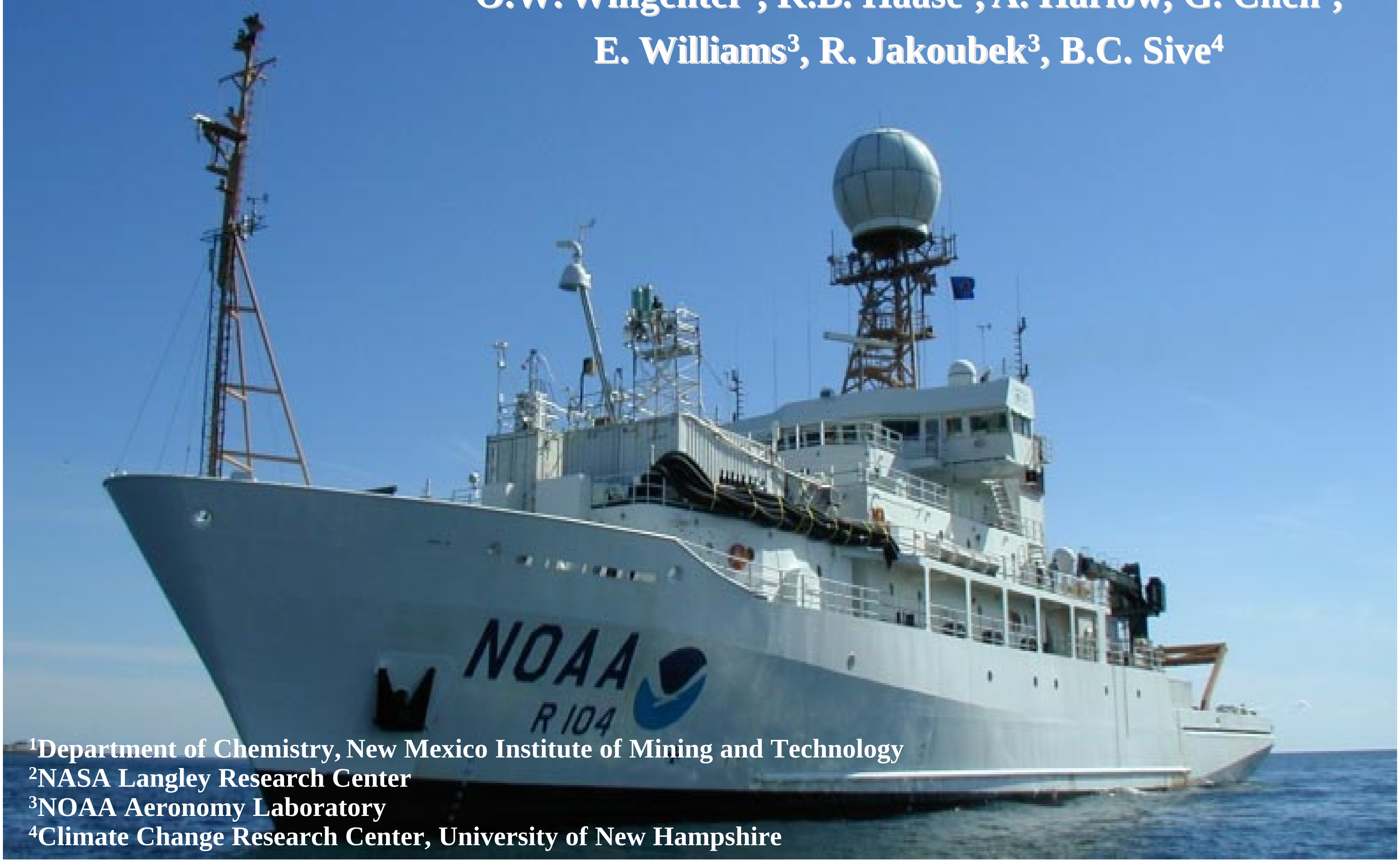
The Photochemical Impact of Oceanic Hydrocarbons on the Atmospheric Marine Boundary Layer over the Gulf of Maine

O.W. Wingenter[1], K.B. Haase[1], A. Harlow, G. Chen[2], E. Williams[3], R. Jakoubek[3], B.C. Sive[4]



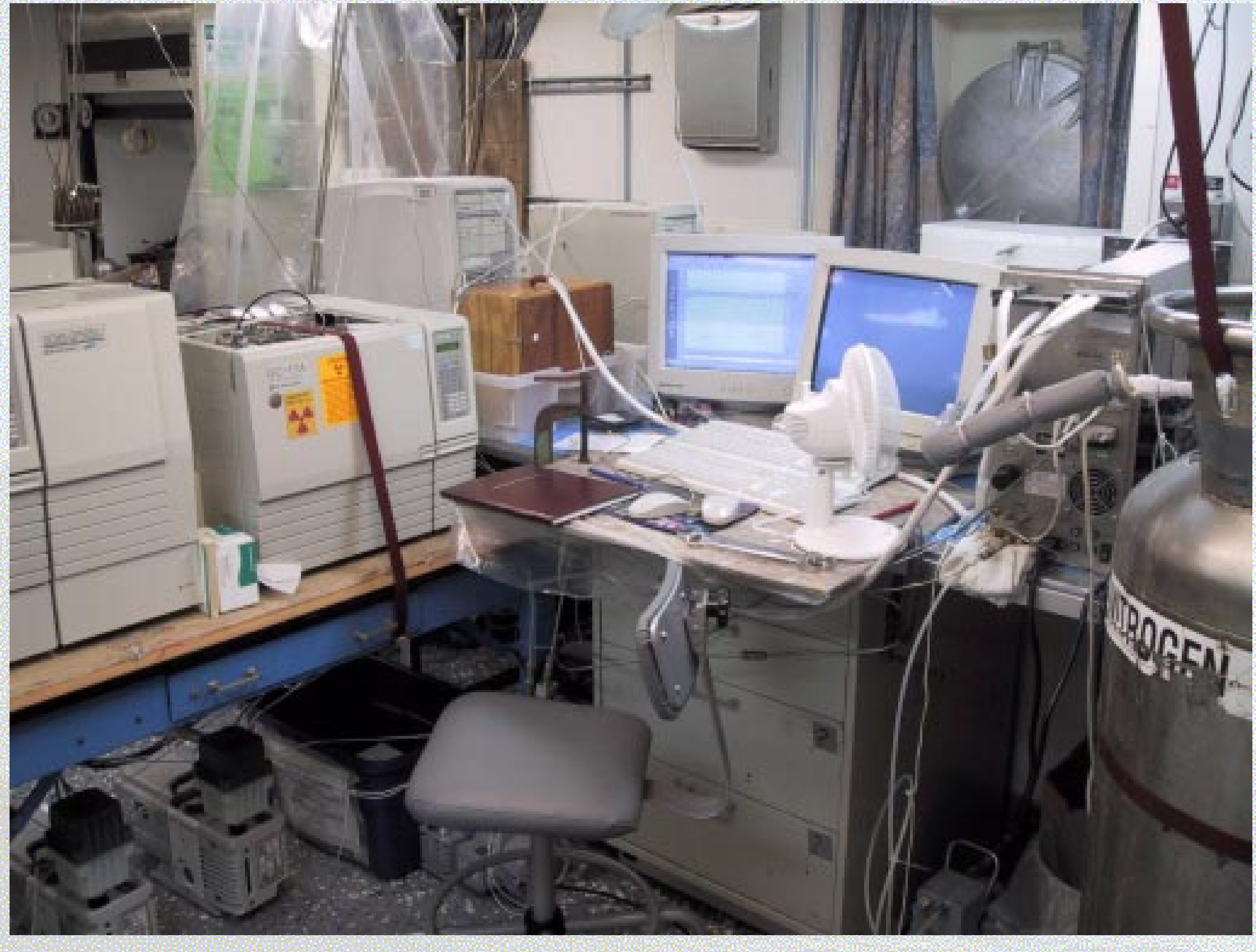
[1]Department of Chemistry, New Mexico Institute of Mining and Technology
[2]NASA Langley Research Center
[3]NOAA Aeronomy Laboratory
[4]Climate Change Research Center, University of New Hampshire

Laboratory Setup

- **Equilibrators**
  - •Smaller version of Weiss design
  - •Marble design tested on Leg 1
    - •Foam produced in coastal waters

Fully Automated Gas Chromatographic System

Two capillary columns were housed in two separately temperature programmed GCs. The PLOT column was coupled to an FID and was used to quantify NMHCs. The DB-624 column was connected to an ECD for separation and detection of halocarbons and alkyl nitrates.



Precision Estimates

Based on reproducibility of 3 consecutive samples taken over 5 hours. Therefore, natural variability is included in the estimates.

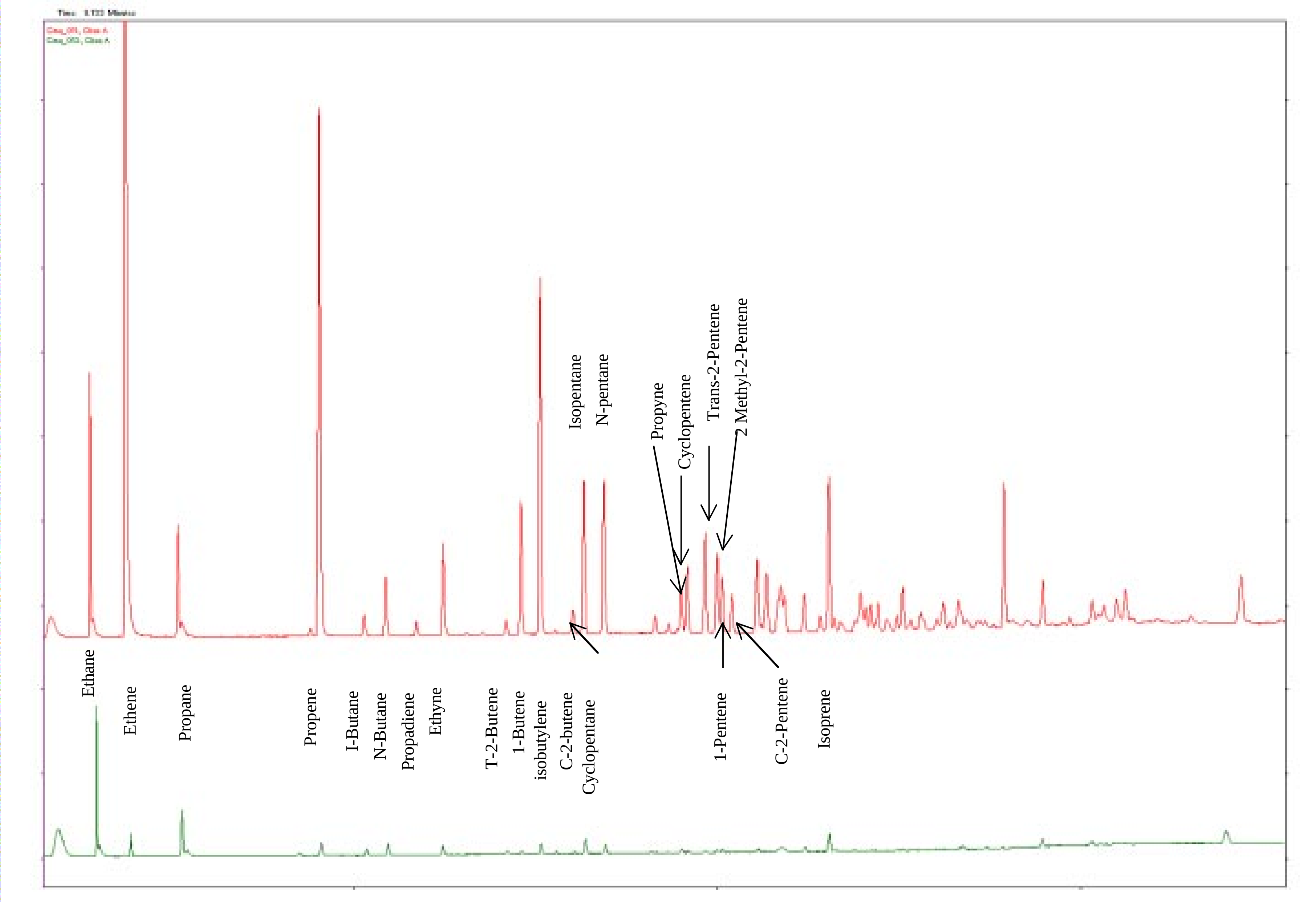
Air

ethene	6%
propene	1%
t-2-butene	2%
1-butene	5%
isobutylene	5%
c-2-butene	3%
isoprene	15%
ethane	2%
i-butane	1%
n-butane	3%
propane	2%
i-pentane	0.4%
n-pentane	3%
cyclopentane	6%
ethyne	2%

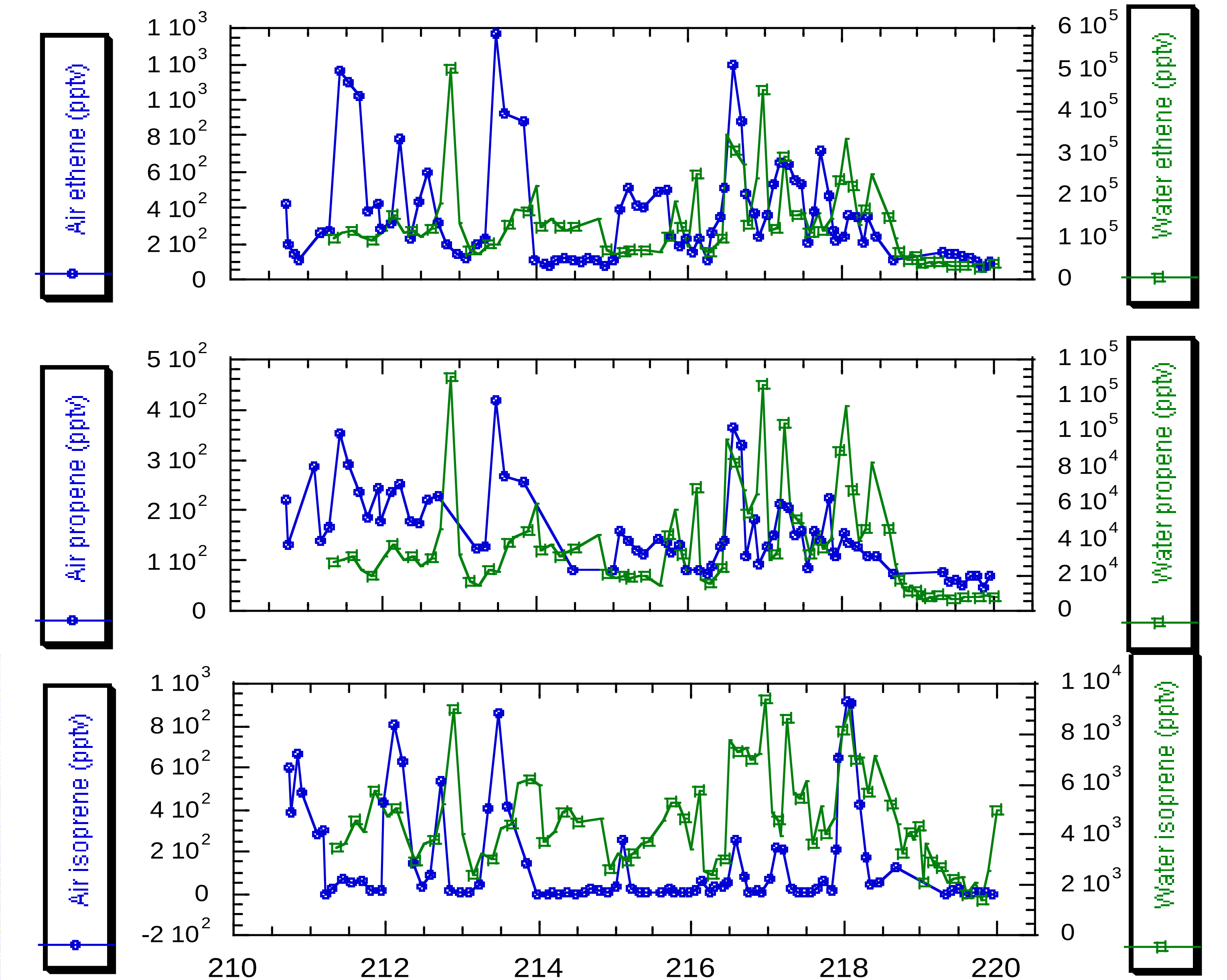
Equilibrator

ethene	1%
propene	2%
t-2-butene	0.3%
1-butene	0.6%
isobutylene	1%
c-2-butene	5%
isoprene	2%
ethane	1%
i-butane	1%
n-butane	2%
propane	0.4%
i-pentane	2%
n-pentane	1%
cyclopentane	5%
ethyne	3%

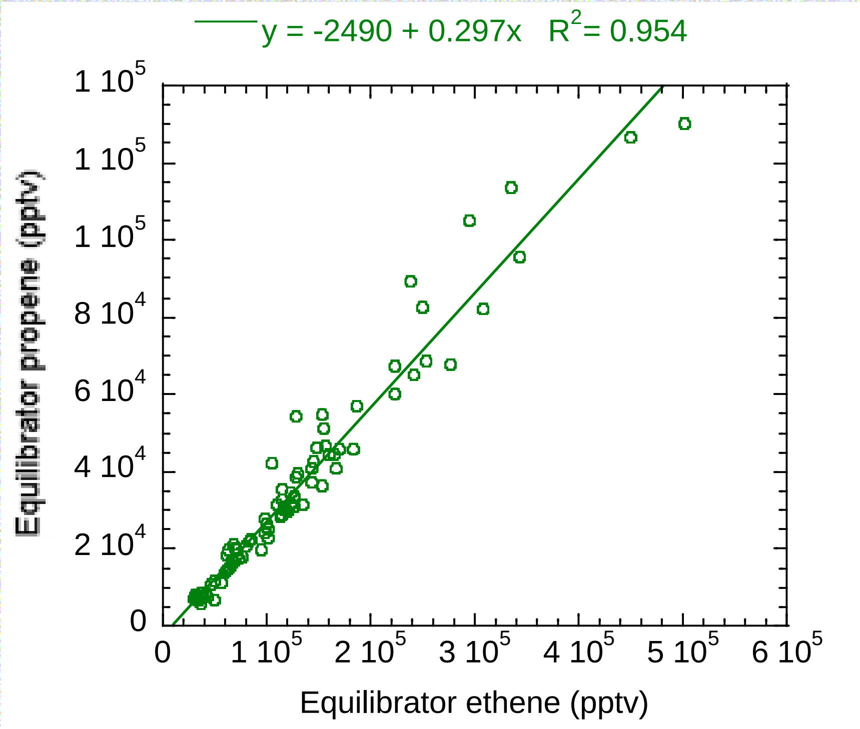
Equilibrator and Air Sample Chromatograms

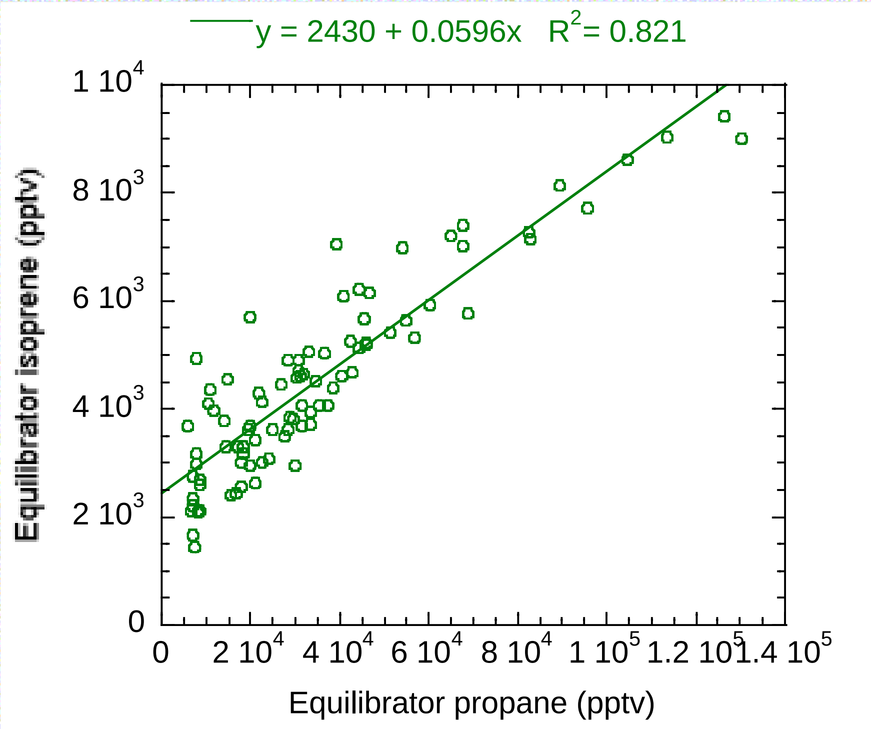


NMHCs Supersaturated in Gulf of Maine



NMHCs Correlations Consistent





For more data, including halocarbons and alkyl nitrates, and experimental description, please see our poster [*Haase et al.* A51D-0712] tomorrow.

Calculation of Land and Seawater NMHCs Contributions

$$\frac{d[Compound]}{dt} = \text{Production} \quad \text{Loss} = 0$$

$$\text{Production} = \text{Loss}$$

$$\text{Loss} = k_{HO}[HO][R] + k_{O_3}[O_3][R]$$

$$\text{Production} = \text{Sea/Air Flux} + \textit{NMHCs transported from Land}$$

Sea - Air Flux was calculated use the Wanninkhof [1997] Flux Relationship

Land Contribution = Photochemical Loss - Seawater Flux

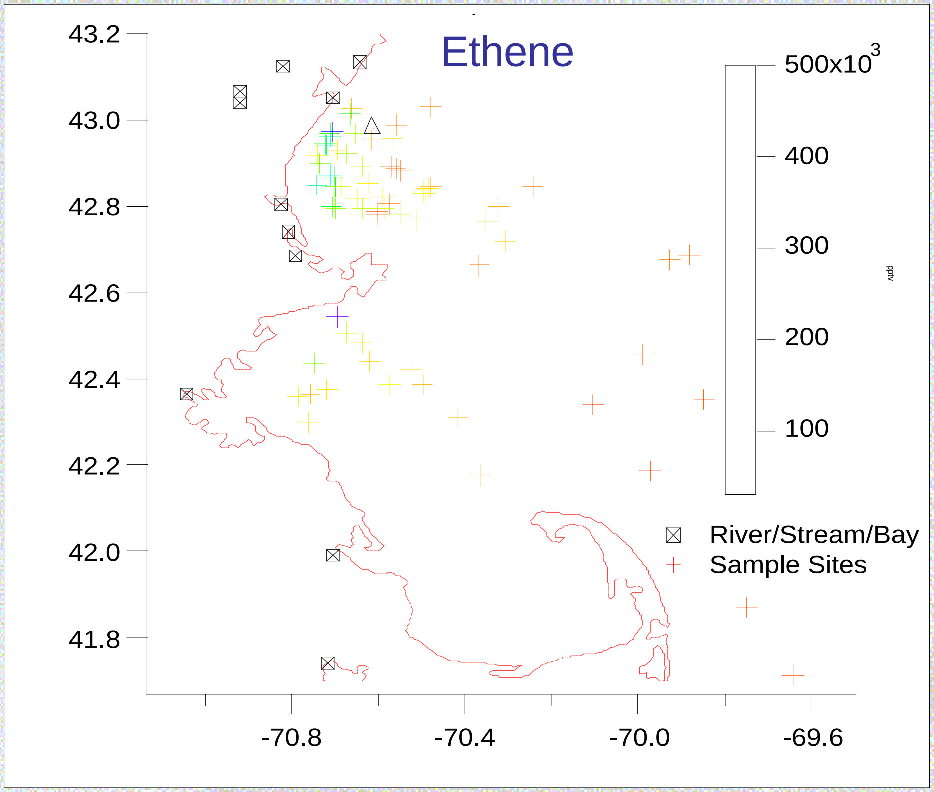
- **100 m used as Marine Boundary Layer Height.**
  - **Typically an inversion started just over the water.**
    - **Average air temperatures in the morning ~ 3K > than water.**
    - **Air 7K > than water in the afternoon.**

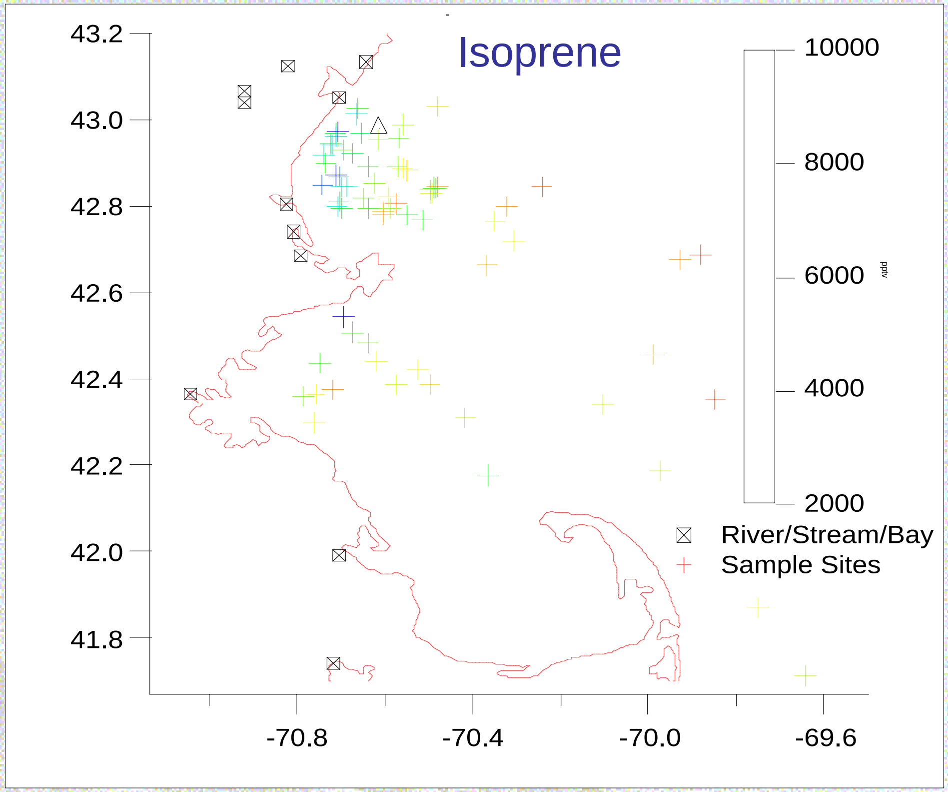
Can we assume steady state? If so at what time of the day?

Georgia Tech/NASA Langley Time Dependant Photochemical Box Model

- Model Constraints: T, Dew Point, O_3, CO (median from Thompson Farm), NO, NMHCs, J-Values (Spectral Radiometer).
- 71 reactions describing H_XO_Y-N_XO_Y-CH_4 chemistry.
- 184 NMHC reactions based on a highly modified CAL scheme [*Lurmann et al.*, 1986].
- Updated $O(^1D)$ quantum yield data [*Talukdar et al.*, 1997].
- Heterogeneous removal of soluble species [*Logan*, 1981].
- Numerical Method: Gear Solver.
- Estimated model uncertainty due to rate coefficients (ks & Js) has been previously estimated to be 25%.

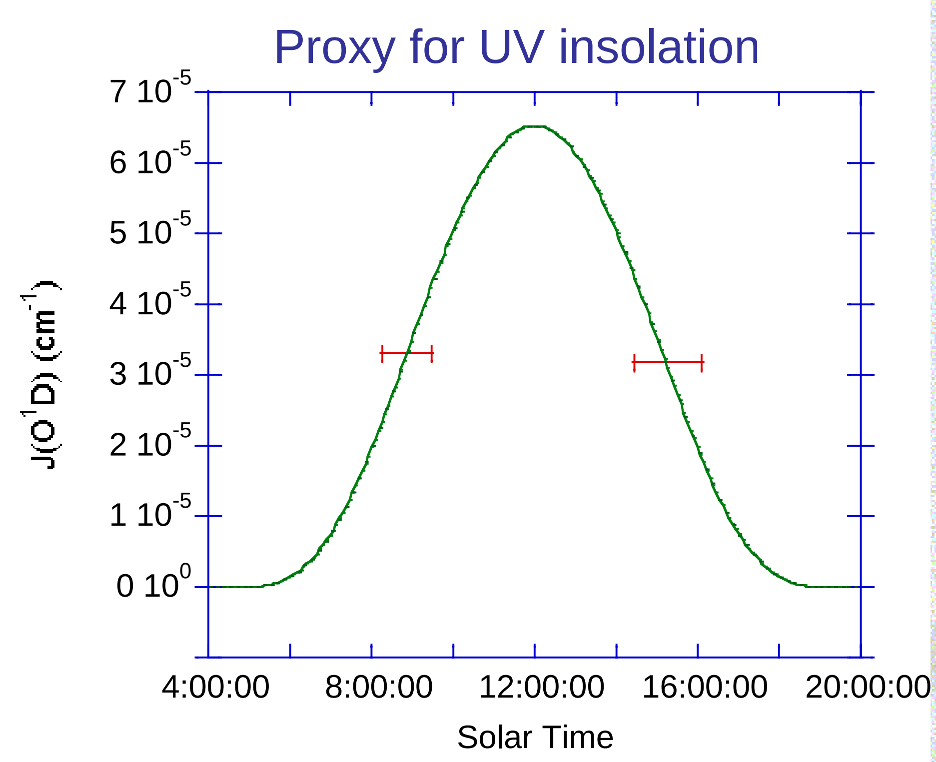
Gulf of Maine Equilibrator Measurements

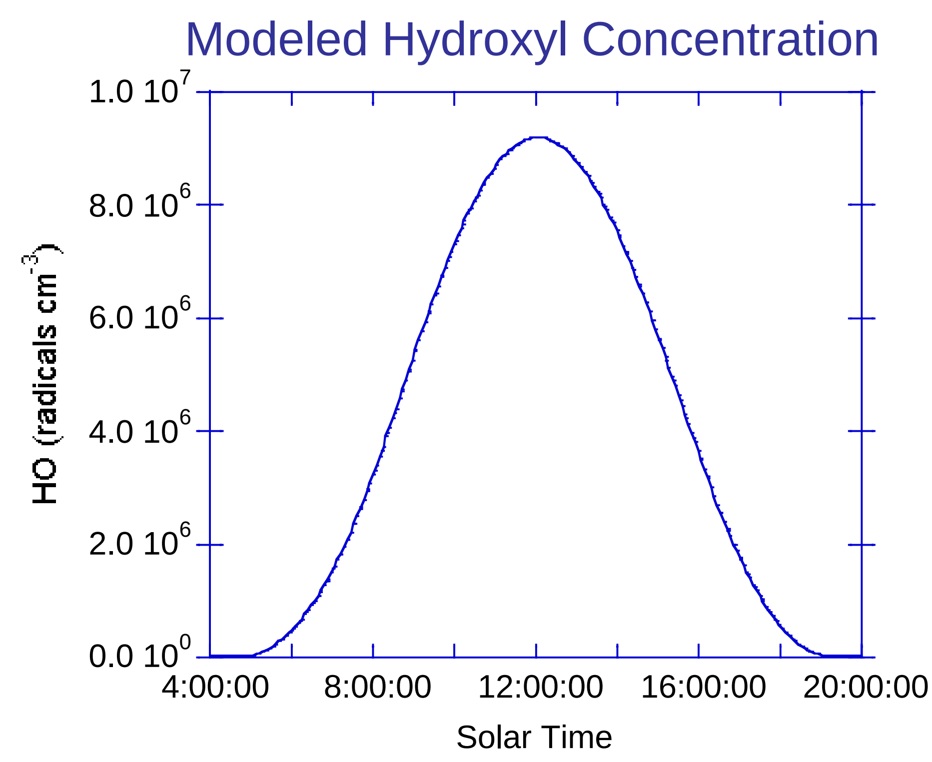




- **Diurnal profiles of seawater NHMCs were not obtained. Typically, during the day the R/V Brown was close to shore and farther out at night.**
- **Although marine NMHCs are produced by photochemistry, their lifetimes in seawater are long and the diurnal cycles are flatter in comparison to HO.**
- **Wind were fairly steady through out the day and night at about 5 m sec^{-1}. Which may have contributed to a flatter amplitude.**

Steady State Approximation





- The chemical loss terms and the NMHCs seawater flux terms have a minimum at dawn and a maximum at about noon (or perhaps early afternoon for seawater flux).
- Therefore, only measurements and model results made at the inflection in the solar day were used in this analysis.

Morning Results

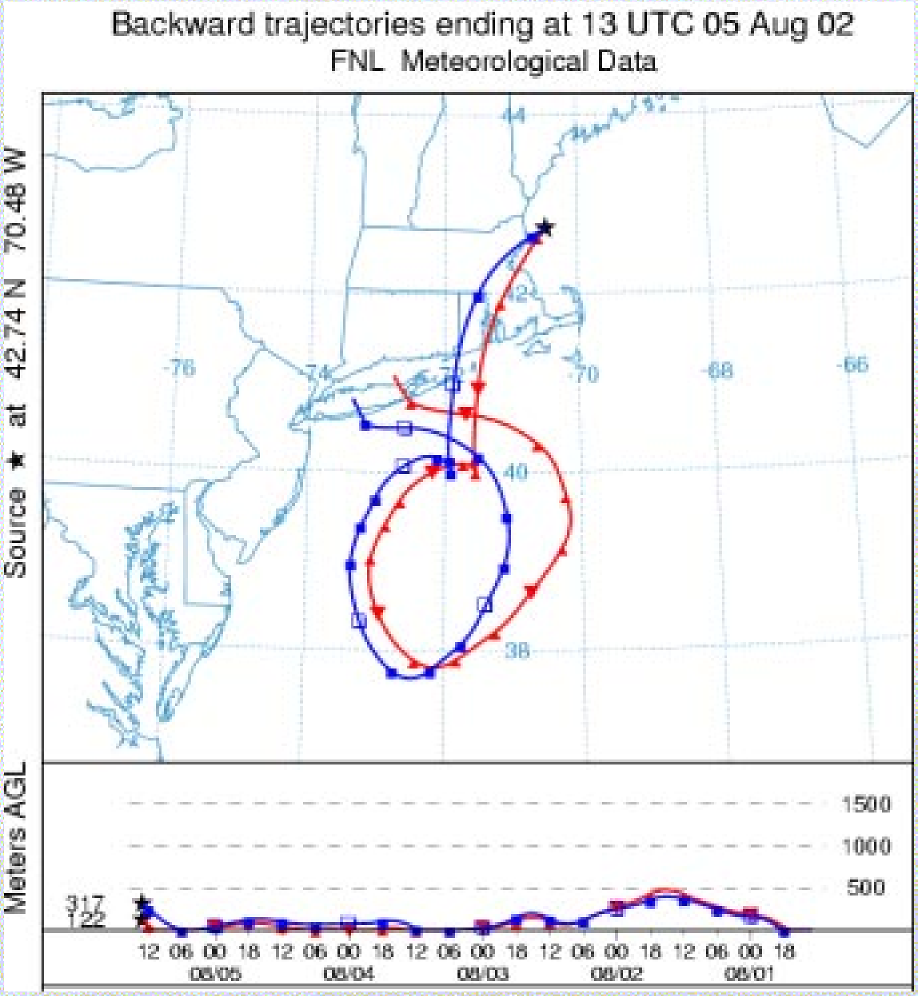
GMT Day of the Year	Measured Mixing Ratios (pptv)						% Contribution from Seawater					
	C2H6	C3H8	ALKA	C2H4	ALKE	ISOP	C2H6	C3H8	ALKA	C2H4	ALKE	ISOP
217.55	1255	649	314	211	191	5	51%	100%	2%	100%	12%	60%
211.54	2520	1799	1703	1099	514	54	18%	27%	0%	11%	2%	4%
216.58	1472	1896	728	516	231	51	9%	7%	0%	9%	3%	2%
213.59	2544	3103	1295	927	537	415	3%	3%	0%	2%	0%	0%

GMT Day of the Year	OH	HO2	CH3O2	k[HO2][NO]	k[CH3O2][NO]	k[RO2][NO]	PO3
217.55	3%	12%	10%	12%	10%	25%	73%
211.54	2%	4%	3%	4%	3%	5%	5%
216.58	0%	2%	2%	2%	2%	3%	3%
213.59	0%	0%	0%	0%	0%	0%	1%

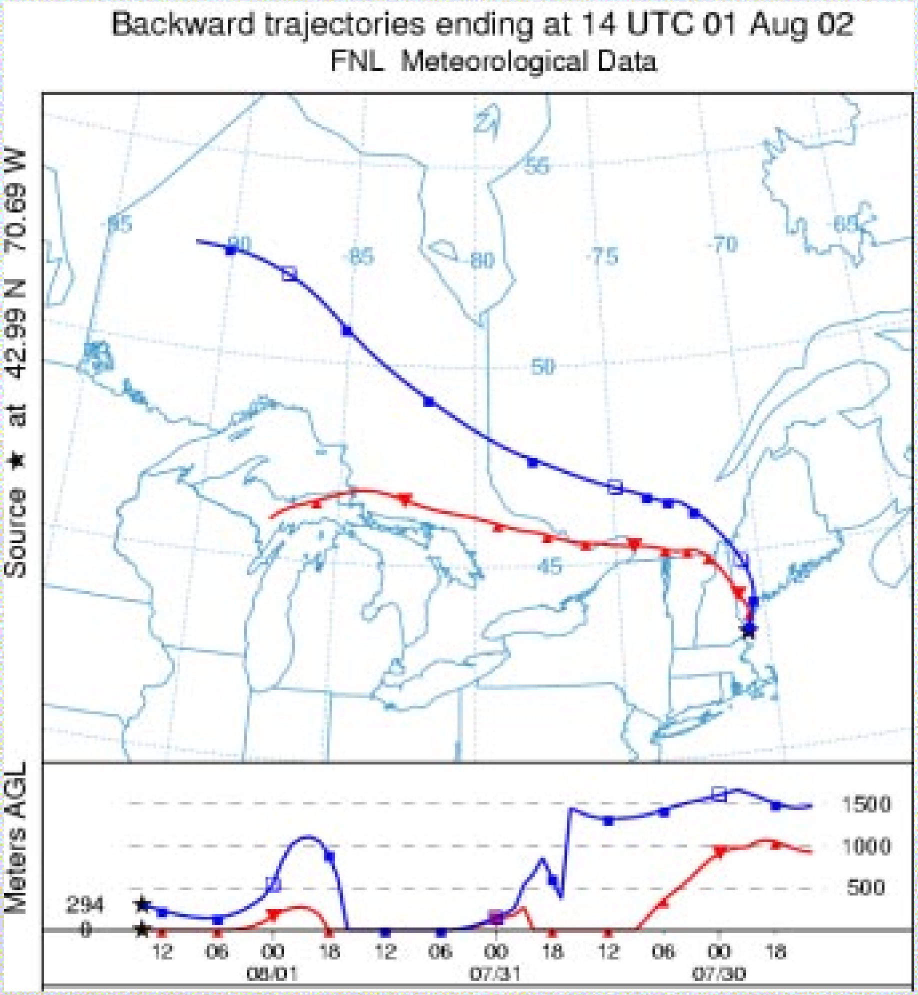
NOAA HYSPLIT Back Trajectories

Day of the Year

217.55



213.59



Afternoon Results

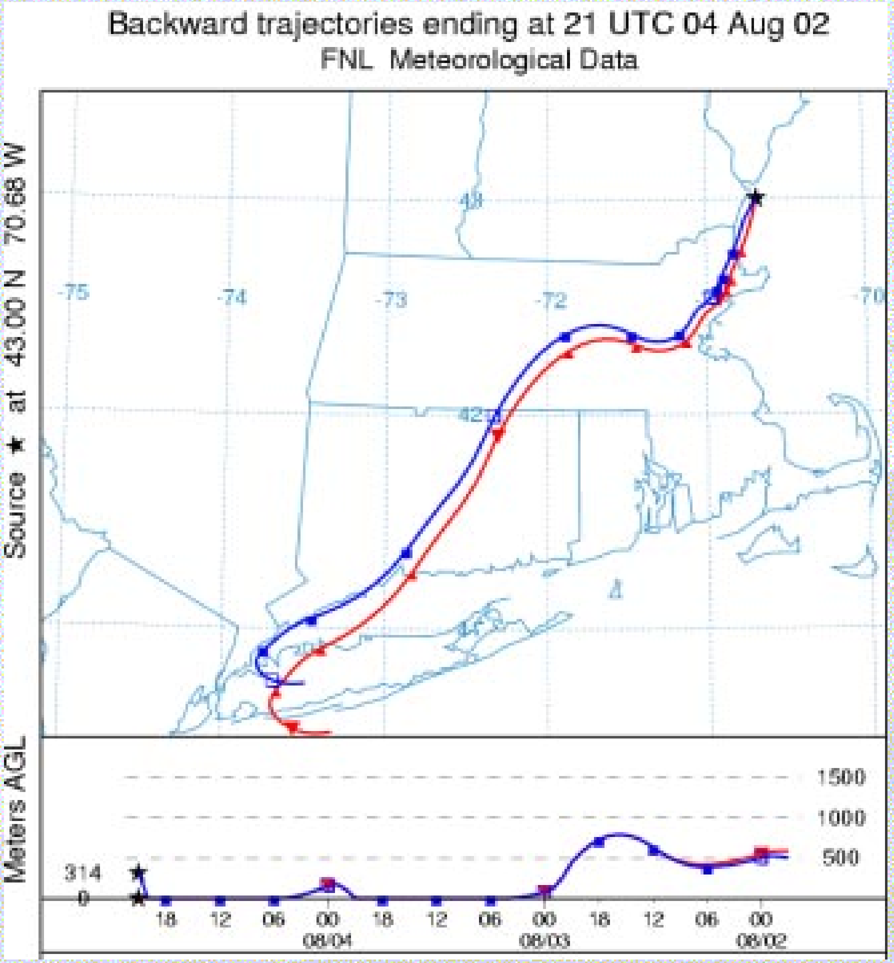
GMT Day of the Year	Measured Mixing Ratios (pptv) C2H6	C3H8	ALKA	C2H4	ALKE	ISOP	% Contribution from Seawater C2H6	C3H8	ALKA	C2H4	ALKE	ISOP
216.86	1582	776	749	367	387	12	40%	47%	1%	53%	6%	50%
212.84	1481	718	487	198	421	10	18%	22%	1%	50%	3%	35%
211.79	2772	1534	1180	377	501	18	4%	9%	0%	10%	1%	6%
214.79	905	259	169	110	219	10	27%	68%	1%	61%	5%	10%
217.83	1868	1087	976	470	504	15	13%	23%	0%	21%	3%	20%
213.85	1789	1099	1792	885	573	142	19%	18%	0%	12%	2%	1%

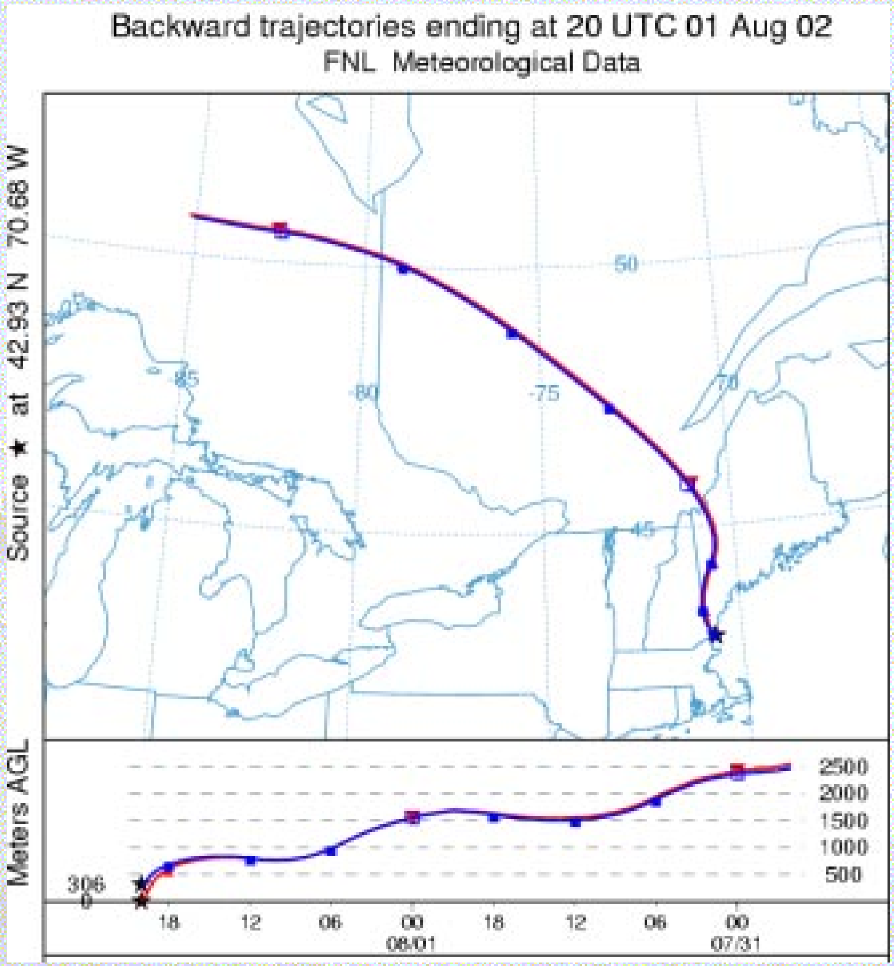
GMT Day of the Year	OH	HO2	CH3O2	k[HO2][NO]	k[CH3O2][NO]	k[RO2][NO]	PO3
216.86	0%	7%	5%	7%	5%	12%	12%
212.84	1%	5%	3%	5%	3%	8%	10%
211.79	0%	1%	1%	1%	1%	2%	3%
214.79	-3%	0%	0%	0%	0%	7%	3%
217.83	-2%	1%	0%	1%	0%	4%	2%
213.85	-1%	1%	0%	1%	0%	1%	1%

NOAA HYSPLIT Back Trajectories

Day of the Year

216.86 **213.85**

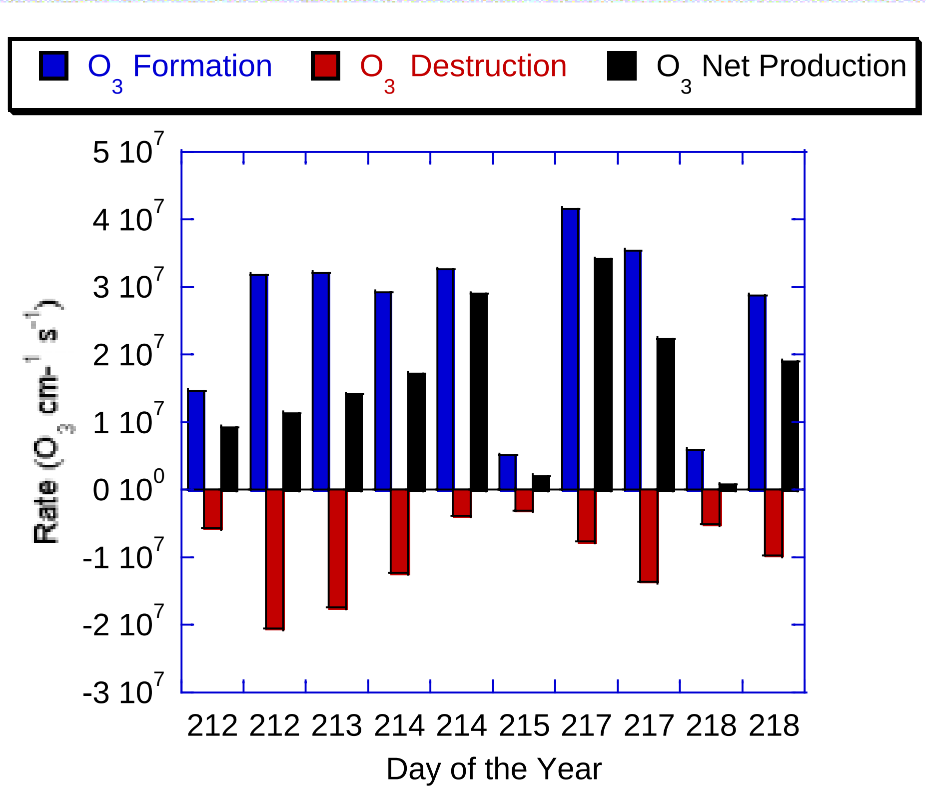




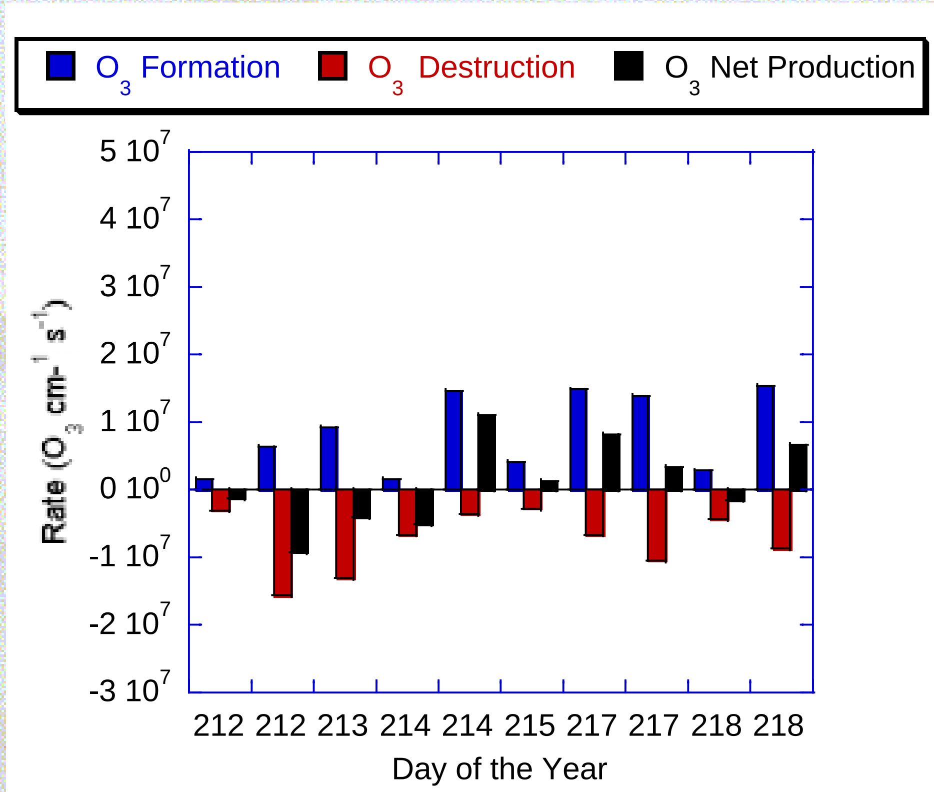
Ozone Formation, Destruction, and Net Production Rates (O_3 cm^{-1} s^{-1})

NMHC input

Terrestrial Origin



Marine Origin



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WERC

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UNIVERSITY of NEW HAMPSHIRE

AIRMAP

- Crew, Researchers, and Facilities at…

NOAA

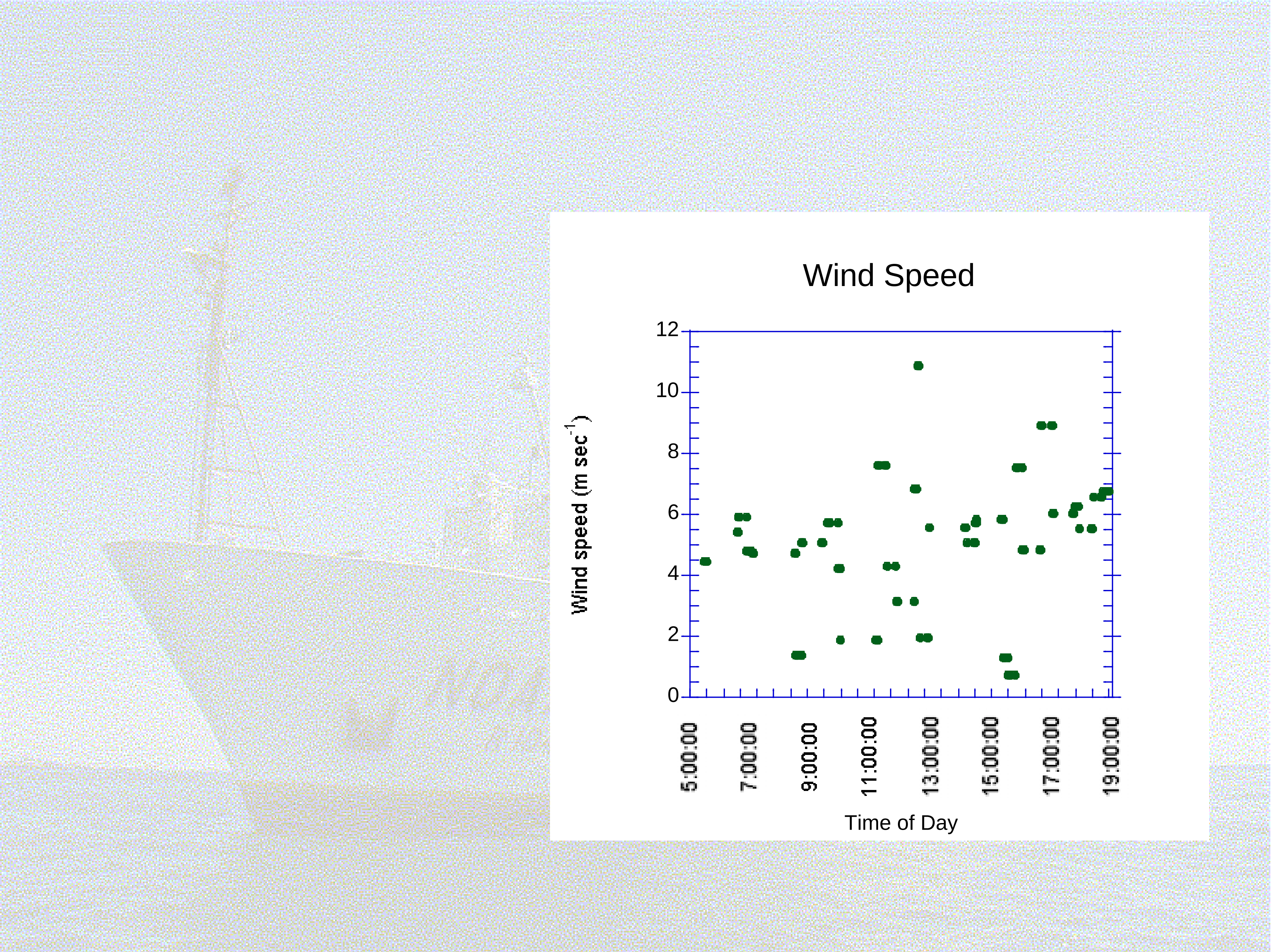
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

U.S. DEPARTMENT OF COMMERCE

and Wynn Norris

- This research is part

surface.ocean us solas lower.atmosphere.study


Wind Speed
Wind speed (m sec-1)
12
10
8
6
4
2
0
5:00:00
7:00:00
9:00:00
11:00:00
13:00:00
15:00:00
17:00:00
19:00:00
Time of Day