

INTRODUCTION

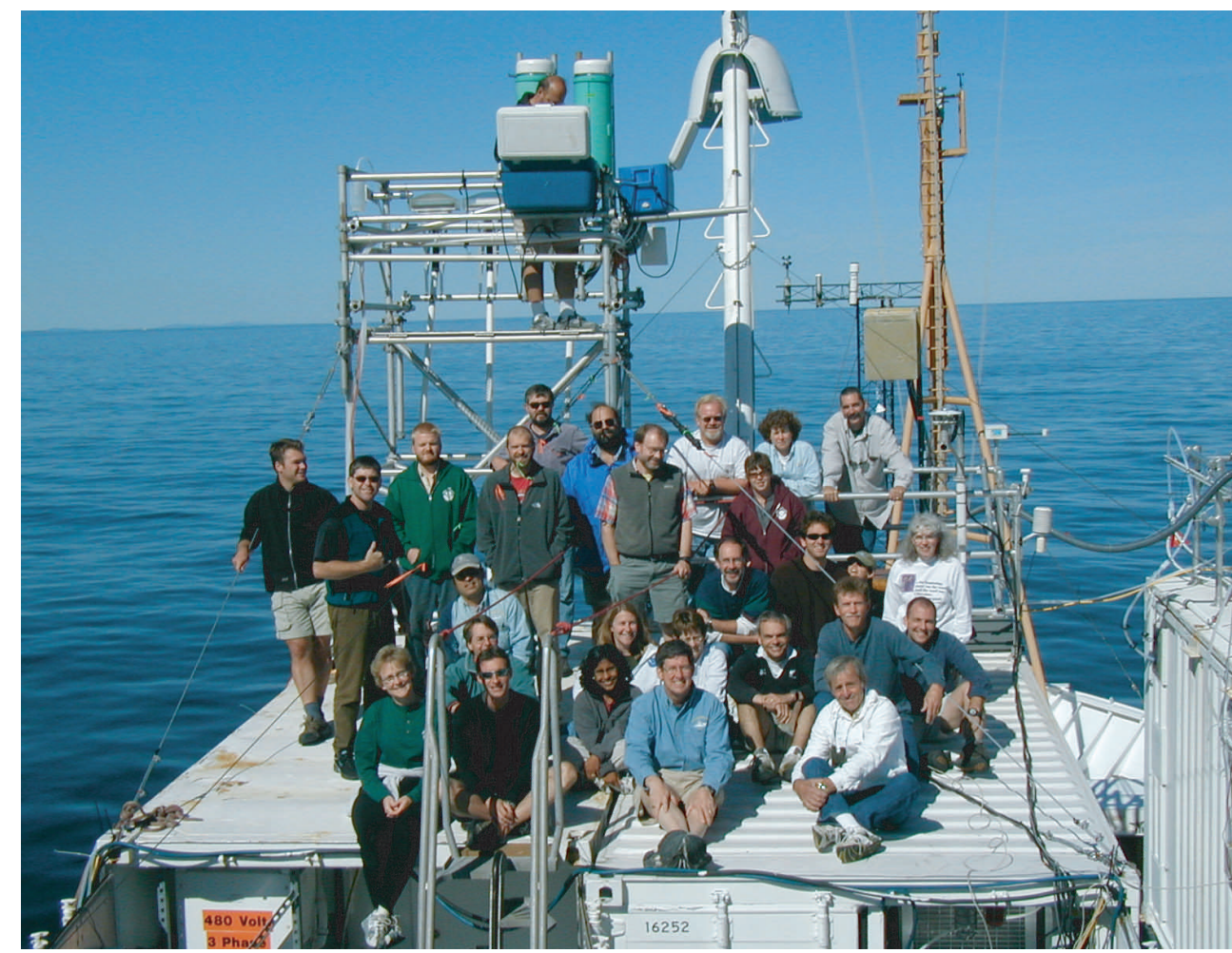
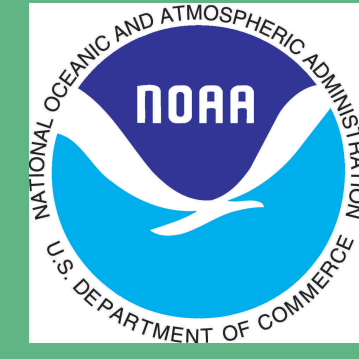
Nitrogen and sulfur emissions from large marine vessels are a significant source of these species to the atmosphere. Since approximately 70% of all ship emissions occur within 400 km of land, marine vessel emissions (MVE) are important to air quality regionally in coastal areas and locally in ports. Sulfur emissions depend on the sulfur content of fuel and nitrogen emissions depend on the vessel engine type. In emissions inventories MVE are calculated from fuel usage and emission factors. The best available emission factors come from a Lloyd's Register of Shipping sponsored emissions research program. Measurements were made of emissions from engines during bench tests and from in-service marine vessels directly at the stack. However, the significance of MVE suggests that additional evaluation of emission factors be conducted.

During the 2002 New England Air Quality Study (NEAQS) measurements were made of MVE off the east coast of the U.S. This poster presents those results and relates them to current emission factor estimates.

MEASUREMENTS OF MARINE VESSEL EMISSIONS

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NEAQS 2002 used a network of ground-based observing sites, the DOE G1 aircraft, and the NOAA research vessel Ronald H. Brown. The ship was equipped to measure a wide variety of gas-phase and aerosol species, meteorological parameters, and vertical profiles of ozone, aerosols, wind, and temperature.

In the summer of 2004 NEAQS will be part of a larger study, called ICARTT, that will examine the transport and transformation of pollutants from North America across the Atlantic Ocean to Europe.



Marine Vessel Emission Characteristics

N emissions: Mostly from combustion (temperature dependent)

S emissions: From fuel S-content (typically <1% to 5% by weight)

C emissions: Virtually complete combustion!! (CO/CO₂ << 1%)

Particulates: Soot; organic (unburned fuel; lube oils); some S

Global N-emissions: 3.08 TgN/yr (~14% of total fossil fuel source)
(~100% of U.S. mobile sources)

Global S-emissions: 4.24 TgS/yr (~5% of total fossil fuel source)
(~20% of global DMS source)

BUT, shipping patterns and activities matter a lot:
MVE are heavily skewed toward the Northern Hemisphere
Meteorology has strong influence on fate of emissions
Emissions at ports (slow-speed; idle) are crucial



Marine Vessel Propulsion Characteristics

Slow-speed diesel: 55% of total fleet: ~58,000 vessels (>95% comm.)
(SSD)
low-grade residual fuels ("bunkers"; high S; cheap!)
power: < 10 MW up to ~100 MW
directly coupled to propeller shaft

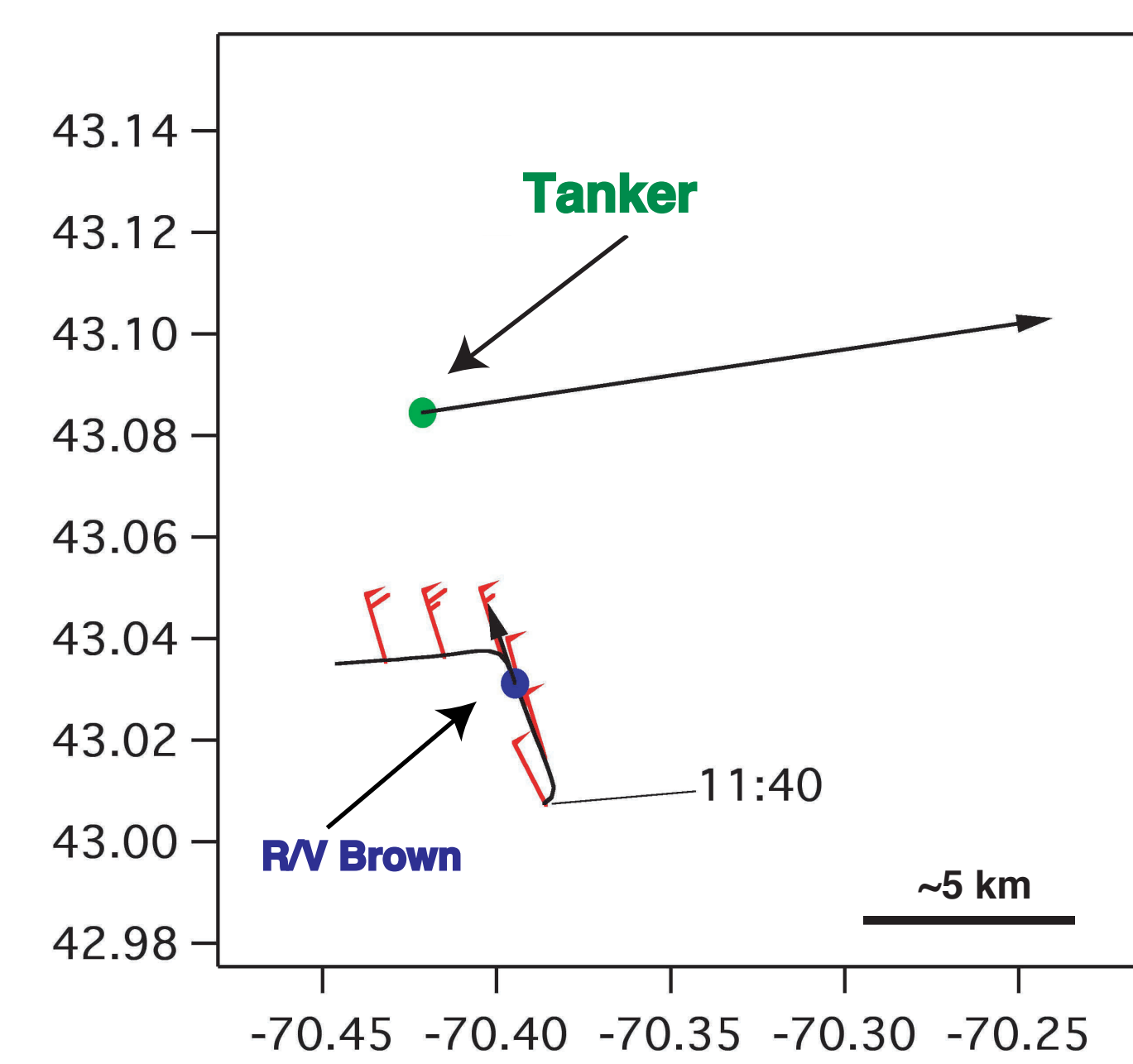
Medium-speed diesel: 40% of total fleet: ~42,000 vessels (40% military)
(MSD)
uses residual or distillate fuels; power: ~1 - 20 MW
diesel-electric - motor powers propeller shaft
coupled via gears to propeller

Steam-turbine: <5% of total fleet: ~5,000 vessels (70% military)
uses distillate fuels (low S; more expensive)
steam generation drives turbine; powers prop.

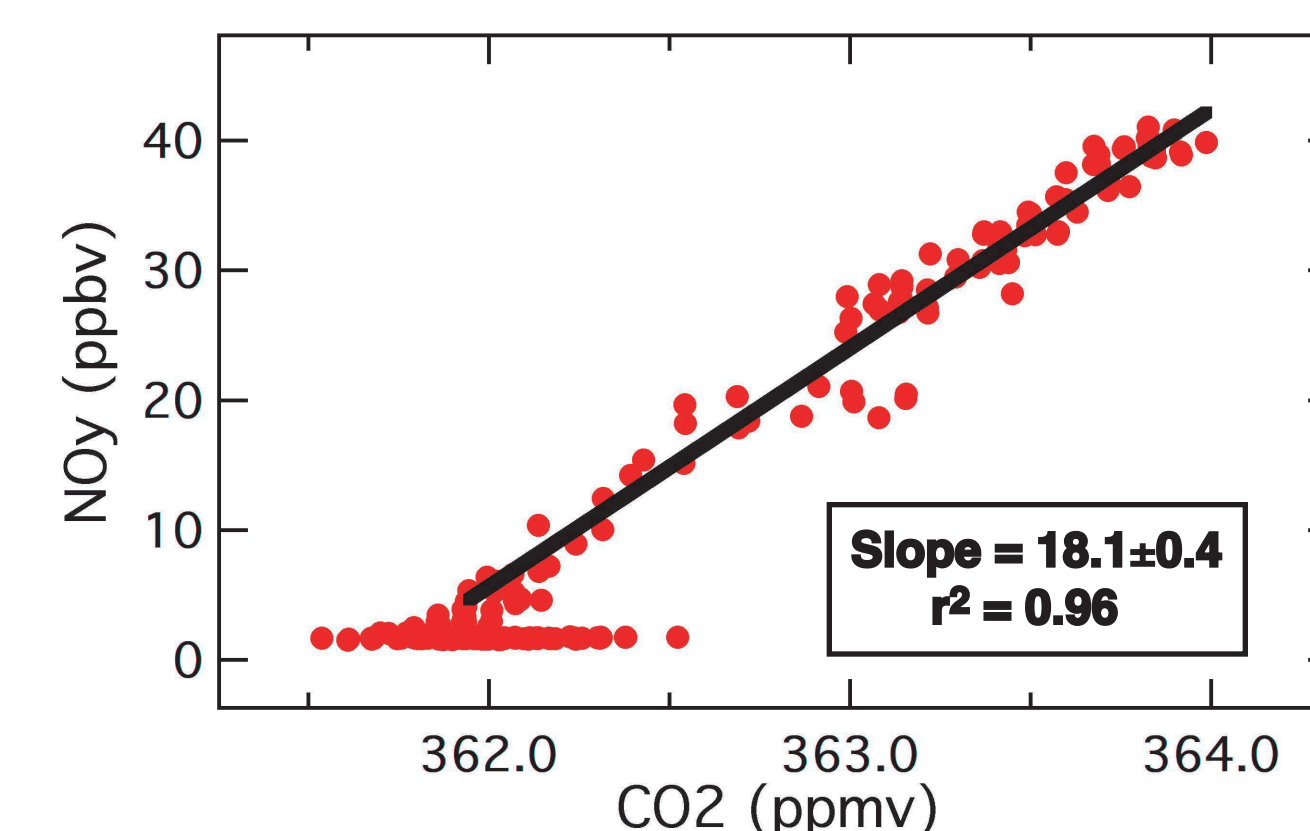
[Ref.: Corbett and Fishbeck, Science, 278, 31 October 1997; and refs]



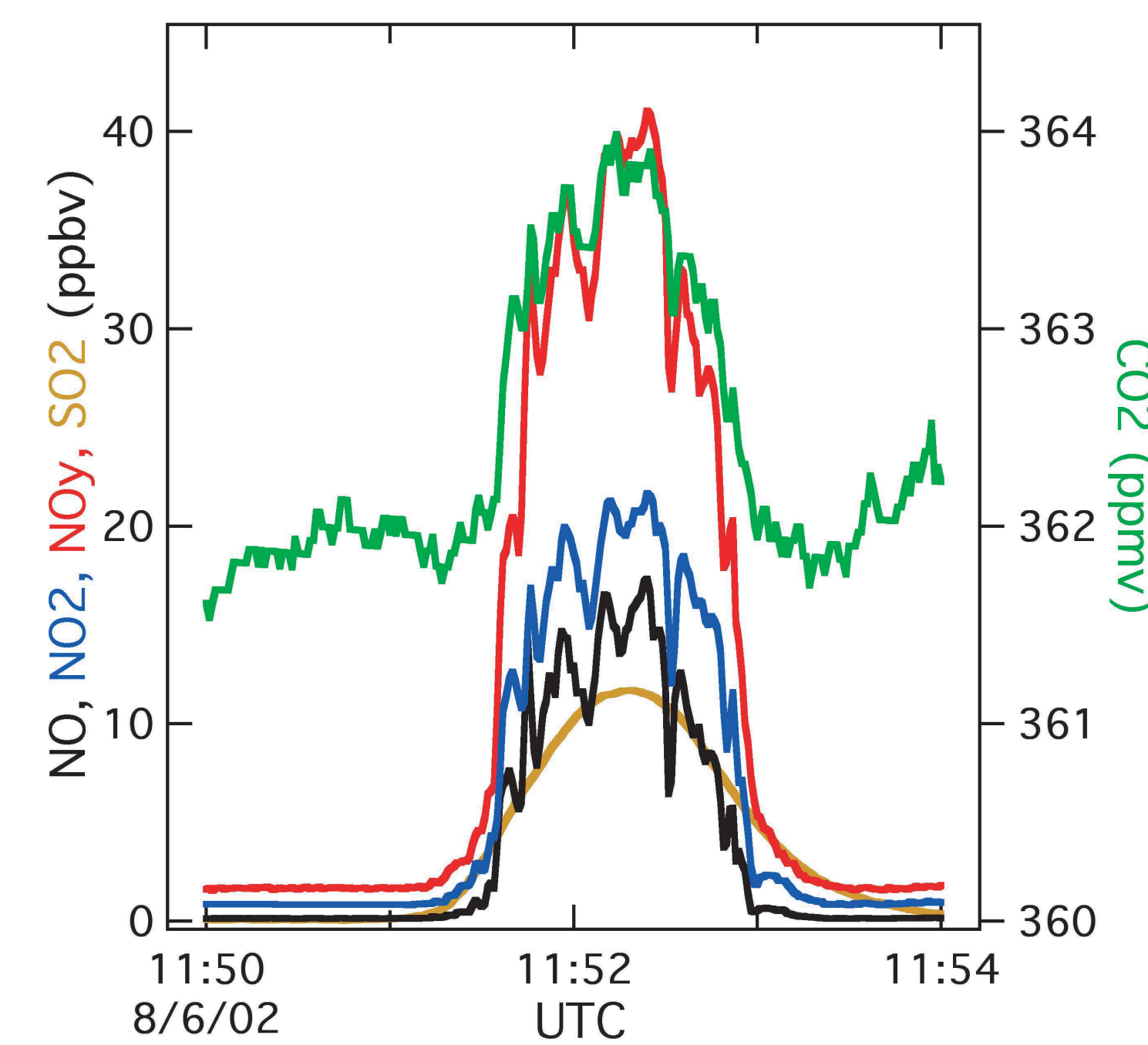
Measurements of NO_y, SO₂, and CO₂ Emissions from a Bulk Tanker



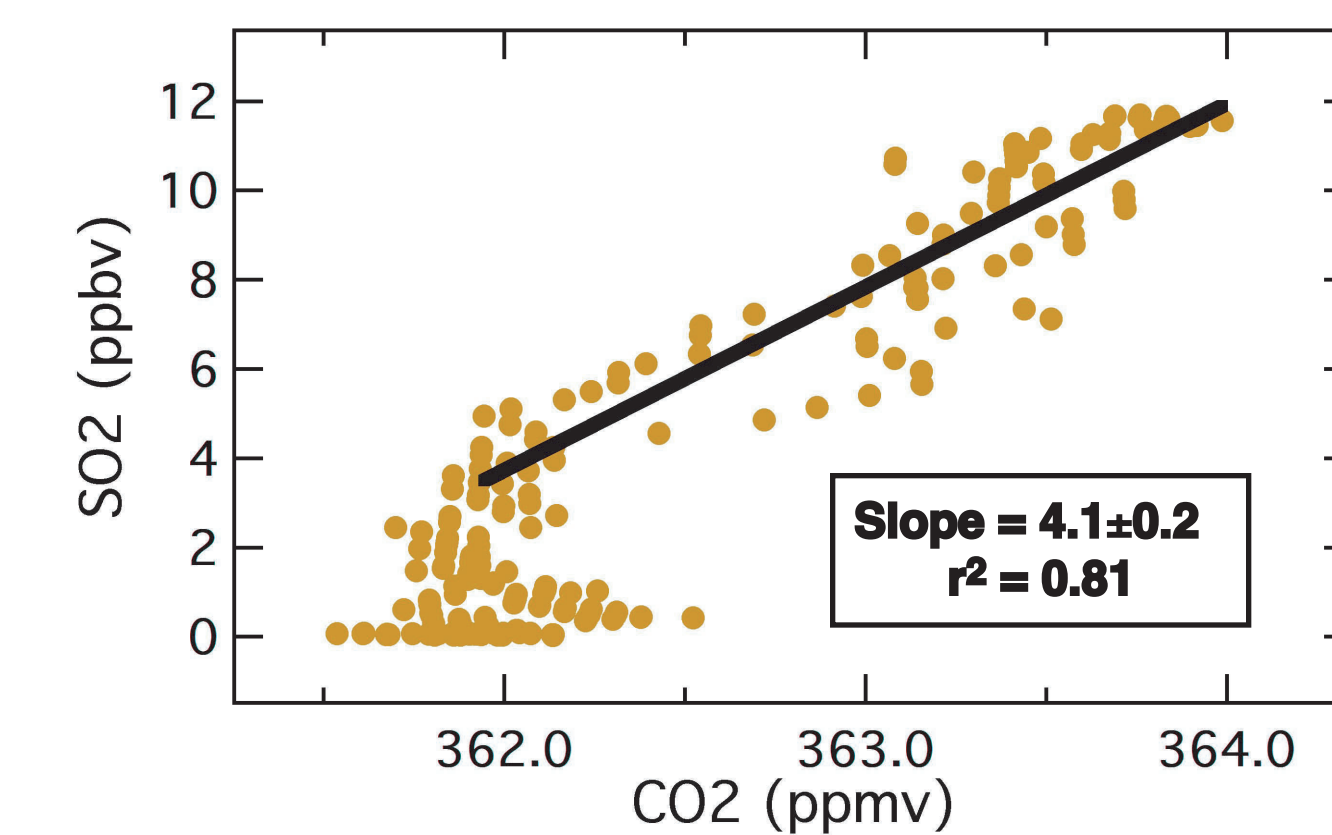
A Canadian tanker was encountered outbound from Portsmouth, NH, on the morning of August 6. The tanker was north of Brown heading east at about 15 kts. The wind was from the north-northwest at about 21 kts. The nearest approach of the tanker to Brown was about 3 nm, so the plume was about 9 minutes old when the measurements were taken.



The slope of the regression between the NO_y and CO₂ data (without background data) allows us to estimate the amount of N emitted relative to CO₂ (i.e., fuel consumed). The fresh nature of the plume means that very little N has been lost (e.g., deposition).



The background air during this encounter was relatively clean, so the plume from the ship exhaust stands out clearly. The data above are 1 second measurements of NO, NO₂, NO_y, SO₂, and CO₂, time-shifted for coincidence. As expected for fresh emissions, the ratio NO_x/NO_y is close to one. The fine structure in the data correlate well for all measurements except SO₂, which is due to slower instrument response.



Though the correlation between SO₂ and CO₂ is not as high as with NO_y, the slope is sufficiently well-defined to provide an estimate of the amount of S emitted relative to CO₂.

Emission Factor Calculations

Emission factors were calculated from the measurements by use of the relationships shown below. The slopes of the regression lines (see plots to lower left) were used with an estimate of the average fuel C content of marine fuel, assuming that all the fuel C was converted to CO₂, that no N or S (or C) is lost in the plume, and that dilution affects all species equally.

Assume average fuel C content: 86±0.5% C or 13.9±0.1 g fuel/mole C
[Average fuel N content: 0.3±0.2%]
[Average fuel S content: 1.5±1.2%]
[Source: Lloyd's Register, 1995]

$$E.F. = \frac{\text{ppmv NO}_y \cdot 46e-3 \text{ kg NO}_x/\text{mole NO}_y \cdot 1000 \text{ kg}}{\text{ppmv CO}_2 \cdot 13.9e-3 \text{ kg fuel/mole CO}_2 \cdot \text{tonne fuel}} = \text{Slope} \cdot 3.31(\pm 0.02)$$

$$E.F. = \frac{\text{ppmv SO}_2 \cdot 64e-3 \text{ kg SO}_2/\text{mole SO}_2 \cdot 1000 \text{ kg}}{\text{ppmv CO}_2 \cdot 13.9e-3 \text{ kg fuel/mole CO}_2 \cdot \text{tonne fuel}} = \text{Slope} \cdot 4.60(\pm 0.03)$$

Marine Vessels: Emission Factor Data

The data below were calculated using the relationships shown above and the measurements from ship encounters that were documented in the ship's log by the bridge crew of Brown. Since we did not have full information for each vessel (e.g., engine type; fuel consumed), we surmise from the SO₂ data that the fishing vessel and the casino boat engines were not the same as the others and are excluded from the average. The entry with the double asterisk is for a plume that coalesced from two vessels. That data point is considered in a separate average.

Date	Time	(per 1000 kg [tonne] fuel)		Vessel type
		kg NO _x	kg SO ₂	
18 Jul	1035	49 (±2)*	~5	Cruise ship
19 Jul	1055	83 (±4)	0.7 (±0.09)	Fishing vessel
30 Jul	2230	75 (±2)	0.7 (±0.04)	Casino boat
6 Aug	1155	60 (±1)*	19 (±1)	Tanker
8 Aug	2230	95 (±4)**	22 (±1)	Container and Freighter
8 Aug	2320	39 (±4)*	6 (±0.5)	Deep-water tanker
8 Aug	2335	67 (±7)*	11 (±2)	Container
9 Aug	0015	41 (±5)*	5 (±0.7)	Container
9 Aug	0115	81 (±7)*	17 (±3)	Freighter
Average		56 ± 16*	11 ± 6	
		62 ± 21**	12 ± 7	

Marine Vessel Emission Factors

Source	(per 1000 kg [tonne] fuel)	
	kg NO _x	kg SO ₂
Lloyd's Register of Shipping, 1995	87 (SSD)	20 X (fuel wt. % S)
Marine Exhaust Emission Research Program	57 (MSD)	
Booz-Allen & Hamilton, 1991	78	22 X (fuel wt. % S)
Inventory of Air Pollutant Emissions from Marine Vessels (EPA; AP-42)		
Environment Canada	39 - 179	4.7 - 64
Port of Vancouver Marine Vessel Emissions Test Program		(calculated)
THIS WORK: Average of 6 ships	56 ± 16	11 ± 6
Range	39 - 95	5 - 22

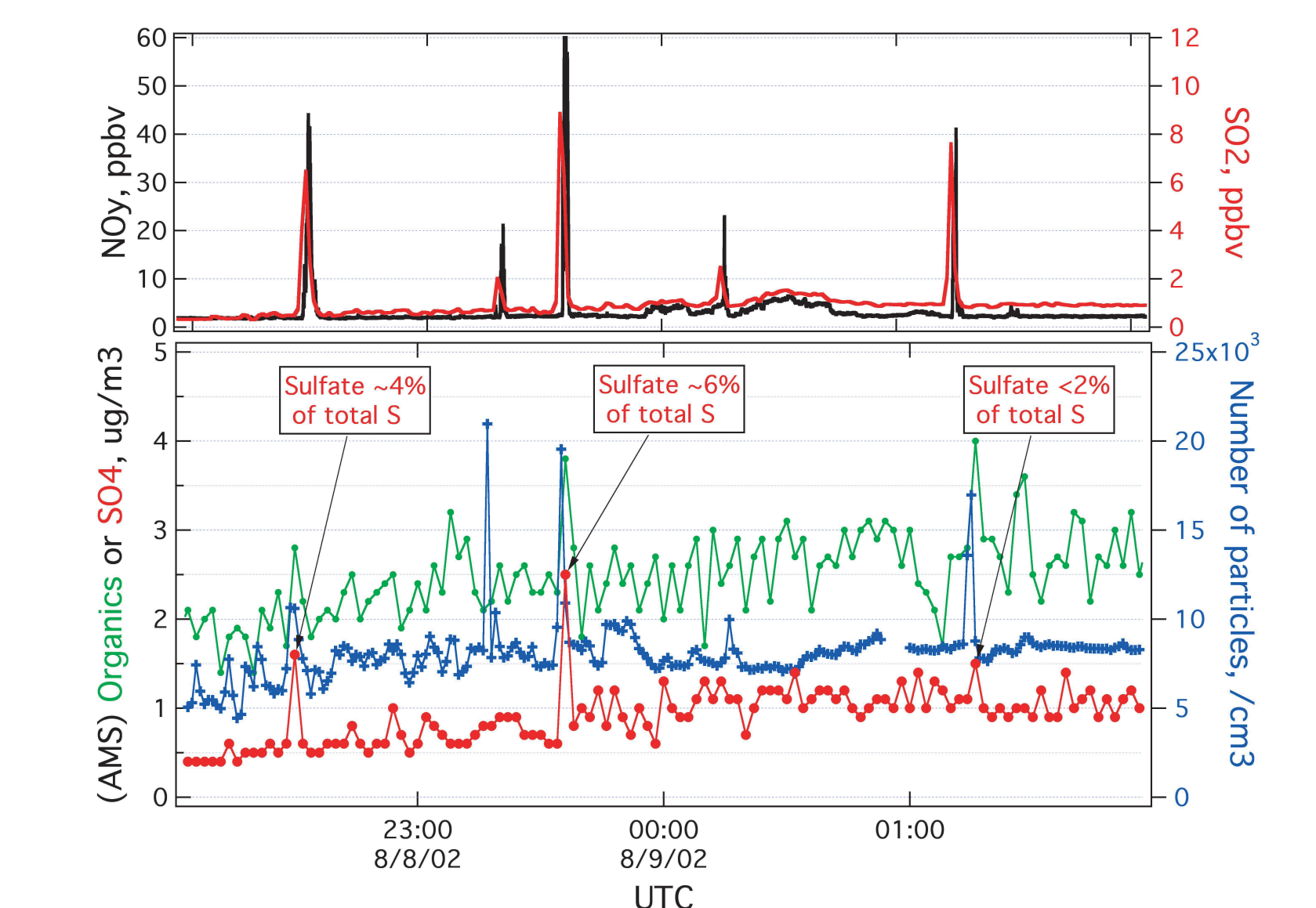
Significance of Emission Factor Measurements

- Emission factors are a key element in emissions inventory development
- emission factors can be a major source of uncertainty
- Measured N emission factors are consistent with literature data:
- our measured factors are appropriate to "underway" conditions (i.e., medium to high engine load)
- need engine/fuel information from each vessel for direct comparison
- N emissions drop significantly for idle conditions: need data here
- Measured S emission factors seem low compared to literature values
- e.g., for fuel with 1% S, calculated emission factor is 20-22
- need fuel S content for each vessel for direct comparison

Acknowledgments

We thank the officers and crew of the NOAA Research Vessel Ronald H. Brown and all of our colleagues on board. We also thank the folks at the University of New Hampshire, especially Mark Twickler, for organizing and hosting the meetings and workshops associated with the New England Air Quality Study.

Particulate Sulfate Emissions



The data shown above were taken south of the sealane in and out of Chesapeake Bay. The top plot shows NO_y and SO₂ from five different vessels, and the bottom plot shows aerosol sulfate and organics data measured with an Aerosol Mass Spectrometer and particle number density. The data traces are slightly offset for clarity. The plume transit times were approximately 20-30 minutes which implies conversion rates of SO₂ to sulfate as high as 18% per hour. The gas-phase SO₂ conversion rate is estimated to be less than ~3% per hour at 2200 UTC and dropping to near 0% after 0030 UTC. Since there were no clouds or fog present during this time, which excludes rapid liquid-phase conversion to sulfate, it is likely that a substantial fraction of the aerosol sulfate in the exhaust plumes was formed at the point of emission. Possible mechanisms for this are SO₃ chemistry in the exhaust gas due to excess O₂ (typically 10-15% excess) or heterogeneous SO₂ conversion on the aerosol surface. There is also a significant organic component to the particles which likely comes from lubrication oils or unburned fuel.

CONCLUSIONS

- Ship-based measurements are an effective means of evaluating emissions of marine vessels under operating conditions
- "Under-way" emission factor measurements are reasonably consistent with literature data
- More data needed at different load conditions (in 2004!!!):
slow speeds; idle ("hoteling")