



1 Improved Prediction of Dimethyl Sulfide (DMS) Distributions in the 2 NE Subarctic Pacific using Machine Learning Algorithms

3 Brandon J. McNabb¹ & Philippe D. Tortell^{1,2}

4 ¹Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, Vancouver, BC V6T 1Z4,
5 Canada

6 ²Department of Botany, University of British Columbia, Vancouver, BC V6T 1Z4, Canada

7 *Correspondence to:* Brandon J. McNabb (bmcnabb@eoas.ubc.ca)



Abstract. Dimethyl sulfide (DMS) is a volatile biogenic gas with the potential to influence regional climate as a source of atmospheric aerosols and cloud condensation nuclei (CCN). The complexity of the oceanic DMS cycle presents a challenge in accurately predicting sea-surface concentrations and sea-air fluxes of this gas. In this study, we applied machine learning methods to model the distribution of DMS in the NE Subarctic Pacific (NESAP), a global DMS hot-spot. Using nearly two decades of ship-based DMS observations, combined with satellite-derived oceanographic data, we constructed ensembles of 1000 machine-learning models using two techniques, random forest regression (RFR) and artificial neural networks (ANN). Our models dramatically improve upon existing statistical DMS models, capturing up to 62% of observed DMS variability in the NESAP and demonstrate notable regional patterns that are associated with mesoscale oceanographic variability. In particular, our results indicate a strong coherence between DMS concentrations, sea surface nitrate (SSN) concentrations, photosynthetically active radiation (PAR) and sea surface height anomalies (SSHA), suggesting that NESAP DMS cycling is primarily influenced by heterogeneous nutrient availability, light-dependent processes and physical mixing. Based on our model output, we derive summertime, sea-air flux estimates ranging between 0.5-2.0 Tg S yr⁻¹ in the NESAP. Our work demonstrates a new approach to capturing spatial and temporal patterns in DMS variability, which is likely applicable to other oceanic regions.

1 Introduction

Dimethyl sulfide (DMS), a volatile biogenic gas, is an important component of the marine sulfur cycle. This molecule contributes the largest fraction of bulk non-sea salt (NSS) sulfate emissions to the atmosphere (Bates et al., 1992), where it is rapidly oxidized to form aerosols that act as cloud condensation nuclei (CCN; Charlson et al., 1987; Hegg et al., 1991; Korhonen et al., 2008), potentially influencing regional albedo and climate (Charlson et al., 1987; Ayers and Cainey, 2007). Given its potential role in climate regulation, and recognized importance to marine microbial metabolism (Vila-Costa et al., 2006) and food web interactions (Nevitt, 2008), substantial research has focused on characterizing DMS dynamics in seawater. This work has revealed considerable complexity in the oceanic DMS cycle, which has limited the development of simple predictive algorithms describing spatial and temporal DMS distributions.

Oceanic DMS production and loss are tightly linked with the biological cycling of the related metabolites dimethyl sulfoniopropionate (DMSP) and dimethyl sulfoxide (DMSO). DMS is believed to be primarily derived from the cleavage of DMSP (Kiene and Linn, 2000), but it can also be cycled through biological DMSO reduction (Spiese et al., 2009) and oxidation (Lidbury et al., 2016), and abiotically by light-dependent reactions (del Valle et



al., 2007; Royer et al., 2016). DMS cycling is influenced by suite of environmental and ecological factors, including release from phytoplankton cells into the dissolved pool via grazing (Dacey and Wakeham, 1986), viral lysis (Malin et al., 1998), or exudation. Oxidative stress generated by other variables such as temperature (Kirst et al., 1991), salinity (Dickson and Kirst, 1987), UV radiation (Kinsey et al., 2016), and nutrient limitation (Bucciarelli et al., 2013; Spiese & Tatarkov, 2014) may also enhance the cycling of DMSP and DMSO, which may regulate DMS concentrations through cascading oxidative pathways (Sunda et al., 2002). Finally, variability in surface wind fields can modulate the rates of DMS sea-air exchange, providing a significant source of heterogeneity in surface water DMS concentrations (Royer et al., 2016). These examples illustrate the complex non-linearity of the oceanic DMS cycle.

Over the past two decades, a number of approaches have been developed to model DMS distributions at both global (Bock et al., 2021; Galí et al., 2018; Simó and Dachs, 2002; Vallina and Simó, 2007) and regional (Watanabe et al., 2007) scales. These models have been largely based on linear regression techniques to estimate DMS using one or two predictors. To date, these studies have focused on a number of variables, including ratio of chlorophyll *a* (Chl-*a*) to mixed layer depth (MLD) (Simó and Dachs, 2002), sea surface temperature (SST) and nitrate (SSN) (Watanabe et al., 2007), solar radiation dose (SRD) (Vallina and Simó, 2007), photosynthetically active radiation (PAR) and modelled DMSP concentrations (Galí et al., 2018). Some of these models have demonstrated reasonably good performance at global scales, but their predictive power is generally diminished at regional scales (Herr et al., 2019), failing to accurately resolve important smaller-scale features (Belviso et al., 2003; Nemcek et al., 2008; Royer et al., 2015; Tortell, 2005b).

In recent years, machine-learning algorithms have been increasingly used to derive predictions for non-linear oceanic systems. For example, these methods have been successfully applied to describe the spatial and temporal patterns of global methane flux (Weber et al., 2019) and carbon export (Roshan and DeVries, 2017). To our knowledge, only two studies have thus far applied machine-learning to describe DMS distributions, with one study focused on the Arctic (Humphries et al., 2012) and the other exploring a global domain (Wang et al., 2020). Despite producing algorithms with reasonable predictive skill, these two studies found limited success in resolving the underlying relationships driving DMS variability. This was partially due to a reliance on indirect sensitivity tests assessing the importance of predictor variables, and also, potentially, from the large-scale averaging applied to the underlying data fields ($1 \times 1^\circ$; 111 km^2). Analyses at higher spatial resolution may reveal mesoscale (roughly 20-200 km) and sub-mesoscale (roughly 1-20 km) patterns that would otherwise be obscured, thereby increasing predictive strength.



Machine learning algorithms require large datasets for the training and testing process. Traditionally, DMS measurements were based on time-consuming ship-board analysis of discrete samples, resulting in sparse data coverage over much of the oceans. More recently, the development of several automated DMS measurement systems (Royer et al., 2014; Saltzman et al., 2009; Tortell, 2005a) has provided marine DMS observations at a significantly higher resolution, yielding greater spatial and temporal data coverage. These new datasets potentially enable new insights into small-scale and regional patterns in oceanic DMS distributions, as well as the characterization of oceanic DMS ‘hot-spots’. One such global DMS hotspot is the northeast subarctic Pacific (NESAP) (Asher et al., 2017; Herr et al., 2019; Lana et al., 2011), a region encompassing both highly productive coastal upwelling regimes, and off-shore, iron-limited waters (Martin and Fitzwater, 1988). Several factors have been proposed to account for the elevated DMS production in the NESAP, including increased productivity from entrainment and upwelling along coastal fronts (Asher et al., 2017), and the stimulation of DMS production in response to oxidative stress in low iron waters (Sunda et al., 2002; Herr et al., 2020). Although multiple studies have examined empirical relationships between DMS and various oceanographic factors in the NESAP (Watanabe et al., 2007; Herr et al., 2019; Asher et al., 2017, 2011), these have all reported low predictive skill based on simple linear correlation approaches. To date, machine-learning approaches have not been applied to describe DMS distributions specifically in this region.

Here, we present an approach to modelling summertime NESAP DMS concentrations and sea-air fluxes using ensemble random forest regression (RFR) and artificial neural network (ANN) machine-learning algorithms. Our statistical models leverage field observations of DMS collected across the NESAP between 1997 to 2017 to generate a summertime DMS climatology mapped at a higher spatial resolution than previous efforts (Simó and Dachs, 2002; Vallina and Simó, 2007; Galí et al., 2018; Watanabe et al., 2007; Humphries et al., 2012; Wang et al., 2020). This new modelling approach represents a significant improvement over previous methods and predicts regional DMS distributions that are coherent with underlying patterns of oceanographic variability. Most notably, the modelled DMS concentrations and sea-air fluxes can be explained, to a large extent, by regional and mesoscale patterns in nutrient supply and physical mixing dynamics. Based on the output of our models, we present summertime sea-air flux estimates in close agreement with previous studies (Herr et al., 2019; Lana et al., 2011), further highlighting the importance of the NESAP as a globally-significant sulfur source to the atmosphere.



94 2 Methods

95 2.1 Data

96 A combination of data sources was used in training our machine-learning models to build a summertime
 97 DMS climatology. For this study, we restricted DMS measurements to the months of June, July and August between
 98 1997 to 2017 in the NESAP (43-60°N, 147-122°W). A total of 26,201 data points were obtained from the NOAA
 99 PMEL repository (<https://saga.pmel.noaa.gov/dms/>; last accessed: February 3, 2021), including measurements
 100 derived from purge and trap gas chromatography and membrane inlet mass spectrometry. The DMS data were
 101 binned to a monthly resolution, regardless of year, and averaged into 0.25 x 0.25° grid cells.

102 Predictor data used to build our machine-learning models included the following variables derived from
 103 the NASA Aqua MODIS satellite at level L3 monthly 0.036° resolution: sea surface temperature (SST), the ratio
 104 of normalized fluorescence line height to chlorophyll a (nFLH:Chl-a), instantaneous and daily observed
 105 photosynthetically active radiation (iPAR and PAR, respectively), particulate inorganic carbon (PIC), the
 106 absorption of gelbstof and detritus at 433 nm ($a_{\text{cdm}}(443)$), and diffuse attenuation coefficients at 490nm (K_d).
 107 Satellite-based PIC is considered as a proxy for the abundance of coccolithophores and other calcified
 108 phytoplankton (Franklin et al., 2010), whereas the $a_{\text{cdm}}(443)$ product is considered a proxy for the distributions of
 109 chromophoric dissolved organic matter (CDOM) (Nelson & Siegel, 2013), which is thought to be an important
 110 photosensitizer of DMS (see Sect. 4.1). For observations prior to 2004, data were from either SeaWiFS or Terra
 111 MODIS when SeaWiFS data was unavailable (e.g. nFLH and iPAR). As described below, K_d and PIC were later
 112 excluded from the final models (see Sect. 2.6).

113 The following predictor variables were also used: 6-day averaged sea surface height anomalies (SSHA)
 114 derived from the TOPEX/Poseidon satellites at 0.17° resolution; Level L4 ESA Sentinel-3 Copernicus monthly-
 115 averaged 0.25° wind speeds; net primary productivity (NPP) from the Vertically-Generalized Production Model
 116 (VGPM; Behrenfeld & Falkowski, 1997) at monthly 0.25° resolution; sea surface nitrate from the 2018 World
 117 Ocean Atlas at monthly 1° resolution (Garcia et al., 2019); and mixed-layer depth (MLD) and sea surface salinity
 118 (SSS) from the MIMOC climatology at 0.5° resolution (Schmidtke et al., 2013). Except for MIMOC data, all
 119 predictors were restricted in time to the corresponding years of DMS sampling (1997 to 2017). Net community
 120 productivity (NCP) was estimated from the algorithm of Li & Cassar, (2016; using NPP and SST). As with DMS
 121 observations, predictor data were interpolated to a 0.25 x 0.25° average monthly resolution using linear radial basis
 122 interpolation functions. Interpolation was constrained to the oceanic region by masking out land pixels using
 123 ETOPO2 bathymetric (0.033° resolution) binned at 0.25 x 0.25° resolution. Data sources can be found in Table 1.



124

125 **Table 1. Data sources and spatial and temporal resolution of predictor variables used to develop the RFR and ANN algorithms. Data**
 126 **processing levels are indicated where relevant. All variables were used as predictors (excluding bathymetry) and post-processed to**
 127 **monthly-averaged, 0.25° resolution (see sections 2.1-2.2).**

Variable	Spatial Resolution (°)	Temporal Resolution	Source	Level
Sea Surface Temperature (SST)	0.036	6-Day Average	SeaWiFS/AquaTERRA (1997-2003) or AquaMODIS(2004-2017): https://oceancolor.gsfc.nasa.gov/13/	3
Chlorophyll-Normalized Fluorescence (nFLH:Chl-a)	0.036	Monthly	SeaWiFS/AquaTERRA (1997-2003) or AquaMODIS (2004-2017): https://oceancolor.gsfc.nasa.gov/13/	3
Instantaneous Photosynthetically Active Radiation (iPAR)	0.036	Monthly	SeaWiFS/AquaTERRA (1997-2003) or AquaMODIS (2004-2017): https://oceancolor.gsfc.nasa.gov/13/	3
Daily Photosynthetically Active Radiation (PAR)	0.036	Monthly	SeaWiFS/AquaTERRA (1997-2003) or AquaMODIS (2004-2017): https://oceancolor.gsfc.nasa.gov/13/	3
Particulate Inorganic Carbon (Calcite; PIC)	0.036	Monthly	SeaWiFS/AquaTERRA (1997-2003) or AquaMODIS (2004-2017): https://oceancolor.gsfc.nasa.gov/13/	3
Absorbtion of Gelbstof and Detritus at 433 nm ($a_{cdm}(443)$)	0.036	Monthly	SeaWiFS/AquaTERRA (1997-2003) or AquaMODIS (2004-2017): https://oceancolor.gsfc.nasa.gov/13/	3
Diffuse Attenuation Coeffiencents at 490 nm (K_d)	0.036	Monthly	SeaWiFS/AquaTERRA (1997-2003) or AquaMODIS (2004-2017): https://oceancolor.gsfc.nasa.gov/13/	3
Sea Surface Height Anomalies (SSHA)	0.17	Monthly	TOPEX/Poseidon: https://podaac.jpl.nasa.gov/dataset/SEA_SURFACE_HEIGHT_ALT_GRID_S_L4_2SATS_5DAY_6THDEG_V_J_PL1812	4
Monthly Wind Speeds	0.25	Monthly	ESA Sentinal-3 Copernicus: https://resources.marine.copernicus.eu/?option=com_csw&view=details&product_id=WIND_GLO_PHY_CLIMAT_E_L4_REP_012_003	N/A



Net Primary Productivity (NPP)	0.25	Monthly	Vertically-Generalized Production Model (VGPM): http://www.science.oregonstate.edu/ocean.productivity/	N/A
Sea Surface Nitrate (SSN)	1	Monthly	World Ocean Atlas 2018 (WO18): https://www.ncei.noaa.gov/access/world-ocean-atlas-2018/	N/A
Mixed Layer Depth (MLD)	0.5	Monthly	MIMOC Climatology: https://www.pmel.noaa.gov/mimoc/	N/A
Sea Surface Salinity (SSS)	0.5	Monthly	MIMOC Climatology: https://www.pmel.noaa.gov/mimoc/	N/A
Bathymetry	0.033	N/A	ETOPO2: https://rda.ucar.edu/datasets/ds759.3/	N/A



129

130 2.2 Machine-learning models

131 We compared the performance of random forest regression (RFR) and artificial neural network (ANN)
 132 models at the regional scale. In both cases, the models were built as an ensemble of either 1000 individual decision
 133 trees or individual networks to minimize bias in predictions. The input data were randomly divided for use in model
 134 training (80%) and external testing (20%). Although RFR is not sensitive to large differences in predictor variance,
 135 predictor data were standardized in both models by normalization to their respective mean and standard deviation.
 136 Additionally, we applied an inverse hyperbolic sine (IHS) transformation to the DMS data prior to training. Testing
 137 results indicated that IHS yielded slightly better performance than the more traditional logarithmic transformations
 138 for both of our models.

139 Both our ANN and RFR models followed a similar design to Weber et al. (2019). Our ANNs were built
 140 using a feed-forward framework consisting of a single input node, two hidden layers each consisting of 30 neurons
 141 (using a sigmoidal activation function), and a single output layer (using a linear activation function). A Bayesian
 142 L2 (Ridge) regularization parameter was tuned to minimize overfitting. Each individual decision tree within the
 143 RFR was trained using the standard CART algorithm and constrained to a max depth of 25 decision splits, the
 144 simplest configuration determined to perform well and minimize overfitting.

145 2.3 Sea-to-air fluxes

146 Sea-air DMS fluxes (F_{DMS} , $\mu\text{mol m}^{-2} \text{d}^{-1}$) were calculated from the monthly-averaged observed and
 147 modelled DMS values for June, July and August. F_{DMS} was calculated using the gas transfer velocity (k , $\text{cm}^3 \text{hr}^{-1}$)
 148 following the modified approach of Webb et al. (2019):

$$149 F_{DMS} = k(DMS)(0.24) \quad (1)$$

150 where the factor of 0.24 converts to the values to daily fluxes. Since our fluxes were calculated from our monthly
 151 averaged models, the gas transfer velocity was calculated using the approach from Simó & Dachs (2002), as
 152 modified by (Nightingale et al., 2000). This approach is necessary to correct for differences due to the non-linear
 153 relationship between DMS and wind speed (Livingstone and Imboden, 1993) when using monthly-averaged,
 154 satellite-derived wind speeds. Assuming a Rayleigh distribution ($\xi=2$), k can be defined as:

$$155 k = [5.88\eta\Gamma(1 + \frac{2}{\xi}) + 1.49\eta\Gamma(s)]Sc_{DMS}^{-0.5} \quad (2)$$



where η is the quotient of the wind speed (m s^{-1}) by the gamma function $\Gamma(s)$ (using $s = 1 + \frac{1}{\xi}$), and Sc_{DMS} is the DMS-specific Schmidt number ($\text{cm}^3 \text{hr}^{-1}$) as defined by Saltzman et al. (1993):

$$Sc_{DMS} = 2674 - 147.12(SST) + 3.72(SST^2) - 0.038(SST^3) \quad (3)$$

Regional summertime fluxes (\bar{F}_{DMS} , Tg) were calculated as the average quantity of DMS-sulfur emitted over 92 days through the area of the mapped study region ($1.28 \times 10^7 \text{ km}^2$ or 85.0% of the total bounded area).

2.4 Comparison against existing algorithms

Simple linear regression (LR) and multiple linear regression (MLR) models were built for comparison against the machine-learning algorithms. We also tested the performance of our RFR and ANN models against the published algorithms of Simó & Dachs (2002), Watanabe et al. (2007), Vallina & Simó, (2007), and Galí et al. (2018) (hereafter referred to as SD02, W07, VS07, and G18, respectively). SRD is calculated here using MLD as described by Vallina & Simó (2007):

$$SRD = \frac{PAR}{K_d \times MLD} \times (1 - e^{-K_d \times MLD}) \quad (4)$$

Each of the four algorithms was assessed using both their original coefficients and coefficients tuned to our NESAP dataset using nonlinear least-squares optimization.

2.5 Controls on DMS variability

Principal component analysis (PCA) was applied to assess the relationships between DMS and the nine predictors used to build the RFR and ANN ensembles. Additionally, non-parametric spearman rank correlations were calculated between each variable and both the modelled and observed DMS concentrations. Correlation analysis was also extended to assess the role of taxonomy on predicted DMS concentrations, using the outputs of a chlorophyll-a based taxonomic algorithm by Hirata et al. (2011) with NESAP-tuned coefficients (Zeng et al., 2018).

2.6 Sensitivity Tests and Predictor Selection

To inform our selection of grid size, we assessed the performance of both the RFR and ANN models using grid cells ranging from 0.25° to 5° (Fig. 1). From this analysis, we found that model accuracy was highest at 0.25° resolution (see Sect. 3.1). Smaller grid sizes would presumably further improve model accuracy, but at a significantly higher computational cost.



We also tested the influence of other biological predictor variables on the performance of the RFR and ANN models, using either NCP, NPP, Chl-a, or PIC. These sensitivity tests indicated no significant difference between the various biological predictor variables, although accuracy was slightly reduced when PIC was used. We therefore selected NCP as the biological predictor variable within our model framework. We also removed K_d as a predictor variable after further sensitivity testing indicated that its exclusion slightly improved results.

The inclusion of nFLH:Chl-a represents a proxy for iron limitation (see Sect. 4.1). However, fluorescence yields corrected for non-photochemical quenching (NPQ) have been suggested to yield a better iron limitation proxy than nFLH:Chl-a (Behrenfeld et al., 2009). We therefore calculated NPQ-corrected fluorescence yields (φ_f) by:

$$\varphi_f = \frac{nFLH}{Chl-a \times \alpha \times S} \times \frac{iPAR}{iPAR} \quad (5)$$

where $\alpha = 0.0147 \times Chl - a^{-0.316}$ and $S = 100 \text{ mW cm}^{-2} \mu\text{m}^{-1} \text{sr}^{-1} \text{m}$ as described by Behrenfeld et al. (2009). Our tests indicated nFLH:Chl-a yielded slightly improved performance overall whereas φ_f decreased both models' performance. We therefore retained nFLH:Chl-a and excluded φ_f in our final model design.

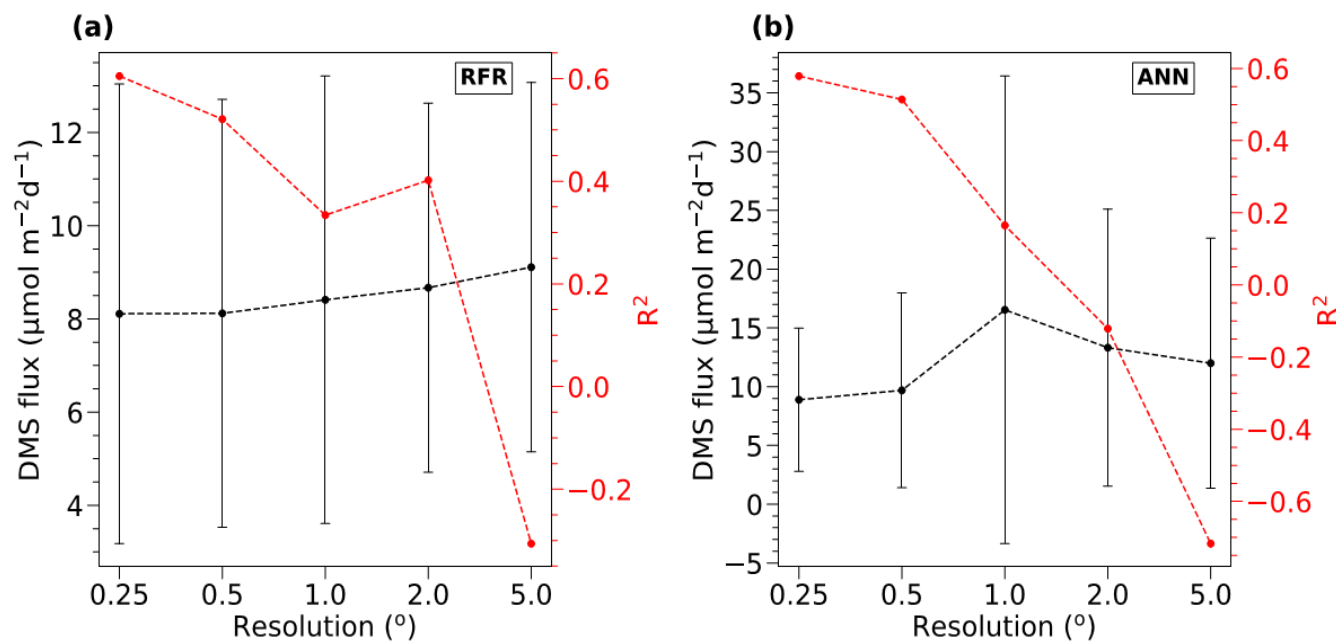


Fig. 1. Sensitivity of RFR and ANN models to grid size resolution. DMS fluxes (green) and R^2 values (red) derived from sensitivity tests of (a) RFR and (b) ANN models to pixels resolutions of 0.25–5°. The negative R^2 values observed at the lowest resolution (largest grid cells) indicate that the predicted values explain less variance than the overall mean of the dataset.



199 **3 Results**

200 **3.1 Model evaluation**

201 To benchmark the performance of our RFR and ANN models, we first evaluated the predictive skill of four
202 existing empirical DMS algorithms (SD02, W07, VS07, & G18), in addition to simple and multiple linear
203 regression models. Previous studies have demonstrated that these empirical algorithms show strong predictive skill
204 ($R^2=0.53-0.84$) over large scales and in some oceanic regions (Simó and Dachs, 2002; Galí et al., 2018; Watanabe
205 et al., 2007), but significantly poorer performance in the NESAP (Herr et al., 2019). Consistent with these results,
206 we found that the SD02, W07, VS07, and G18 did not accurately predict NESAP DMS distributions, even with
207 regionally tuned coefficients (Fig. 2, $R^2=0-0.01$). We also found that simple and multiple linear regressions
208 performed poorly ($R^2=0-0.05$; Fig. 2, 3), yielding virtually no explanatory power for surface water DMS
209 distributions in the NESAP ($R^2\leq 0.05$).

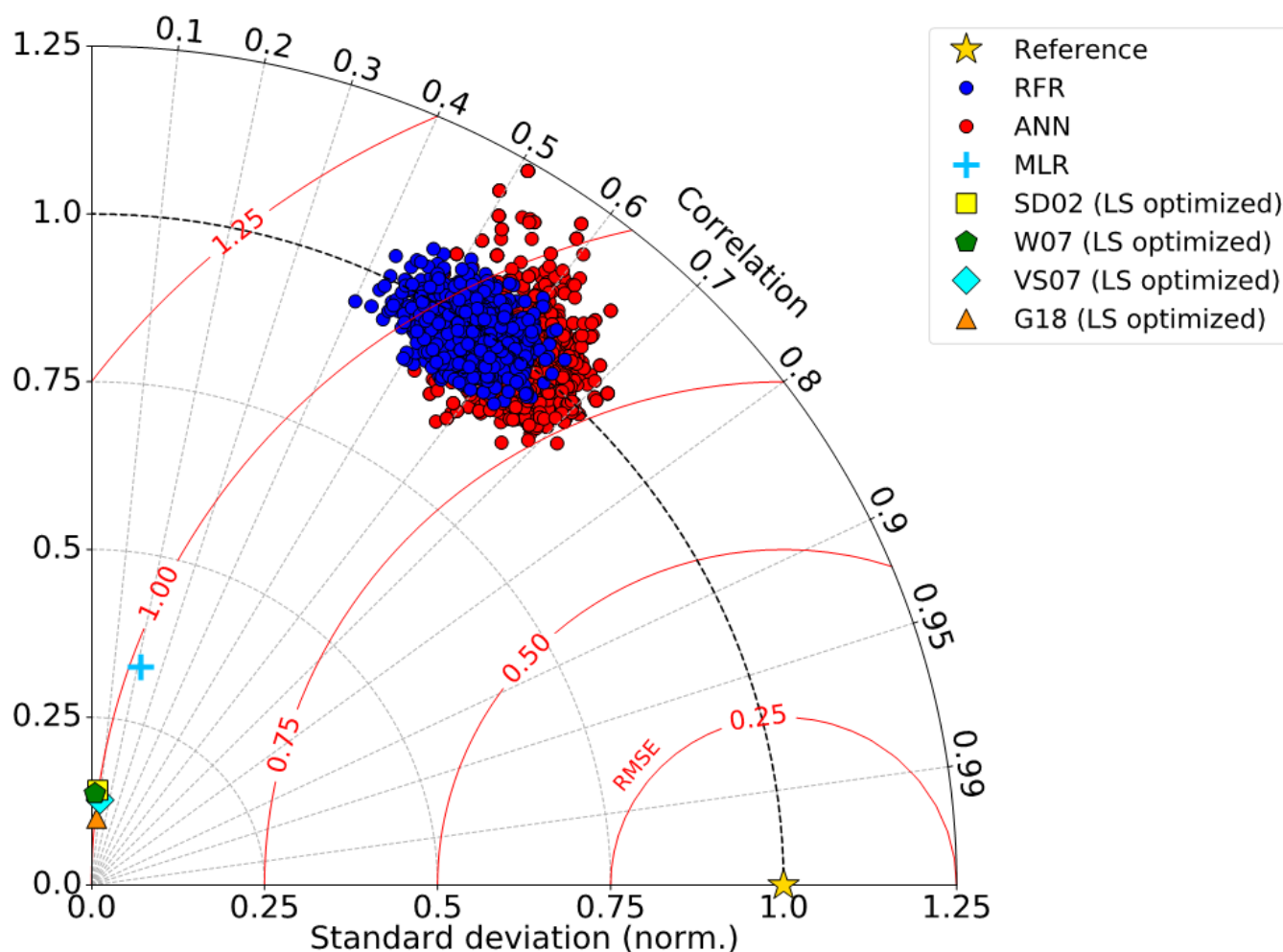


Fig. 2. Taylor Diagram showing comparative performance metrics of each individual Random Forest Regression (RFR) and Artificial Neural Network (ANN) model (1000-model ensembles) against multiple linear regression (MLR) and other statistical DMS models (See sections 2.1 and 2.4). The Pearson correlation coefficients (“Correlation”; outer radius), root mean squared error (“RMSE”; red radial contours), and standard deviations (SDs; grey radial contours from origin) are all computed with respect to the observed DMS samples after inverse hyperbolic sine (IHS) transformation. The reference of a perfect model fit is shown with a gold star. SDs of the model outputs are normalized to the SDs of the DMS observations. RMSE represents a normalized trigonometric derivation from both the correlation coefficients and normalized SDs. Performance of the SDO2, W07, VS07, and G18 algorithms reported here are calculated using regionally tuned coefficients to the NESAP derived from non-linear least-squares optimization (see section 2.4).

Relative to other published modelling approaches, both the RFR and ANN models dramatically improved the representation of NESAP DMS variability, achieving significantly higher predictive accuracy (Fig. 2, 3). The collective ensembles of both the RFR and ANN models yielded strong performance, explaining up to 62% of the observed DMS variability ($R^2=0.61-0.62$; Fig. 3). For individual models within the ensembles, the ANN method



provided slightly better results ($R^2=0.16-0.50$), compared to the individual RFR models ($R^2=0.16-0.43$). As observed for predicted DMS concentrations, the models showed lower predictive power for sea-air DMS fluxes at coarser resolution (Fig. 1).

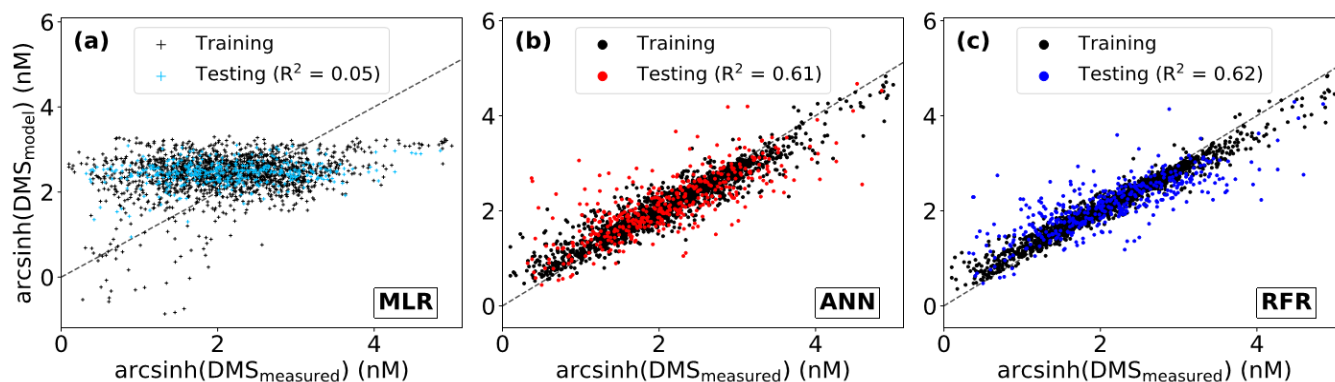


Fig. 3. Performance of three modelling approaches in predicting observed DMS distributions; (A) multiple linear regression (MLR) (B) ensemble of Artificial Neural Networks (ANN) and (C) ensemble of Random Forest Regression (RFR). For consistency, all predictions are partitioned by the Training and Testing datasets used to build the ensembles (see section 2.2). Model performance (R^2) is computed only for the Testing dataset predictions. The dashed line demonstrates a 1:1 relationship.

3.2 DMS distributions and sea-air fluxes

The predicted spatial distribution of DMS was generally consistent between observations and the RFR and ANN methods (Fig. 4a,c,d). The average model derived DMS concentrations was 4.0 ± 2.1 nM and 4.7 ± 3.0 nM (mean \pm SD) for the RFR and ANN ensemble models, respectively, with a similar range from 0.3 to 84.3 nM. In both models, the highest DMS concentrations were largely constrained to coastlines and within the Alaska Gyre adjacent to the Aleutian Islands (Fig. 4b-c, 8C). The greatest discrepancy between DMS concentrations from the two models was observed in these regional ‘hotspots’, where the ANN models emphasize high DMS within the Alaska gyre, while the RFR models emphasize elevated coastal DMS concentrations (Fig. 4b). The models deviated on average by 0.49 nM, with the greatest offsets observed in an area of particularly sparse DMS observations in the Alaska Gyre (Fig. 4a,b). Future observational data in this region should help improve model performance.



June – August

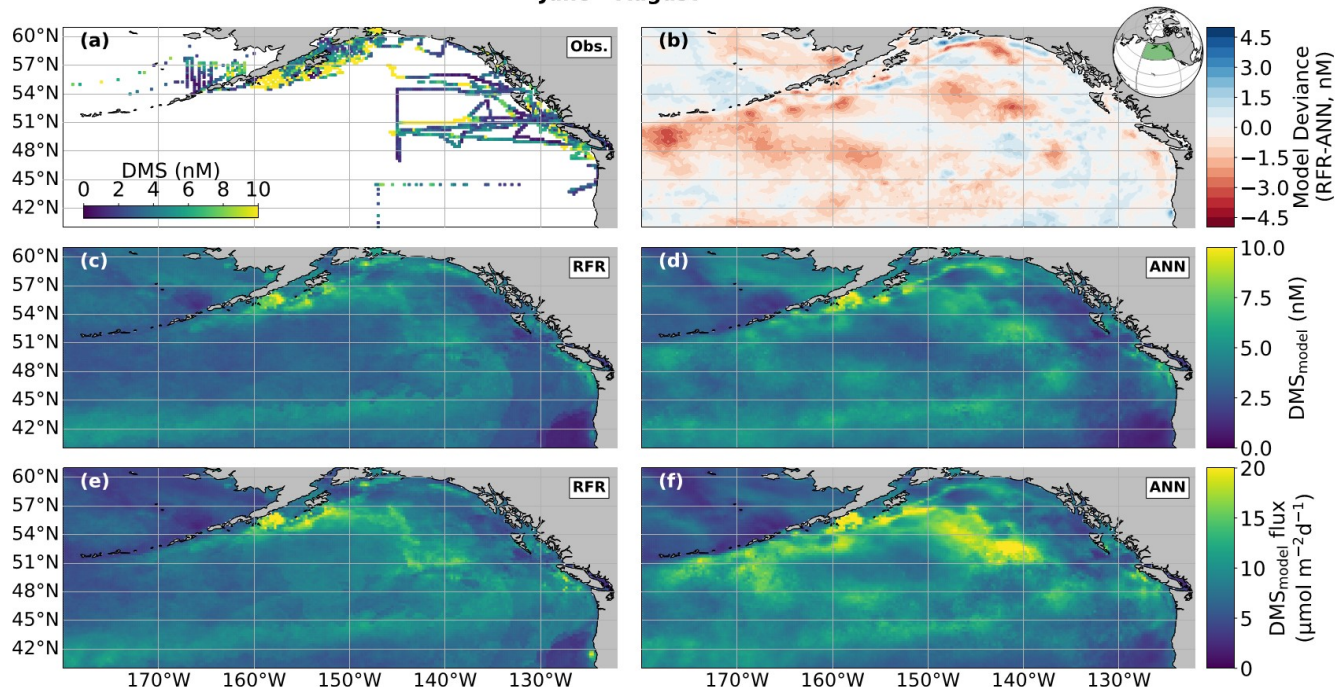


Fig. 4. Predicted maps of sea surface DMS concentrations and sea-air fluxes. (a) Ship-based observations of mean summertime (June-August) DMS concentrations used to construct the predictive models. (b) Differences between the (c) Random Forest Regression (RFR) and (d) Artificial Neural Network (ANN) ensemble predicted DMS concentrations. (e,f) DMS sea-air fluxes derived from the predicted DMS concentrations. Colormap ranges are restricted to illustrate trends, with <1% of DMS data exceeding the colorbar limits. The inset map in (b) shows the NESAP study region as a shaded green patch in a global orthographic projection.

Sea-air DMS fluxes (Fig. 4e,f) derived from ANN predictions were 18% higher, on average, than RFR predictions, largely due to higher predicted values in the Alaska Gyre (Fig. 4d-e, Table 2). The distribution of ANN sea-air fluxes was also closer to ship-based observations (Fig. 5). Predicted regional fluxes ranged from 0.7 to 107 $\mu\text{mol m}^{-2}\text{d}^{-1}$ between the two models (Fig. 4e,f, 5), with the highest predicted DMS emissions in August, when derived sea-air fluxes were approximately 1.5-fold greater than in June and July (Table 2). Our models yielded a summertime integrated sea-air flux of 0.31 ± 0.19 Tg DMS-derived sulfur (equivalent to 0.5 to 2.0 Tg S yr^{-1} ; Table 2), in good agreement with recent estimates based on compiled ship-based observations (0.3 Tg; Herr et al., 2019) and existing climatological estimates (Table 2; Lana et al., 2011). This summertime mean value is equivalent to ~4-8% of total global DMS sea-air emissions annually, assuming an uncertainty ranging between 15 to 28 Tg S yr^{-1} in global estimates (Bock et al., 2021). This result further emphasizes the NESAP as a globally significant DMS source to the atmosphere.



Table 2. Monthly and mean summertime NESAP sea-air DMS fluxes. Fluxes (mean \pm SD) are calculated from the Random Forest Regression (RFR) and Artificial Neural Network (ANN) model predictions (based on an ensemble of 2000 models). NESAP sea-air flux derived from the Lana et al. (2011) climatology is shown for comparative purposes.

	Annual Sulfur Emissions			
	RFR	ANN	This Study	Lana et al. (2011)
	$\mu\text{mol m}^{-2} \text{d}^{-1}$	$\mu\text{mol m}^{-2} \text{d}^{-1}$	Tg S	Tg S
June	5.9 ± 3.7	6.0 ± 3.9	0.22 ± 0.13	0.44 ± 0.20
July	6.5 ± 3.0	7.7 ± 3.8	0.26 ± 0.12	0.33 ± 0.17
August	10.8 ± 3.0	14.0 ± 3.8	0.45 ± 0.21	0.54 ± 0.21
June-August	7.7 ± 2.4	9.2 ± 3.4	0.31 ± 0.19	0.44 ± 0.21

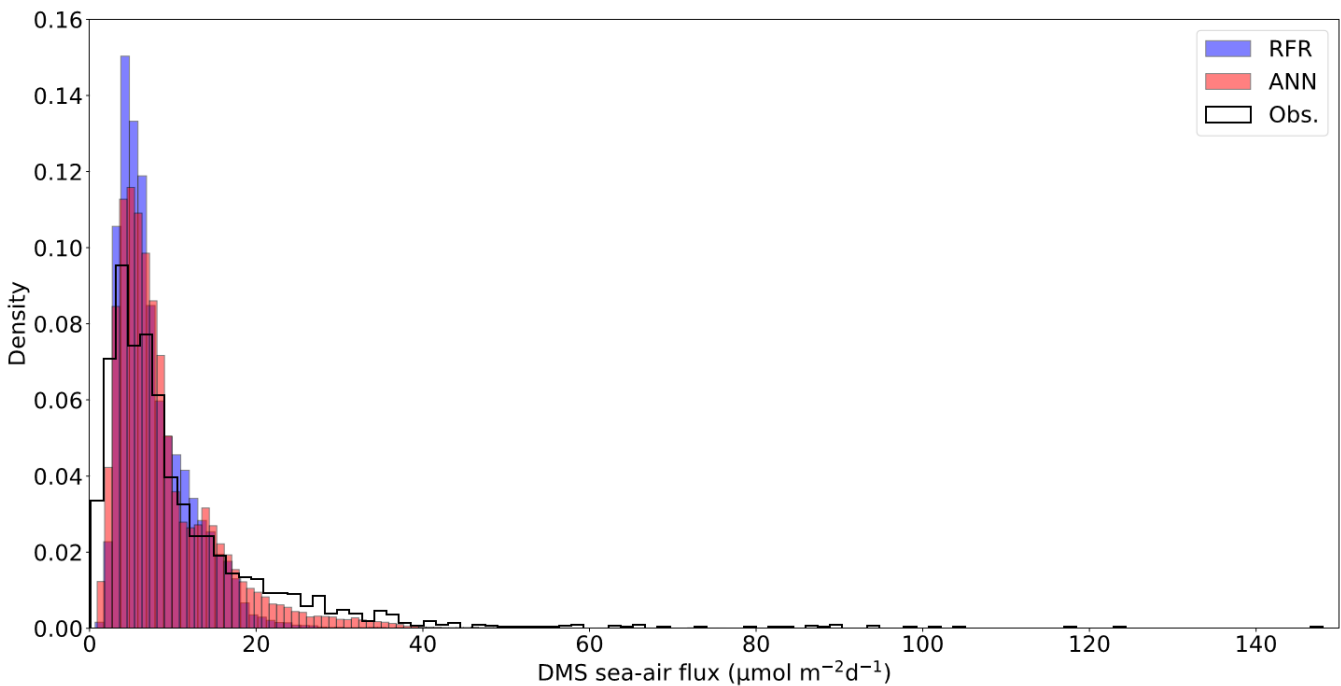


Fig. 5. Histograms of DMS sea-air flux distributions derived from the 1000-model ensemble random forest regression (RFR) and artificial neural network (ANN) predictions as well as cruise observations (Obs.). The sample sizes of both models are equivalent ($n=49,632$) and are significantly higher than the observational dataset ($n=2063$). Note that the ANN better predicts the upper tail of DMS observations greater than 20 nM.

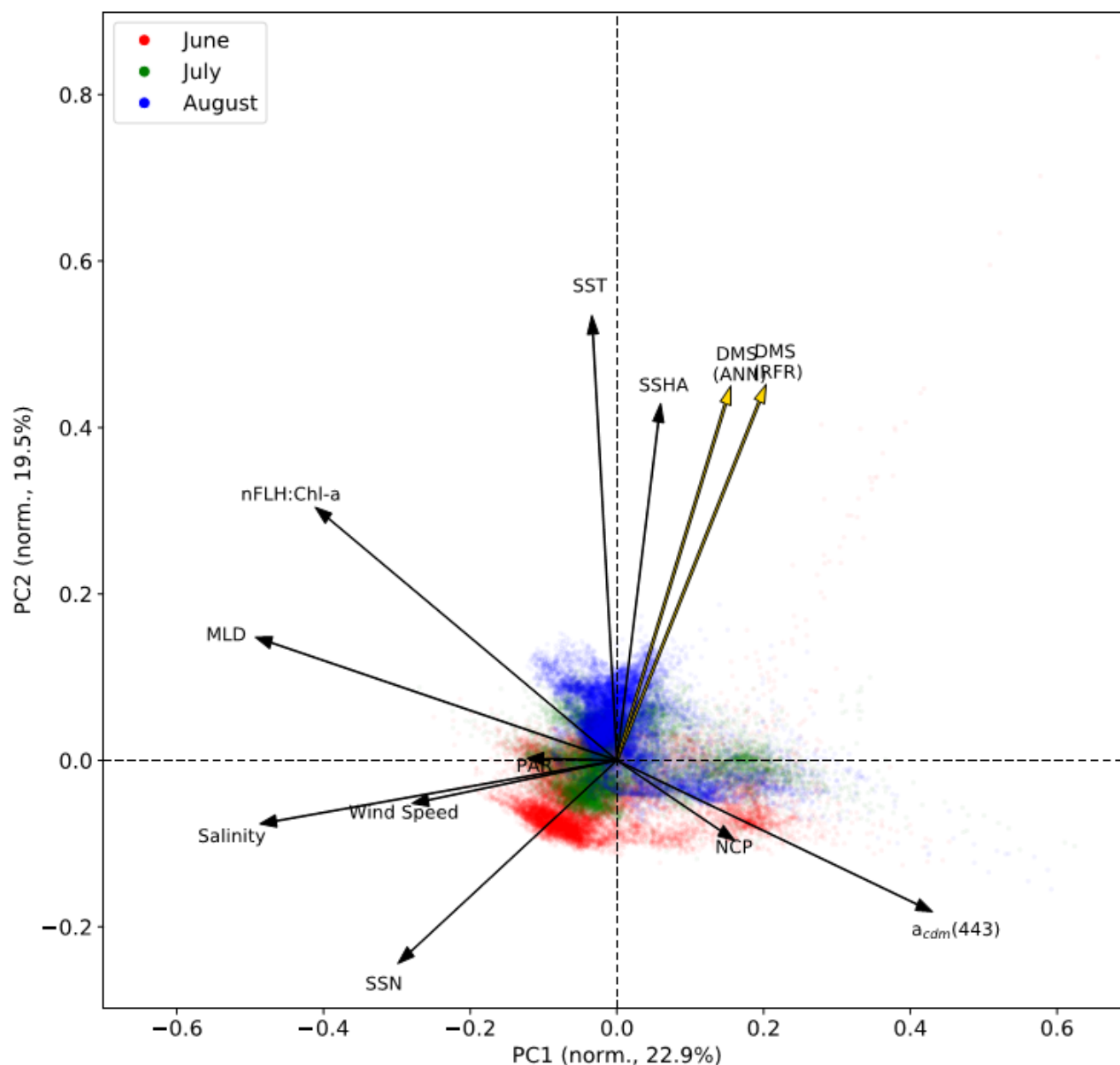


275 3.4 Drivers of DMS variability

276 In addition to modelling the spatial and temporal distribution of surface water DMS in the NESAP, we
277 examined the influence of different oceanographic variables as model predictors. As expected based on previous
278 work (Herr et al., 2019), no single predictor was found to exert a dominant control on modelled DMS distributions
279 from either the RFR or ANN models (Fig. 6, 7). Rather, the relationship between DMS and other oceanographic
280 variables exhibited significant region-specific patterns. One of the most compelling regional signatures was the
281 apparent relationship between DMS and SSHA. In both models, we found significant positive correlations between
282 DMS and SSHA ($\rho=0.35, 0.41$ for RFR and ANN, respectively) across the full spatial domain, with a particularly
283 notable relationship along the northern Alaskan coastline (Fig. 8, 9). Here, strong winds (Fig. 9j-l), coupled with
284 the northeastern Alaska current flow, produce two characteristic oceanographic features in the NESAP: strong,
285 semi-permanent mesoscale eddies collectively referred to as the Haida, Sitka and Yakutat eddies (Fig. 8a), and the
286 formation of the high nutrient, low chlorophyll (HNLC) Alaska Gyre (Fig. 8c; Okkonen et al., 2001; Whitney et
287 al., 2005). Both the monthly (Fig. 9a-i) and summertime-averaged (Fig. 8a,b) RFR and ANN-derived DMS
288 concentrations are low where these downwelling eddies form. In contrast, elevated DMS concentrations were
289 associated with the negative SSHA coastal upwelling areas (Fig. 8a,b), where phytoplankton productivity is
290 stimulated by nutrient inputs into the mixed layer.



291



292

293 **Fig. 6. Principal Component Analysis (PCA) showing the relationships between variables used to construct the**
 294 **predictive algorithms. Eigenvectors (arrows) are superimposed over the principal components (PCs; data points) for**
 295 **the first two significant modes obtained from PCA. PCs are normalized and clustered by month (June-August, see**
 296 **legend for colors), while the eigenvectors are grouped by ensemble model predictions (gold) and nine predictor**
 297 **variables (black). The percentage of variance explained by each mode is indicated along the axes.**

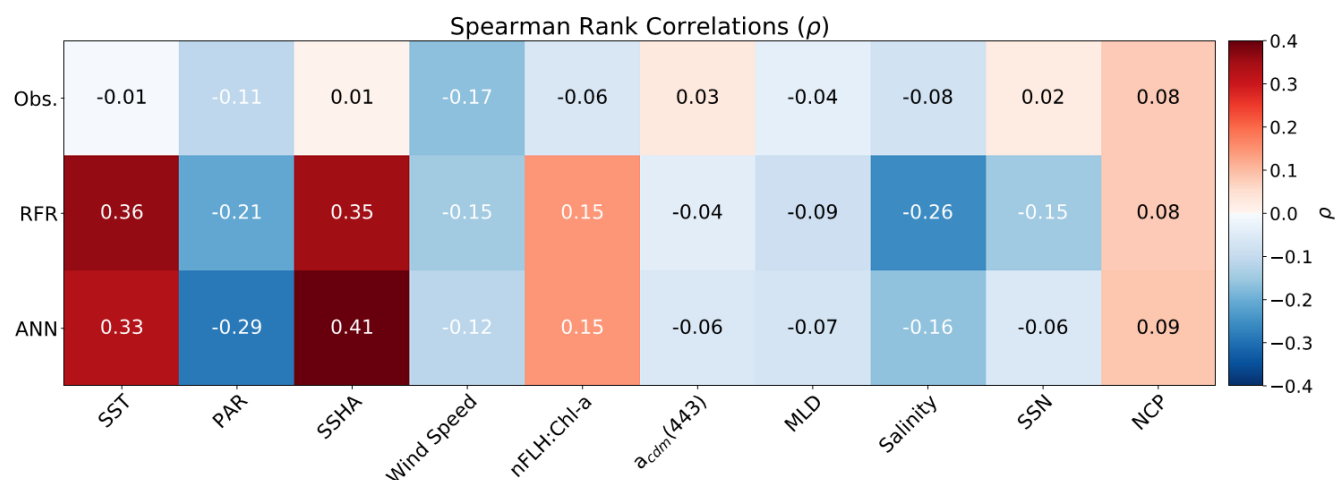
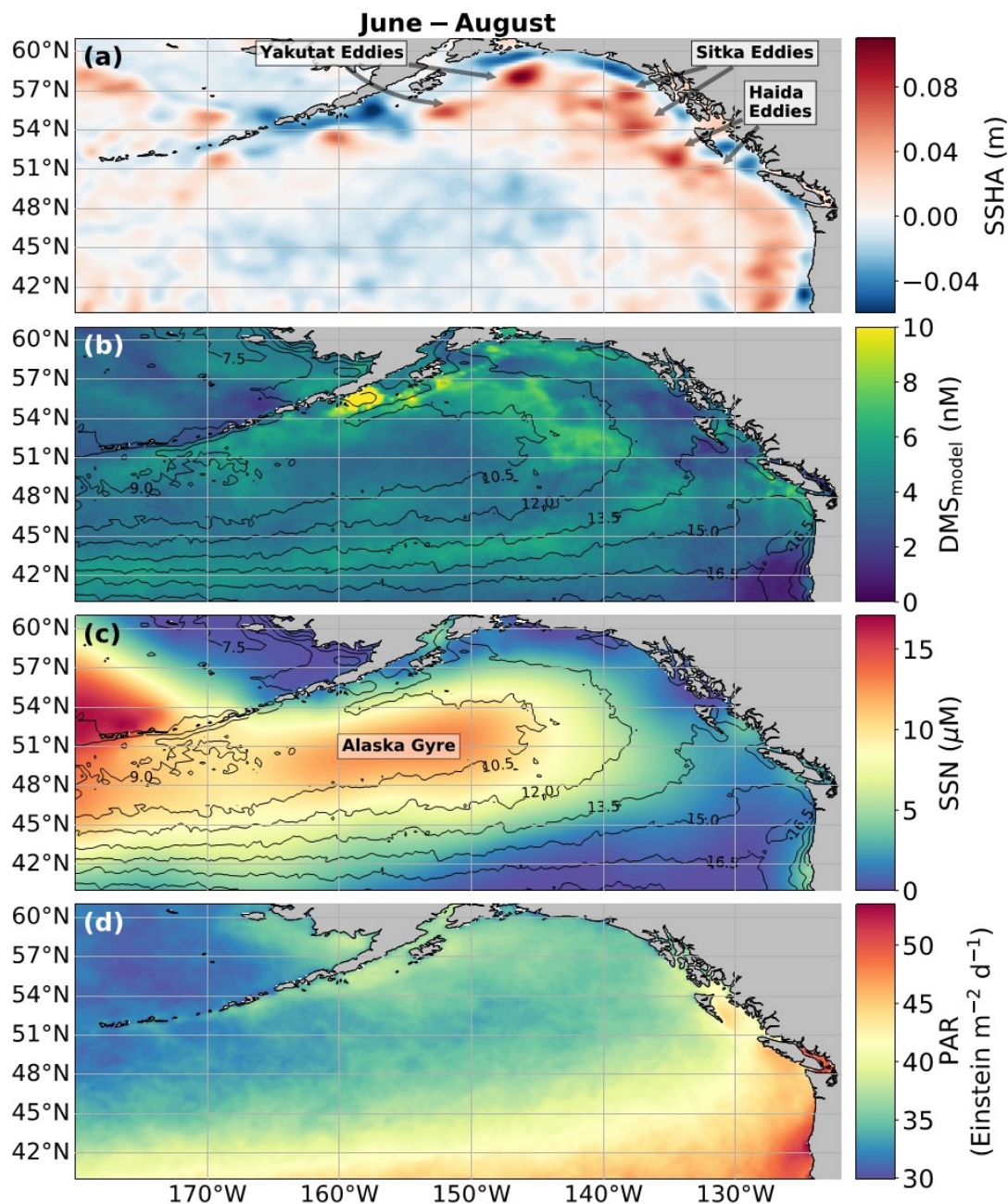


Fig. 7. Heatmap of Spearman rank correlations (ρ). Top row: observed DMS concentrations; middle row: RFR model predictions; bottom row: ANN model predictions. All model correlations are computed on the 1000-model ensembles.

Modelled DMS concentrations also significantly correlated with hydrographic frontal patterns. We found significant correlations between DMS and SST ($\rho=0.36$, 0.33 for RFR and ANN, respectively) which suggested the central Alaska Gyre is an area of elevated DMS variability. Both models predict high DMS levels in the northern frontal zone of the gyre (140°W - 145°W) between the 10.5 and 12°C isotherms and the southern frontal zone between (42°N - 45°N) between the 13.5 and 15°C isotherms (Fig. 8b,c). By comparison, our models suggest that DMS concentrations are predominantly low in relation to high sea surface nitrate (SSN) concentrations within the HNLC gyre (Fig. 8, 9). As discussed below, the relationship between DMS and macronutrient concentrations in the HNLC waters of the central Gulf of Alaska could indicate an important role for iron limitation as a controlling factor in the DMS cycle. The presence of elevated summer nutrients in offshore waters is taken as a proxy for iron limitation, which increases over the course of the summer growing season.



311
 312 **Fig. 8. Physical drivers of summertime (June-August) NESAP DMS distributions.** (a) Sea surface height anomalies
 313 (SSHA), (b) predicted DMS concentrations derived from the mean of all 2000 RFR and ANN machine learning models,
 314 (c) sea surface nitrate (SSN) and (d) photosynthetically active radiation (PAR). Contours in (b,c) show sea surface
 315 temperature (SST) isotherms. Coherent features of elevated sea-surface height indicate the presence of mesoscale
 316 eddies, whereas nearshore low SSHAs features reveal areas of upwelling. Colormaps ranges are restricted to illustrate
 317 trends with <1% of data exceeding the colorbar limits.



318 Other variables appear to exhibit a more localized or minimal influence on DMS cycling. For instance,
319 both NCP and DMS are elevated in productive nearshore waters, but NCP generally correlates weakly with both
320 RFR- and ANN-derived DMS concentrations ($\rho=0.08$, 0.09 for RFR and ANN, respectively). Similarly, modelled
321 phytoplankton taxonomic composition (Hirata et al., 2011; Zeng et al., 2018) was not significantly correlated with
322 predicted DMS concentrations ($\rho<0.1$). Although strong, persistent winds appear to sustain low DMS
323 concentrations off the coast of Oregon and Vancouver Island (Fig. 9), wind speeds only weakly correlate with DMS
324 overall for the region ($\rho=-0.15$ and -0.12 for RFR and ANN, respectively). Additionally, high PAR in these areas
325 correspond with low DMS concentrations (Fig. 6d) and there is an overall negative correlation between PAR and
326 DMS for the region (Fig. 6, 7; $\rho=-0.21$ and -0.29 for RFR and ANN, respectively). Finally, despite hypothesized
327 links between DMS cycling and iron limitation in the NESAP (Levasseur et al., 2006; Merzouk et al., 2006),
328 nFLH:Chl-a ratios (taken as a proxy for phytoplankton iron stress; Behrenfeld et al., 2009; Westberry et al., 2013)
329 did not exhibit any coherent spatial patterns and only weakly correlated to our modelled DMS concentrations
330 ($\rho=0.15$ for both RFR and ANN, respectively).

331

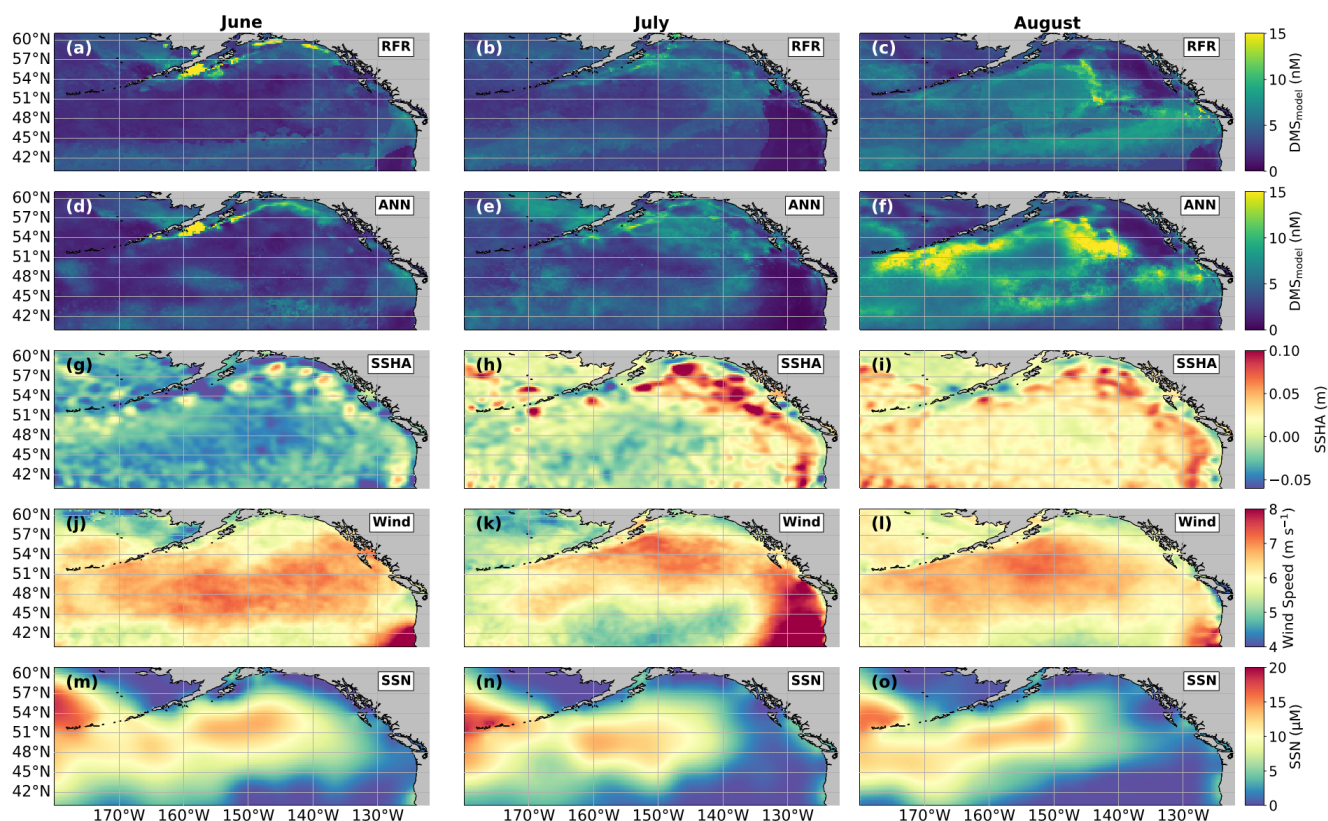


Fig. 9. Predicted spatial and temporal (June-August) DMS distribution in relation to underlying oceanographic variables. DMS concentrations predicted from (a-c) the Random Forest Regression (RFR) and (d-f) the Artificial Neural Network (ANN) ensemble models are mapped alongside the monthly-averaged (g-i) sea surface height anomalies (SSHA), (j-l) wind speeds (Wind), and (m-o) sea surface nitrate (SSN) for each month. Colormap ranges are restricted to illustrate trends, with at most 1.5% of the data beyond the colorbar limits.

4 Discussion

The relative sparsity of DMS data in many oceanic regions and the complexity of DMS cycling have limited previous attempts to model oceanic distributions of this compound (Simó and Dachs, 2002; Vallina and Simó, 2007; Galí et al., 2018; Watanabe et al., 2007; Herr et al., 2019). Taking advantage of expanding data resources, we employed a new approach to statistically describe DMS distributions in the NESAP. Our results show that both our RFR and ANN models substantially improved predictive strength over traditional empirical approaches (Fig. 2, 3), while identifying several key DMS relationships and regional patterns across the NESAP (Fig. 8, 9). Although our statistical approach does not directly elucidate the underlying mechanisms driving these relationships, we can



nonetheless make some reasonable inductive inferences. These inferences are discussed below, along with the implications of the improved predictive performance observed here.

4.1 Relationships with other oceanographic variables

Among the more prominent spatial relationships we observed was the coherence between predicted DMS concentrations and SST, and the negative correlation between predicted DMS concentrations and sea surface nitrate (SSN) within and surrounding the Alaska Gyre (Fig. 6-9). The DMS-nitrate relationship may be partially explained by the so-called sulfur overflow hypothesis (Stefels, 2000), which suggests that nutrient-limited phytoplankton increase DMSP production and its subsequent cleavage to DMS, in order to regulate intracellular sulfur quotas when protein synthesis is limited (Hatton & Wilson, 2007; Kinsey et al., 2016; Simó & Vila-Costa, 2006; Spiese & Tatarkov, 2014; Stefels, 2000). This pathway may help explain the higher predicted DMS concentrations predicted at the northern extent of the Alaska Gyre, where SSN concentrations begin to decrease (Fig. 6). The apparent relationship between DMS and nitrate could also result indirectly from the underlying effects of iron limitation. Excess summertime nitrate concentrations are taken as evidence for iron limitation in the NESAP (Boyd and Harrison, 1999; Boyd et al., 2004; Martin and Fitzwater, 1988; Whitney et al., 2005). Under iron-limiting conditions, DMS is thought to function, together with DMSP and DMSO, as part of an antioxidant response to oxidative stress (Sunda et al., 2002). This hypothesis suggests that iron limitation should stimulate net production of DMS and DMSP (Bucciarelli et al., 2013; Sunda et al., 2002), which is inconsistent with the negative dependence predicted between DMS and SSN (Fig. 8b,c).

Satellite-based, chlorophyll-normalized fluorescence has been suggested as an additional proxy for iron limitation. Low iron conditions can lead to both a reduction in photosystem I relative to photosystem II (Strzepek and Harrison, 2004), and an apparent increase in energetically-decoupled light harvesting complexes (Allen et al., 2008; Behrenfeld & Milligan, 2013), resulting in elevated fluorescence-to-chlorophyll a ratios (nFLH:Chl-a) (Westberry et al., 2013). To our knowledge, this proxy has not been widely investigated with respect to DMS cycling. In our analysis, we found that nFLH:Chl-a ratios, and the NPQ-corrected fluorescence yields (ϕ_f), exhibited only weak positive correlations with the RFR and ANN predicted DMS concentrations (Fig. 6, 7). Moreover, neither of these metrics exhibited coherent spatial patterns with predicted DMS concentrations, suggesting a limited role for iron in driving spatial patterns of DMS cycling within the NESAP. However, it is important to note the potential temporal mismatch between our monthly DMS predictions and these more instantaneous metrics of iron limitation, which reflect short-term physiological changes (days to weeks; (Behrenfeld et al., 2009; Westberry et al., 2019) that depend on sporadic iron loading (e.g. aerosol deposition; Mahowald et al., 2009). Indeed, both natural



376 and artificial iron-fertilization events have thus far been detected from satellite-derived nFLH:Chl-a at daily
 377 resolution (Westberry et al., 2013), in contrast to the monthly-averaged data used here. Therefore, modelling
 378 frameworks utilizing shorter temporal scales may find a clearer connection between DMS cycling and iron
 379 limitation using the chlorophyll-a fluorescence proxy.

380 Beyond nutrient limitation effects, ambient light fields are believed to exert significant direct and indirect
 381 effects on DMS cycling (del Valle et al., 2007). Ultraviolet radiation has been noted to induce high DMS production
 382 and turnover through a proposed cascading oxidation pathway, which acts to remove harmful reactive oxygen
 383 species (Sunda et al., 2002; Archer et al., 2010). In contrast, more recent evidence has indicated the potential for
 384 elevated DMS production in the NESAP from the reduction of DMSO due to light-induced oxidative stress over
 385 diurnal cycles (Herr et al., 2020). However, our modelled DMS concentrations exhibited a negative correlation
 386 with PAR (Fig. 6, 7), suggesting that incident light may predominantly drive DMS loss in the NESAP through
 387 photolysis (del Valle et al., 2007) on regional and longer-term scales.

388 Since DMS does not have strong light absorption properties, the presence of photosensitisers is necessary for
 389 the abiotic photooxidation of DMS (Brimblecombe and Shooter, 1986). To account for this process, our models
 390 incorporated nitrate (SSN) and $a_{\text{cdm}}(443)$ (as a proxy for CDOM; Nelson & Siegel, 2013), both of which are thought
 391 to be dominant photosensitisers of DMS in marine systems (Taalba et al., 2013; Bouillon and Miller, 2004, 2005;
 392 Galí et al., 2016). In the NESAP, nitrate appears to exert a stronger influence than CDOM on the apparent quantum
 393 yields (AQY) of DMS (Bouillon and Miller, 2004). In support of this, our results suggest a stronger negative
 394 dependence of predicted DMS concentrations on nitrate compared to CDOM within the NESAP (Fig. 6, 7). We
 395 note, however, that the DMS-nitrate relationship likely also reflects physiological impacts of nutrient limitation, as
 396 discussed above. Nonetheless, our results are consistent with elevated rates of DMS photo-oxidation in the nitrate-
 397 replete, low iron waters of the Alaska Gyre, where photolysis, coupled with potentially high DMS oxidation rates
 398 due to iron-induced oxidative stress (Sunda et al., 2002), may explain the low predicted DMS concentrations (Fig.
 399 8, 9). Further *in situ* work will be required to resolve the relative contributions of these biotic and abiotic processes
 400 to DMS cycling within these areas.

401 Among all the statistical relationships we observed, perhaps the most striking was the association of DMS
 402 variability with SSHA, particularly along the Alaskan coast and in relation to mesoscale eddies (Okkonen et al.,
 403 2001; Whitney et al., 2005; Fig. 8, 9). To our knowledge, only one other study has linked SSHA to DMS within
 404 the NESAP. Herr et al., (2019) demonstrated contrasting positive and negative correlations between DMS and
 405 SSHA in offshore and coastal waters, respectively, in general agreement with our results. Presently, the underlying
 406 mechanisms explaining the relationship between SSHA and DMS cycling remain unclear, yet it is likely that



physical mixing processes are important. For example, enhanced biological production is known to be stimulated by eddy re-supply of iron and macronutrients via vertical advection and diffusion (Whitney et al., 2005; Bailey et al., 2008). These nutrient supply processes would also be expected to influence DMS cycling, as outlined above. Elevated abundances of high DMS-producers within eddies have been noted in the Sargasso Sea (Bailey et al., 2008), while eddy-induced vertical transport likely supplements nearshore, current-driven upwelling that can also resupply iron into the coastal waters of the NESAP (Cullen et al., 2009; Freeland et al., 1984). In addition, eddy propagation can allow cross-shelf transport, distributing micronutrients to offshore waters (Fiechter and Moore, 2012), potentially contributing to the apparent elevated DMS concentrations in the outer Alaska gyre between the 10.5 and 12°C isotherms (Fig. 8). These mixing and transport mechanisms could partially explain the influence of elevated productivity in driving increased nearshore and northern NESAP DMS concentrations (Fig. 4, 7-9), representing a novel source of DMS variability in this region.

The taxonomic composition of plankton assemblages is also a likely source of variability influencing DMS cycling. Significant changes to DMS production and consumption rates within the NESAP are expected in response to variable microbial and phytoplankton taxonomy (Vila-Costa et al., 2006; Lidbury et al., 2016; Sheehan and Petrou, 2020). Such taxonomic variability may, in turn, reflect transient community composition shifts in response to mixing (Bailey et al., 2008), nitrate (Bouillon and Miller, 2004), and iron availability (Levasseur et al., 2006; Merzouk et al., 2006). The monthly averaging used in our data processing removes autocorrelation associated with individual sampling expeditions (Wang et al., 2020), but it may preclude capturing these transient taxonomic responses. For instance, coccolithophores have long been believed to influence DMS cycling in the NESAP (Herr et al., 2019; Asher et al., 2011), yet averaged calcite distributions did not yield increased predictive strength for DMS concentrations in our analysis (see Sect. 2.6). Similarly, applying a chlorophyll-a based taxonomic algorithm (Hirata et al., 2011; Zeng et al., 2018) yielded no further explanation of the DMS variability predicted. The influence of taxonomic composition thus remains cryptic within our modelling framework.

4.2 Implications of Improved Predictive Power

As noted above, both the RFR and ANN approaches demonstrate significantly improved accuracy, explaining up to 62% of observed DMS variability (Fig. 2, 3). This model performance is somewhat lower than that achieved in the prediction of methane fluxes (Weber et al., 2019) and dissolved inorganic carbon dynamics (Roshan and DeVries, 2017), where R^2 values ranging from 0.7 to 0.95 were obtained. Nonetheless, the dramatic accuracy improvement of our algorithms over traditional methods (Fig. 2, 3) encourages the further use of these techniques in modelling DMS distributions.



Improved predictive accuracy provides opportunities to gain insight into the mechanisms driving DMS cycling. Our approach has yielded accurate DMS predictions at a 4 to 40-fold higher resolution than previous algorithms (Simó and Dachs, 2002; Vallina and Simó, 2007; Galí et al., 2018; Watanabe et al., 2007), enabling the description of mesoscale patterns and processes (Fig. 8). Extending these methods to sub-mesoscale resolution will enable investigations into the dependence of DMS on finer-scale hydrographic processes, particularly stratification and frontal dynamics, which have been increasingly linked to DMS cycling but remain unresolved mechanistically (Asher et al., 2011; Royer et al., 2015). Moreover, coupling machine learning algorithms with biophysical and tracer export models holds promise to resolve the contributions of eddy dynamics and upwelling intensity on DMS variability, likely through nutrient availability and physiological mechanisms (Asher et al., 2011; Bailey et al., 2008; Cullen et al., 2009). Recent work has also developed a new database of DMS apparent quantum yields (Galí et al., 2016). As the availability of these measurements increases, simultaneous mapping of both DMS quantum yields and concentrations will become feasible, enabling future studies to better parse out the contribution of photolysis, physical mixing, and biological drivers of DMS cycling.

Although used in a diagnostic capacity here, our statistical models also hold potential for prognostic applications. Frameworks utilizing shorter time scales will likely be able to detect underlying mechanisms driving observed diel cycling (Galí et al., 2013; Royer et al., 2016), even if the underlying mechanisms are still unresolved. We note, however, that caution will need be exercised as machine learning models have a tendency to overfit noise (Weber et al., 2019; Roshan and DeVries, 2017; Wang et al., 2020), thus requiring appropriately large training datasets and the use of known “future” observations to validate predictive accuracy in this context. The significant variability in DMS cycling across oceanic regimes will likely also render predictions more successful at regional, rather than global, scales (Galí et al., 2018; Royer et al., 2015). Nonetheless, prognostic applications of these algorithms should be investigated to aid in the future development of improved mechanistic models.

5 Conclusions

We have presented a statistical approach to modelling DMS distributions, which provides significantly higher accuracy than traditional methods (Simó and Dachs, 2002; Vallina and Simó, 2007; Galí et al., 2018; Watanabe et al., 2007; Lana et al., 2011), and yields estimates of the summertime NESAP DMS sea-air fluxes to 0.5-2.0 Tg S yr⁻¹ in agreement with previous findings (Herr et al., 2019; Lana et al., 2011). Our results further underscore the importance of the NESAP to global DMS production and motivate further observations in



traditionally under-sampled areas such as the Alaska Gyre and Aleutian Islands. Although we are unable to directly examine the mechanistic drivers of DMS variability, our findings suggest nutrient limitation, light-driven processes, and eddy-induced mixing are potentially key drivers of DMS cycling in the NESAP. Future studies will benefit from using such statistical algorithms, in conjunction with field-based process studies and mechanistic models, to better understand the underlying dynamics and driving factors in the oceanic DMS cycle.

Code availability. The analysis in this study makes extensive use of the Numpy, Matplotlib, & Scikit-Learn libraries in Python. The custom codes used can be downloaded at https://github.com/bjmcnabb/DMS_Climatology/tree/main/NESAP or are available upon request from the corresponding author.

Data Availability. DMS observations and predictor datasets are described in the Methods with relevant links to repositories. Data from the Lana et al. (2011) climatology used for comparison in Table 2 are available via the SOLAs project (retrieved from www.bodc.ac.uk/solas_integration/implementation_products/group1/dms/), where the DMS sea-air fluxes were calculated as described in Sect. 2.3. The gridded climatologies produced from each algorithm in this study can be obtained at https://github.com/bjmcnabb/DMS_Climatology/tree/main/NESAP/Climatologies.

Author Contribution. BM and PT designed the study. Model code was written and implemented by BM. BM prepared the manuscript with significant contributions from PT.

Competing Interests. The authors declare that they have no conflict of interest.

Acknowledgements. We would like to thank Dr. Valentina Radic for her advice in model design. This work was supported by grants to BM and PT from the Natural Sciences and Engineering Research Council of Canada (NSERC).



488 References

- 489 Allen, A. E., LaRoche, J., Maheswari, U., Lommer, M., Schauer, N., Lopez, P. J., Finazzi, G., Fernie, A. R., and
 490 Bowler, C.: Whole-cell response of the pennate diatom *Phaeodactylum tricornutum* to iron starvation,
 491 *Proceedings of the National Academy of Sciences*, 105, 10438–10443, <https://doi.org/10/cs9k8x>, 2008.
- 492 Archer, S. D., Ragni, M., Webster, R., Airs, R. L., and Geider, R. J.: Dimethyl sulfoniopropionate and dimethyl
 493 sulfide production in response to photoinhibition in *Emiliania huxleyi*, *Limnology and Oceanography*, 55, 1579–
 494 1589, <https://doi.org/10/dvpwqb>, 2010.
- 495 Asher, E. C., Merzouk, A., and Tortell, P. D.: Fine-scale spatial and temporal variability of surface water
 496 dimethylsulfide (DMS) concentrations and sea–air fluxes in the NE Subarctic Pacific, *Marine Chemistry*, 126, 63–
 497 75, <https://doi.org/10/chmbhk>, 2011.
- 498 Asher, E. C., Dacey, J. W., Ianson, D., Peña, A., and Tortell, P. D.: Concentrations and cycling of DMS, DMSP,
 499 and DMSO in coastal and offshore waters of the Subarctic Pacific during summer, 2010–2011, *J. Geophys. Res.*
 500 *Oceans*, 122, 3269–3286, <https://doi.org/10.1002/2016JC012465>, 2017.
- 501 Ayers, G. P. and Cainey, J. M.: The CLAW hypothesis: a review of the major developments, *Environ. Chem.*, 4,
 502 366, <https://doi.org/10/b7p54b>, 2007.
- 503 Bailey, K. E., Toole, D. A., Blomquist, B., Najjar, R. G., Huebert, B., Kieber, D. J., Kiene, R. P., Matrai, P.,
 504 Westby, G. R., and del Valle, D. A.: Dimethylsulfide production in Sargasso Sea eddies, *Deep Sea Research Part*
 505 *II: Topical Studies in Oceanography*, 55, 1491–1504, <https://doi.org/10/fnqb6j>, 2008.
- 506 Bates, T. S., Lamb, B. K., Guenther, A., Dignon, J., and Stoiber, R. E.: Sulfur emissions to the atmosphere from
 507 natural sources, *J Atmos Chem*, 14, 315–337, <https://doi.org/10/chmgt6>, 1992.
- 508 Behrenfeld, M. J. and Falkowski, P. G.: Photosynthetic rates derived from satellite-based chlorophyll
 509 concentration, *Limnology and Oceanography*, 42, 1–20, <https://doi.org/10/cg5x4k>, 1997.
- 510 Behrenfeld, M. J. and Milligan, A. J.: Photophysiological Expressions of Iron Stress in Phytoplankton, *Annu.*
 511 *Rev. Mar. Sci.*, 5, 217–246, <https://doi.org/10.1146/annurev-marine-121211-172356>, 2013.
- 512 Behrenfeld, M. J., Westberry, T. K., Boss, E. S., O'Malley, R. T., Siegel, D. A., Wiggert, J. D., Franz, B. A.,
 513 McClain, C. R., Feldman, G. C., Doney, S. C., Moore, J. K., Dall'Olmo, G., Milligan, A. J., Lima, I., and
 514 Mahowald, N.: Satellite-detected fluorescence reveals global physiology of ocean phytoplankton,
 515 *Biogeosciences*, 6, 16, <https://doi.org/10/fdn3f2>, 2009.
- 516 Belviso, S., Sciandra, A., and Copin-Montégut, C.: Mesoscale features of surface water DMSP and DMS
 517 concentrations in the Atlantic Ocean off Morocco and in the Mediterranean Sea, *Deep Sea Research Part I:*
 518 *Oceanographic Research Papers*, 50, 543–555, [https://doi.org/10.1016/S0967-0637\(03\)00032-3](https://doi.org/10.1016/S0967-0637(03)00032-3), 2003.
- 519 Bock, J., Michou, M., Nabat, P., Abe, M., Mulcahy, J. P., Olivié, D. J. L., Schwinger, J., Suntharalingam, P.,
 520 Tjiputra, J., van Hulten, M., Watanabe, M., Yool, A., and Séférian, R.: Evaluation of ocean dimethylsulfide
 521 concentration and emission in CMIP6 models, *Biogeosciences*, 18, 3823–3860, <https://doi.org/10/gk6fw8>, 2021.



- 522 Bouillon, R.-C. and Miller, W. L.: Determination of apparent quantum yield spectra of DMS photo-degradation
 523 in an in situ iron-induced Northeast Pacific Ocean bloom: AQY of DMS in an iron-induced bloom, *Geophys.*
 524 *Res. Lett.*, 31, n/a-n/a, <https://doi.org/10/d96wkn>, 2004.
- 525 Bouillon, R.-C. and Miller, W. L.: Photodegradation of Dimethyl Sulfide (DMS) in Natural Waters: Laboratory
 526 Assessment of the Nitrate-Photolysis-Induced DMS Oxidation, *Environ. Sci. Technol.*, 39, 9471–9477,
 527 <https://doi.org/10/d2j84c>, 2005.
- 528 Boyd, P. and Harrison, P. J.: Phytoplankton dynamics in the NE subarctic Pacific, *Deep Sea Research Part II:*
 529 *Topical Studies in Oceanography*, 46, 2405–2432, <https://doi.org/10/fkg4mz>, 1999.
- 530 Boyd, P. W., Law, C. S., Wong, C. S., Nojiri, Y., Tsuda, A., Levasseur, M., Takeda, S., Rivkin, R., Harrison, P.
 531 J., Strzepek, R., Gower, J., McKay, R. M., Abraham, E., Arychuk, M., Barwell-Clarke, J., Crawford, W.,
 532 Crawford, D., Hale, M., Harada, K., Johnson, K., Kiyosawa, H., Kudo, I., Marchetti, A., Miller, W., Needoba, J.,
 533 Nishioka, J., Ogawa, H., Page, J., Robert, M., Saito, H., Sastri, A., Sherry, N., Soutar, T., Sutherland, N., Taira,
 534 Y., Whitney, F., Wong, S.-K. E., and Yoshimura, T.: The decline and fate of an iron-induced subarctic
 535 phytoplankton bloom, *Nature*, 428, 549–553, <https://doi.org/10/fkgnf4>, 2004.
- 536 Brimblecombe, P. and Shooter, D.: Photo-oxidation of dimethylsulphide in aqueous solution, *Marine Chemistry*,
 537 19, 343–353, <https://doi.org/10/bqwpc9>, 1986.
- 538 Bucciarelli, E., Ridame, C., Sunda, W. G., Dimier-Hugueney, C., Cheize, M., and Belviso, S.: Increased
 539 intracellular concentrations of DMSP and DMSO in iron-limited oceanic phytoplankton *Thalassiosira oceanica*
 540 and *Trichodesmium erythraeum*, *Limnology and Oceanography*, 58, 1667–1679,
 541 <https://doi.org/10.4319/lo.2013.58.5.1667>, 2013.
- 542 Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic phytoplankton, atmospheric
 543 sulphur, cloud albedo and climate, *Nature*, 326, 655–661, <https://doi.org/10.1038/326655a0>, 1987.
- 544 Cullen, J. T., Chong, M., and Ianson, D.: British Columbian continental shelf as a source of dissolved iron to the
 545 subarctic northeast Pacific Ocean, *Global Biogeochem. Cycles*, 23, <https://doi.org/10/b489x8>, 2009.
- 546 Dacey, J. W. H. and Wakeham, S. G.: Oceanic Dimethylsulfide: Production During Zooplankton Grazing on
 547 Phytoplankton, *Science*, 233, 1314–1316, <https://doi.org/10.1126/science.233.4770.1314>, 1986.
- 548 Dickson, D. M. J. and Kirst, G. O.: Osmotic Adjustment in Marine Eukaryotic Algae: The Role of Inorganic Ions,
 549 Quaternary Ammonium, Tertiary Sulphonium and Carbohydrate Solutes, *New Phytologist*, 106, 645–655,
 550 <https://doi.org/10.1111/j.1469-8137.1987.tb00165.x>, 1987.
- 551 Fiechter, J. and Moore, A. M.: Iron limitation impact on eddy-induced ecosystem variability in the coastal Gulf of
 552 Alaska, *Journal of Marine Systems*, 92, 1–15, <https://doi.org/10/bvqv4d>, 2012.
- 553 Franklin, D., Steinke, M., Young, J., Probert, I., and Malin, G.: Dimethylsulphoniopropionate (DMSP), DMSP-
 554 lyase activity (DLA) and dimethylsulphide (DMS) in 10 species of coccolithophore, *Mar. Ecol. Prog. Ser.*, 410,
 555 13–23, <https://doi.org/10/fk7hmj>, 2010.



- 556 Freeland, H. J., Crawford, W. R., and Thomson, R. E.: Currents along the pacific coast of Canada, *Atmosphere-*
 557 *Ocean*, 22, 151–172, <https://doi.org/10.1080/07055900.1984.9649191>, 1984.
- 558 Galí, M., Simó, R., Vila-Costa, M., Ruiz-González, C., Gasol, J. M., and Matrai, P.: Diel patterns of oceanic
 559 dimethylsulfide (DMS) cycling: Microbial and physical drivers, *Global Biogeochem. Cycles*, 27, 620–636,
 560 <https://doi.org/10.1002/gbc.20047>, 2013.
- 561 Galí, M., Kieber, D. J., Romera-Castillo, C., Kinsey, J. D., Devred, E., Pérez, G. L., Westby, G. R., Marrasé, C.,
 562 Babin, M., Levasseur, M., Duarte, C. M., Agustí, S., and Simó, R.: CDOM Sources and Photobleaching Control
 563 Quantum Yields for Oceanic DMS Photolysis, *Environ. Sci. Technol.*, 50, 13361–13370,
 564 <https://doi.org/10/f9jg2w>, 2016.
- 565 Galí, M., Levasseur, M., Devred, E., Simó, R., and Babin, M.: Sea-surface dimethylsulfide (DMS) concentration
 566 from satellite data at global and regional scales, *Biogeosciences*, 15, 3497–3519, <https://doi.org/10/gdrm6n>, 2018.
- 567 Garcia, H. E., Weathers, K. W., Paver, C. R., Smolyar, I., Boyer, T. P., Locarnini, M. M., Zweng, M. M.,
 568 Mishonov, A. V., Baranova, O. K., and Seidov, D.: *World Ocean Atlas 2018. Vol. 4: Dissolved Inorganic*
 569 *Nutrients (phosphate, nitrate and nitrate+ nitrite, silicate)*, 35pp., 2019.
- 570 Hatton, A. D. and Wilson, S. T.: Particulate dimethylsulphoxide and dimethylsulphoniopropionate in
 571 phytoplankton cultures and Scottish coastal waters, *Aquat. Sci.*, 69, 330–340, <https://doi.org/10/dbxk6n>, 2007.
- 572 Hegg, D. A., Radke, L. F., and Hobbs, P. V.: Measurements of Aitken nuclei and cloud condensation nuclei in
 573 the marine atmosphere and their relation to the DMS-Cloud-climate hypothesis, *J. Geophys. Res. Atmos.*, 96,
 574 18727–18733, <https://doi.org/10/d6fwx9>, 1991.
- 575 Herr, A. E., Kiene, R. P., Dacey, J. W. H., and Tortell, P. D.: Patterns and drivers of dimethylsulfide
 576 concentration in the northeast subarctic Pacific across multiple spatial and temporal scales, *Biogeosciences*, 16,
 577 1729–1754, <https://doi.org/10.5194/bg-16-1729-2019>, 2019.
- 578 Herr, A. E., Dacey, J. W. H., Kiene, R. P., McCulloch, R. D., Schuback, N., and Tortell, P. D.: Potential roles of
 579 dimethylsulfoxide in regional sulfur cycling and phytoplankton physiological ecology in the NE Subarctic Pacific,
 580 *Limnology and Oceanography*, <https://doi.org/10/ghfstm>, 2020.
- 581 Hirata, T., Hardman-Mountford, N. J., Brewin, R. J. W., Aiken, J., Barlow, R., Suzuki, K., Isada, T., Howell, E.,
 582 Hashioka, T., Noguchi-Aita, M., and Yamanaka, Y.: Synoptic relationships between surface Chlorophyll-a and
 583 diagnostic pigments specific to phytoplankton functional types, *Biogeosciences*, 8, 311–327,
 584 <https://doi.org/10.5194/bg-8-311-2011>, 2011.
- 585 Humphries, G. R. W., Deal, C. J., Elliott, S., and Huettmann, F.: Spatial predictions of sea surface
 586 dimethylsulfide concentrations in the high arctic, *Biogeochemistry*, 110, 287–301, <https://doi.org/10/fx778z>,
 587 2012.
- 588 Kiene, R. P. and Linn, L. J.: The fate of dissolved dimethylsulphoniopropionate (DMSP) in seawater: Tracer
 589 studies using ³⁵S-DMSP, *Geochimica et Cosmochimica Acta*, 64, 2797–2810, [https://doi.org/10.1016/S0016-](https://doi.org/10.1016/S0016-7037(00)00399-9)
 590 [7037\(00\)00399-9](https://doi.org/10.1016/S0016-7037(00)00399-9), 2000.



- 591 Kinsey, J. D., Kieber, D. J., and Neale, P. J.: Effects of iron limitation and UV radiation on *Phaeocystis antarctica*
 592 growth and dimethylsulfoniopropionate, dimethylsulfoxide and acrylate concentrations, *Environ. Chem.*, 13,
 593 195–211, <https://doi.org/10.1071/EN14275>, 2016.
- 594 Kirst, G. O., Thiel, C., Wolff, H., Nothnagel, J., Wanzek, M., and Ulmke, R.: Dimethylsulfoniopropionate
 595 (DMSP) in icealgae and its possible biological role, *Marine Chemistry*, 35, 381–388,
 596 [https://doi.org/10.1016/S0304-4203\(09\)90030-5](https://doi.org/10.1016/S0304-4203(09)90030-5), 1991.
- 597 Korhonen, H., Carslaw, K. S., Spracklen, D. V., Mann, G. W., and Woodhouse, M. T.: Influence of oceanic
 598 dimethyl sulfide emissions on cloud condensation nuclei concentrations and seasonality over the remote Southern
 599 Hemisphere oceans: A global model study, *J. Geophys. Res. Atmos.*, 113, <https://doi.org/10/cfrz46>, 2008.
- 600 Lana, A., Bell, T. G., Simó, R., Vallina, S. M., Ballabrera-Poy, J., Kettle, A. J., Dachs, J., Bopp, L., Saltzman, E.
 601 S., Stefels, J., Johnson, J. E., and Liss, P. S.: An updated climatology of surface dimethylsulfide concentrations
 602 and emission fluxes in the global ocean, *Global Biogeochem. Cycles*, 25, <https://doi.org/10/dbqjrm>, 2011.
- 603 Levasseur, M., Scarratt, M. G., Michaud, S., Merzouk, A., Wong, C. S., Arychuk, M., Richardson, W., Rivkin, R.
 604 B., Hale, M., Wong, E., Marchetti, A., and Kiyosawa, H.: DMSP and DMS dynamics during a mesoscale iron
 605 fertilization experiment in the Northeast Pacific-Part I: Temporal and vertical distributions, *Deep Sea Research*
 606 Part II: Topical Studies in Oceanography, 53, 2353–2369, <https://doi.org/10.1016/j.dsr2.2006.05.023>, 2006.
- 607 Li, Z. and Cassar, N.: Satellite estimates of net community production based on O_2 /Ar observations and
 608 comparison to other estimates, *Global Biogeochem. Cycles*, 30, 735–752, <https://doi.org/10/f8v6bh>, 2016.
- 609 Lidbury, I., Kröber, E., Zhang, Z., Zhu, Y., Murrell, J. C., Chen, Y., and Schäfer, H.: A mechanism for bacterial
 610 transformation of dimethylsulfide to dimethylsulfoxide: a missing link in the marine organic sulfur cycle,
 611 *Environ. Microbiol.*, 18, 2754–2766, <https://doi.org/10.1111/1462-2920.13354>, 2016.
- 612 Livingstone, D. M. and Imboden, D. M.: The non-linear influence of wind-speed variability on gas transfer in
 613 lakes, *Tellus B*, 45, 275–295, <https://doi.org/10/bbc4n3>, 1993.
- 614 Mahowald, N. M., Engelstaedter, S., Luo, C., Sealy, A., Artaxo, P., Benitez-Nelson, C., Bonnet, S., Chen, Y.,
 615 Chuang, P. Y., Cohen, D. D., Dulac, F., Herut, B., Johansen, A. M., Kubilay, N., Losno, R., Maenhaut, W.,
 616 Paytan, A., Prospero, J. M., Shank, L. M., and Siefert, R. L.: Atmospheric Iron Deposition: Global Distribution,
 617 Variability, and Human Perturbations, *Annu. Rev. Mar. Sci.*, 1, 245–278, <https://doi.org/10/fsn8tj>, 2009.
- 618 Malin, G., Wilson, W. H., Bratbak, G., Liss, P. S., and Mann, N. H.: Elevated production of dimethylsulfide
 619 resulting from viral infection of cultures of *Phaeocystis pouchetii*, *Limnology and Oceanography*, 43, 1389–1393,
 620 <https://doi.org/10/bw7vjf>, 1998.
- 621 Martin, J. H. and Fitzwater, S. E.: Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic,
 622 *Nature*, 331, 341–343, <https://doi.org/10/bvtg6v>, 1988.
- 623 Merzouk, A., Levasseur, M., Scarratt, M. G., Michaud, S., Rivkin, R. B., Hale, M. S., Kiene, R. P., Price, N. M.,
 624 and Li, W. K. W.: DMSP and DMS dynamics during a mesoscale iron fertilization experiment in the Northeast
 625 Pacific-Part II: Biological cycling, 53, 2370–2383, <https://doi.org/10.1016/j.dsr2.2006.05.022>, 2006.



- 626 Nelson, N. B. and Siegel, D. A.: The Global Distribution and Dynamics of Chromophoric Dissolved Organic
 627 Matter, *Annu. Rev. Mar. Sci.*, 5, 447–476, <https://doi.org/10/dwcwbk>, 2013.
- 628 Nemcek, N., Ianson, D., and Tortell, P. D.: A high-resolution survey of DMS, CO₂, and O₂/Ar distributions in
 629 productive coastal waters, *Global Biogeochem. Cycles*, 22, 1–13, <https://doi.org/10.1029/2006gb002879>, 2008.
- 630 Nevitt, G. A.: Sensory ecology on the high seas: the odor world of the procellariiform seabirds, *Journal of*
 631 *Experimental Biology*, 211, 1706–1713, <https://doi.org/10/d2rdz3>, 2008.
- 632 Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S., Liddicoat, M. I., Boutin, J., and Upstill-
 633 Goddard, R. C.: In situ evaluation of air-sea gas exchange parameterizations using novel conservative and
 634 volatile tracers, *Global Biogeochem. Cycles*, 14, 373–387, <https://doi.org/10/d9dztz>, 2000.
- 635 Okkonen, S. R., Jacobs, G. A., Joseph Metzger, E., Hurlburt, H. E., and Shriver, J. F.: Mesoscale variability in
 636 the boundary currents of the Alaska Gyre, *Continental Shelf Research*, 21, 1219–1236, <https://doi.org/10/dc2n79>,
 637 2001.
- 638 Roshan, S. and DeVries, T.: Efficient dissolved organic carbon production and export in the oligotrophic ocean,
 639 *Nat Commun*, 8, 2036, <https://doi.org/10/gcrfdg>, 2017.
- 640 Royer, S.-J., Galí Tàpias, M., Saltzman, E., McCormick, C., Bell, T., and Simó, R.: Development and validation
 641 of a shipboard system for measuring high-resolution vertical profiles of aqueous dimethylsulfide concentrations
 642 using chemical ionisation mass spectrometry, *Environmental Chemistry*, <https://doi.org/10/f6c3qp>, 2014.
- 643 Royer, S.-J., Mahajan, A. S., Galí, M., Saltzman, E., and Simó, R.: Small-scale variability patterns of DMS and
 644 phytoplankton in surface waters of the tropical and subtropical Atlantic, Indian, and Pacific Oceans, *Geophys.*
 645 *Res. Lett.*, 42, 475–483, <https://doi.org/10/gkxzf6>, 2015.
- 646 Royer, S.-J., Galí, M., Mahajan, A. S., Ross, O. N., Pérez, G. L., Saltzman, E. S., and Simó, R.: A high-resolution
 647 time-depth view of dimethylsulphide cycling in the surface sea, *Sci. Rep.*, 6, 32325,
 648 <https://doi.org/10.1038/srep32325>, 2016.
- 649 Saltzman, E. S., King, D. B., Holmen, K., and Leck, C.: Experimental determination of the diffusion coefficient
 650 of dimethylsulfide in water, *J. Geophys. Res. Oceans*, 98, 16481–16486, <https://doi.org/10/c73n5b>, 1993.
- 651 Saltzman, E. S., Bruyn, W. J. D., Lawler, M. J., Marandino, C. A., and McCormick, C. A.: A chemical ionization
 652 mass spectrometer for continuous underway shipboard analysis of dimethylsulfide in near-surface seawater,
 653 *Ocean Sci.*, 10, <https://doi.org/10/bv59ng>, 2009.
- 654 Schmidtko, S., Johnson, G. C., and Lyman, J. M.: MIMOC: A global monthly isopycnal upper-ocean climatology
 655 with mixed layers, *J. Geophys. Res. Oceans*, 118, 1658–1672, <https://doi.org/10/ggqp4h>, 2013.
- 656 Sheehan, C. E. and Petrou, K.: Dimethylated sulfur production in batch cultures of Southern Ocean
 657 phytoplankton, *Biogeochemistry*, 147, 53–69, <https://doi.org/10/ghjqgm>, 2020.



- 658 Simó, R. and Dachs, J.: Global ocean emission of dimethylsulfide predicted from biogeophysical data, *Global*
 659 *Biogeochem. Cycles*, 16, 26-1-26-10, <https://doi.org/10/cmqrh2>, 2002.
- 660 Simó, R. and Vila-Costa, M.: Ubiquity of algal dimethylsulfoxide in the surface ocean: Geographic and temporal
 661 distribution patterns, *Marine Chemistry*, 100, 136–146, <https://doi.org/10/bg5bph>, 2006.
- 662 Spiese, C. and Tatarkov, E.: Dimethylsulfoxide reduction activity is linked to nutrient stress in *Thalassiosira*
 663 *pseudonana* NCMA 1335, *Mar. Ecol. Prog. Ser.*, 507, 31–38, <https://doi.org/10.3354/meps10842>, 2014.
- 664 Spiese, C. E., Kieber, D. J., Nomura, C. T., and Kiene, R. P.: Reduction of dimethylsulfoxide to dimethylsulfide
 665 by marine phytoplankton, *Limnology and Oceanography*, 54, 560–570,
 666 <https://doi.org/10.4319/lo.2009.54.2.0560>, 2009.
- 667 Stefels, J.: Physiological aspects of the production and conversion of DMSP in marine algae and higher plants,
 668 *Journal of Sea Research*, 43, 183–197, [https://doi.org/10.1016/S1385-1101\(00\)00030-7](https://doi.org/10.1016/S1385-1101(00)00030-7), 2000.
- 669 Strzepek, R. F. and Harrison, P. J.: Photosynthetic architecture differs in coastal and oceanic diatoms, *Nature*,
 670 431, 689–692, <https://doi.org/10/fk2fs7>, 2004.
- 671 Sunda, W. G., Kieber, D., and Kiene, R. P.: An antioxidant function of DMSP and DMS in marine algae *Oceanic*
 672 *dimethylsulfide (DMS) photolysis*, *Nature*, 418, 317–320, <https://doi.org/10.1038/nature00851>, 2002.
- 673 Taalba, A., Xie, H., Scarratt, M. G., Bélanger, S., and Levasseur, M.: Photooxidation of dimethylsulfide (DMS)
 674 in the Canadian Arctic, *Biogeosciences*, 10, 6793–6806, <https://doi.org/10/f5jhsv>, 2013.
- 675 Tortell, P. D.: Dissolved gas measurements in oceanic waters made by membrane inlet mass spectrometry,
 676 *Limnology and Oceanography: Methods*, 3, 24–37, <https://doi.org/10/drmjv5>, 2005a.
- 677 Tortell, P. D.: Small-scale heterogeneity of dissolved gas concentrations in marine continental shelf waters,
 678 *Geochemistry, Geophysics, Geosystems*, 6, <https://doi.org/10/bgqvs9>, 2005b.
- 679 del Valle, D. A., Kieber, D. J., Bisgrove, J., and Kiene, R. P.: Light-Stimulated Production of Dissolved DMSO
 680 by a Particle-Associated Process in the Ross Sea, Antarctica, *Limnology and Oceanography*, 52, 2456–2466,
 681 <https://doi.org/10.4319/lo.2007.52.6.2456>, 2007.
- 682 Vallina, S. M. and Simó, R.: Strong relationship between DMS and the solar radiation dose over the global
 683 surface ocean, *Science*, 315, 506–508, <https://doi.org/10.1126/science.1133680>, 2007.
- 684 Vila-Costa, M., Valle, D. A. D., González, J. M., Slezak, D., Kiene, R. P., Sánchez, O., and Simó, R.:
 685 Phylogenetic identification and metabolism of marine dimethylsulfide-consuming bacteria, 8, 2189–2200,
 686 <https://doi.org/10.1111/j.1462-2920.2006.01102.x>, 2006.
- 687 Wang, W.-L., Song, G., Primeau, F., Saltzman, E. S., Bell, T. G., and Moore, J. K.: Global ocean dimethyl
 688 sulfide climatology estimated from observations and an artificial neural network, *Biogeosciences*, 17, 5335–5354,
 689 <https://doi.org/10/ghn33p>, 2020.



- 690 Watanabe, Y. W., Yoshinari, H., Sakamoto, A., Nakano, Y., Kasamatsu, N., Midorikawa, T., and Ono, T.:
 691 Reconstruction of sea surface dimethylsulfide in the North Pacific during 1970s to 2000s, *Marine Chemistry*,
 692 103, 347–358, <https://doi.org/10/bzz33z>, 2007.
- 693 Webb, A. L., van Leeuwe, M. A., den Os, D., Meredith, M. P., J. Venables, H., and Stefels, J.: Extreme spikes in
 694 DMS flux double estimates of biogenic sulfur export from the Antarctic coastal zone to the atmosphere, *Sci.*
 695 *Rep.*, 9, 2233, <https://doi.org/10/ghjqgc>, 2019.
- 696 Weber, T., Wiseman, N. A., and Kock, A.: Global ocean methane emissions dominated by shallow coastal
 697 waters, *Nat. Commun.*, 10, 4584, <https://doi.org/10/gf9pc7>, 2019.
- 698 Westberry, T. K., Behrenfeld, M. J., Milligan, A. J., and Doney, S. C.: Retrospective satellite ocean color analysis
 699 of purposeful and natural ocean iron fertilization, *Deep Sea Research Part I: Oceanographic Research Papers*, 73,
 700 1–16, <https://doi.org/10/f4rcbn>, 2013.
- 701 Westberry, T. K., Shi, Y. R., Yu, H., Behrenfeld, M. J., and Remer, L. A.: Satellite-Detected Ocean Ecosystem
 702 Response to Volcanic Eruptions in the Subarctic Northeast Pacific Ocean, *Geophys. Res. Lett.*, 46, 11270–11280,
 703 <https://doi.org/10/ggr9ms>, 2019.
- 704 Whitney, F. A., Crawford, W. R., and Harrison, P. J.: Physical processes that enhance nutrient transport and
 705 primary productivity in the coastal and open ocean of the subarctic NE Pacific, *Deep Sea Research Part II:*
 706 *Topical Studies in Oceanography*, 52, 681–706, <https://doi.org/10/dkn9sn>, 2005.
- 707 Zeng, C., Rosengard, S. Z., Burt, W., Peña, M. A., Nemcek, N., Zeng, T., Arrigo, K. R., and Tortell, P. D.:
 708 Optically-derived estimates of phytoplankton size class and taxonomic group biomass in the Eastern Subarctic
 709 Pacific Ocean, *Deep Sea Research Part I: Oceanographic Research Papers*, 136, 107–118,
 710 <https://doi.org/10.1016/j.dsr.2018.04.001>, 2018.

711