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Supplementary material

A steady-state physiological model for intracellular dimethylsulfoxide in marine phytoplankton

Michel Lavoie,[A] *Maurice Levasseur*[A,C] *and William G. Sunda*[B]

[A]Québec-Océan and Unité Mixte Internationale Takuvik Ulaval–Centre national de recherche scientifique (CNRS), Département de Biologie, Université Laval,
Québec, QC, G1K 7P4, Canada.

[B]Beaufort Laboratory, National Oceanic and Atmospheric Administration,
Beaufort, NC 28516, USA.

[C]Corresponding author. Email: maurice.levasseur@bio.ulaval.ca

Estimation of the intracellular DMS concentration

In the present study, we neglected the oxidation of DMS as a DMSO source based on the very low modelled intracellular DMS concentration of 1 to 40 nmol L^{-1} cell volume published by Spiese.[1] This intracellular DMS range was obtained from a steady-state model that accounted for the production of DMS through the oxidation of DMSP to DMSO and subsequent enzymatic reduction of DMSO to DMS, DMS losses from its reaction with $^{\bullet}OH$ radicals, and its cellular efflux across the outer cell membrane. The cellular efflux of DMS was estimated using an experimentally measured DMS octanol/water partition coefficient (k_{ow} = 18.6 ± 1.1).

The enzymatic conversion of DMSP to DMS by the DMSP lyase enzyme was neglected in estimating the intracellular DMS concentration because this enzyme is not thought to exist in diatoms.[2] And in most prymnesiophytes or dinoflagellates in which DMSP lyase has been detected, the enzyme is thought to be inactive or largely inactive under optimal growth conditions[3,4] and contributes only a low proportion of the intracellular DMS.[1,2]

Spiese[1] has empirically estimated very low intracellular DMS concentrations in a marine dinoflagellate. This estimate was based on similar rates of extracellular accumulation of dissolved DMS and DMSO in cultures of *Amphidinium carterae*[5] despite a computed three to four orders of magnitude-higher permeability of DMS than DMSO across the outer cell membrane. They argued that because of the similarity in accumulation rates of dissolved DMS and DMSO and the orders of magnitude-higher membrane permeability of DMS, the intracellular DMS concentration would have to be three to four orders of magnitude lower than the intracellular DMSO concentration to explain the results. Note that even accounting for significant DMS loss from

photolysis in the algal culture medium, the observations still suggest that the intracellular DMS concentration is much lower than that of DMSO.

Our model calculations also neglected other potential enzymatic reactions that could affect DMS production and loss, such as those catalysed by DMS monooxygenase, thiol-*S*-methyltransferase and DMS dehydrogenase. Although these enzymatic reactions have been shown to occur in bacteria and higher plants, there is no current evidence that these reaction pathways contribute significantly to DMS production and loss in algal cells. The studies of Attieh et al.[6,7] have shown that hydrogen sulphide can be converted to DMS in higher plants. In bacteria, there is some evidence that DMS may be oxidised to DMSO by DMS dehydrogenase[8,9] and that DMS may be oxidised to formaldehyde and methanethiol by DMS monooxygenase. Even though the biochemical pathways leading to DMS production in algae may well be more complicated than Spiese[1] assumed when modelling the intracellular DMS concentrations in algal cells, the much higher membrane permeability of DMS than DMSO along with the similar low rates of extracellular accumulation of these two molecules strongly suggest that the intracellular DMS concentration in algae is very low as assumed in our model.

Comparison of modelled and measured intracellular DMSO concentrations

Table S1. Comparison of modelled (present study) and published measured intracellular DMSO concentrations [DMSOp] in a range of phytoplanktonic species grown in batch cultures in the laboratory under optimal conditions

Note that even though the measured [DMSOp] in several species can be produced with our model within the model range of hydroxyl radical concentrations, that measured [DMSOp] requires an unreasonably high rate of DMSP oxidation to DMSO, an impossibly high rate of DMSP production and an impossibly high steady-state intracellular DMSP concentration (see *Discussion* in the main text body for further details)

Phytoplankton species	Strain	Measured [DMSOp] (mmol L^{-1} cell volume)	Analytical methods	Modelled [DMSOp] (mmol L^{-1} cell volume)	Modelled [$^{\bullet}$OH] (nmol L^{-1} cell volume)	References of measured DMSOp
Skeletonema costatum	CCAP1077/3	0.17	Enzyme-linked	~0.13	>1	Hatton and Wilson[10]
Thalassiosira oceanica	CCMP1005	0.86	$TiCl_3$ reduction	~0.13	>1	Spiese et al. [2]
Phaeodactylum tricornutum	CCAP1052/1A	1.1	Enzyme-linked	~0.13	>1	Hatton and Wilson[10]
Isochrysis galbana	CCMP1323	0.069	$TiCl_3$ reduction	0.07	5×10^{-4}	Spiese et al. [2]
Emiliania huxleyi	CCMP374	1.3	$TiCl_3$ reduction	1.3	0.01	Spiese et al.[2]
E. huxleyi	AC472	17	$NaBH_4$ reduction			Hatton and Wilson[10]
I. galbana	CCAP927/1	12	$NaBH_4$ reduction			Hatton and Wilson[10]
Amphidinium operculatum	CCAP1102/6	73	$NaBH_4$ reduction			Hatton and Wilson[10]

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