Exploring halogen species in power plant plumes

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WINTER Flight + Science Teams

WINTER Science Meeting
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Why *do* we care about HCl?

Source: Coal combustion, waste incineration, sea spray, biomass burning

Lifetime: Several hours to few day (deposition)

Troposphere implication: acidity, ecosystems & particles

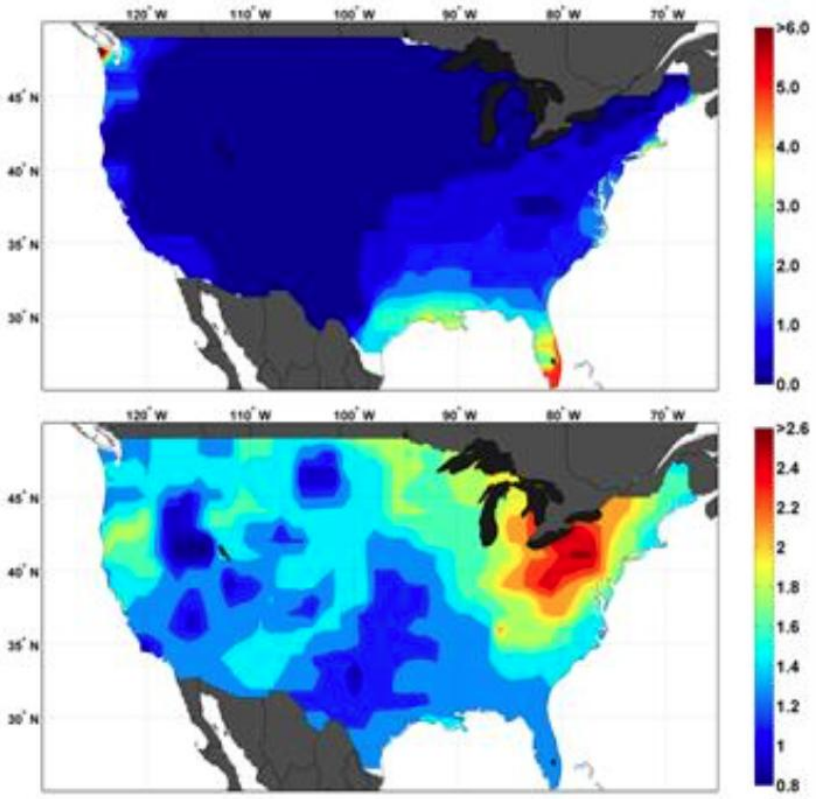
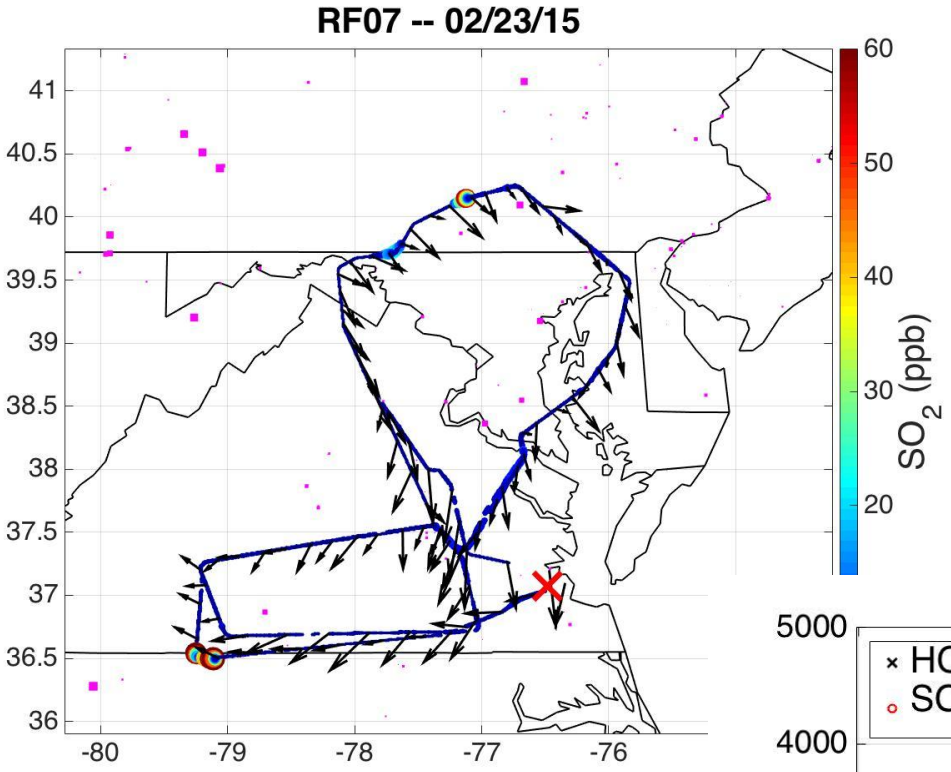


Figure 9. *Annual mean (1996–2010) wet deposition of chloride (mg/yr, top) and the mole ratio of chloride to sodium (bottom) measured in precipitation by the National Atmospheric Deposition Program (NADP); ratios >1.2 are higher than that in seawater.*

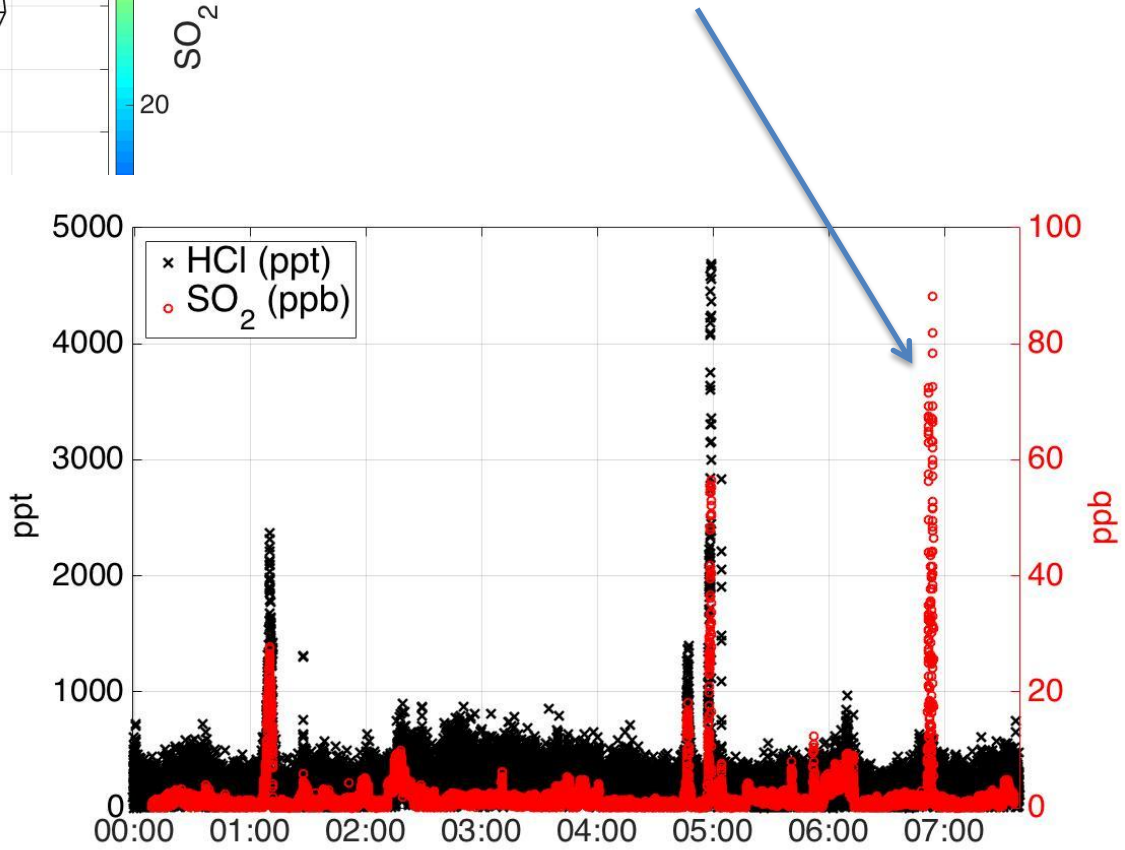
Picture: *J. Thornton*

WINTER White Paper

Research Flight 7



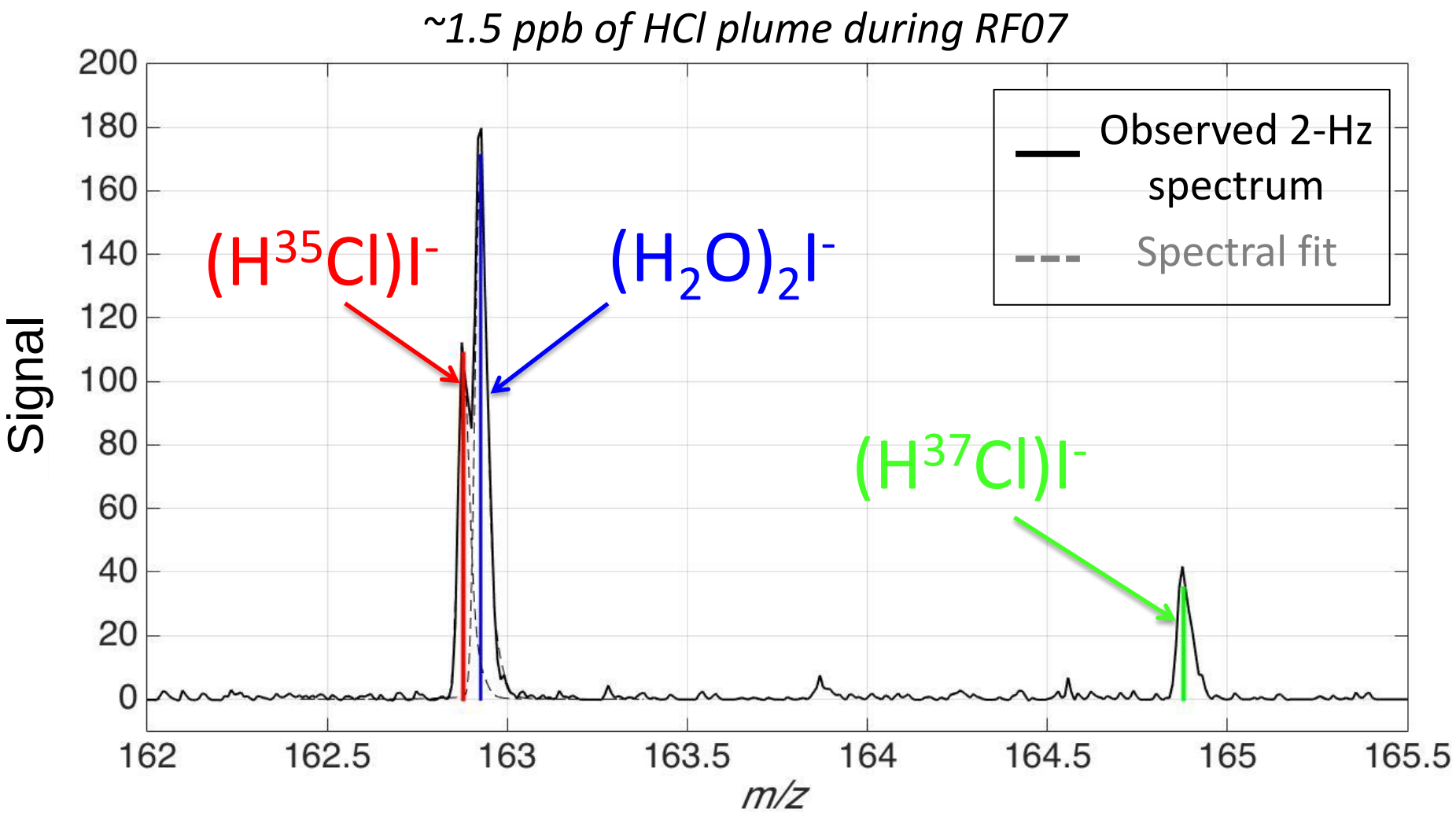
Not all plumes containing elevated SO_2 exhibit enhanced HCl



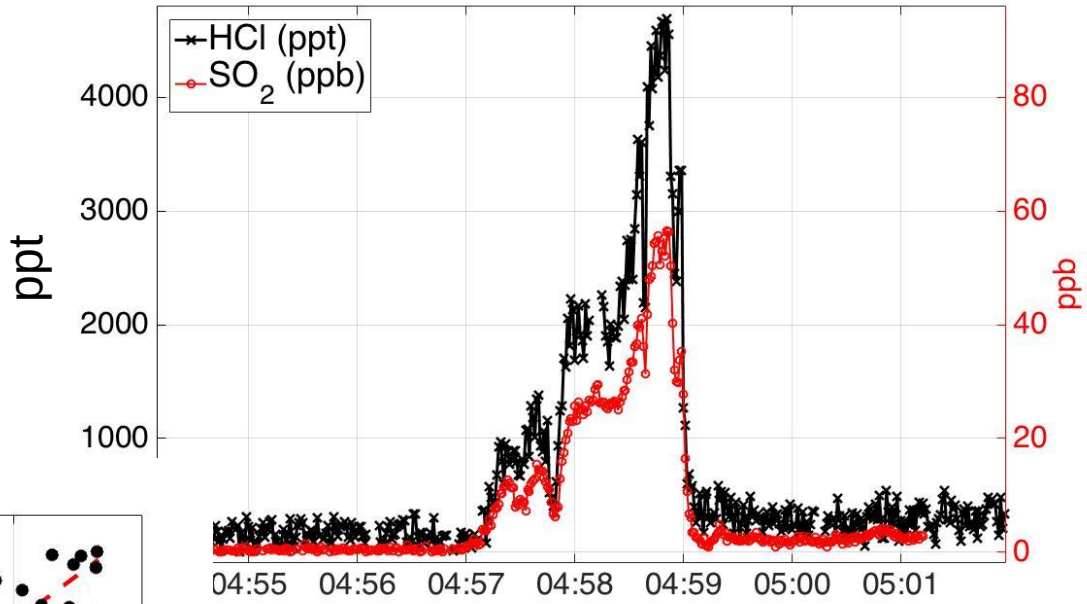
SO_2: *J. Green, M. Fiddler, J. Holloway (NOAA CSD)*

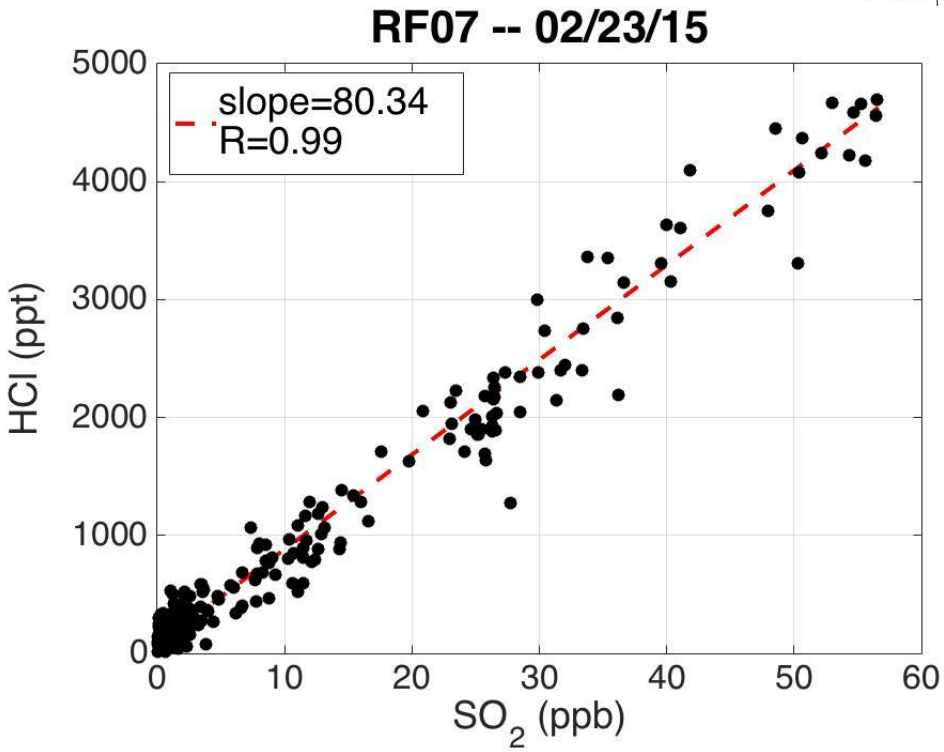
HCl detection

Iodide HRToF-CIMS LOD (1-sec 3-σ) of **$H^{35}Cl$: 750 ppt**



HCl versus SO_2





WINTER versus NEI (2011) inventory: **HCl**

WINTER

Mean +/- Std of 3 plumes intercepted during RF07

(HCl mol / SO_2 mol) 0.065 ± 0.011

NEI 2011

Coal combustion: commercial/institutional

0.043

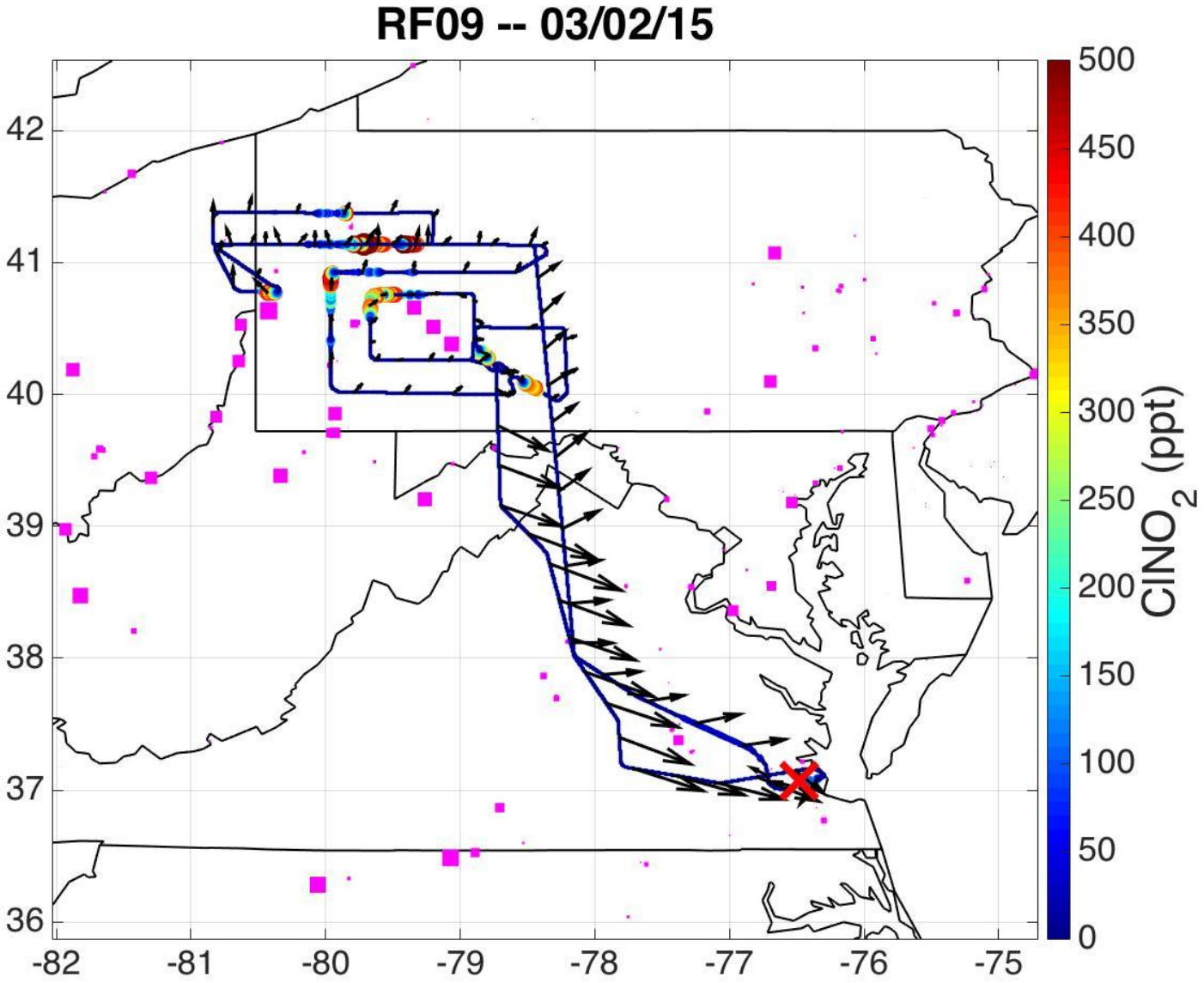
Coal combustion: electricity production

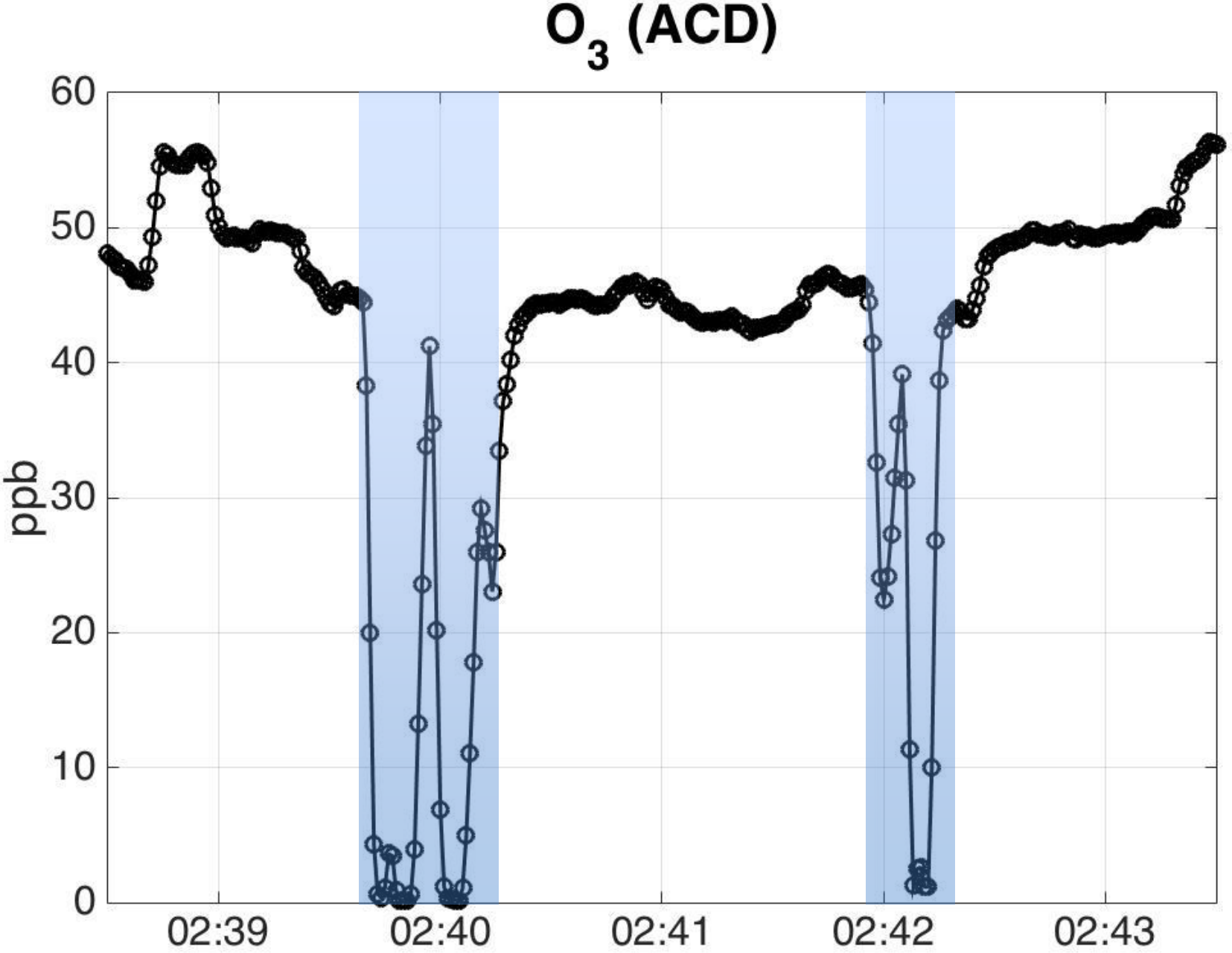
0.026

Coal combustion: industrial boilers

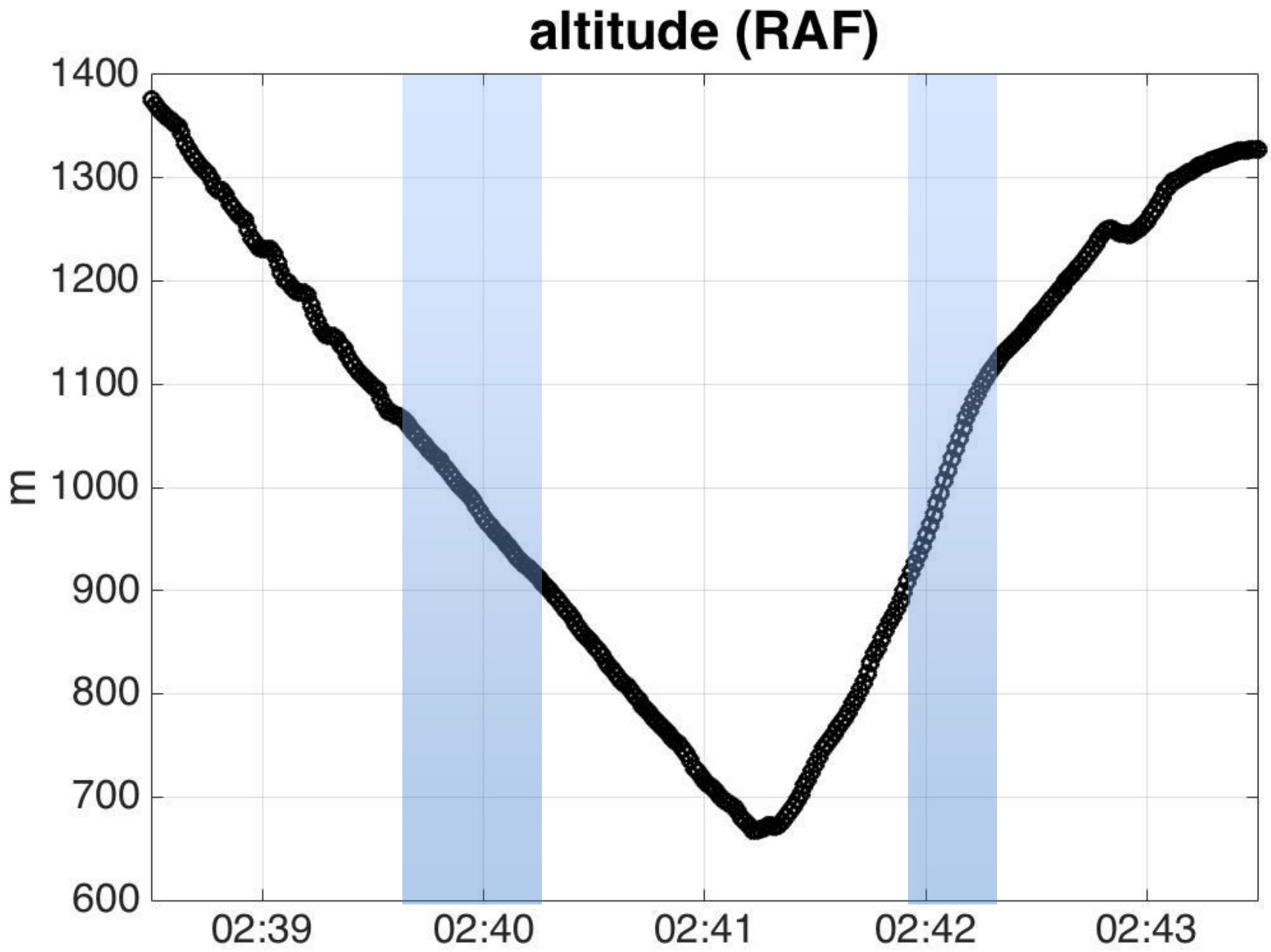
0.046

Halogens *et al.* in/around PP plumes

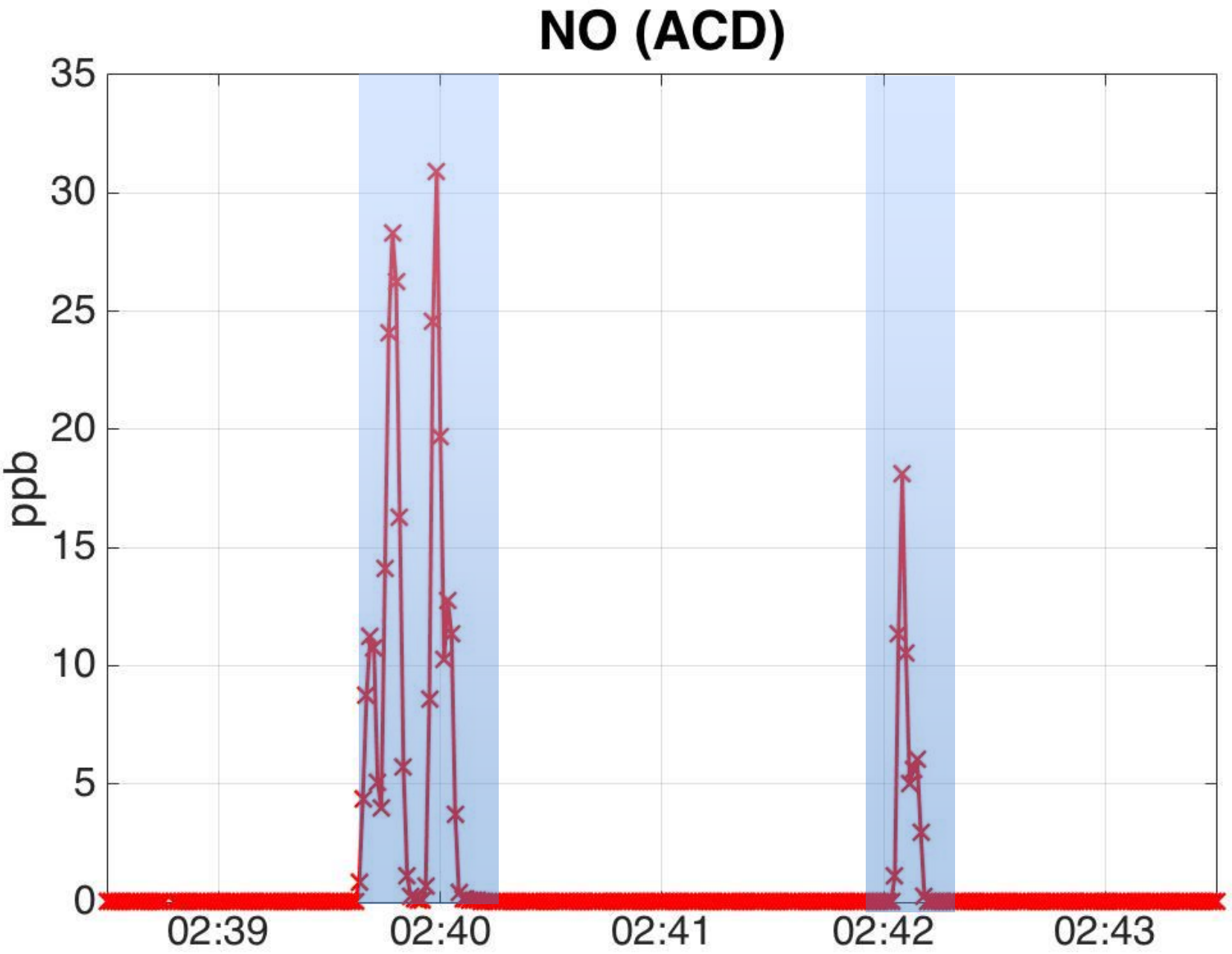




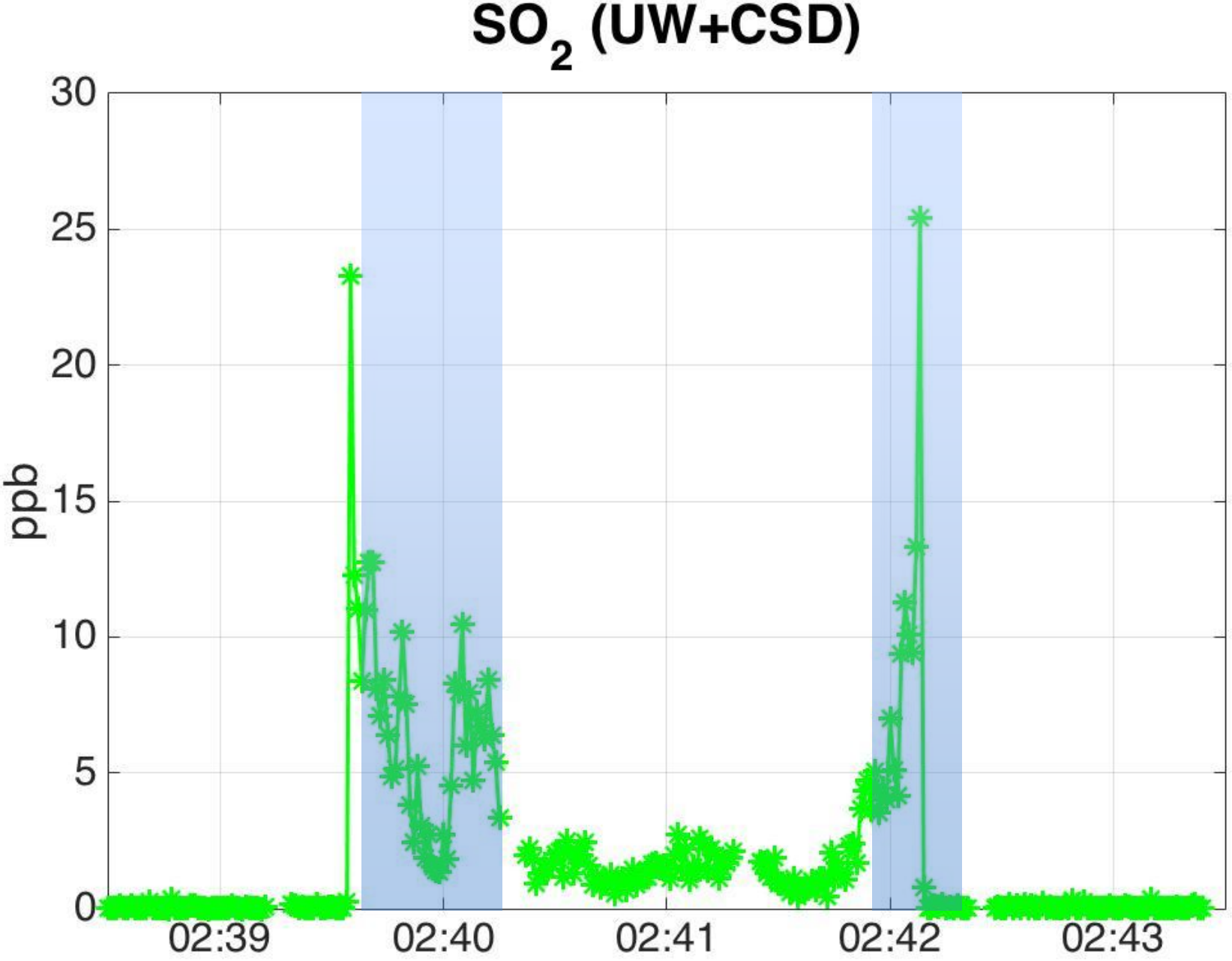
O_3 titrated in these plumes



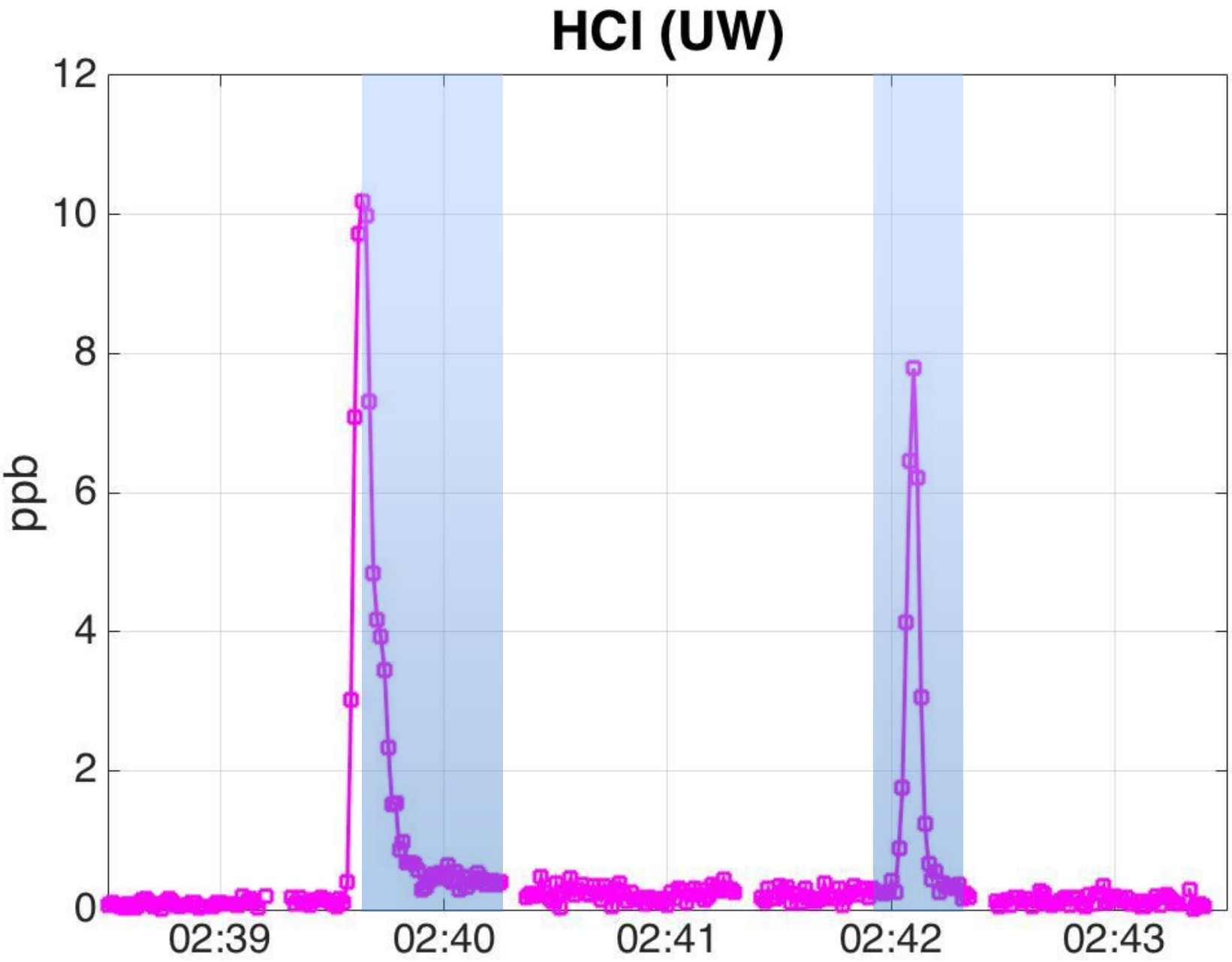
Dipped low (~700 m pressure alt.) then back up



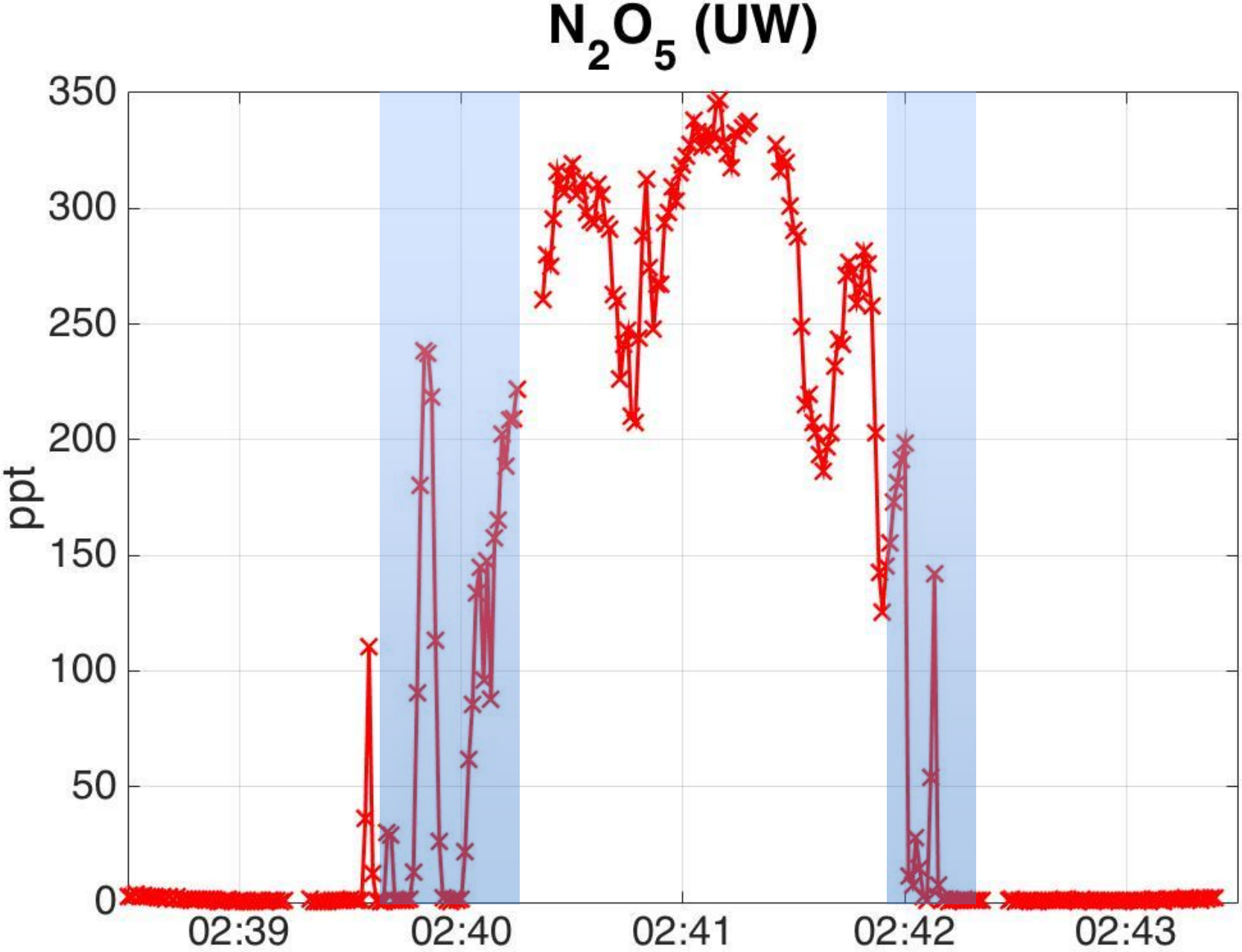
NO still present



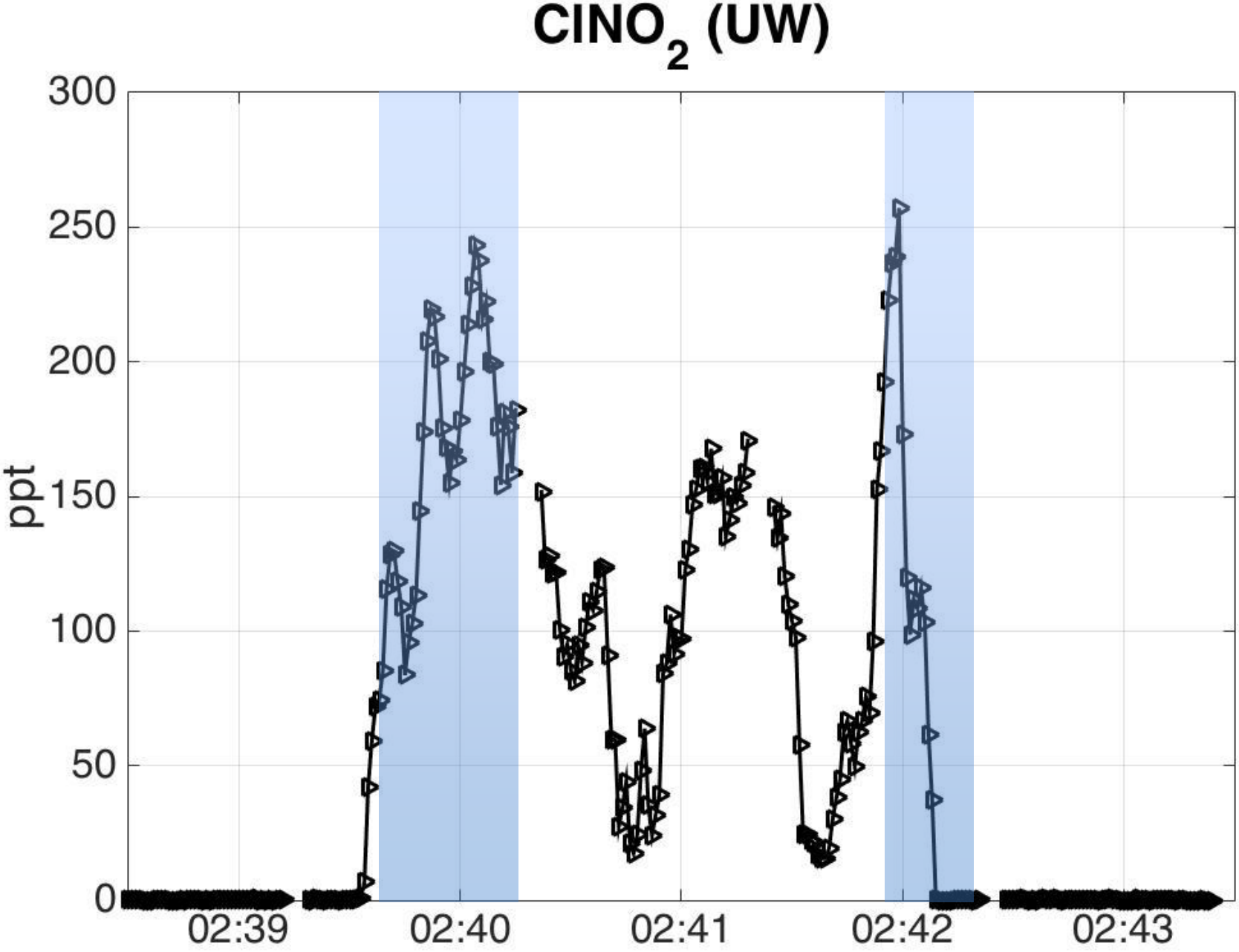
Power plant plumes intercepted



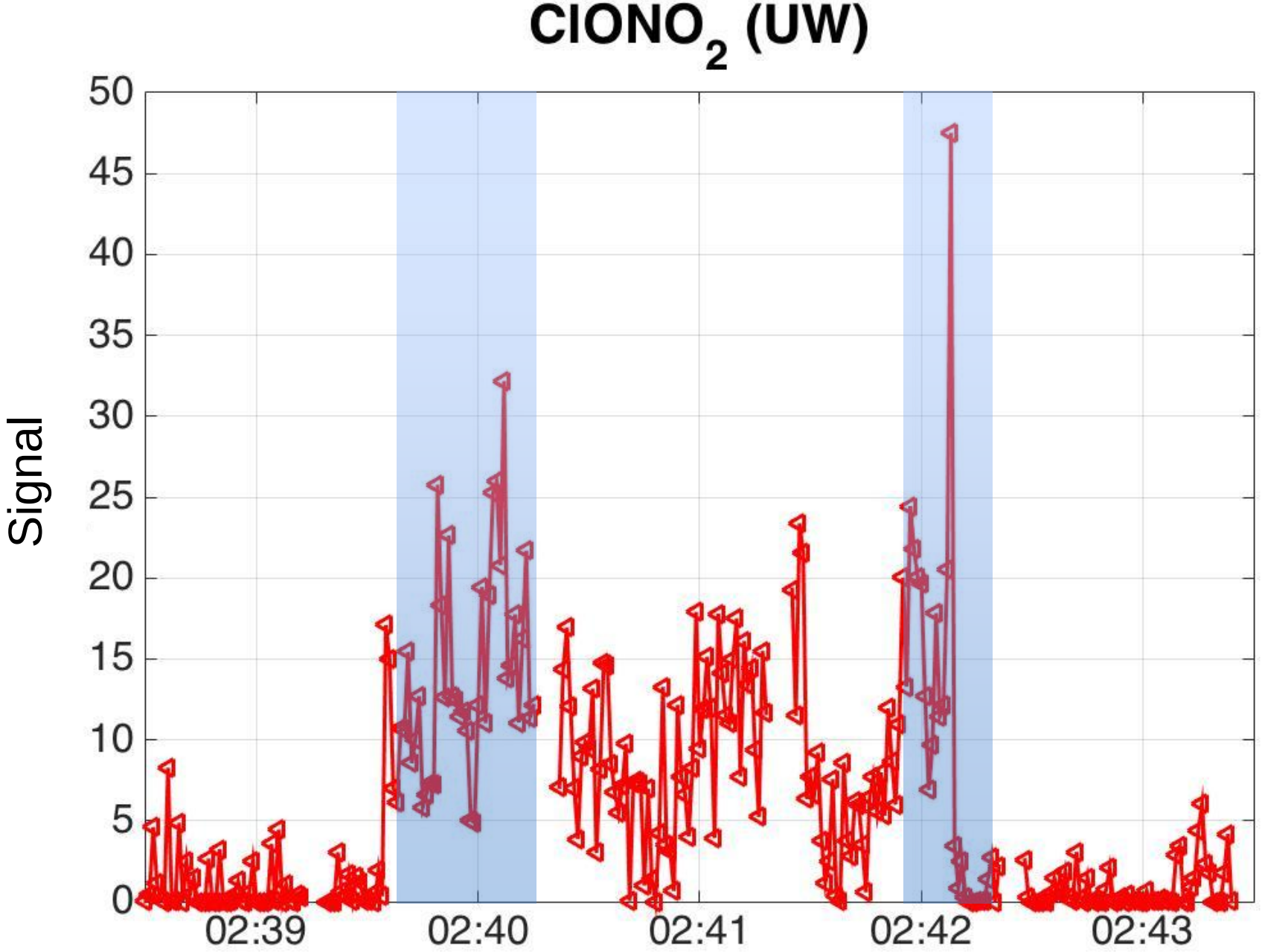
HCl enhanced in PP plumes



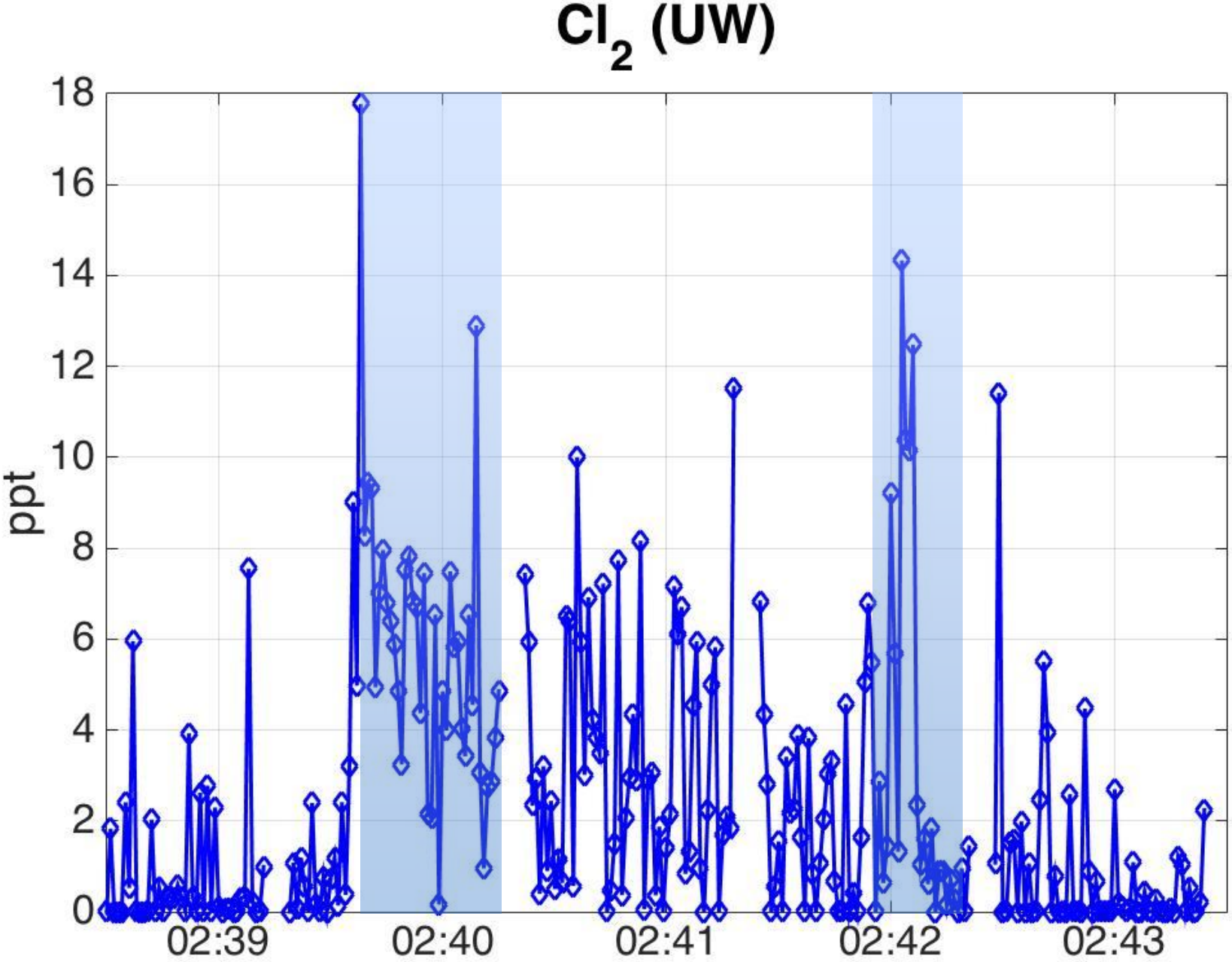
N_2O_5 nearly devoid in these PP plumes



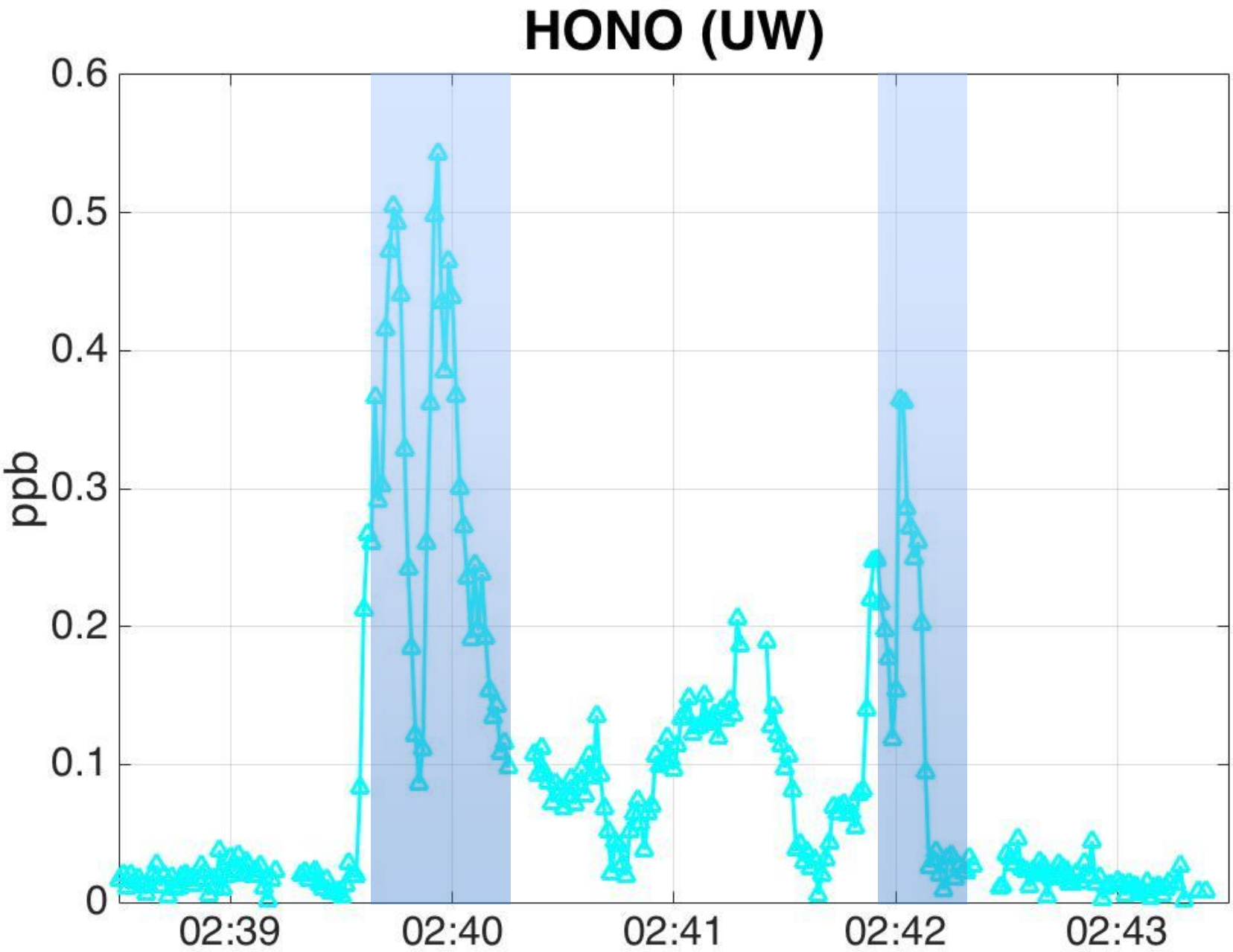
$ClNO_2$ elevated even with N_2O_5 near zero in these PP plumes



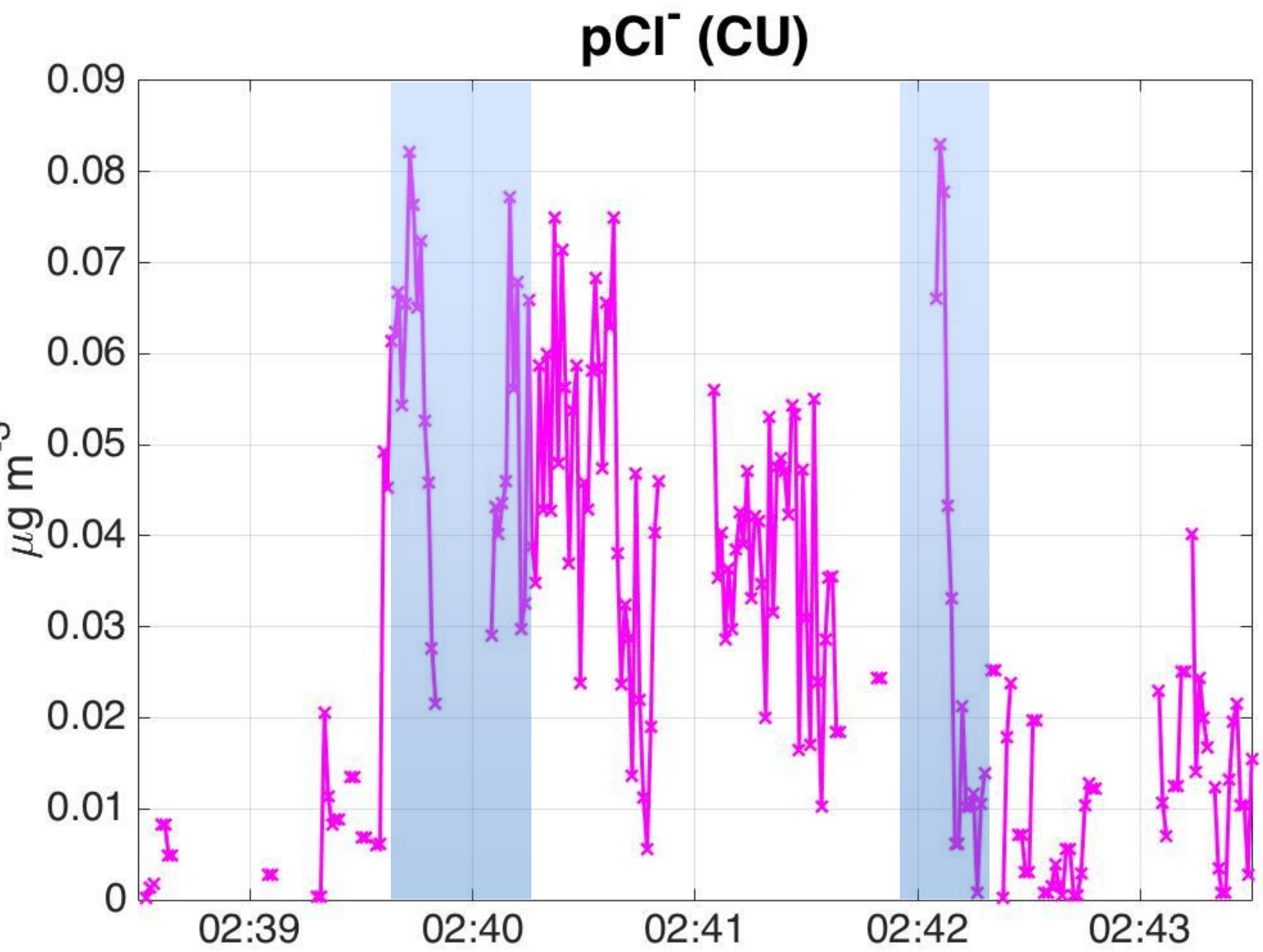
Similarly with $ClONO_2$



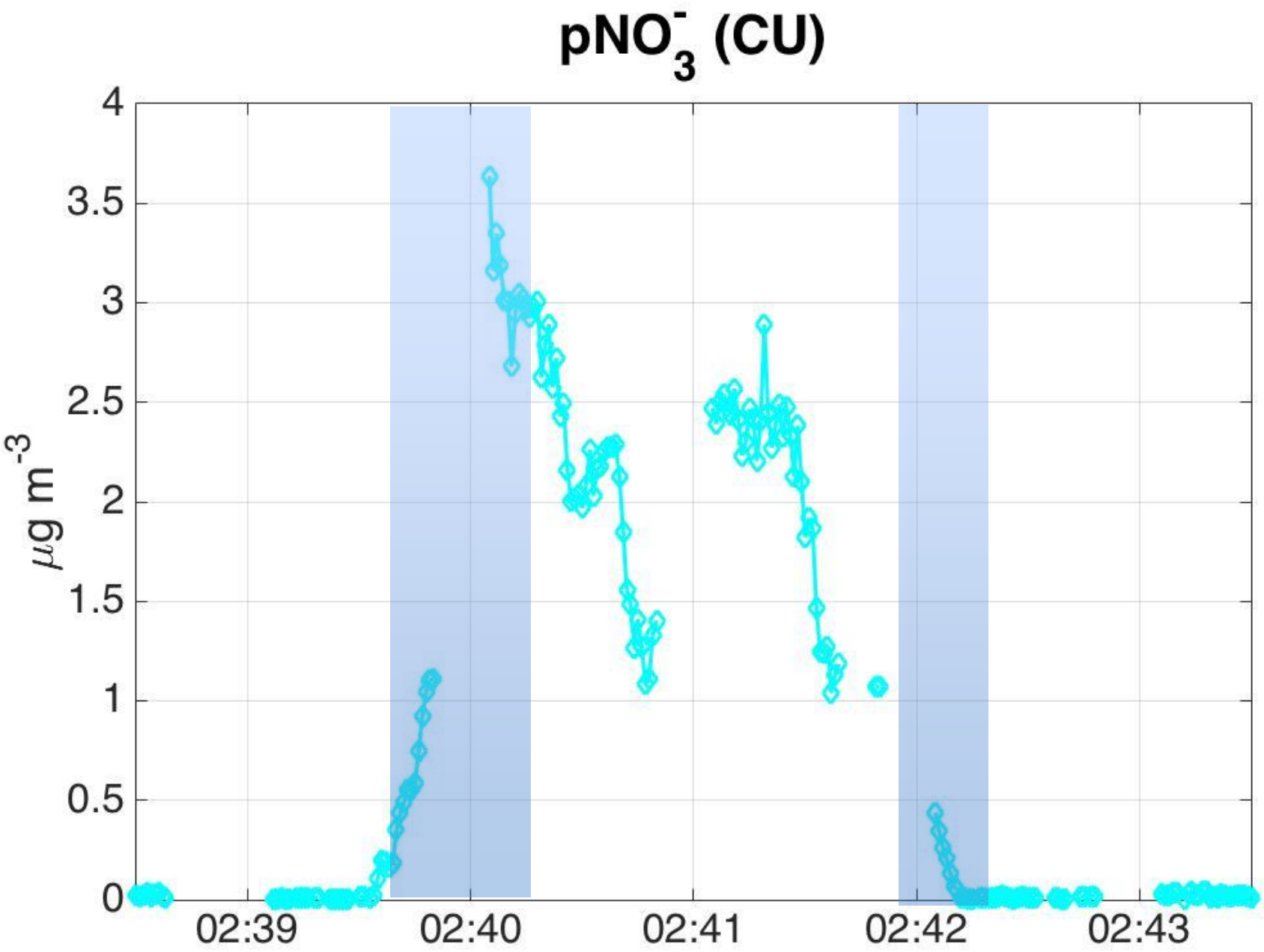
Similarly with Cl_2…?



Well correlated with $ClNO_2$, produced from OH + NO (+M) gas-phase reaction, so is $ClNO_2$ produced *via* radical chemistry?



Particles elevated, cannot rule out heterogeneous chemistry



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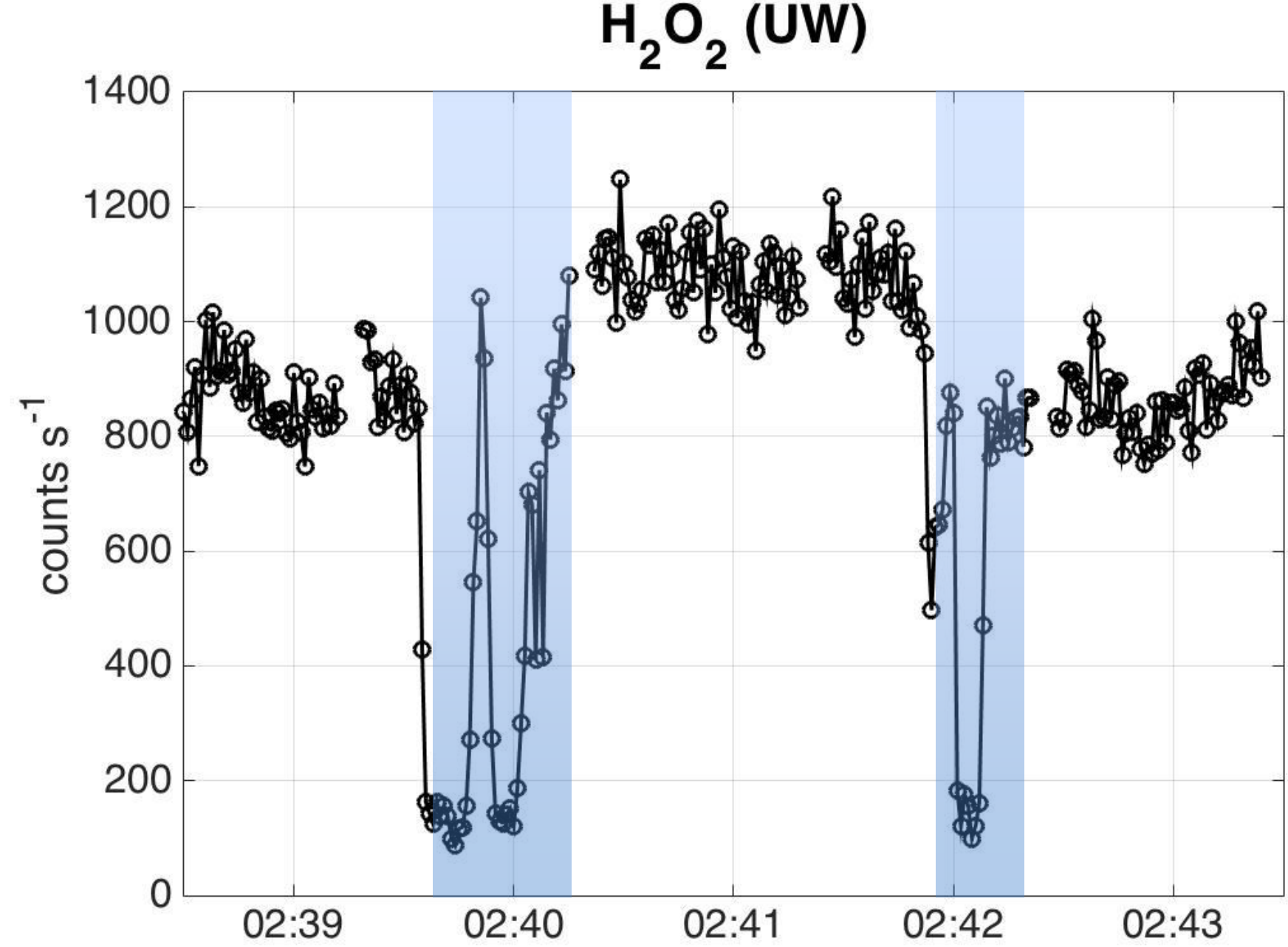
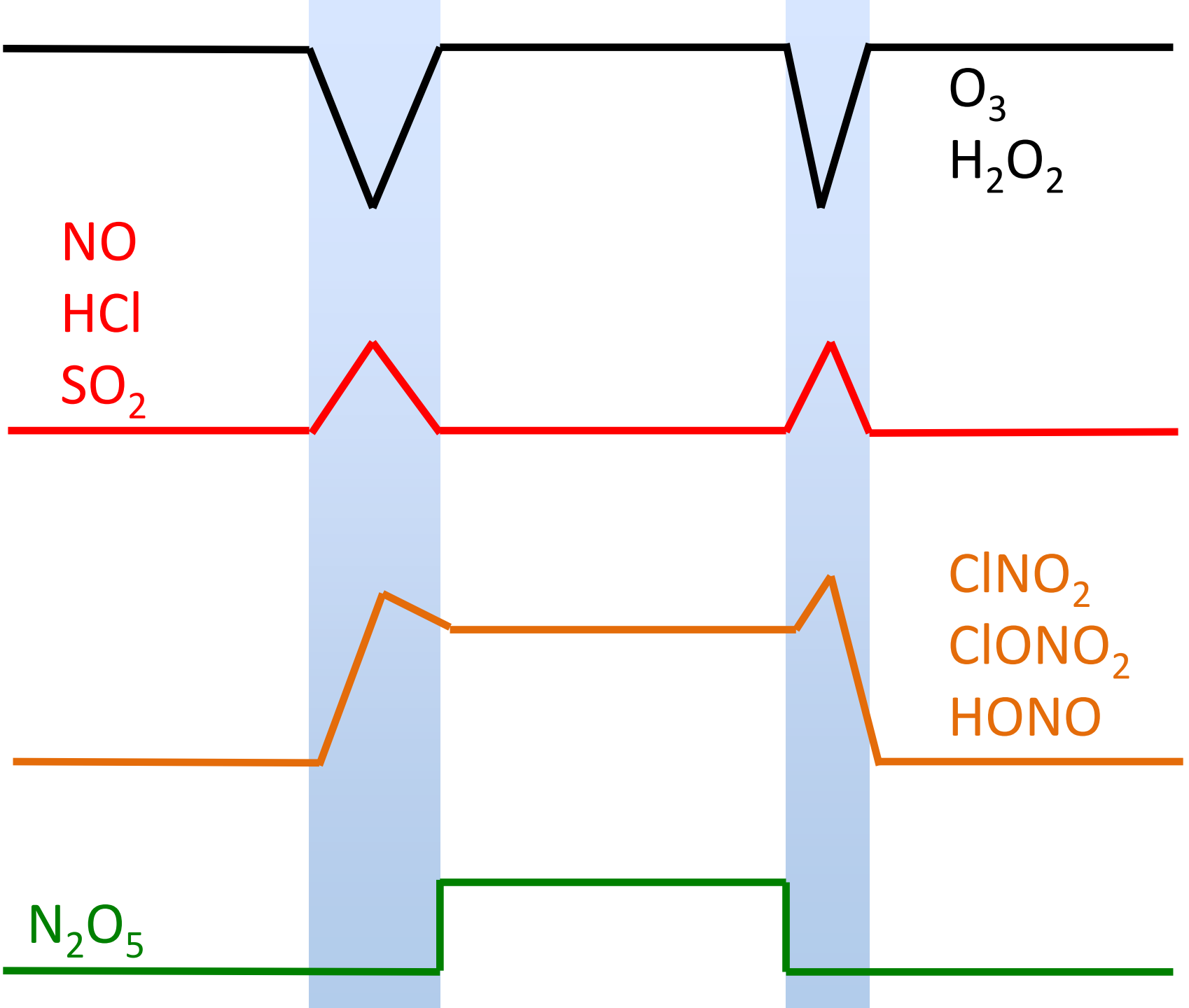


H_2O_2 depleted in PP plumes, possibly Cl or OH oxidation


O_3
H_2O_2
NO
HCl
SO_2
$ClNO_2$
$ClONO_2$
HONO
N_2O_5

"Direct emission" of $ClNO_x$?

$$NO + OH + M \rightarrow HONO$$

$$HCl + OH \rightarrow Cl$$

$$Cl + NO_2 \rightarrow ClNO_2$$

$$Cl + O_3 \rightarrow ClO$$

$$ClO + NO_2 \rightarrow ClONO_2$$

Next steps

- Assign intercepted plumes to specific power plant (or regional emission ratio average) to compare observations to inventory
- Need to decipher PP chemistry/dynamics ($ClNO_2$, $ClONO_2$, HONO, *etc.*)
- Model plume chemistry (OH, HO_2, Cl, ClO …) to reproduce observations
- What is total Cl emission from PP? What form?

FOURIER TRANSFORM IR SPECTROSCOPIC OBSERVATION OF CHLORINE NITRITE, ClONO, FORMED VIA Cl + NO_2 (+M) → ClONO(+M)

H. NIKI, P.D. MAKER, C.M. SAVAGE and L.P. BREITENBACH
Research Staff, Ford Motor Company, Dearborn, Michigan 48121, USA

Received 12 June 1978

Using the FTIR method, chlorine nitrite (ClONO) and nitryl chloride ($ClNO_2$) were identified as reaction products in the photolysis of Cl_2–NO_2 mixtures. The observed yields of ClONO (> 80%) and $ClNO_2$ (< 20%) suggest that Cl atom adds mainly to the O atom rather than the N atom of NO_2 molecule.

$$Cl + NO_2 \xrightarrow{M} \begin{cases} ClNO_2, & \Delta H \approx -30 \text{ kcal mole}^{-1}; \text{ (1)} \\ ClONO, & \Delta H \approx -20 \text{ kcal mole}^{-1}. \text{ (2)} \end{cases}$$

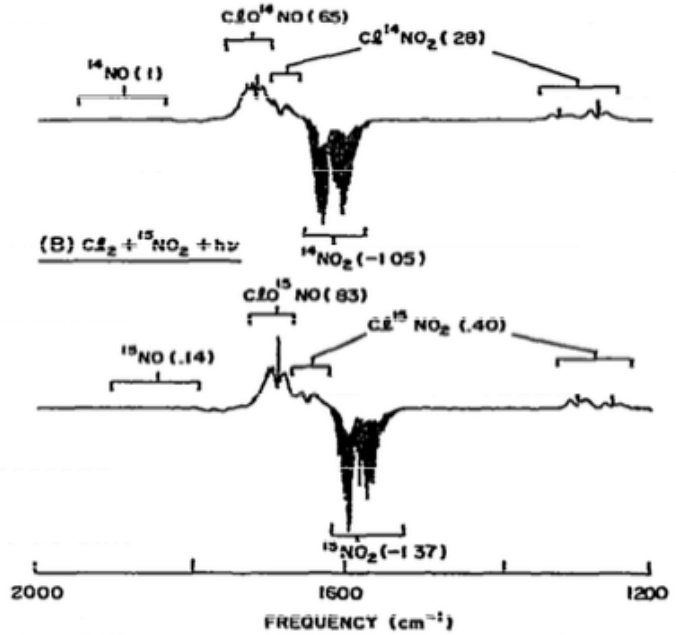
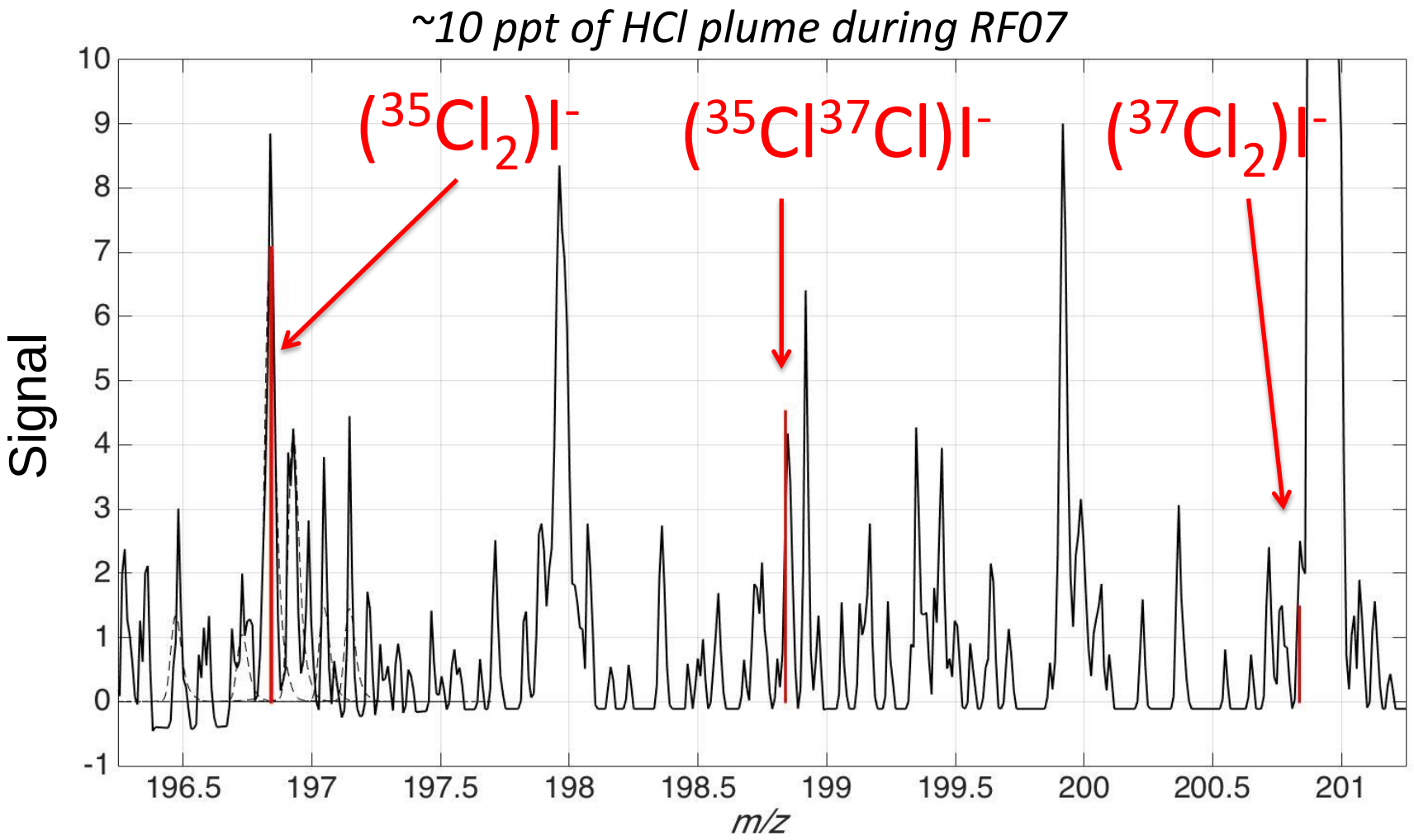


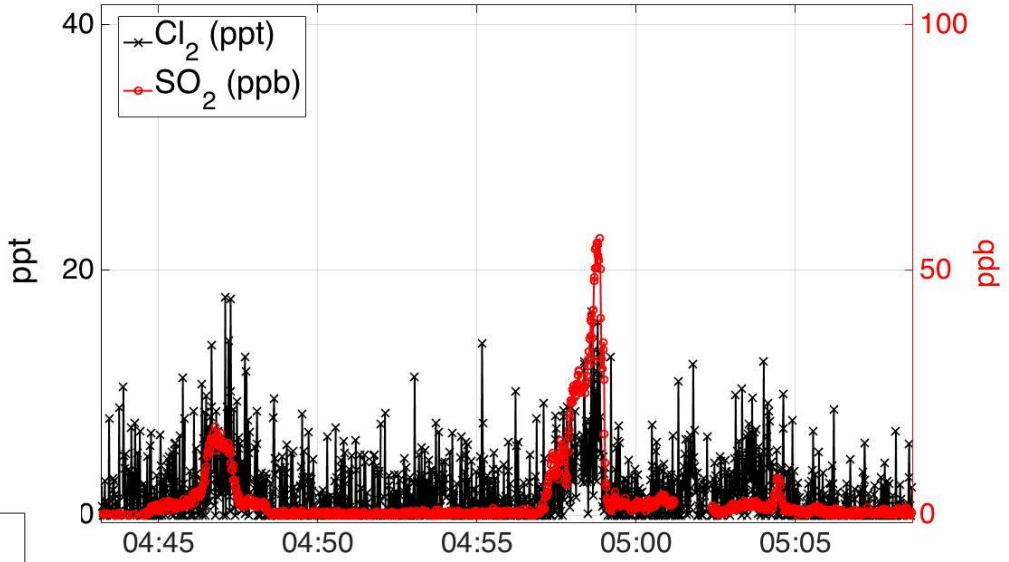
Fig. 1. Difference spectra in the frequency range of 1200–2000 cm^{-1} in the photolysis of (A): Cl_2(33 mtorr)–$^{14}NO_2$(5.7 mtorr) in 700 torr air, and (B): Cl_2 (38 mtorr)–$^{15}NO_2$(5.3 mtorr) in 700 torr air. The spectra were recorded during 0–80 s irradiation.

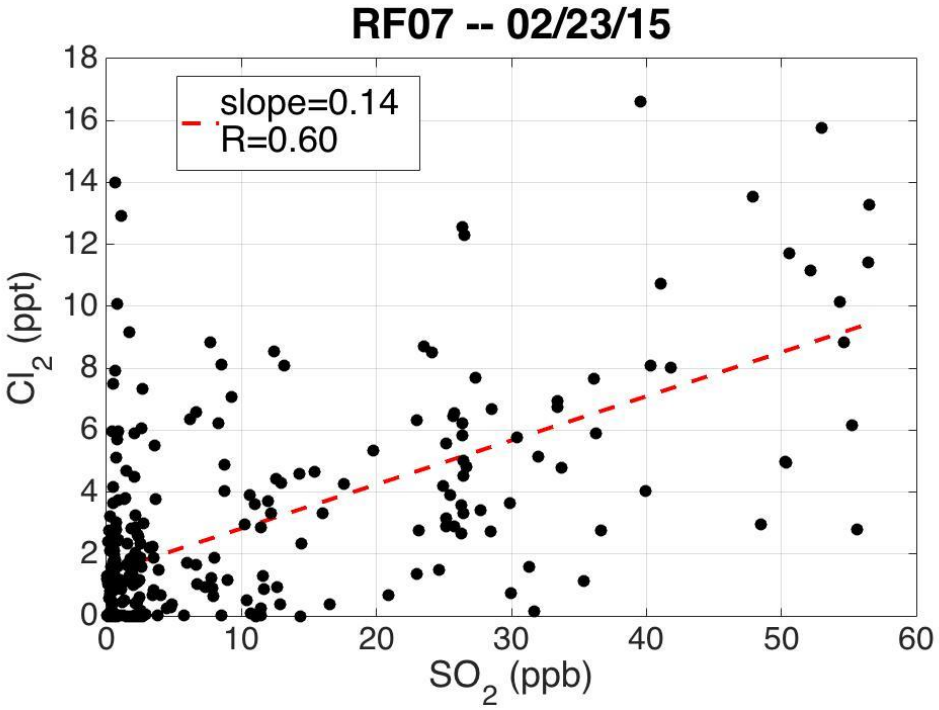
Cl_2 detection

Iodide HRToF-CIMS sensitivity (1-sec 3-σ) of **Cl_2: 30 ppt**



Cl_2 versus SO_2





WINTER versus NEI (2011) inventory: Cl_2

WINTER

Mean +/- Std of 3 plumes intercepted during RF07

$(1.59 \pm 0.20) \times 10^{-4}$

NEI 2011

Coal combustion: commercial/institutional

3.72×10^{-5}

Coal combustion: electricity production

1.45×10^{-5}

Coal combustion: industrial boilers

7.49×10^{-5}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