華東師範大學
EAST CHINA NORMAL UNIVERSITY

# Large NO and HONO emissions from biological soil crusts regulated by drying-wetting cycles and temperature

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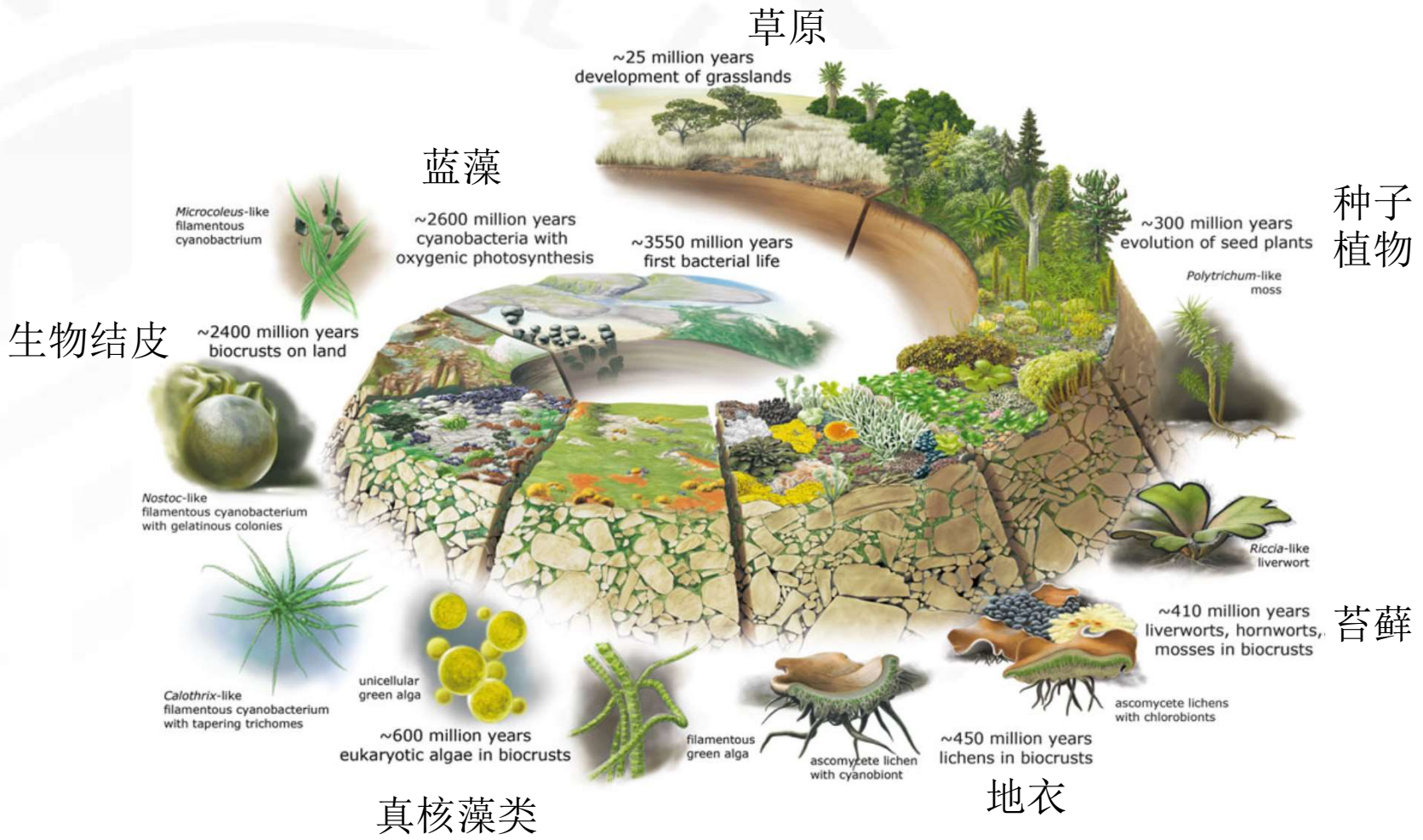
# Introduction

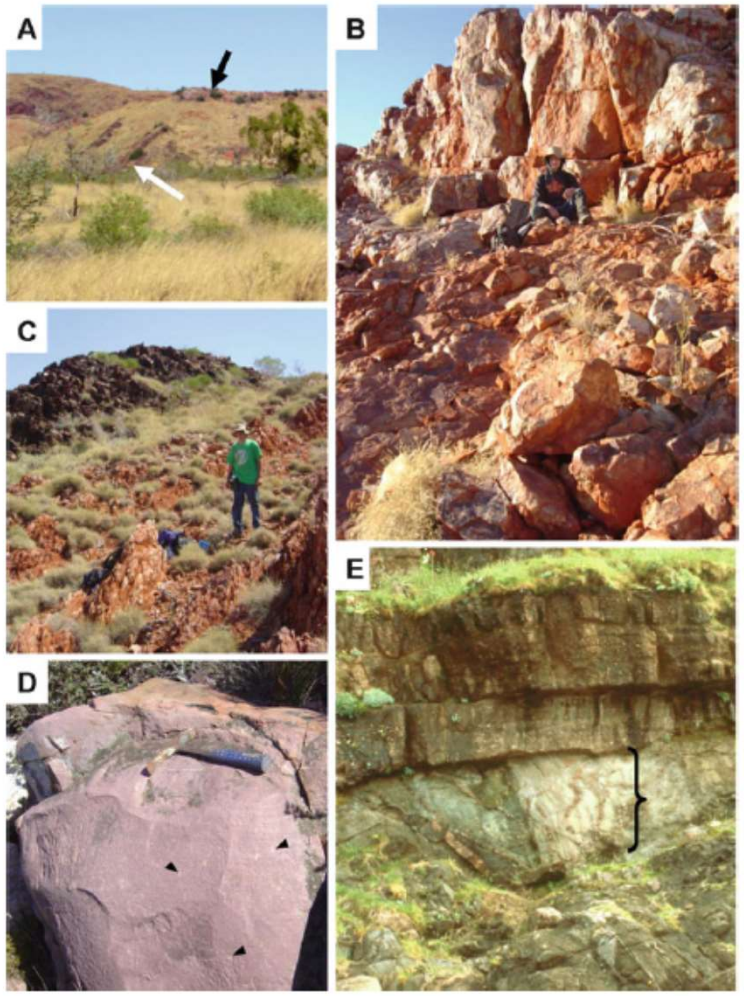
## 土壤生物结皮（Biological Soil Crusts)




(drawing by B. Buedel and F. Spindler)

# Introduction

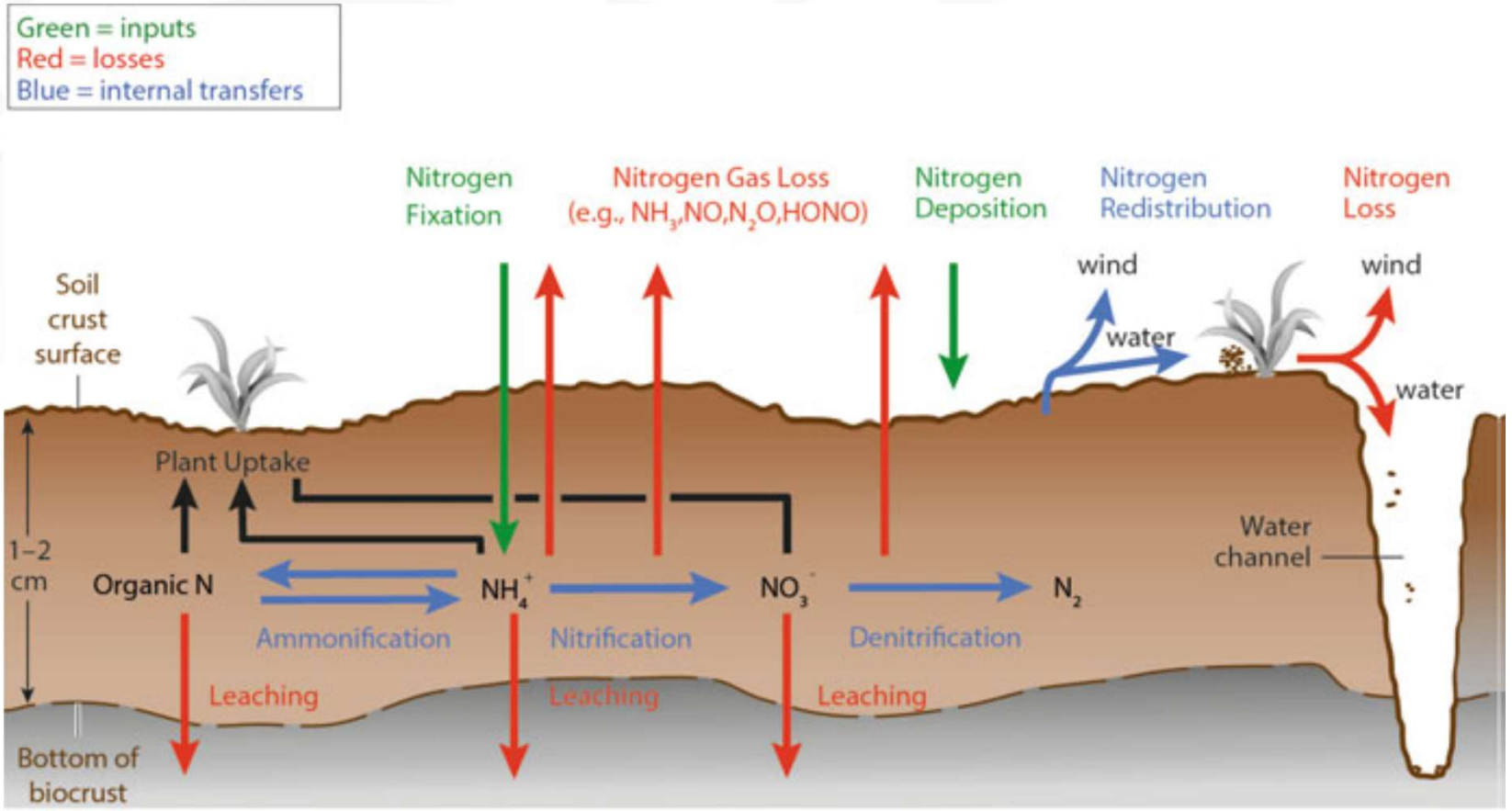
## 土壤生物结皮（Biological Soil Crusts)


(from Elbert et al., 2012, Nature Geoscience; Weber et al., 2016)

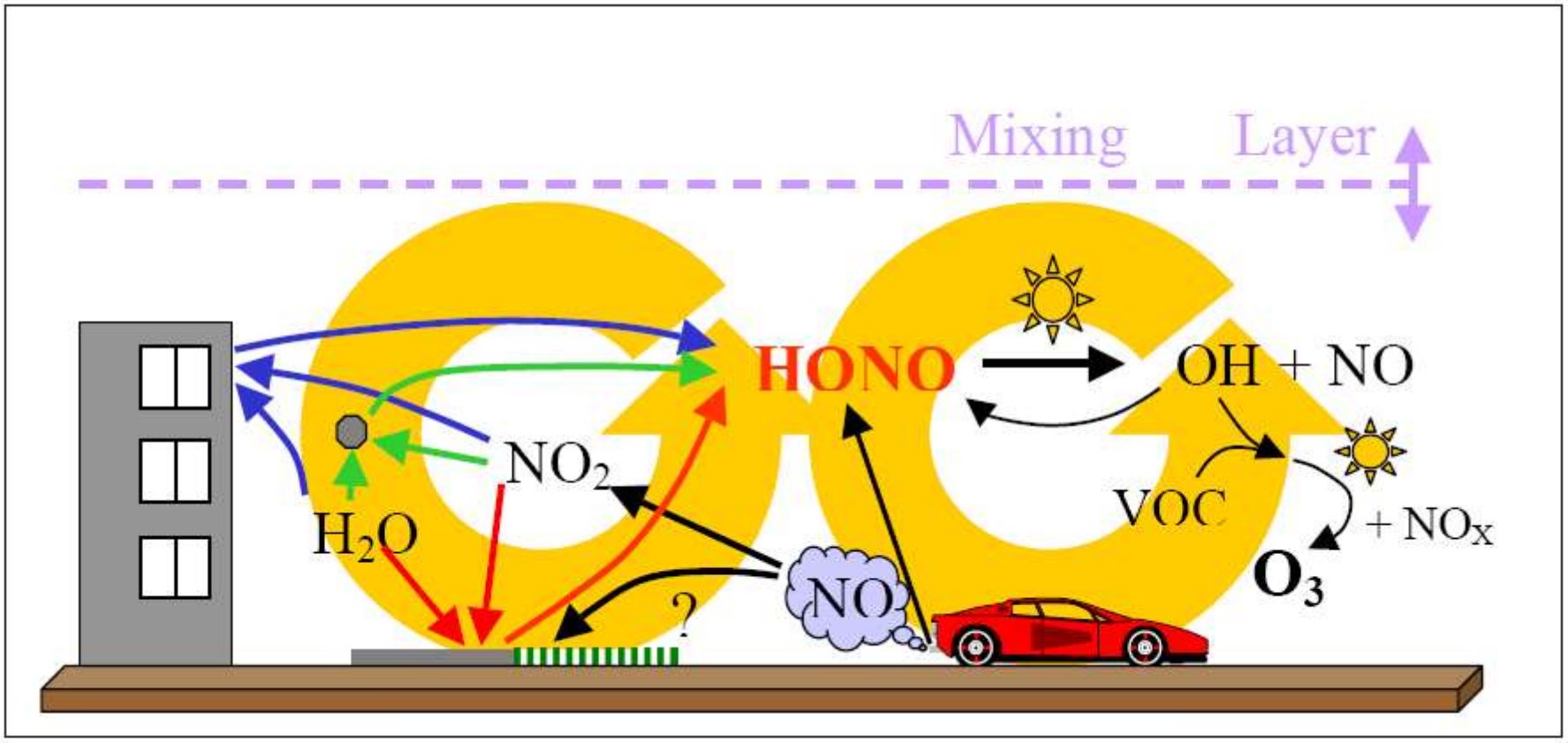
# Introduction

## 土壤生物结皮与氮循环 BSCs on nitrogen cycling




(from Barger et al., 2016)

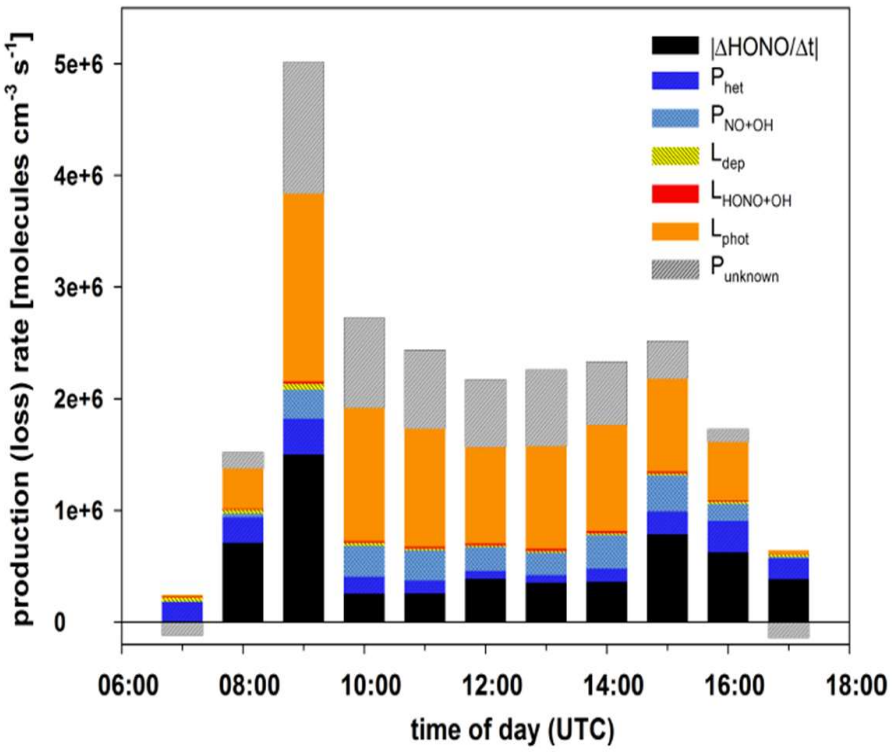
## HONO与城市大气化学 Urban chemistry of HONO




(from Trick, 2004, PhD thesis)

# Introduction

## 大气HONO的未知源 Unknown daytime sources of HONO




(Sörgel et al., 2011, Atmospheric Chemistry and Physics)

Sources:

$NO + OH\cdot \longrightarrow HONO$

$NO_2 + \text{Humic acid} \longrightarrow HONO$

$2NO_2 + H_2O \rightarrow HONO + HNO_3$

$NO_2^- + H^+ \longrightarrow HONO$

Sinks:

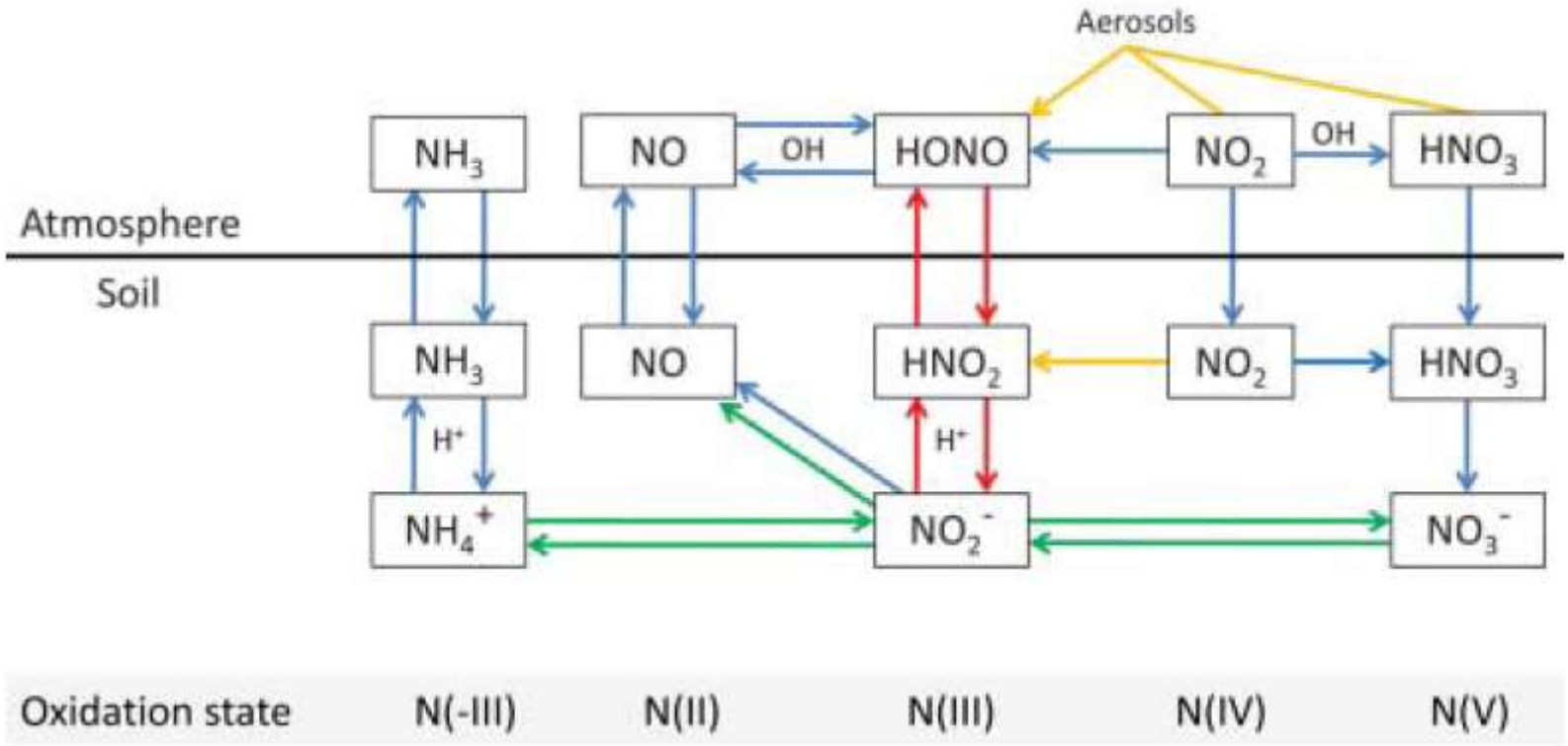
$HONO \xrightarrow{h\nu} OH\cdot + NO$

$HONO + OH\cdot \longrightarrow NO_2 + H_2O$

$HONO + NO_2 \rightarrow HNO_3 + NO$

# Introduction

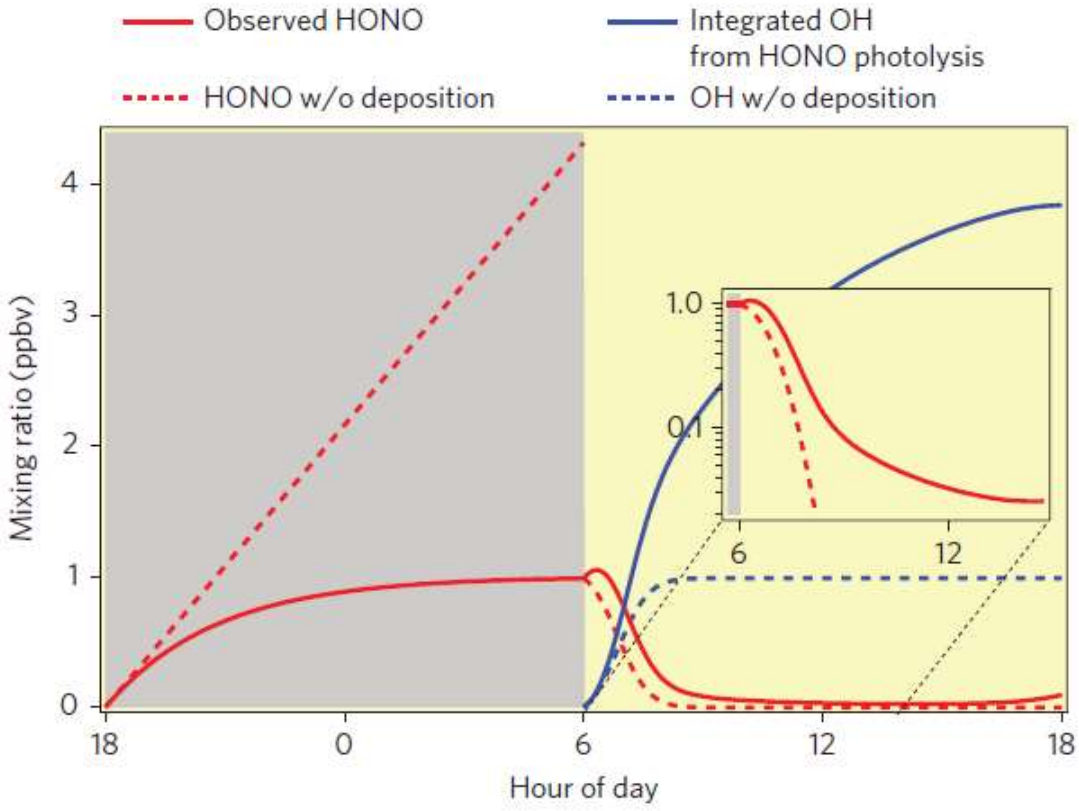
## 土壤排放HONO
## HONO emissions from soil



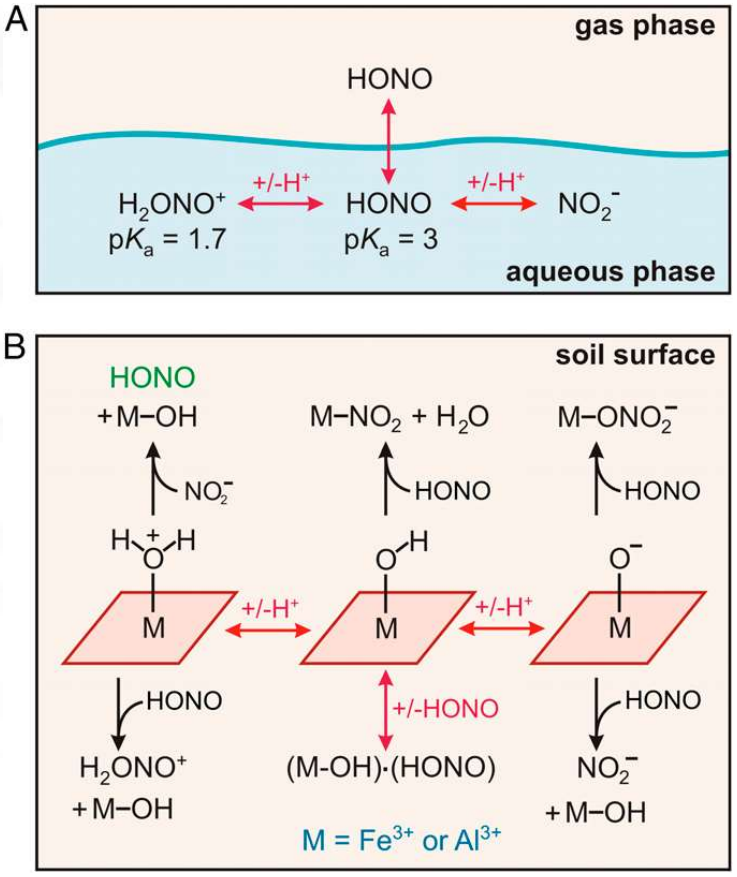

(from Su et al., 2011, Science)

# Introduction

## 土壤排放HONO的机理探讨
## The mechanisms of HONO emission from soil



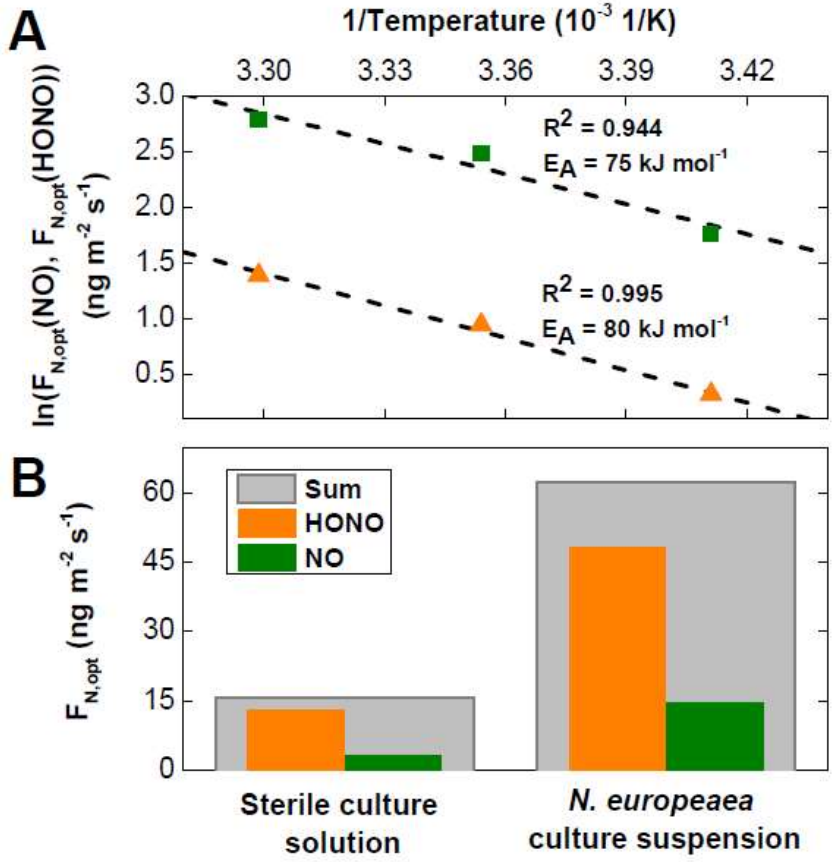

(from VandenBoer et al., 2015, Nature Geoscience)

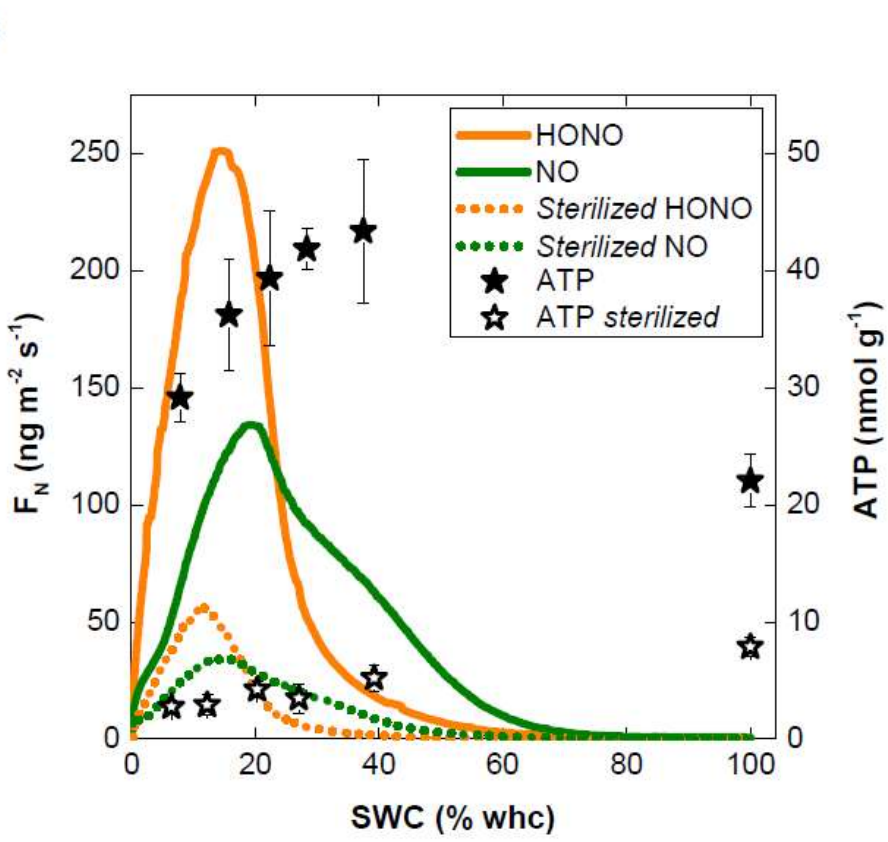



(from Donaldson et al., 2014, PNAS)

# Introduction

## 土壤微生物对HONO排放的贡献
## AOB can emit HONO



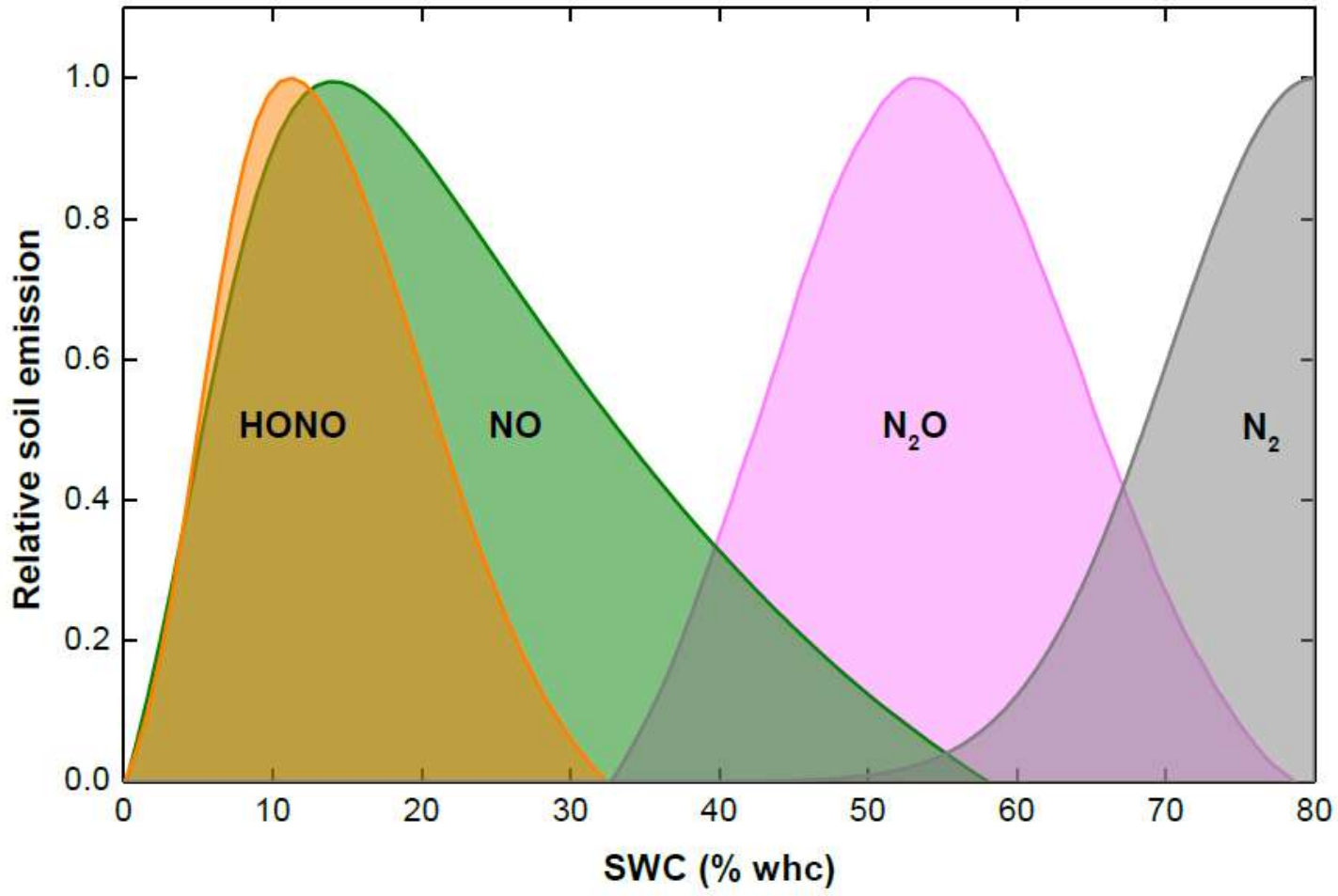




(from Oswald et al., 2013, Science)

# Introduction

## 土壤活性氮气体排放

## Reactive nitrogen gases emission from soil



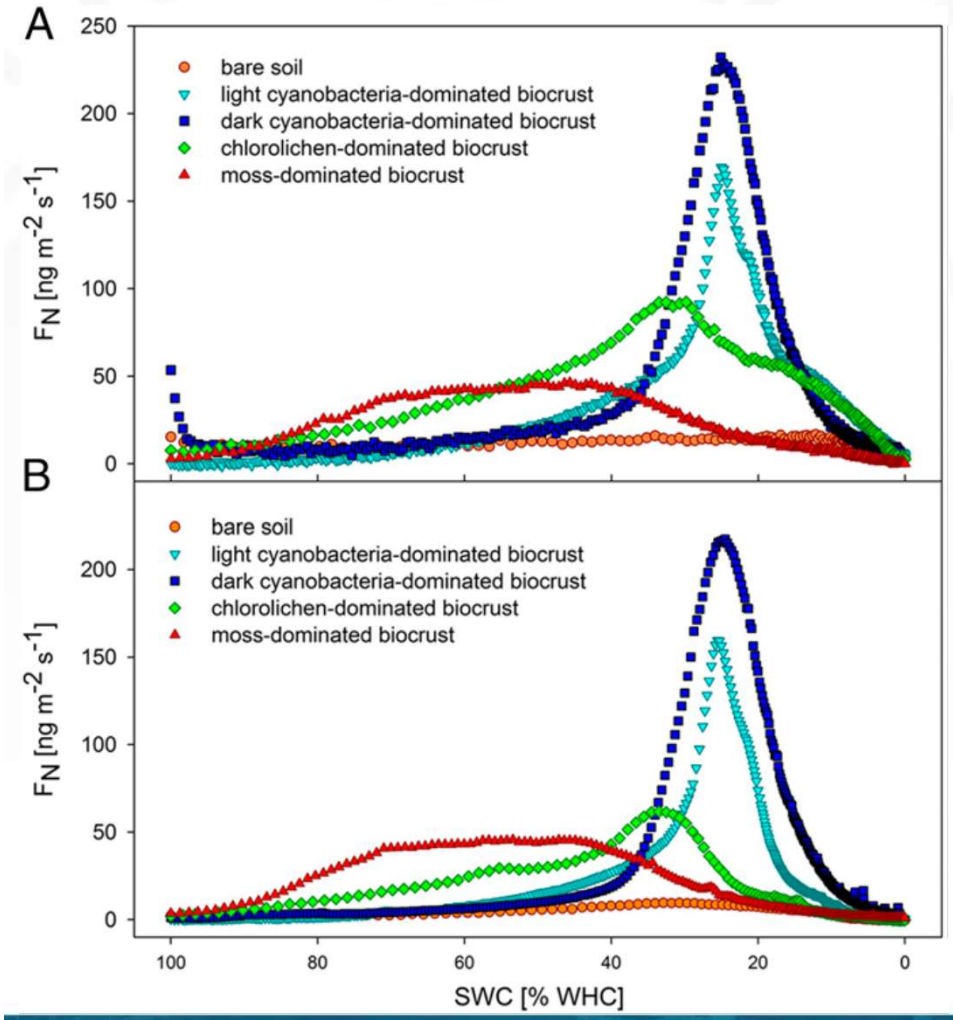

(from Oswald et al., 2013, Science)

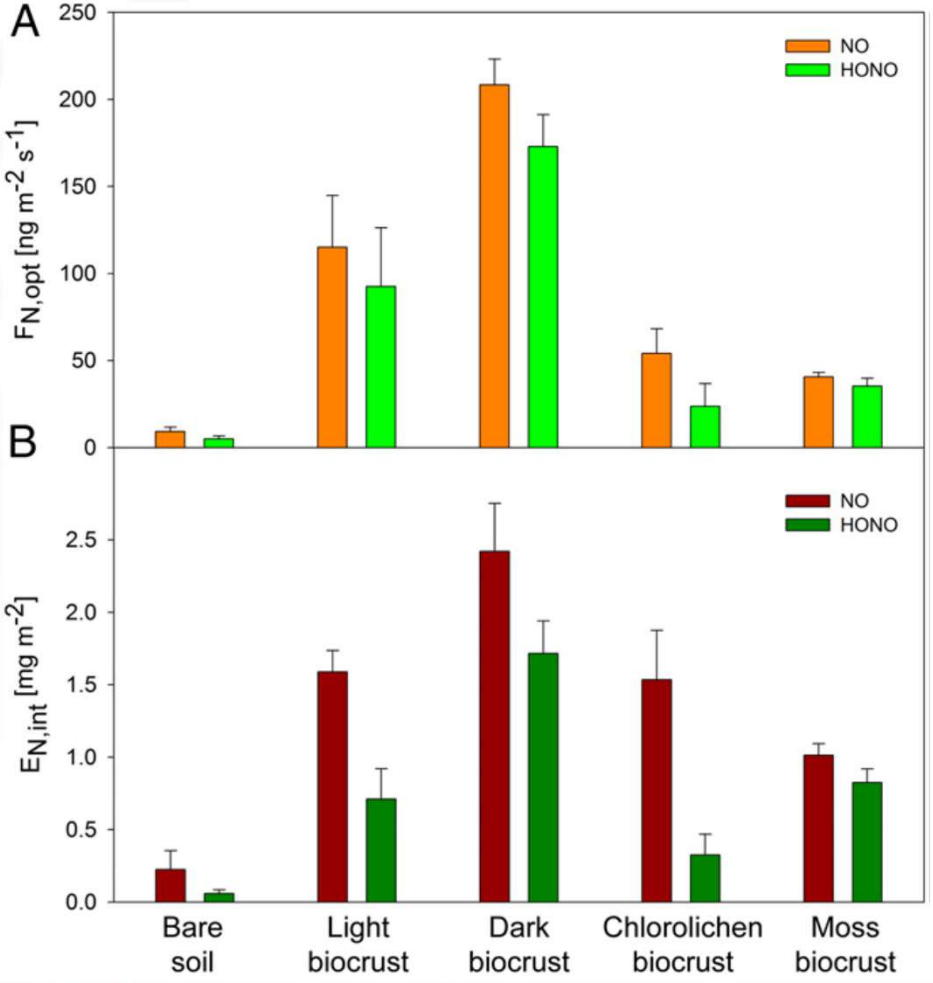
# Methods

动态箱系统
**Dynamic Chamber System**

# Results

## 土壤生物结皮HONO和NO排放
## HONO and NO released from BSCs




(from Weber et al., 2015, PNAS)

# Results

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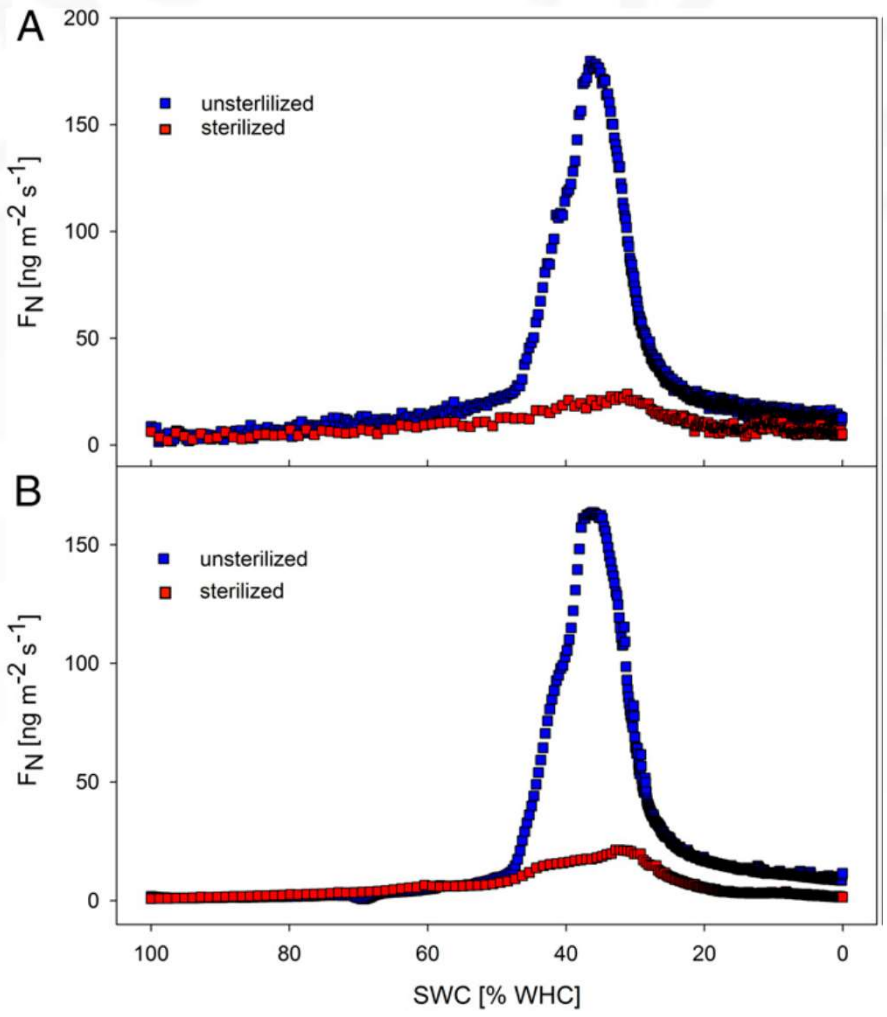
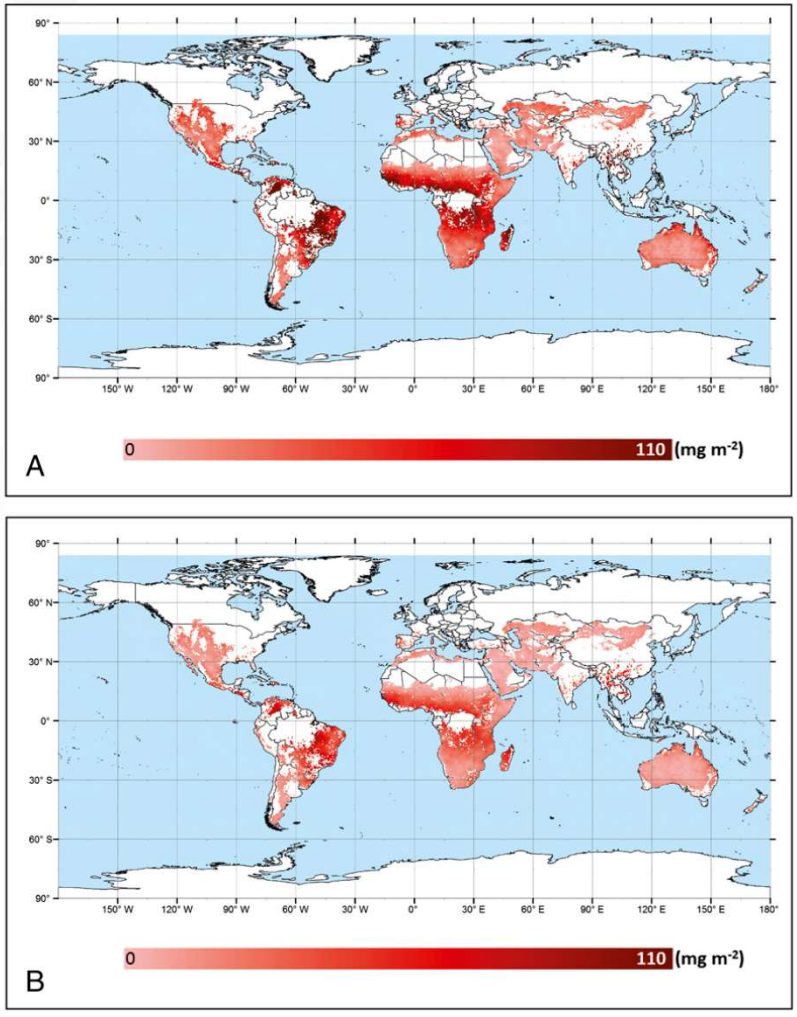
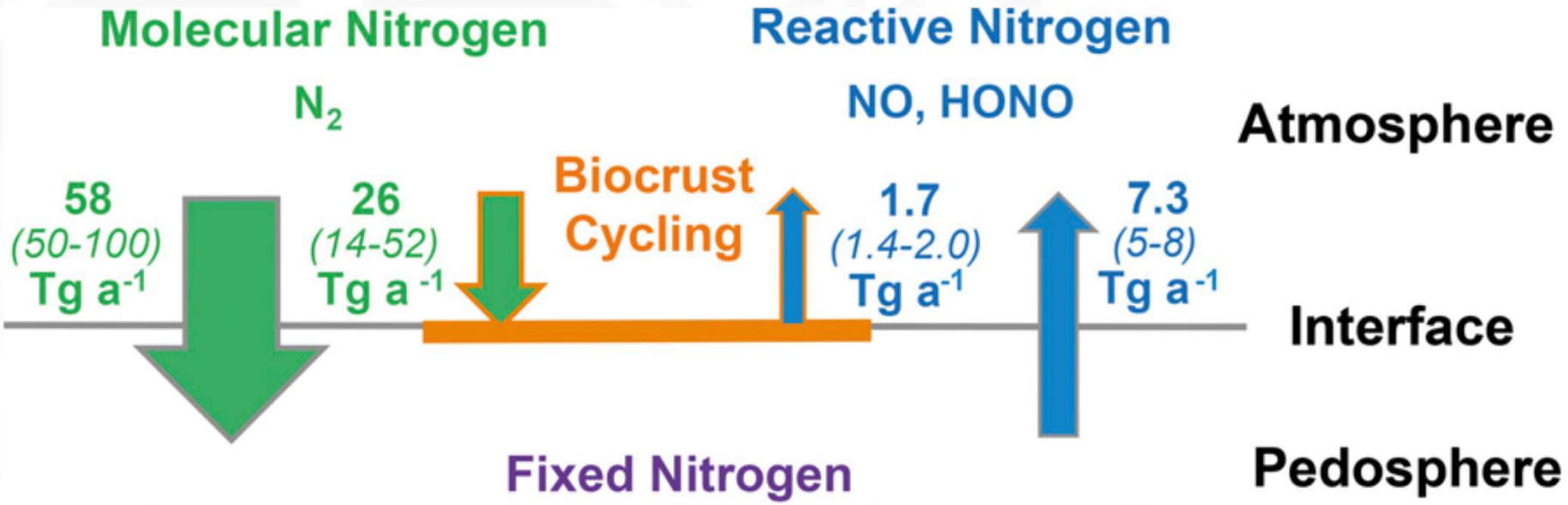



(from Weber et al., 2015, PNAS)

# Results

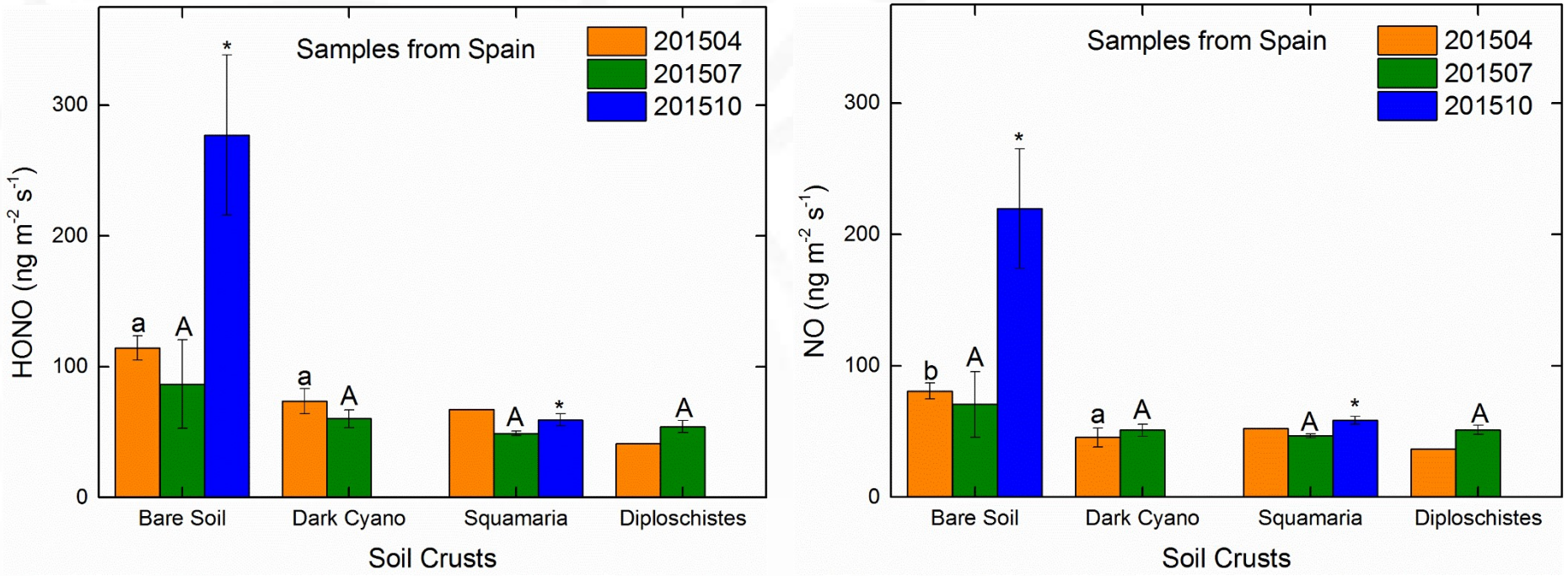
## 土壤生物结皮HONO和NO排放
## HONO and NO released from BSCs




(from Weber et al., 2015, PNAS)

# Results

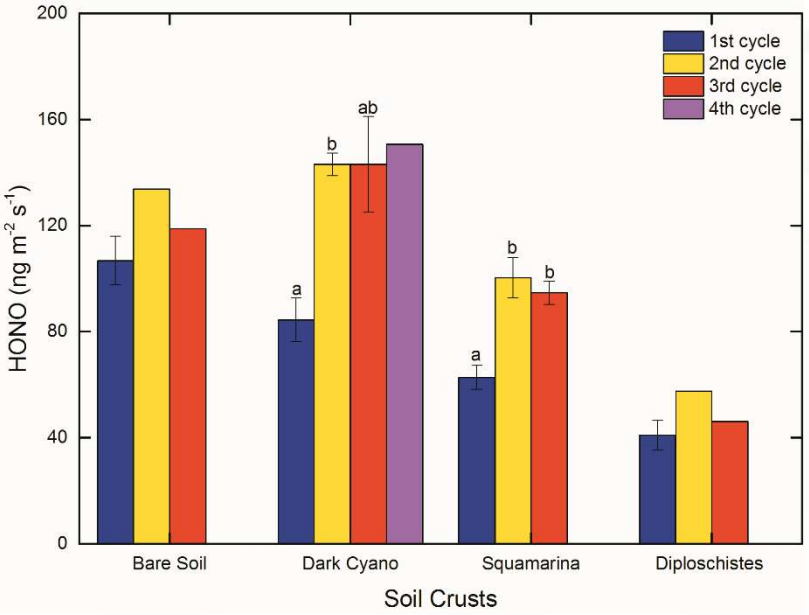
## HONO and NO emission from Spain BSCs

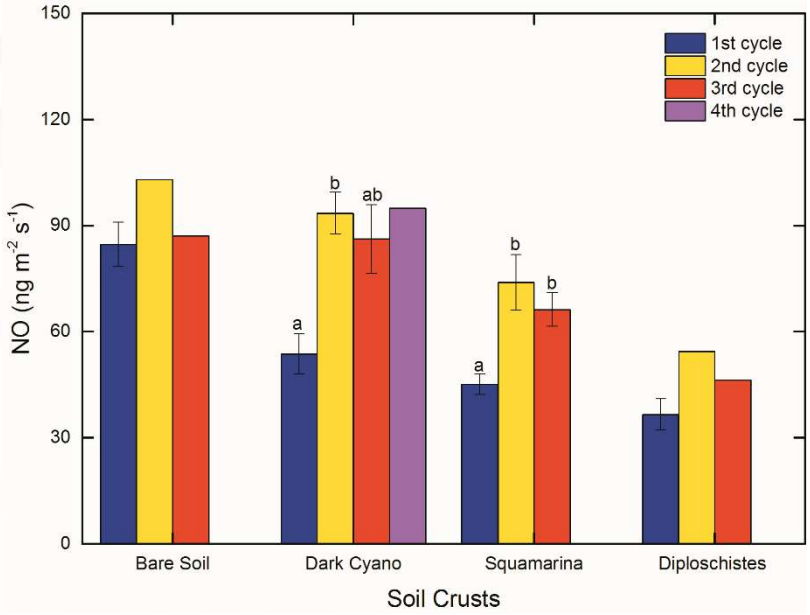



- There is a non-significant tendency that HONO and NO emission from bare soil are higher than other types of biocrusts,
- Potential reasons:
  - Nutrients concentration in bare soil are higher than that in biocrusts samples
  - Storage time

# Results

## 干湿交替次数对HONO和NO排放通量的影响
## Drying-wetting cycles on HONO and NO flux

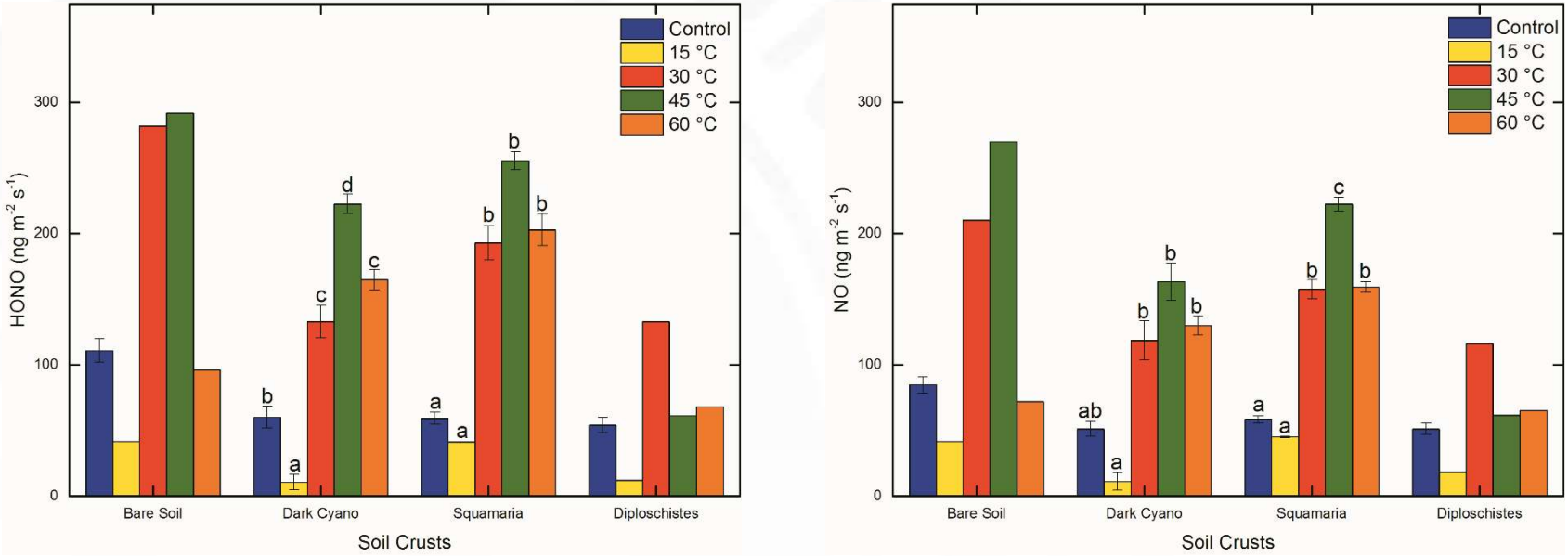



- HONO and NO emission increased during the 2nd cycle of drying-wetting, and kept stable for the next cycles.

# Results

## 干燥温度对HONO和NO排放通量的影响
## Pre-experimental drying at different temperatures on HONO and NO flux



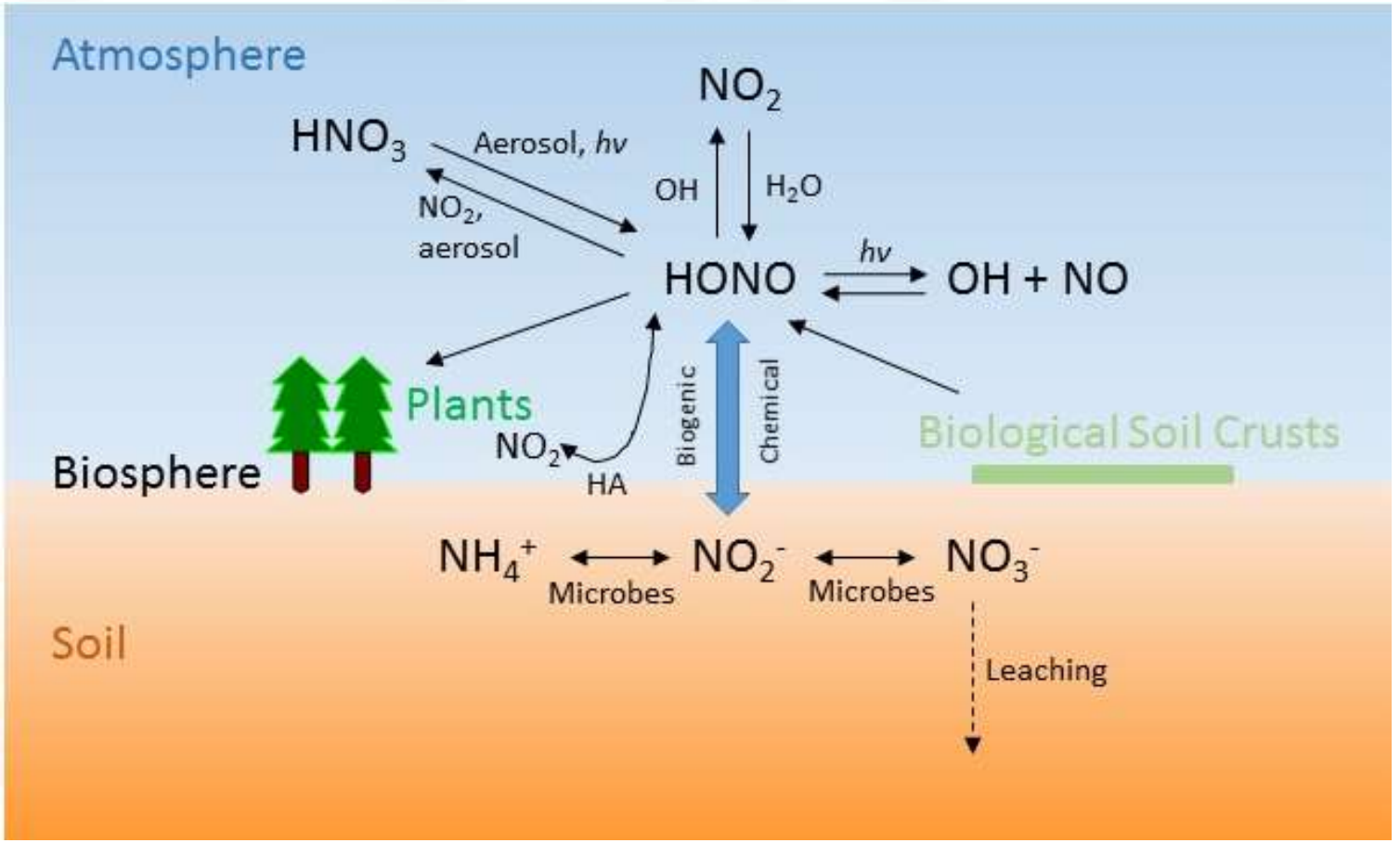

- HONO and NO emission increased up to 45 ºC, and then decreased at 60 ºC.
- Potential reasons:
  - High temperature inhibited microbial activity
  - The optimum temperature for the biocrusts is ~ 45 ºC

# Summary

- Biological soil crusts (biocrusts) are emitters of nitric oxide (NO) and nitrous acid (HONO).
- Based on laboratory, field, and satellite measurement data, we obtain a best estimate of ~1.7 Tg per year for the global emission of reactive nitrogen from biocrusts (1.1 Tg $a^{-1}$ of NO-N and 0.6 Tg $a^{-1}$ of HONO-N), corresponding to ~20% of global nitrogen oxide emissions from soils under natural vegetation.
- High HONO and NO emission from Spain bare soil may caused by high nitrate concentration from N deposition, from nutrient-rich rocks or microbial community.
- HONO and NO emission increased by the 2$^{nd}$ drying-wetting cycle, but kept stable for the 3$^{rd}$ cycle.
- HONO and NO emission increased with temperature increase up to 45 ºC and then decreased at 60 ºC, which indicates microbiological processes are still dominant HONO and NO emission even at high soil temperature, and also implies large HONO and NO emission with global temperature increased.

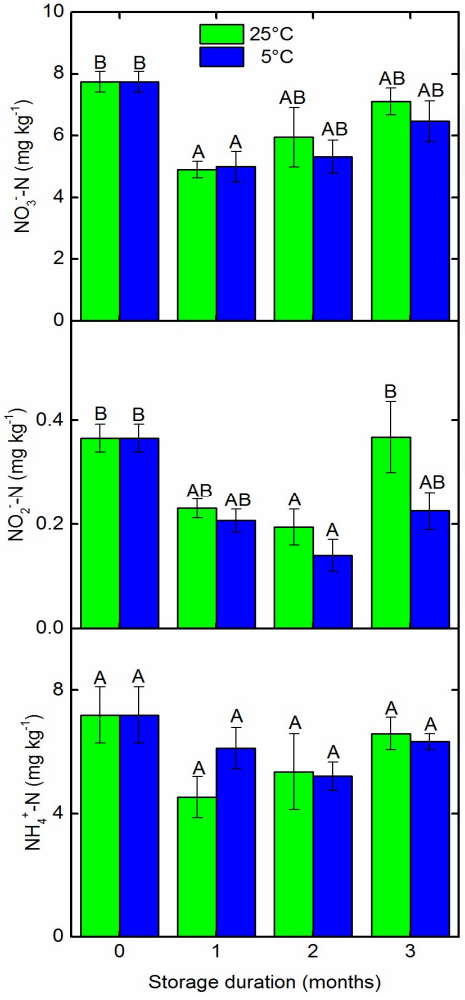
**Acknowledgements:**

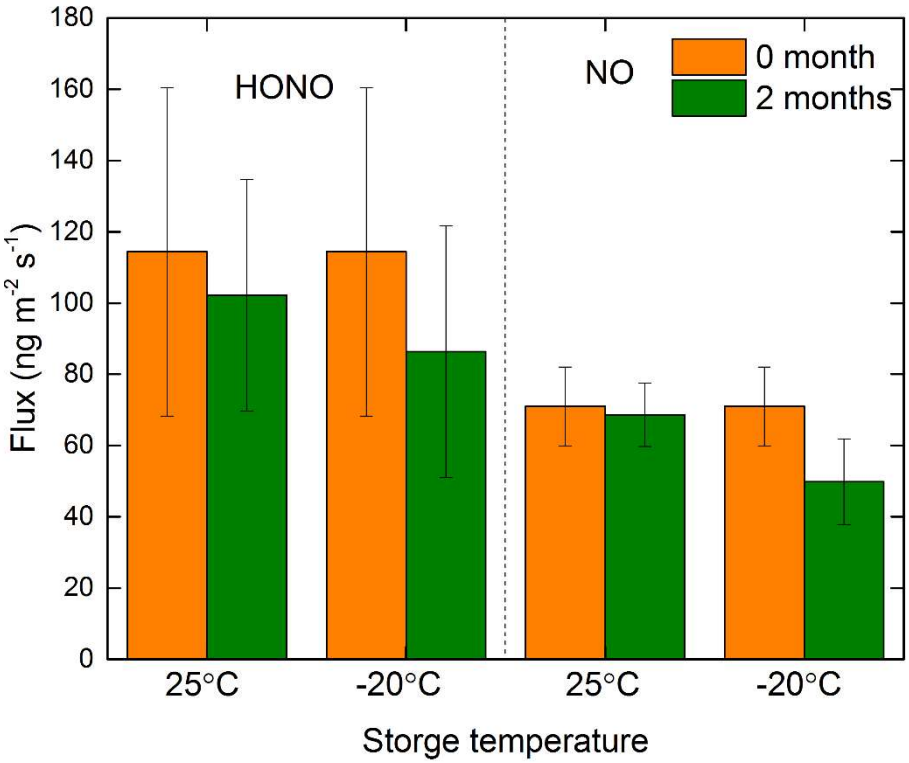
Organizing Committees, IGSNRR of CAS, East China Normal University,
Max Planck Institute for Chemistry



# Results

## Effects of storage temperature and duration on HONO and NO flux



# 研究背景

## HONO在水溶液中的化学反应

Ostwald process:

$$3\ HONO \rightleftharpoons NO_3^- + 2\ NO + H_3O^+$$

weak Brønsted acid, behaves amphoteric like water

$$HONO + H_2O \rightleftharpoons H_3O^+ + NO_2^-$$

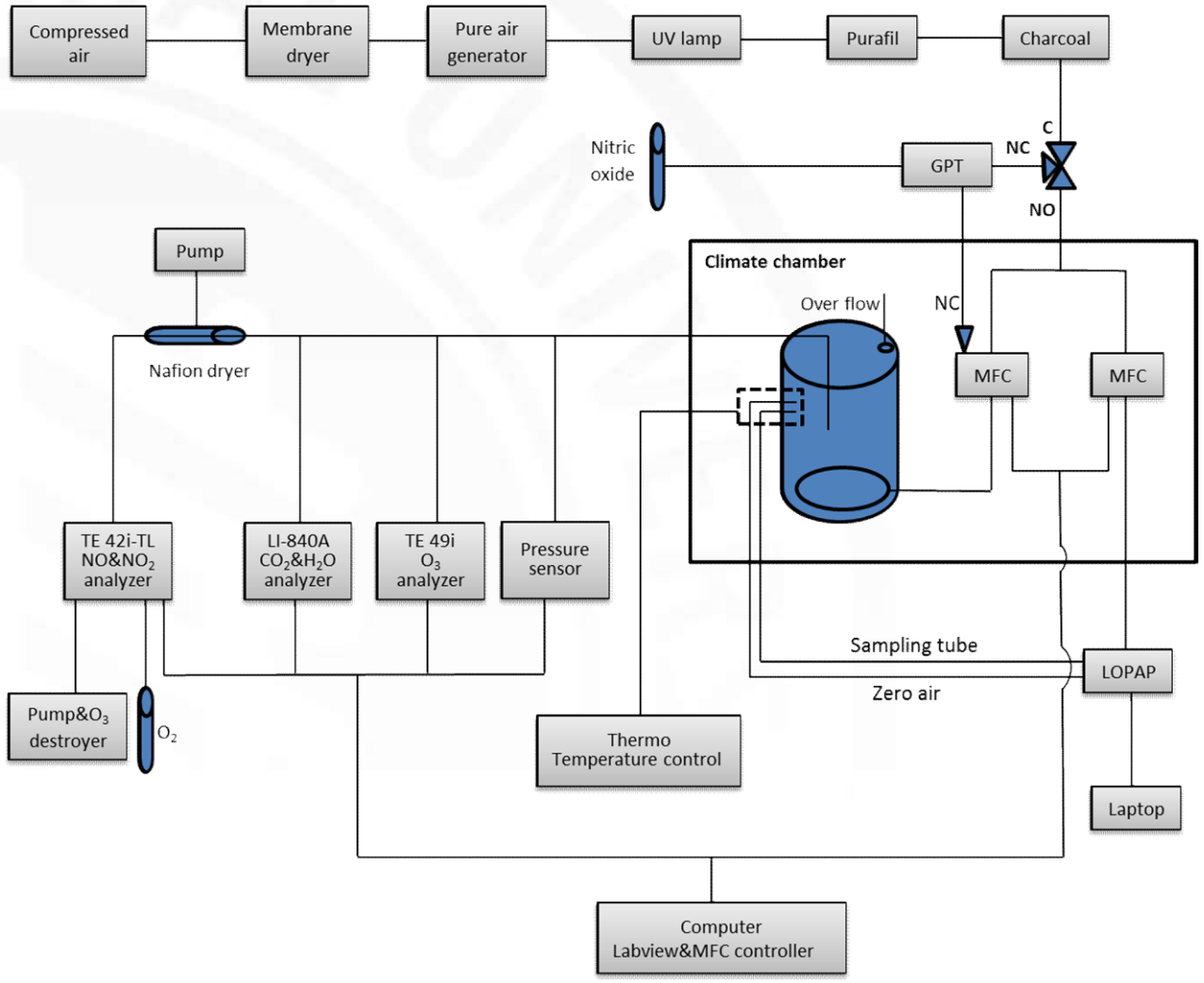
$$HONO + H_3O^+ \rightleftharpoons H_2ONO^+ + H_2O \rightleftharpoons 2\ H_2O + NO^+$$

$$pK_a = -\log\left(\frac{[H_3O^+]\times[NO_2^-]}{[HONO]}\right)$$

$pK_a$ value 3.16 at room temperature

# 研究方法

动态箱系统


Compressed air
Membrane dryer
Pure air generator
UV lamp
Purafil
Charcoal
Nitric oxide
GPT
C
NC
NO
Pump
Climate chamber
Over flow
NC
Nafion dryer
MFC
MFC
TE 42i-TL NO&NO2 analyzer
LI-840A CO2&H2O analyzer
TE 49i O3 analyzer
Pressure sensor
Sampling tube
LOPAP
Zero air
Pump&O3 destroyer
O2
Thermo Temperature control
Laptop
Computer Labview&MFC controller