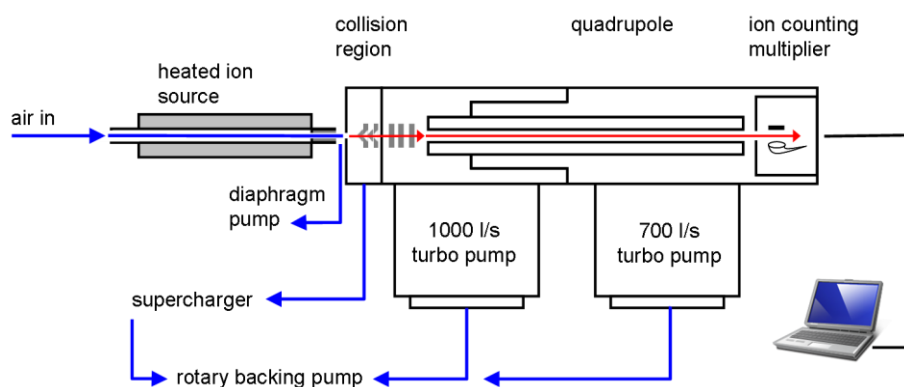


1 Supplementary Materials

2 Atmospheric API-CIMS

3 The atmospheric API-CIMS is a downsized version of the instrument used and described by
4 Marandino et al. (2007). A schematic of the main components is given in Figure S1. The ion
5 source consists of a heated and temperature-controlled glass-lined stainless steel tube
6 containing a radioactive ^{63}Ni foil, as described in Saltzman et al. (2009). Lens voltages for
7 ion optics were supplied by a Gamma custom multichannel DC power supply and the
8 quadrupole supply was an Extrel QPS500 DC/RF power supply and mass command board.
9 Ions were detected using an ion multiplier and discriminator/preamplifier. The primary
10 difference between this instrument and the earlier CIMS instrument is the replacement of a
11 turbo-pumped vacuum stage (1000 L s^{-1} ; 5×10^{-3} Torr) in the vacuum system with a turbo
12 charger/rough pumped (50 L s^{-1} ; 1 Torr) collision chamber. The collision chamber is an
13 Extrel API collision chamber with modified entrance configuration. A custom Labview™
14 program and multichannel A/D interface (NI USB-6343, X Series DAQ) were used to
15 provide the mass command signal and to acquire the ion counts. The same interface was
16 used to acquire the saw tooth synchronizing signal and to output the ion counts as analog
17 signals for logging by the multichannel data logger described above.

18 The gas standard was supplied from a cylinder (11.79 ppm) at a mass flow-controlled flow
19 rate of $3\text{--}6\text{ ml min}^{-1}$, resulting in a d3-DMS level of 440 – 885 ppt in the air stream. The gas
20 standard was delivered using $1/32''$ ID Teflon tubing and a low volume 3-way solenoid valve
21 located at the base of the foremast. Gas flow rates were controlled and logged via a custom
22 PC-controlled 8-channel mass flow controller circuit board.



23
24 Figure S1: mesoCIMS instrument schematic

25 *DMS gas standards*

26 Isotopically-labeled DMS gas standards in the range of 1-10 ppm were prepared by injecting
27 liquid d3-DMS (Cambridge Isotope Laboratory) into dry, evacuated 6 L high pressure
28 aluminum cylinders. The cylinders were pressurized to 1000 psi with N₂. Three cylinders
29 were used to calibrate the API-CIMS instruments on the Knorr_11 cruise. These were
30 calibrated against a temperature-controlled, gravimetrically calibrated permeation tube (Vici
31 Metronics) in the laboratory before and after the cruise and intercompared during the cruise.
32 The gas standard used for atmospheric DMS measurements and the aqueous DMS standard
33 used for seawater measurements were regularly intercompared during the cruise. This was
34 done by stopping the flow of aqueous d3-DMS standard and introducing a gas standard into
35 the air stream from the seawater equilibrator for a period of 5 minutes every 2 hours.
36 Seawater DMS concentrations were calculated using the gas standard assuming that air and
37 seawater were fully equilibrated in the equilibrator. We compared the seawater DMS
38 concentrations from the gas standards (DMS_{gas}) to the adjacent measurements using the liquid
39 standard (DMS_{liq}). The mean ratio of these measurements (DMS_{gas} / DMS_{liq}) was 1.07 ± 0.18
40 ($1\sigma, n=52$). The variance in the ratio includes a contribution from temporal variability in
41 ambient DMS, as the two measurements were offset by several minutes.

42 *DMS Flux Quality Control*

43 DMS flux intervals that met any of the following criteria were excluded:

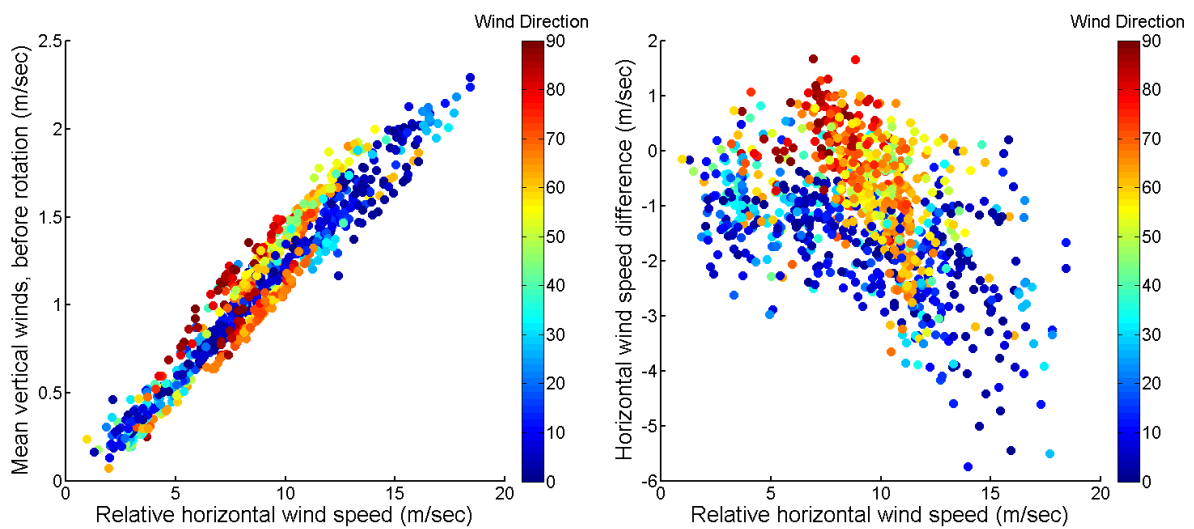
- 44 • $F_{sum} \geq 0.45$ at $f_{norm} = 0.027$ (0.02 Hz at $U_{10m}=10 \text{ m s}^{-1}$)
- 45 • $F_{sum} \leq 0$ at $f_{norm} = 0.014$ (0.01 Hz at $U_{10m}=10 \text{ m s}^{-1}$)
- 46 • $F_{sum} \geq 1.05$ at $f_{norm} = 0.73$ (1 Hz at $U_{10m}=10 \text{ m s}^{-1}$).

47 *Flow distortion*

48 Field measurements and computational fluid dynamics simulations demonstrate flow
49 distortion and vertical displacement of flow fields over the bow of research vessels (Yelland
50 et al., 2002). The magnitude of this effect varies as a function of relative wind direction and
51 can have a significant impact on the measurement of momentum flux or drag coefficients. To
52 minimize this effect, a variety of wind sector limits have been used in previous shipboard

53 eddy covariance gas exchange studies: $\pm 120^\circ$ (Blomquist et al., 2006); $\pm 50^\circ$ (Huebert et al.,
54 2010); and $\pm 60^\circ$ (Marandino et al., 2007; Yang et al., 2011).

55 On Knorr_11, flow distortion was indicated by the presence of an apparent positive mean
56 vertical wind measured by the sonic anemometers after correction for ship motion and sensor
57 orientation but prior to coordinate rotation (Figure S2a). Flow distortion was also indicated
58 by systematic variations in horizontal wind speed measured at various heights on the
59 foremast, reflecting vertical displacement of the winds. Horizontal wind speed differences of
60 up to 4 m sec^{-1} were found between our sensors and the ship's 2D sonic and cup
61 anemometers mounted 2 meters higher on the foremast (Figure S2b). The highest sensor
62 should experience the least flow distortion, so the ship's 2D sonic winds were used to
63 calculate U_{10} . Transfer coefficients for momentum (C_{D10}) and sensible heat (C_{H10}) were
64 computed using fluxes from our sonic anemometers and U_{10} from the ship's 2D sonic winds.
65 Transfer coefficients computed in this way show good agreement with those calculated using
66 the COARE model (Figure 5a).



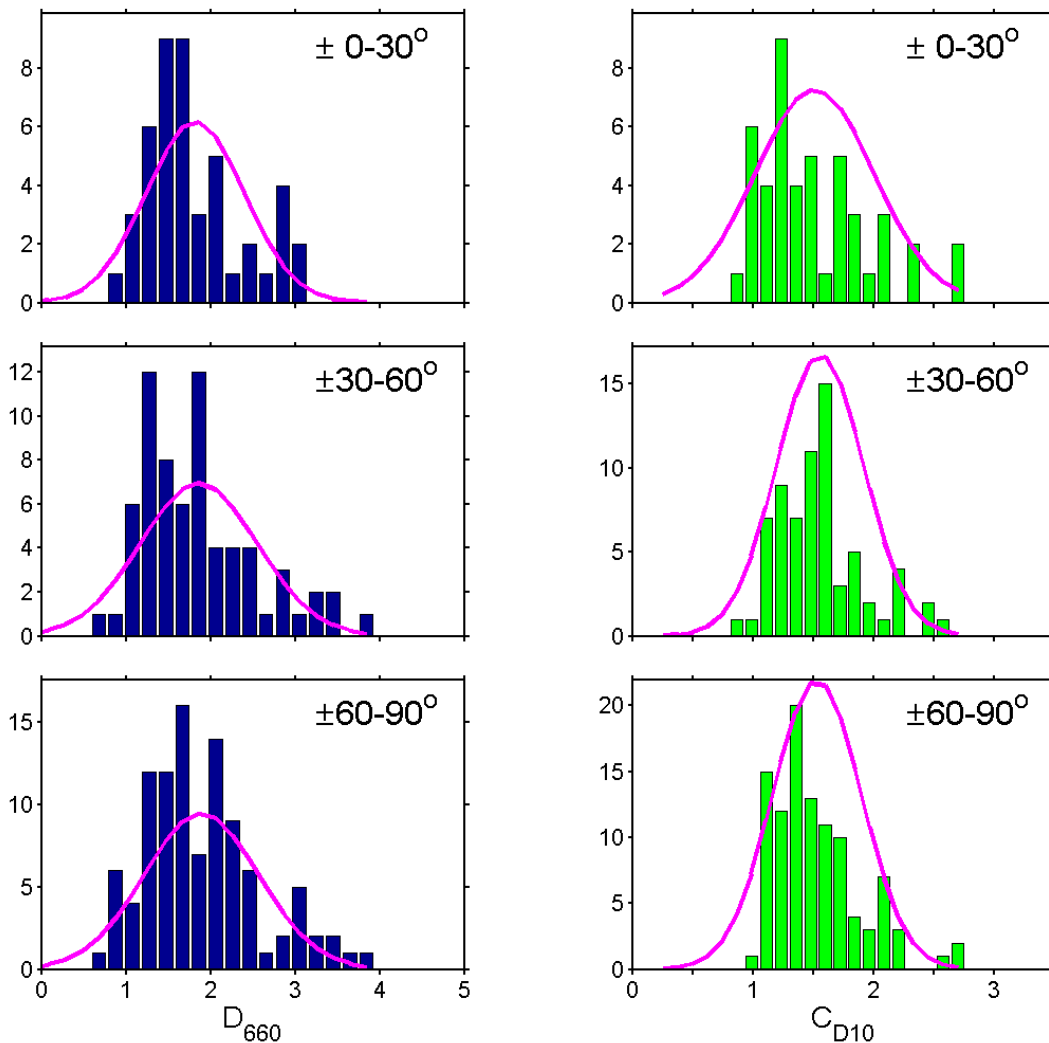
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68 Figure S2: Evidence of flow distortion on the Knorr_11 foremast. Left panel: Mean
69 vertical wind speed before coordinate rotation vs. relative horizontal wind speed, with symbol
70 color indicating apparent absolute wind direction relative to the bow. Right panel: difference
71 in horizontal wind speed. CSAT3 sonic (13.6 m height) minus ship's 2D sonic (15.5 m
72 height), with symbol color indicating apparent absolute wind direction relative to the bow.

73

74 The influence of relative wind direction on momentum flux and gas flux was examined
75 during a portion of the cruise where the relative wind direction varied while wind speed

76 (U_{10n}) and DMS_{sw} remained fairly constant (DOY 184.5-187, $U_{10n} = 9.7 \pm 1.4 \text{ m s}^{-1}$; $DMS_{sw} =$
77 $4.0 \pm 1.9 \text{ nM}$). Frequency distributions of Dalton number ($D_{660} = k_{660}/U_{10n}$) and the drag
78 coefficient ($C_{D10} = w'u'/U_{10n}^2$) for relative wind sectors $\pm 0-30^\circ$, $\pm 30-60^\circ$, and $\pm 60-90^\circ$ are
79 shown for this period in Figure S3. The data show no statistically significant bias between
80 the relative wind sectors for D_{660} or C_{D10} (unequal variance t-test; $\alpha < 0.01$). These results
81 suggest that flow distortion on the R/V Knorr bow mast is a relatively small source of
82 variance in D_{660} and C_{D10} at least during this period of fairly constant conditions. In this
83 paper, data from $\pm 0-90^\circ$ are presented.



84

85 Figure S3: Frequency distribution of D_{660} (left, $\text{cm s hr}^{-1} \text{ m}^{-1}$) and C_{D10} (right) from
86 Knorr_11 DOY 184.5-187. Data is shown for three relative wind direction sectors: $\pm 0-30^\circ$,
87 $\pm 30-60^\circ$, and $\pm 60-90^\circ$.

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