Supplement:

Methods: Analytical Techniques

Samples for the measurement of DMS/P/O concentrations and turnover rates were collected from sack hole brines (Thomas and Papadimitriou et al. 2003), ice covered seawater, surface slush, and melt ponds using a Rule Pump (02 bilge pump 1500GPH). Briefly, sack holes were drilled using an electric ice auger with a coring diameter of ~ 30 cm. The sack holes were covered for 10-20 minutes, so that brine could percolate in from the surrounding ice walls while minimizing exposure full solar irradiance and inhibiting gas exchange. For depth profiles, the auger was lowered to several pre-determined depths below the ice surface. Snow and brine depth (cm) were measured from the sea ice surface with a meter stick. After complete drilling to the bottom of the sea ice, we lowered the pump to the seawater – ice interface to sample seawater immediately below the ice. In one case, we also collected surface seawater (~5 m depth) using the research vessel's underway seawater system. All samples were transferred into UV transparent (UVT), gas tight Welch Fluorocarbon 0.005" PFA bags, the headspace was removed, and the bags were clamped shut with Teflon closures. Samples were placed in opaque plastic bags and taken back to the shipboard laboratory for analysis within one hour of collection. Prior to analysis, samples were stored at 4˚C.

Ancillary measurements were made on ice cores drilled within <1m from DMS/P/O depth profile cores. Chl *a* was measured fluorometrically [Holm-Hansen et al. 1965] using a Turner Fluorometer 10-AU (Turner Designs, Inc.) in triplicate subsamples from 10cm ice core sections (7cm diameter), which were thawed in the dark in 2L of 0.2 mm filtered seawater (Arrigo et al., 2003). Samples were filtered onto 25mm GF/Fs, and the

filters were placed in 5mL of 90% acetone for 24 h extraction in the dark at 4ºC. Filtration volumes ranged from ~25ml to 250ml, depending on the biomass of samples. Chl *a* concentrations from depths ≤ the sack hole brine depth were averaged for comparisons between Chl *a* levels with DMSPt because sackhole brine percolates from overlying and adjacent sea-ice brine channels. Ice temperature was measured immediately following core extraction on the ice and brine salinity was measured on board using a refractometer.

The analysis of DMS, $DMSP_t$, $DMSP_d$ and $DMSO_t$ concentrations was conducted using a purge and trap gas chromatographic separation method, coupled to a capillary inlet mass spectrometer (PT-CIMS). Briefly, 30 ml subsamples were transferred from the Teflon bags into gas tight vials with Teflon-faced butyl seals. The vials were connected to a 16-position manifold valve (VICI Valco Instruments) and sequentially sparged for 5 min at a rate of 450 ml min^{-1} with UHP He to extract DMS onto a Carbopack-X trap held at room temperature. When the sparging was complete, the trap was rapidly heated to ~210˚C to desorb DMS onto a fused capillary column. The effluent from the column was introduced, via capillary bypass inlet, into the electron impact ion source of a quadropole mass spectrometer (Hiden Analytical HAL 301), for detection using a secondary electron multiplier, with a voltage gain of 950 V. DMSP samples were analyzed after purging background DMS out of solution for ~10min with 450ml/min of UHP He (until no DMS remained) and a subsequent > 6 hour alkaline hydrolysis to DMS in 1M KOH. Samples for $DMSP_d$ determination were gently (~15 ml min-1) syringe filtered (Acrodisc 0.2μm) following the procedures described by [*Kiene and Slezak*, 2006] to minimize cell lysis.

46 $DMSO_t$ concentrations were measured using $TiCl_3$ reduction method to convert DMSO to
47 DMS on samples stored at -20 ˚C for 6 weeks according to Kiene and Gerard [1994].

48 Unequal variance t-tests on the ranks (rather than Student's t-tests or Mann-Whitney U
49 tests) were used to evaluate the difference between DMS/P/O concentrations in sea-ice
50 and in ice-covered seawater because histograms of DMS/P/O data across the SIZ showed
51 considerable skew and unequal variances between the groups [*Ruxton*, 2006]. We
52 conducted four separate tests on the ranks of DMS, $DMSP_t$, $DMSP_d$, $DMSO_t$ across these
53 two groups, and thus adopted an alpha of 0.001 for hypothesis testing. In addition to
54 Pearson correlations, we used two multiple regressions between concentrations of
55 DMS/P/O and ancillary parameters to probe for patterns in the observed variance: we
56 regressed DMS against $DMSO_t$ and $DMSP_t$, and we regressed $DMSP_t$ against Chl *a* and
57 depth.

58 We quantified the rates of key production and consumption pathways in the DMS
59 cycle using a multi-isotope tracer approach in sea ice brines (Fig S2). Sack hole brine
60 samples were amended with deuterium-labeled dimethyl $^2H_3$-DMS (CDN Isotopes, 99%
61 purity), $^2H_6$-$DMSP_d$ (synthesized from $^2H_3$-DMS, CDN Isotopes, 99% purity) and Fluka
62 3-bromopropionic acid using the method of Challenger and Simpson (1948) (*Dacey and*
63 *Stefels*, 2005), and $^{13}C_2$-$DMSO_d$ (Icon Isotopes, 97% purity). Tracers were added to
64 obtain final concentrations ~10% of natural concentrations. All tracers were added
65 simultaneously into duplicate or triplicate experimental bags, which were incubated for 3-
66 4 hours outside in coolers packed with ice to maintain in situ temperatures (-1°C). We
67 used various layers of neutral density screening in addition to snow cover (mimicking *in*

68 *situ* thickness) to reduce ambient irradiance in the coolers to levels similar to those at
69 various depths within the ice.
70 We replicated *in situ* temperatures and irradiance levels as closely as possible during
71 these incubations to examine natural rates of DMS cycling, although it is possible that
72 certain phytoplankton and larger organisms that adhere onto the sidewalls of sea ice brine
73 channels may have been under sampled during our incubations (Thomas and
74 Papadimitriou et al. 2003). Nevertheless, we deemed sack hole brine sample collection
75 for these incubations our best option for these incubations. Slowly melting of sea ice
76 (Arrigo et al., 2003), would likely alter the rates of DMS consumption and production by
77 influencing microbial dynamics, and promoting gas exchange. Similarly, sample
78 collection based on ice crushing (*Tison et al.*, 2010), perturbs the ecosystems maintained
79 within brine channels.
80 During experiments, subsamples were extracted from each bag with 60 ml syringes
81 every ~30-40 minutes, filtered with sterile 0.45 mm syringe filters into 50 ml amber
82 serum bottles, capped with Teflon-faced butyl septa and loaded onto a multiport valve for
83 analysis as described above. Between uses, UVT incubation bags were rinsed once with
84 ~10% HCL, fresh MQ, and twice with each sample to avoid contamination. In addition,
85 serum bottles used for analysis were soaked in ~5% HCl for ~24 hrs, rinsed with fresh
86 MQ, and dried in a muffled heater at 125°C for ~1hr prior to use [*Kiene and Gerard*,
87 1994].
88 DMS produced from DMSP and DMSO was analyzed as described above.
89 Concentrations of isotopically-labeled species ($^{13}C_2$-DMS, $^{2}H_3$-DMS, and $^{2}H_6$-DMS)
90 were calculated by integrating chromatogram signals of different isotopic DMS species

measured by peak jumping the mass spectrometer between m/z 62, 64, 65 and 68. Final concentrations were calculated from standard curves using known concentrations of both unlabeled and labeled DMS with a working background detection of 0.1nM for 30 ml samples. Integrated peak areas were converted to DMS concentrations using standard additions of DMS prepared in deep seawater (>1500m), with intermediate dilutions prepared in milli-Q water. Tracer production and consumption rates were quantified with linear regressions of averaged concentrations for 2-3 replicates (one for each bag that was incubated) over 4-5 time points and converted to nM d^{-1}. Rates that were not statistically different from 0 (with $p>0.1$) were considered below the detection limit. To scale the rates of tracer consumption and production to *in situ* values, the calculated rates were divided by the concentration of added tracers (yielding first order rate constants, d^{-1}) and multiplied by the concentration of the natural DMS /$DMSP_d$ /$DMSO_d$ pools respectively. Concentrations of unlabeled $DMSO_d$ and DMS were measured at the start of each incubation, and $DMSP_d$ concentrations were inferred from our depth profile measurements. Net DMSO turnover rates were calculated from the difference in $^{13}C_2$-DMSO concentrations at the beginning and end of the incubations, and converted into nM/day. DMSO-DMS yields were then estimated as the fraction of DMSO converted to DMS. The calculated DMSO-DMS yield are subject to significant uncertainty due error propagation and analytical variability. The rates of change of deuterated and ^{13}C-labeled stable isotope tracers are assumed to be representative of natural DMS cycling because isotope discrimination between species of DMS, favoring lighter isotopes, appears minimal (<10%; Asher unpublished data).

114 **References**

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Supplementary Figures

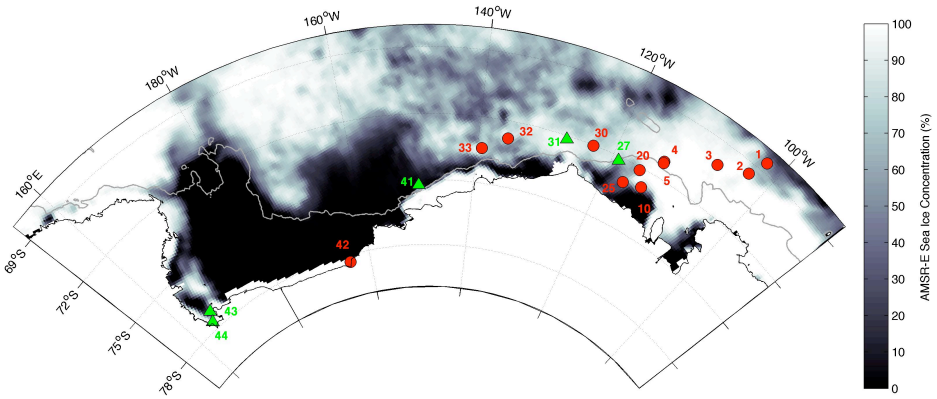
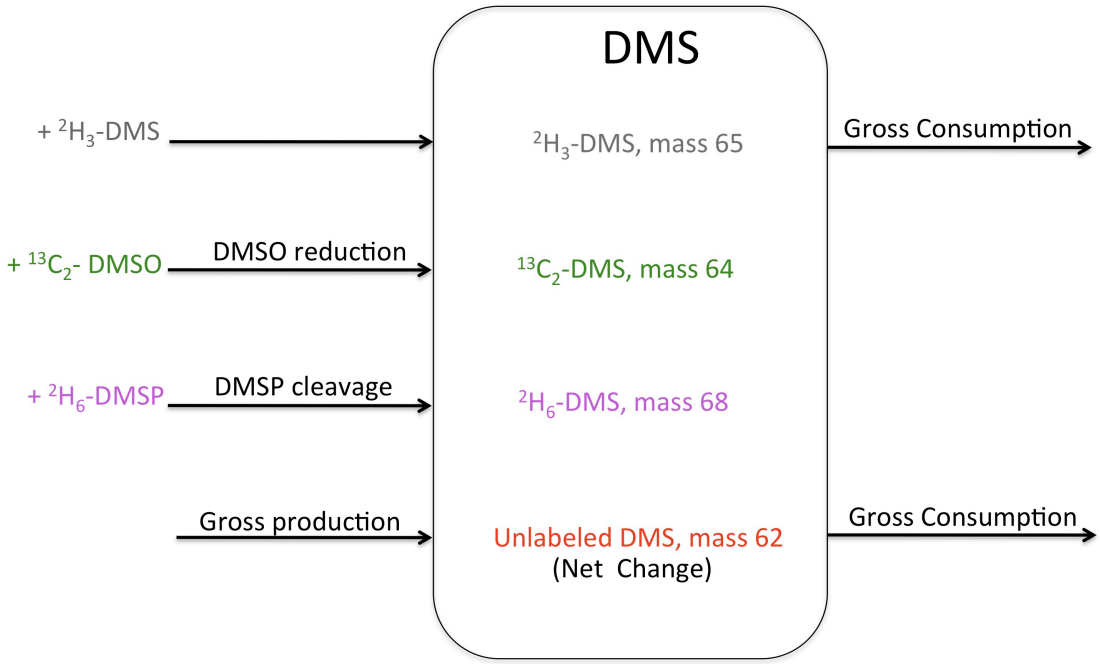


Figure S1. Map of sampling stations across an east to west transect through the SIZ of the Amundsen Sea and Ross Sea between December 16, 2010 and January 10, 2011.

153 Station numbers appear next to station locations. Green triangles denote stations where
154 isotope tracer experiments were conducted in addition to DMS/P/O measurements. Red
155 circles denote stations where only concentration measurements were made. The
156 background black and white color scale shows the mean sea ice concentrations during the
157 period of our survey derived from the AMSR-E satellite [Cavelieri et al. 2004].



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159 Fig. S2. Schematic diagram of the DMS tracer method. Tracers, shown in gray, green,
160 and purple are added to the ambient DMS, $DMSO_d$ and $DMSP_d$ pools, respectively, and
161 detected in the in DMS pool. Labeled black arrows denote measured production and
162 consumption processes affecting each isotopic mass of DMS.

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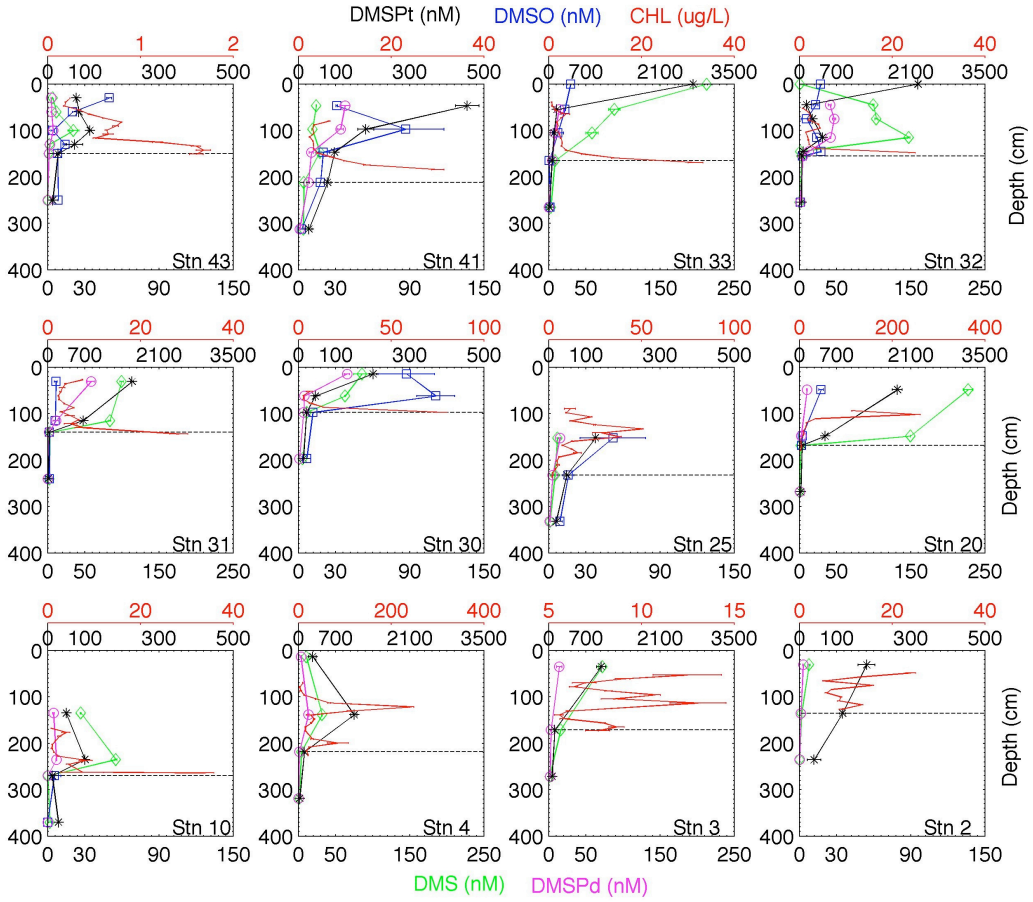

Fig. S3. Depth profiles of methylated S compounds at 12 sea ice stations with chlorophyll *a* concentrations (in red) for comparison. Blue squares and lines denote $DMSO_t$ concentrations, while black stars represent $DMSP_t$ (plotted along the top *x*-axis). Green diamonds and lines represent DMS and magenta circles represent $DMSP_d$, which are plotted along the bottom *x*-axis. Dashed horizontal lines on the plots show the sea-ice/seawater interface, and station numbers are marked in the bottom right of each subplot. Note that all subplots do not have identical *x*-axes.

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