Photolysis of Particulate Nitrate: a Daytime HONO Source and a Re-NOx-ification Pathway in the Troposphere (TROPospheic HONO: TROPHONO)

A Component of NOMADSS (Nitrogen, Oxidants, Mercury, and Aerosol Distributions, Sources and Sinks) Field Campaign

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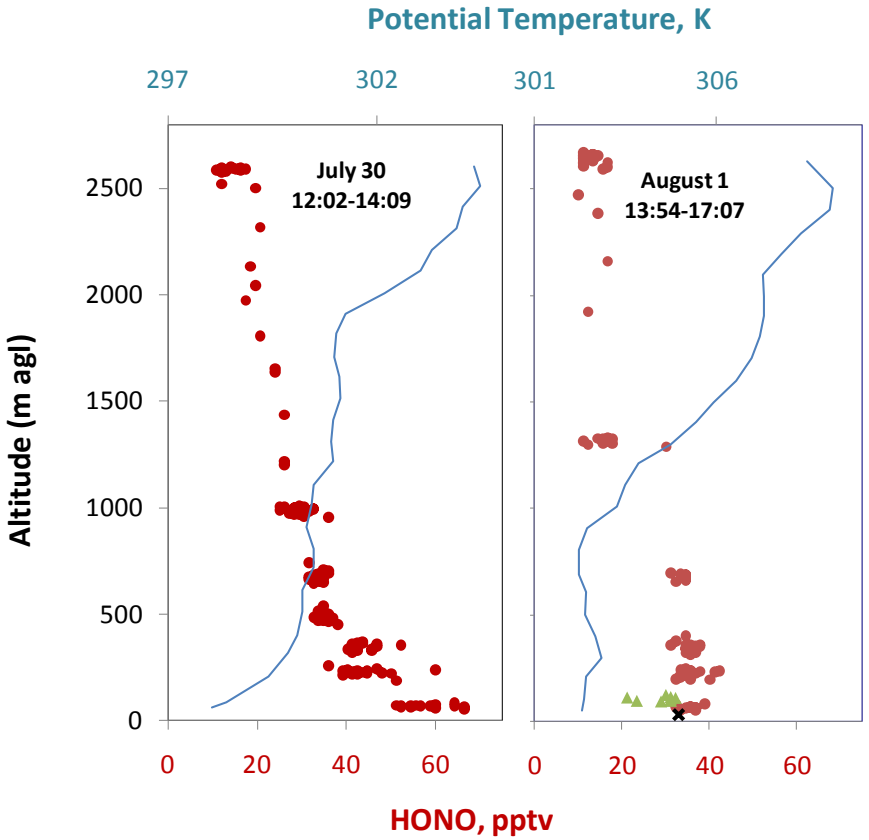
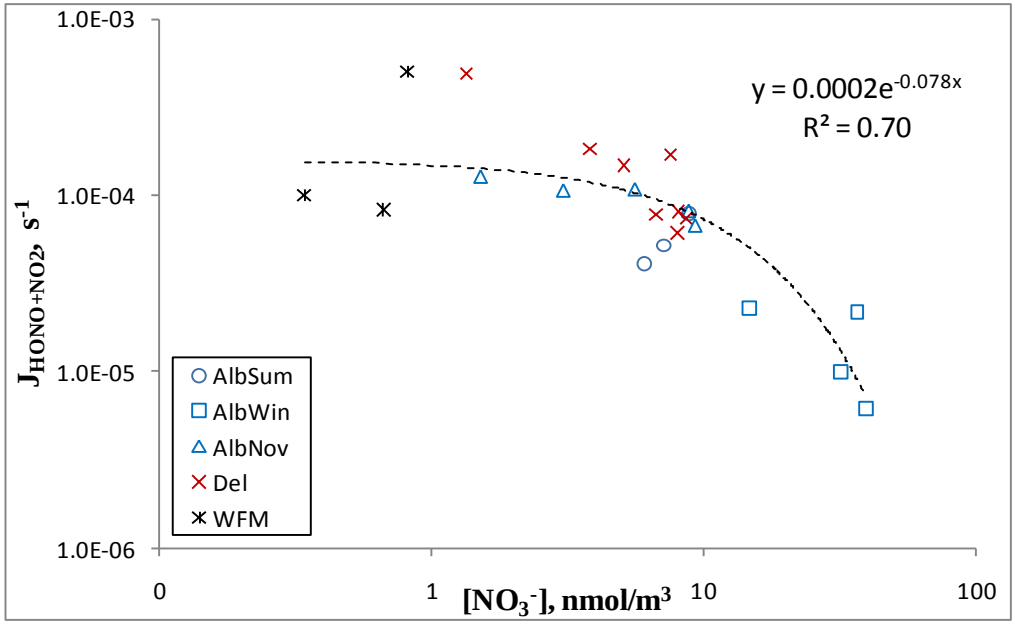
Objective: To investigate the role of particulate nitrate photolysis in the cycling of reactive nitrogen species in the troposphere, focusing on HONO as an intermediate product.

Hypothesis 1: Photolysis of particulate nitrate in aerosol particles, and, to a lesser extent, NO_2 conversion on organic aerosol, are major sources of HONO in the low-NOx troposphere above the surface boundary layer.

Hypothesis 2: Photolysis of particulate nitrate in aerosol particles represents an important pathway to recycle HNO_3/nitrate back to photochemically reactive NO_x (re-NOx-ification) in the troposphere.

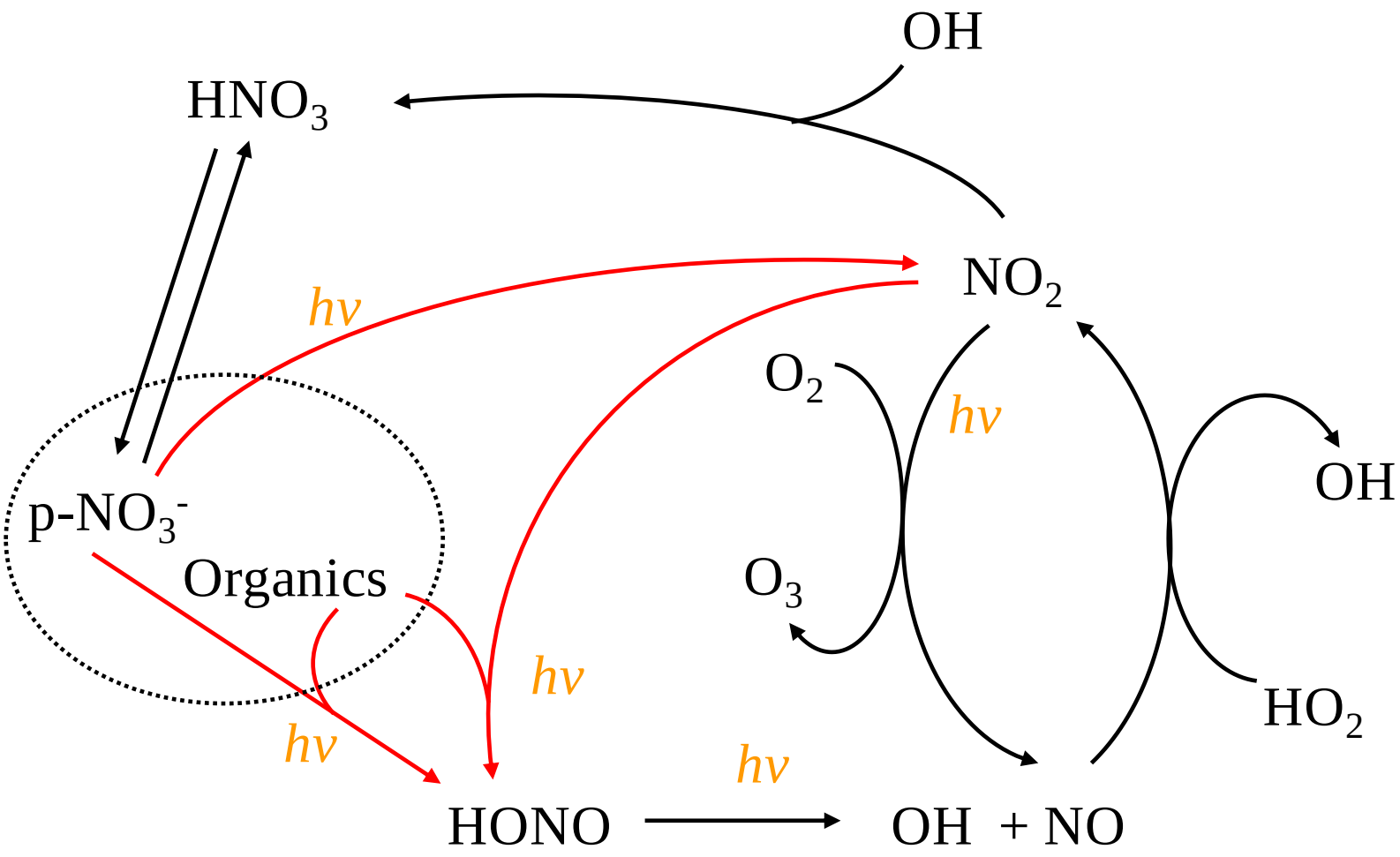
Supporting Evidences





- Substantial daytime HONO exists in the upper atmospheric boundary layer and free troposphere → require a strong daytime HONO source in the air column.
- Photolysis of particulate nitrate (pNO_3) in aerosol is fast, with a lifetime of ~1.4 hr for pNO_3, with HONO as a dominant product ($HONO/NO_2$ = 3 - 9)

Potential impact of p-NO_3 photolysis on tropospheric photochemistry



Flight Strategy/Experimental Designs

1. Daytime horizontal transects and vertical profiling over land and ocean:

   To establish daytime distributions of HONO and its production rate, and their relationships with pNO_3, NO_x, pOrganics, aerosols, and O_3 in different air masses.

2. Daytime HONO production in urban plumes:

   To study daytime HONO production in the urban plumes as a function of photochemical ages, and to establish the maximum HONO contribution from the NO_x precursor.

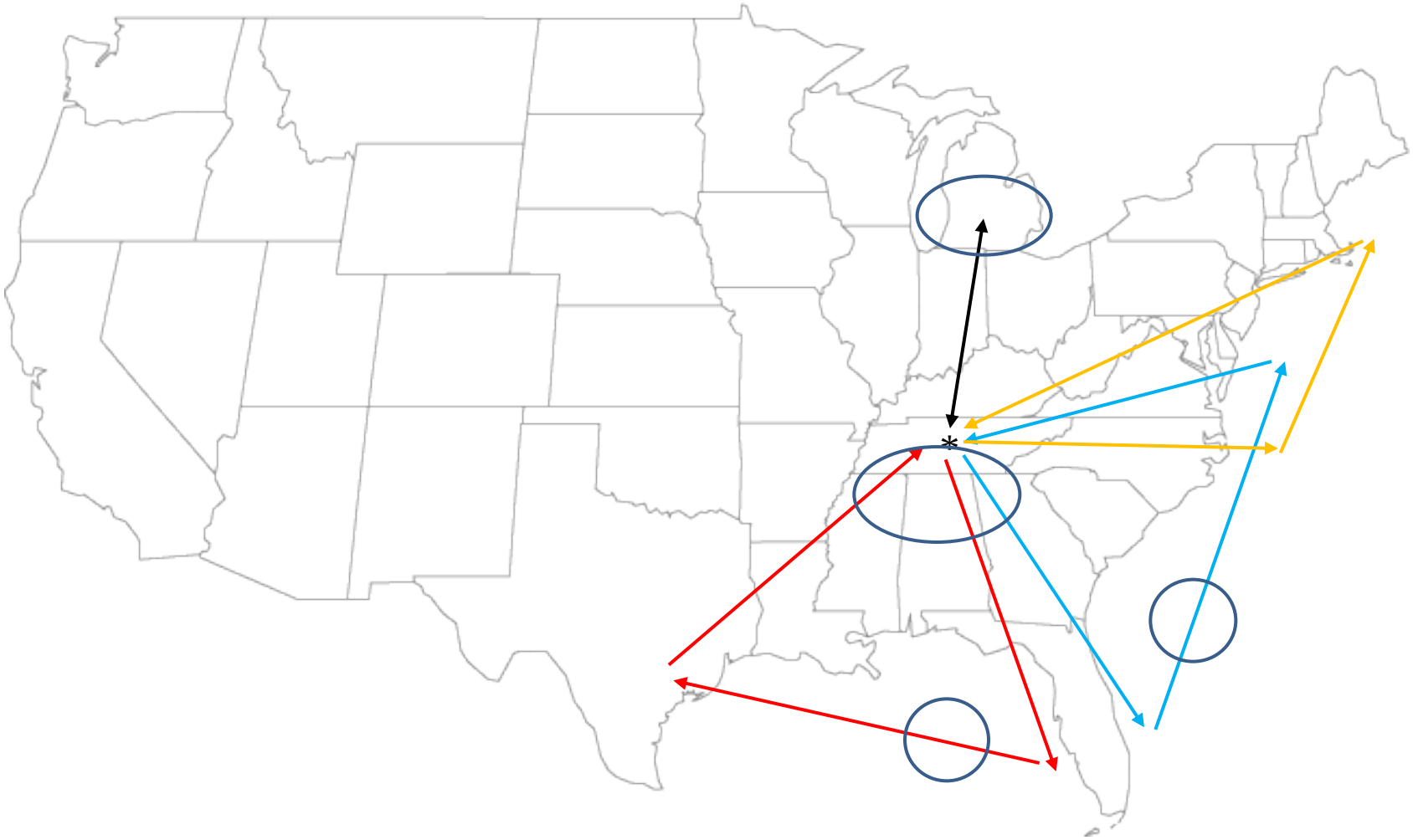
3. Nighttime HONO accumulation/early morning decay:

   To study nighttime accumulation and morning hour decay of HONO . The HONO formation rates during the day and the night will be compared.

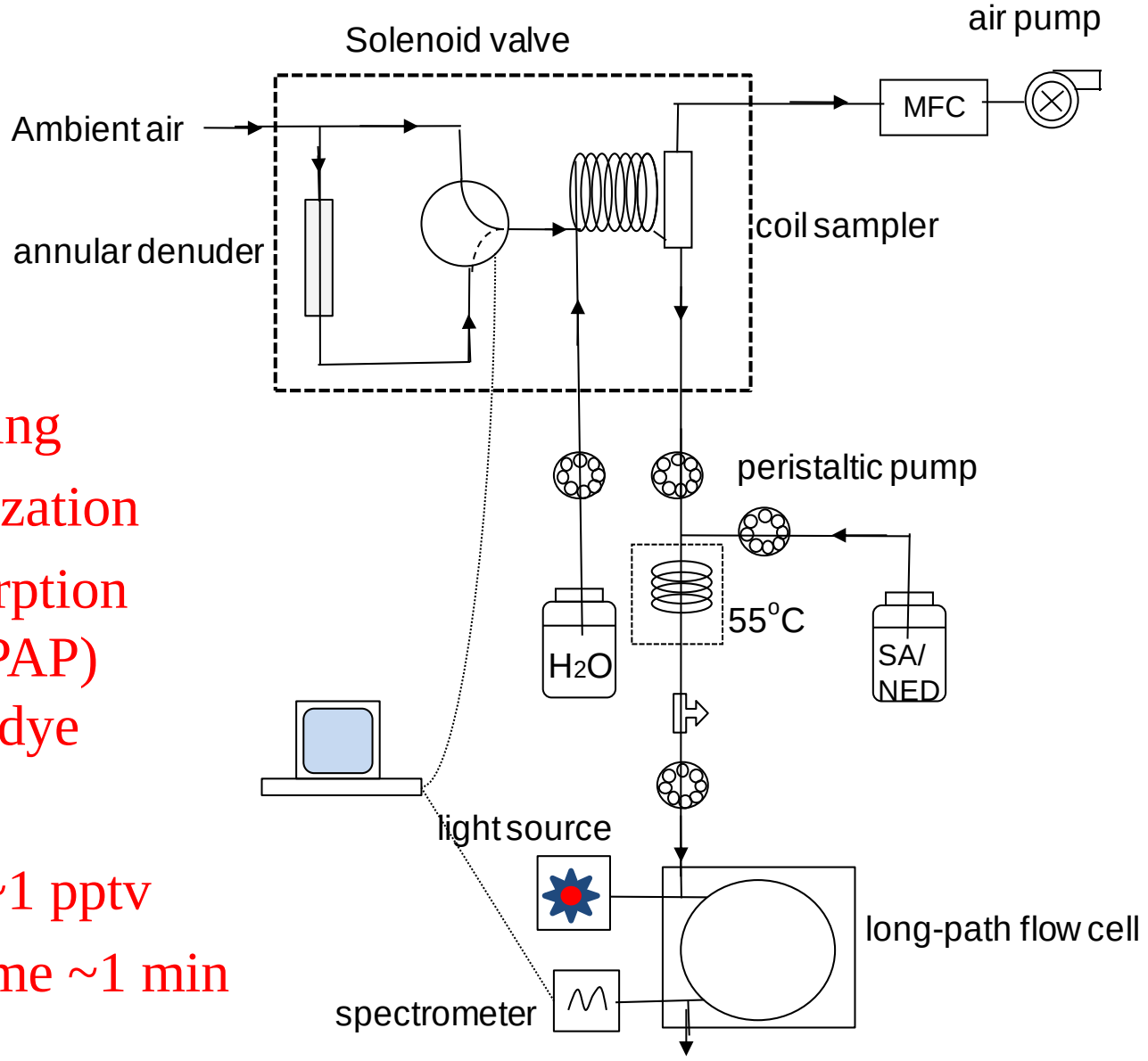
4. Bulk aerosol sampling:

   To collect aerosol samples for laboratory pNO_3 photolysis experiments.

horizontal transects and vertical profiles



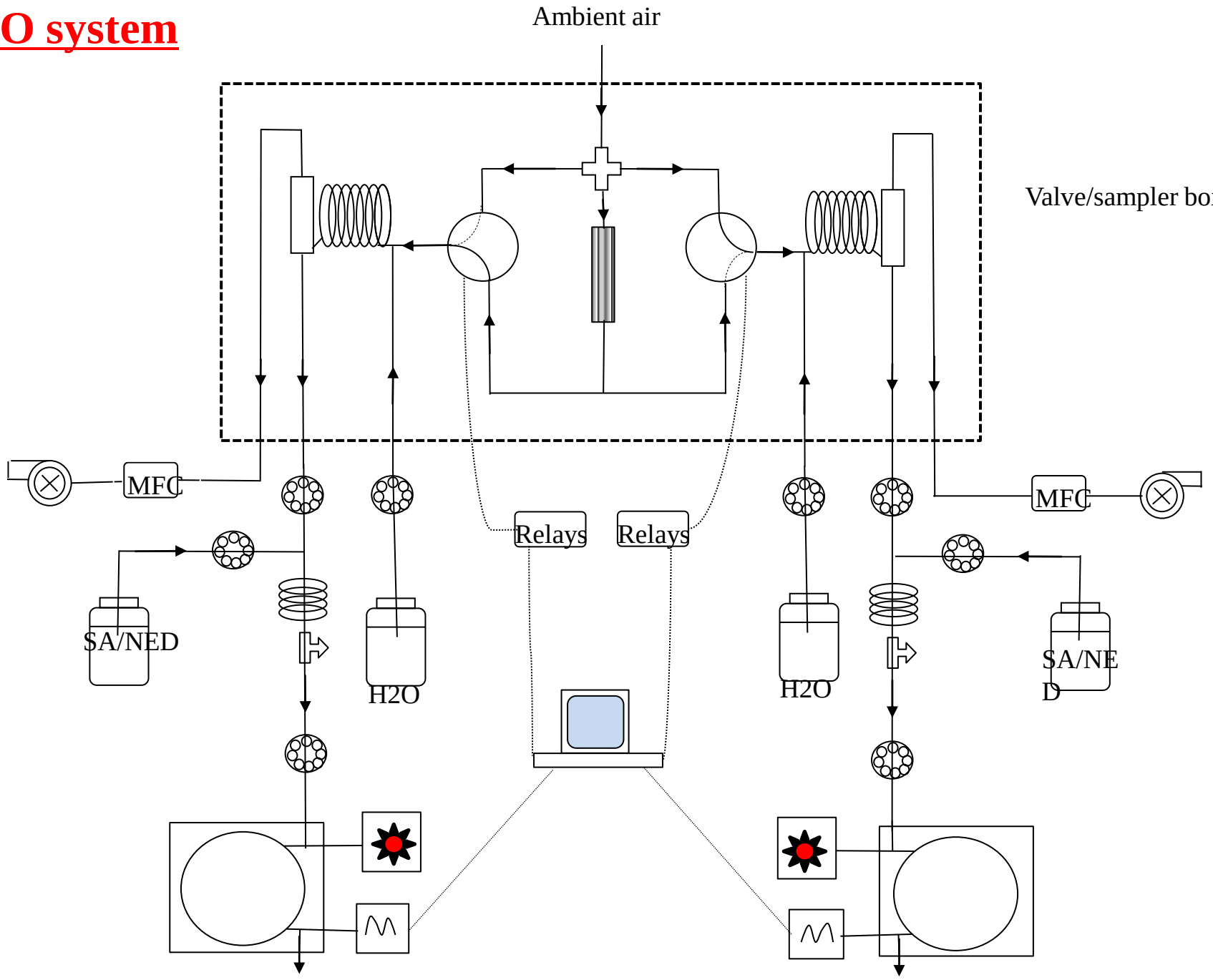
HONO system



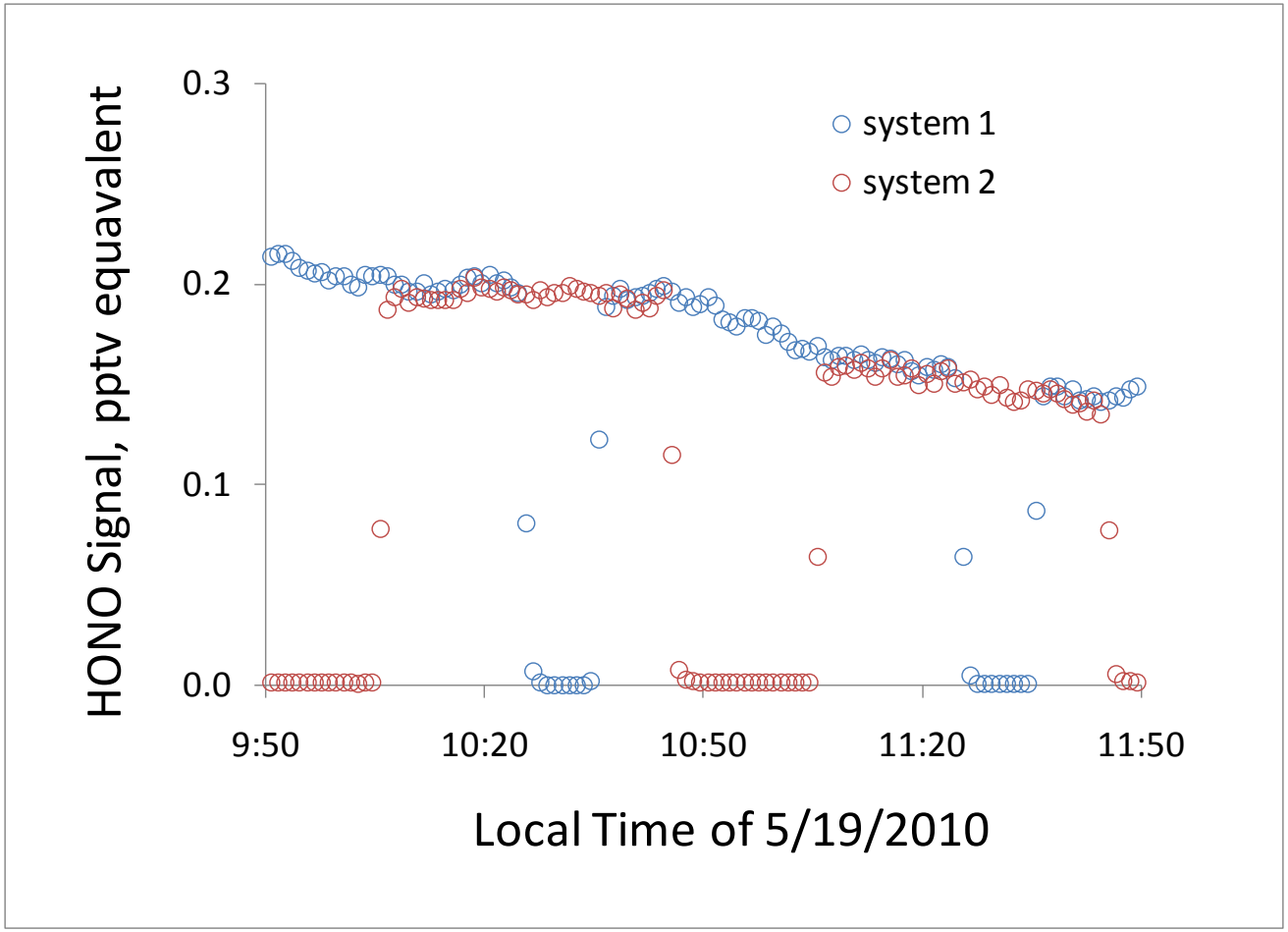
- Aqueous scrubbing
- Azo dye derivatization
- Long-Path Absorption Photometric (LPAP) detection of azo dye

- Detection limit ~1 pptv
- 90% response time ~1 min

HONO system


Ambient air
Valve/sampler box
MFC
MFC
Relays
Relays
SA/NED
H2O
H2O
SA/NE
D

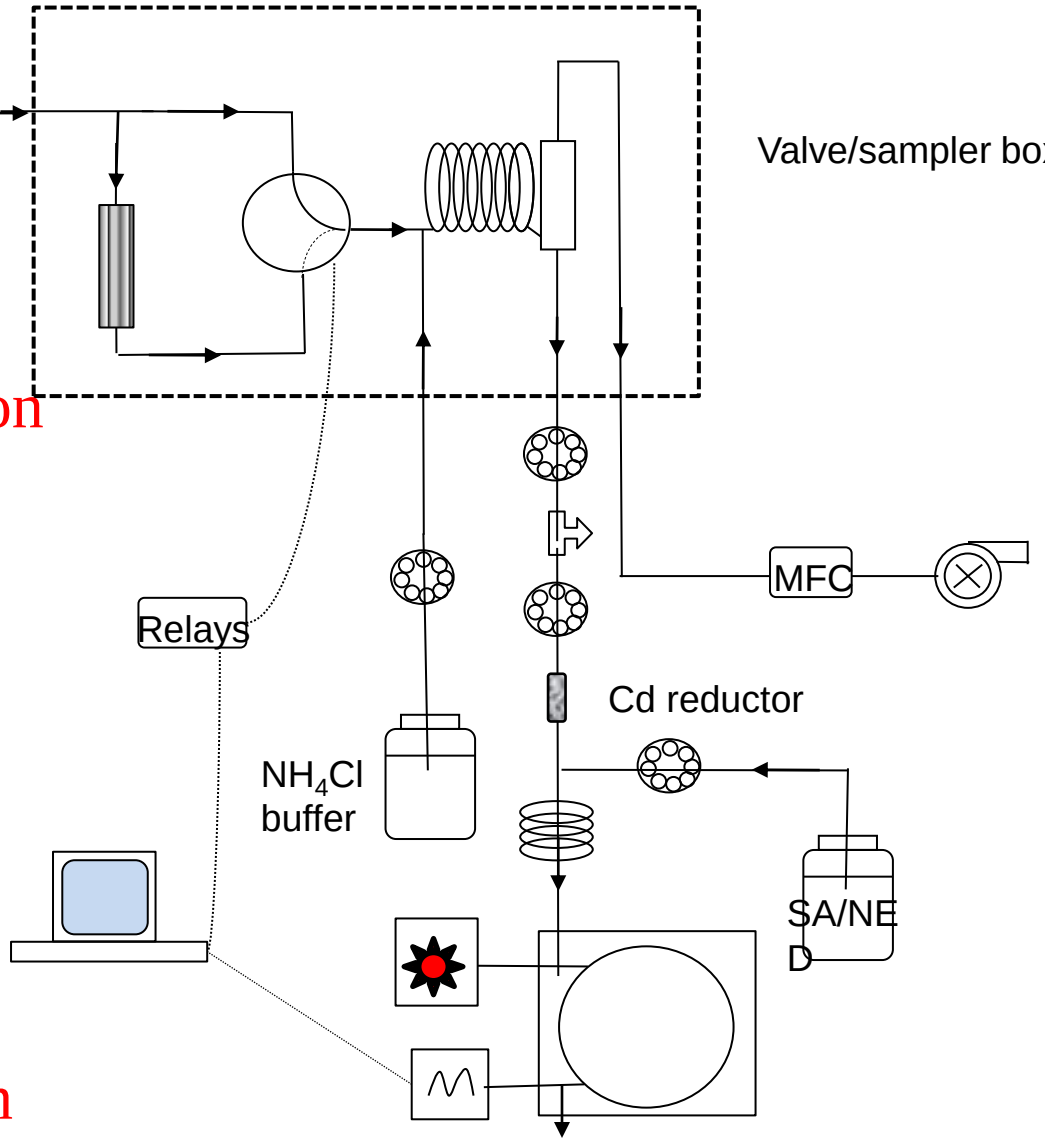
HONO data from two HONO systems



HNO_3 system

- Aqueous scrubbing
- NO_3^- to NO_2^- conversion on Cd-reductor
- Azo dye derivatization
- Long-Path Absorption Photometric (LPAP) detection of azo dye

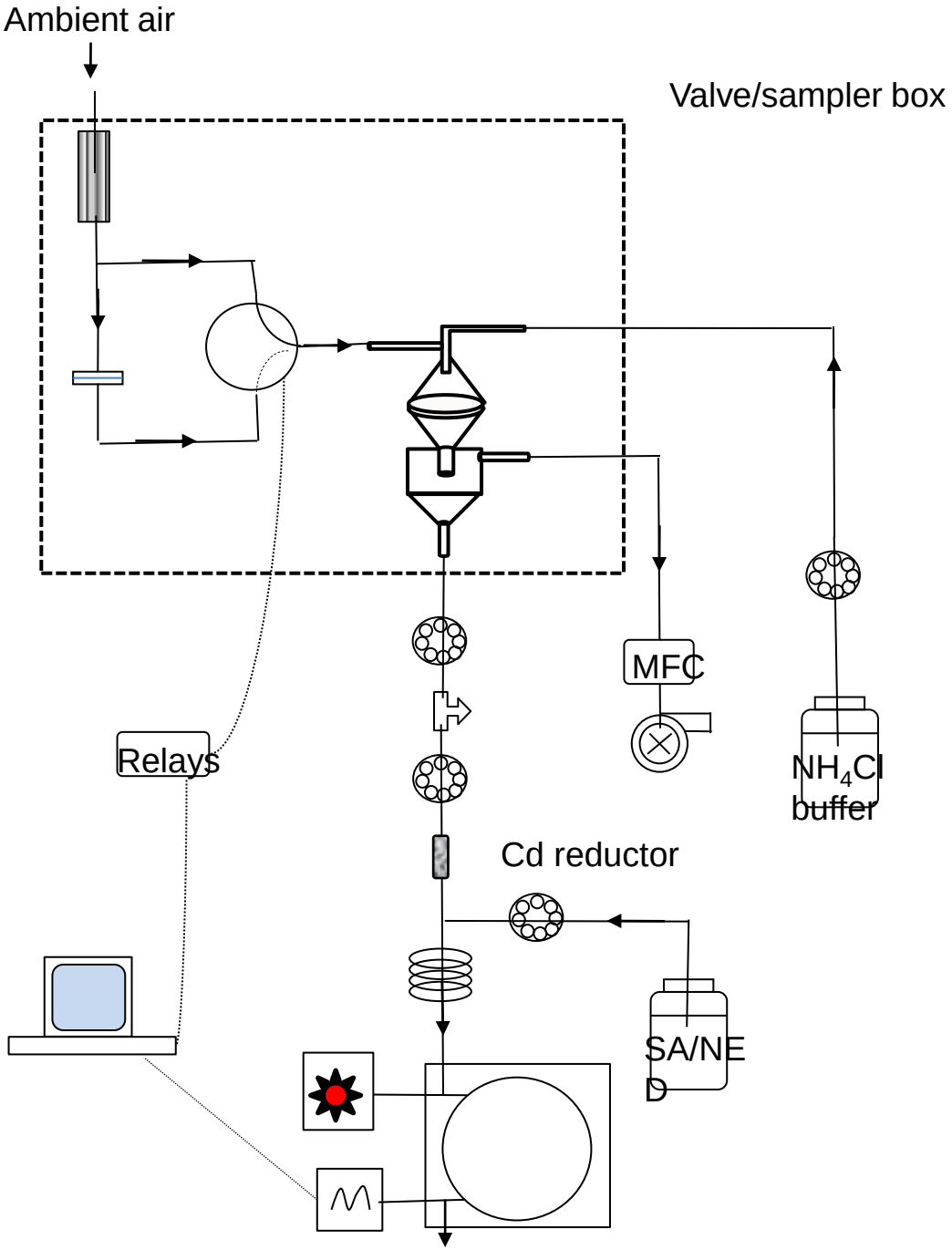
- Detection limit ~20 pptv
- 90% response time ~1 min



PNO_3 system

- Aqueous scrubbing
- NO_3^- to NO_2^- conversion on Cd-reductor
- Azo dye derivatization
- Long-Path Absorption Photometric (LPAP) detection of azo dye

- Detection limit ~20 pptv
- 90% response time ~1 min



P-Organics system

- Aqueous scrubbing
- Long-Path Absorption measurement a 300 nm