陆地生态系统N_2O排放研究方法

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2012.12.27, 南京信息工程大学

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- Atmospheric N_2O & its effects
- Global budget & uncertainties
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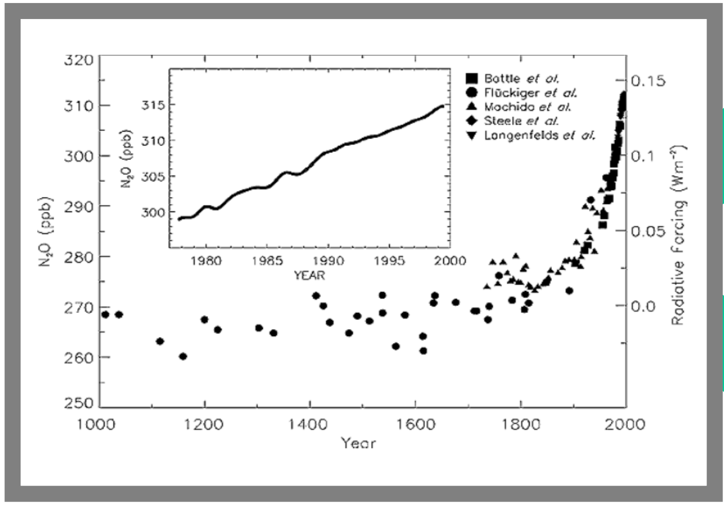
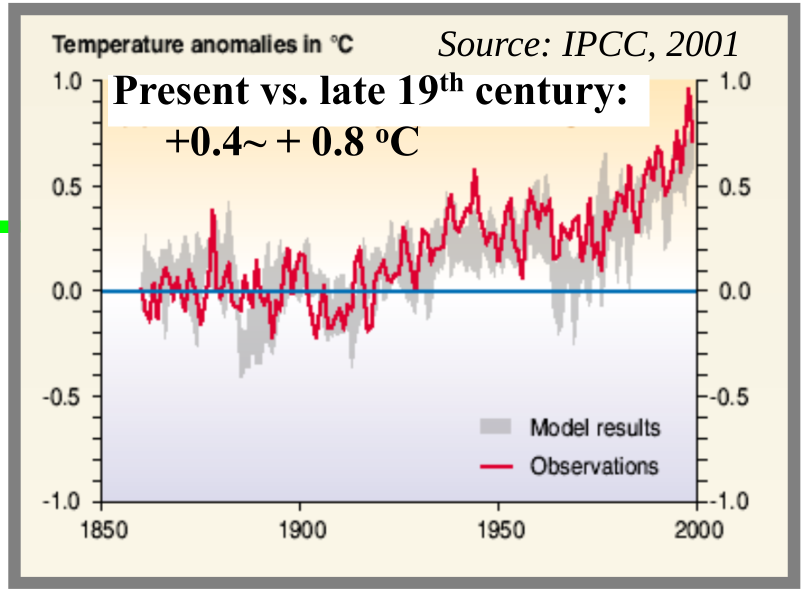
- Process study
- Field measurement
- Model simulation

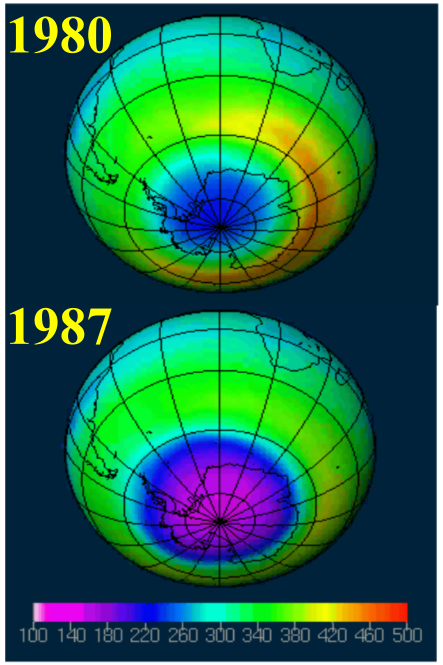
Research methodologies

N_2O effects





O_3
Hole



N_2O

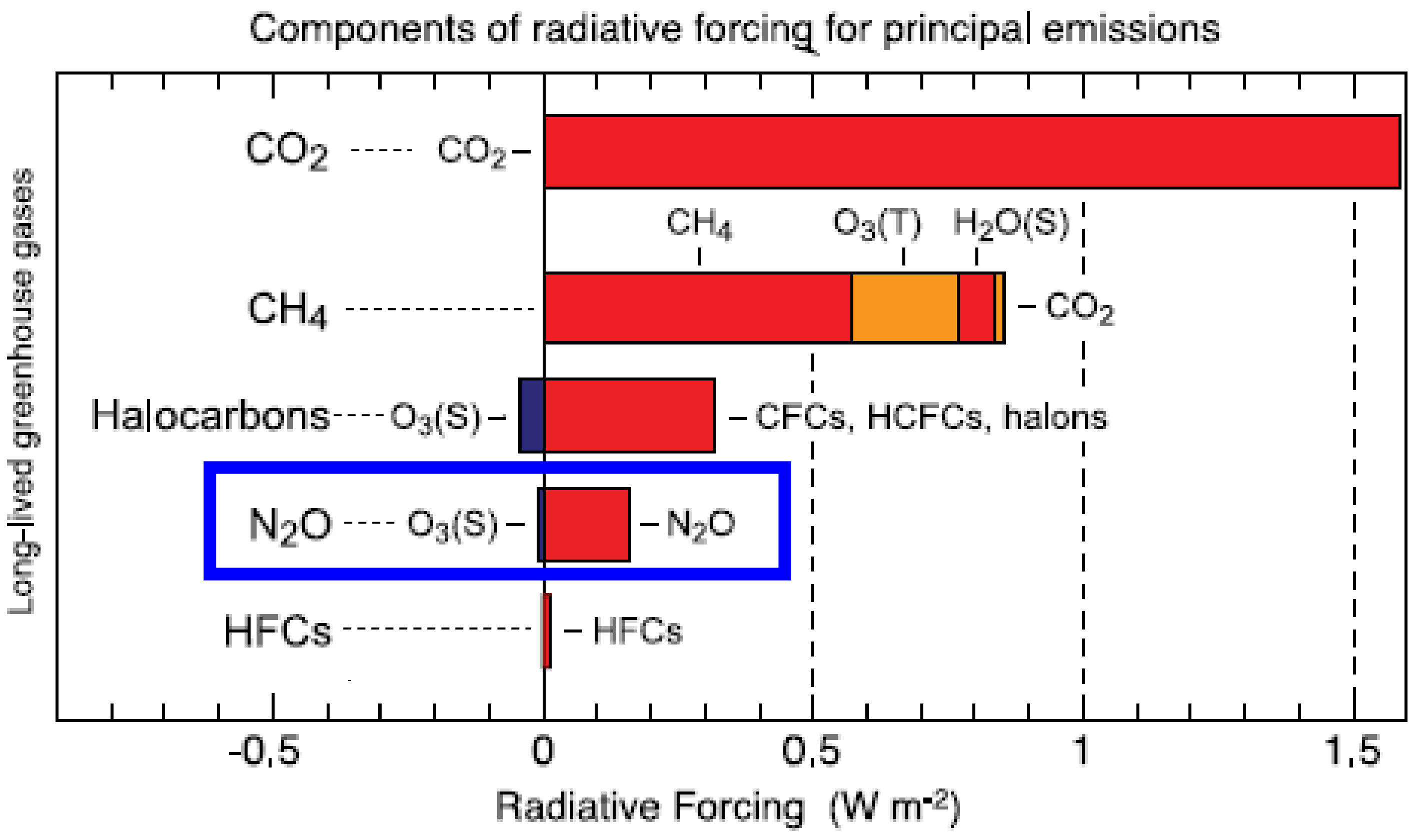
Environmental N enrichment
due to anthropogenic activity

N_2O: a long-lived greenhouse gas in troposphere

	N_2O	CH_4	CO_2
Pre-industrial era con. (ppbv):	~ 275	~700	~280000
Present con. (ppbv):	319	1774	379000
Annual inrease (%/yr^{-1}):	0.25	0.6	0.4
Life time (yr):	114	12	50-200
Specific GWP (100 yr):	298	25	1

Source: IPCC, 2007

Warming effect of N_2O

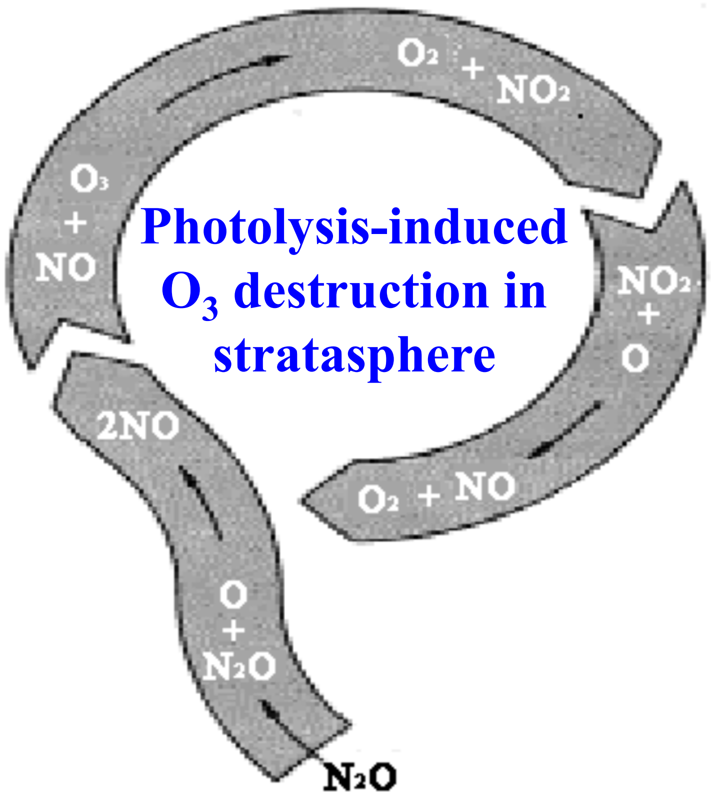


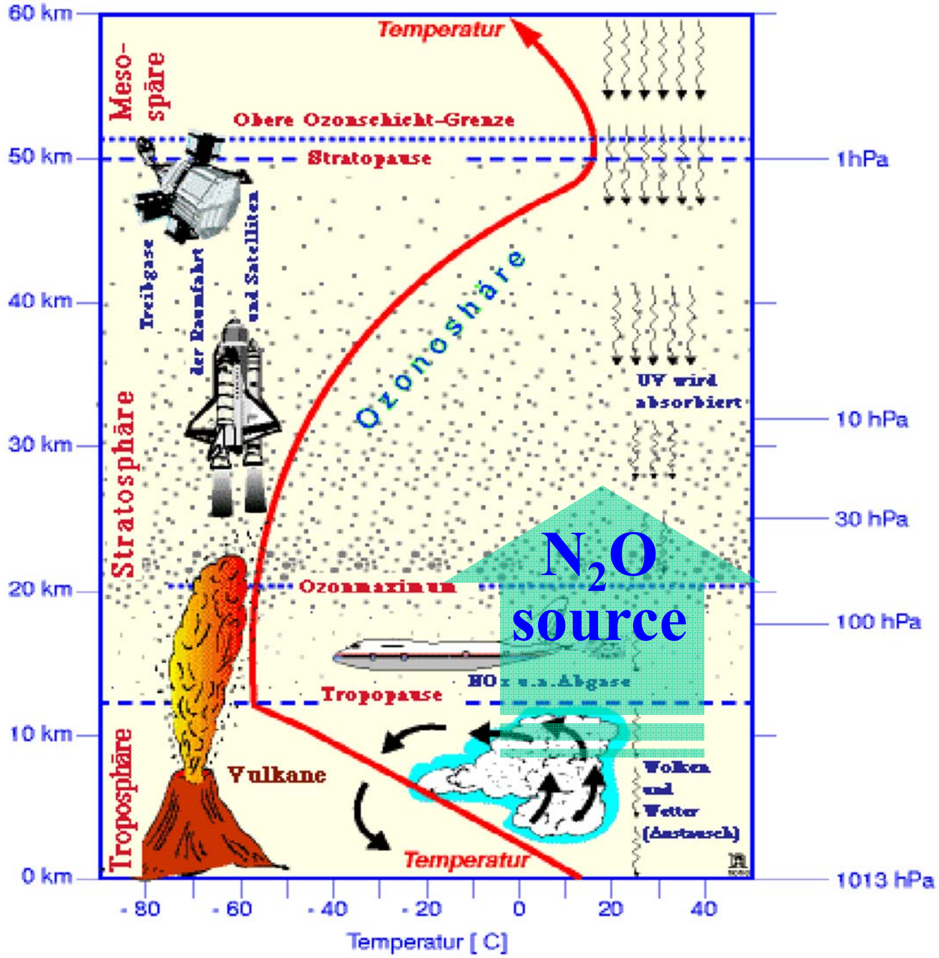
Net radiative forcing of N_2O (since 1750): 0.16 w m^{-2}

(~ 6% of long-lived GHG's radiative forcing)

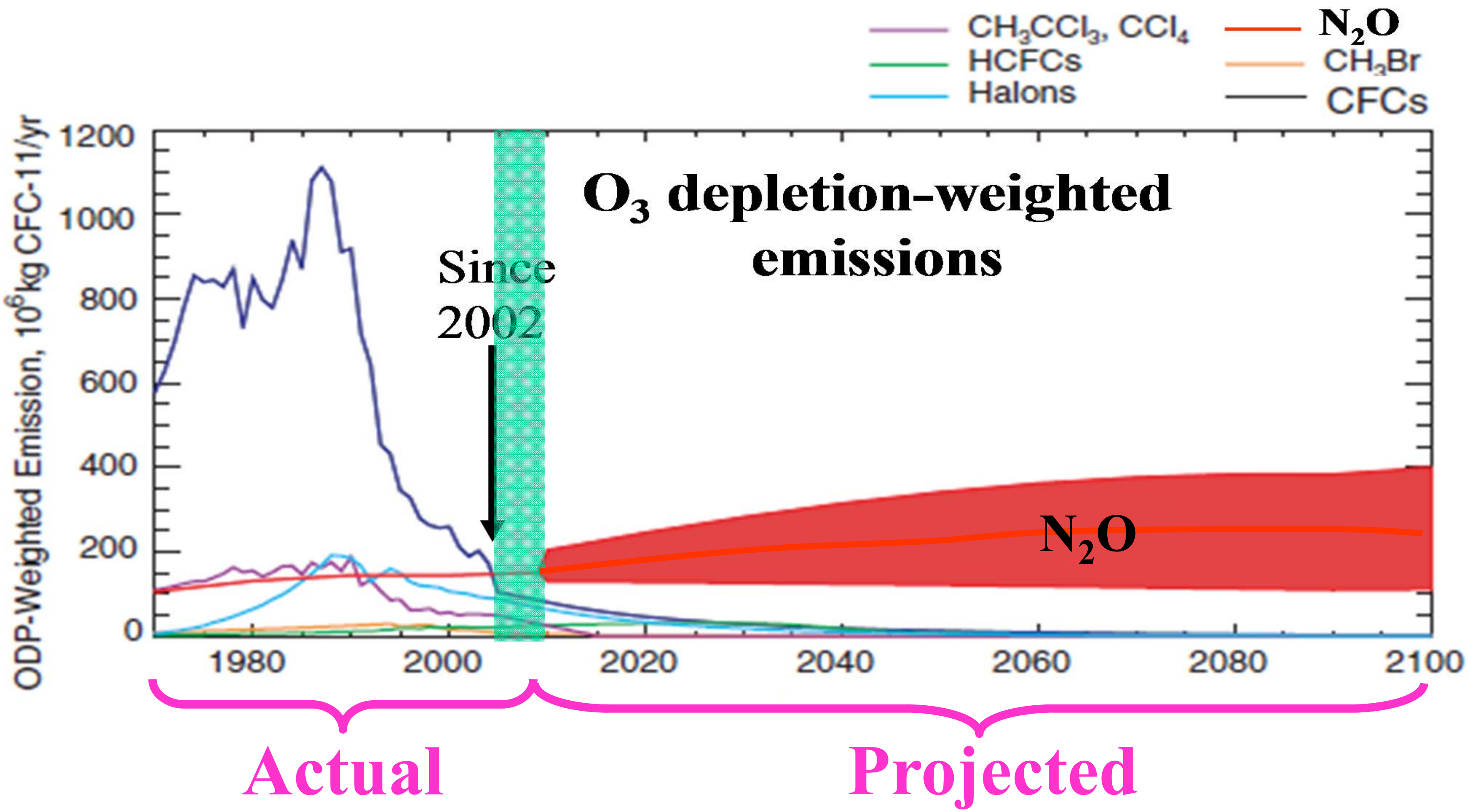
Source: IPCC, 2007

N_2O -induced O_3 depletion in stratasphere





N_2O release: the primary anthrop. emission of O_3-depletion matter



Source: Ravishankara et al. (2009, Science)

Global budget & contributions of individual sources (%)

Unit: Tg N yr^{-1}		Anthrop.
Source	17.7	6.7 (38%)
Sink	12.6	
Increase	5.1	

Natural sources	
Ocean	21%
Soils under natural vegetation	37%
Atmospheric chemistry	3%

Anthropogenic sources	
Agriculture	16%
Aquatic ecosystem	10%
Combustion & industrial processes	4%
Biomass and bio-fuel burning	4%
Atmospheric deposition	3%
Human exctreta	1%

12 %

Source: *IPCC, 2001,2007*

Uncertainty of estimates for N_2O emission of different source categories

Sources	Tg N yr^{-1} Range	Mean (Uncert.)
Natural soils	3.3 ~ 9.7	6.6 (-50 ~ 47%)
Agriculture	1.7 ~ 4.8	2.8 (-39 ~ 71%)
Aquatic ecosys. (Rivers, estuaries, coastal zones)	0.5 ~ 2.7	1.7 (-71 ~ 59%)
Other anthrop. sources	0.8 ~ 5.0	2.2 (-64 ~ 127%)

Source: IPCC, 2007

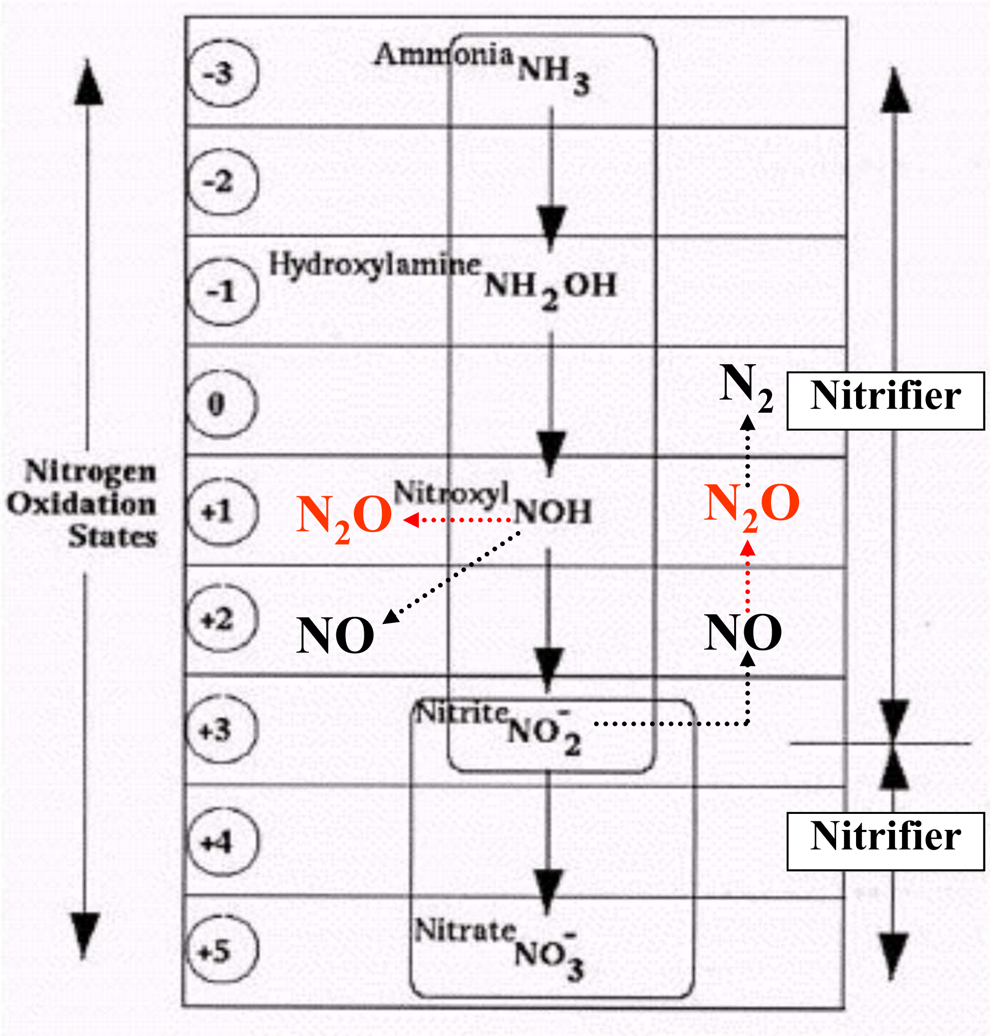
Key questions

- **How to reduce the uncertainties?**
- **How to mitigate the anthrop. emissions?**

Accurate quantification

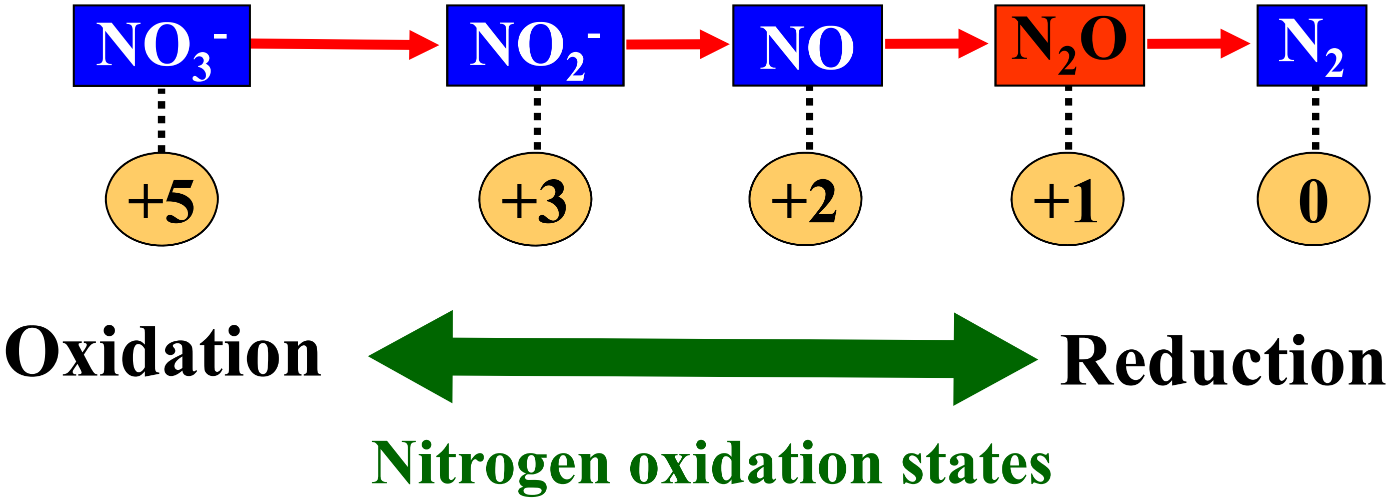
- **Process study**
- **Field study**
- **Model simulation & upscaling**

Microbial nitrification



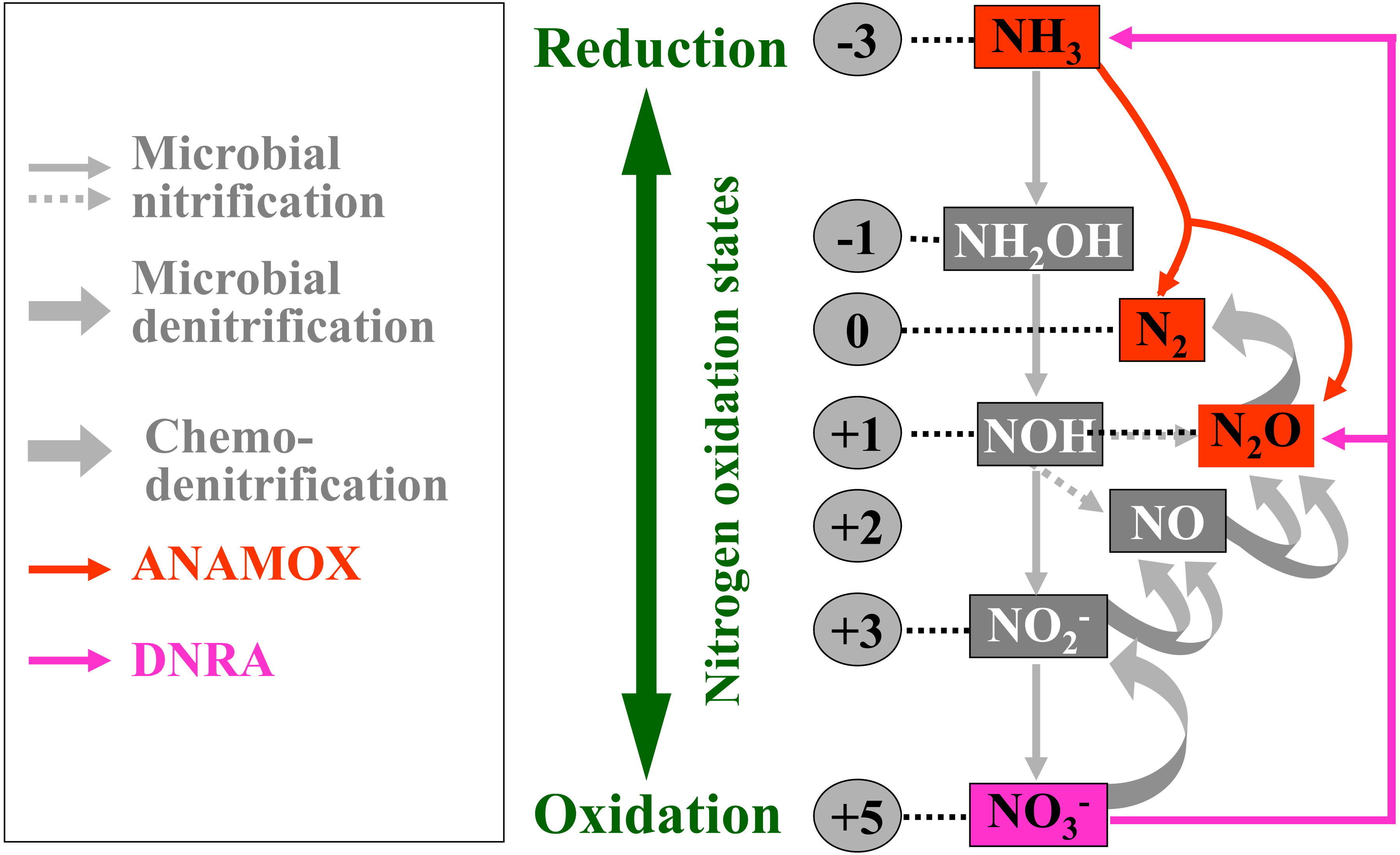
- **Autotrophic nitrifiers**
- **Heterotrophic nitrifiers**

Microbial denitrification

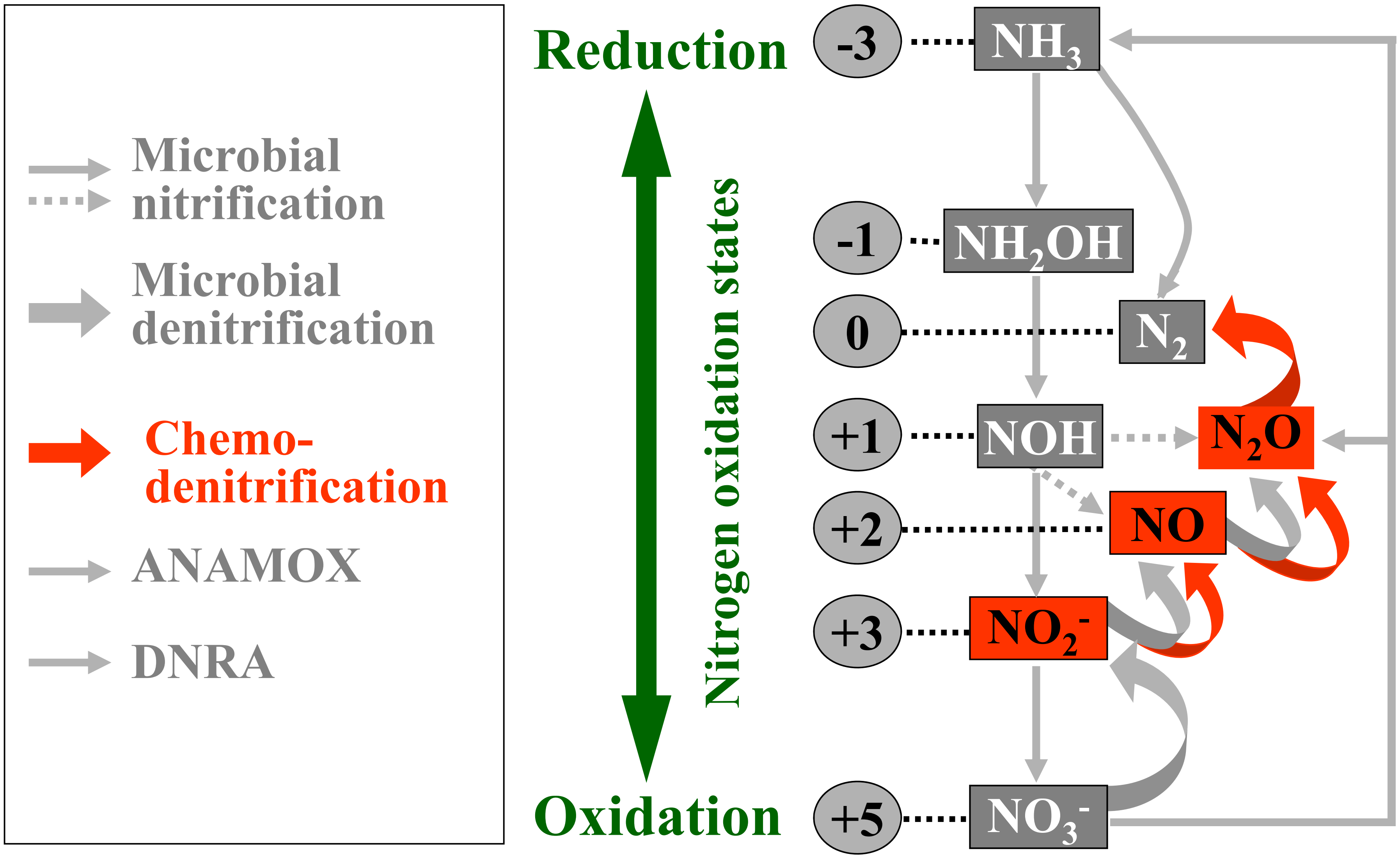


Denitrifiers: heterotrophic

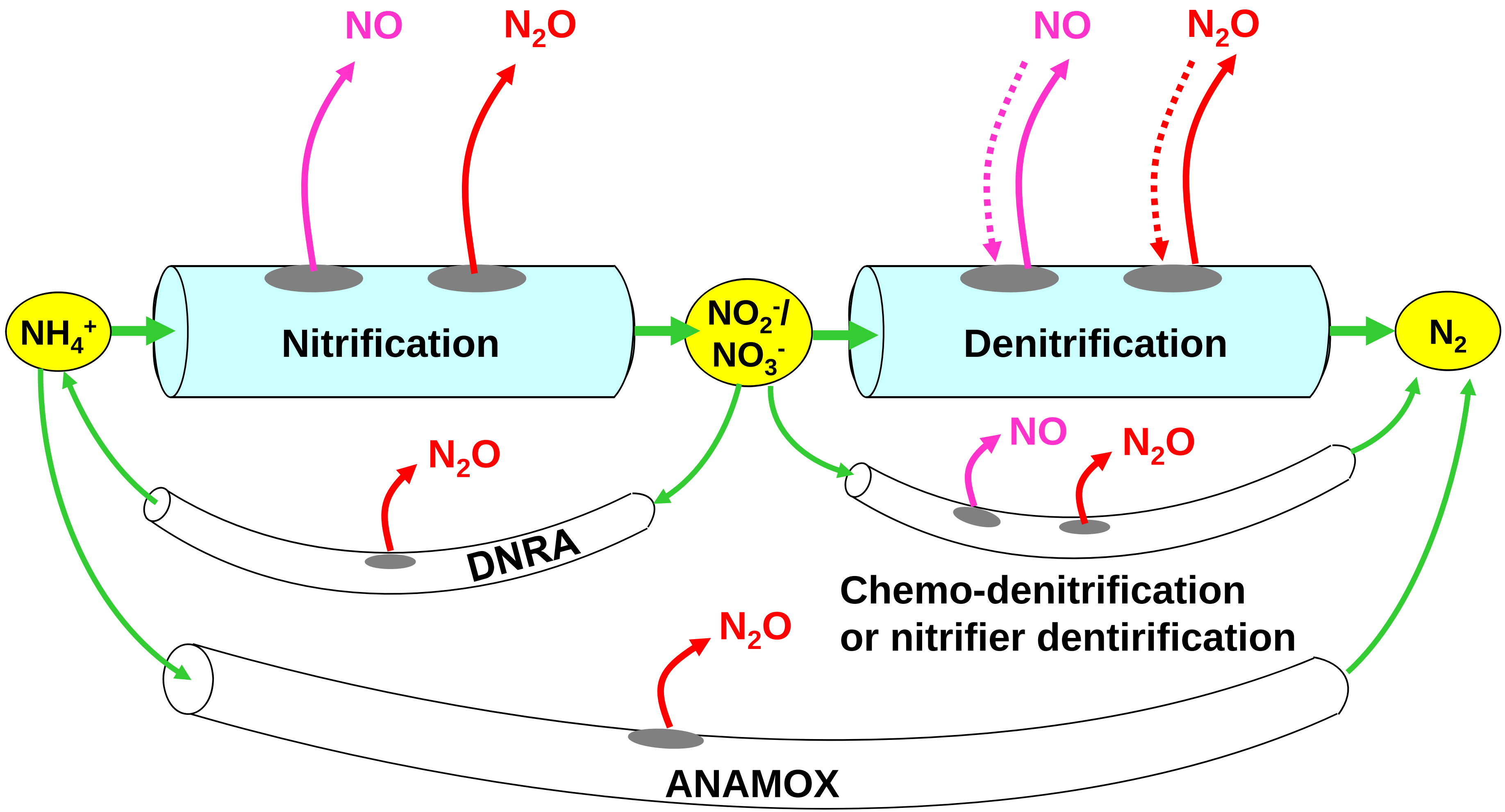
Microbial DNRA & ANAMOX



Non-microbial process



Processes producing N_2O in soil/water



Measured N_2O from a soil may result from multiple processes

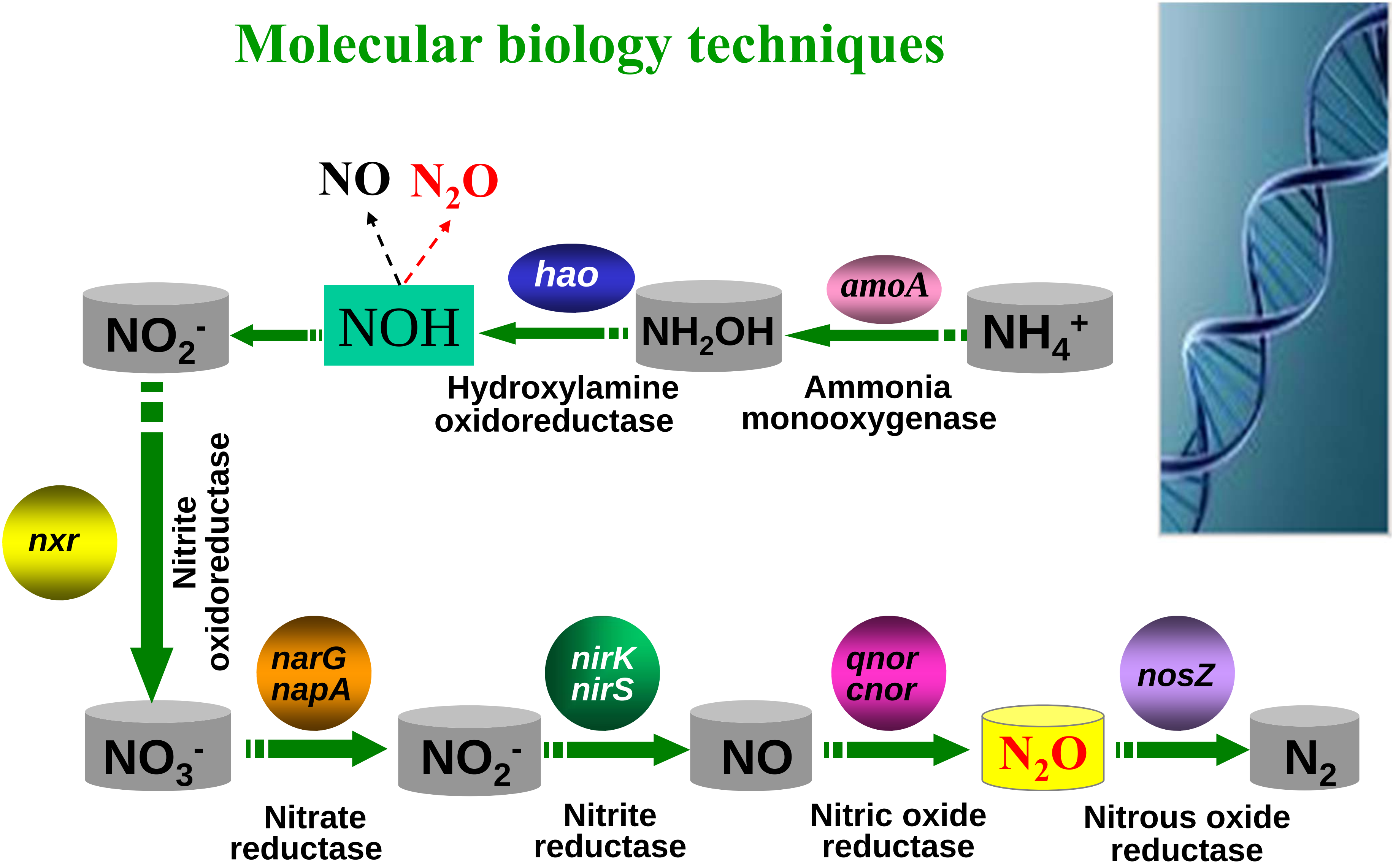
Needs of process study

- **To know the importance of individual processes in overall soil/water N_2O emission:** nitrification, denitrification, nitrifiers denitrification, dissimilatory nitrate reduction to ammonium (DNRA), anaerobic ammonium oxidation (ANAMOX), chemo-denitrification
- **To understand the effects of key factors on N_2O production in individual processes:** microbes, substrates, environmental conditions (temperature, moisture, soil properties)
- **To quantify the ratios of N_2O production rate to rates of nitrogen turnover processes** (e.g. denitrification or gross nitrification)

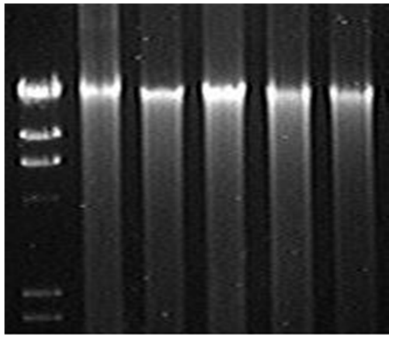
Techniques for process study

- **Molecular biology techniques:** to detect and count functional microbes responsible for individual processes of N_2O production in soil/water.
- **Isotopic signature techniques:** to quantify contribution of nitrification and denitrification, using site preference and isotopologue enrichment factors
- **^{15}N pool dilution techniques:** to measure gross nitrification rate, ammonization rate, and NH_4^+ and NO_3^- immobilization
- **Gas-flow-soil-core/C_2H_2/O_2 inhibition techniques:** to measure denitrification/nitrification and its production ratios

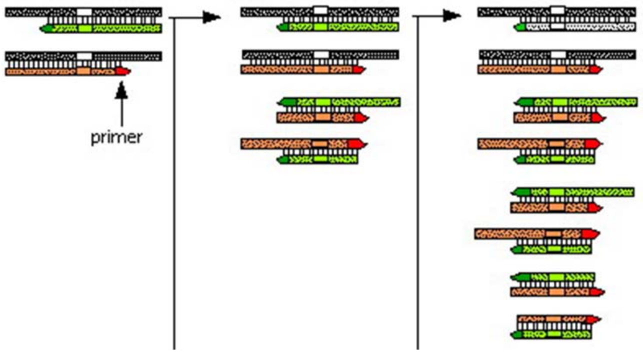
Molecular biology techniques



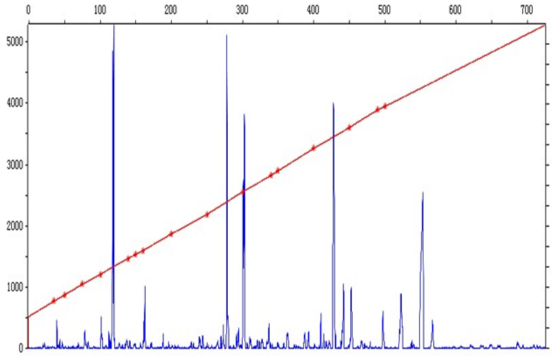
Molecular biology techniques



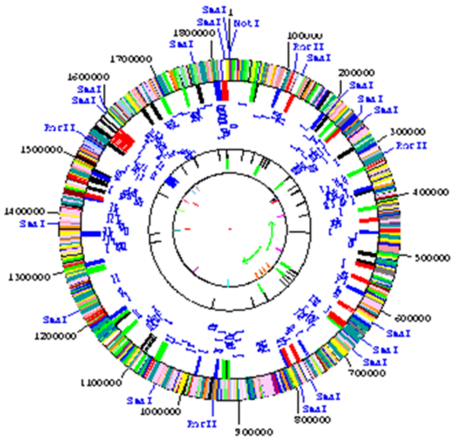
DNA或RNA提取
（DNA/RNA extraction）



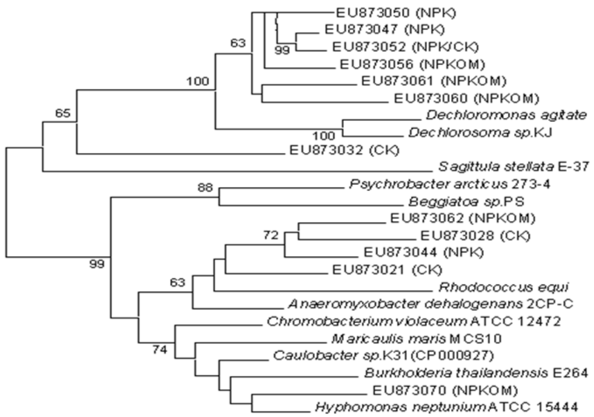
聚合酶链式反应
（PCR amplification）



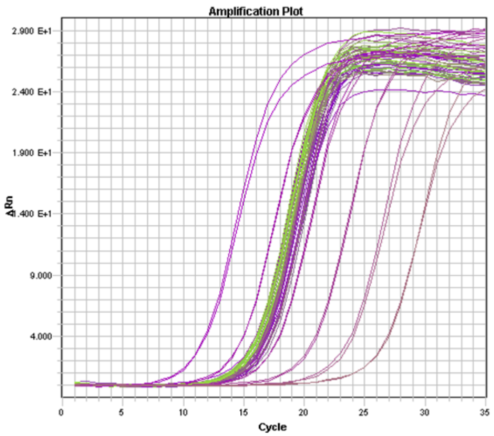
末端限制性片段多态性分析（T-RFLP analysis）



宏基因组学
（Metagenomics）

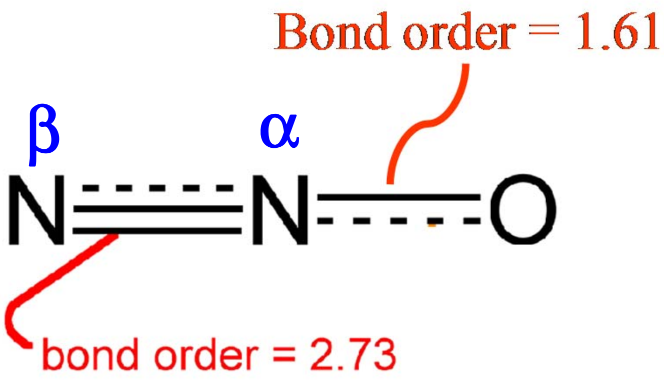


系统发育分析
（Phylogenetic analysis）



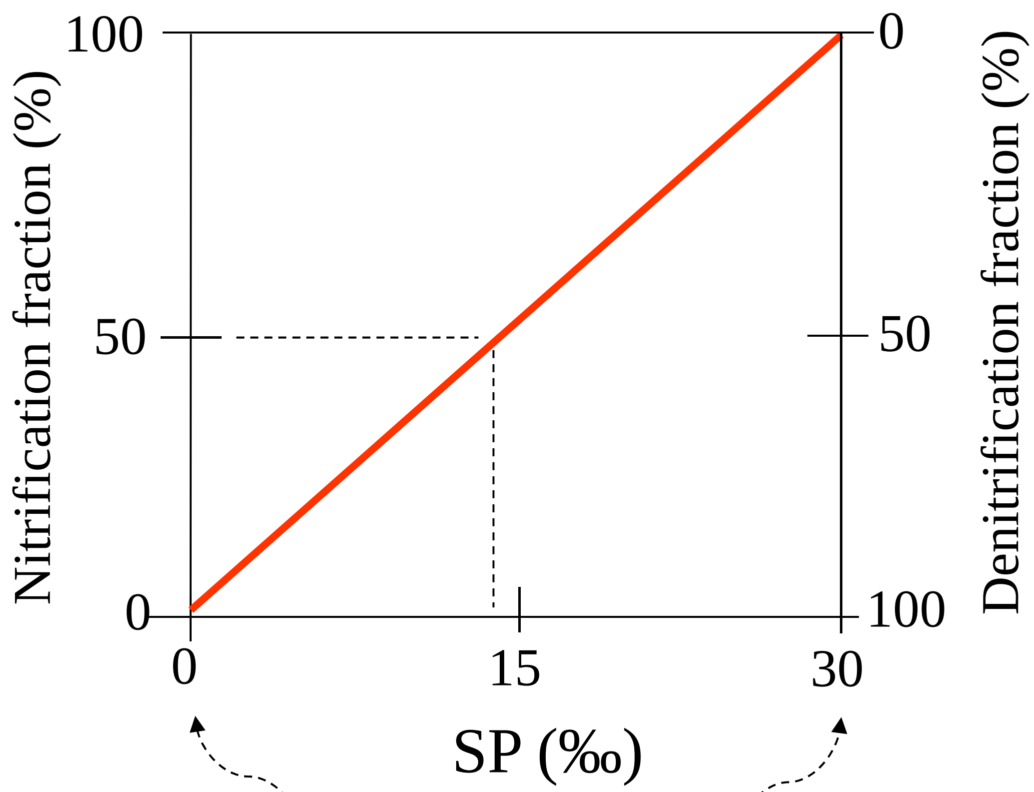
定量聚合酶链式反应
（Real-time PCR）

Isotopic signature techniques



$$\mathbf{SP = \delta^{15}N^{\alpha} - \delta^{15}N^{\beta}}$$

Isotopomer



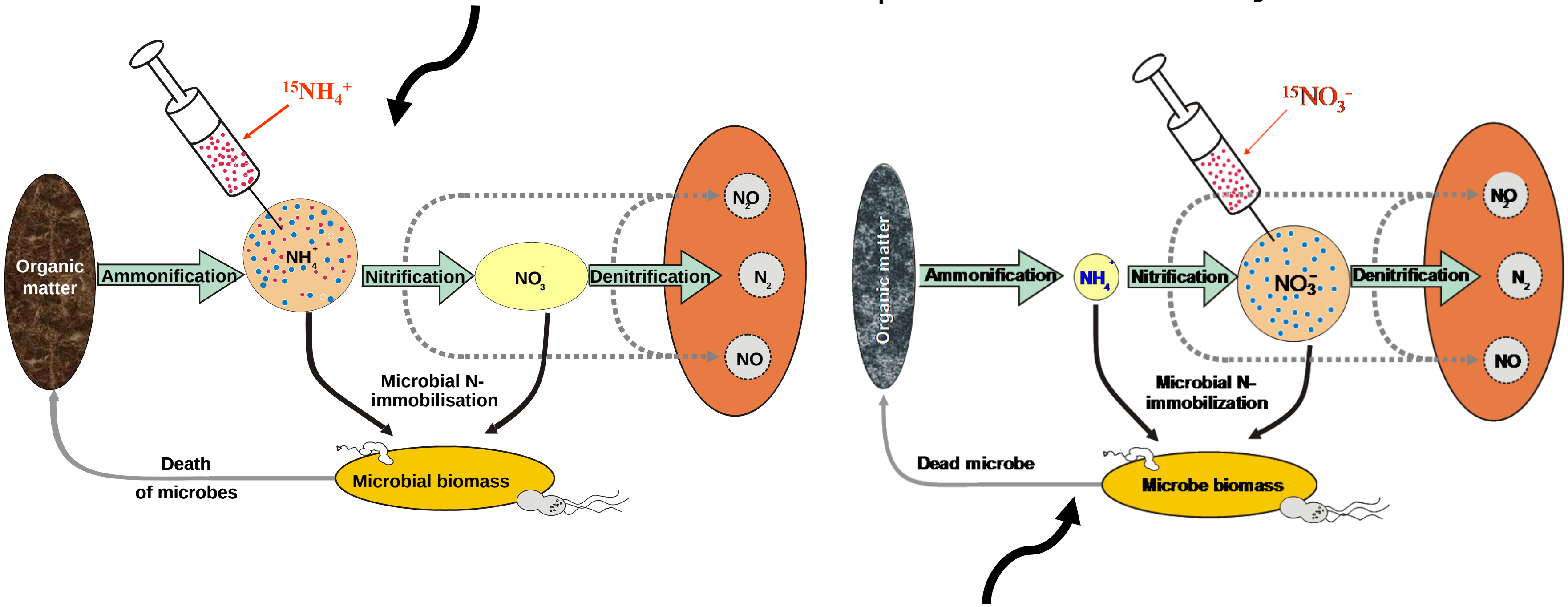
Denitrification by bacteria

Nitrification by bacteria

^{15}N pool dilution techniques

Gross ammonization rate

- $\Delta\ NH_4^+$ between t = 0 and 40 h
- NH_4^+ immobilized by microbes



Gross nitrification rate

- $\Delta\ NO_3^-$ between t = 0 and 40 h
- NO_3^- immobilized by microbes

Source: Klaus Butterbach-Bahl

C_2H_2 / O_2 inhibition techniques

- Denitrification rates (10% C_2H_2): $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \cancel{\rightarrow} N_2$
- Separation of N_2O production processes (C_2H_2 and O_2):

Processes \ Treatments	Control (1)	10 Pa C_2H_2 (2)	21% O_2 (3)	10 Pa C_2H_2 21% O_2 (4)
Nitrification	✓	×	✓	×
Denitrification	✓	✓	×	×
Nitrifier denitrification	✓	×	×	×
Other processes	✓	✓	✓	✓

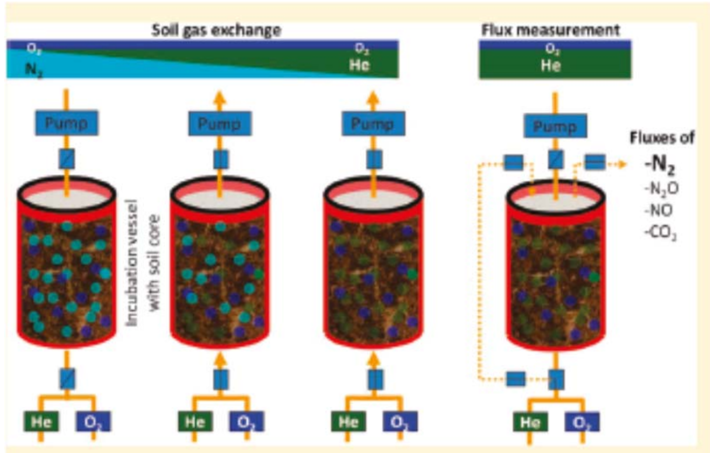
(3) - (4): nitrification
(2) - (4): denitrification
(1) - (2) - (3) + (4): nitrifier denitrification
(4): other processes

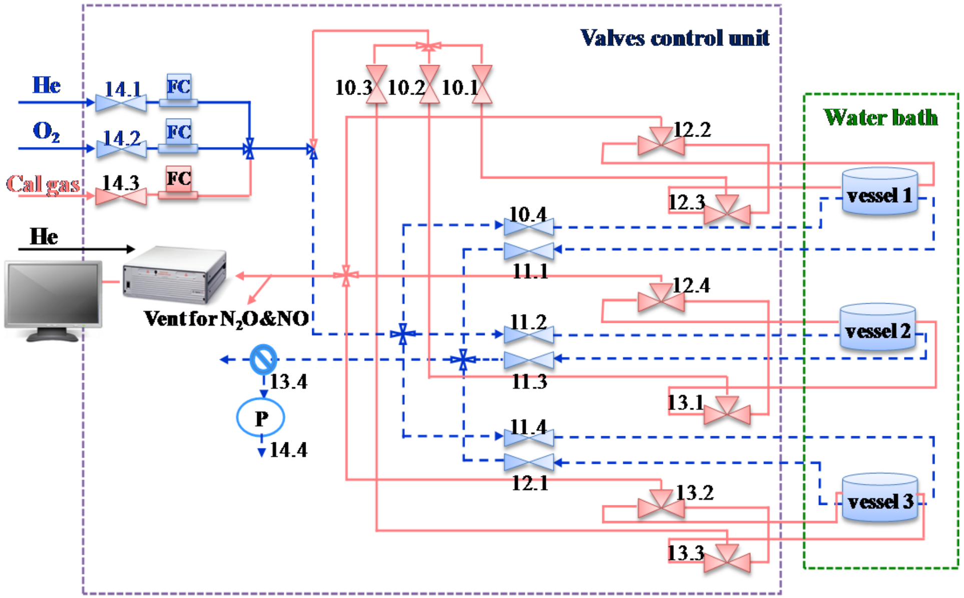
✓ not inhibited
× inhibited

Source: e.g. Wrage et al., 2004

Gas-flow-soil-core technique

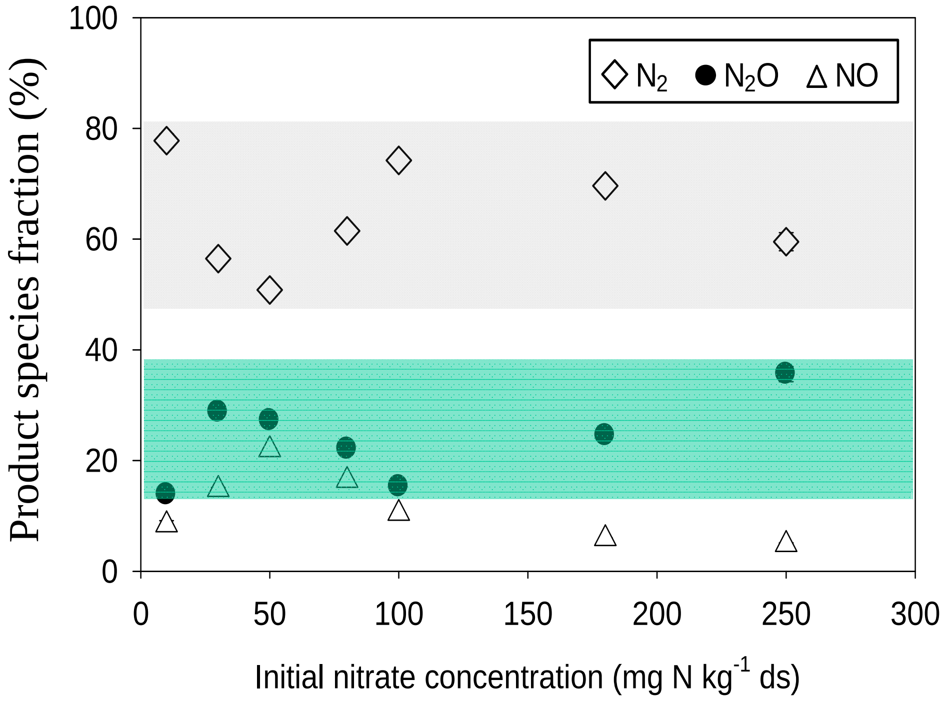
	accuracy	detection limit	
	(µmol mol^{-1})	(µg N h^{-1} kg^{-1} ds)	(µg N m^{-2} h^{-1})
N_2	0.2	0.23	8.6
N_2O	5×10^{-3}	0.02	0.6
NO	1×10^{-3}	0.08	2.7

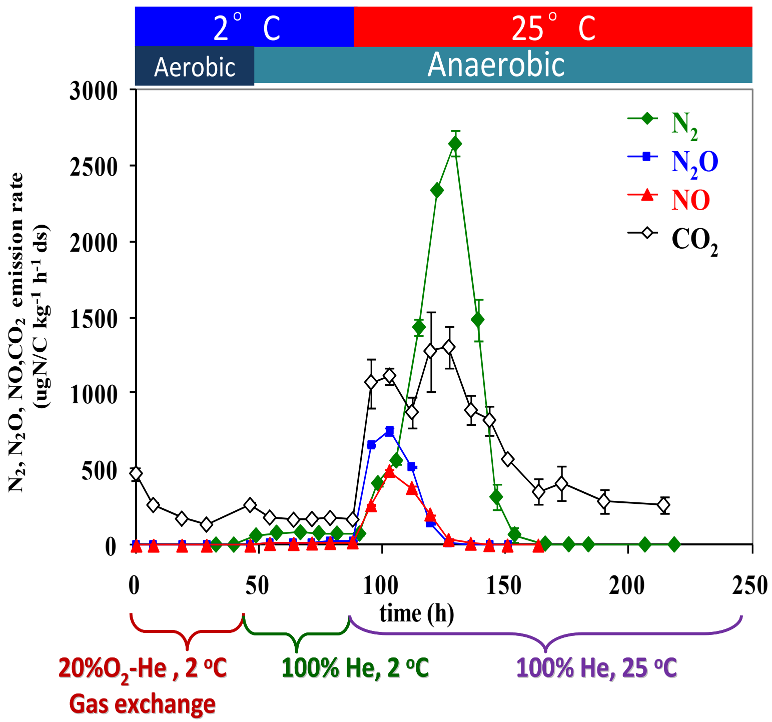




Source: Wang et al., 2011, EST

Gas-flow-soil-core technique





Denitrification potential measurement

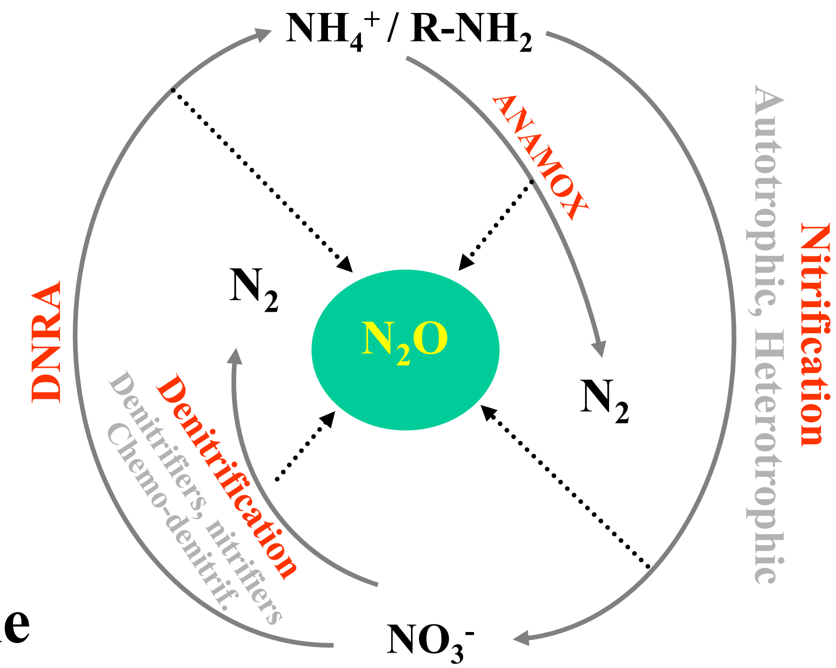
Daily measurements of NH_4^+, NO_3^-, NO_2^-, DOC, and microbial carbon and nitrogen during incubation are necessary to link laboratory study with field N_2O flux and its model simulation.

Source: Wang et al., 2012, Plant Soil

Techniques for measuring field N_2O fluxes

- ➢Static chamber technique
- ➢Eddy covariance technique

Overall N_2O fluxes, which integrate emissions of multiple processes occurring in field conditions



Static chamber-based field measurement

Automatic translucent chamber

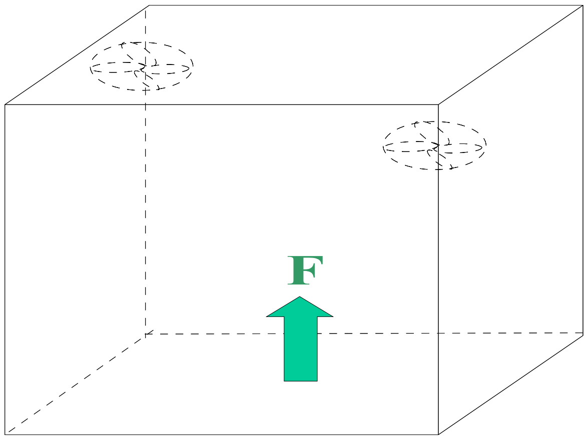
Manual opaque/translucent chamber

- **Gas chromatography-electron capture detector (GC-ECD) is usually used to analyze (online or offline) air samples from chamber (automatic, manual) headspace.**
- **Researchers start recently to use laser/FTIR detectors.**

Static chamber-based field measurement

Static chamber technique

$$F = (dC/dt)V/A$$



F: field N_2O flux

dC/dt: initial change rate of N_2O concentration during enclosure

V: headspace volume

A: measured land area

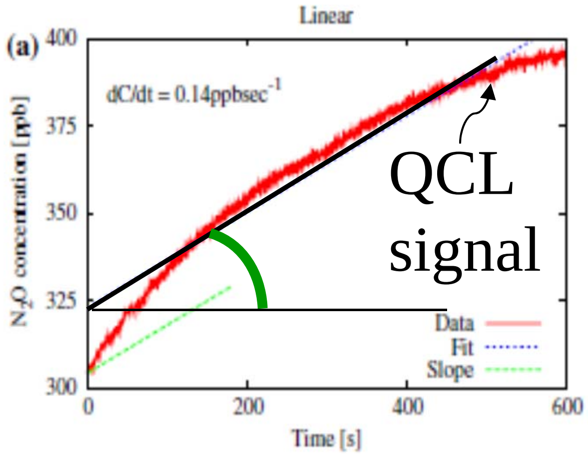
Nonlinear relationship occurs between N_2O concentration and sampling time, as chamber enclosure

a) **reduces concentration gradient ($\partial C/\partial z$), and**

b) **prevents air mass flow driven by wind.**

Chamber-based measurement: Con. → flux

$$F = (dC/dt) \cdot V/A \cdot \rho_{N2O} \cdot P/P_0 \cdot T_0/T$$

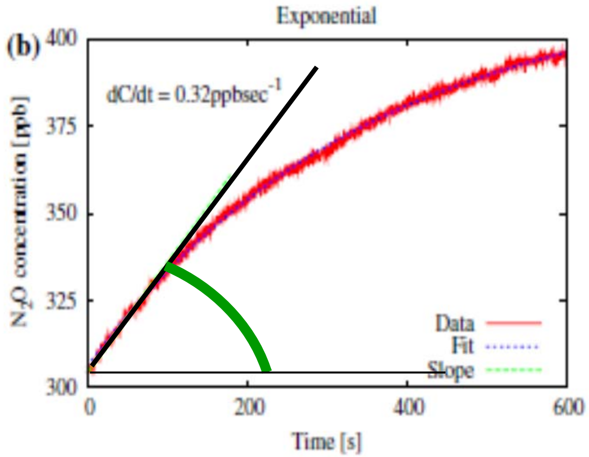


Linear model:

$$dC/dt = a$$

$$C_t = a \cdot t + b$$

(used almost for all available dataset)



Nonlinear model:

$$F = (dC/dt) \cdot V/A \cdot \rho_{N2O} \cdot P/P_0 \cdot T_0/T$$

$$dC/dt = a - b \cdot C_0$$

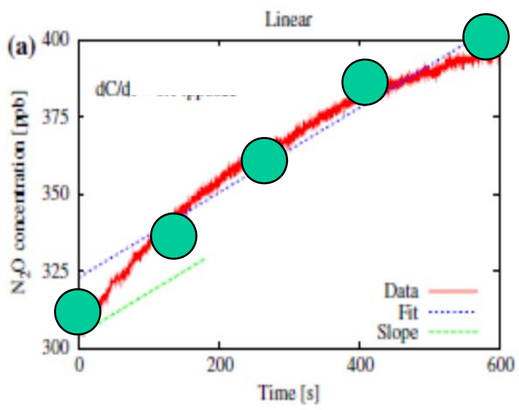
$$C_t = a/b + (C_0 - a/b) \cdot e^{-b.t}$$

(seldom used, yet)

Source: Kroon et al., 2008, NCA; Valente et al., 1995, JGR; Wang et al., 2012, AFM

Chamber-based measurement: flux bias

- **Linear model has to be used in case nonlinearity detection fails** (offline concentration analysis or usage of GC, as a slow-response detector, prevent high-frequency concentration measurements during enclosure; usually using only 5 observations to detect nonlinearity in GC-based measurement).



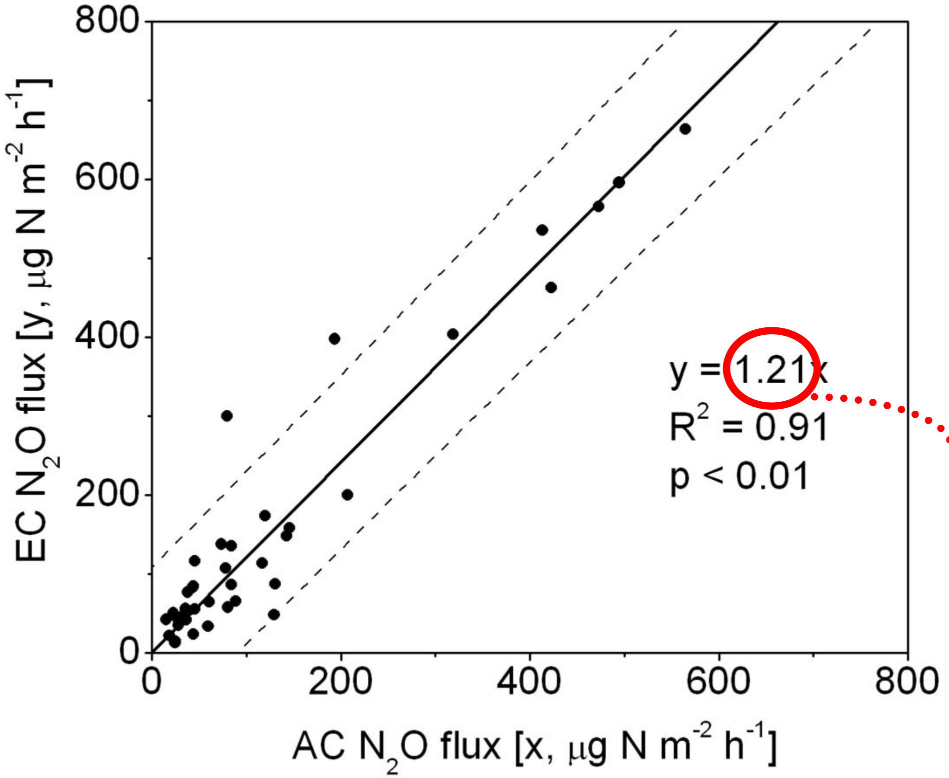
- **Linear model has to be used** since too fewer concentration measurements (≤ 4 times) prevent use of nonlinear model.

- **Flux bias: using of wrong model and failure in nonlinearity detection could underestimate annual N_2O fluxes by 0~ 30%** (for a fertilized cotton case).

Result from chamber data

Source: Wang et al., 2012, AFM

Chamber-based measurement: flux bias



Result from comparison between chamber and EC data

AC < EC by 17 ~ 20

AC: automatic chamber fluxes (nonlinear model was used for detected nonlinearity cases)

EC: eddy covariance (TDL) fluxes with wind from chamber location

Source: Wang et al., 2012, AFM

Chamber-based measurement: flux bias

Flux bias due to wrong GC method

Carrier gas:

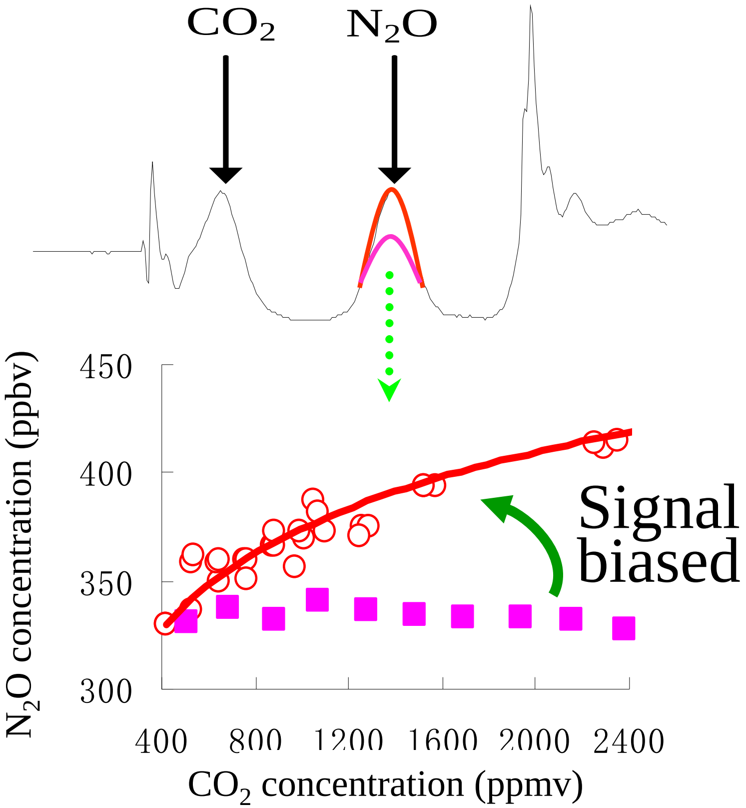
- **Argon-methane mixture (5-10% CH_4 in Ar) is better to be used as carrier (AM method);**
- **If Ar-CH_4 mixture is substitute with N_2 alone (DN method), ascarite (which may lead to negative flux for marginal emission) is not recommended to use as filter of CO_2 (DN-Ascarite method). Instead, we recommend to let 10% CO_2 in pure N_2 flow through ECD cell at ~2 ml min^{-1} as a buffer gas (DN-CO_2 method).**

Source: Zheng et al., 2008, Plant Soil; Wang et al., 2010, AAS

Chamber-based measurement: flux bias

Flux bias due to wrong GC method

N_2 as carrier gas in GC-ECD (DN method)



$$\beta + N_2 \rightarrow \beta' + N_2^+ + e$$

$$N_2O + e \rightarrow N_2 + O^-$$

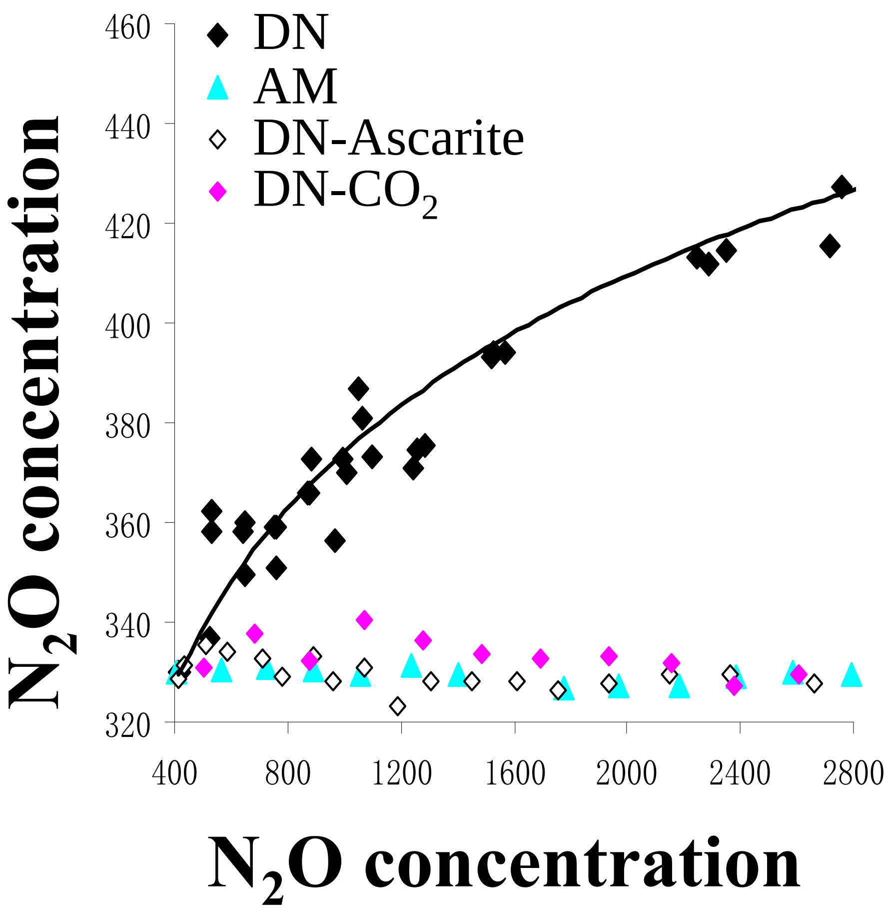
$$\beta + CO_2 \rightarrow \beta' + CO_2^+ + e$$

N_2	15.6[a]
Ar	15.8[a]
He	24.6[b]
CO_2	13.6[c]
N_2O	12.9[c]
NH_3	10.2[d]
H_2O	12.6[e]
H_2S	10.4[f]
O_2	12.1[g]
CH_4	12.5[a, g]
NO	9.3[h]
CS_2	10.1[i]
COS	11.2[j]

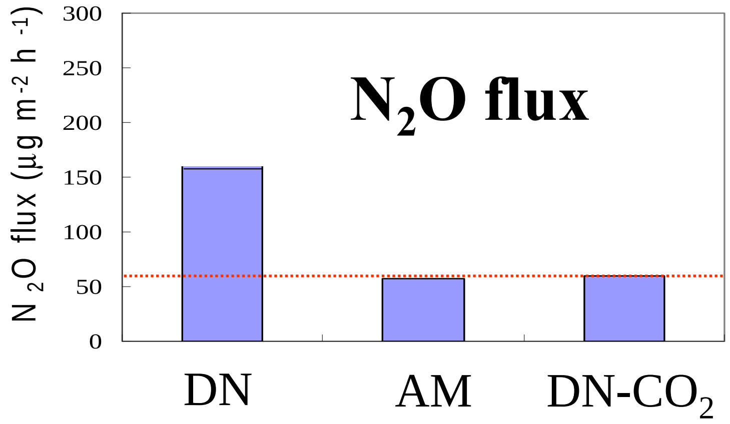
Source: Zheng et al., 2008, Plant Soil

Chamber-based measurement: flux bias

Flux bias due to wrong GC method



Source: Wang et al., 2010, AAS

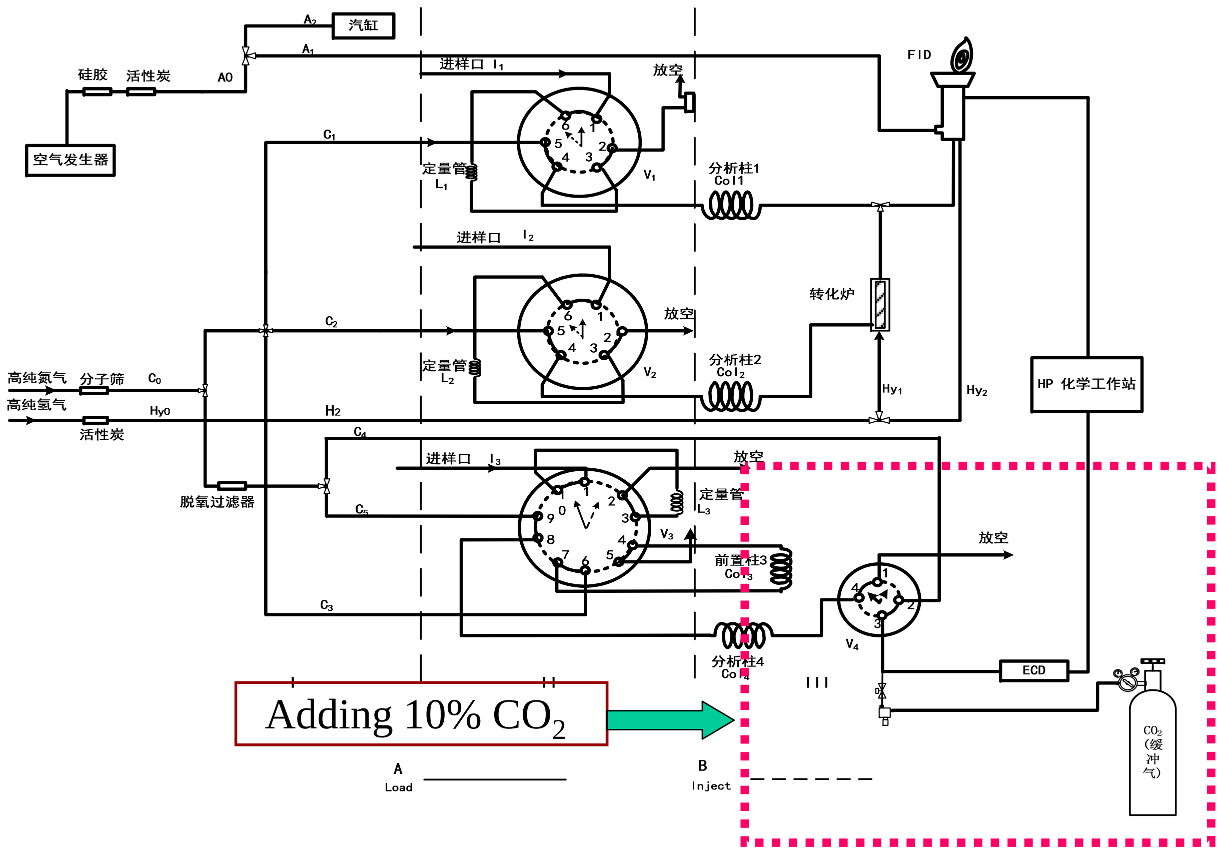


GC-ECD method	Precision for 300 ppbv N_2O (%)
DN	**1.6 - 2.3**
DN-CO_2	**0.2 - 0.7**

Not able to detect low fluxes

Chamber-based measurement: flux bias

Gas-flow system in GCs for simultaneous analysis of N_2O, CH_4 and CO_2, using DN-CO_2 for N_2O



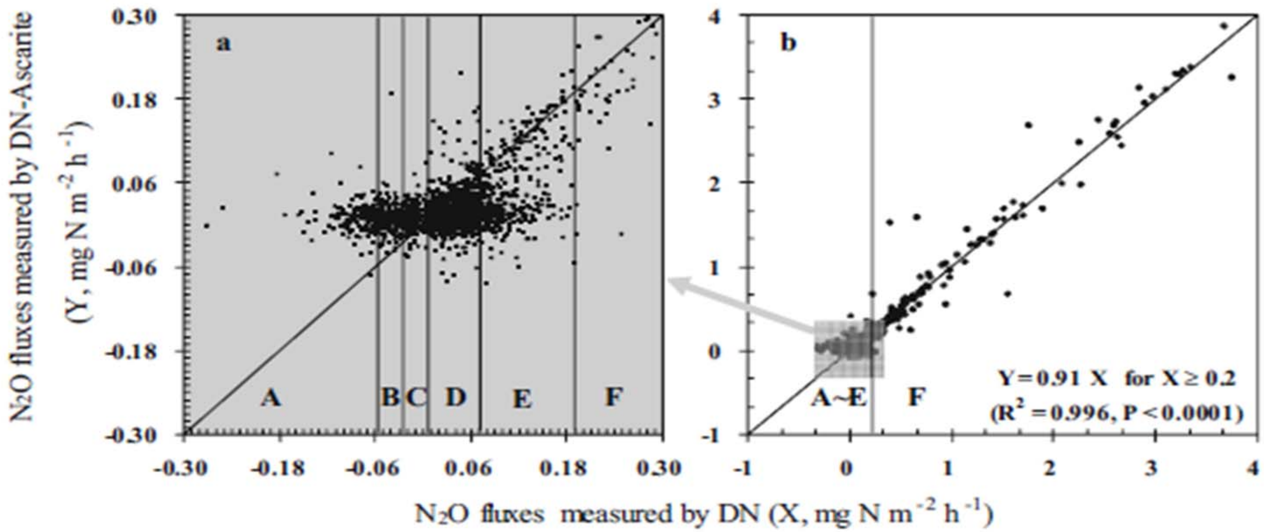
- Precision of each gas: 0.2 ~ 0.7% for ambient air samples.
- > 90% of GCs in China using this method.

Source: Wang et al., 2010, AAS

Chamber-based measurement: flux bias

Flux bias due to wrong GC method

Ranges of N_2O fluxes measured by DN ($\mu g\ N\ m^{-2}\ h^{-1}$)		N_2O fluxes ($\mu g\ N\ m^{-2}\ h^{-1}$)						Pair number	Significance level
		DN (apparent)		DN-Ascarite		$Y-X$	Y/X		
		Mean (X)	SD	Mean (Y)	SD				
A	<−30	−63	34	8	22	72	–	301	***
B	−30~0	−14	7	8	15	22	–	254	***
C	0~30	17	25	12	25	−5	0.72	551	***
D	30~100	57	19	19	27	−38	0.34	882	***
E	100~200	136	27	72	65	−64	0.53	212	***
F	>200	2,872	6,999	2,713	6,324	−159	0.94	163	ns



Correction term for DN-measured N_2O fluxes

Source: Zheng et al., 2008, Plant Soil

Chamber-based measurement: flux bias

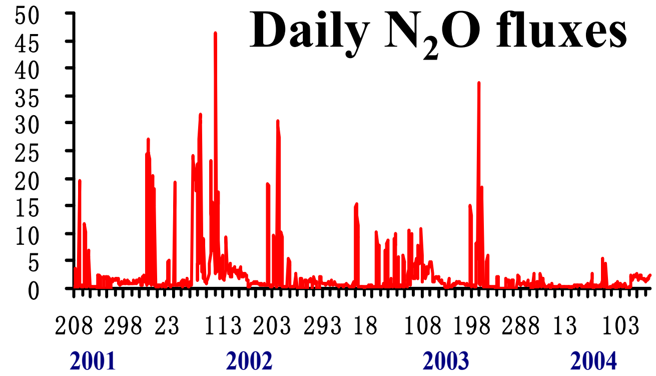
Case study of a rice-wheat rotation ecosystem

(relative to six 6 measurements d^{-1})

Fixed frequency	Annual flux bias（%）
Once every 3 d	-19 ± 10
Once every 4 d	-23 ± 15
Once every 5 d	-24 ± 12
Once every 7 d	-30 ± 18
Once every 10 d	-30 ± 13

Most field measurements

Source: Zheng et al., 2004



Frequency-related biases are variable with ecosystems

Chamber-based measurement: advantages

a) **High sensitive:** detection limit could be **1 ~ 11** (mean: 4.6) μg N m^{-2} h^{-1} for 50 cm chamber height (95% confidence interval), being more sensitive than other approaches by 1-2 order of magnitude.

b) **Flexible applicability:** applicable for all field plot sizes of uniform or non-uniform land surface.

c) **Very practical:** simple principle, easy operation, and low cost.

Source: Wang et al., 2012, AFM

Chamber-based measurement: disadvantages

a) **Negative bias:** due to failure in nonlinearity detection and prevent of mass flow.

b) **Low temporal resolution** (manual) and **poor representativeness for spatial variability** (automatic).

c) **Very labor-consuming**.

Source: Wang et al., 2012, AFM

Chamber-based measurement: avoiding bias

a) **Using AM or DN-CO_2** if GC has to be adopted.

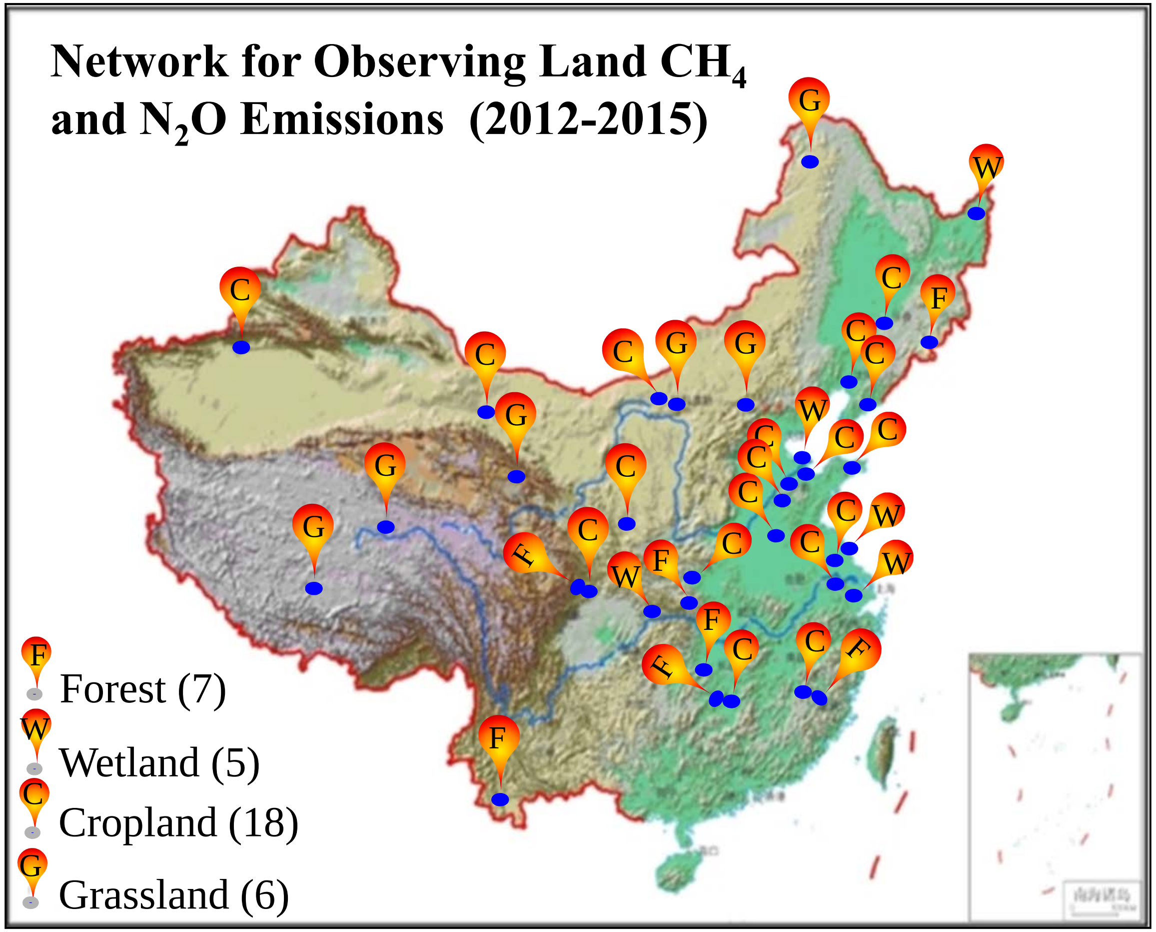
b) **Enlarging sample size** of concentration measurements during chamber enclosure.

c) **Using** high-precision, **fast-response detectors** for online concentration analysis.

d) Using **flexible** measurement **schedule**: daily measurement for a few days to a few weeks following flux-stimulating events (e.g., fertilization, irrigation, rainfall, …), but weekly otherwise.

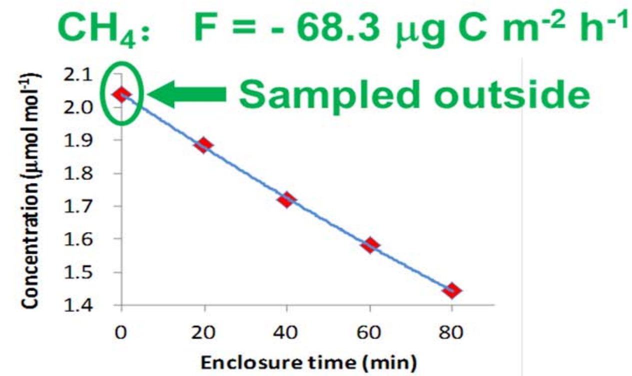
中国陆地CH_4和N_2O排放通量箱法观测网

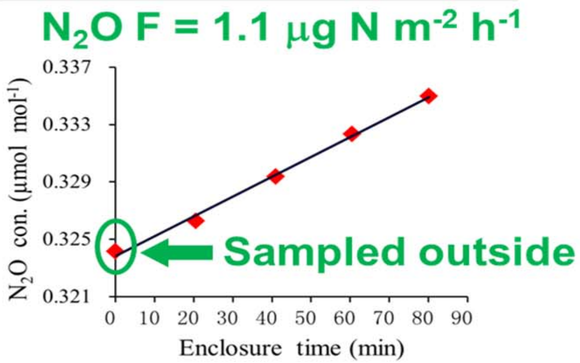
制定并采用了统一的测定方法与数据质控规范，为过程规律与模型研究提供具有可比性的高质量通量数据



行业（农业）科研专项项目（首席邱建军）的大部分站点
中科院先导（碳）专项项目（首席蔡祖聪）和973项目（首席郑循华）的所有站点

➢观测网数据质量控制：中科院大气所数据质控人员及时收集和处理各站点气体通量数据，诊断存在问题，提出问题解决方案，并负责或协助解决。





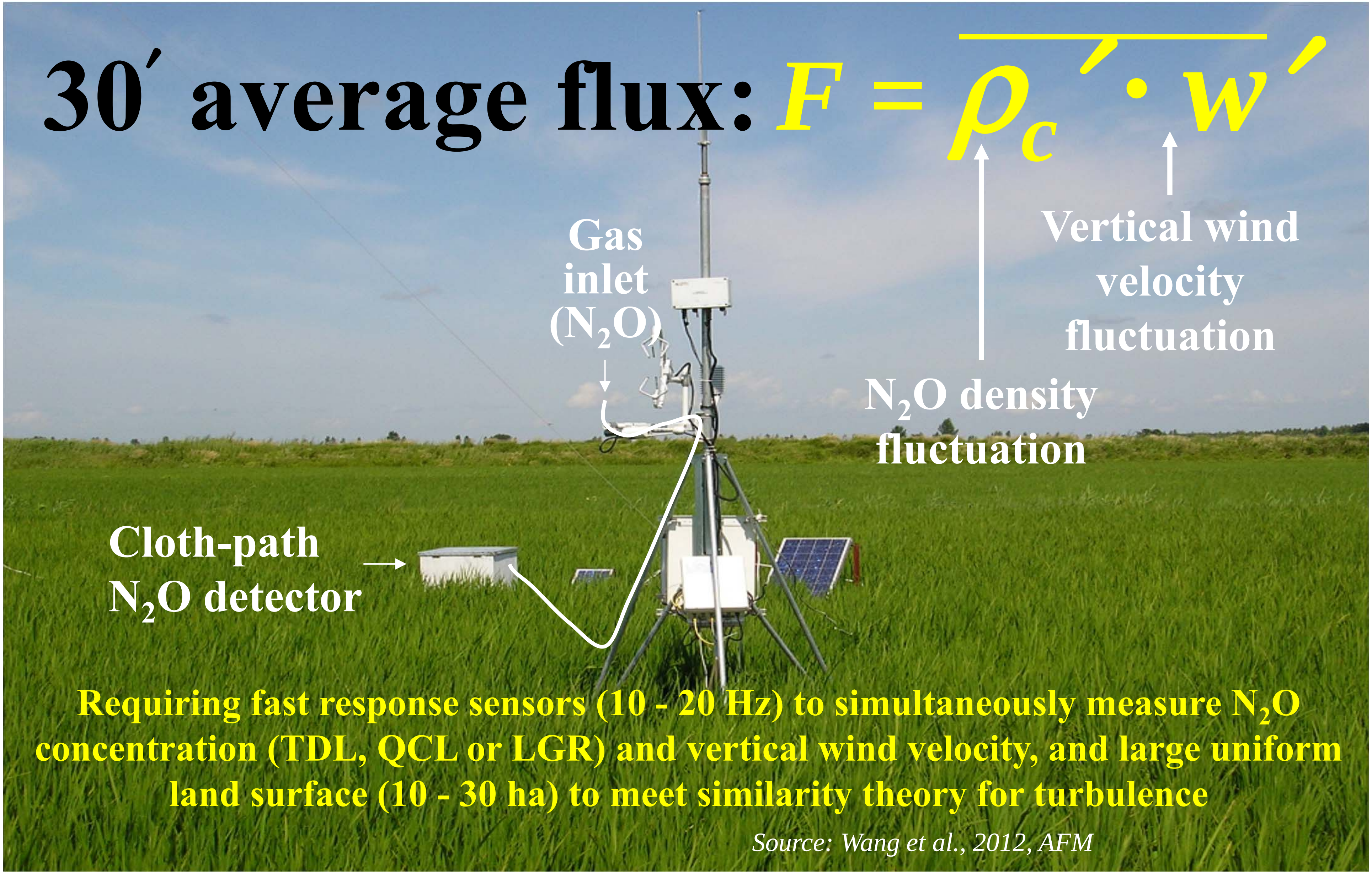
海北严重退化高寒草甸的通量数据的有效率（n = 300）：

CH_4 97%

N_2O 65%

箱高：40 cm;采样时间：80′; GC精度：0.2% ~ 0.8%

Eddy covariance measurement of N_2O fluxes



Eddy covariance measurement of N_2O fluxes

➢ **Corrections** and **quality control** to determine 30-min fluxes:

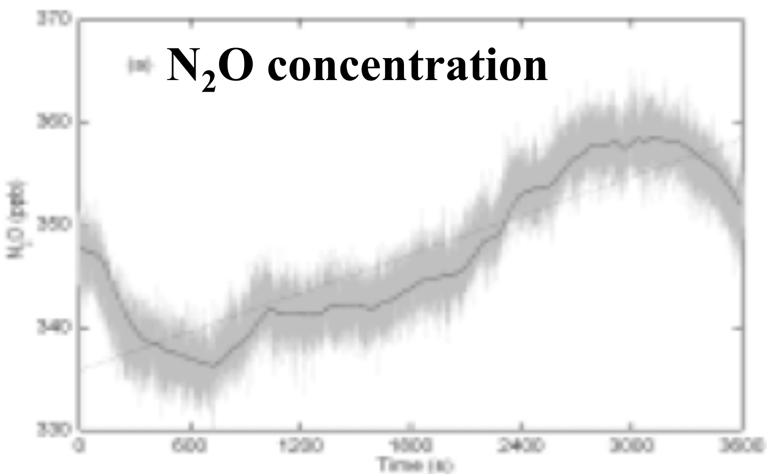
a) **Coordinate rotation** for two-dimension wind velocity;

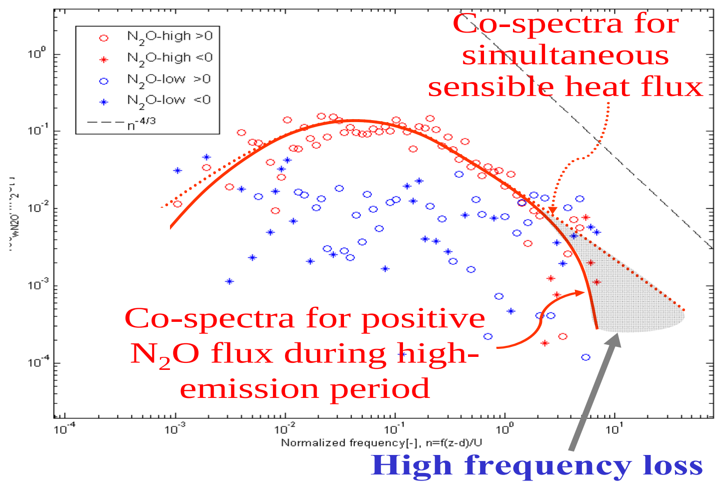
b) **Detrending** vertical wind velocity & N_2O concentration;

c) Correcting **lag time** between N_2O concentration & wind velocity;

d) Correcting **flux loss** at high-frequency.

e) Using **friction velocity (u*) filter** to reject fluxes from area beyond footprint of the EC mast.

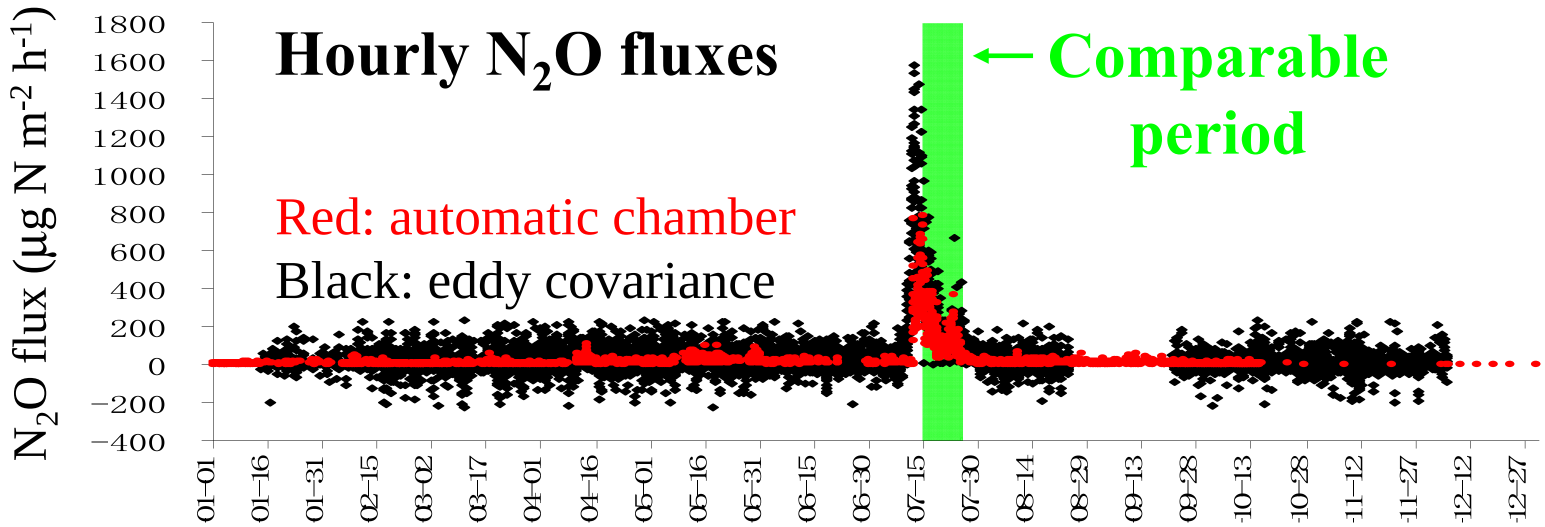




Source: Wang et al., 2012, AFM

Eddy covariance measurement of N_2O fluxes

- **N_2O flux detection limit** of eddy covariance technique (TDL): **36 ~ 108** μg N m^{-2} h^{-1} (**95%** confidence interval).
  Versus chamber: 1 ~ 11 μg N m^{-2} h^{-1}
- **Hourly flux uncertainty:** ±676 and ±569 μg N m^{-2} h^{-1} during the high and low emission periods, respectively (**95%** confidence interval).
  Versus chamber: -62 ~ 15 (high) & -6 ~ 3 (low) μg N m^{-2} h^{-1}



- **Applicability of eddy covariance** technique is still questionable for low to moderate levels of N_2O fluxes.

Source: Wang et al., 2012, AFM

Eddy covariance measurement of N_2O fluxes

- **Advantages:**
  - a) Good representativeness of spatial variability for the area within footprint fetch.
  - b) Easy operation *in situ* & labor-saving.
- **Disadvantages:**
  - a) Low sensitivity, yielding not reliable fluxes from low emission sources.
  - b) Not applicable for manipulation field experiment with small plots & non-uniform land surface.
  - c) Complexity in principles and data processing
  - d) Expensive detectors.
- **Promising application:** 1) long-term observation; and, 2) developing correction factors for chamber flux biases

Source: Wang et al., 2012, AFM

Modeling approach: scaling up and scenario study

- **Field measurements:** never sufficient in terms of N_2O emisison management;
- **Process-oriented modeling approach:** necessary way to link process understandings at molecular/microsite scales, field measurements at site scale, and management decision at regional scale.

Process-oriented modeling approach

DNDC (US)

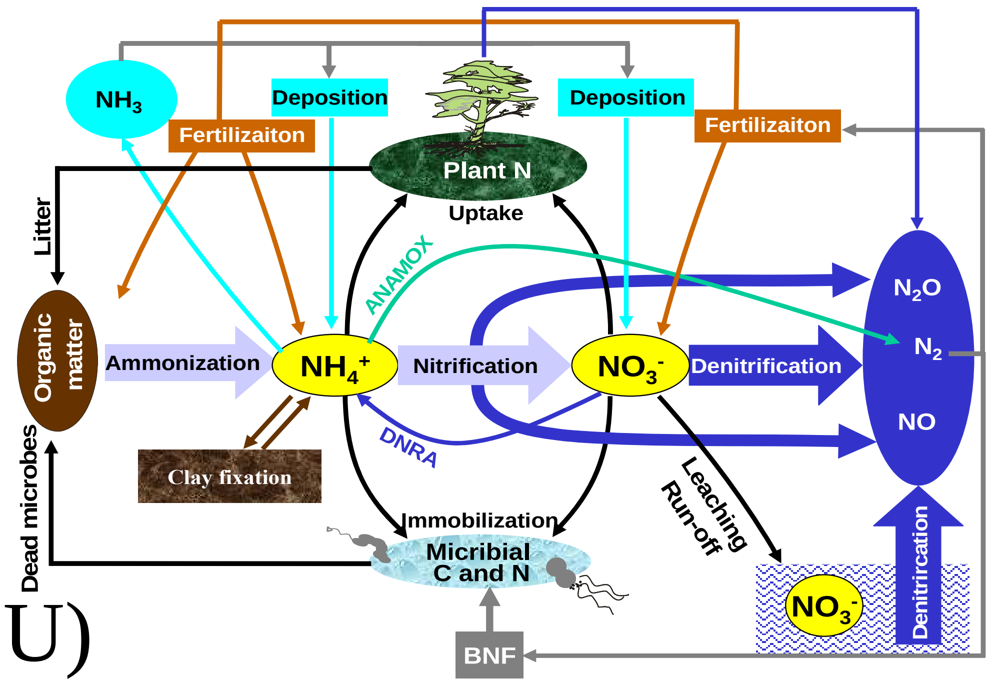
Daycent (US)

PaSim (EU)

WNMM (Australia)

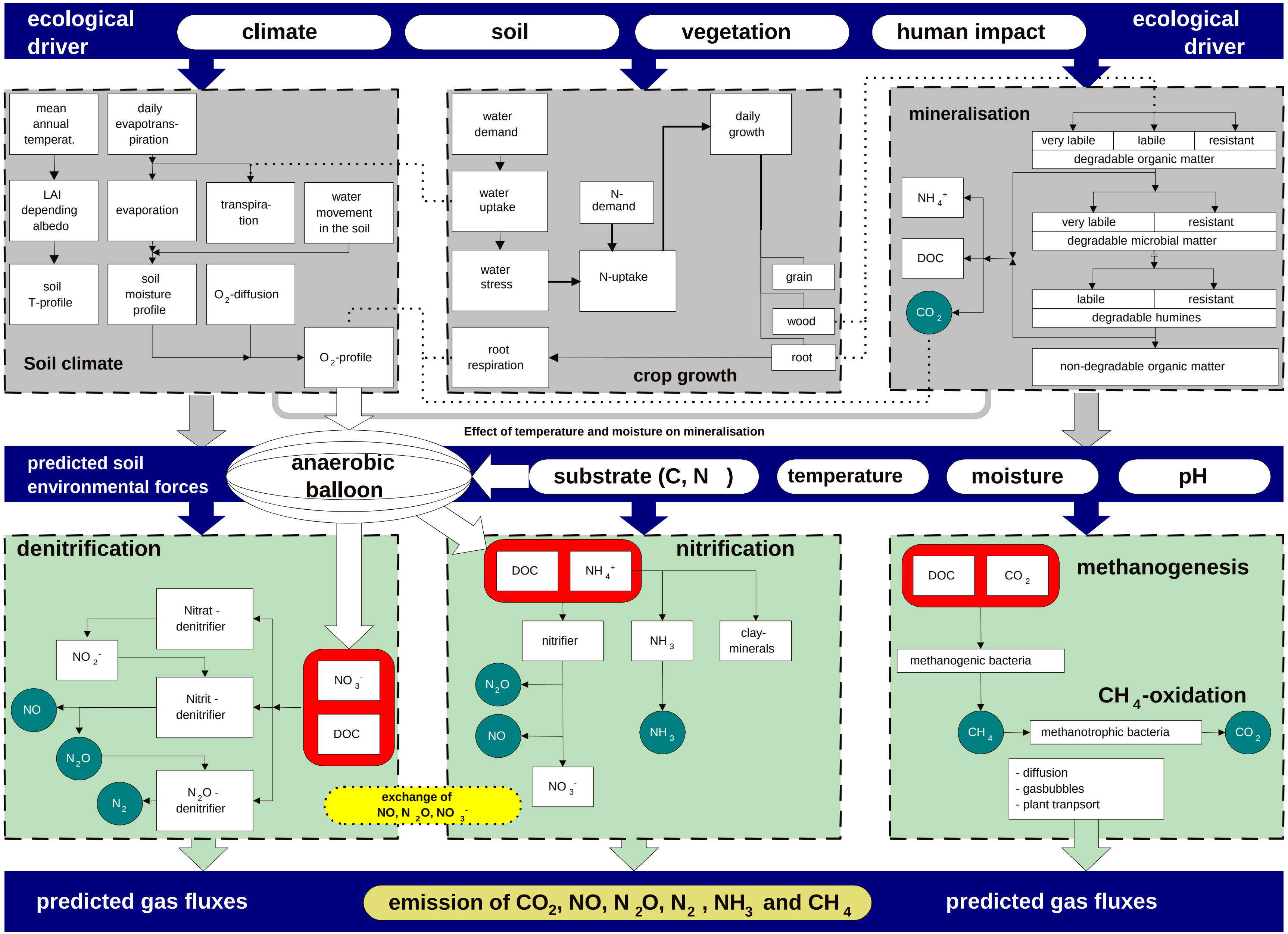
Landscape DNDC (EU)

……

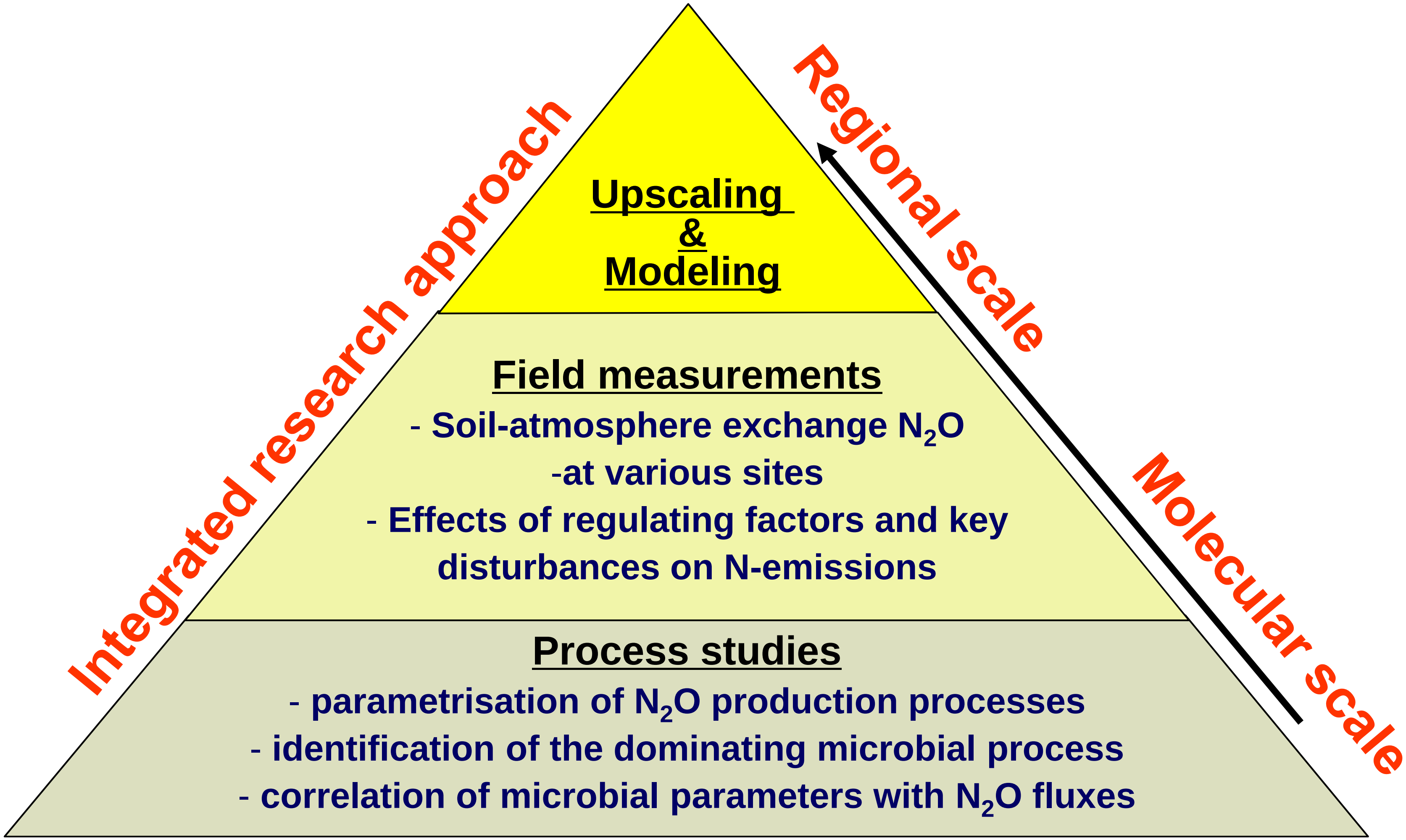


Models are designed to describe the nitrogen/carbon cycling processes from site to regional/catchment scale, so as to predict management effects of given scenarios.

DNDC9.5 模型 (一维过程)



Modeling approach: scaling up and scenario study



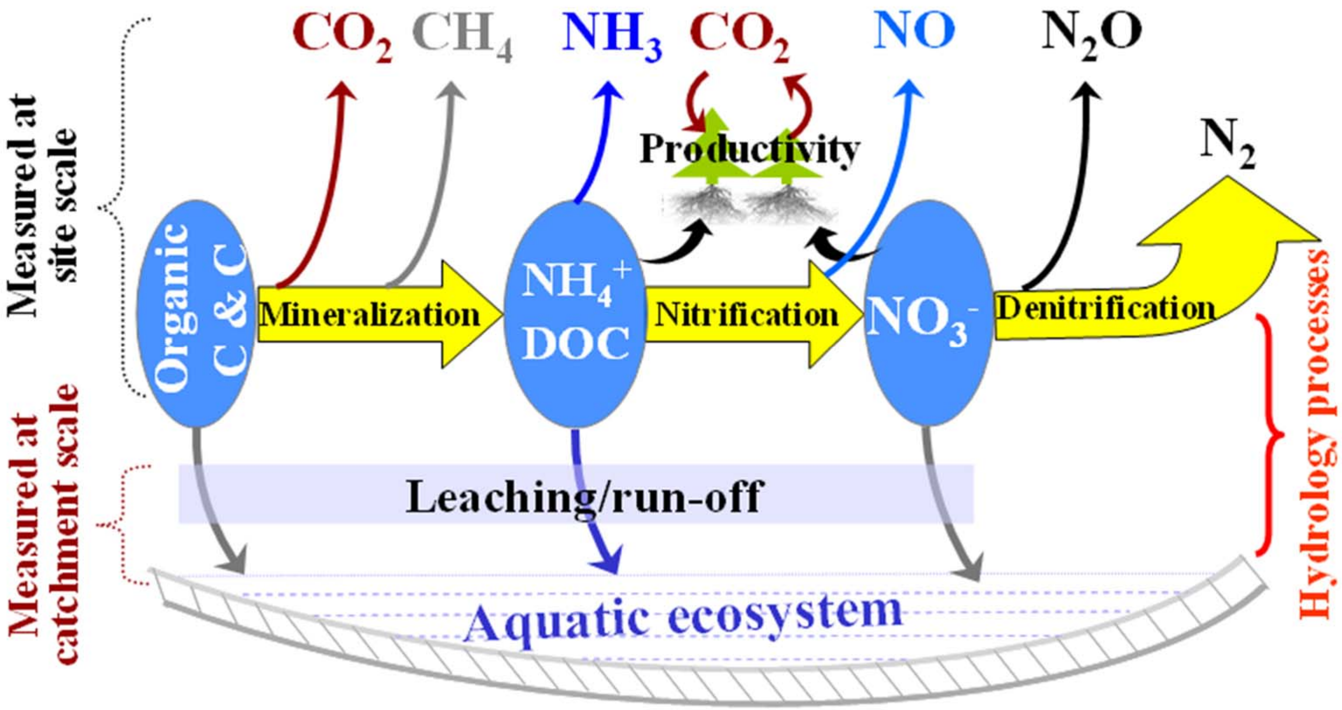
Source: Klaus Butterbach-Bahl

Modeling approach: scaling up and scenario study

Challenges

1) Long-term (replicated years) flux validation of multiple carbon- and nitrogen-gases including N_2O, NH_3, NO, CO_2 and CH_4 with multiple field treatments of site scale: no successful case so far.
2) Simultaneous simulation of multiple gas emissions, hydrology and productivity at catchment scale: model development is undergoing, e.g. Landscape DNDC, WNMM.
3) Available measurement dataset for model test, calibration, and validation in terms of simultaneously measured variables and/or parameters: not sufficient.

Modeling approach: scaling up and scenario study

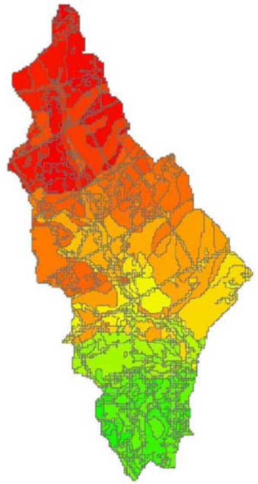


Close cooperation of experimental and model scientists are strongly required to integrate the studies from site, ecosystem to catchment scales !

Modeling approach: scaling up and scenario study

DNDC-SCS-MULSE model application

Slope runoff（SCS curve）:



$$Q_{surf} = \frac{\left(R_{day} - I_a\right)^2}{\left(R_{day} - I_a + S\right)} \qquad S = 25.4\left(\frac{1000}{CN} - 10\right)$$

Erosion（MULSE）:

$$sed = 11.8 \cdot \left(Q_{surf} \cdot q_{peak} \cdot area_{hru}\right)^{0.56} \cdot K_{USLE} \cdot C_{USLE} \cdot P_{USLE} \cdot LS_{USLE} \cdot CFRG$$

N retention and runoff in stream:

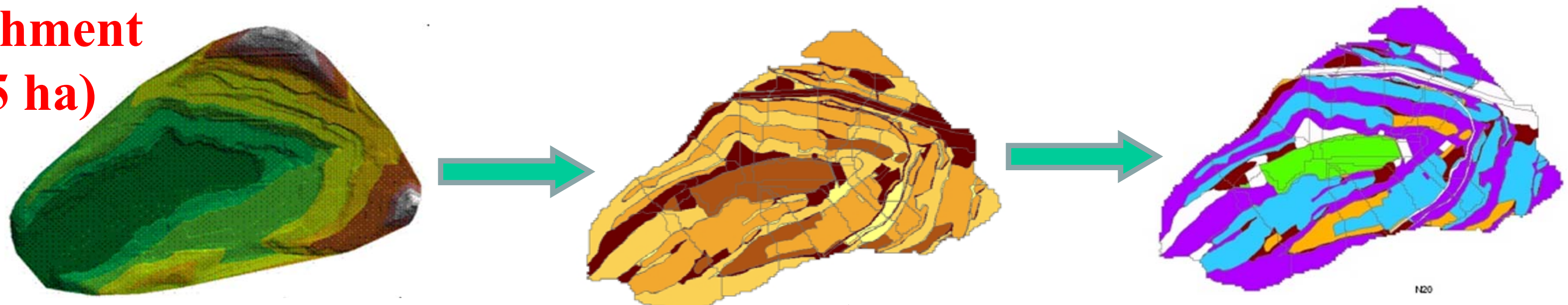
$$orgN_{surf} = 0.001 \cdot conc_{orgN} \cdot \frac{sed}{area_{hru}} \cdot \varepsilon_{N:sed}$$

(Deng et al., 2011, JGR; 2011, Biogeosciences)

Modeling approach: scaling up and scenario study

DNDC-SCS-MULSE model application

Catchment (35 ha)

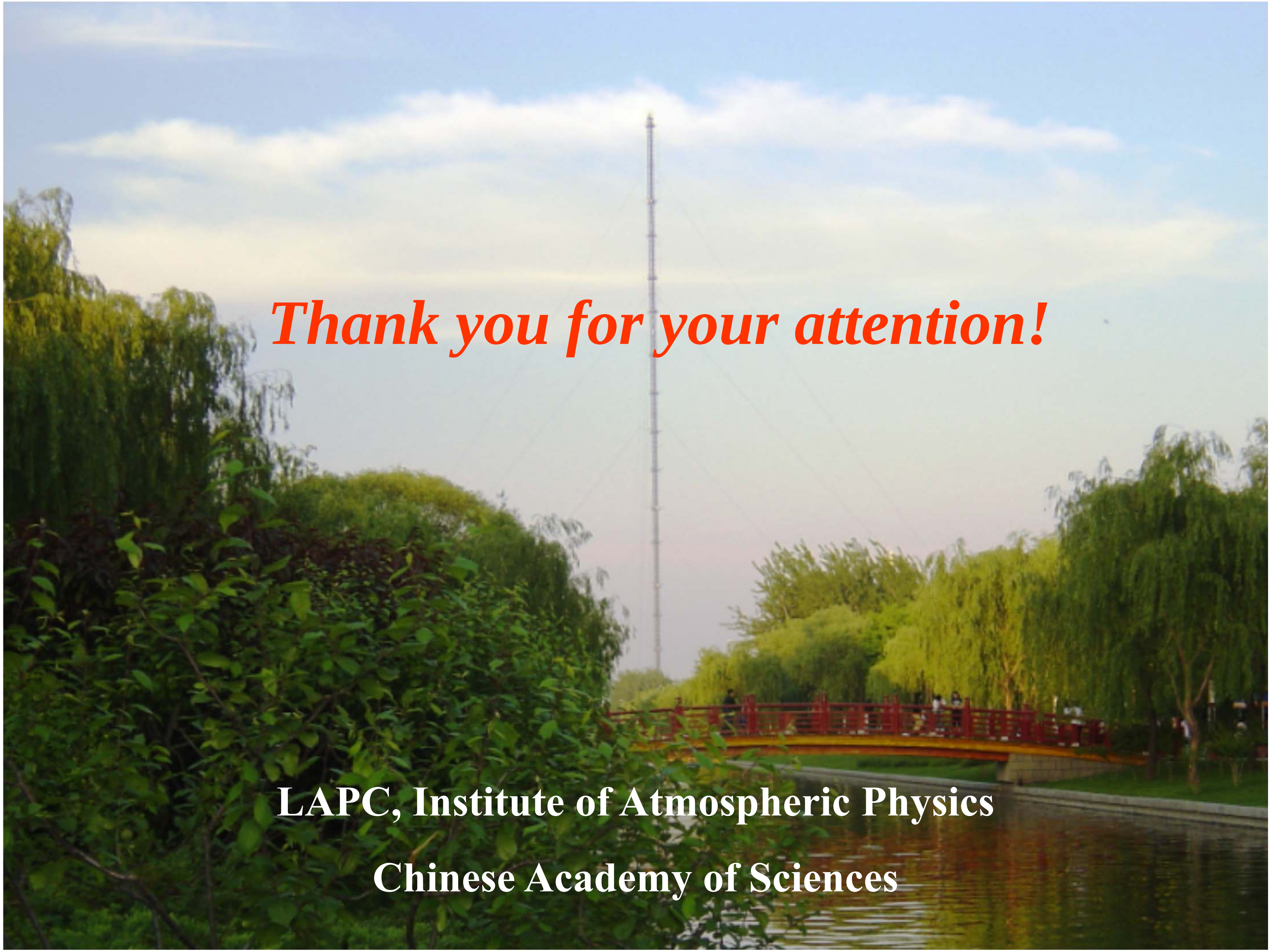


DEM → N leaching/runoff → N_2O emission

Land types	N losses (kg N yr^{-1})				
	N_2O	NO	N_2	TN	NH_3
Dry cropland	27.0	4.5	7.5	525	1350
Rice-based rotation	4.5	0.8	29.5	48	93
Winter-flooded paddy	0.2	0.2	5.9	31	34
Grassland	0.2	0.1	0.2	5	2
Forest	2.2	0.0	8.8	121	0
Residence area				174	
Total	**34**	**6**	**52**	**904**	**1479**

41% fertilizer nitrogen lost from the catchment by NH_3 emission and leaching or run-off

Source: Deng et al, 2011, JGR; Deng et al., 2011, Biogeosciences


Thank you for your attention!
LAPC, Institute of Atmospheric Physics
Chinese Academy of Sciences