Nitrous acid (HONO) exchanges at the *Zea mays* leaf – atmosphere interface

A. Marion, J. Morin,
A. Gandolfo, E. Ormeno,
S. Boiry, B. D'Anna, H. Wortham

Why is HONO interesting ?

- Source of hydroxyl radicals $HONO + h\nu \rightarrow HO^{\bullet} + NO^{\bullet}$
  - Main atmospheric oxidants during the day
  - Key species in the formation of ozone and particulate matter

→ Need to model HONO formation to predict OH concentrations

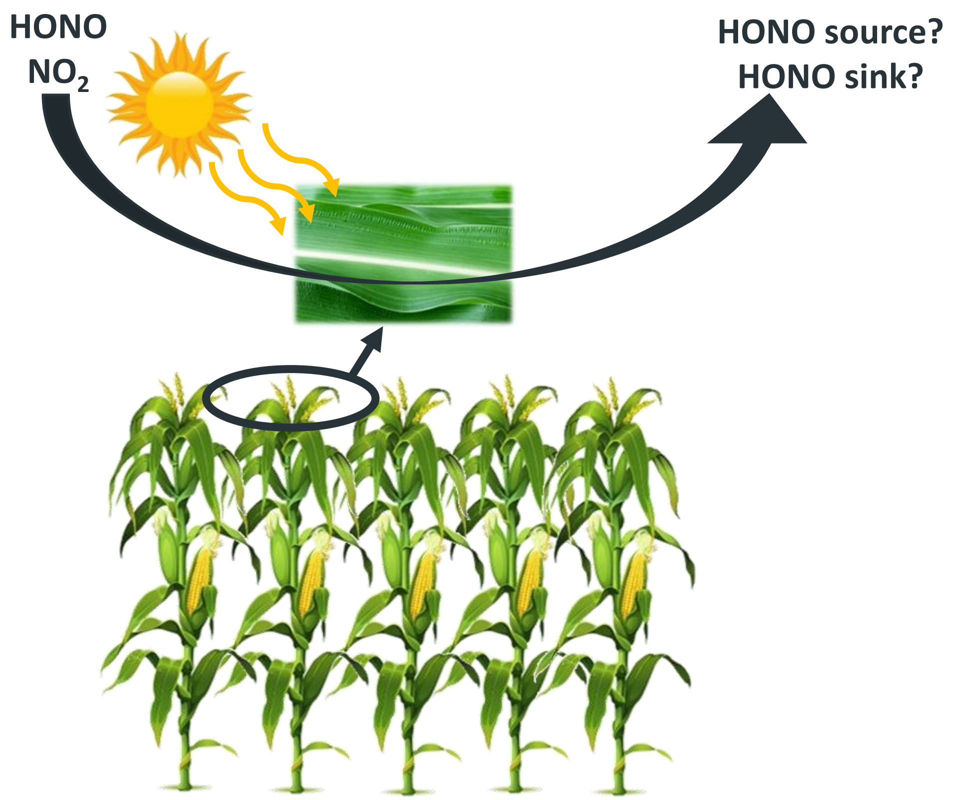
- Models underestimate HONO concentration
  - Unknown source of HONO : maximal around midday, correlated to NO_2 concentration

[HONO] above the canopee > **[HONO] above the ground**

→ Formation on leaves ?

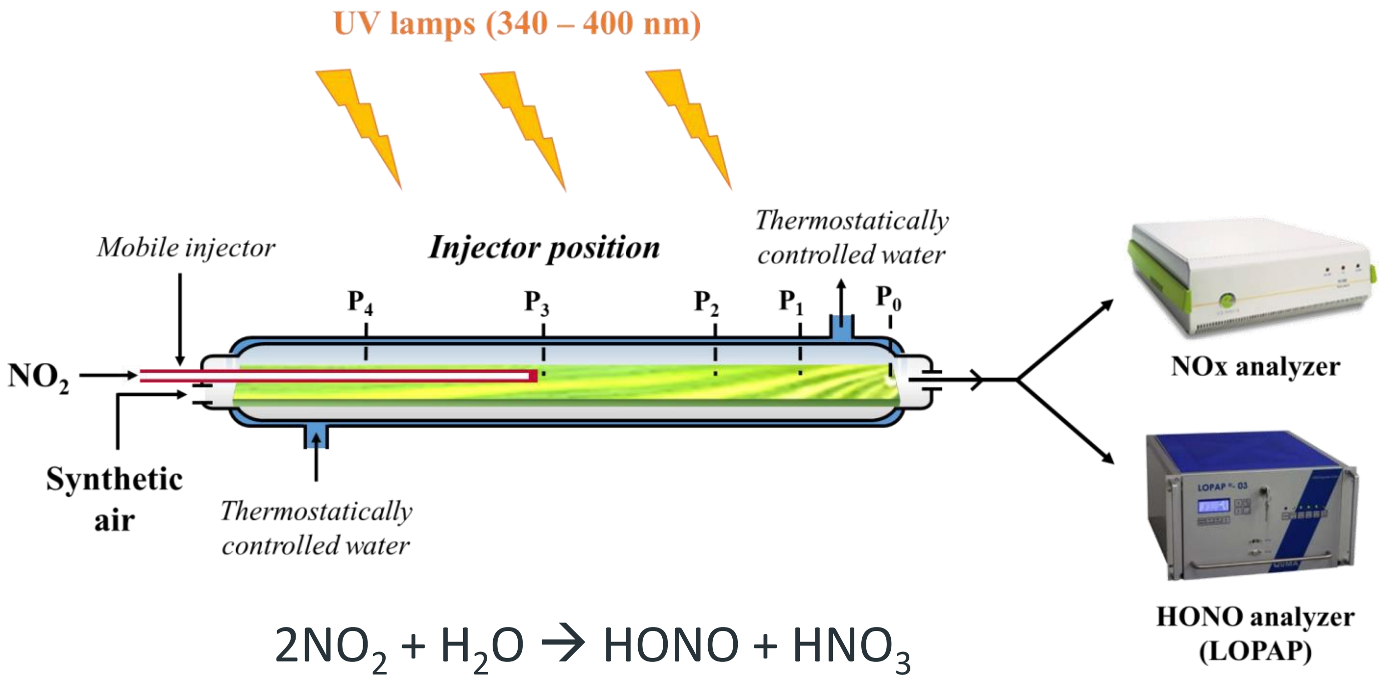
Objective

$2NO_2 + H_2O \rightarrow HONO + HNO_3$



A. Marion, J. Morin,
A. Gandolfo, E. Ormeno,
S. Boiry, B. D'Anna, H. Wortham

1/ HONO production by reduction of nitrogen dioxide (NO_2) on *Zea mays* leaf surfaces in laboratory varying temperature



$2NO_2 + H_2O \rightarrow HONO + HNO_3$

Temperature : 288 K to 313 K

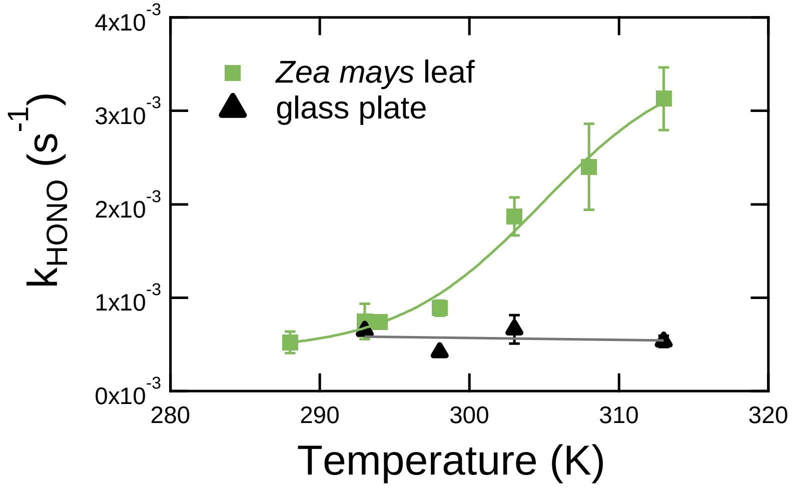


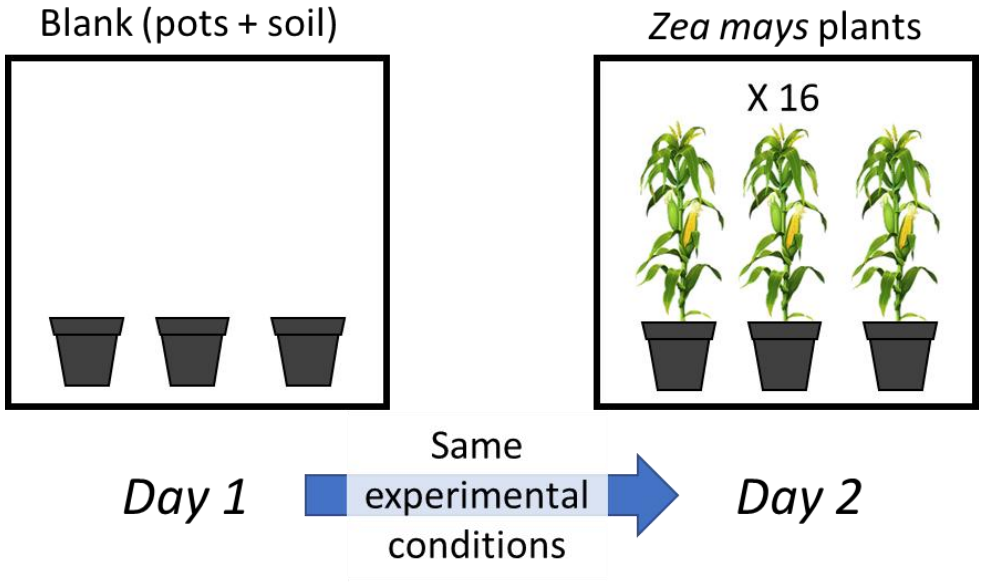
Figure 1: Rate constant for HONO formation on Zea mays leaves under controlled conditions : RH = 40% , NO_2 = 40 ppb, Light intensity = 20 W m^{-2}

- Important increase of HONO rate constant with temperature
- Increase of reaction and/or desorption step

Nitrous acid (HONO) exchanges at the Zea mays leaf – atmosphere interface

A. Marion, J. Morin,
A. Gandolfo, E. Ormeno,
S. Boiry, *B. D'Anna, H. Wortham*

2/ HONO production and consumption by living *Zea mays* plants



Controlled parameters:

- Temperature
- Relative humidity
- NO_2 and CO_2 concentration
- Light intensity

Measurement of :

- CO_2 consumption
- Leaf surfaces
- [HONO]

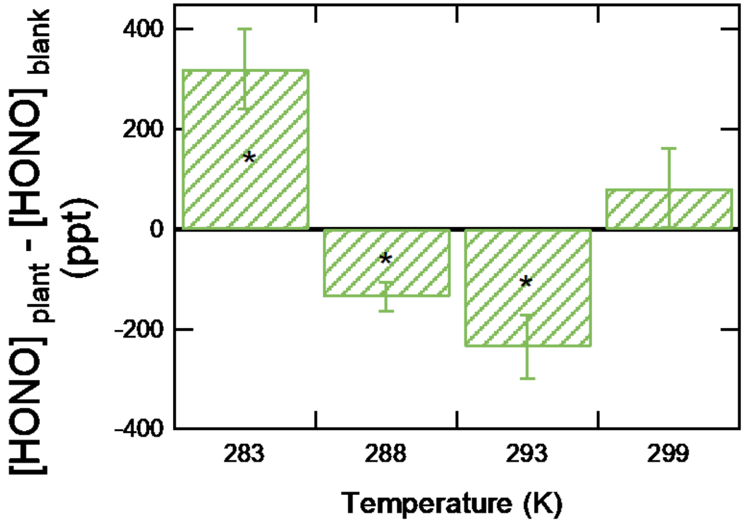


Figure 2: $[HONO]_{plant}$ – $[HONO]_{blank}$ (ppt) as a function of temperature (K)

** Statistically different from blank*

- HONO emission > HONO consumption at 283 K
- HONO consumption > HONO emission at 288 and 293 K
- HONO emission = HONO consumption at 299 K

A. Marion, J. Morin,
A. Gandolfo, E. Ormeno,
S. Boiry, B. D'Anna, H. Wortham

First order rate constant for HONO uptake by the plants (k_{plant}) and deposition velocities

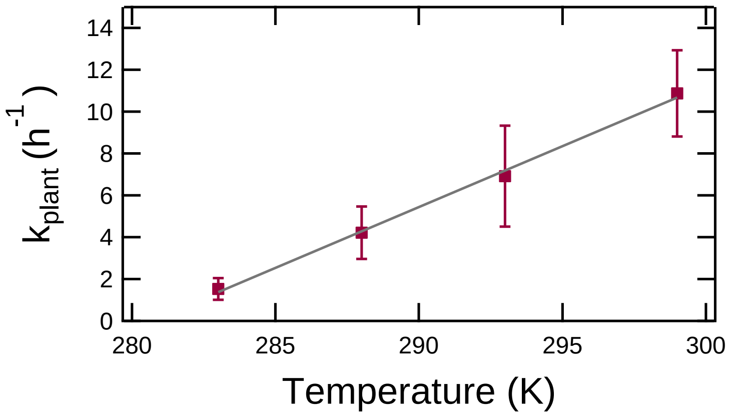


Figure 3: Rate constant for HONO uptake by the plants (k_{plant}) as a function of temperature – leaf surface 2.83m²

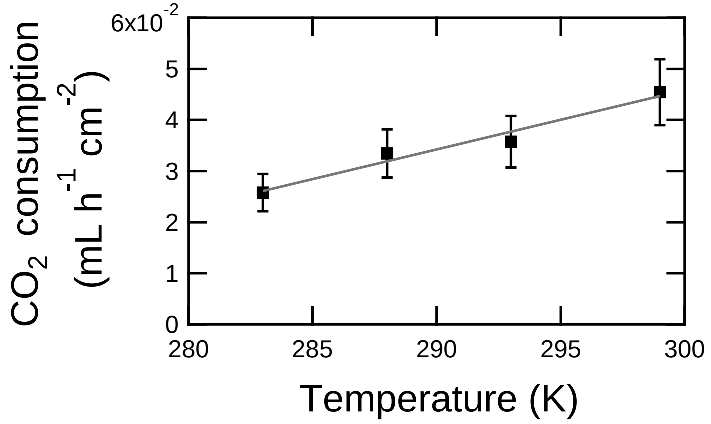


Figure 4: CO_2 consumption by the plant as a function of temperature

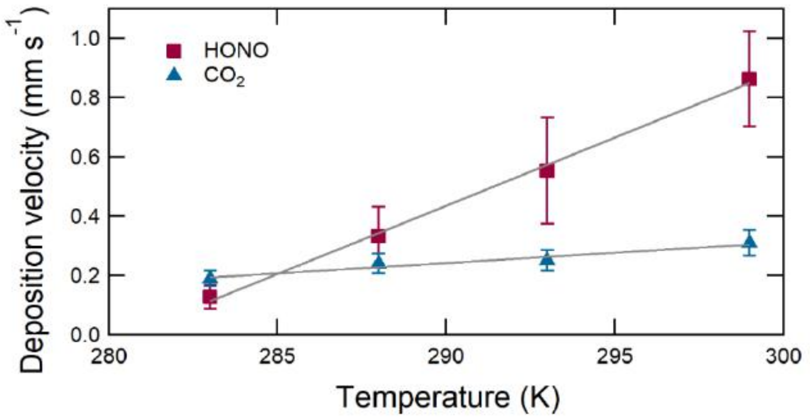


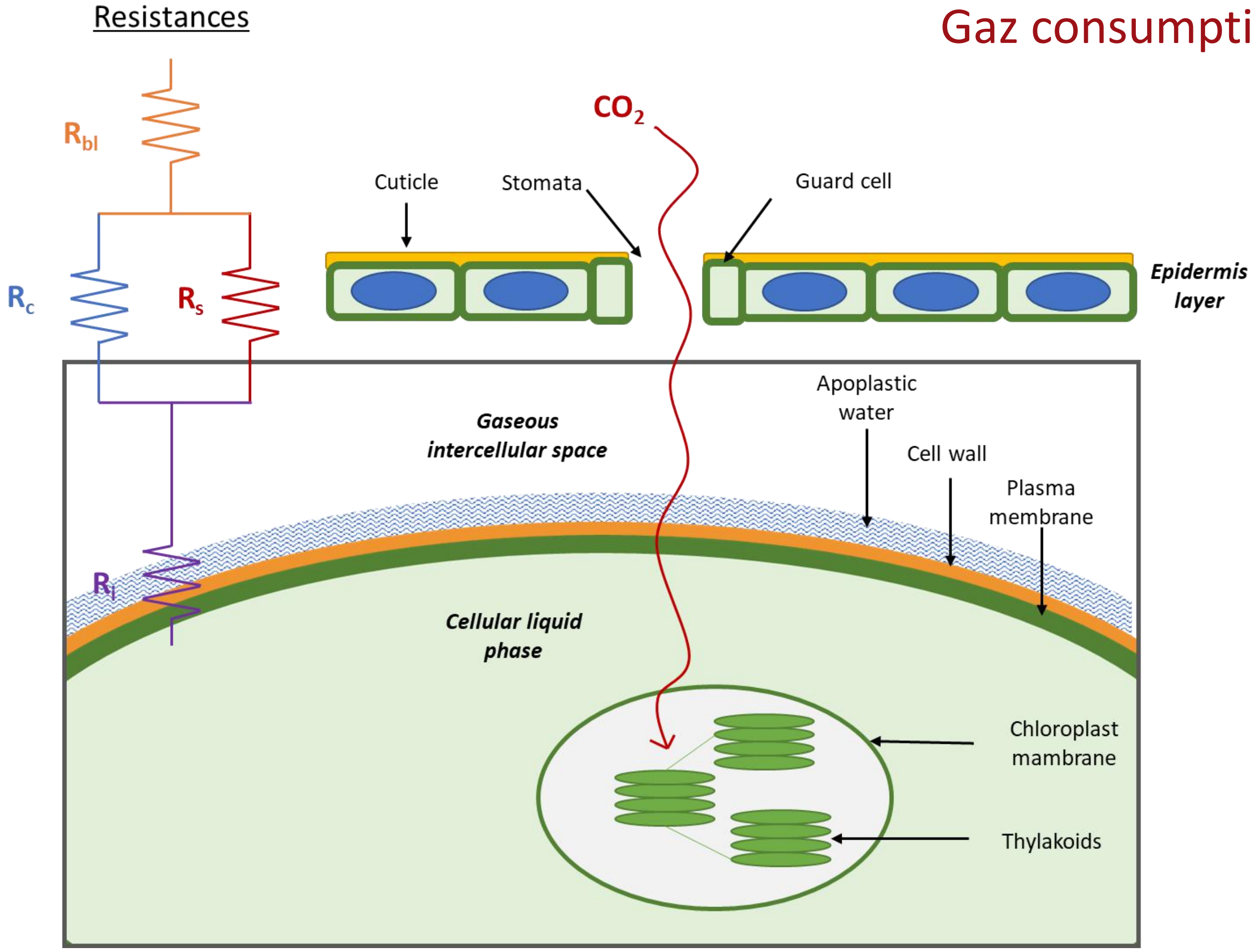
Figure 5: HONO and CO_2 deposition velocities

- The rate constant for HONO uptake by the plant (k_{plant}) is increasing linearly with temperature (Fig. 3)
- k_{plant} is correlated to CO_2 consumption, representing stomatal opening (Fig. 4) → HONO uptake controlled by stomatal opening
- HONO deposition velocity is higher than CO_2 deposition velocity for most temperatures (Fig. 5) → smaller internal resistance (see next slide)

Nitrous acid (HONO) exchanges at the Zea mays leaf – atmosphere interface

A. Marion, J. Morin,
A. Gandolfo, E. Ormeno,
S. Boiry, B. D'Anna, H. Wortham

Gaz consumption by leaves



Gaz consumption by leaves can be modeled by a resistance system (R):

- Boundary layer resistance(R_{bl}) (negligible due to the use of a fan in the chamber)
- Cuticule resistance (R_c) (considered negligible for RH<70%)
- Stomatal resistance (R_s)
- Internal/mesophyll resistance (R_i)

Gaz phase diffusion coefficient:

$D_{CO_2} air = 0{,}139$ cm² s^{-1}

$D_{HONO} air = 0{,}154$ cm² s^{-1}

Henry's constant (298 K):

$H_{CO_2} air = 3{,}4 \times 10^{-2}$ M atm^{-1}

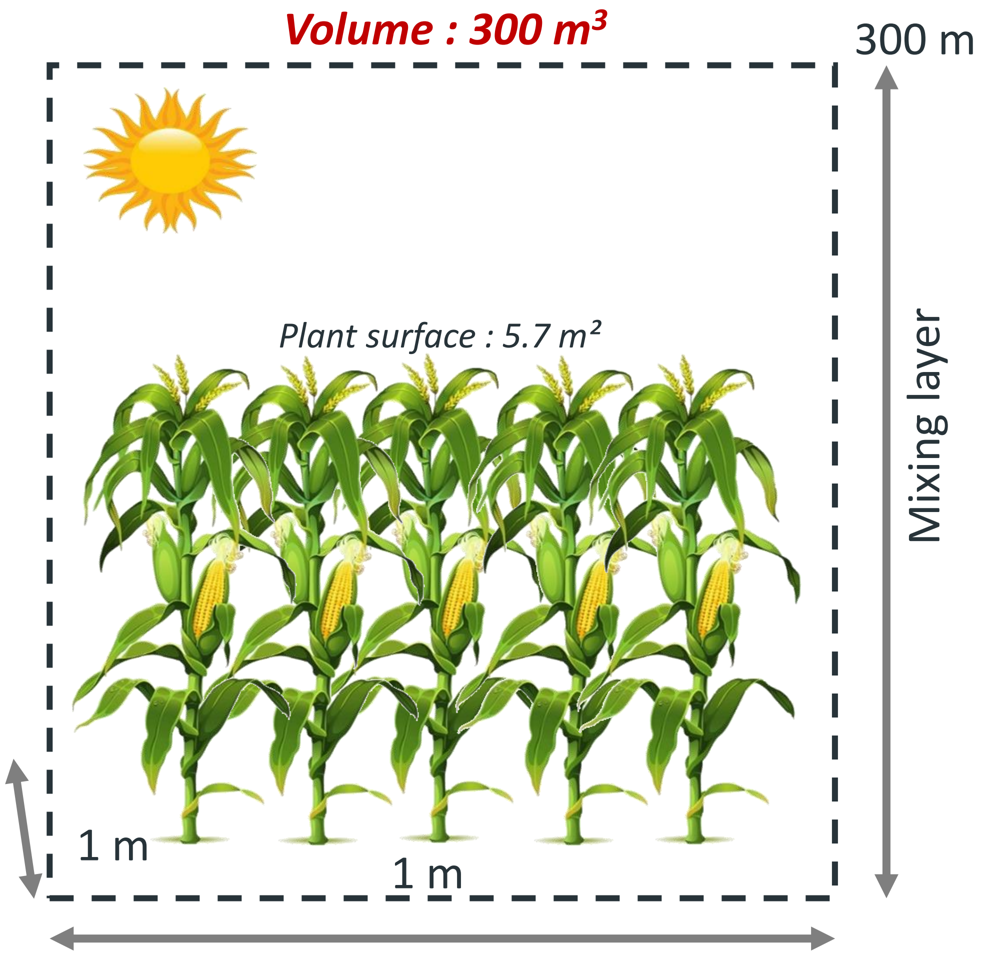
$H_{HONO} air = 49$ M atm^{-1}

- Henry's constants could explain internal resistance differences between HONO and CO_2

Nitrous acid (HONO) exchanges at the Zea mays leaf – atmosphere interface

A. Marion, J. Morin,
A. Gandolfo, E. Ormeno,
S. Boiry, B. D'Anna, H. Wortham

HONO emission/uptake in the atmosphere



Temperature (K)	[HONO] atmosphere ppb	Plant surface (m^2/m^2)	Mixing layer (m)	HONO production minus HONO consumption (ppt h^{-1})
283	0,4	5,7	300	**1.8 ± 0.6**
288	0,4	5,7	300	**0.7 ± 0.2**
293	0,4	5,7	300	**4.7 ± 1.7**
299	0,4	5,7	300	**26.8 ± 6.4**

- Small emission or uptake from 283 to 293 K
- Significant HONO emission at 299 K

Nitrous acid (HONO) exchanges at the *Zea mays* leaf – atmosphere interface

A. Marion, J. Morin,
A. Gandolfo, E. Ormeno,
S. Boiry, B. D'Anna, H. Wortham

- HONO production is occuring on *Zea mays* leaves and increasing with temperature
- HONO can be assimilated by the plants and the assimilation is correlated with stomatal opening
- Estimations of HONO production/consumption in the environment showed that *Zea mays* plants are expected to be a source of HONO at 299 K