Supplementary Materials

Sea-Air fluxes of dimethyl sulphide and methanethiol from mesocosm studies of natural seawaters from the South-West Pacific

M. Rocco[1,2*], E. Dunne[3], A. Saint-Macary[4,7], M. Peltola[1], T. Barthelmeß[5], N. Barr[4], K. Safi[4A], A. Marriner[4], S. Deppeler[4], J. Harnwell[3], A. Engel[5], A. Colomb[1], A. Saiz-Lopez[6], M. Harvey[4], C. S. Law[4,7], and K. Sellegri[1]

[1] Université Clermont Auvergne, CNRS, Laboratoire de Météorologie Physique (LaMP), 63000, Clermont-Ferrand, France
[2] Now at Instituto de Astronomia, Geofísica e Ciências Atmosféricas/IAG - Universidade de São Paulo - Laboratório de Estudos Ambientais/IPA, São Paulo, Brazil
[3] CSIRO Ocean & Atmosphere, Aspendale, Australia
[4] National Institute of Water and Atmospheric Research, Wellington, New Zealand
[4A] National Institute of Water and Atmospheric Research, Hamilton, New Zealand
[5] GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany
[6] National Center for Atmospheric Research, NCAR, Boulder, USA
[7] Department of Marine Science, University of Otago, New Zealand

Correspondence to: Karine Sellegri (karine.sellegri@uca.fr); Manon Rocco (rocco.manon@gmail.com)

Supplementary methods:

We analyzed the seawater biogeochemistry for Dissolved Organic Carbon (DOC) composition, including Amino Acids, Fatty acids, Chromophoric and Fluorescent DOM, and phytoplankton speciation using Flow Cytometry, optical microscopy and Flowcam. Further details of these seawater measurements are provided in Sellegri et al. (2022) and in the supplementary of this paper.

Phytoplankton community structure was determined for cells >5 µm using a Flowcam (Fluid Imaging Technologies Inc). A sample of 250 mL of seawater was filter concentrated using a 47-mm diameter 3-µm polycarbonate filter to 10 mL final volume and stored at 4 °C until analysis. One mL of 25 times concentrated seawater sample was run through a 80-µm depth Field of View flow cell (FC80FV) at 0.050 mL min^{-1} and 20 frames per second, with an imaging efficiency of 61.9 ± 2%. Images were taken using a 10 objective on AutoImage mode. Total run time for each sample was 20 min. Images were classified into cell size and class groupings using VisualSpreadsheet v4.16.7 software, by size category (<10 µm; 10 to 20 µm; 20 to 50 µm and >50 µm), and the results given as total phytoplankton biovolume of each size class.

For microscopic analysis of phytoplankton community composition, 500 mL of seawater was preserved at 1% (final concentration) Lugol's iodine solution, with samples stored at room temperature in the dark. Phytoplankton community composition and cell numbers for phytoplankton >5 µm were determined using optical microscopy, following the method described in Safi et al. (2007) and references herein. Briefly, 100 mL subsamples were settled for 24 hours and the supernatant then carefully syphoned with 10 mL transferred to Utermohl chambers and resettled (Edler and Elbrächter, 2010). Where possible, all abundant organisms were identified to genus or species level before being counted. Phytoplankton biovolume estimates were calculated from the dimensions of each taxa and approximated geometric shapes (spheres, cones, ellipsoids) initially following Olenina (2006). The biovolumes were subsequently used to calculate cell carbon (mg C m^{-3}) using equations from the literature; Olenina (2006) and Montagnes and Franklin (2001) for diatoms, and Olenina (2006) and Menden-Deuer and Lessard

(2000) for dinoflagellates and nanoflagellates. Menden-Deuer and Lessard (2000) was also applied to other low biomass unidentified groups referred to as small flagellates.

For DMSw and DMSP measurements, seawater was sampled in 125 mL amber bottles. DMSw was analysed following sampling. The DMSw samples were injected through a 25-mm glass microfiber filter (GF/F) into a 1-mL loop, before transfer to a silanized sparging tower, where the sample was sparged for 5 minutes with N_2 at a flow rate of 50 mL min^{-1}. Nafion® dryers removed the water vapor from the gas samples before DMS preconcentration at 110 ℃ on a Tenax® trap. The trap was then heated to 120 ℃ to release the DMS onto an Agilent Technology 6850 Gas Chromatography coupled to an Agilent 355 Sulfur Chemiluminescent Detector (GC-SCD). The daily sensitivity and detection limit of the detector were confirmed using VICI® methyl ethyl sulfide and DMS permeation tubes. The average detection limit during the voyage was 0.14 (± 0.03) pgS sec^{-1}. For total DMSP measurements, 20 mL glass vials were filled with seawater and two pellets of sodium hydroxide added before gas-tight sealing the vials, which were stored at ambient temperature in the dark. DMSP was analysed one day after sampling using the same semi-automated purge and trap system followed by GC-SCD, as described above. A wet standard calibration curve was made daily from a stock solution of DMSP diluted in Milli-Q® water, with calibration concentrations ranging from 0.1 to 95 nmol L^{-1}. These were decanted into 20 mL gas tight glass vials, hydrolysed with two pellets of sodium hydroxide and then injected into the sparging unit and processed as with the samples.

Supplementary references:

Edler, L. and M. Elbrächter (2010). "The Utermöhl method for quantitative phytoplankton analysis." Microscopic and molecular methods for quantitative phytoplankton analysis 110: 13-20.

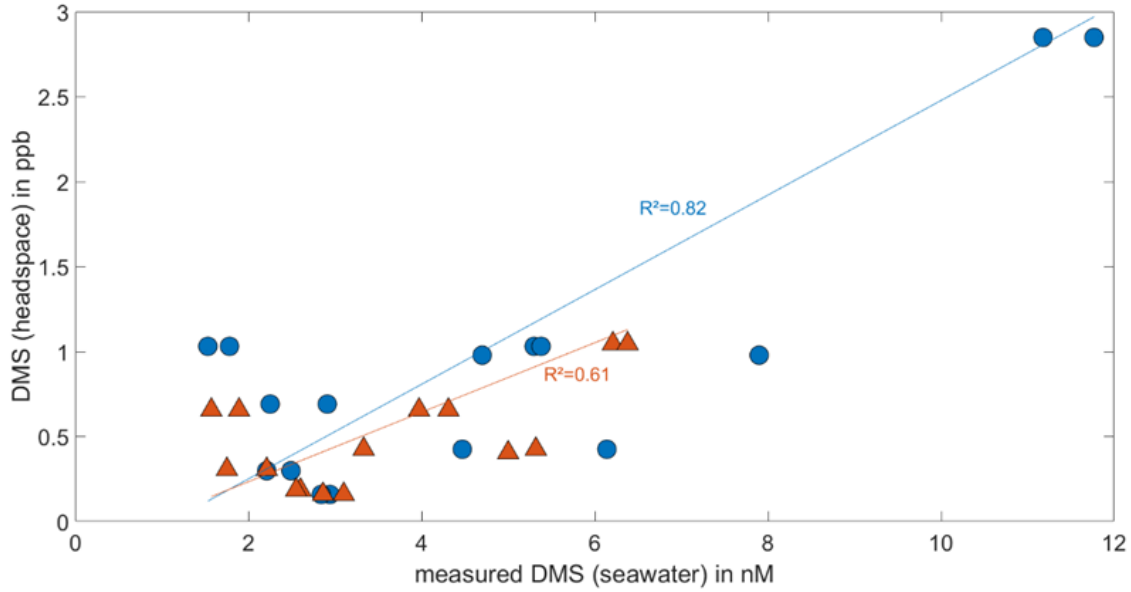
Menden-Deuer, S. and E. J. Lessard (2000). "Carbon to volume relationships for dinoflagellates, diatoms, and other protist plankton." Limnology and Oceanography 45(3): 569-579.

Montagnes, D. J. S. and D. J. Franklin (2001). "Effect of temperature on diatom volume, growth rate, and carbon and nitrogen content : Reconsidering some paradigms." Limnology and Oceanography 46(8): 2008-2018.

Olenina, I., et al. (2006). Biovolumes and size-classes of phytoplankton in the Baltic Sea. HELCOM Baltic Sea Environment Proceedings. 106: 144.

Safi, K. A., et al. (2007). "Microzooplankton composition, biomass and grazing rates along the WOCE SR3 line between Tasmania and Antarctica." Deep Sea Research Part I: Oceanographic Research Papers 54(7): 1025-1041.

Supplementary figures:



ASIT-control : slope = 0.28 ± 0.41; intercept = -0.31 ± 0.08; r = 0.82

ASIT-O_3: slope = 0.21 ± 0.32; intercept = -0.17 ± 0.08; r = 0.61

Figure S. 1: Reduced major axis (RMA) of measured ASITs DMS (seawater) vs. DMS (headspace).

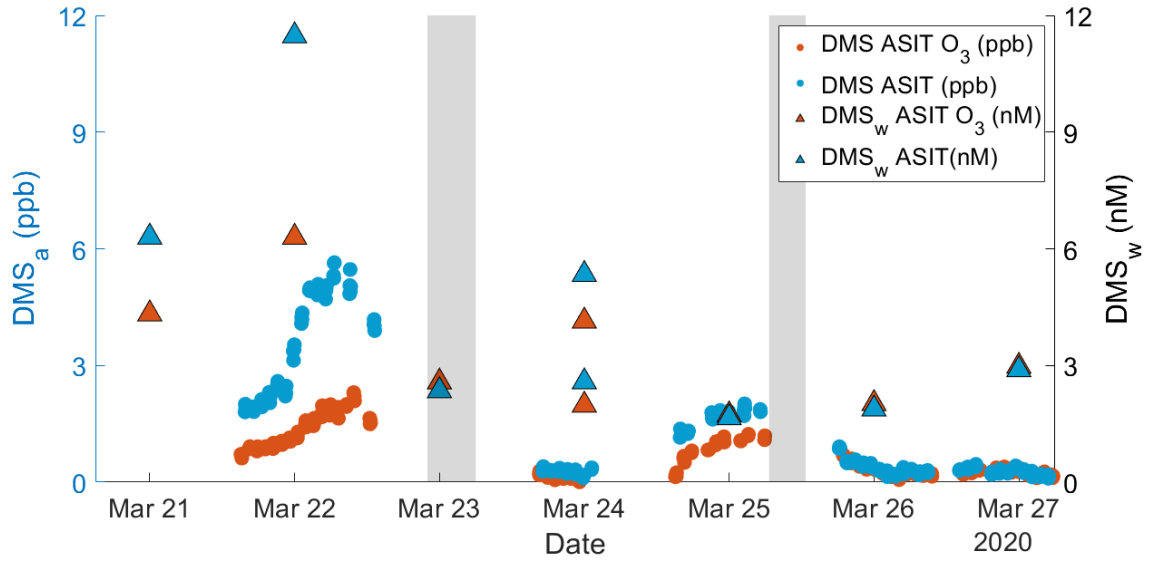


Figure S.2: Concentration of DMS in seawater (nM) and air (ppbv) in ASIT-control (blue) and ASIT-O_3 (orange). ~20min average DMS headspace mixing ratios (ppbv, dots) in ASIT-control (blue) and ASIT-O_3 (orange) and dissolved DMS in ASITs seawater samples(nM, triangles).

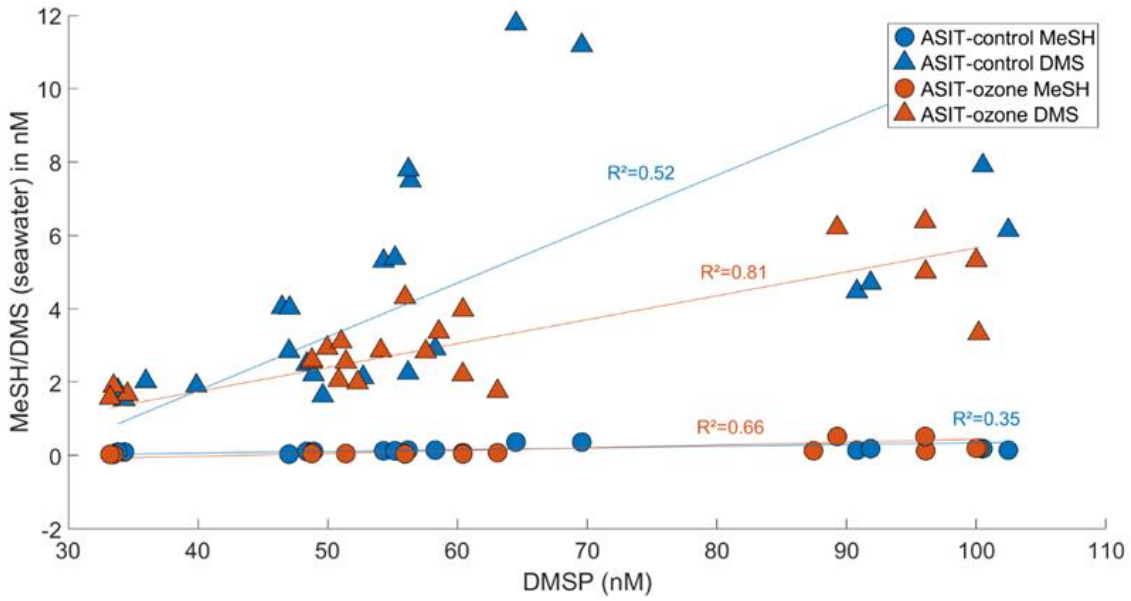


Figure S. 3: Measured ASITs DMSP (seawater) versus measured DMS (seawater) and calculated MesH (seawater).

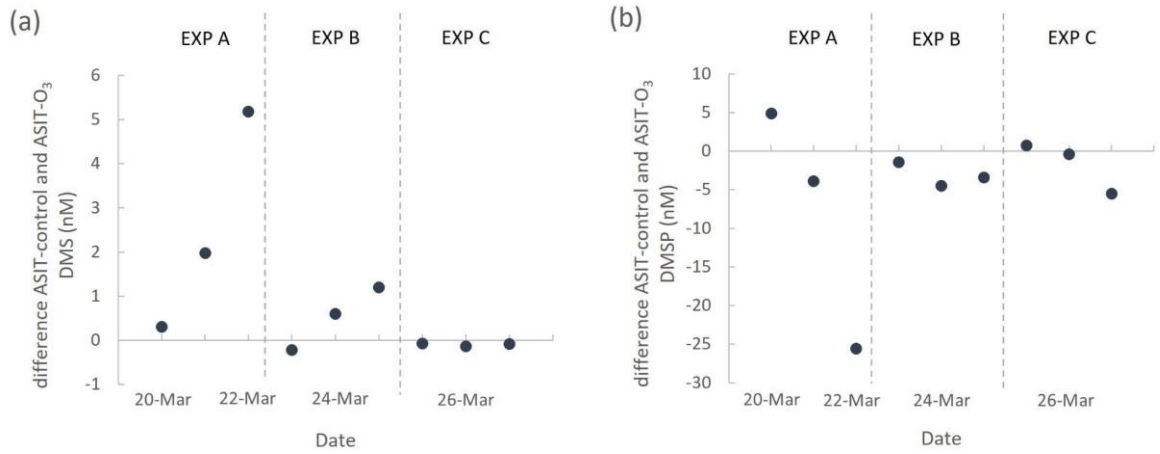


Figure S.4. Difference in concentration of DMS and DMSP in seawater (nM) between ASIT-O_3 and ASIT-control. Note the inverse scale for DMSP.

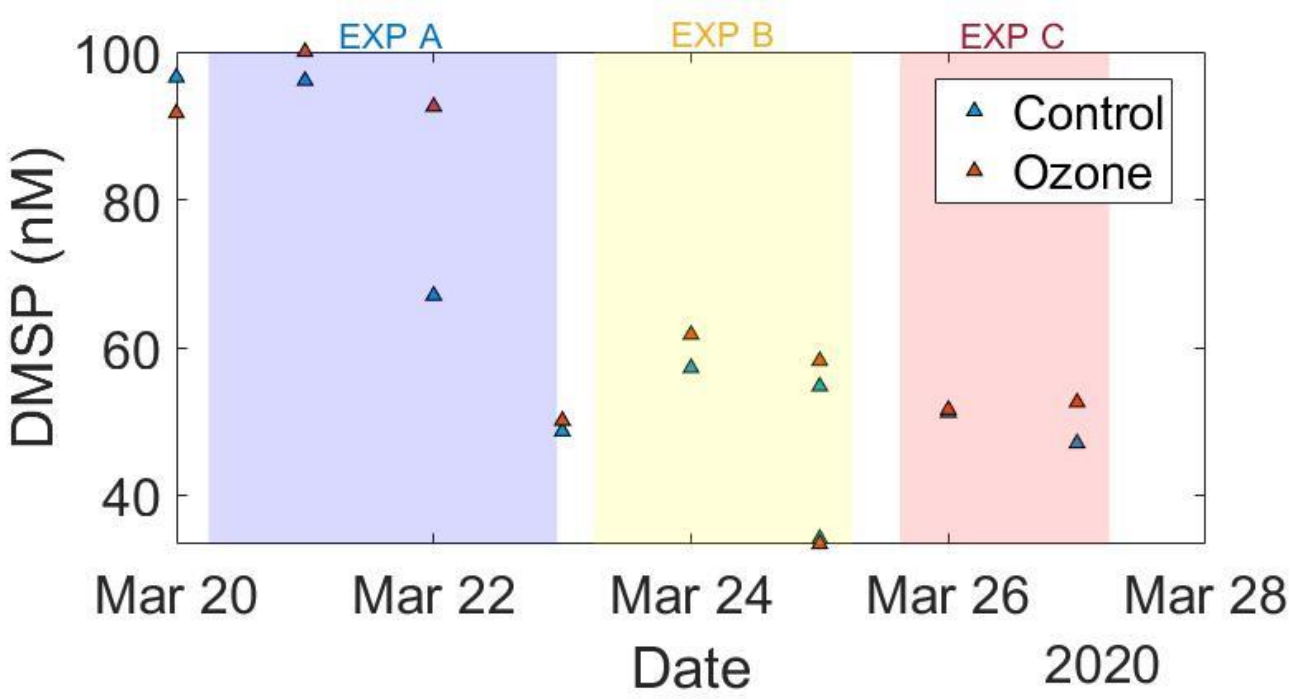


Figure S.5: Concentrations of DMSP in seawater (nM).

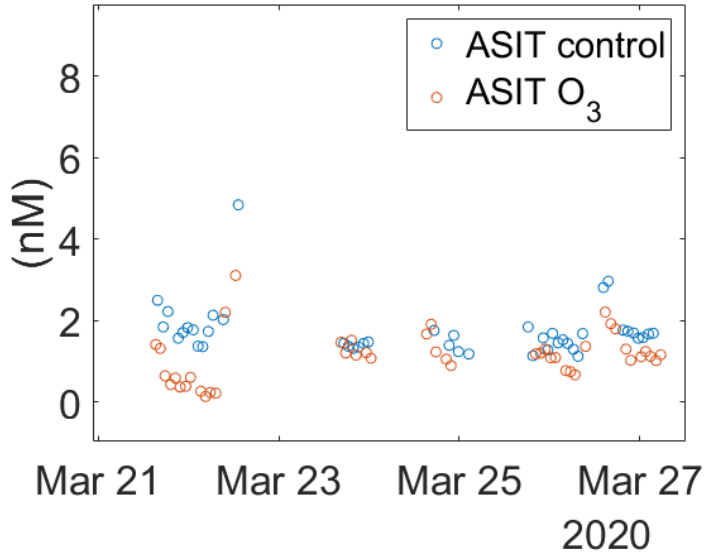


Figure S.6: Calculated concentrations of MeSH in seawater (nM).

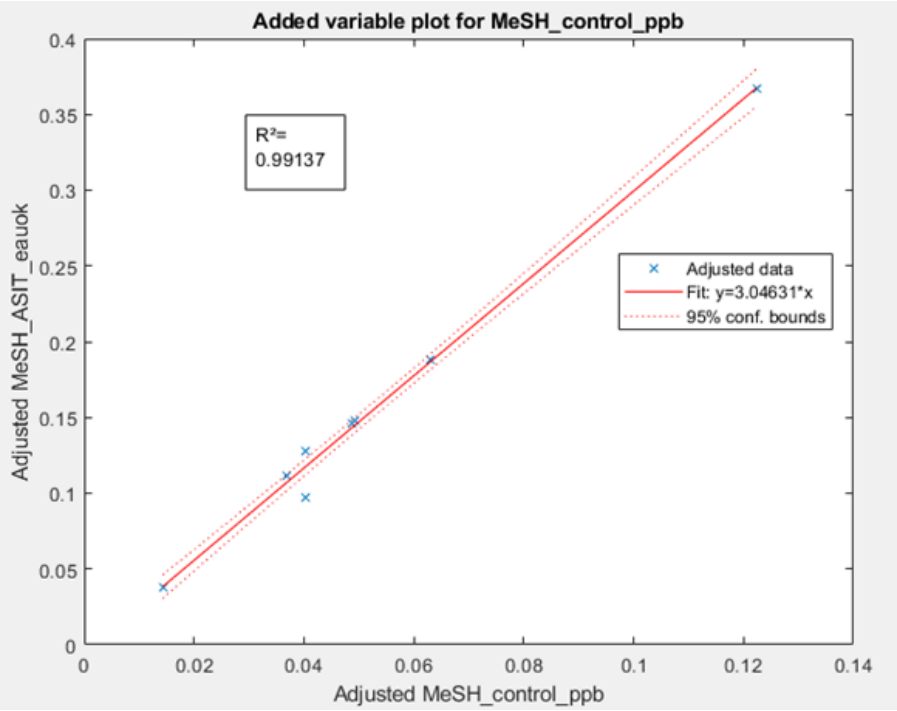


Figure S. 7: Correlations with measured (headspace) and calculated MeSH (seawater).

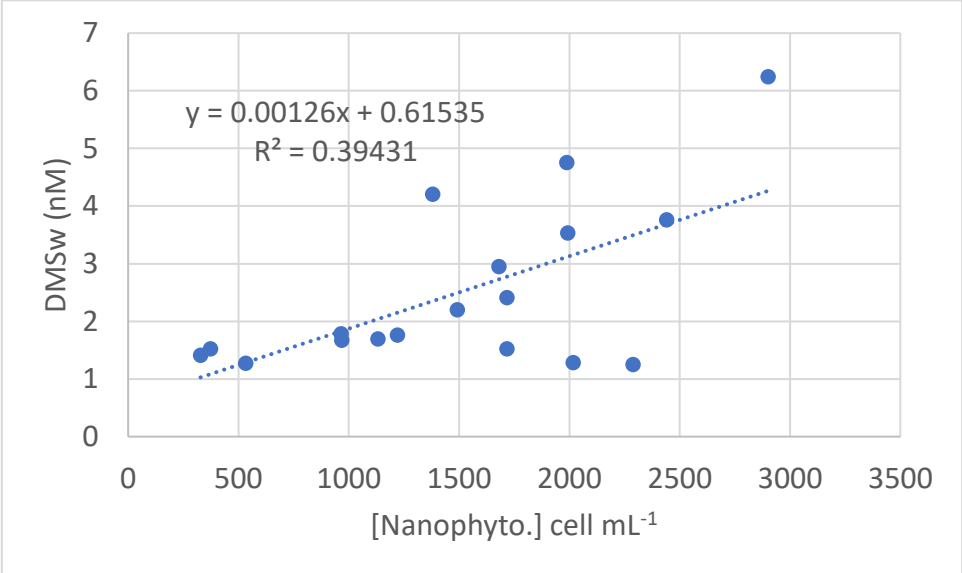


Figure S.8: Concentration of DMS (nM) in seawater during CTD and workboat measurements VS nanophytoplankton cells (cell mL^{-1}).

Supplementary tables:

	r^2	'DMS'	MeSH'
real time	corr PAR ASIT	0.00	0
	corr PAR ASIT O3	0.00	0.03
h+2	corr PAR ASIT	0.02	0.01
	corr PAR ASIT O3	0.09	0.07
h+4	corr PAR ASIT	0.09	0.11

	corr PAR ASIT O3	0.16	0.12
h+6	corr PAR ASIT	0.12	0.14
	corr PAR ASIT O3	0.15	0.16
h+8	corr PAR ASIT	0.11	0.14
	corr PAR ASIT O3	0.06	0.06
h+10	corr PAR ASIT	0.00	0.00
	corr PAR ASIT O3	0.07	0.08
h+12	corr PAR ASIT	0.00	0.00
	corr PAR ASIT O3	0.00	0.00

Table S. 1: Correlation of DMS and MeSH fluxes with PAR and shifted PAR every two hours.

		Chl-a (mg/m3)	Bacteria	Dinoflagellates	Diatoms	Flagellates
all ASITs						
DMSP	r	0.32	0.61	0.77	0.63	0.50
	p	<0.001	<0.001	<0.001	<0.001	<0.001
ASIT-control						
DMSP	r	0.44	0.63	0.34	0.03	0.30
	p	<0.001	<0.001	<0.001	<0.001	<0.001

ASIT-O_3						
DMSP	r	0.14	0.74	0.40	0.20	0.22
	p	<0.001	<0.001	0.063	0.035	0.004

Table S.2: Correlations and p_{value} of DMSPw with Chl-a, bacteria, dinoflagellates, diatoms and flagellate's species.