Influences of Halogen Chemistry on Processing of North American Pollutant Outflow

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Goals

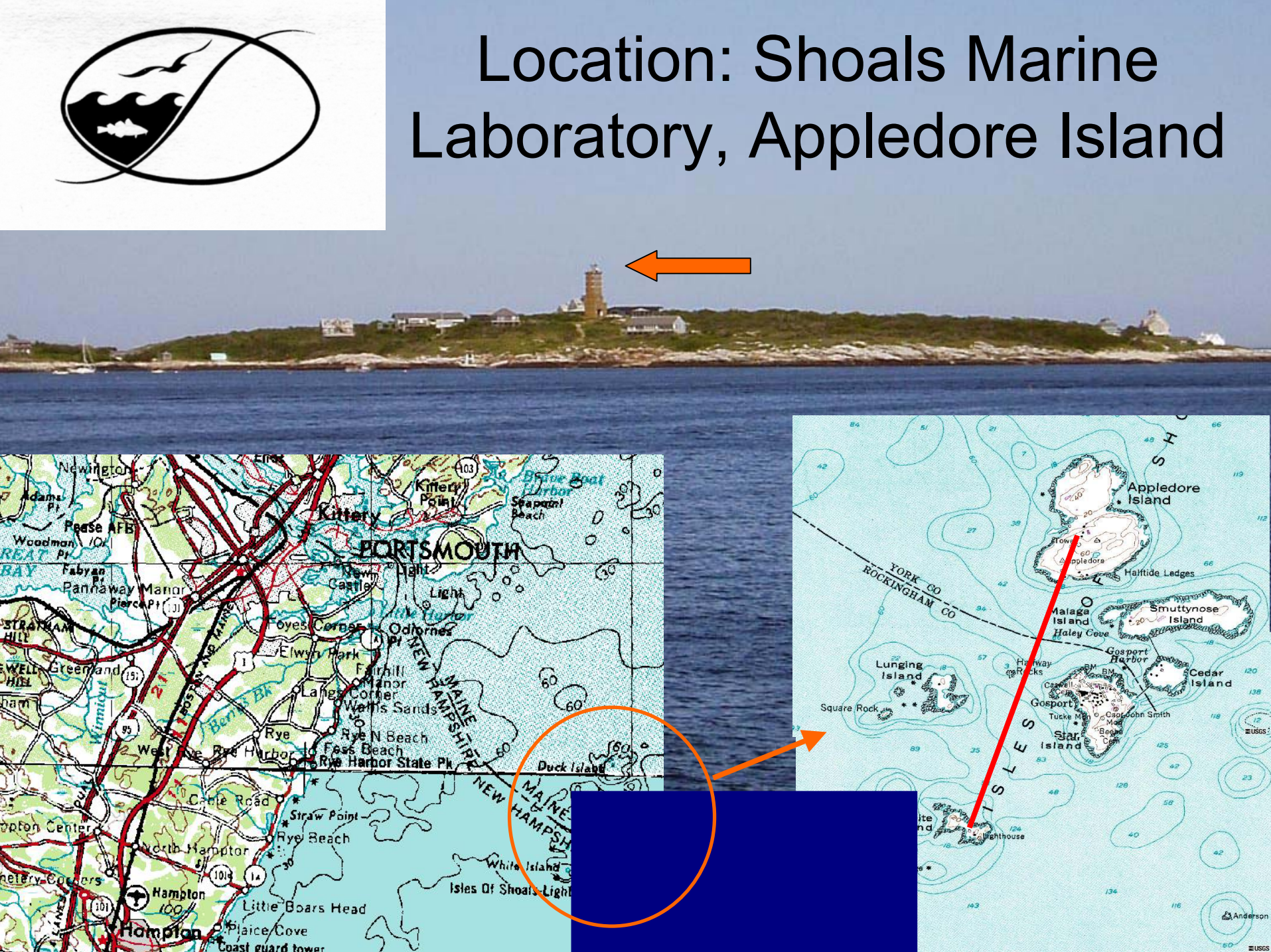
- *To quantify the influences of halogen radicals on ozone production/destruction in polluted air along the New England east coast during summer.*

- *To investigate the influence of nocturnal radical chemistry, i.e. NO_3 and N_2O_5, on halogen levels.*

- *To investigate the role of halogens in the production and chemical evolution of aerosols over the Gulf of Maine.*

- *To assess potential implications of the outflow on the chemistry in the MBL over the Gulf of Maine.*

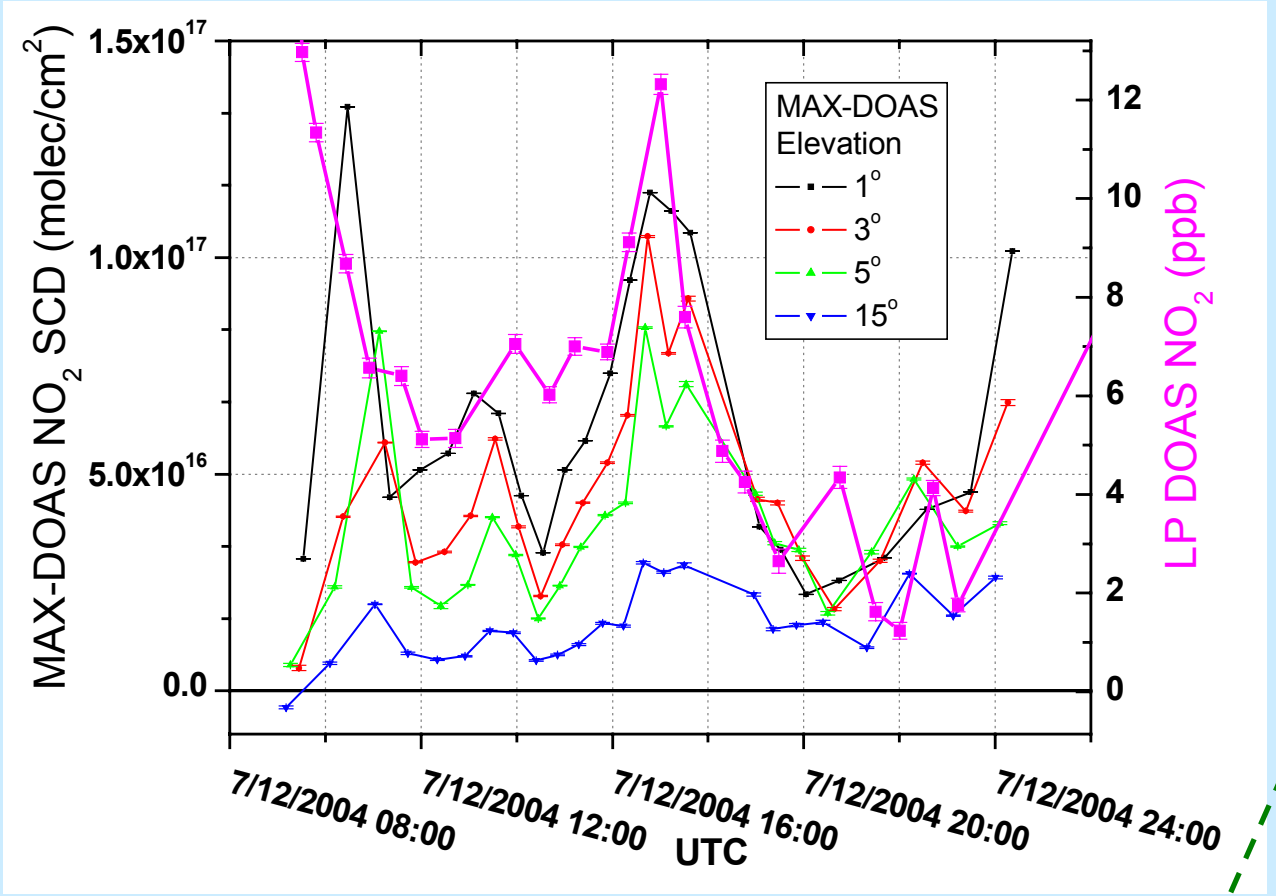
Location: Shoals Marine Laboratory, Appledore Island

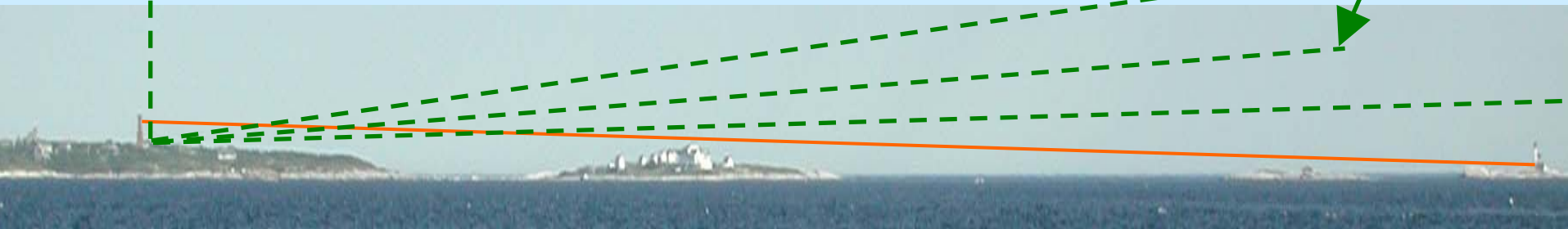


Instrument Overview

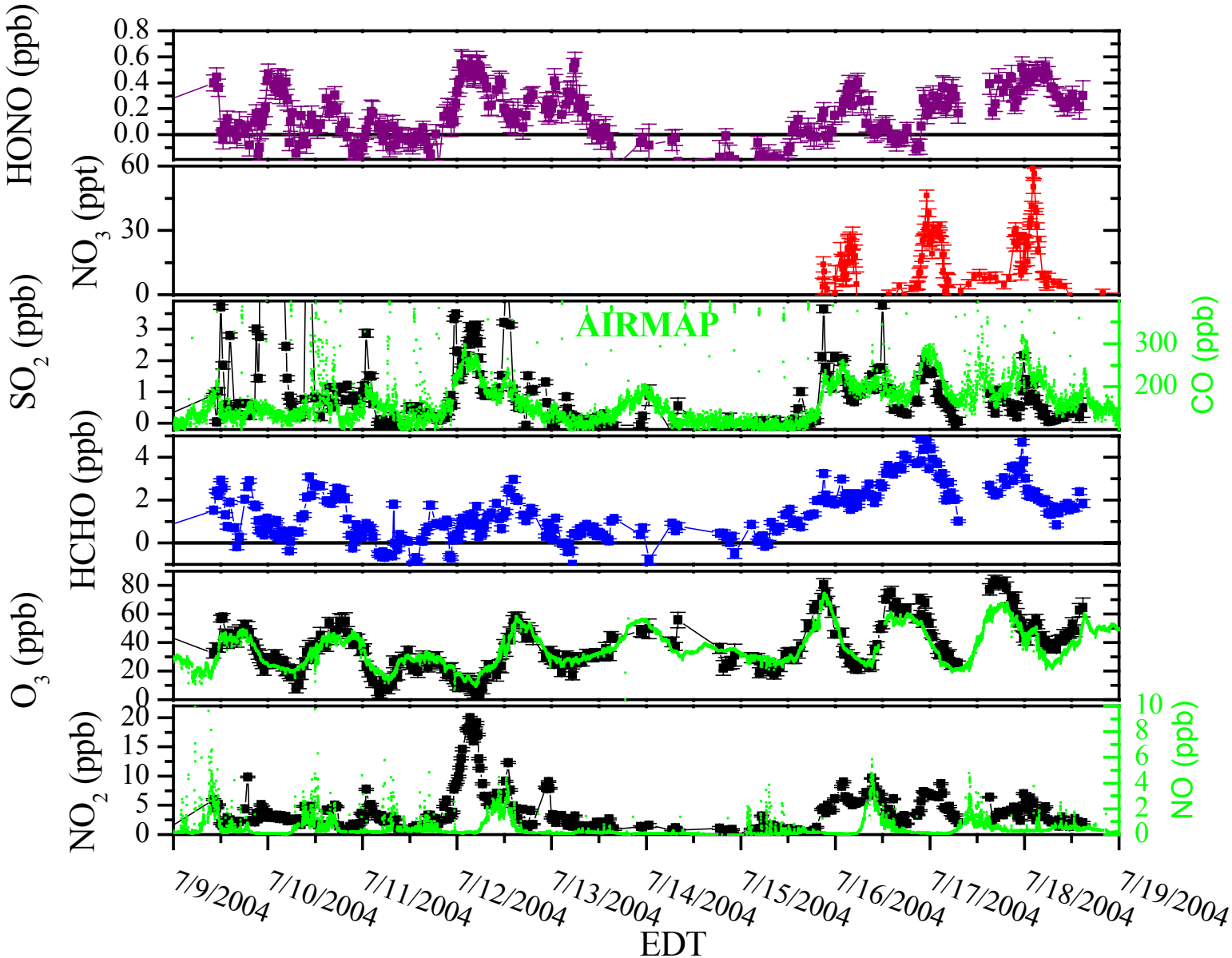
- **O_3, CO, NO, VOC** (PTRMS), **CO_2, CH_4** through AIRMAP
- LP- and MAX-DOAS: **O_3, NO_2, SO_2, HCHO, NO_3, BrO, IO, OIO, I_2**
- Inorganic gaseous chlorine: **HCl* (primarily HCl) and Cl* (including Cl_2 + HOCl),** by tandem mist chambers
- soluble trace gases (**HNO_3, NH_3, SO_2, HCl, HCOOH, and CH_3COOH**) by second tandem mist chamber system
- Total **gaseous inorganic Br and I** by daytime/nighttime filter packs
- **C_2-C_{10} hydrocarbons, C_1-C_5 alkylnitrates, halocarbons**
- Organic and inorganic ionic constituents (**NO_3^-, SO_4^{2-}, $CH_3SO_3^-$, Cl^-, Br^-, $HCOO^-$, CH_3COO^-, $C_2O_42^-$, Na^+, K^+, Mg^{2+}, and Ca^{2+}**) and **total Na, Cl, Br, and I** in daytime/nighttime size segregated aerosol samples
- **Particle number-size distributions (6 to 800 nm)** at 40% RH by multistaged particle sizing spectrometer and DMA
- **Photolysis rates** by spectroradiometer

Multi Axis DOAS

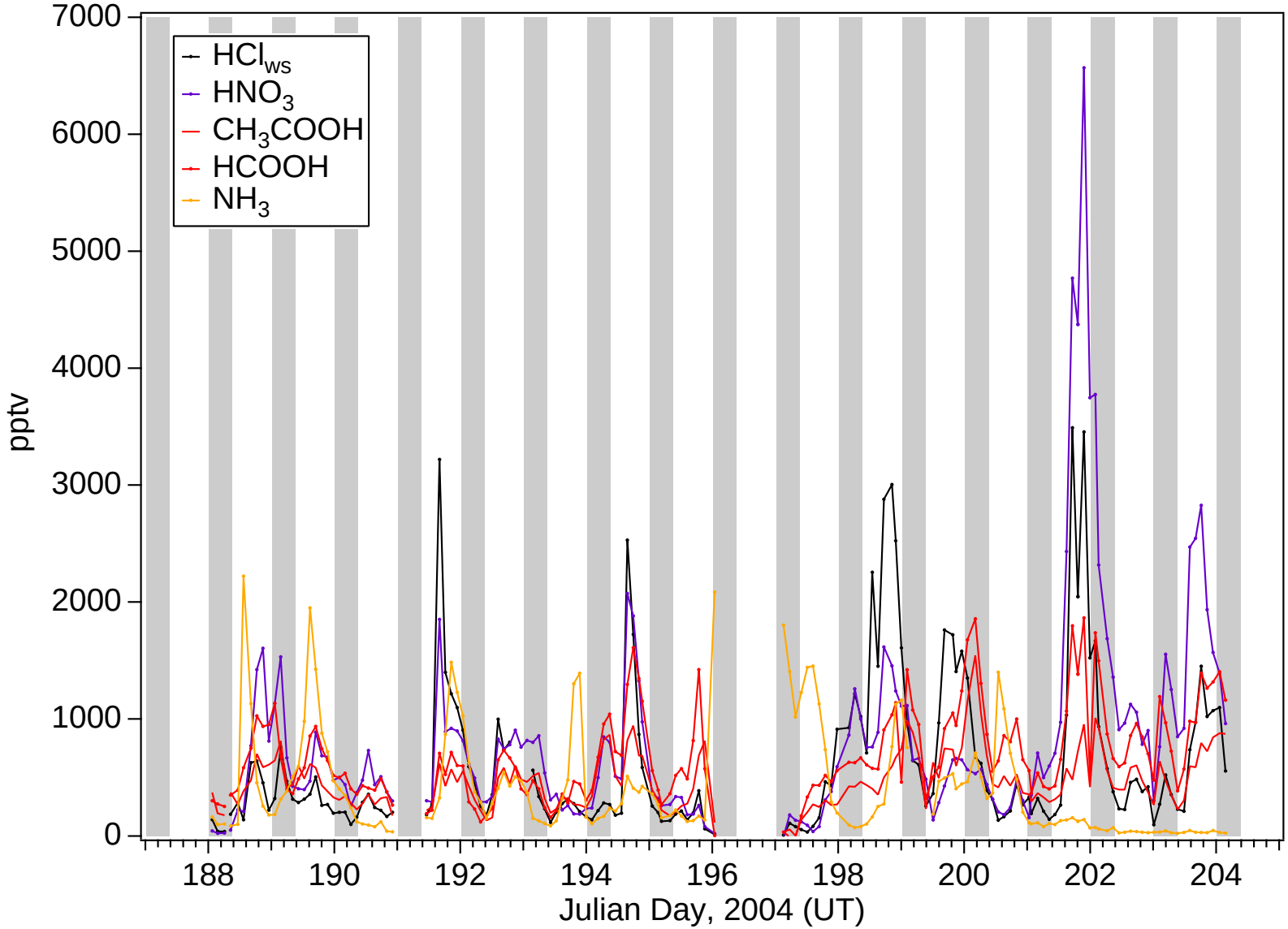




LP-DOAS / AIRMAP Data Overview

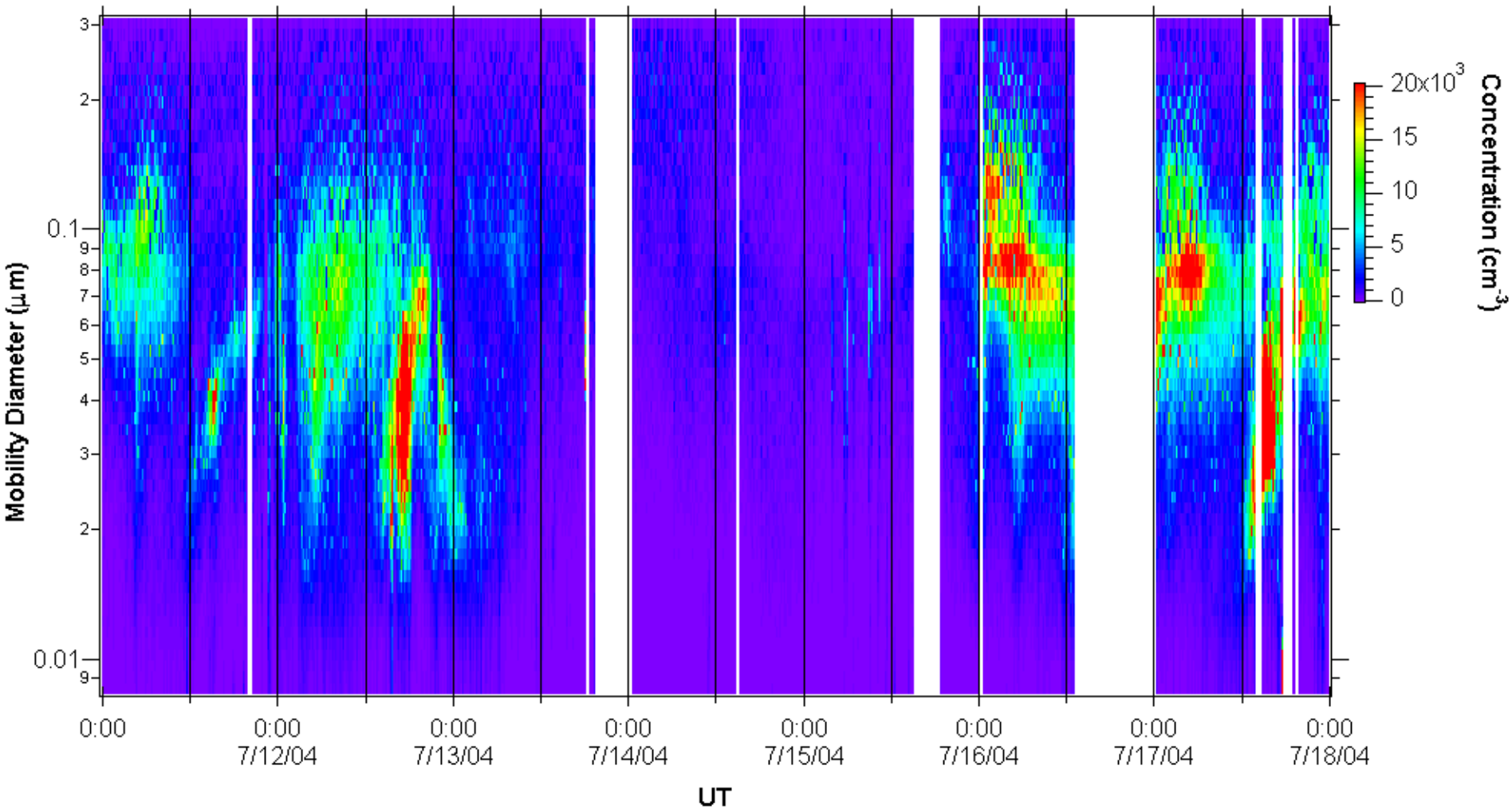


Water Soluble Gases

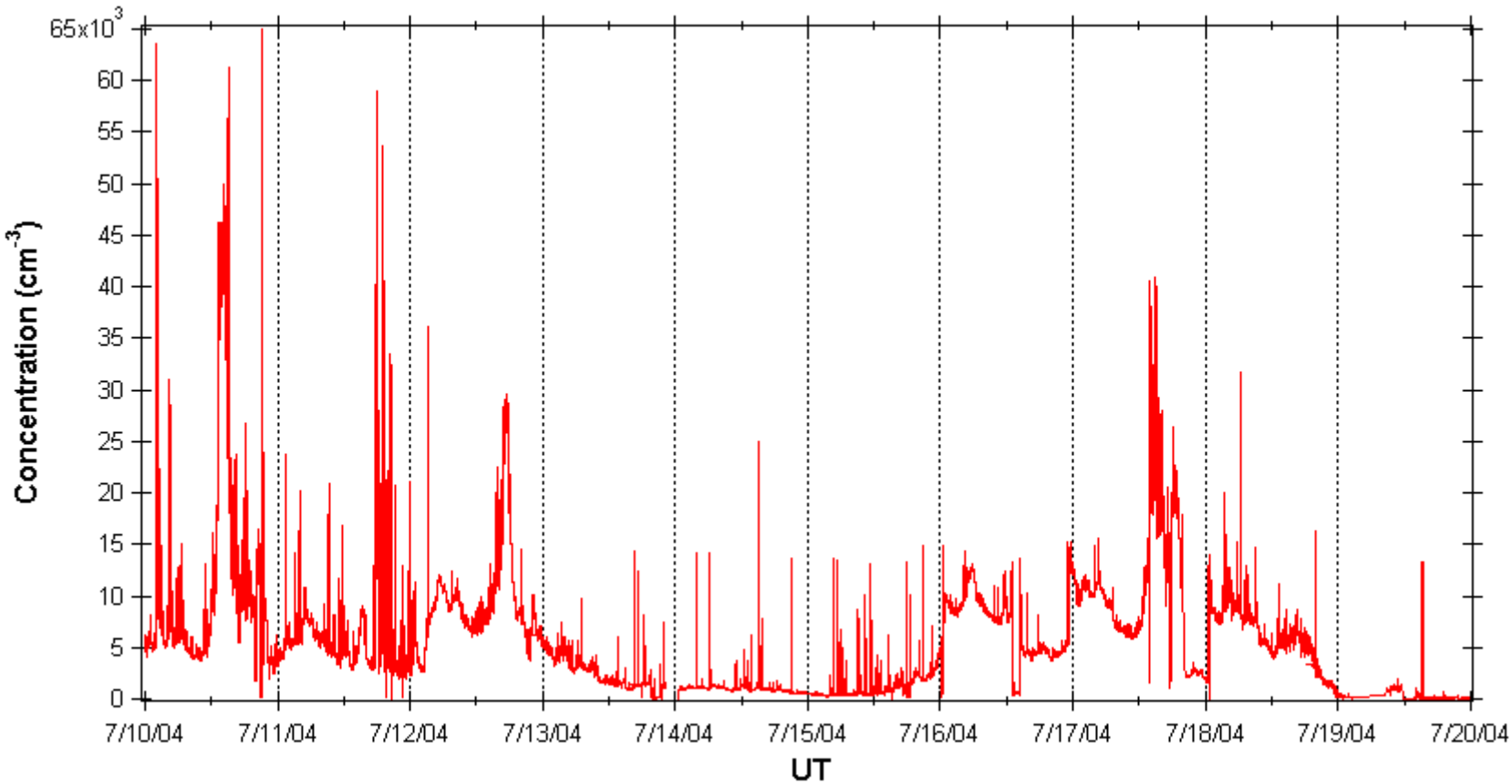


Day 188 = 7/6/2004

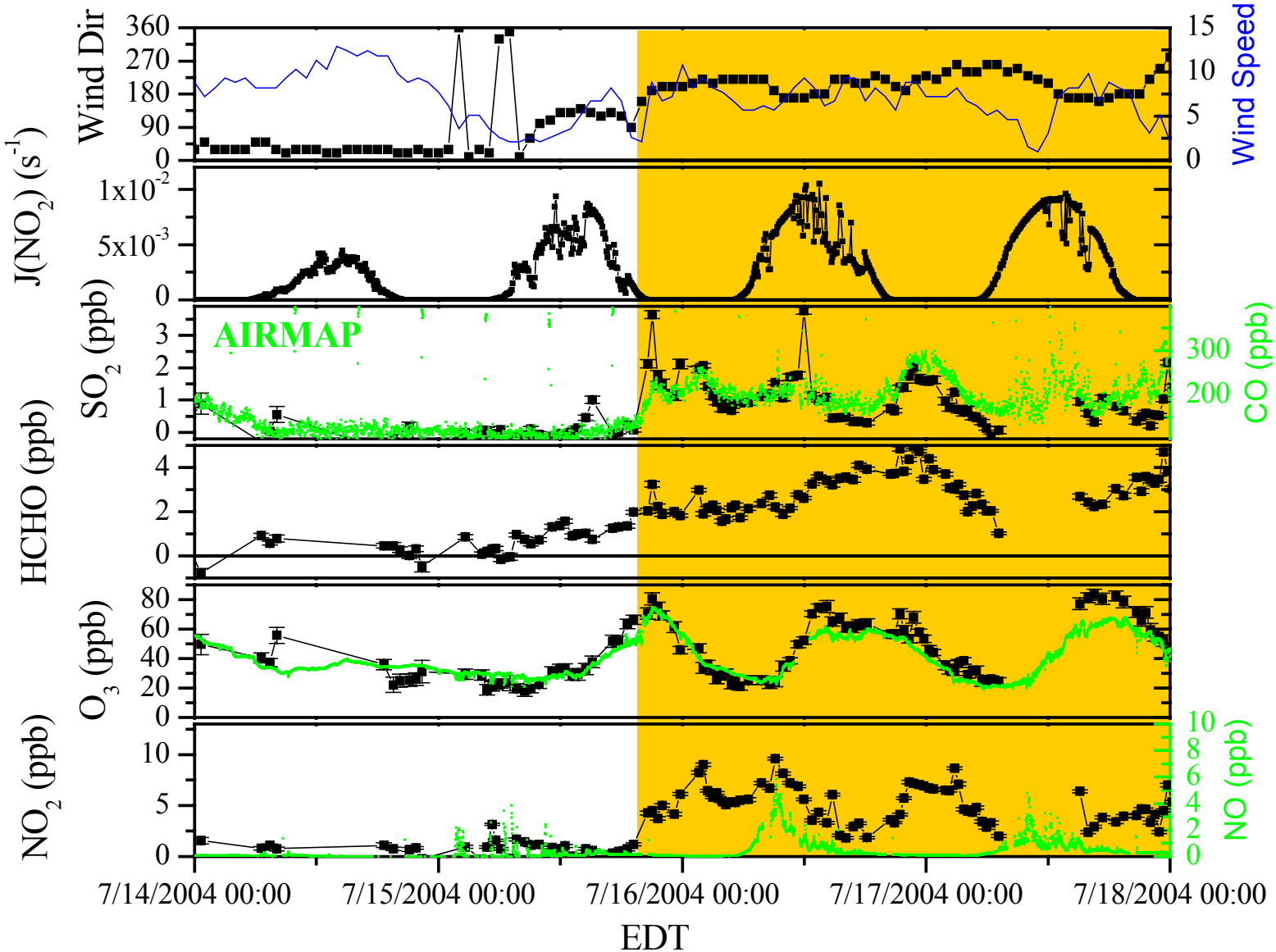
SMPS Aerosol Data



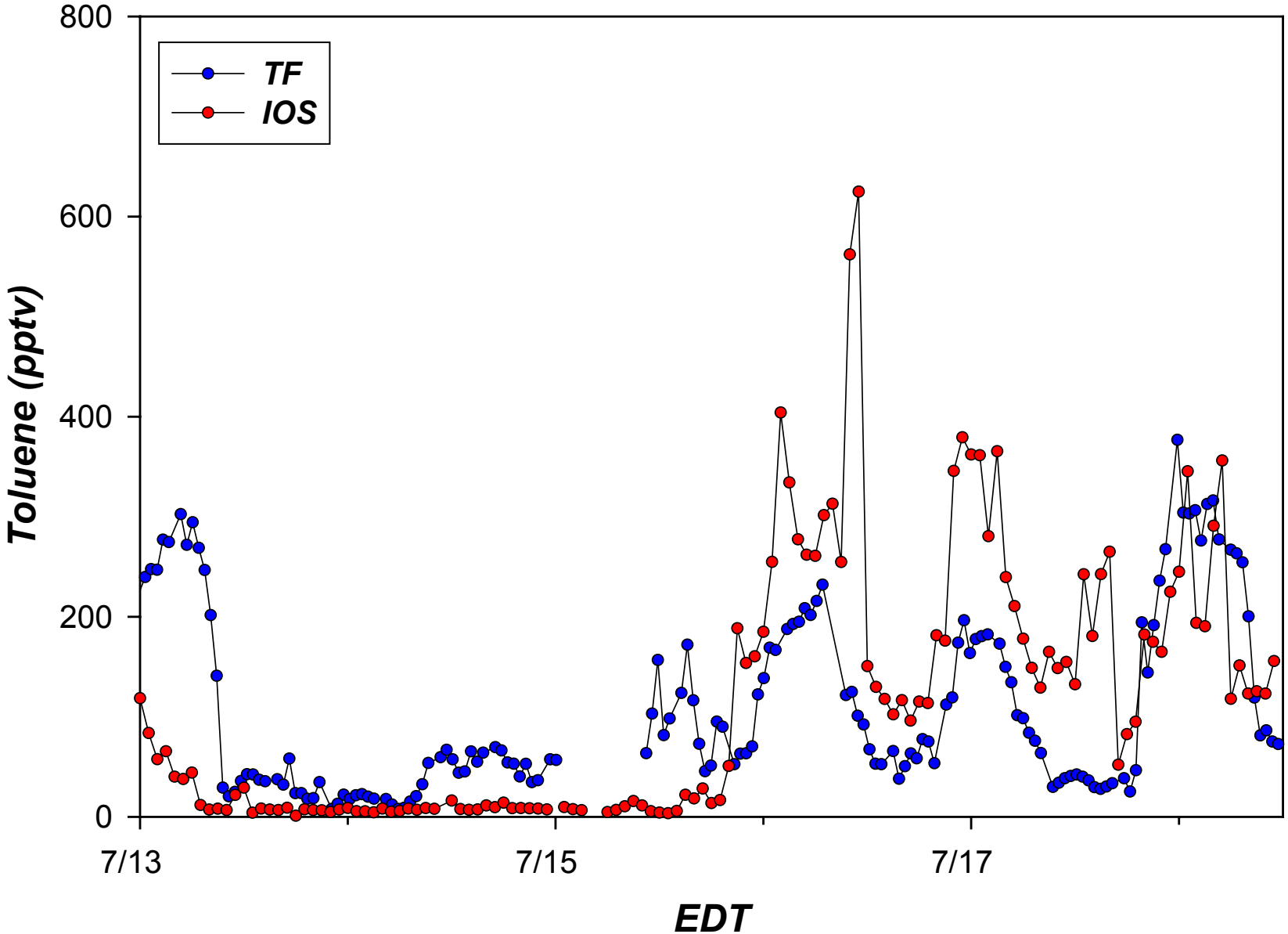
Ultrafine Particle CPC



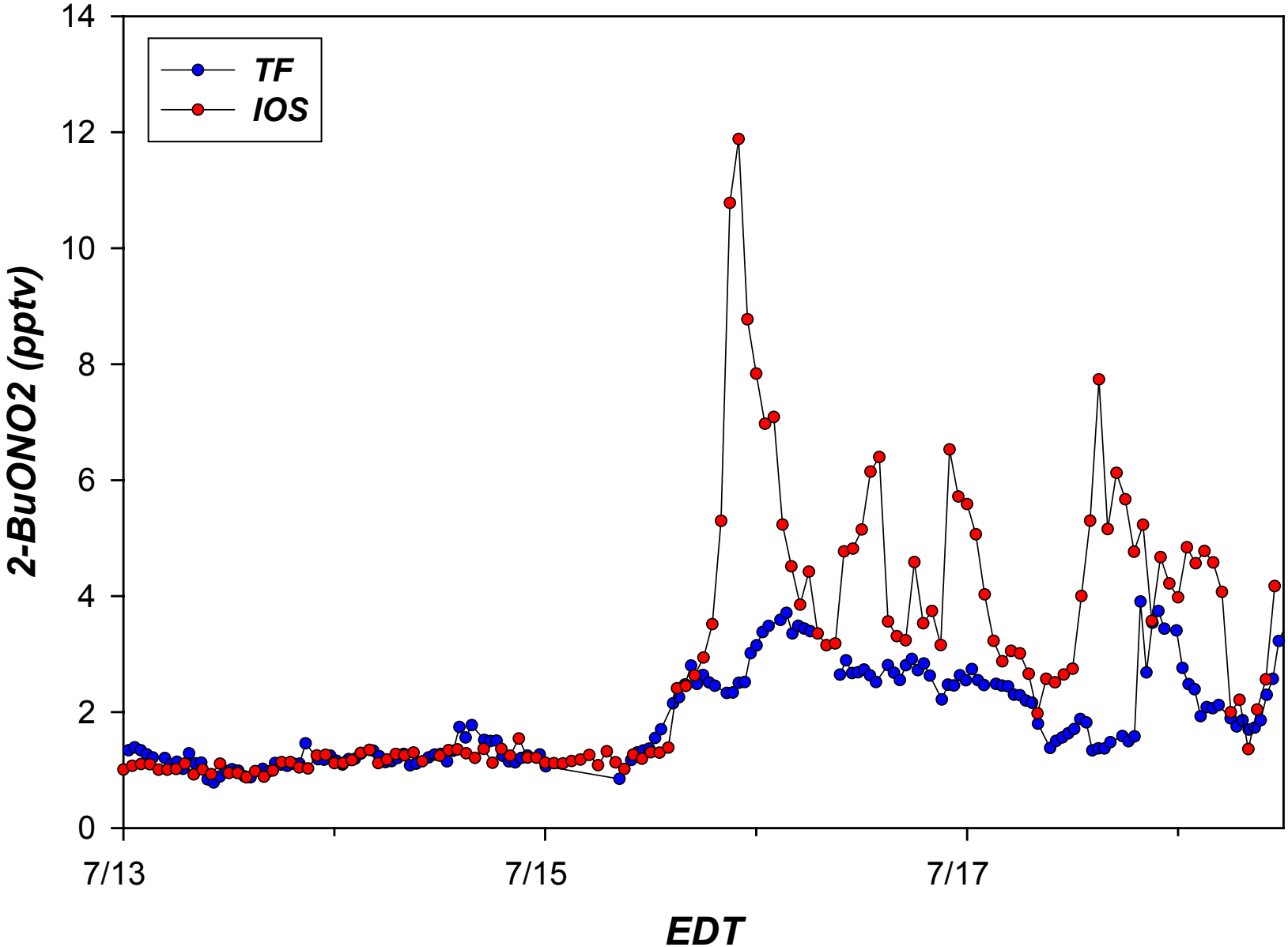
Transition on 7/15/04



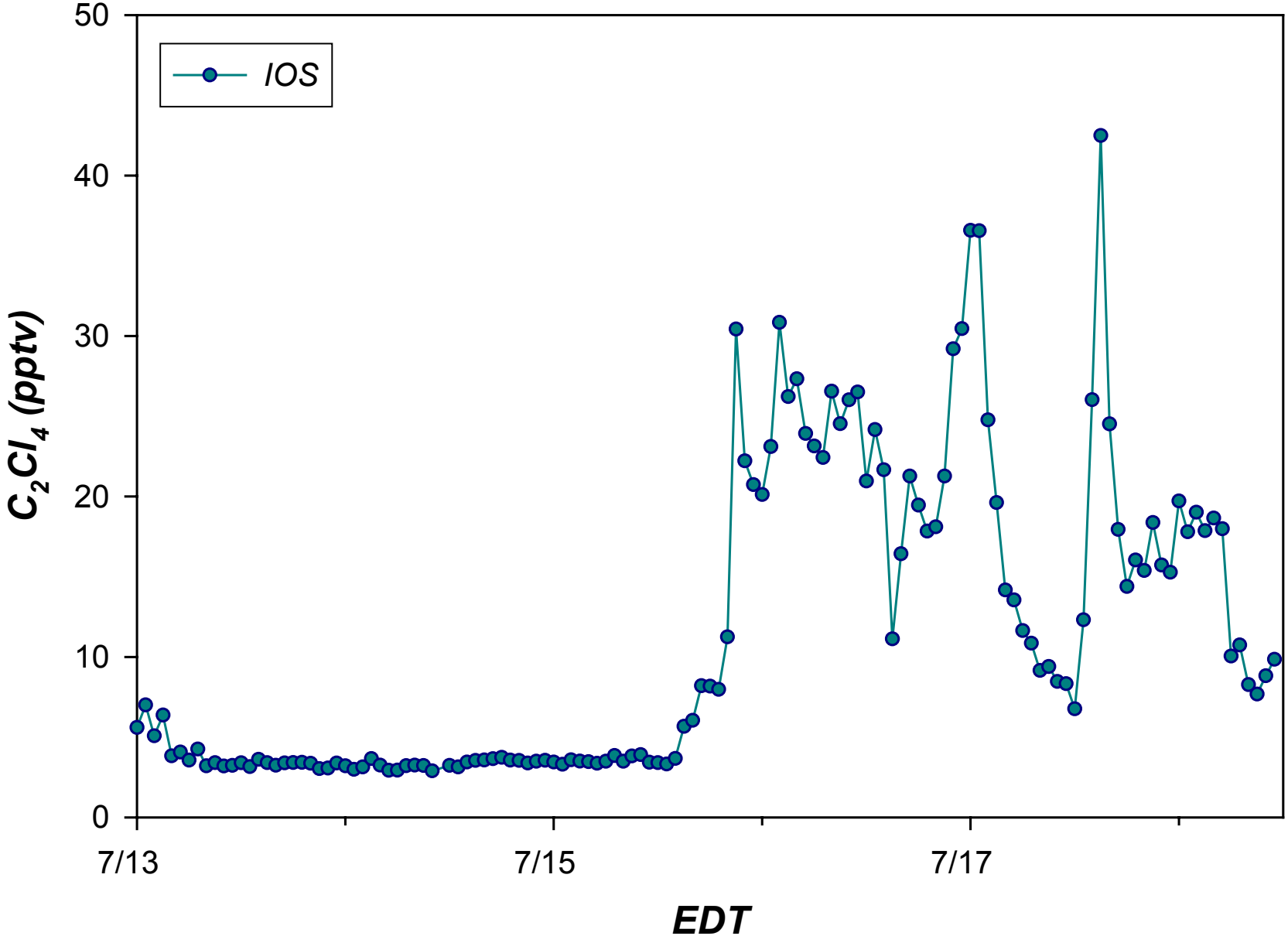
Toluene at the Isles of Shoals and Thompson Farm



2-$BuONO_2$ at the Isles of Shoals and Thompson Farm

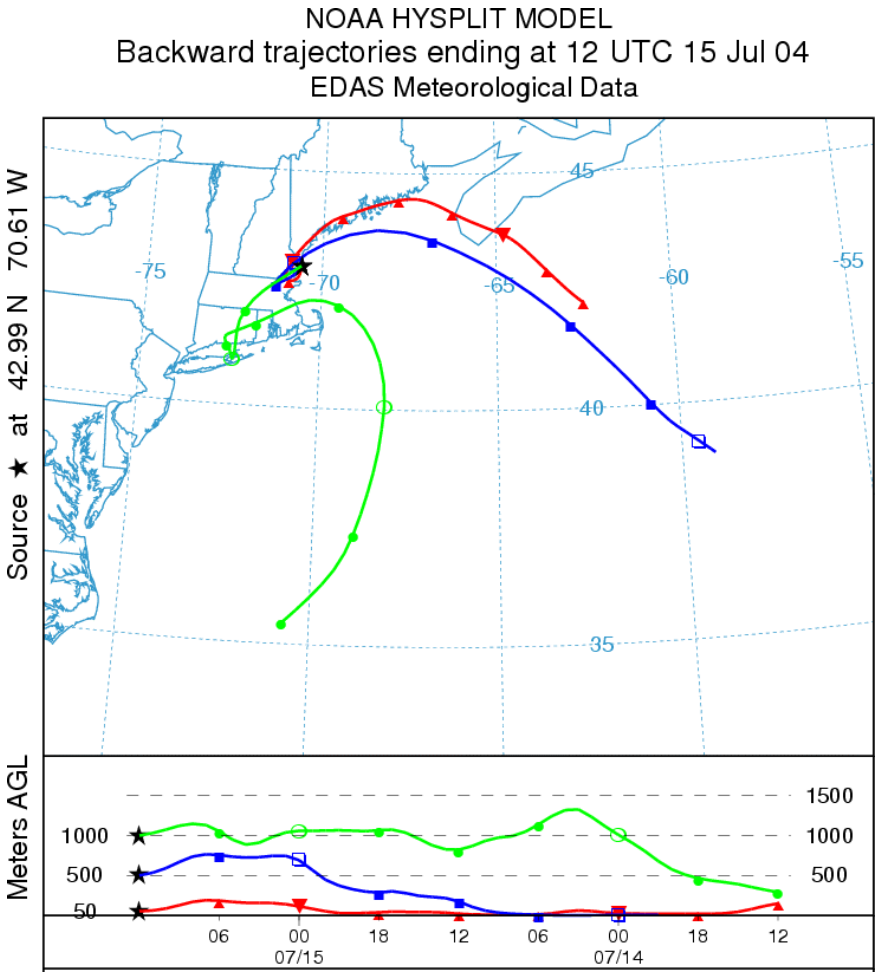


C_2Cl_4 at the Isles of Shoals

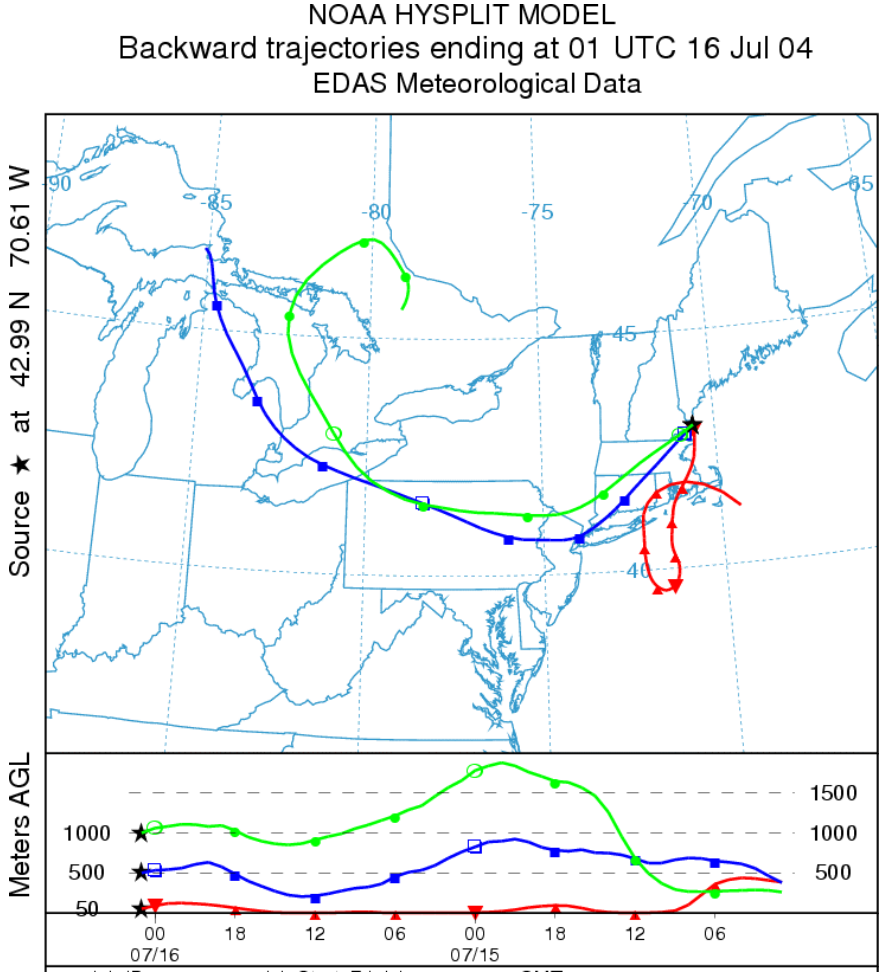


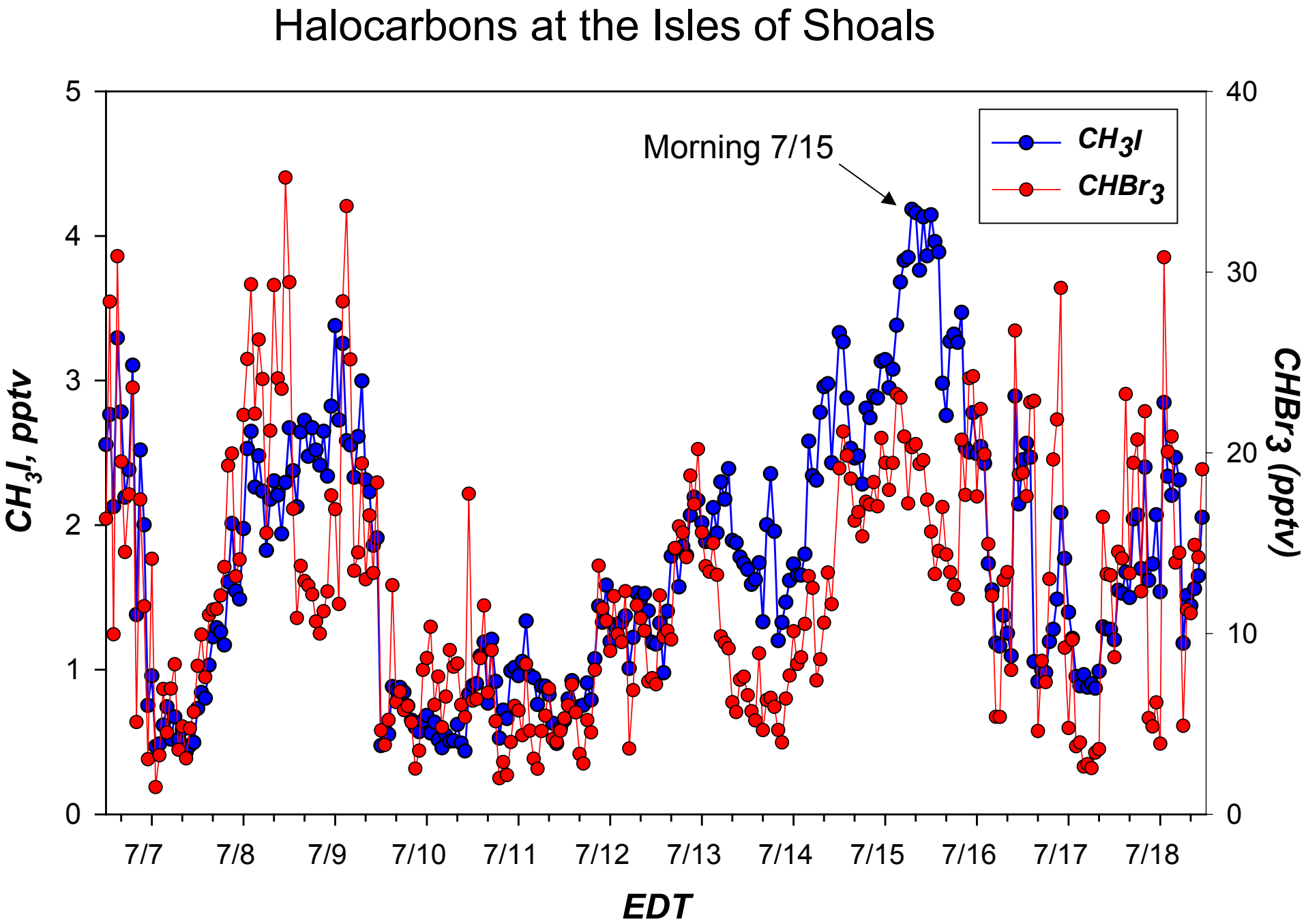
Back-Trajectories

Clean Period
8am EDT 7/15/04

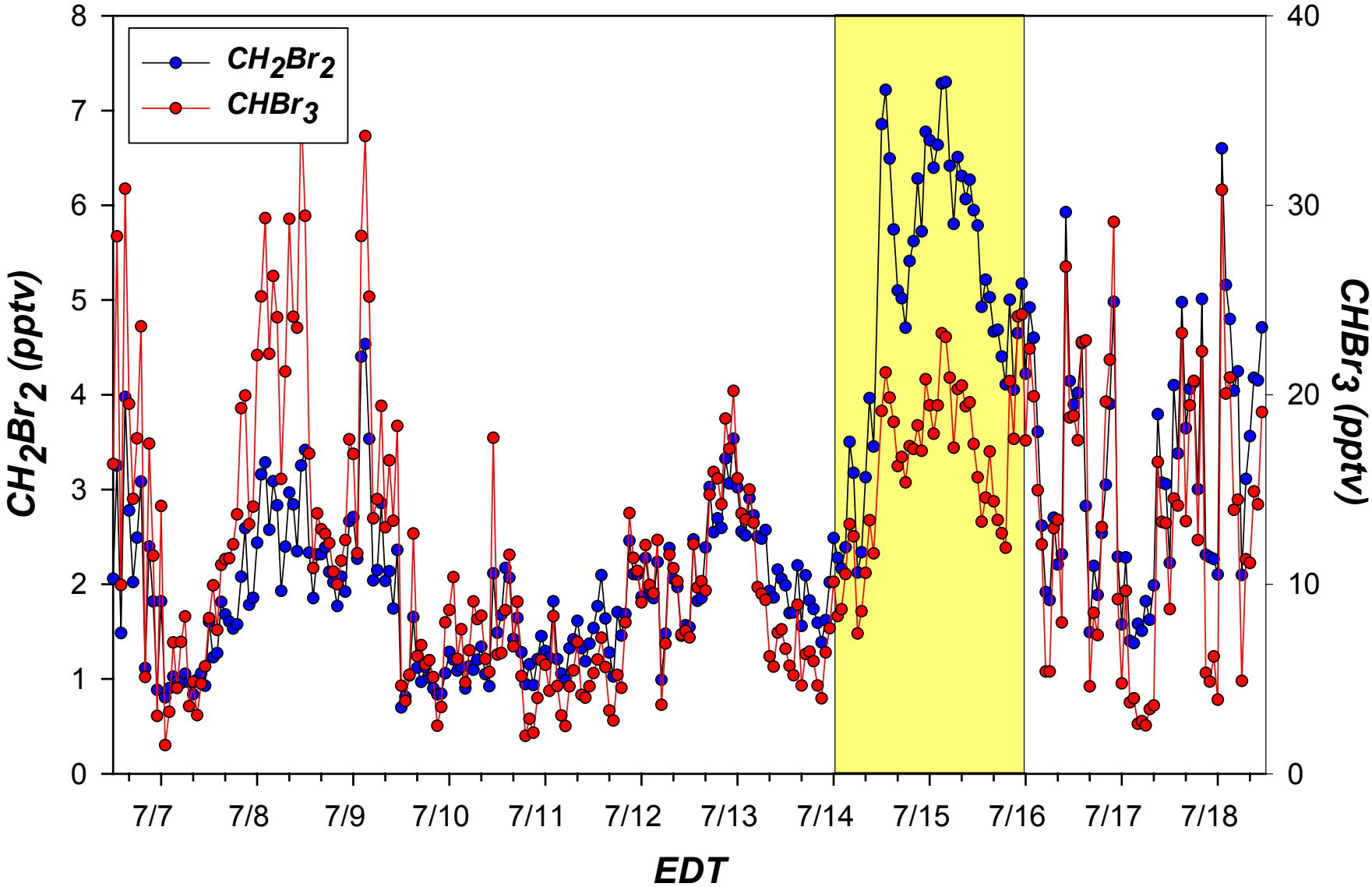


Polluted Nocturnal Period
9pm EDT 7/15/04

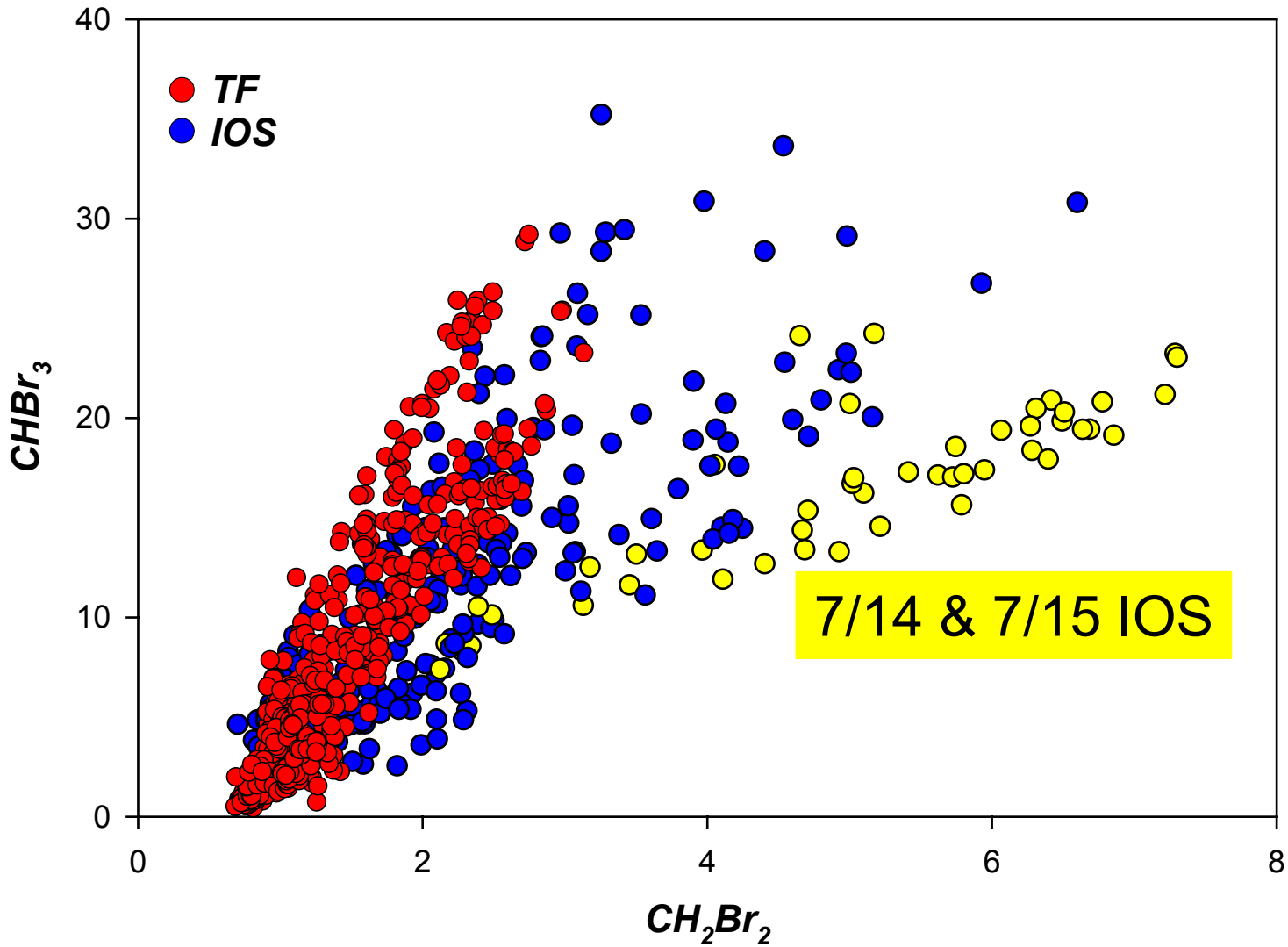



Halocarbons at the Isles of Shoals
Morning 7/15
CH3I
CHBr3
CH3I, pptv
CHBr3 (pptv)
EDT
0
1
2
3
4
5
0
10
20
30
40
7/7
7/8
7/9
7/10
7/11
7/12
7/13
7/14
7/15
7/16
7/17
7/18

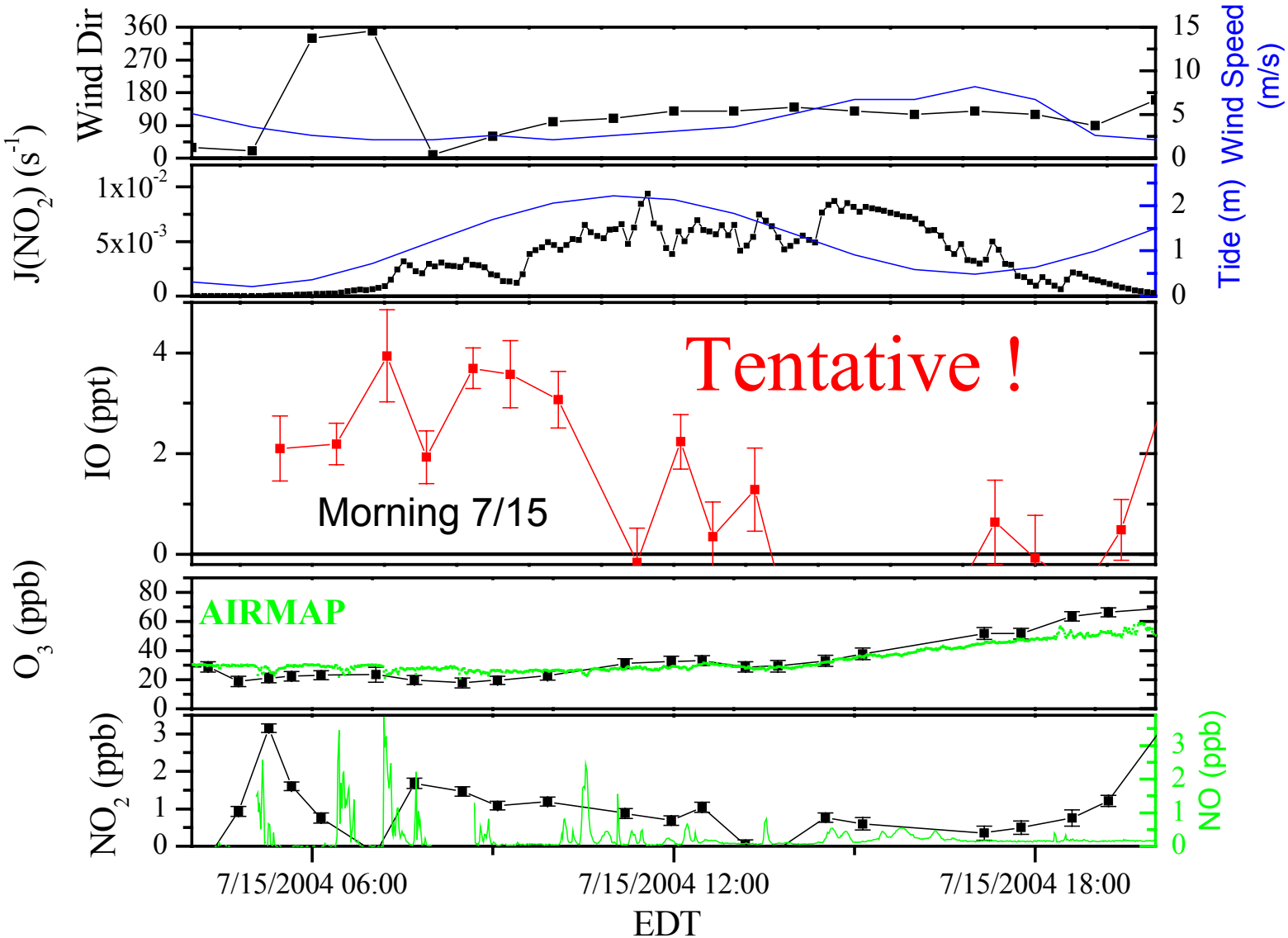
Halocarbons at the Isles of Shoals



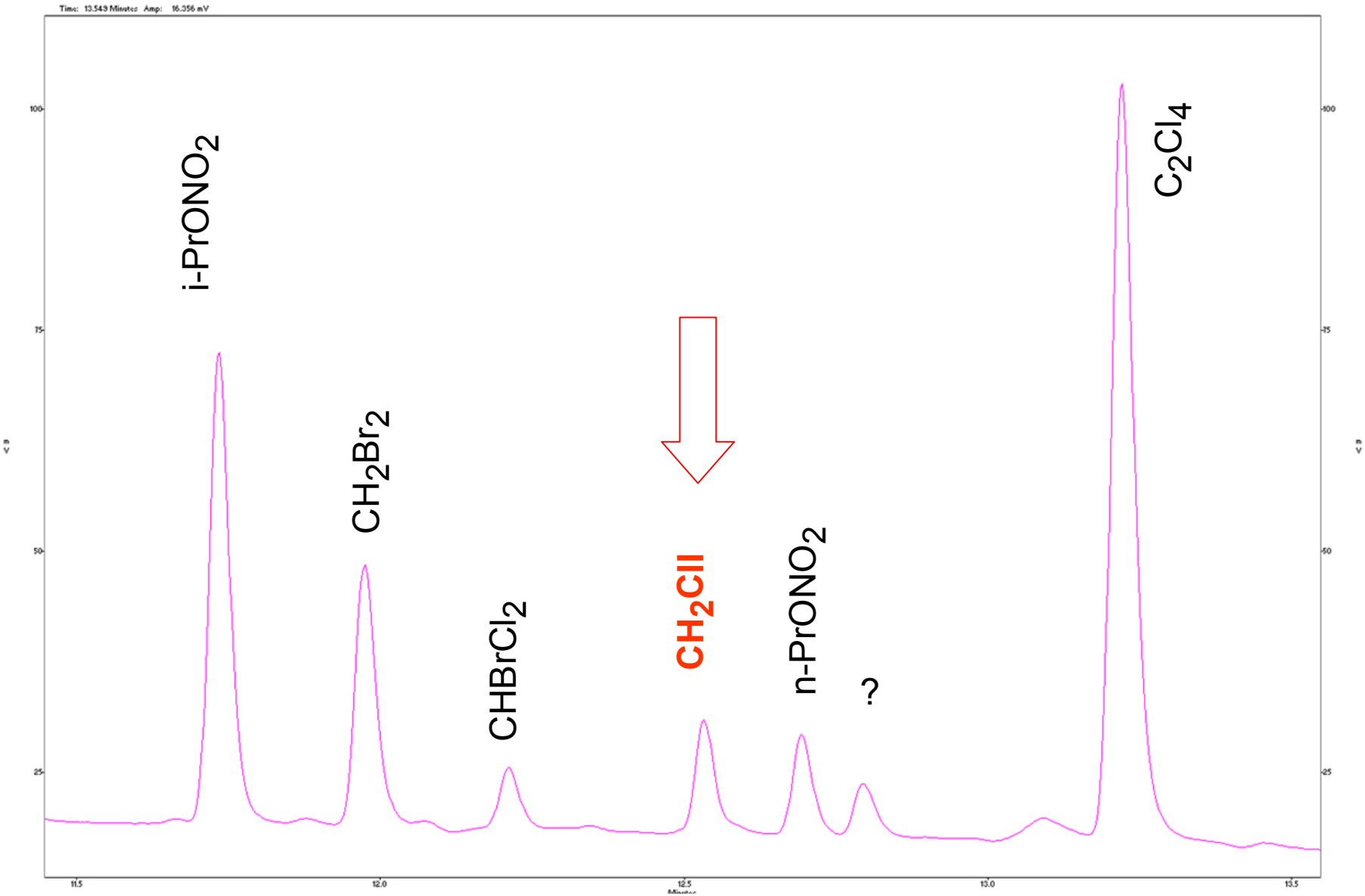
$CHBr_3$ / CH_2Br_2 correlation



Reactive Halogens ?



CH_2ClI in Chromatograms



Conclusions

- Measurements show periods of clean marine influence and polluted continental air
- Clean periods (7/14 & 7/15) show elevated halocarbons, tentatively reactive iodine and precursors
- Night of 7/16 the Boston/NYC plume was observed, with high VOC, O_3, NO_x, NO_3, soluble gases, and aerosol

The CHAiOS Crew

Chemistry of Halogens at the Isles of Shoals