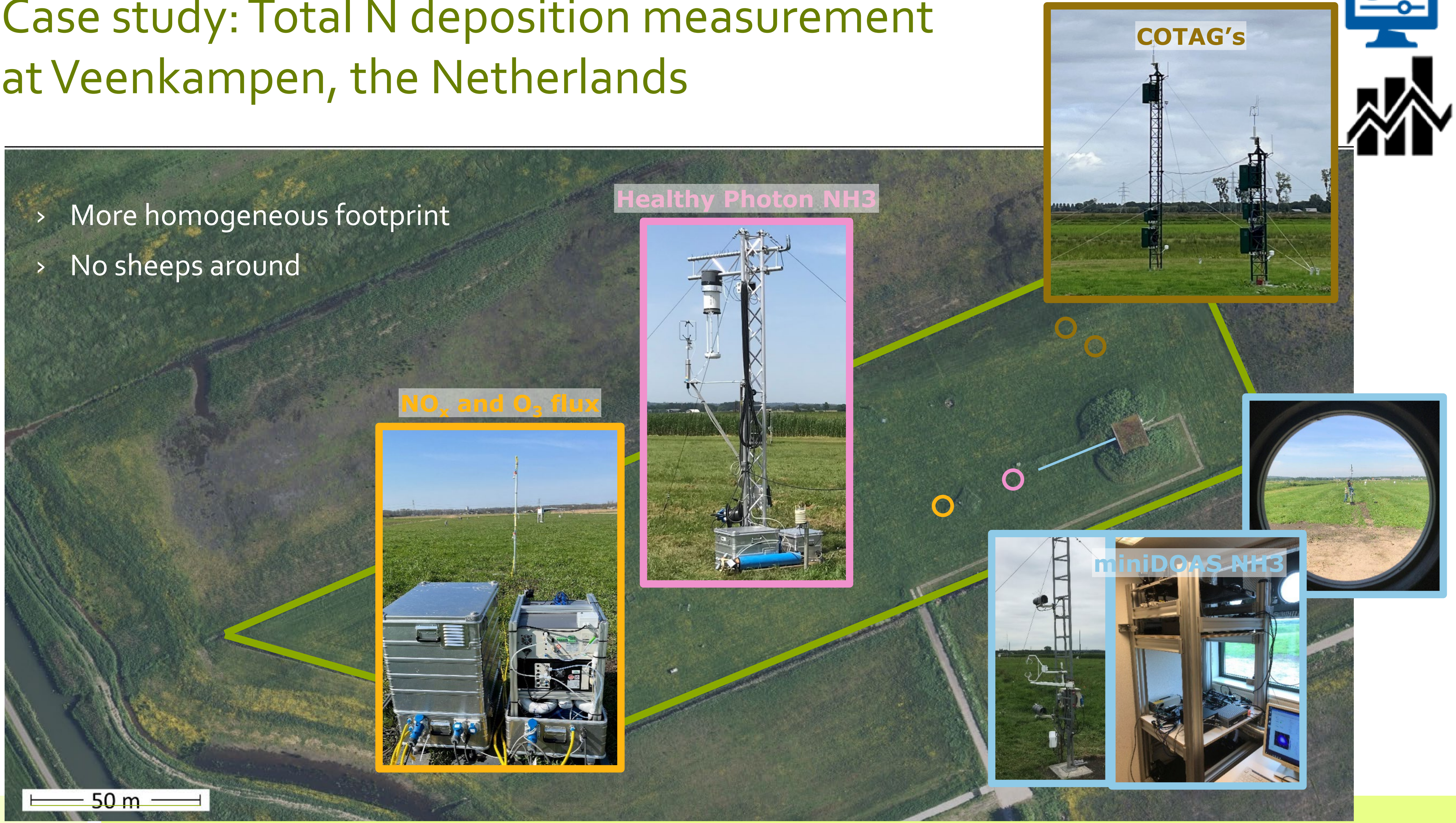


- There is high correlation between the observed daytime NH3 emissions and LE (0.70) and the photosynthetically active radiation (PAR, 0.72). These results provide a first order quantification of stomatal emission of NH_3.
- It shows that collocated flux measurements of CO_2 and water vapor are appropriate variables to ***distinguish stomatal NH_3 exchange from non-stomatal exchange***.

The 2nd case study in the Netherlands

Case study: Total N deposition measurement at Veenkampen, the Netherlands

- More homogeneous footprint
- No sheeps around



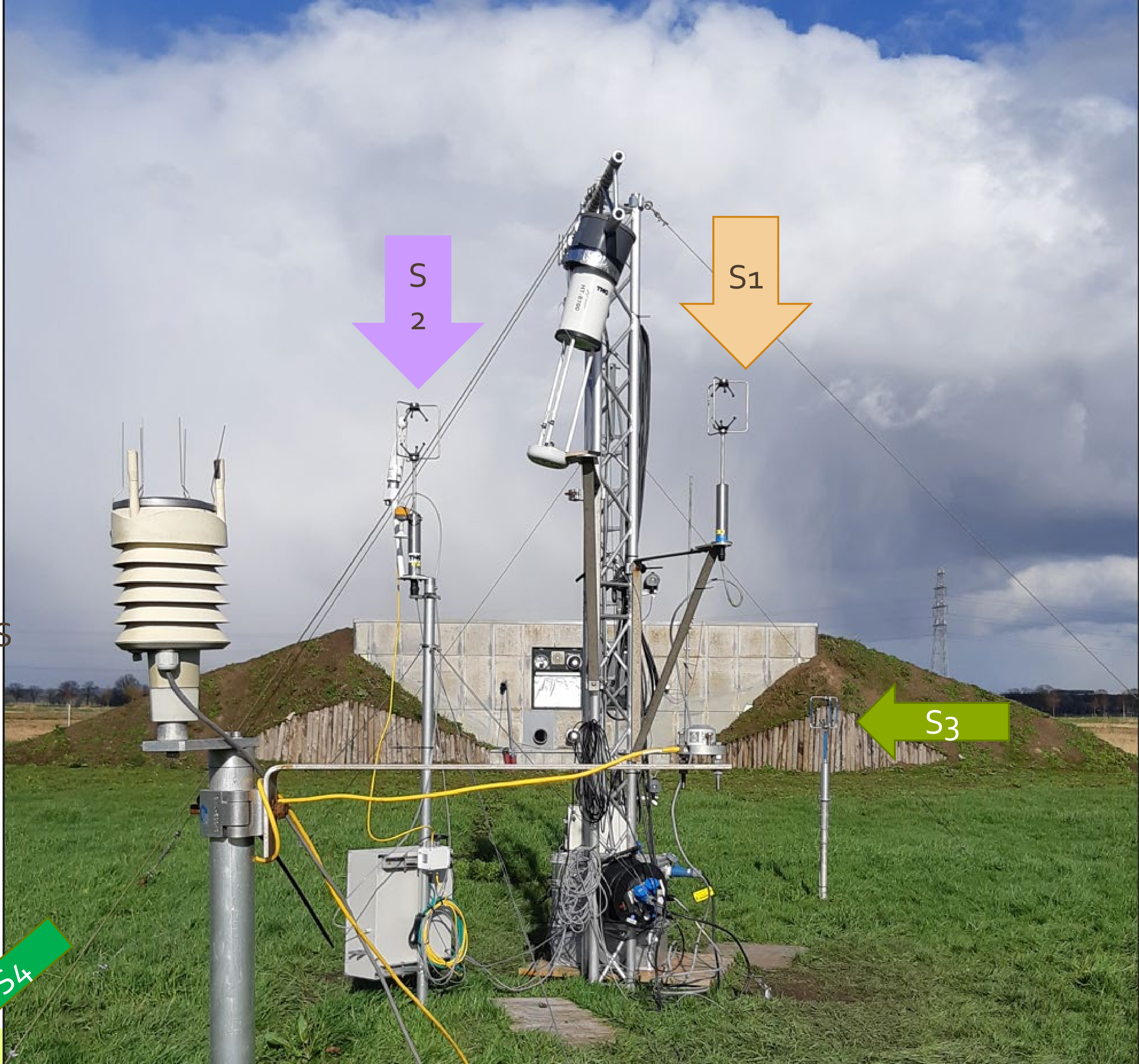
Veenkampen

2 sonics from TNO at 2.6 m , 2.8 m height

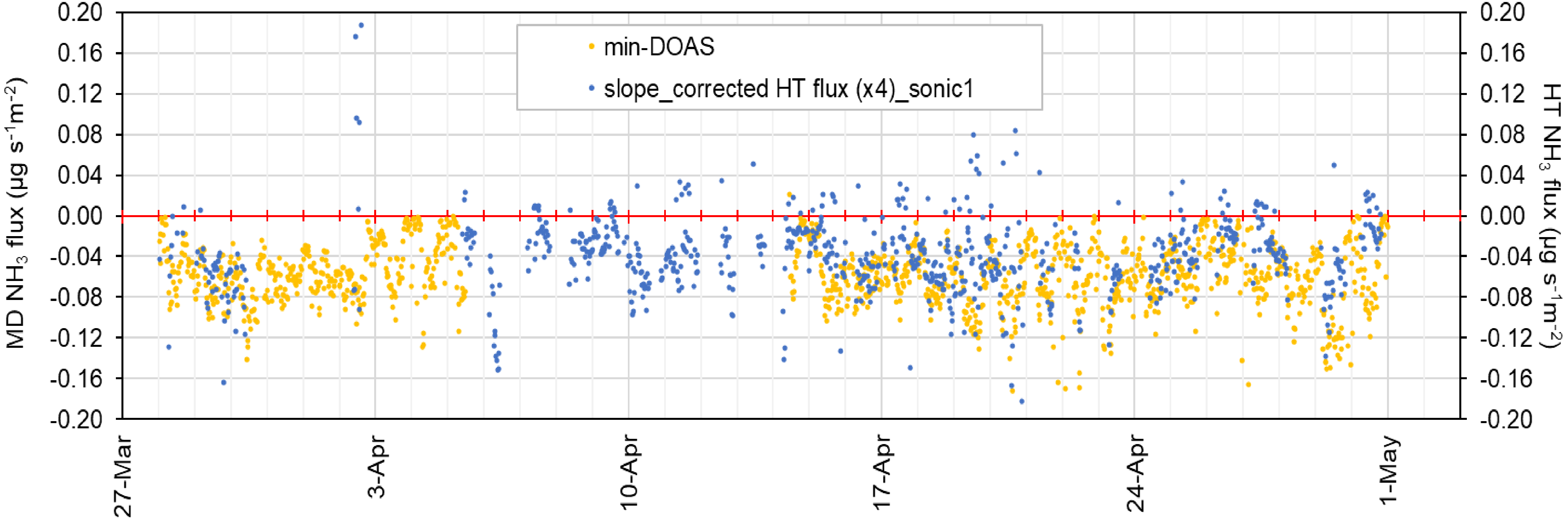
SONIC 1_72 cm from HT_165 cm from LICOR-7500
SONIC 2_65 cm from HT_15 cm from LICOR7500

S3: from RIVM at 1.6 m height: close to miniDOAS

S4: from WUR at xx height, > 50 m away in SW



Compare HT*-MD measured fluxes
(note: corrected HT flux as primary result)



Two systems – two methods both show deposition flux at the site.

Auto-NH_3 Chamber measurement ?

2023 August
Evergreen Needleleaf Forests
NH_3 flux measuring at ICOS station

ICOS- the Integrated Carbon Observation System, is a European-wide greenhouse gas research infrastructure

ICOS NETHERLANDS

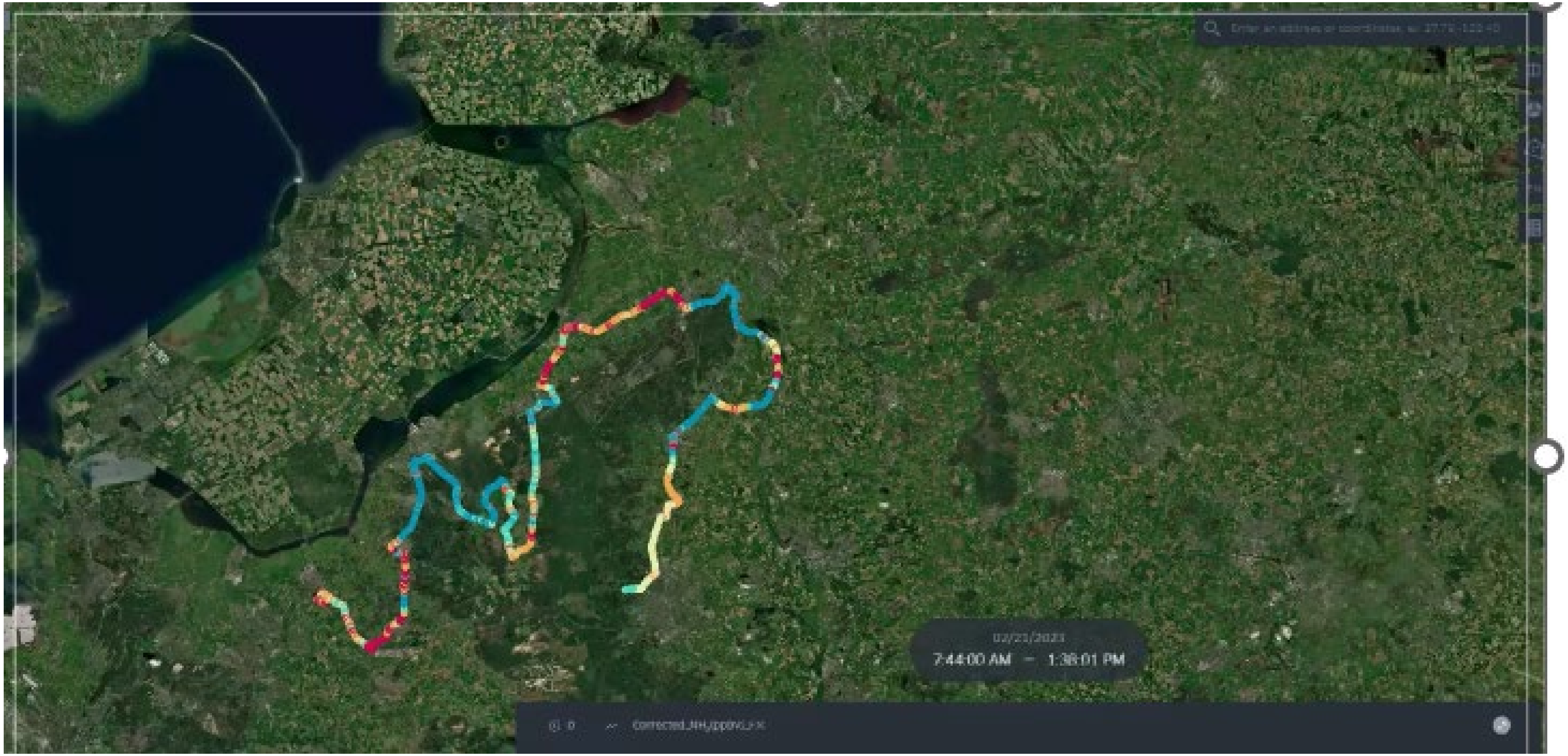
Loobos

ONE OF THE WORLD'S OLDEST CONTINUOUSLY RUNNING MEASUREMENT SITES


Ammonia deposition impacts on biodiversity ?
NH3 emission source inventory through mobile measurement

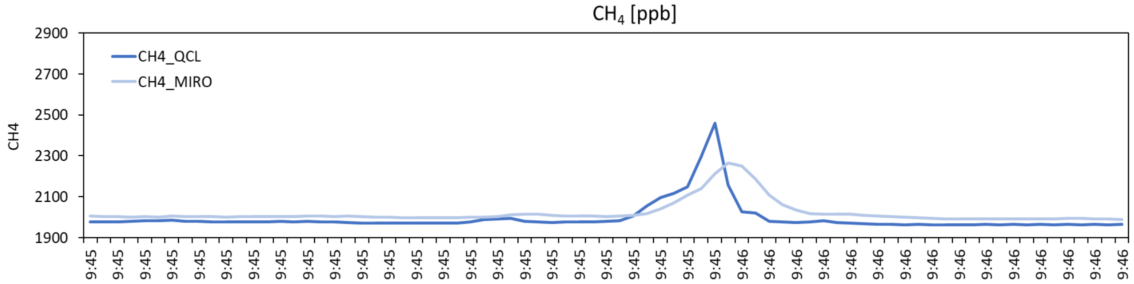

TNO
Ruisdael
observatory
Environmental Research; Petten, The Netherlands
HT-8700

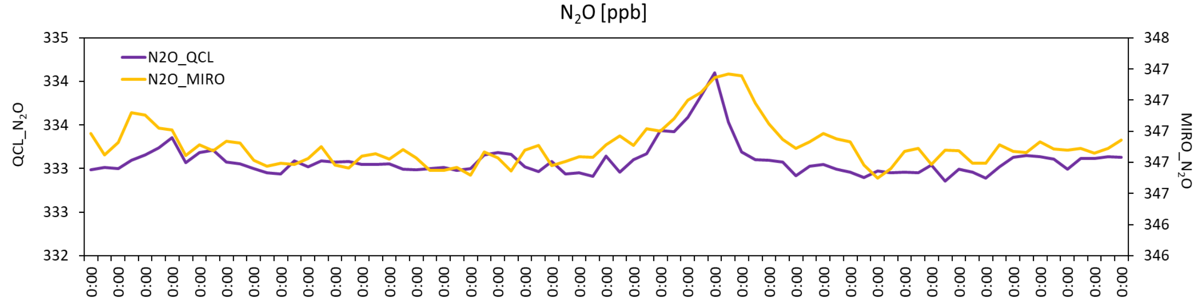

HT measured NH_3 concentration at Veluwe area

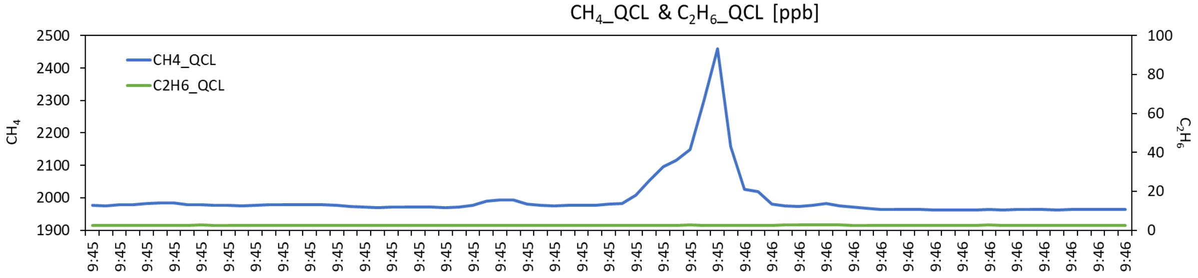


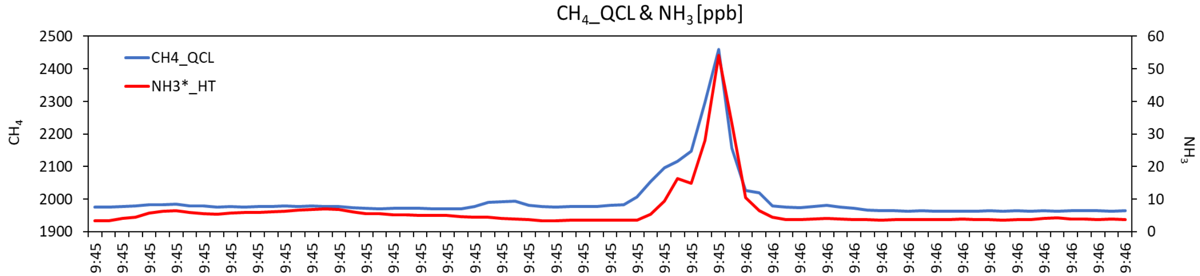
Peak #1: upwind is a pig farm

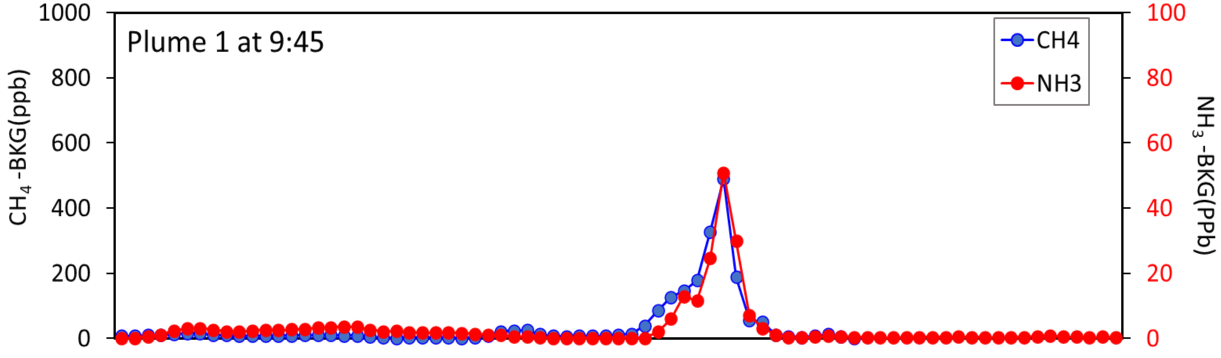
peak #1: Upwind is a pig farm

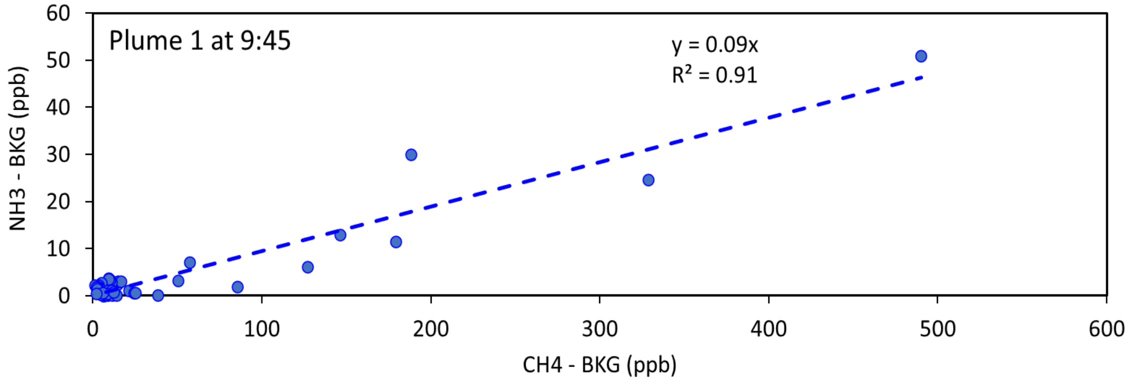








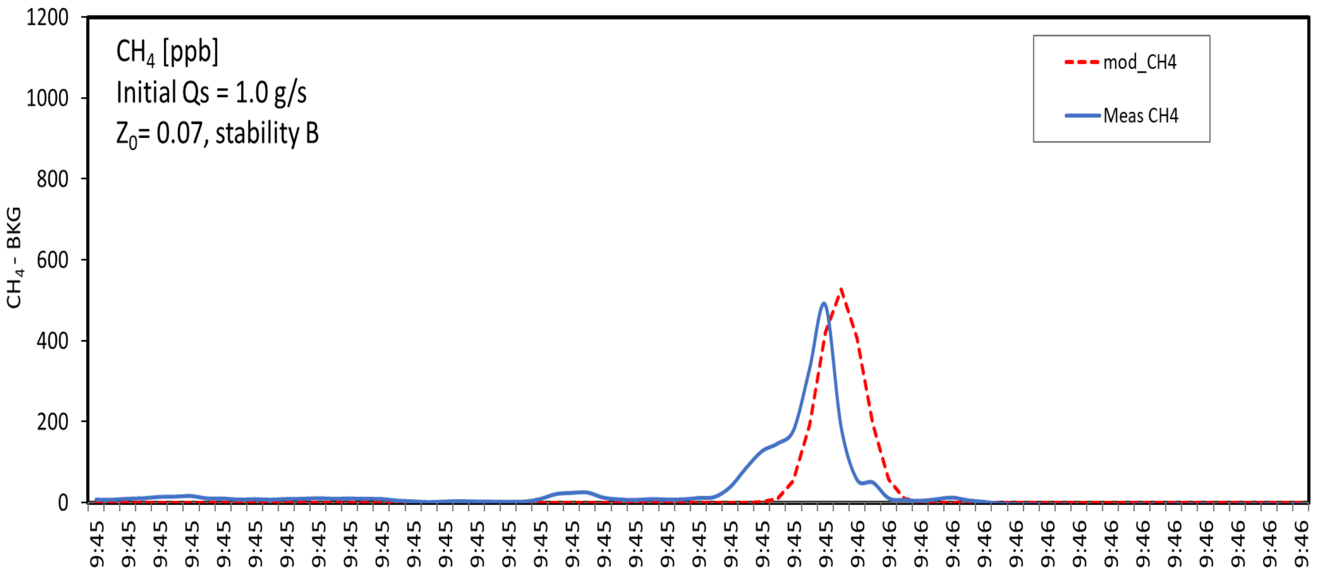




*N_2O peak from the same source – possible with open wet soil.

Modelled emission

Plume No.	Possible source type	Modelled NH3 emission (g/s)	Modelled CH4 emission (g/s)	NH_3/CH_4 concentration peaks ratio	NH_3/CH_4 emission ratio
1	pig farm	**0.13**	**1.08**	0.09	0.12



Conclusions

- Climate change and Nitrogen crisis is strongly connected.
- Dry NH_3 deposition contributes to a large portion to total nitrogen deposition.
- NH_3 are the most challenging gas to be measured.
- Innovative equipment is available to use now.
- The methods (even EC method) to calculate N – fluxes still have their limitations.
- Development are still needed in both flux measurement instruments and analytical methods.
- Bridges between **C**arbon – **N**itrogen communication still need to be established.

innovation for life

Thanks for your attention!

Acknowledgement:
Dr. Kai Wang from CAS, Atmospheric Science, CN
Prof. dr. Arjan Hensen, Dr. Pascal Wintjen, Drs. Arnoud Frumau, Pim van den Bulk from TNO, NL
Dr. Daan Swart, Dr. Susanna Jonker, Dr. Ruben Schulte, Dr. Shelley van der Graaf, Dr. Stijn Berkhout, René van der Hoff, Marty Haaima, Thomas van Goethem from RIVM, NL