THE HONG KONG POLYTECHNIC UNIVERSITY
香港理工大學

Significant production of $ClNO_2$ and possible source of Cl_2 from N_2O_5 uptake at a suburban site in eastern China

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Introduction:

1. **N_2O_5 het. chemistry, Cl activation.**

2. **Key factors of N_2O_5 chem**:

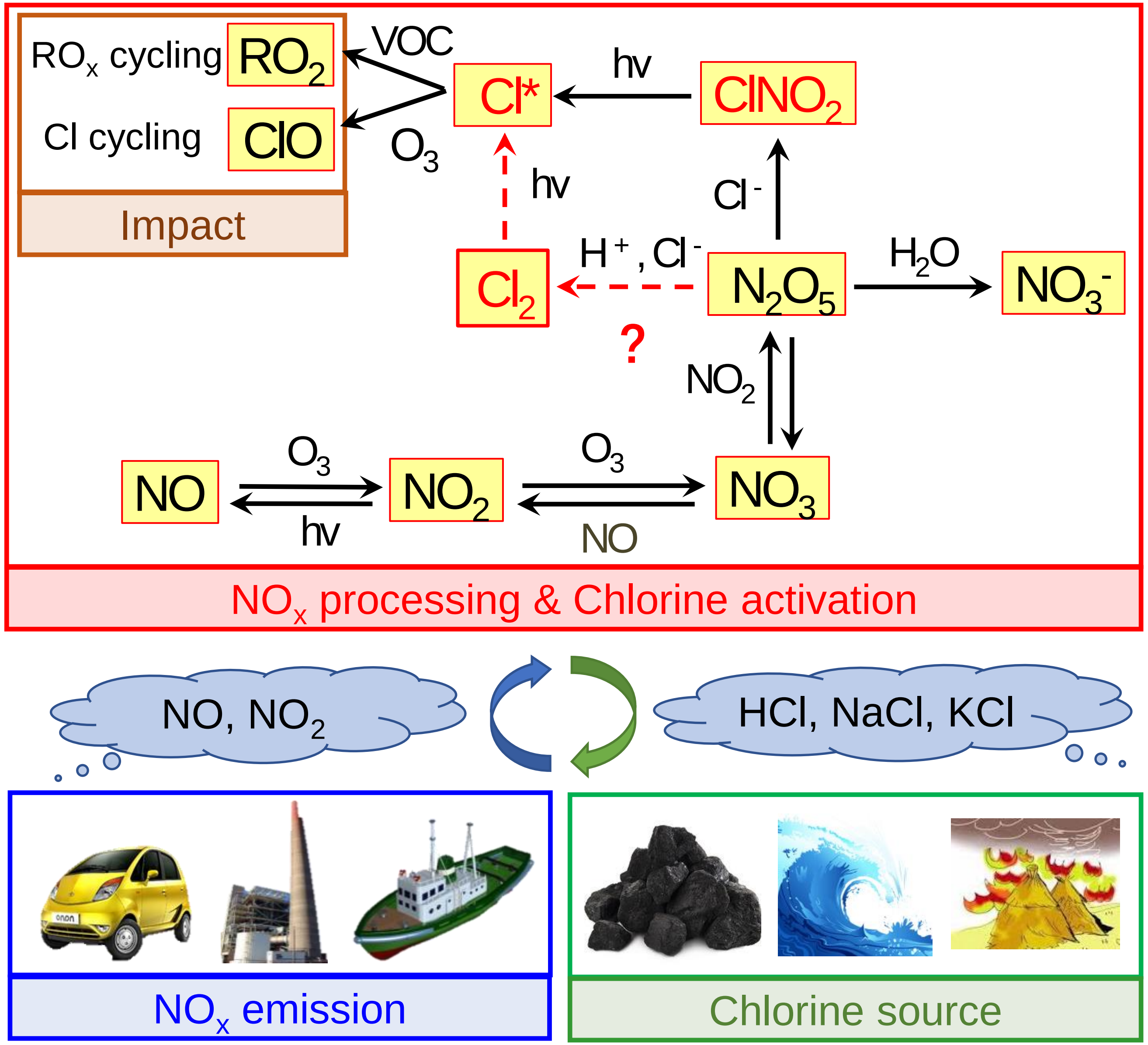
   1) $\gamma(N_2O_5)$, H_2O, Cl^-, nitrate, many studies;
   2) $\varphi(ClNO_2)$, less concerned; nucleophiles;
   3) knowledge gap of $\varphi(ClNO_2)$.

3. **"New" products of N_2O_5 uptake-Cl_2**

   1) limited: abundance, impact less known;
   2) het. source highly uncertain.

4. **This study:**

   1) N_2O_5 het. process: abundance, profile, discuss air mass change.
   2) N_2O_5 het chem & product: $ClNO_2$ & Cl_2; toward parameterization.



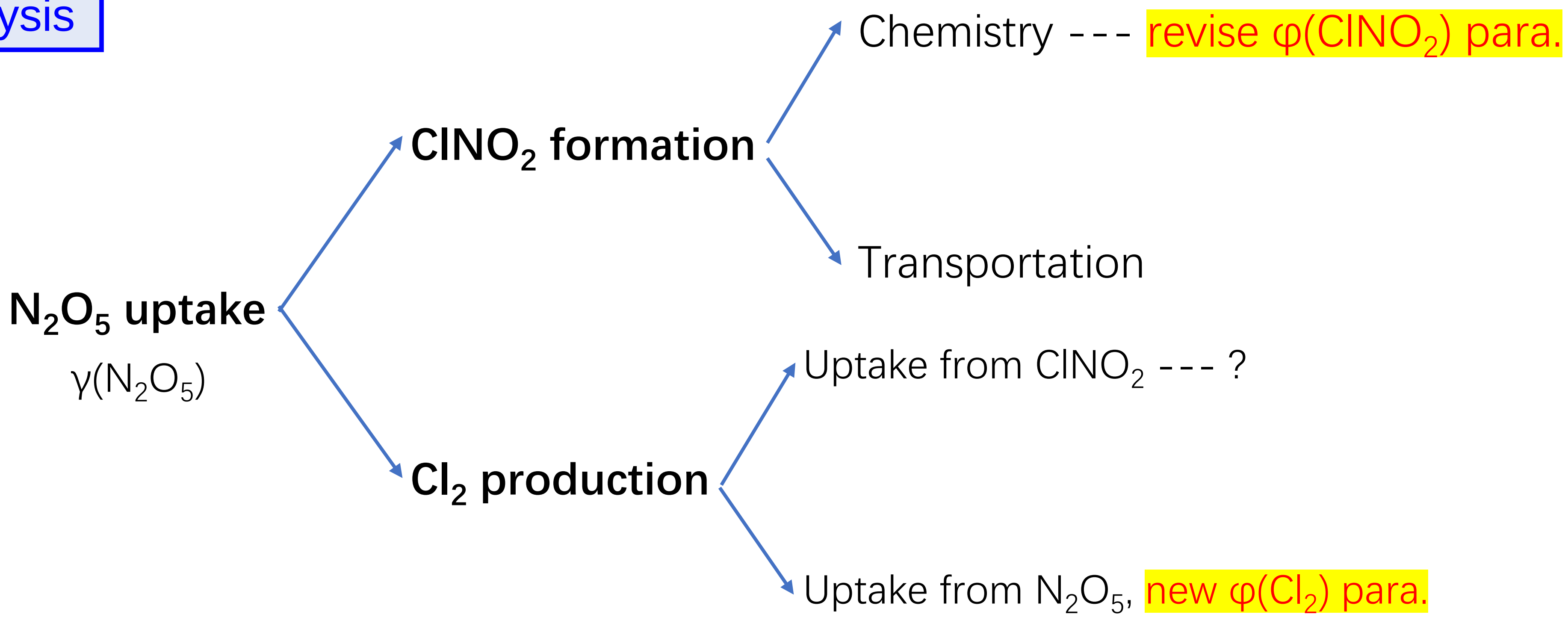
Schematic diagram of this study

Report observations

Overall: notable N_2O_5 het. chemistry

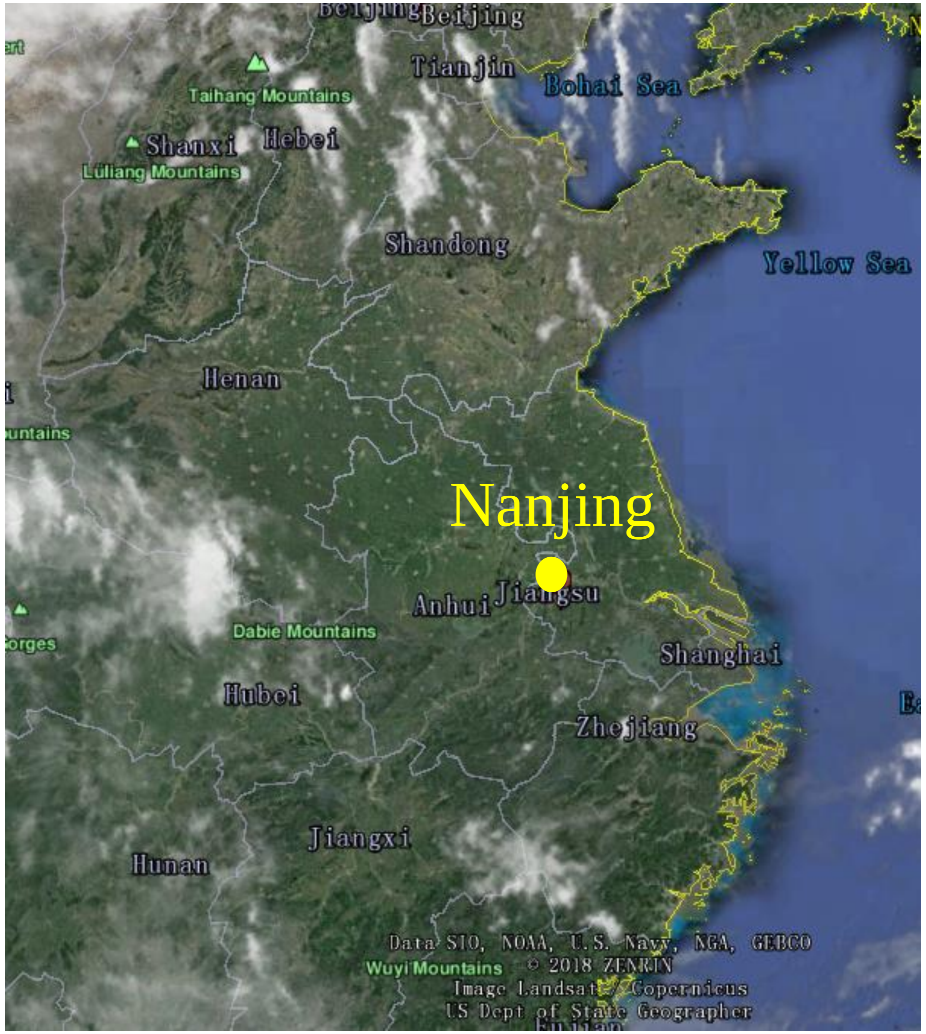
1. $ClNO_2$: diurnal profiles; air mass changes.
2. Nitrate: correlated with $ClNO_2$;
3. Cl_2: higher at night; correlated with $ClNO_2$.

Further analysis

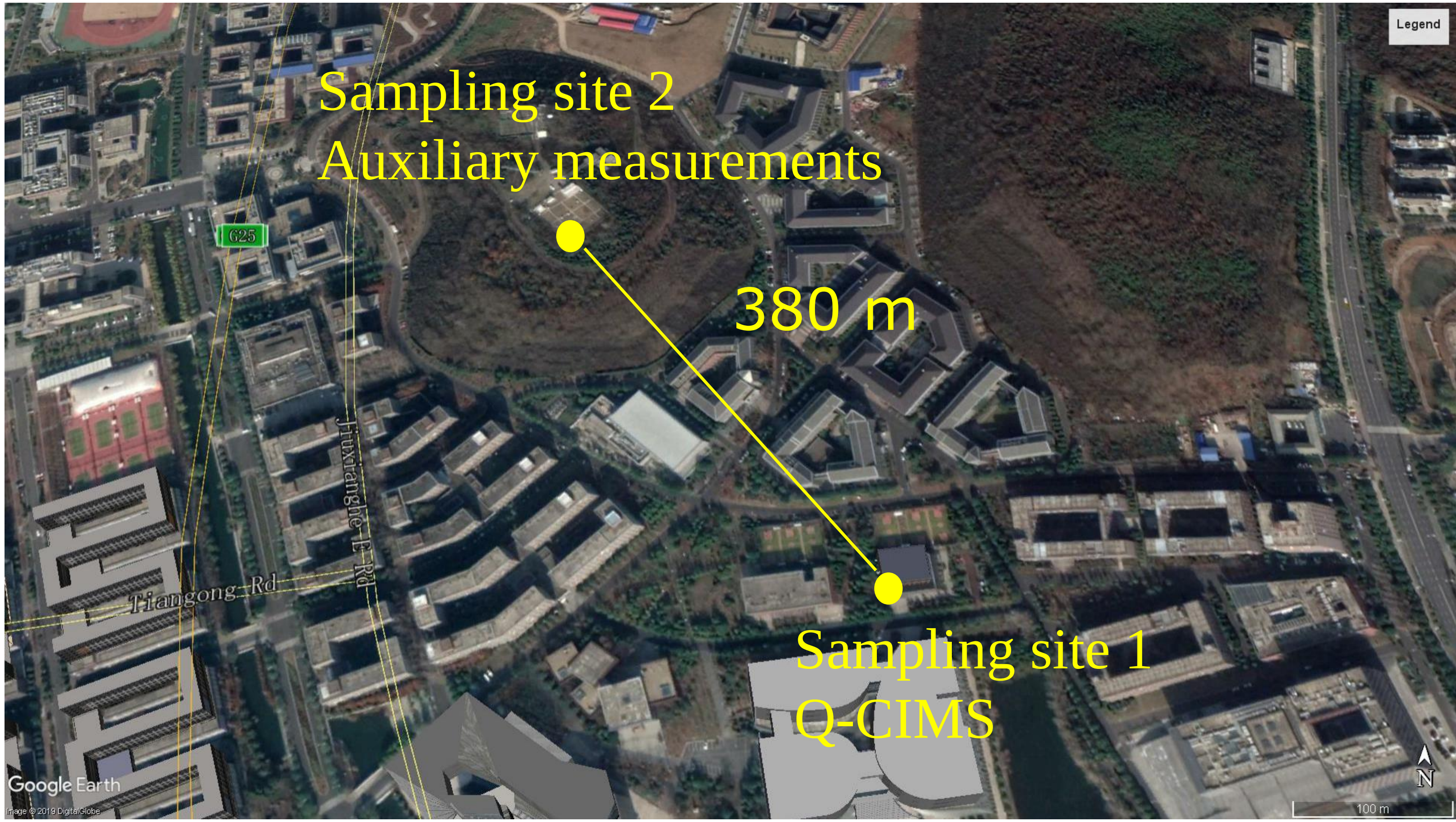


Method: 2018 Apr Nanjing campaign

Sampling time: 2018 Apr 11~26, spring season
Sampling site: rural site in Nanjing city

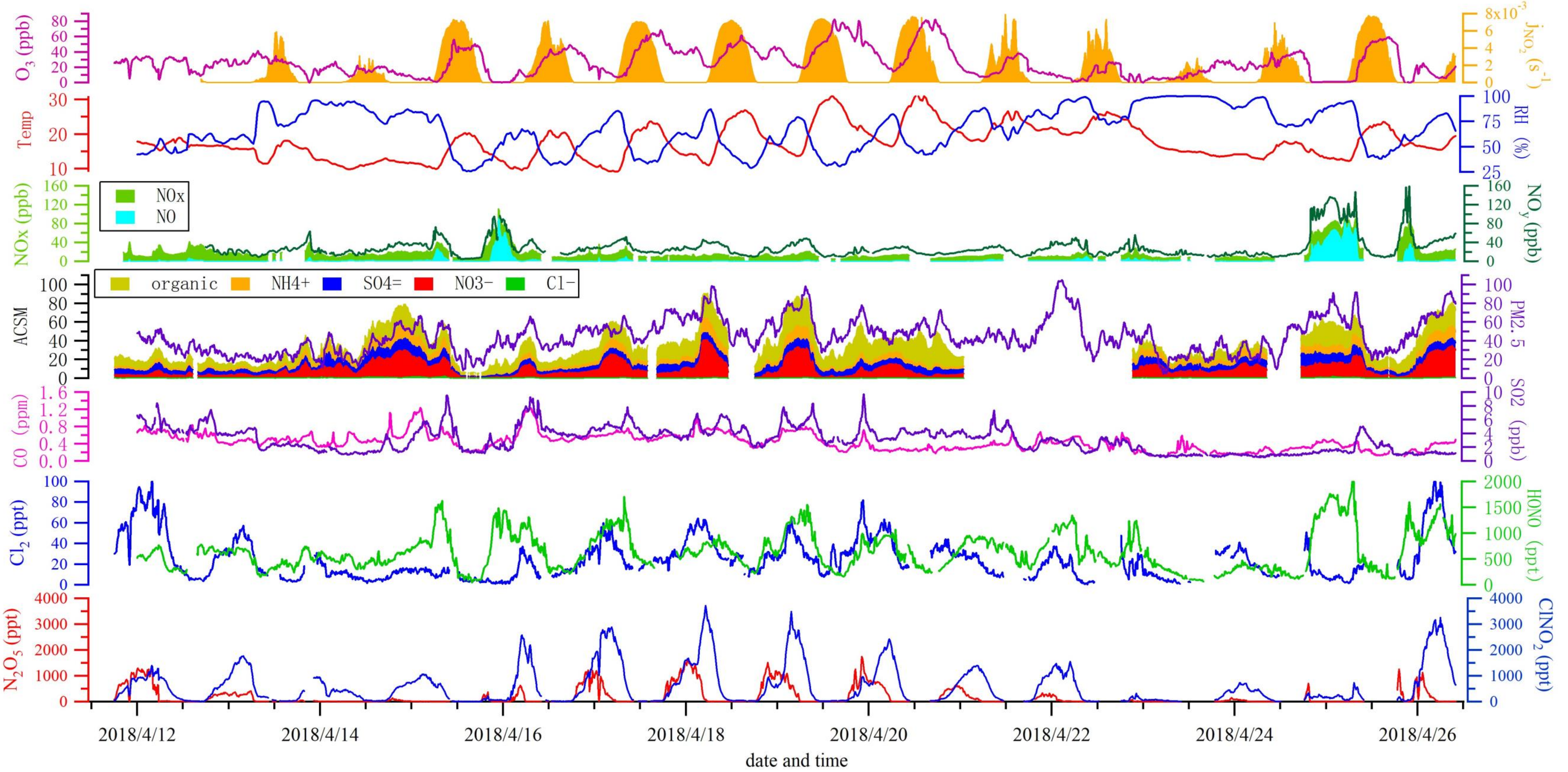


Nanjing city in Yangtze river delta (YRD)

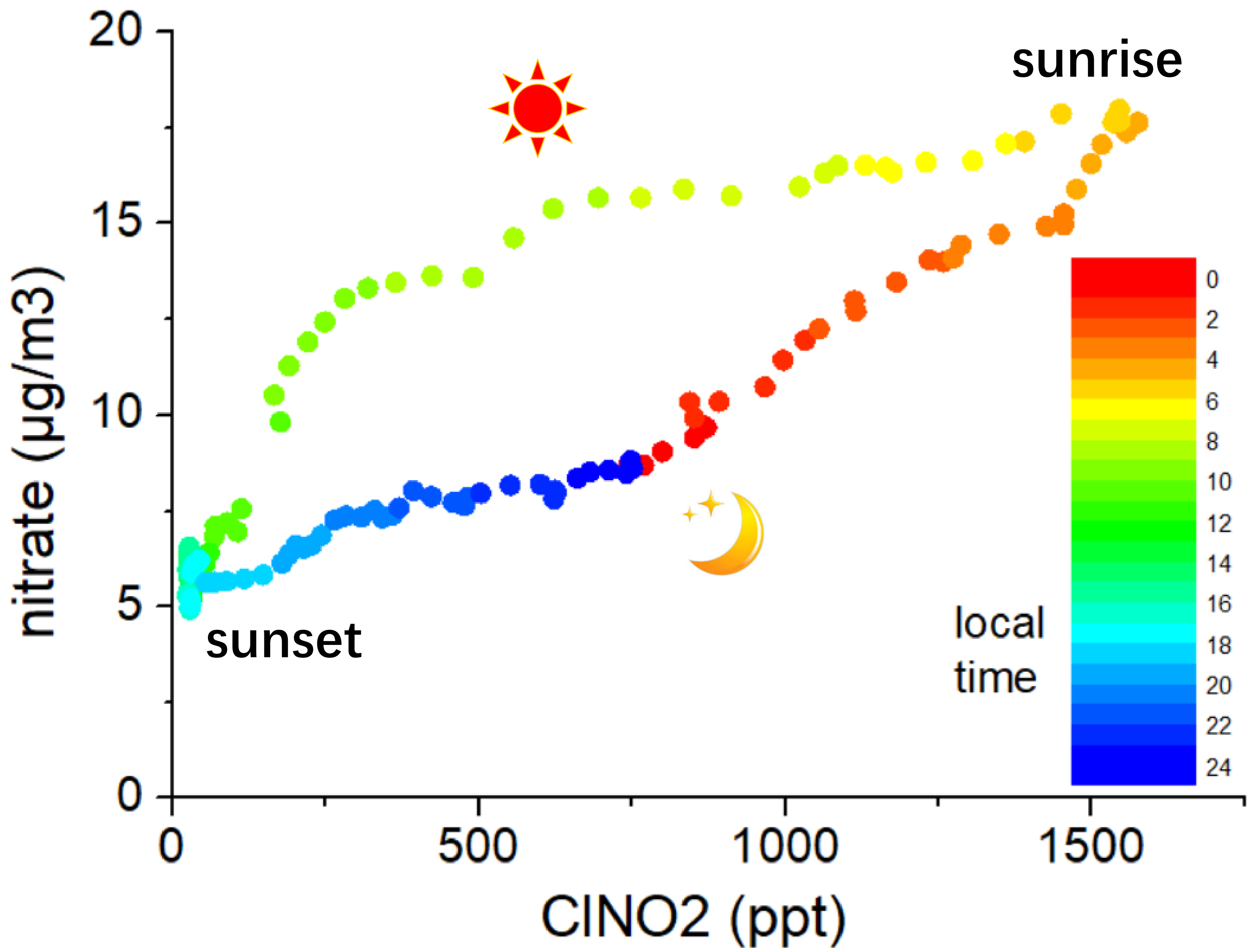


Sampling sites --- Nanjing University campus
vicinity environment: traffic, commercial, residential.
Surrounding downtown Nanjing: industrial facilities.

Result: 18 Apr Nanjing campaign overall observations



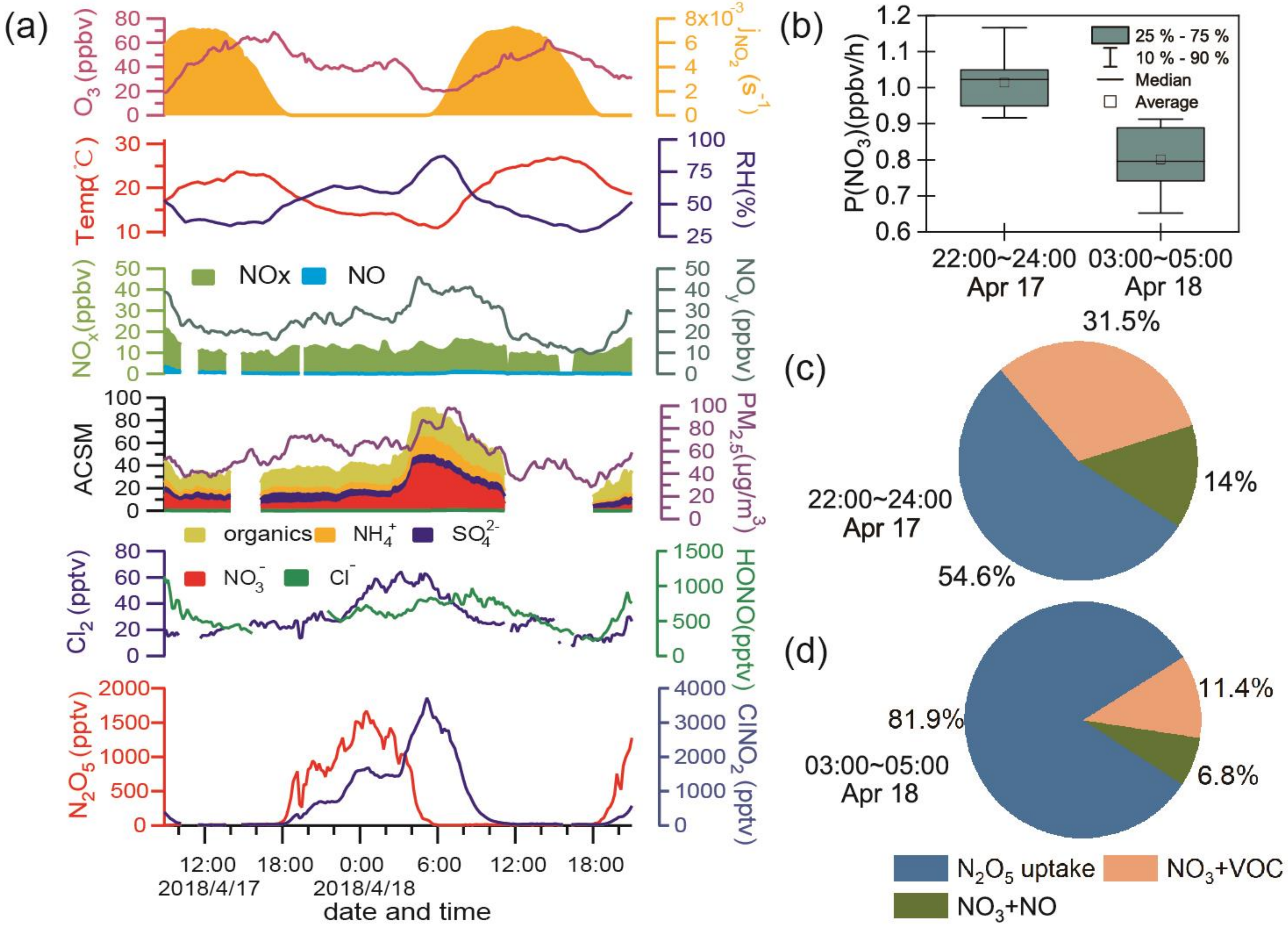
Overall relationship of $ClNO_2$ and nitrate



Tips

1. Good diurnal profiles
2. Nighttime $ClNO_2$ and nitrate well correlated.
3. Higher nitrate increase after midnight.

Elevated $ClNO_2$ and nitrate during air mass shift process --- **comparison & discussion**

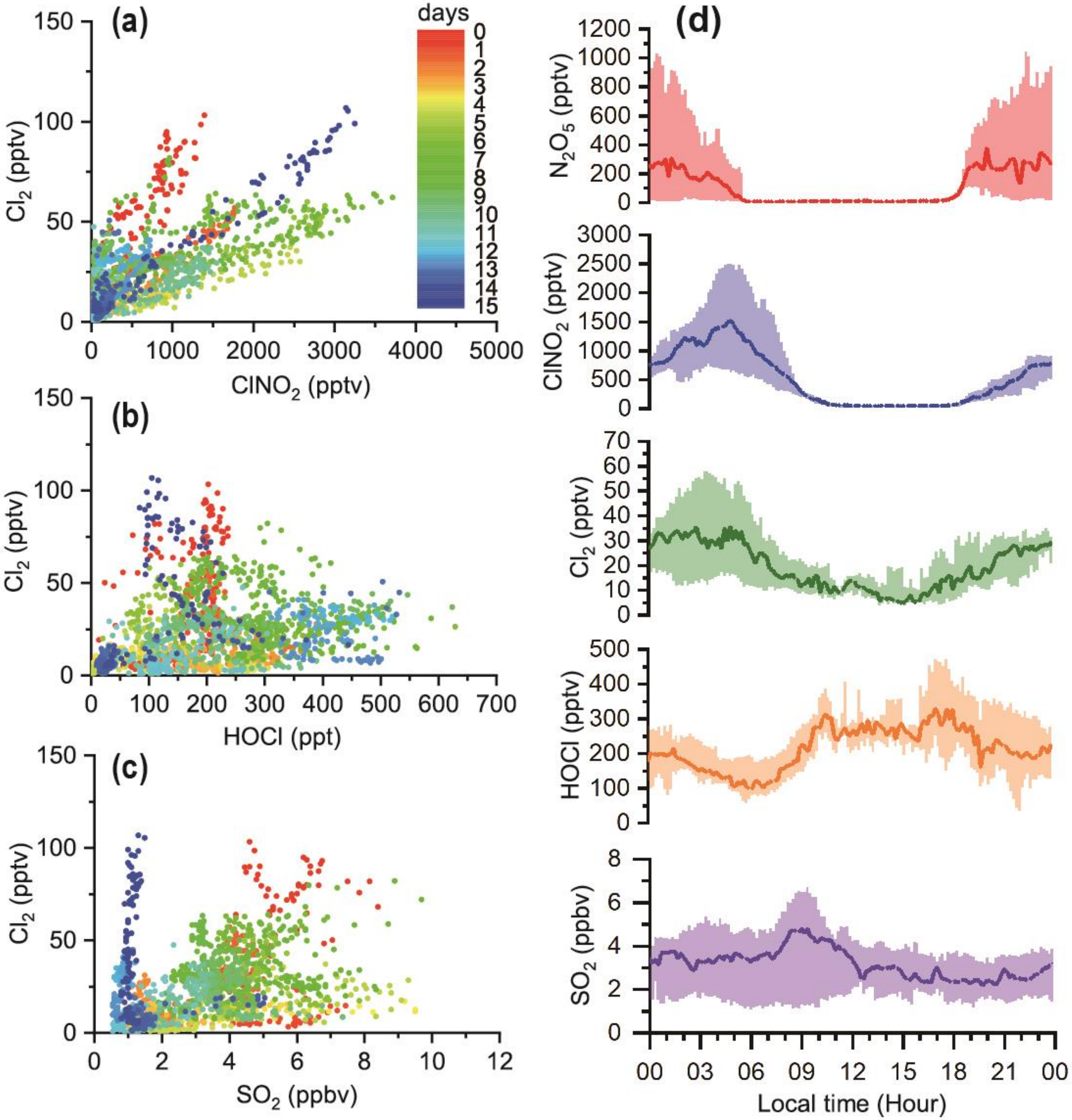


After midnight

NO_3 production slightly lower

Backward trajectory: The same (not shown here)

N_2O_5 het. loss much higher



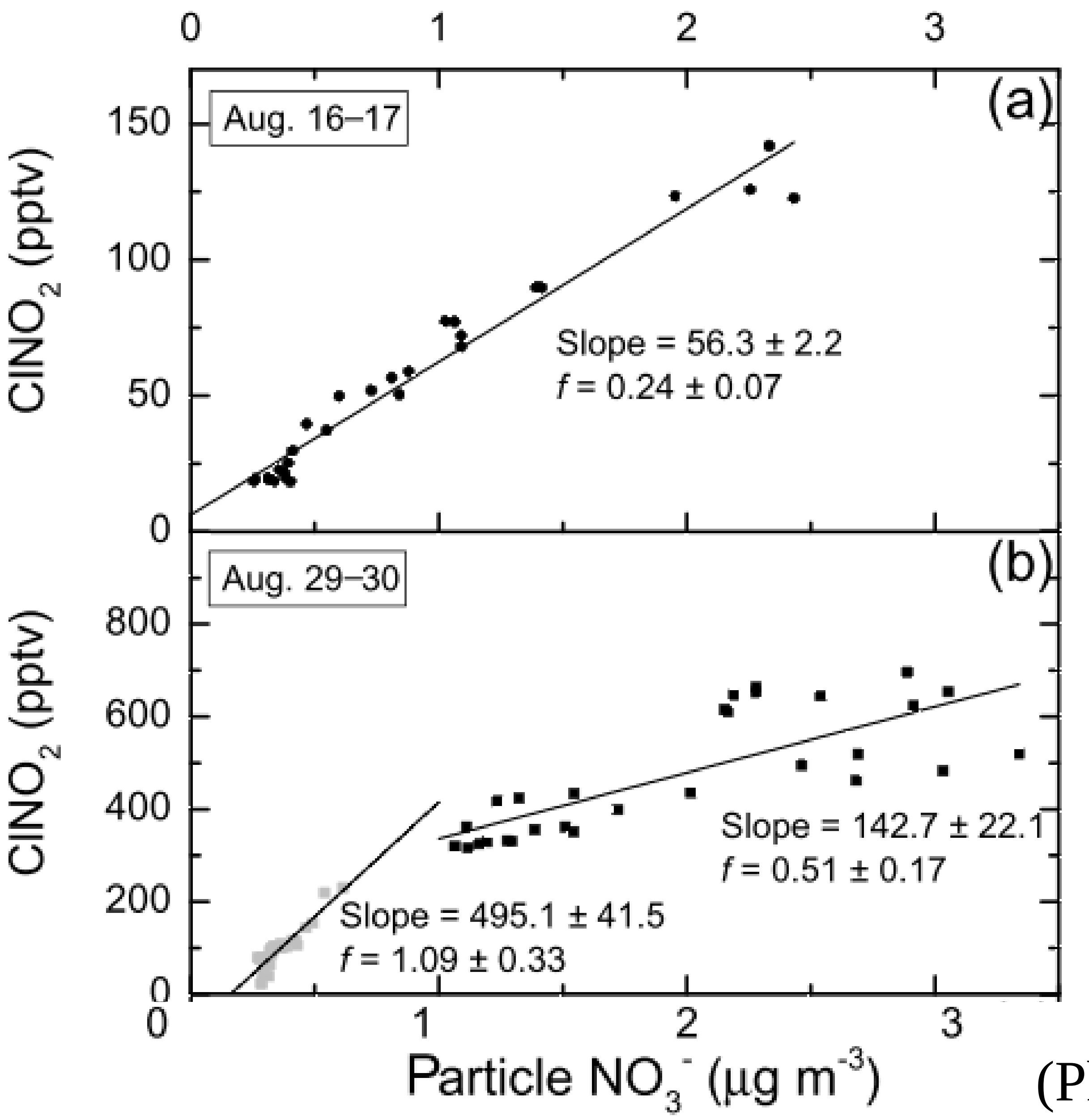
Investigation of Cl_2 sources --- correlations of Cl_2 study

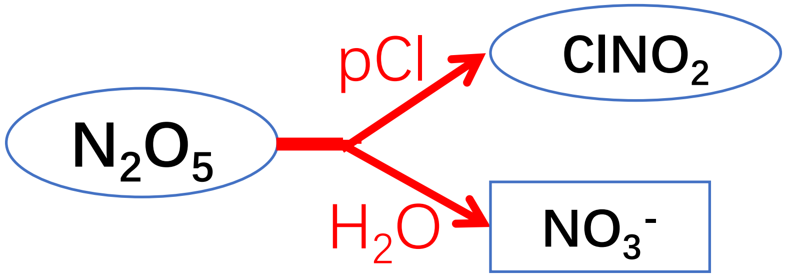
1. N_2O_5 uptake

2. HOCl uptake

3. Coal burning

Estimate N_2O_5 uptake coefficient and $ClNO_2$ yield





Basic assumption

- Nitrate increasing is mostly attributable to N_2O_5 uptake.

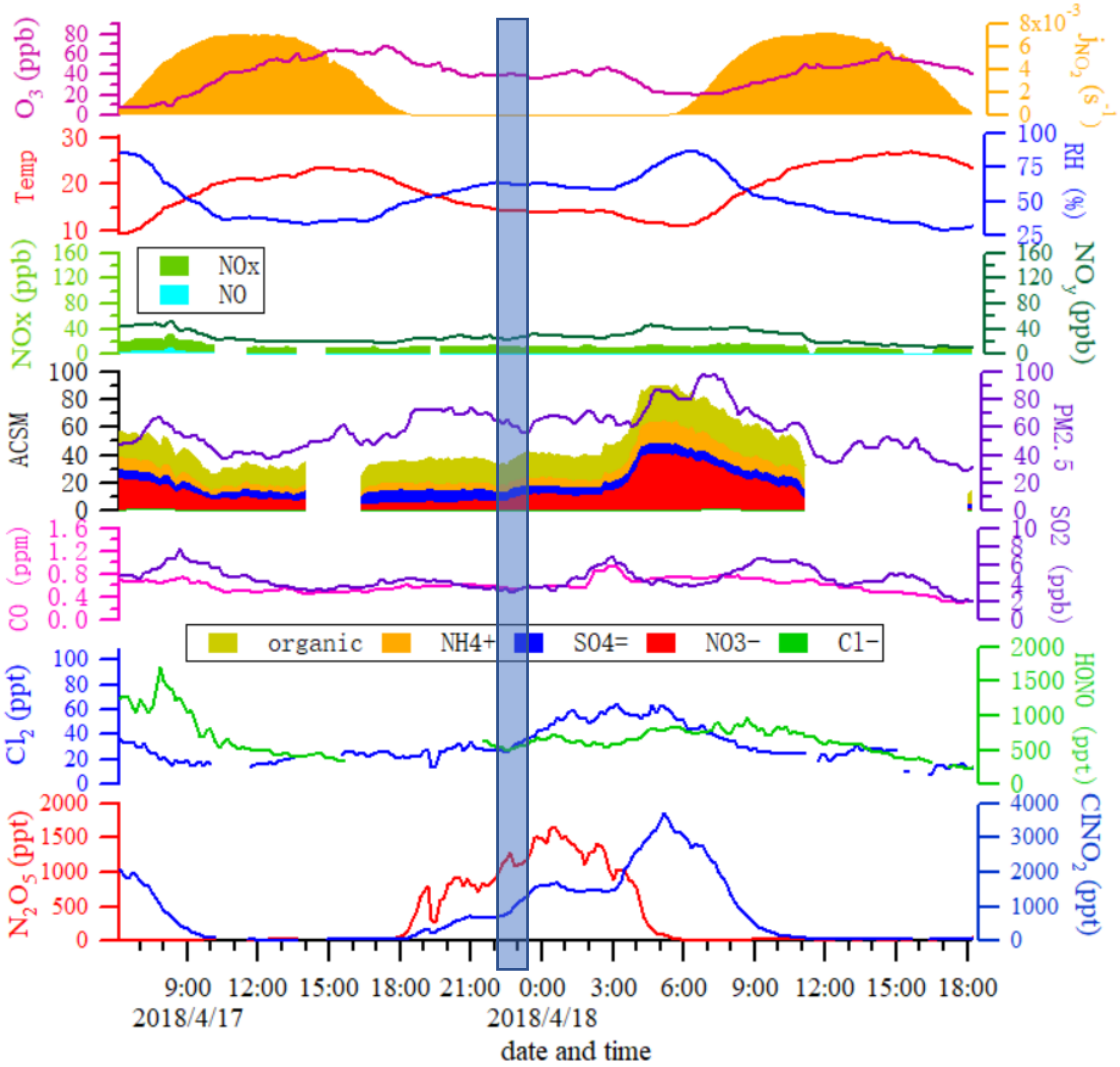
$$pClNO_2 = \frac{d[ClNO_2]}{dt} = f\,(0.25\gamma \bar{c} A\,[N_2O_5]).$$

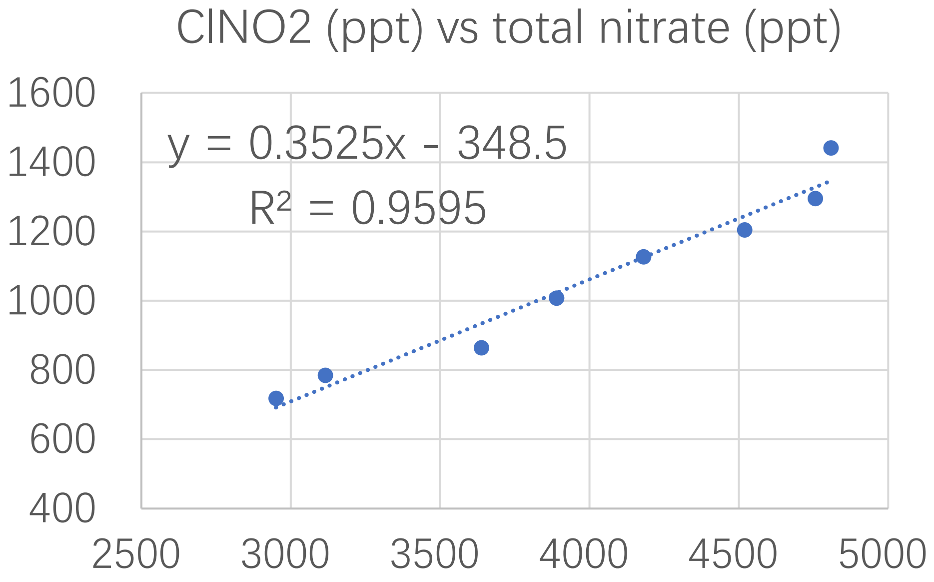
$$\varphi(ClNO_2) = 2\left(\frac{pNO_3^-}{pClNO_2} + 1\right)^{-1}$$

(Phillips et al., 2016)

Case study to investigate $\gamma(N_2O_5)$, $\varphi(ClNO_2)$ and Cl_2 production

Selection criteria: stable plumes (CO, SO_2, wind); increasing Cl_2; increasing $ClNO_2$ and nitrate; NO<0.1 ppb; duration > 30 min.

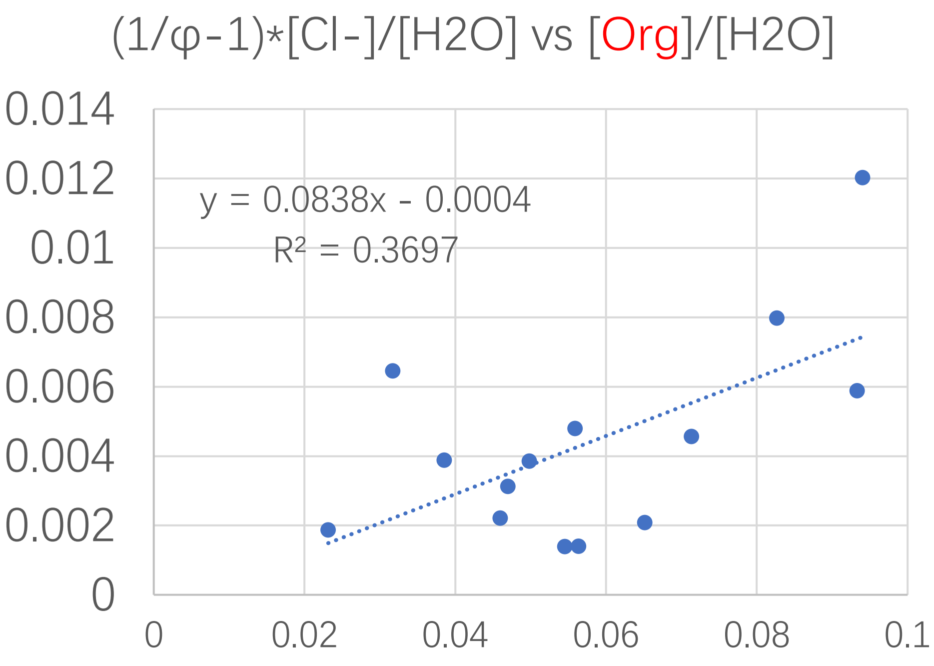




Apr 17 22:20~23:30

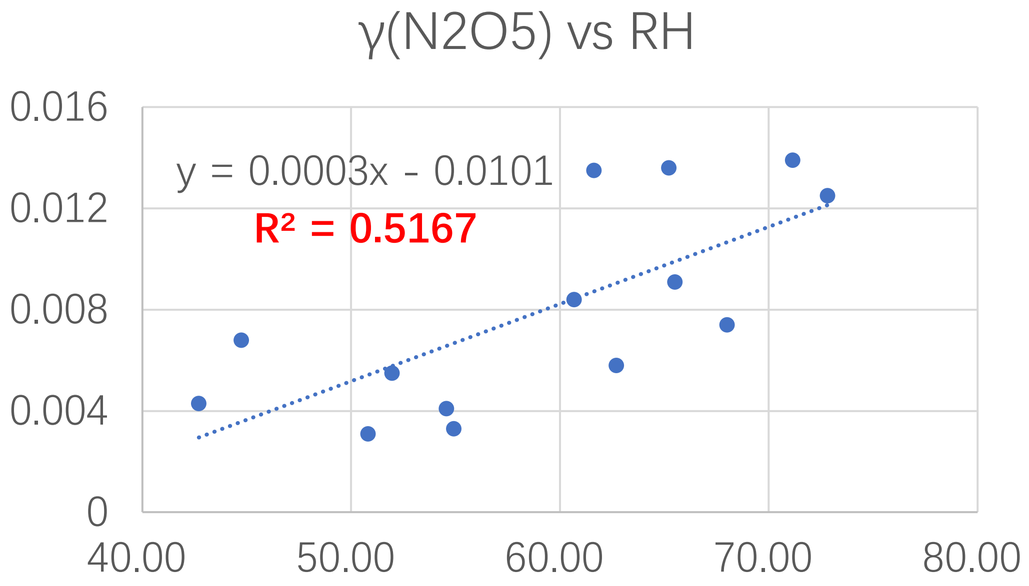
$\gamma(N_2O_5)$=0.0058, $\varphi(ClNO_2)$=0.521

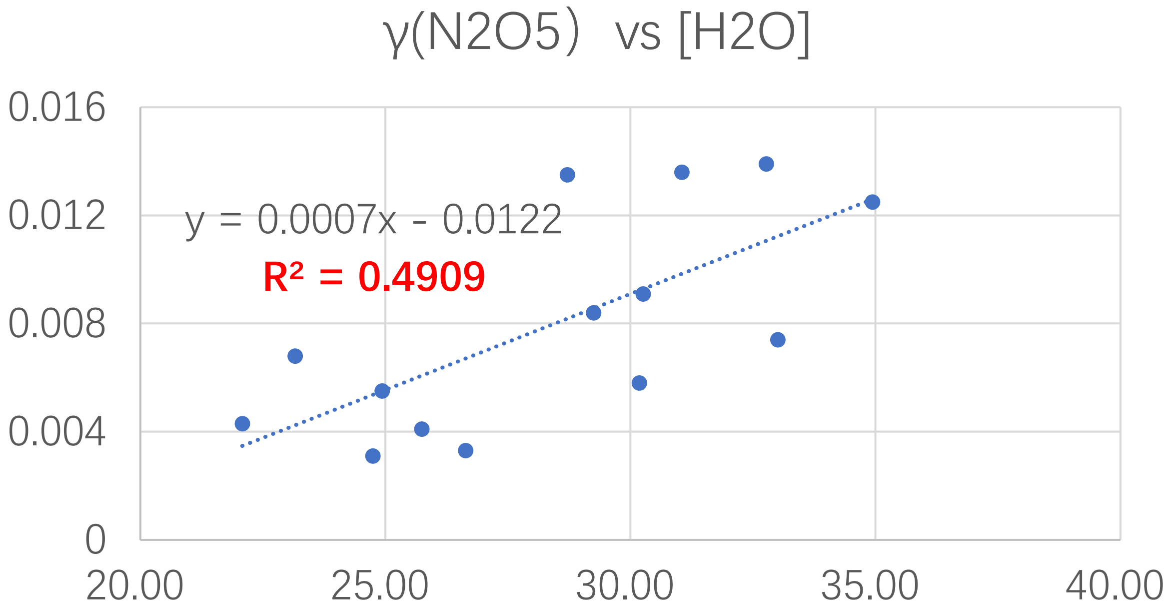
Case study to investigate $\gamma(N_2O_5)$, $\varphi(ClNO_2)$ and Cl_2 production

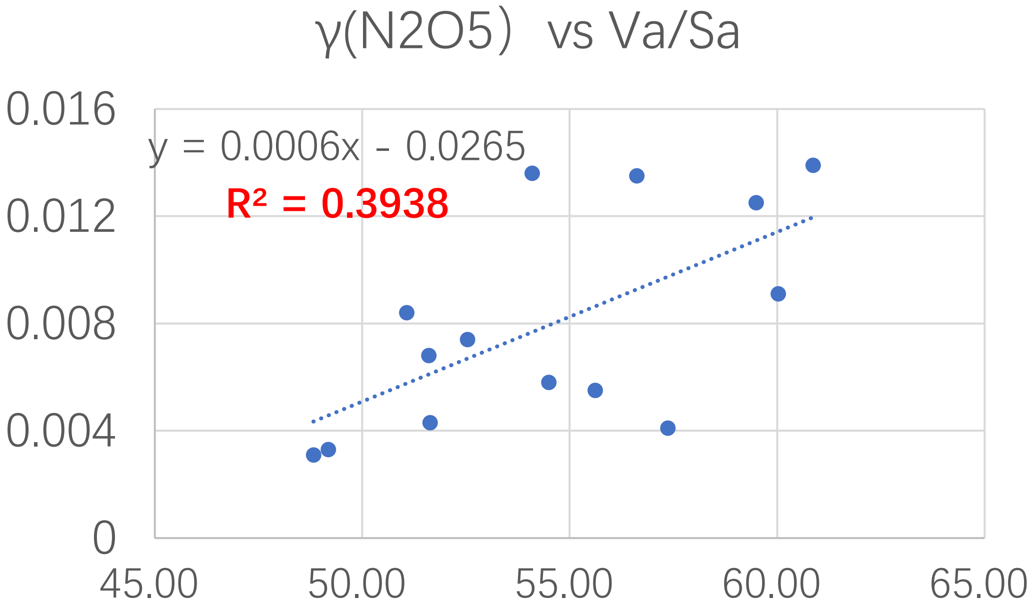


plume	start	end	γ(N2O5)	φ(ClNO2)
1	4/12/18 2:10	4/12/18 3:00	0.0043	0.885
2	4/12/18 3:10	4/12/18 3:40	0.0068	0.716
3	4/12/18 21:40	4/13/18 0:40	0.0061	0.853
4	4/16/18 19:50	4/16/18 20:30	0.0031	0.378
5	4/16/18 20:40	4/16/18 21:20	0.0033	0.541
6	4/17/18 22:20	4/17/18 23:40	0.0058	0.521
7	4/18/18 3:00	4/18/18 3:50	0.0135	0.483
8	4/18/18 4:10	4/18/18 4:40	0.0139	0.187
9	4/19/18 0:00	4/19/18 0:40	0.0055	0.280
10	4/19/18 0:40	4/19/18 1:40	0.0041	0.523
11	4/19/18 2:00	4/19/18 3:00	0.0091	0.769
12	4/20/18 1:00	4/20/18 2:00	0.0084	0.641
13	4/20/18 2:10	4/20/18 2:50	0.0074	0.647
14	4/26/18 1:20	4/26/18 2:00	0.0136	0.468
15	4/26/18 2:30	4/26/18 3:20	0.0125	0.533
average±standard deviation			0.008±0.004	0.562±0.197

Estimate N_2O_5 uptake coefficient and $ClNO_2$ yield --- influencing factors

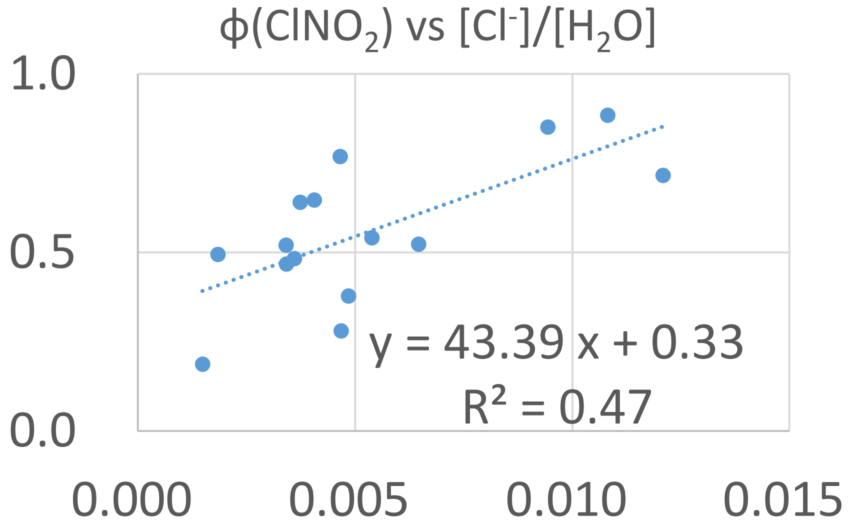


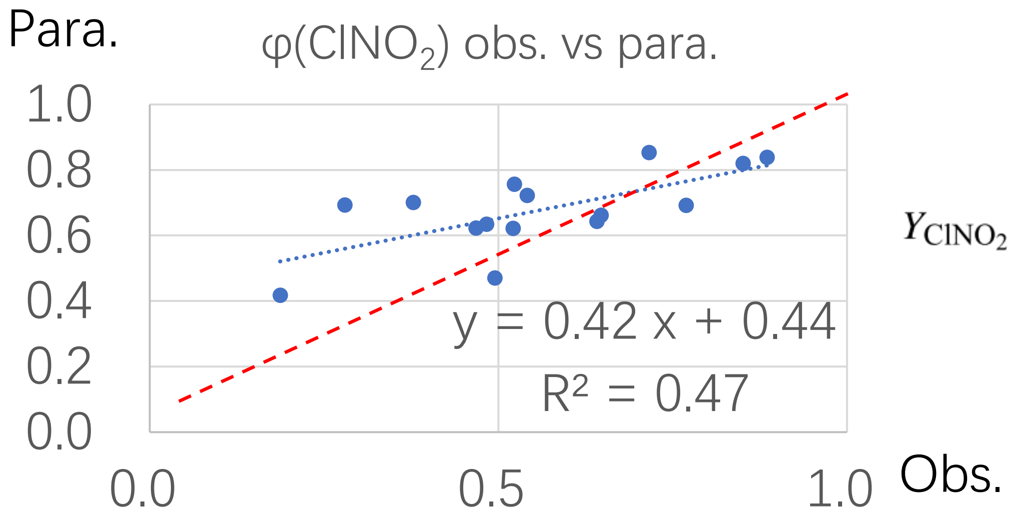




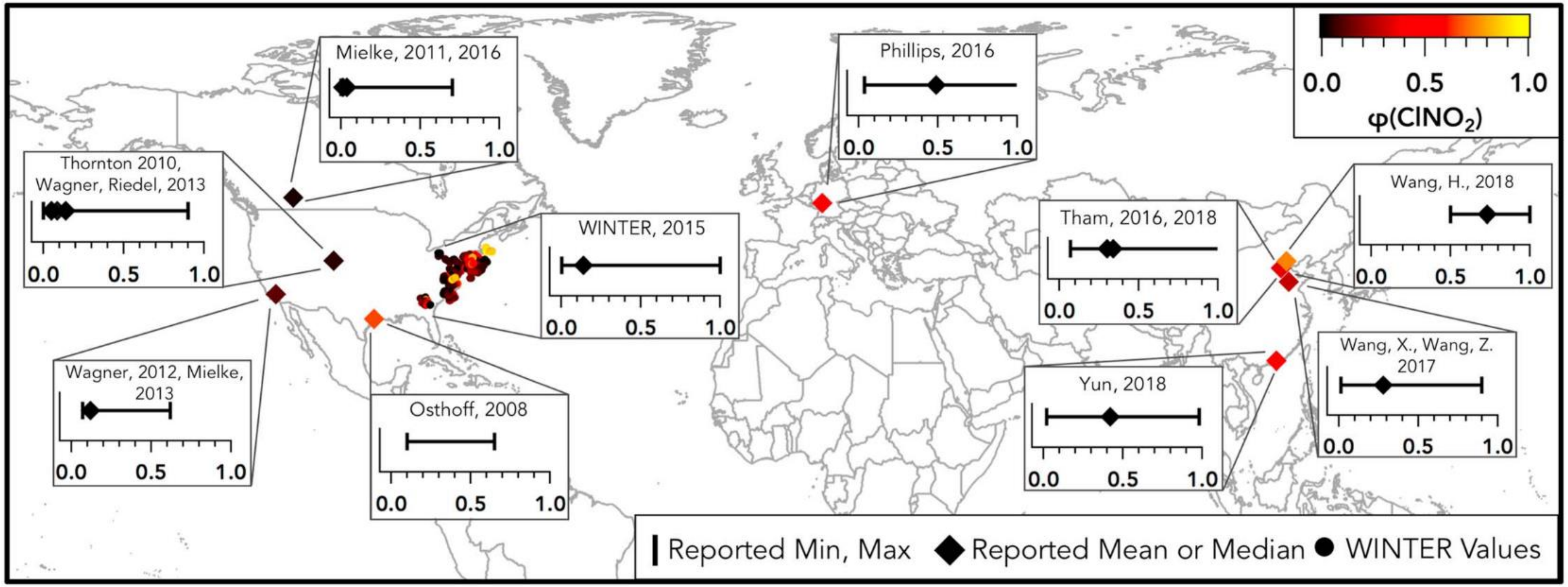
Other factors have no significant impact.

Investigation of high φ($ClNO_2$)





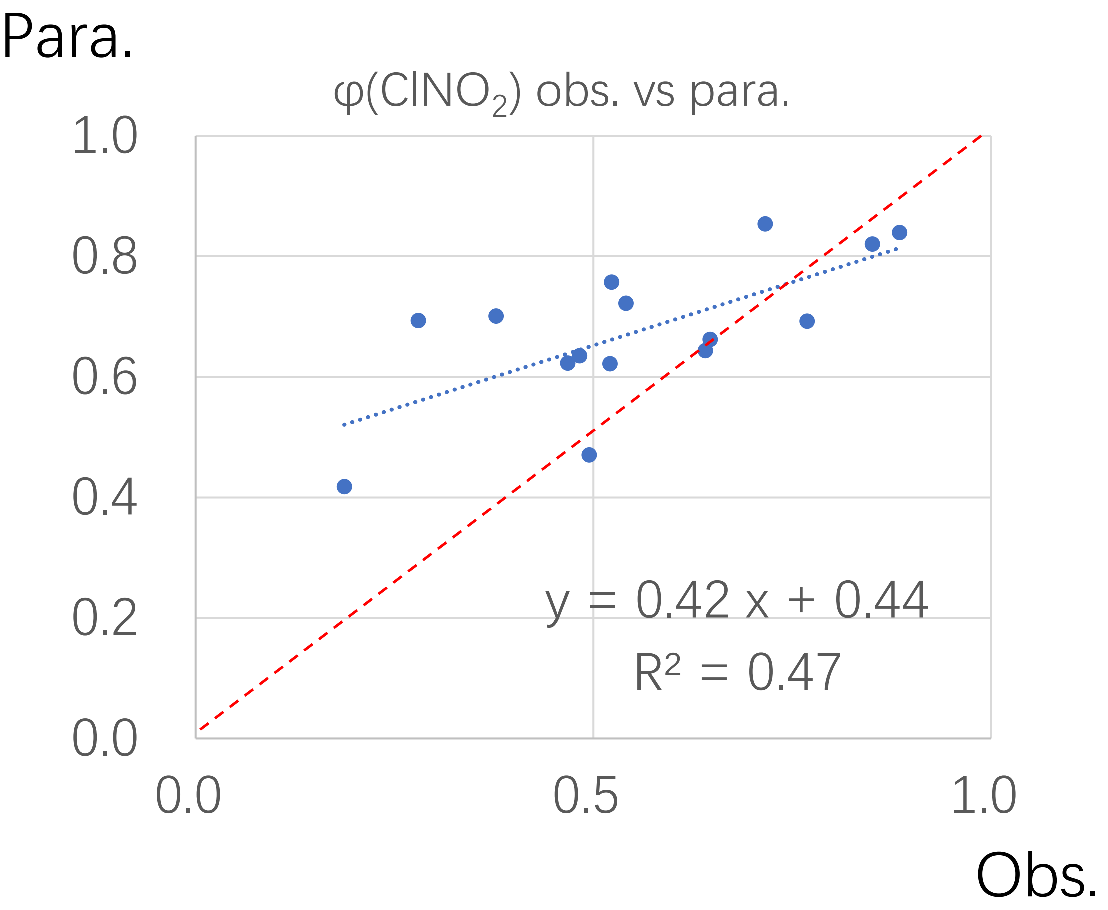
$$Y_{ClNO_2} = \frac{\Delta ClNO_2}{\Delta N_2O_5} = \left(1 + \frac{k_3\,[H_2O(l)]}{k_4\,[Cl^-]}\right)^{-1}$$



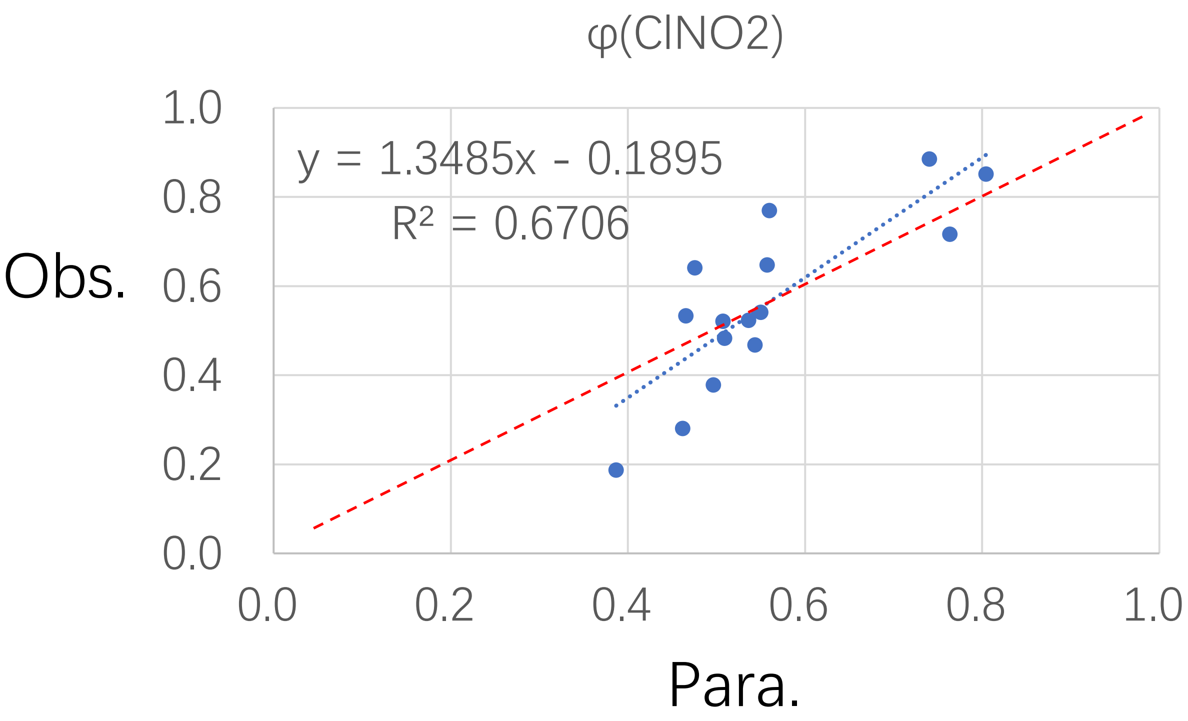
Why $ClNO_2$ yield is high in Nanjing?

1. Cl^-/H_2O
2. competitors for NO_2^+

Revise parameterizations of $\Phi(ClNO_2)$ by incorporating organics.



$\Phi(ClNO_2)=1/(1+[H_2O]/483*[Cl^-]+[Org]/235*[Cl^-])$



Revise parameterizations of Φ($ClNO_2$) by incorporating organics.

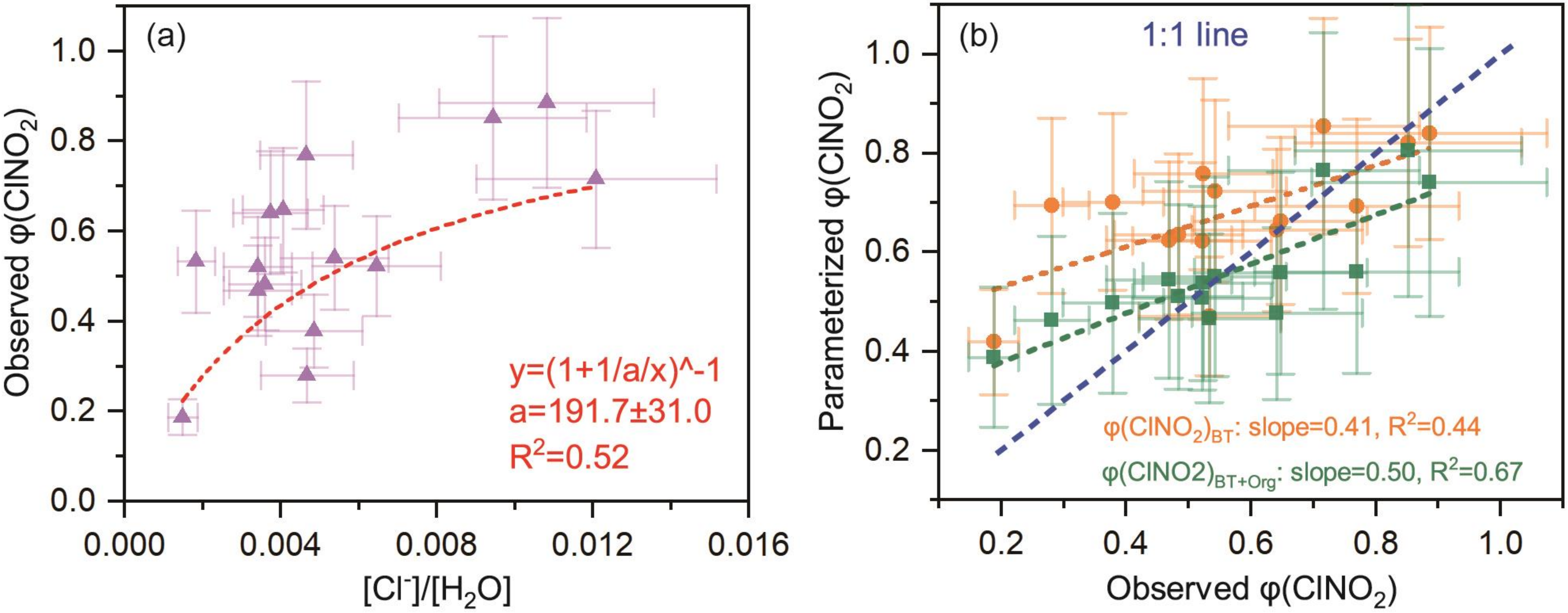
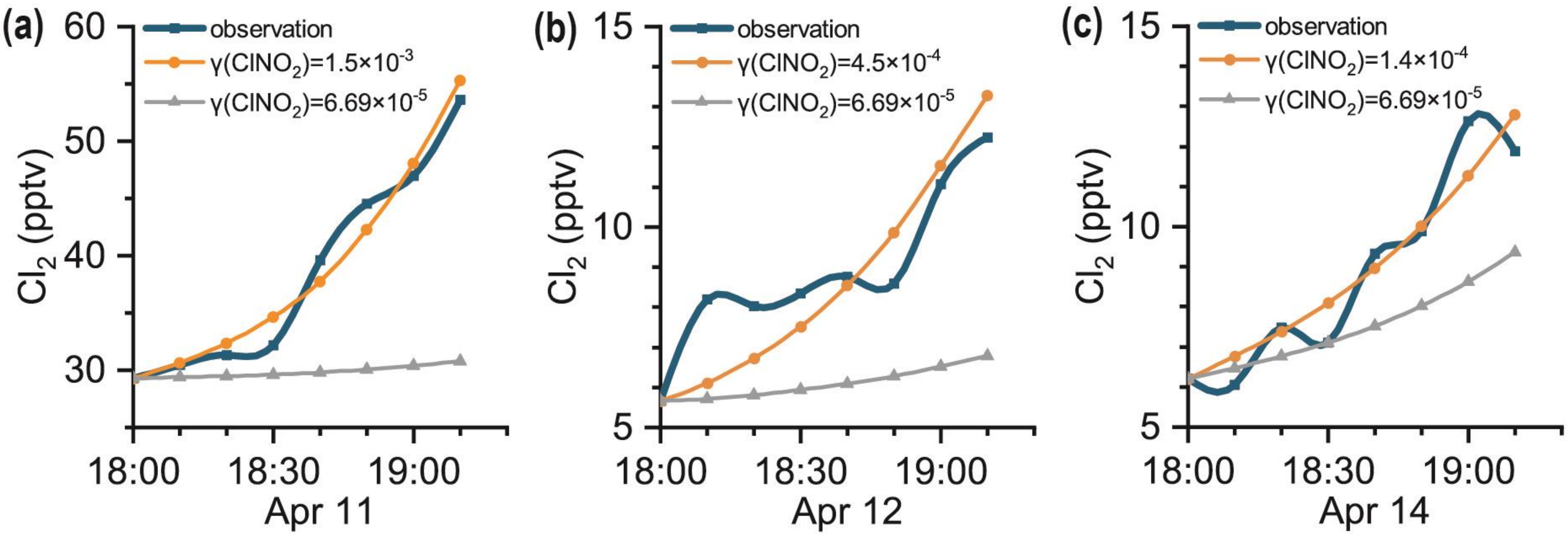
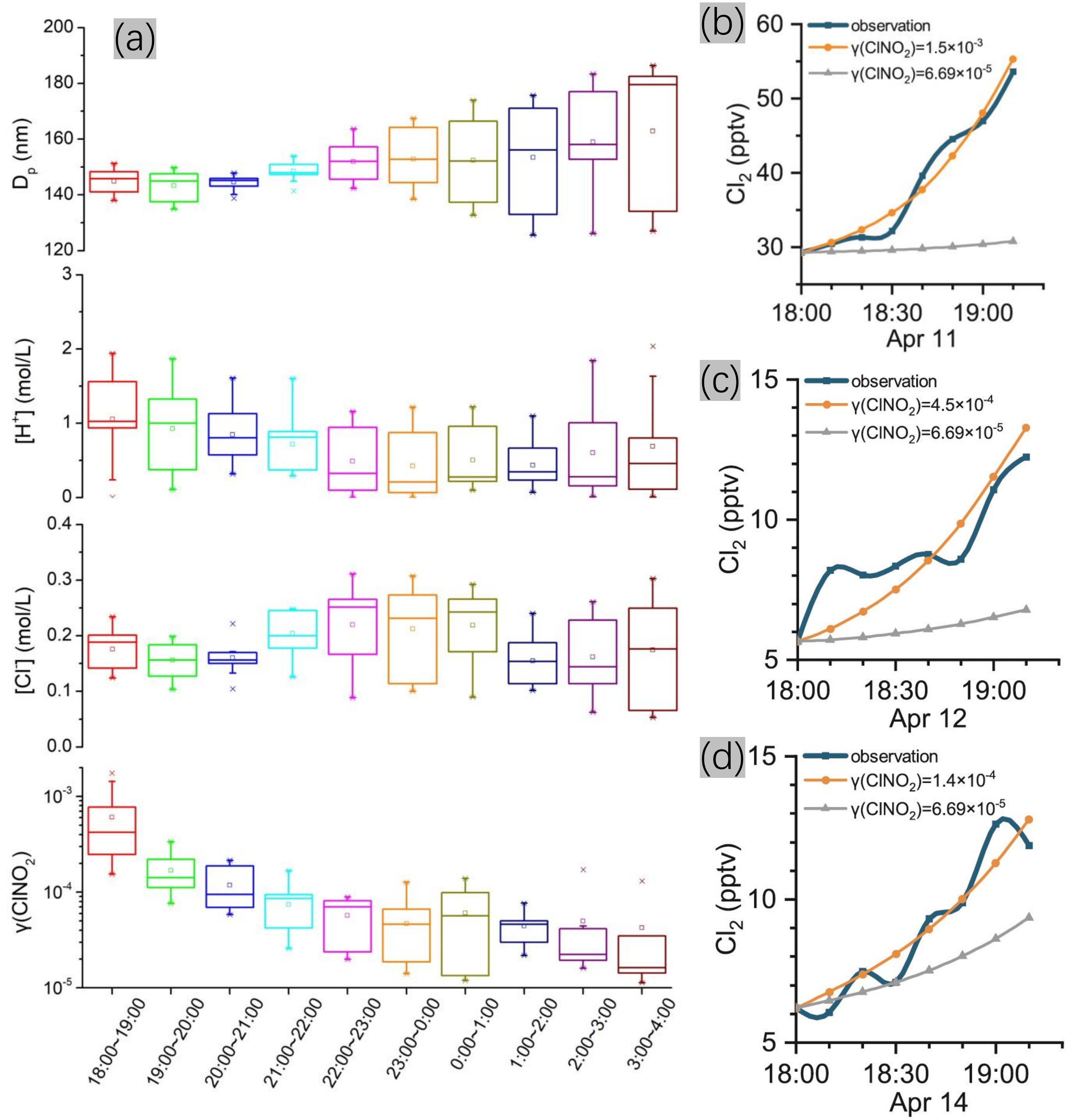


Figure used in manuscript

$ClNO_2$ uptake alone cannot explain Cl_2 increase during early night

$$d[Cl_2]/dt=\frac{1}{4}c(ClNO_2)\ S_a\gamma(ClNO_2)[ClNO_2]$$

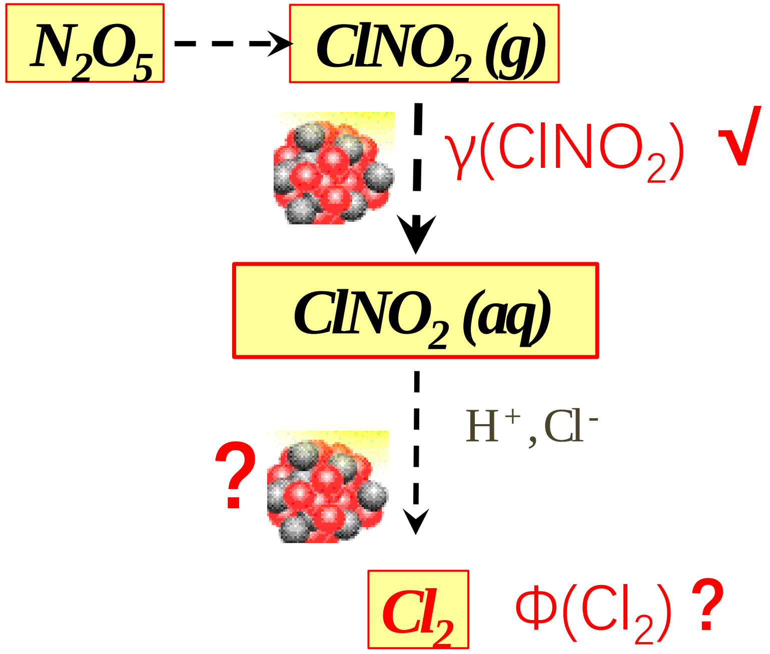




(a)
D_p (nm)
$[H^+]$ (mol/L)
$[Cl^-]$ (mol/L)
$\gamma(ClNO_2)$
18:00~19:00
19:00~20:00
20:00~21:00
21:00~22:00
22:00~23:00
23:00~0:00
0:00~1:00
1:00~2:00
2:00~3:00
3:00~4:00
(b)
observation
$\gamma(ClNO_2)=1.5\times10^{-3}$
$\gamma(ClNO_2)=6.69\times10^{-5}$
Cl_2 (pptv)
Apr 11
(c)
observation
$\gamma(ClNO_2)=4.5\times10^{-4}$
$\gamma(ClNO_2)=6.69\times10^{-5}$
Cl_2 (pptv)
Apr 12
(d)
observation
$\gamma(ClNO_2)=1.4\times10^{-4}$
$\gamma(ClNO_2)=6.69\times10^{-5}$
Cl_2 (pptv)
Apr 14

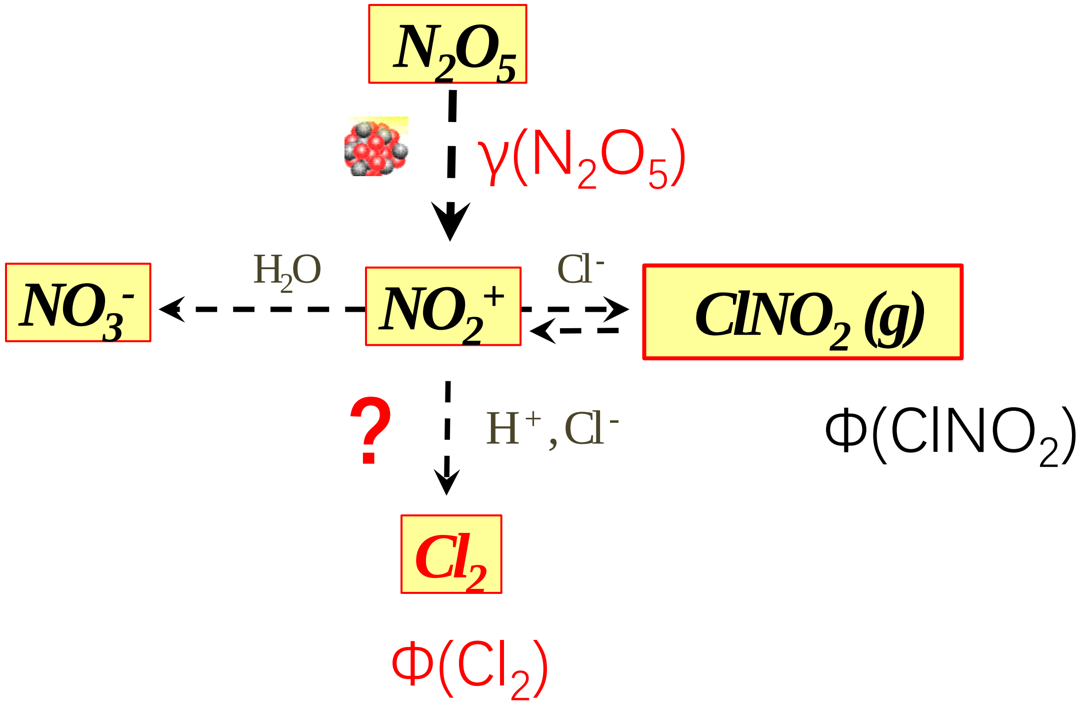
Heterogeneous Cl_2 formation from $N_2O_5/ClNO_2$ chemistry

Previous scheme



Based on above analysis,
Consider $ClNO_2$ only to estimate
Cl_2 formation is not reasonable

Newly proposed scheme



Our proposed mechanism:
Cl_2 is ultimately converted from NO_2^+.

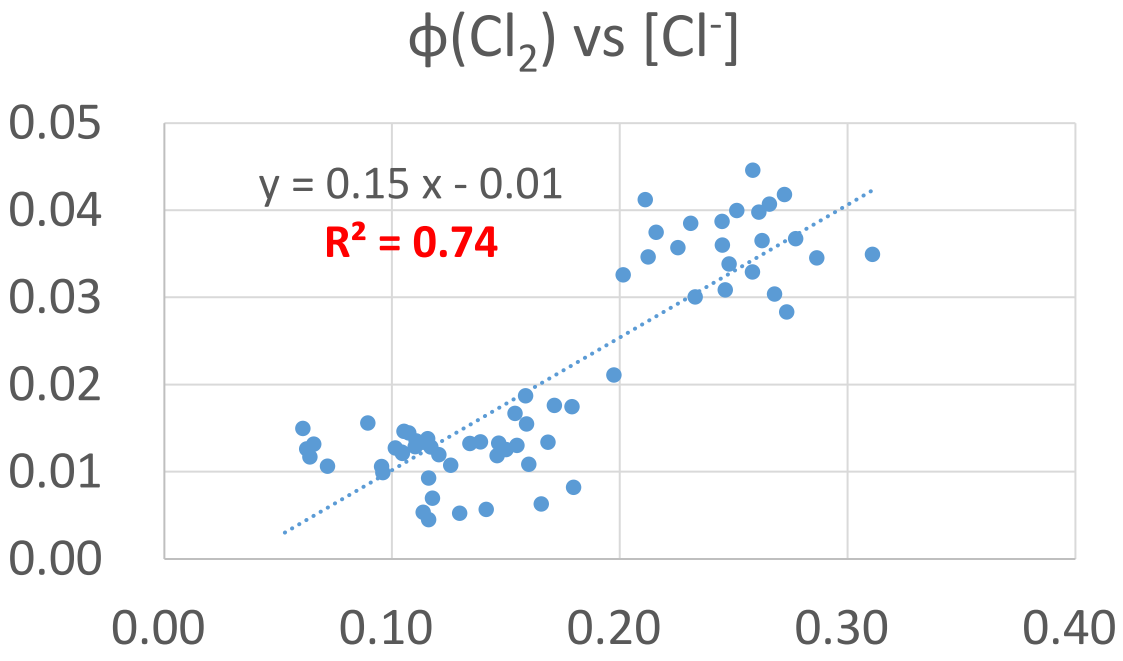
(Ammann et al., 2013) (Haskins et al., submitted to JGR)

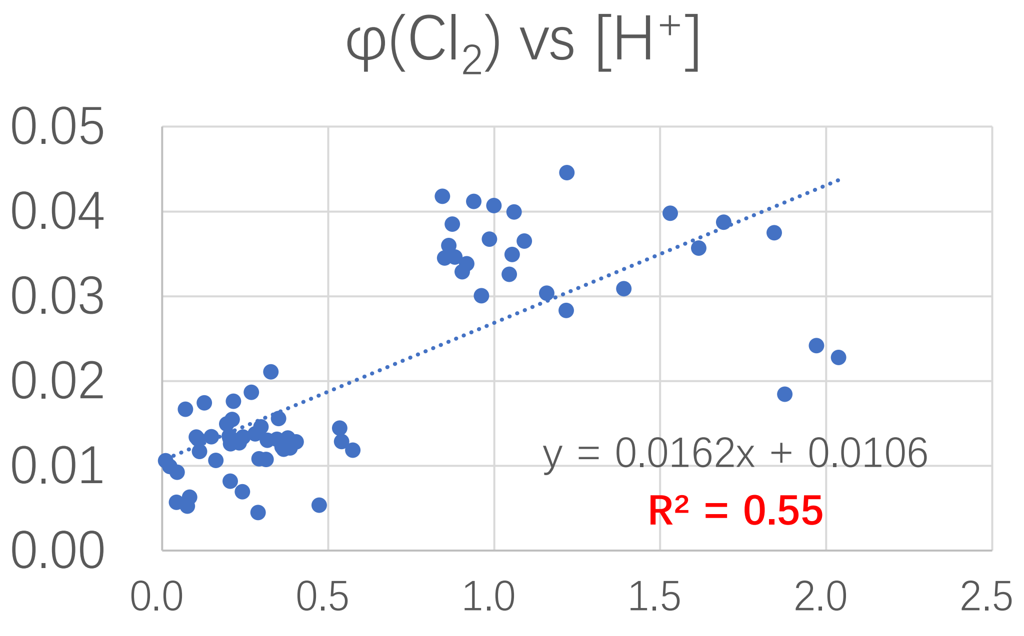
(derived in this study, see next slides)

New method: regard Cl_2 as direct oxidation product from N_2O_5 uptake we can **define Cl_2 yield from N_2O_5 uptake**

$$\varphi(ClNO_2)=\frac{\Delta[ClNO_2]}{\int k(N_2O_5)_{het}[N_2O_5]dt} \;\Rightarrow\; \varphi(Cl_2)=\frac{\Delta[Cl_2]}{\int k(N_2O_5)_{het}[N_2O_5]dt}$$

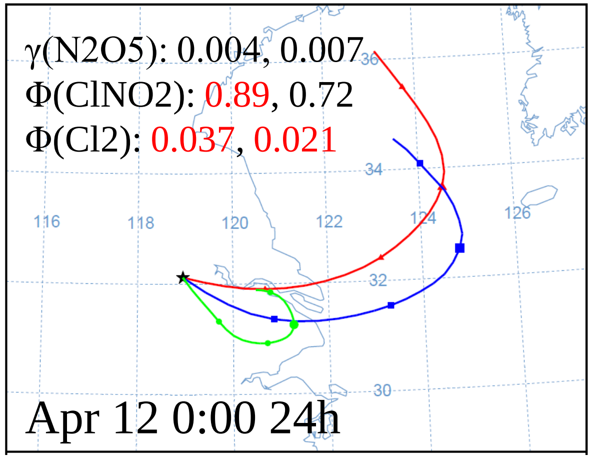
Dependence of $\varphi(Cl_2)$ shows better correlation with $[Cl^-]$ and $[H^+]$ --- more reasonable



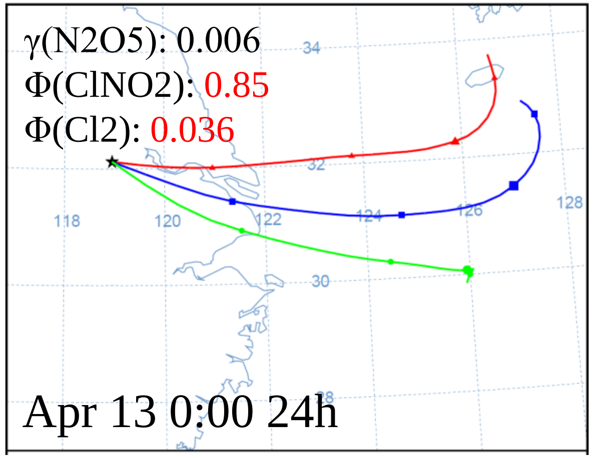


Investigate high $\varphi(Cl_2)$ plumes

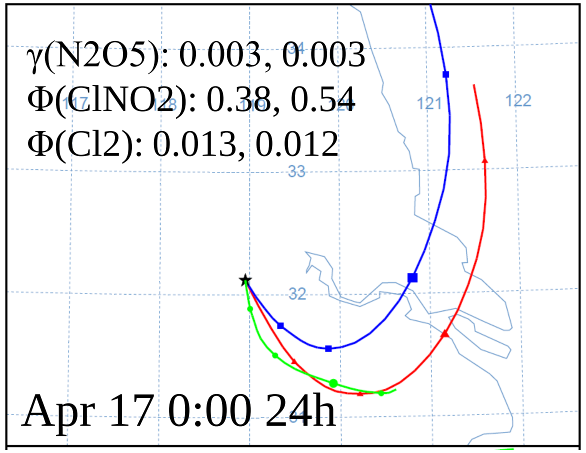
Max Cl_2: 103 ppt



Max Cl_2: 57 ppt



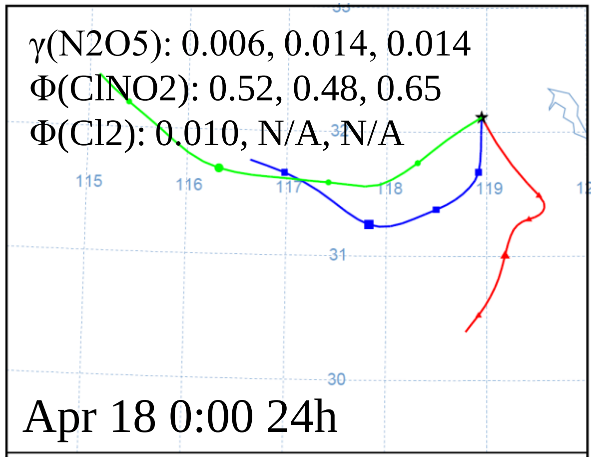
Max Cl_2: 60 ppt



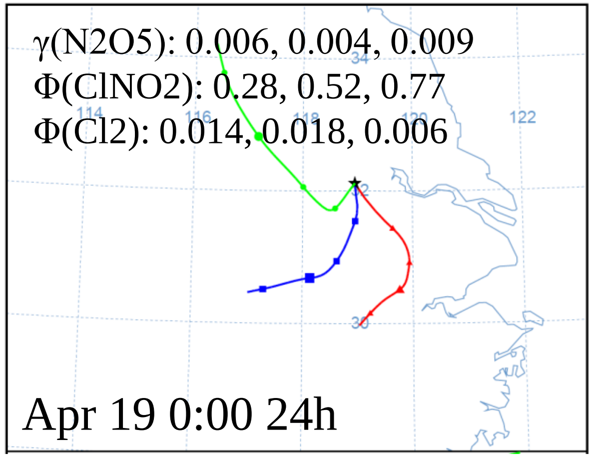
Marine air masses have higher $\varphi(Cl_2)$

Continental air masses

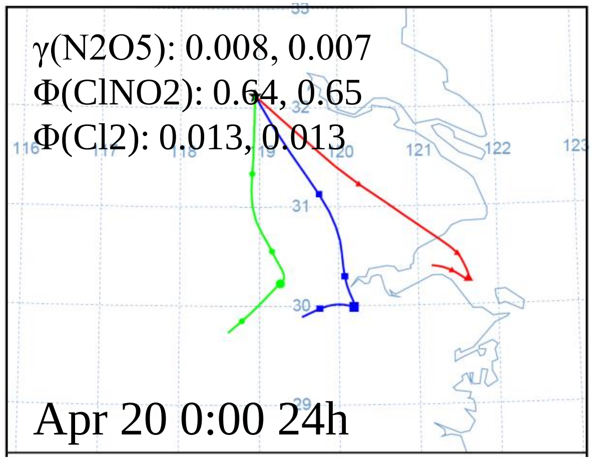
Max Cl_2: 64 ppt



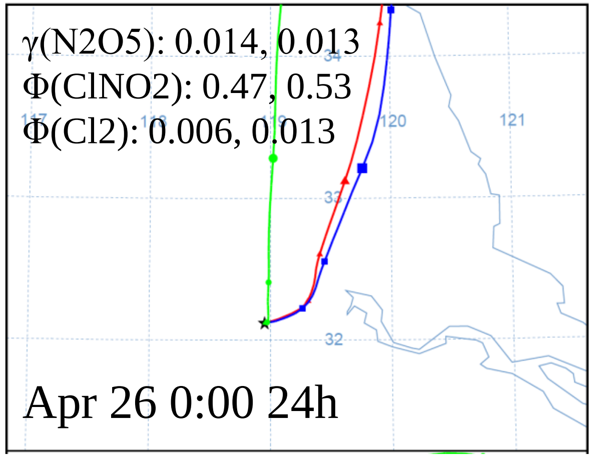
Max Cl_2: 64 ppt

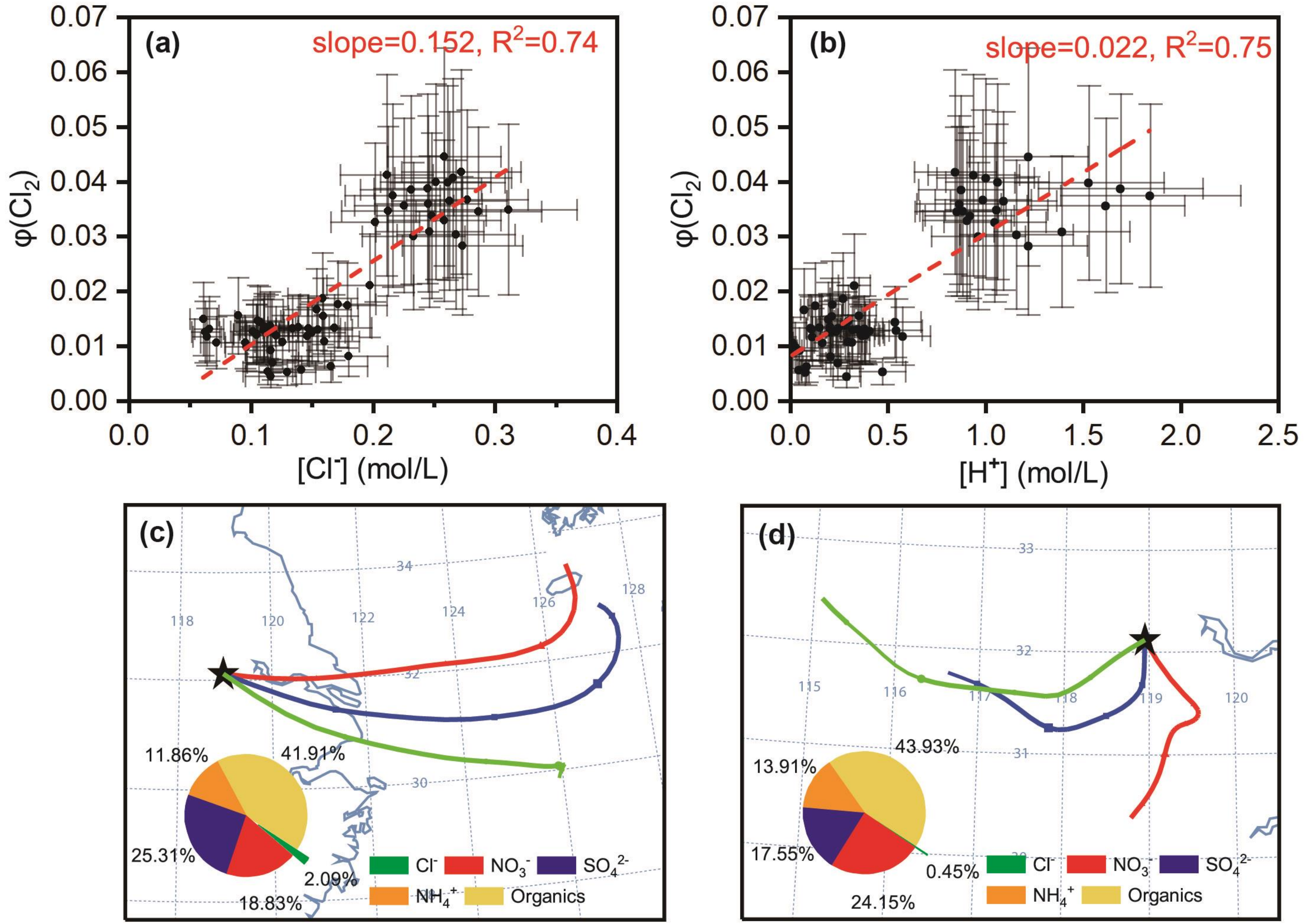


Max Cl_2: 82 ppt



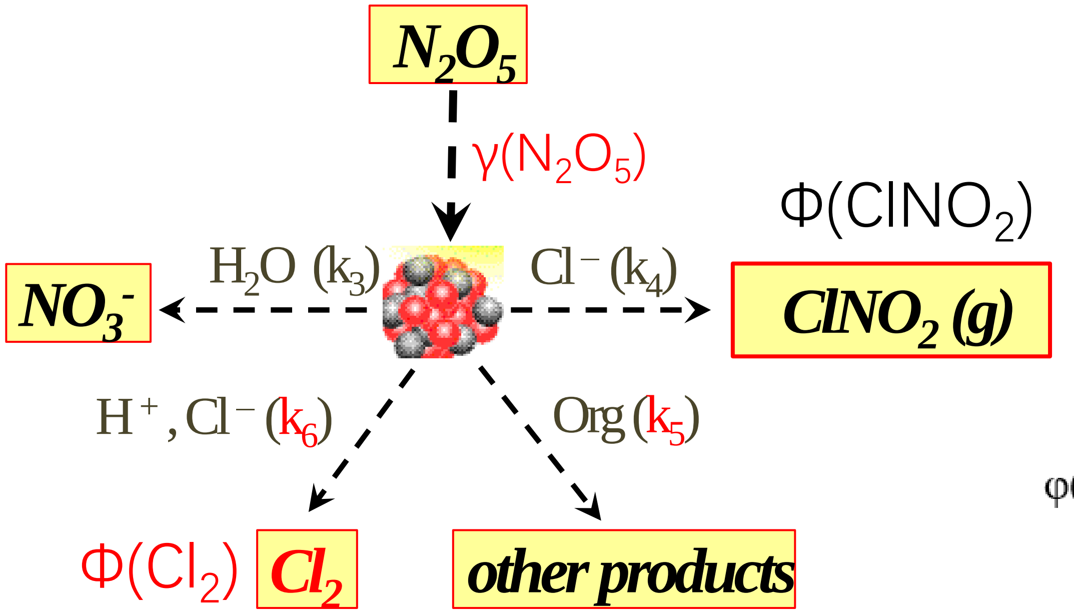
Max Cl_2: 107 ppt





(a)
slope=0.152, R2=0.74
φ(Cl2)
[Cl-] (mol/L)
(b)
slope=0.022, R2=0.75
φ(Cl2)
[H+] (mol/L)
(c)
11.86%
41.91%
25.31%
2.09%
18.83%
Cl-
NO3-
SO42-
NH4+
Organics
(d)
43.93%
13.91%
17.55%
0.45%
24.15%
Cl-
NO3-
SO42-
NH4+
Organics

Parameterization of Φ(Cl_2) --- step 1: determine the activity of Org (k_5/k_3)
--- step 2: derive k_6/k_3



$d[NO_3^-]/dt=k_3[NO_2^+][H_2O]$

$d[ClNO_2]/dt=k_4[NO_2^+][Cl^-]$

$d[Cl_2]/dt=k_6[NO_2^+][Cl^-][H^+]$

$d[Org]/dt=k_5[NO_2^+][Org]$

$$\varphi(Cl_2)=\frac{\frac{d[Cl_2]}{dt}}{\frac{d[Cl_2]}{dt}+\frac{d[ClNO_2]}{dt}+\frac{d[NO_3^-]}{dt}+\frac{d[Org]}{dt}}=\frac{k_6[Cl^-][H^+]}{k_6[Cl^-][H^+]+k_4[Cl^-]+k_3[H_2O]+k_5[Org]}$$

From φ($ClNO_2$) study, we have

$$\varphi(ClNO_2)_{BT+Org}=\left(1+\frac{[H_2O]}{483[Cl^-]}+\frac{[Org]}{235[Cl^-]}\right)^{-1}$$

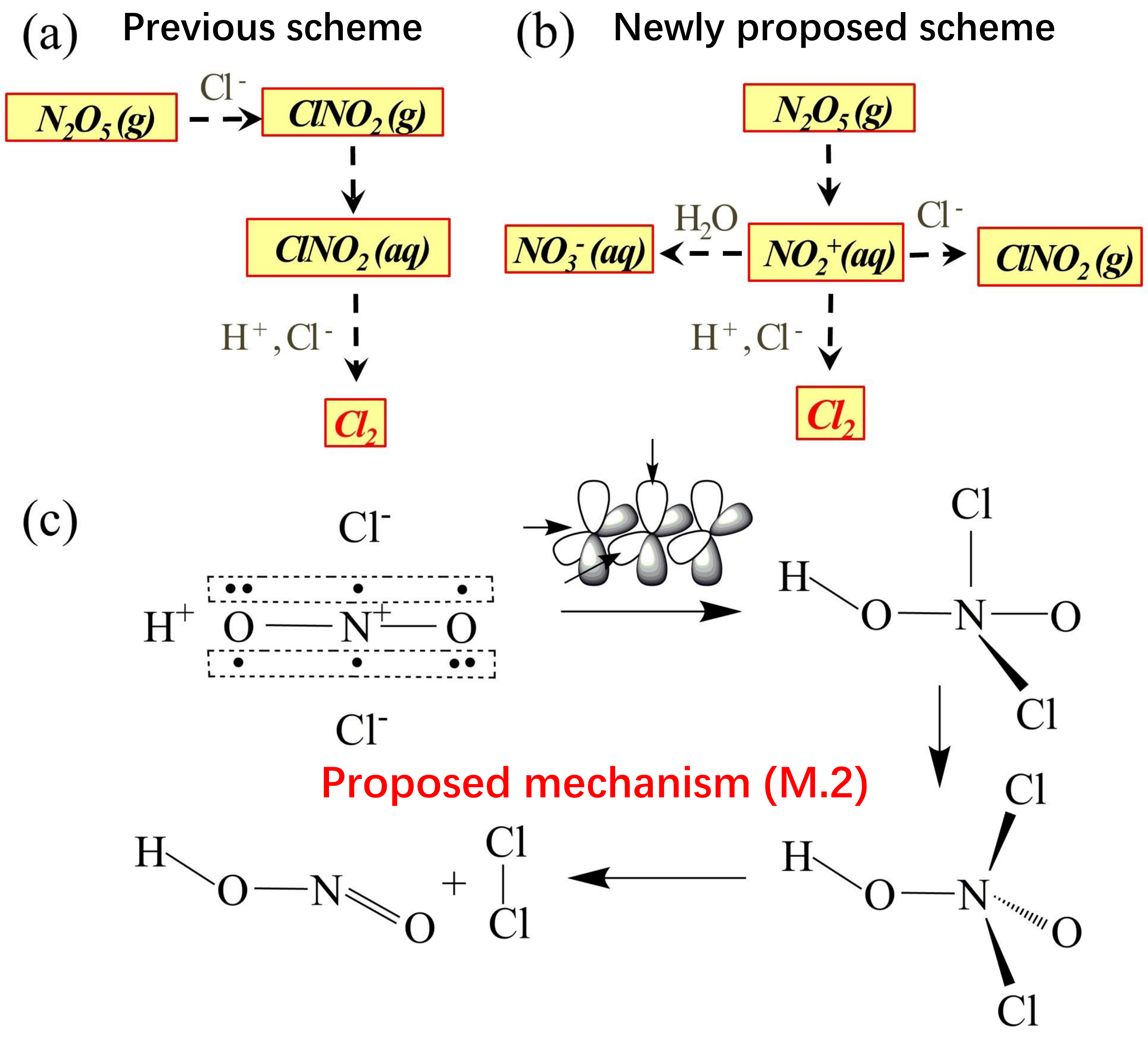
$k_5/k_3=2.05$

$k_4/k_3=483$ (Bertram and Thornton, 2009)

Non-linear regression, adjust k_6/k_3 to match para. Φ(Cl_2) and obs. Φ(Cl_2)

$$\varphi(Cl_2)=\frac{19.38[H^+][Cl^-]}{19.38[H^+][Cl^-]+483[Cl^-]+[H_2O]+2.05[Org]}$$

Schematic diagram and proposed mechanism



Revised Cl_2 formation mechanism:

Initial NO_2^+ production from N_2O_5:

$N_2O_5 + H_2O = NO_2^+(H_2O) + NO_3^-$

$NO_2^+(H_2O) + Cl^- = ClNO_2 + H_2O$

NO_2^+ regeneration from aqueous $ClNO_2$ hydrolysis

$ClNO_2 + H_2O = NO_2^+(H_2O) + Cl^-$

Cl_2 production from NO_2^+

M.1) $NO_2^+ + H_2O + Cl^- = HOCl + NO_2^- + H^+$

$HOCl + Cl^- + H^+ = Cl_2 + H_2O$

M.2) $NO_2^+ + 2Cl^- + H^+ = Cl_2 + HONO$

Future work is needed to verify our proposed mechanism.

Summary and Conclusions:

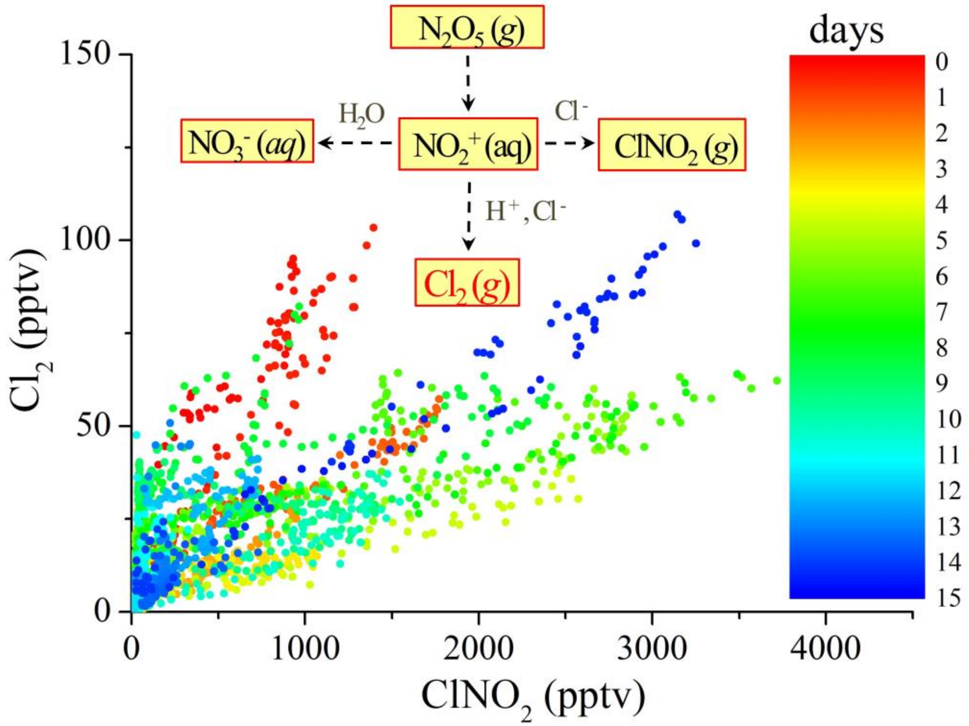
1. Elevated levels of $ClNO_2$ (3 ppb) and Cl_2 (100 ppt) at a rural site in Nanjing.

2. ClNO2 yield para. revised by including organics.

3. $ClNO_2$ and Cl_2 were closely correlated and exhibited clear diurnal patterns.

4. $ClNO_2$ uptake alone cannot explain the Cl_2 formation

5. A new parameterization of Cl_2 yield ($\varphi(Cl_2)$) from N_2O_5 uptake, applicable in models.



This work has been submitted to and just accepted by *Atmospheric Chemistry and Physics* (acp-2019-1130).

Final thinking and outlook:

1. Kinetic parameters (such as $\varphi(ClNO_2)$ and $\varphi(Cl_2)$) are intrinsically linked to each other. The investigation of $\varphi(ClNO_2)$ here is a prerequisite of parameterizing $\varphi(Cl_2)$.

$$\varphi(ClNO_2)_{BT+Org} = \left(1 + \frac{[H_2O]}{483[Cl^-]} + \frac{[Org]}{235[Cl^-]}\right)^{-1}$$

Constraining reaction rate of [Org] →

$$\varphi(Cl_2) = \frac{19.38[H^+][Cl^-]}{19.38[H^+][Cl^-] + 483[Cl^-] + [H_2O] + 2.05[Org]}$$

2. Exact Cl_2 formation mechanism from N_2O_5 uptake is not clear, which may be a direction of future research.

Cl_2 production from NO_2^+

M.1) $NO_2^+ + H_2O + Cl^- = HOCl + NO_2^- + H^+$

$HOCl + Cl^- + H^+ = Cl_2 + H_2O$

M.2) $NO_2^+ + 2Cl^- + H^+ = Cl_2 + HONO$

3. Loss pathway of Cl_2 remains unexplored.

Acknowledgement

This study was supported by the National Natural Science Foundation of China (NSFC) project (grant number: 91544213 and D0512/41675145), and the Hong Kong Research Grants Council (T24-504/17-N)


View of Mt Tai
Bring back the blue sky!
Thank you!