Detection of alkyl nitrates (ANs) and peroxyacyl nitrates (PNs) by a TD-CEAS (thermal dissociation - cavity enhanced absorption spectrometer) system

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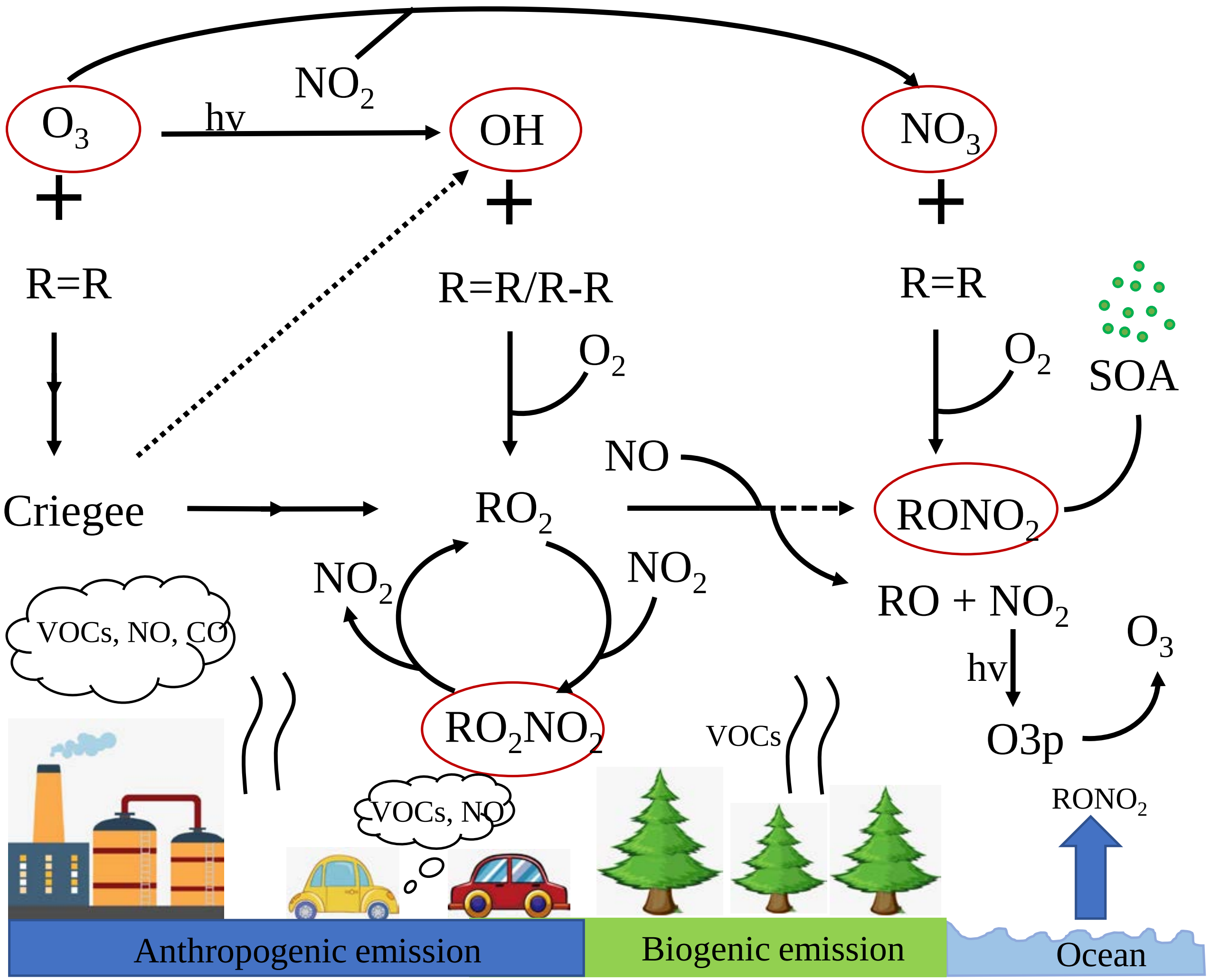
1. Introduction



- Organic nitrates (ONs) include PNs (RCO_3NO_2) & ANs ($RONO_2$);
- The formation of ONs is initiated by O_3, OH and NO_3;
- ONs can be very useful indicators for the kinetic regime determination and mechanism development;
- ONs have an effect on the formation of O_3;
- ONs are the important precursors of SOA.

2. Characterization of the Cavity Enhanced Absorption Spectrometer

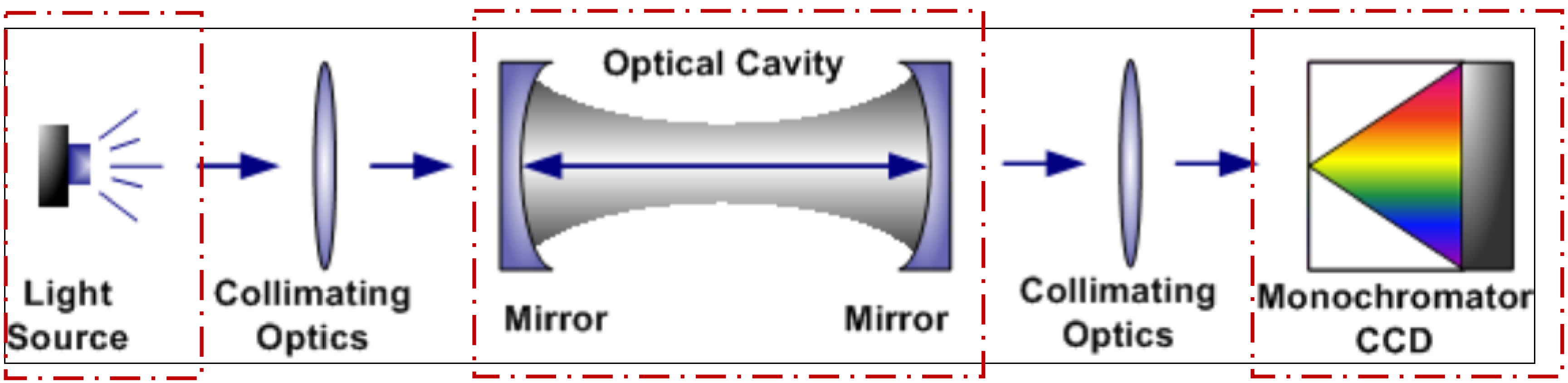
NO_2 has distinct absorption peaks at 300-500 nm, so a single-colour LED centered at 450nm is used as the light source.

Lambert Beer's law: $\log\left(\frac{I_0}{I}\right) = \sigma \times L \times C$

Cavity technology to increase the optical path.---L

$$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1\right)\left(\frac{1 - R(\lambda)}{d_{\text{eff}}}\right) = \sum_i n_i \times \sigma_i(\lambda) + \alpha_{\text{Mie}}(\lambda) + \alpha_{\text{Rayl}}(\lambda)$$

(extinction coefficient) **(Mie scattering)(Rayleigh scattering)**

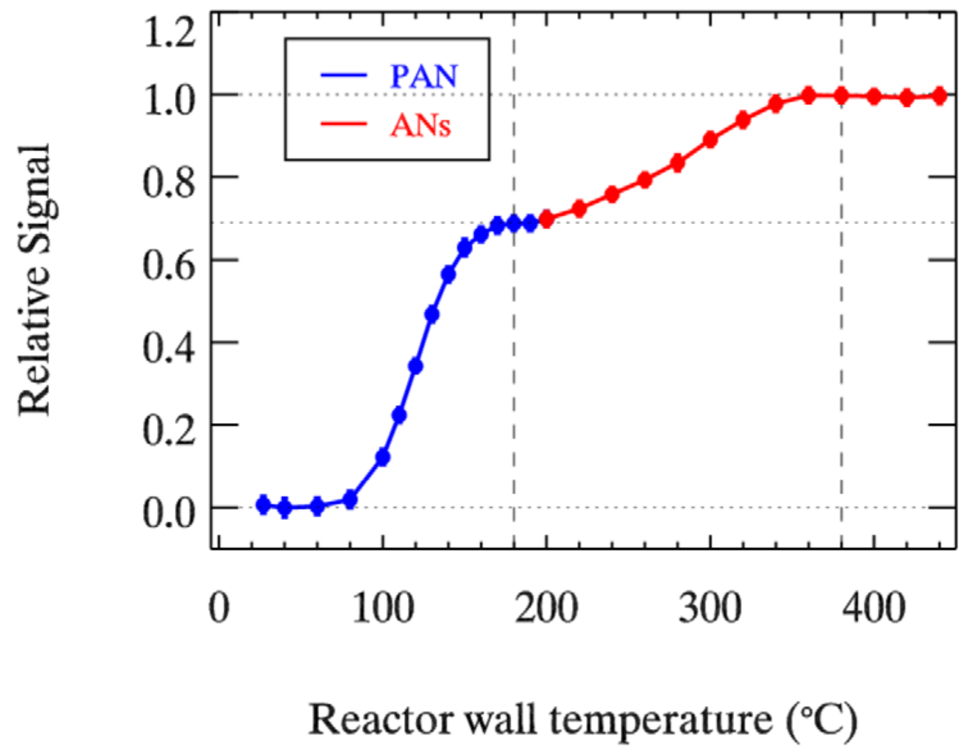


3. TD-CEAS characterization — Efficiency of Thermal Dissociation

- **Photochemical source：** PAN in zero air are generated by acetone photolysis at 285 nm in the presence of O_2 and NO.

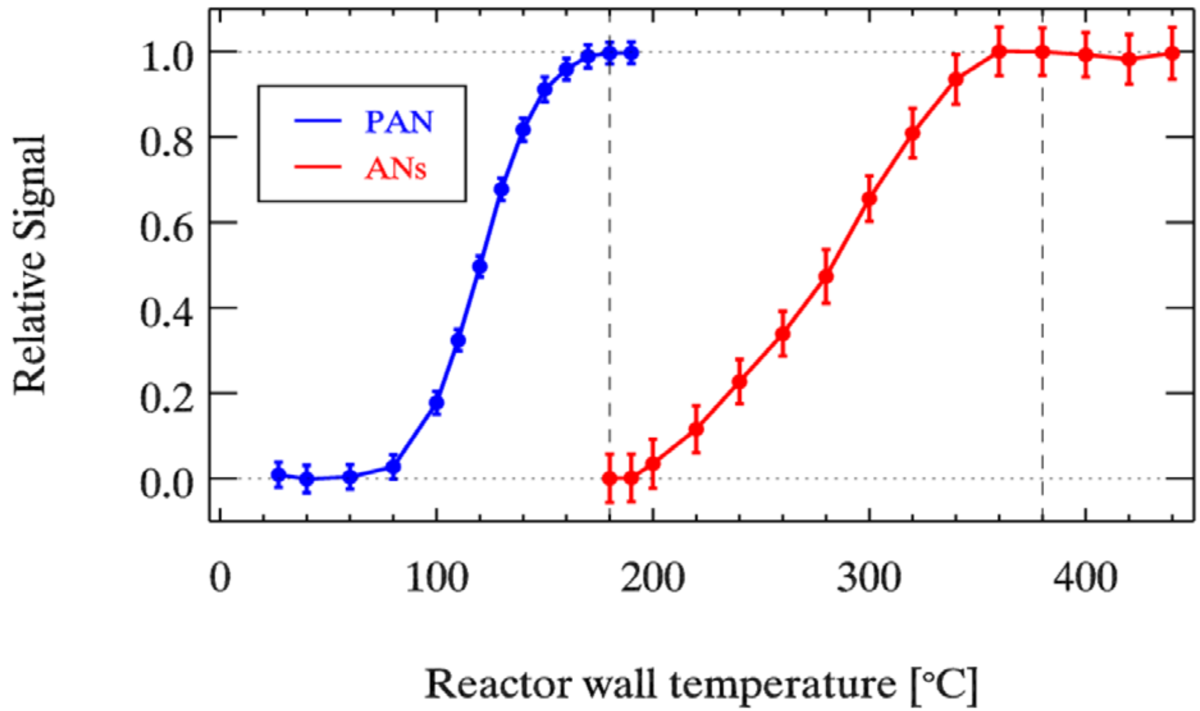
$$CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3$$
$$CH_3CO + O_2 \rightarrow CH_3COO_2$$
$$CH_3COO_2 + NO_2 \rightarrow PAN$$

- **PAN:MeN=2:1**. Fused silica enclosure to house Hg lamp does not attenuate the output in the near-UV, which promotes further reactions of CH_3 to generate methyl nitrate (MeN).



- Normalized TD signals of thermal dissociation of standard source based on the total concentration of ONs.

3. TD-CEAS characterization — Efficiency of Thermal Dissociation

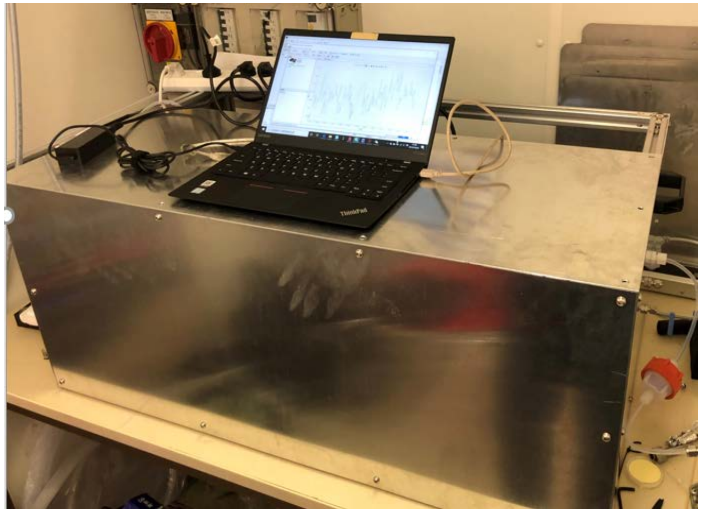


- At 180 °C, PAN (blue line) is completely pyrolyzed and MeN is not pyrolyzed at all. ANs (red line) is pyrolyzed totally when the temperature is above 360 °C.
- Quartz tubes to measure PNs/ANs are heated at 180 °C/ 380 °C, which is similar to previous pyrolysis temperature.

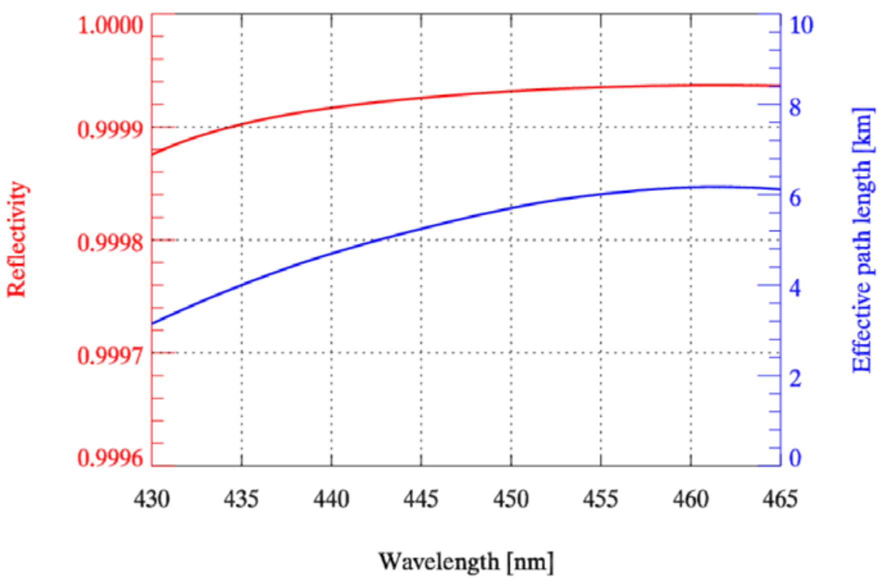
3. TD-CEAS characterization

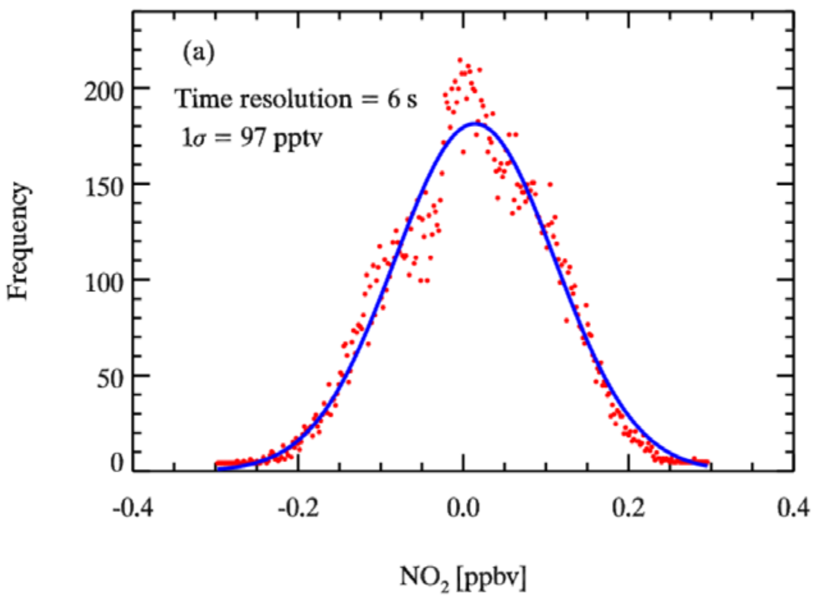
- Instrument: 110cm x 60cm x 50cm, ~300w;
- Sample gas: 2.4 L/min;
- Detection limit and time resolution:

  1σ =97 pptv, time resolution = 6 s
- Reflectivity： N_2 and He



$$R(\lambda) = 1 - d \times \left(\frac{I_{N_2}(\lambda) \times n_{N_2} \times \sigma_{Rayl,N_2}(\lambda) - I_{He}(\lambda) \times n_{He} \times \sigma_{Rayl,He}(\lambda)}{I_{He}(\lambda) - I_{N_2}(\lambda)} \right)$$

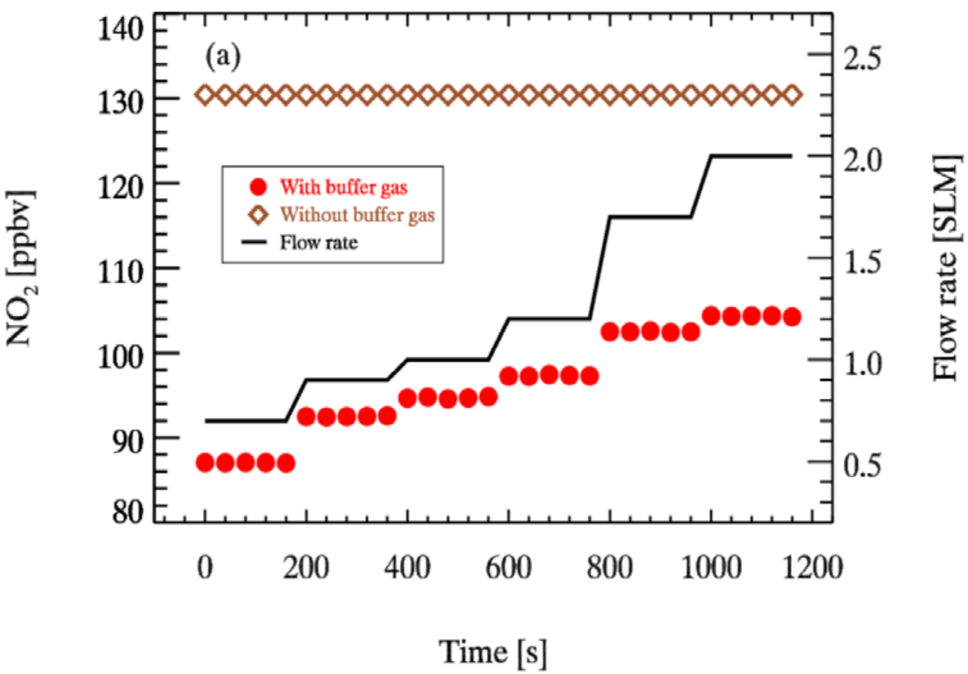


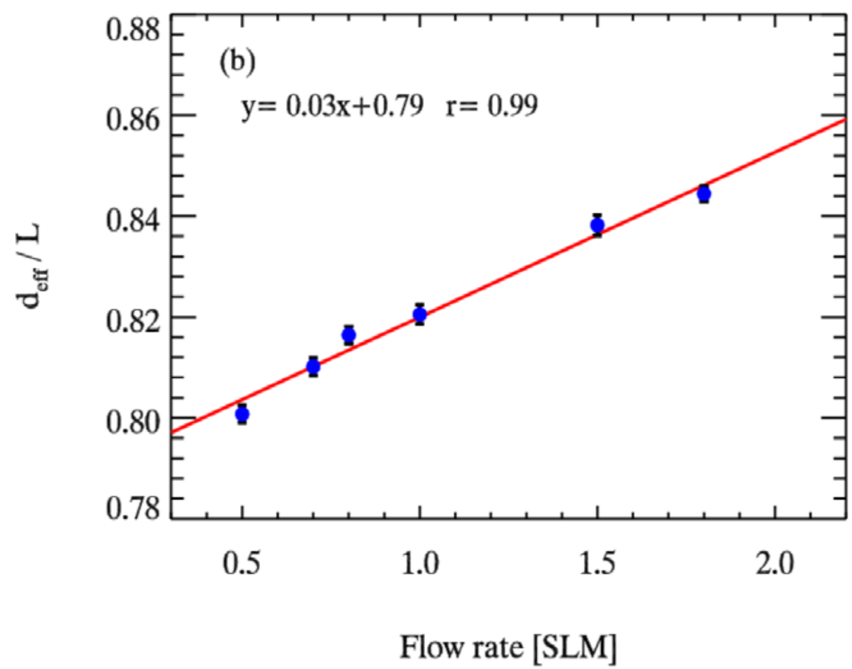


3. TD-CEAS characterization

- Purge gas to prevent the HR mirrors from pollution: 100 sccm × 2;
- d_{eff}: the effective cavity length due to the purge gas;
- Experiment in Lab: determination of $[NO_2]$ under two conditions with or without purge in the cavity by using the same NO_2 stand source(≈130 ppbv).

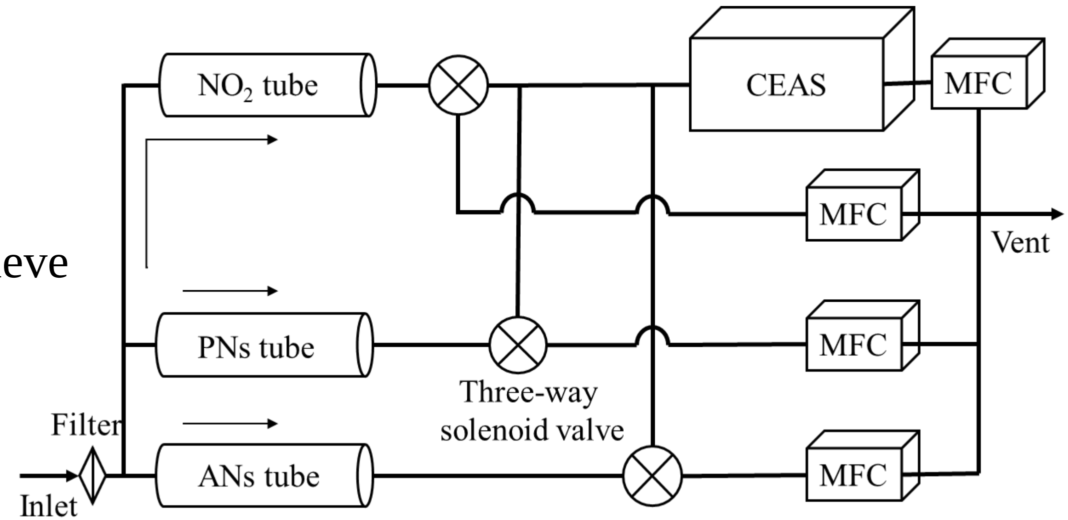
$$d_{eff} / L = [NO_2]_{with} / [NO_2]_{without}$$

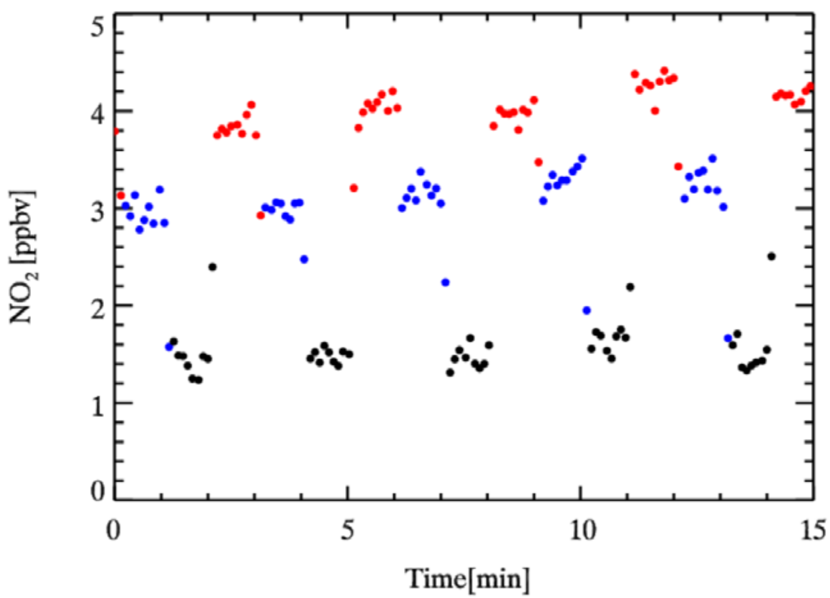




3. TD-CEAS characterization

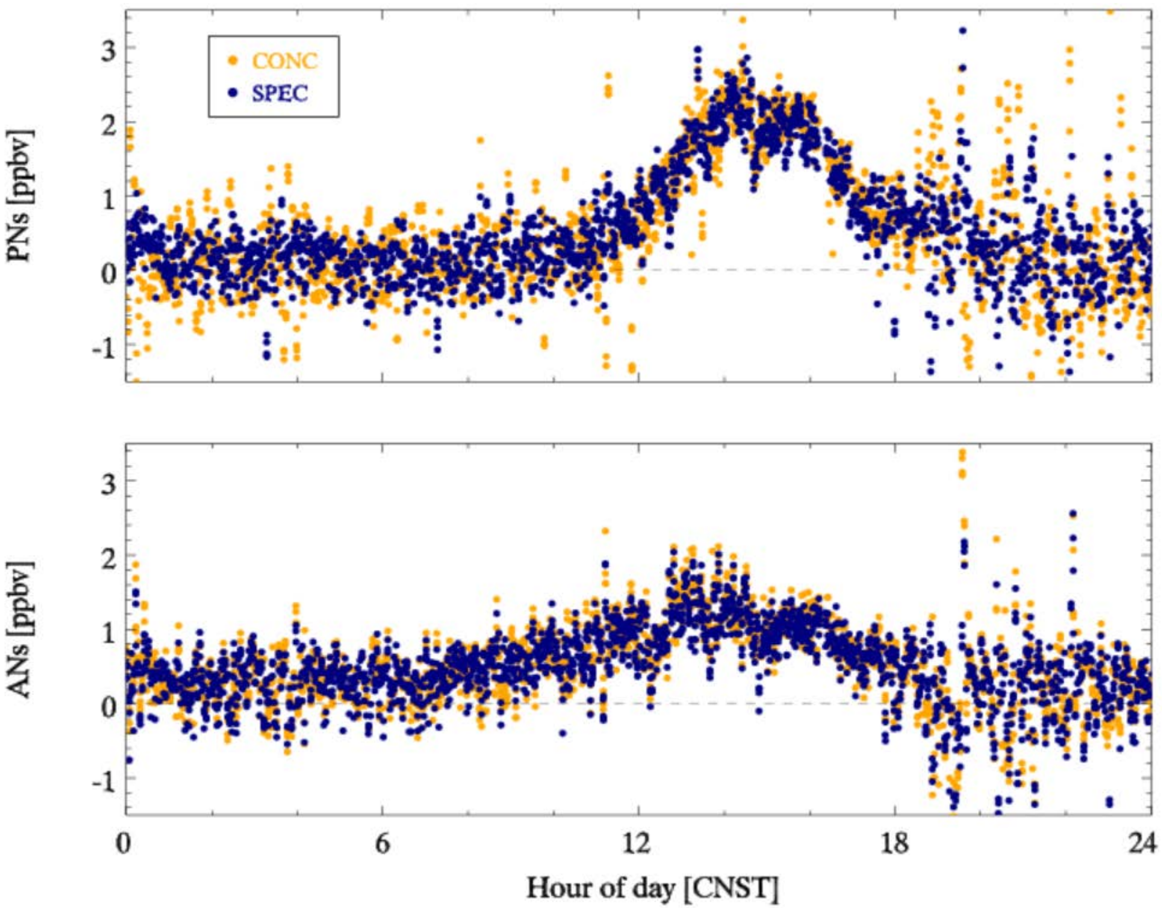
- One CEAS is used to detect;
- Multiple components (solenoid value, T-shaped tee) aim to achieve alternate measurement;
- Airflow is stable in 3 channels.





- One measurement cycle for 3 min, including 3 measurement phases;
- Time resolution: 6 s;
- red dots: [ANs]+[PNs]+[NO_2], blue dots: [PNs]+[NO_2], black dots: [NO_2]

3. TD-CEAS characterization



- The data is the measurement results of CHOOSE campaign on September 8, 2019.

- According to the spectral fitting of CEAS, [ANs] and [PNs] can be determined by two methods;
- 'CONC' method:

$$\alpha_{TD380} = \left(\frac{I_{TD380}}{I_{N_2}} - 1\right)\left(\frac{1-\mathrm{R}(\lambda)}{d_{eff}}\right)$$

$$\alpha_{TD180} = \left(\frac{I_{TD180}}{I_{N_2}} - 1\right)\left(\frac{1-\mathrm{R}(\lambda)}{d_{eff}}\right)$$

- 'SPEC' method:

$$\alpha_{[ANs]} = \left(\frac{I_{TD380}}{I_{TD180}} - 1\right)\left(\frac{1-\mathrm{R}(\lambda)}{d_{eff}}\right)$$

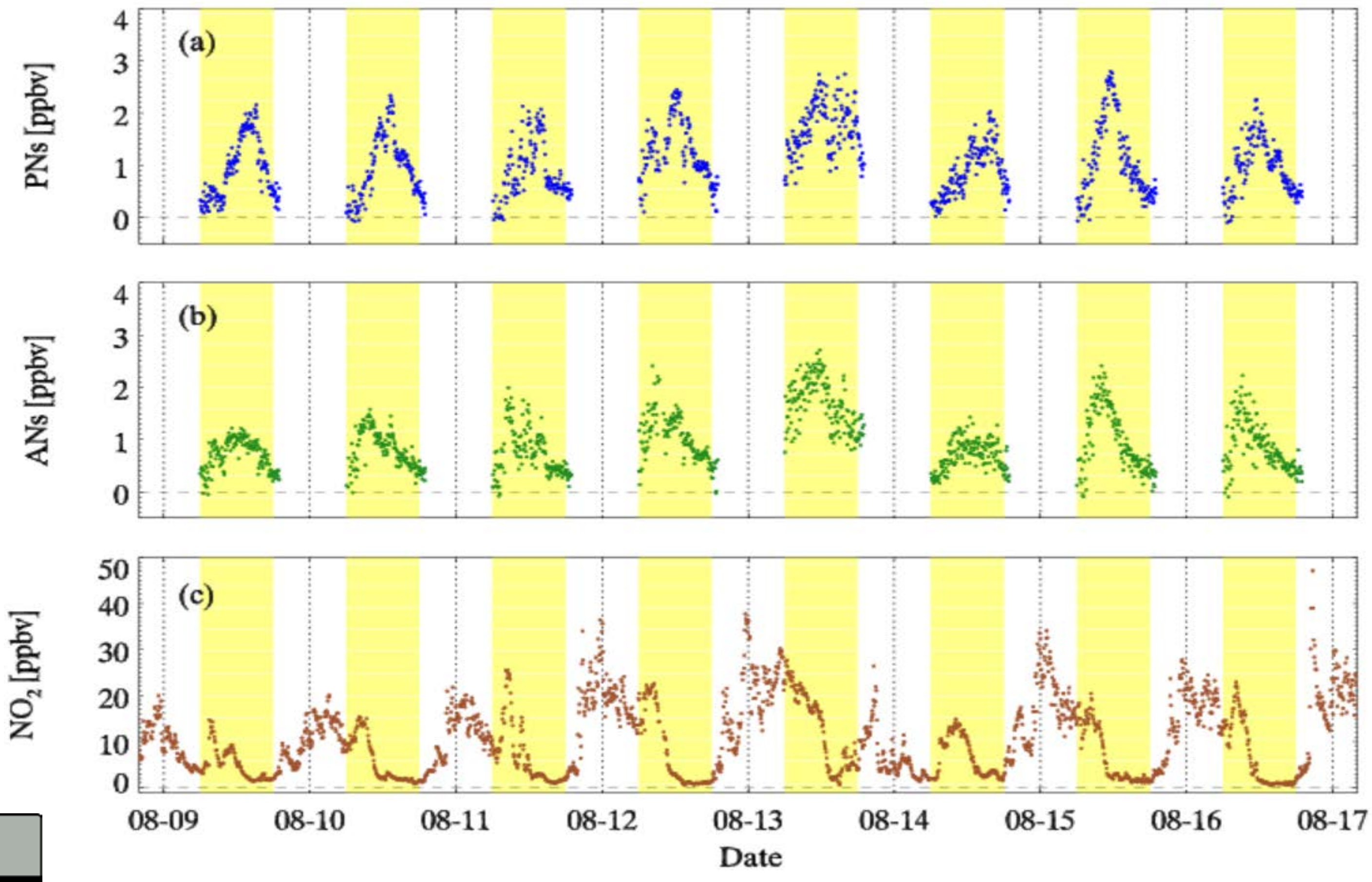
$$\alpha_{[PNs]} = \left(\frac{I_{TD180}}{I_{NOR}} - 1\right)\left(\frac{1-\mathrm{R}(\lambda)}{d_{eff}}\right)$$

Comparison to other ANs/PNs instrument

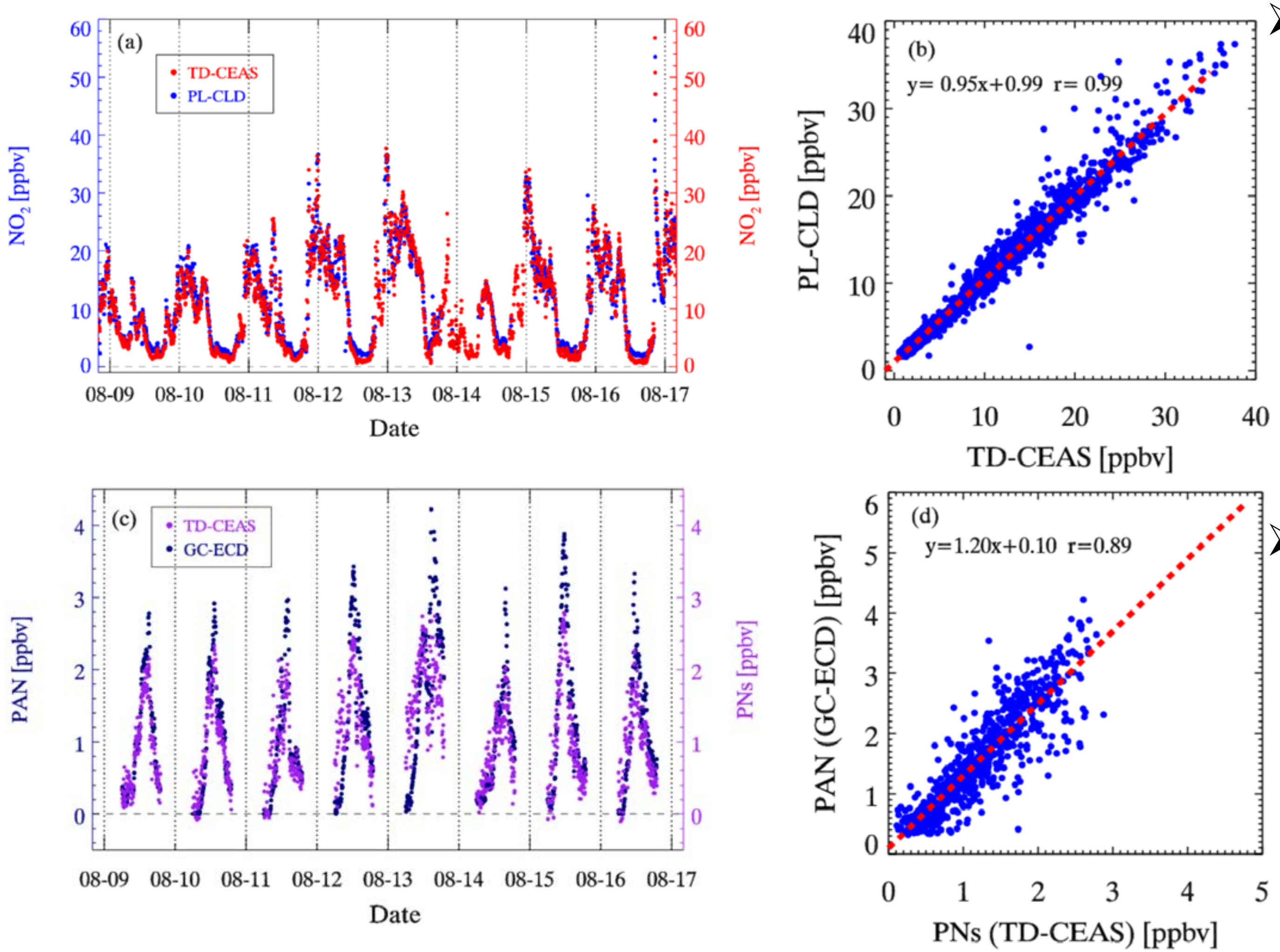
Tech	Measuring Parameter	Measure species	Calibration	Temporal/ Spatial resolution	DL	Accuracy	Main interference	Ref
TD-LIF	Fluorescence spectrum	ANs, PNs, NO_2	PAN/ethyl nitrate/n-propyl nitrate/NO_2 standard source	10 s	90 pptv	10-15%	Thermal interference	Day et al., 2002
TD-CIMS	Mass spectrum	PiBN, PAN, PPN ， MPAN	PAN/MPAN/PPN standard source	1-15 s	3-7 pptv	20%	Acetone, acetic acid, peracetic acid	Slusher et al., 2004
TD-CAPS	Phase shift	ANs, PNs, NO_2	PAN/PPN/methyl, ethyl, isopropyl, isobutyl, n-pentyl nitrates/NO_2 standard source	2 min	21 pptv		Thermal interference	Sadanaga et al., 2016
TD-CRDS	Ring-down time	ANs, PNs, NO_2	2-propyl nitrate/PAN/NO_2 standard source	1 s	28 pptv,	6%+20 pptv +(20pptv*RH /100)	Thermal interference, RH	Thieser et al., 2016
TD-CRDS	Ring-down time	ANs, PNs, NO_2	2-propyl nitrate/i-butyl nitrate/PAN/NO_2 standard source	1 s	80 pptv, 94 pptv, 59 pptv	8%	Thermal interference	Sobanski et al., 2016
TD-PERCA-CRDS	Ring-down time	PNs	NO_2/PAN standard source	1 s	2.6 pptv	9%	Thermal interference	Taha et al., 2018
TD-CEAS	Absorption spectrum	ANs, PNs, NO_2	PAN /MeN standard source	6 s	97pptv	8%	Thermal interference	This study

4. Field observations

- The first field observation named CHOOSE was deployed in XINJIN, Chengdu, China, in 2019;
- An example time series of [NO_2], [PNs] and [ANs] measured during an ozone pollution in CHOOSE campaign.

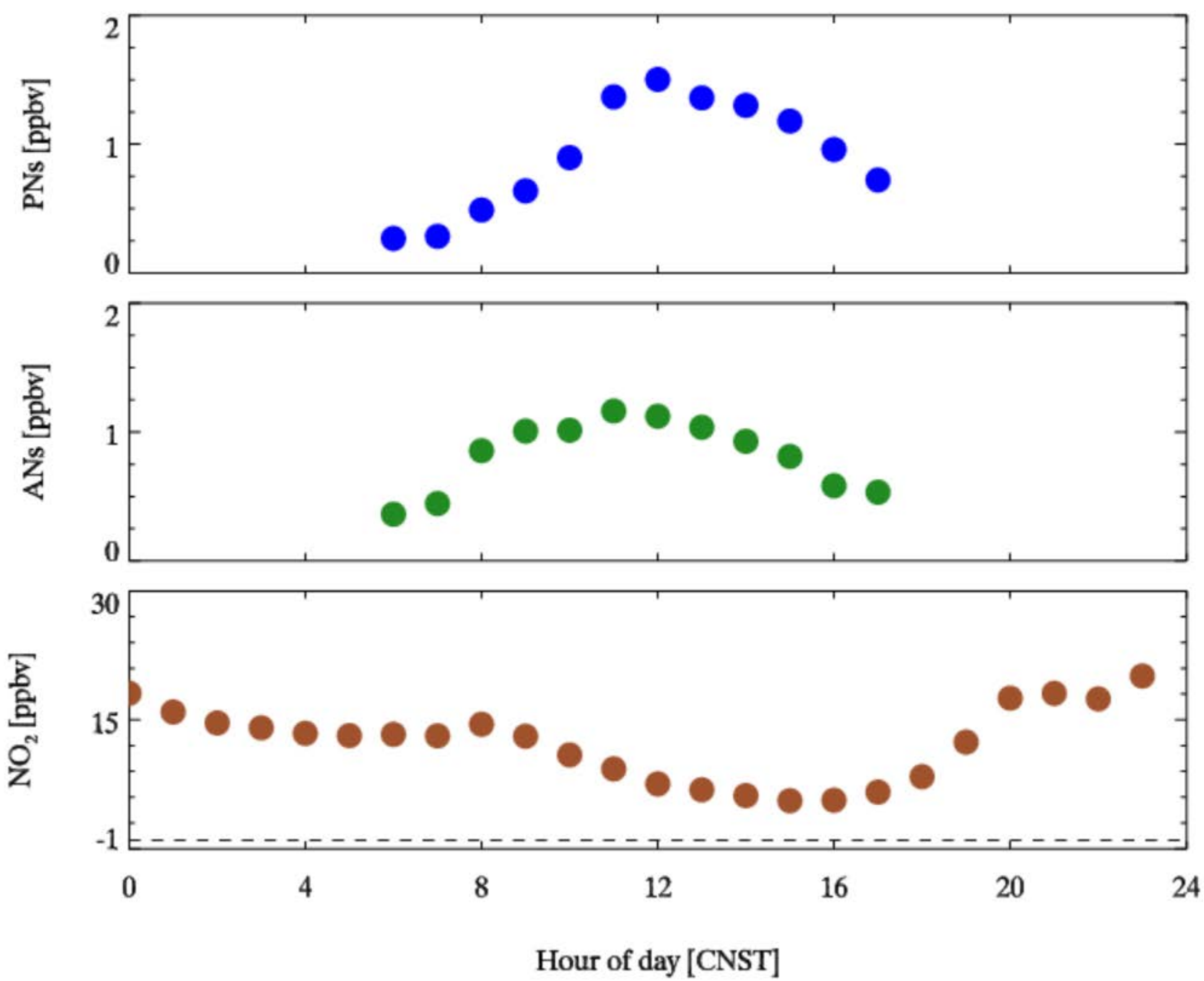


Field intercomparison of NO_2 and PAN



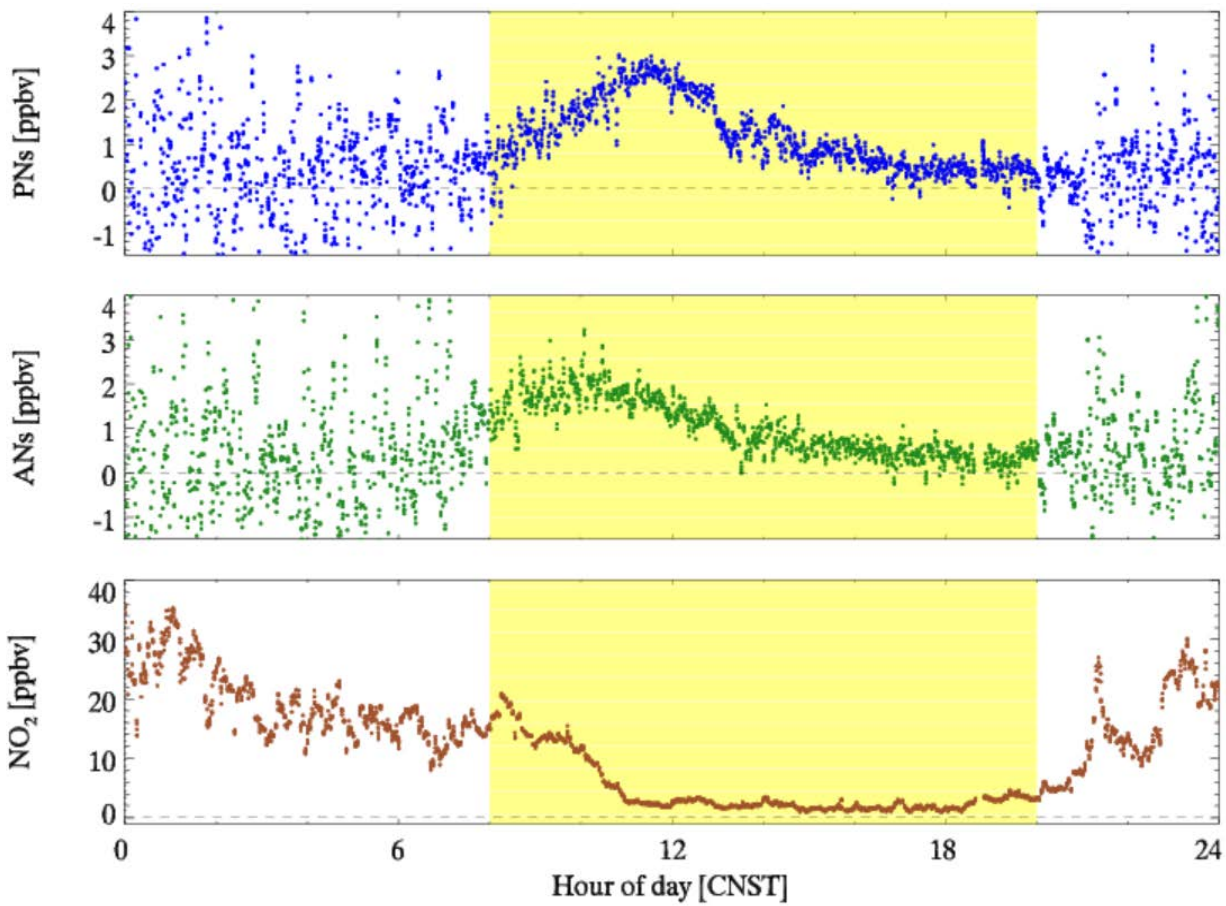
- The results of TD-CEAS is a little higher than PL-CLD, which may be due to the different sampling position;
- GC-ECD used the PAN source generated by the photochemical reaction for calibration, which may make the sensitivity high.

Diurnal variations



- [ANs] / [PNs] had peak during the day, [ANs] at 11am , [PNs] at 12am;
- The high value of [ANs] lasted longer during the day than [PNs];
- [NO_2] kept high concentration at nigh, and started to fall at 8am.

The limitations of the current single channel TD-CEAS



- The data is the measurement results of CHOOSE campaign on August 15, 2019.

- ➢ [NO_2] shows irregular jitters at night, and the corresponding [PNs] and [ANs] had larger errors;
- ➢ [NO_2], [PNs] and [ANs] all had small jitter during the day;
- ➢ when the [NO_2] change drastically, the difference in [NO_2] between adjacent measurement phases in a cycle will be large, resulting in larger errors.

5. Conclusion

- A single channel TD-CEAS system is successfully developed for the selective measurement of NO_2, ANs and PNs sequentially.

- The instrument can be calibrated and characterized with a conventional PAN calibration source which contains both PAN and MeN.

- During its field deployment, the measured NO_2 and PNs showed good agreement with the corresponding observed values from CLD and GC-ECD, respectively.

- More characterization are still required to account the influence of the side reactions which take place at the thermal dissociation tube.

THANK YOU!