

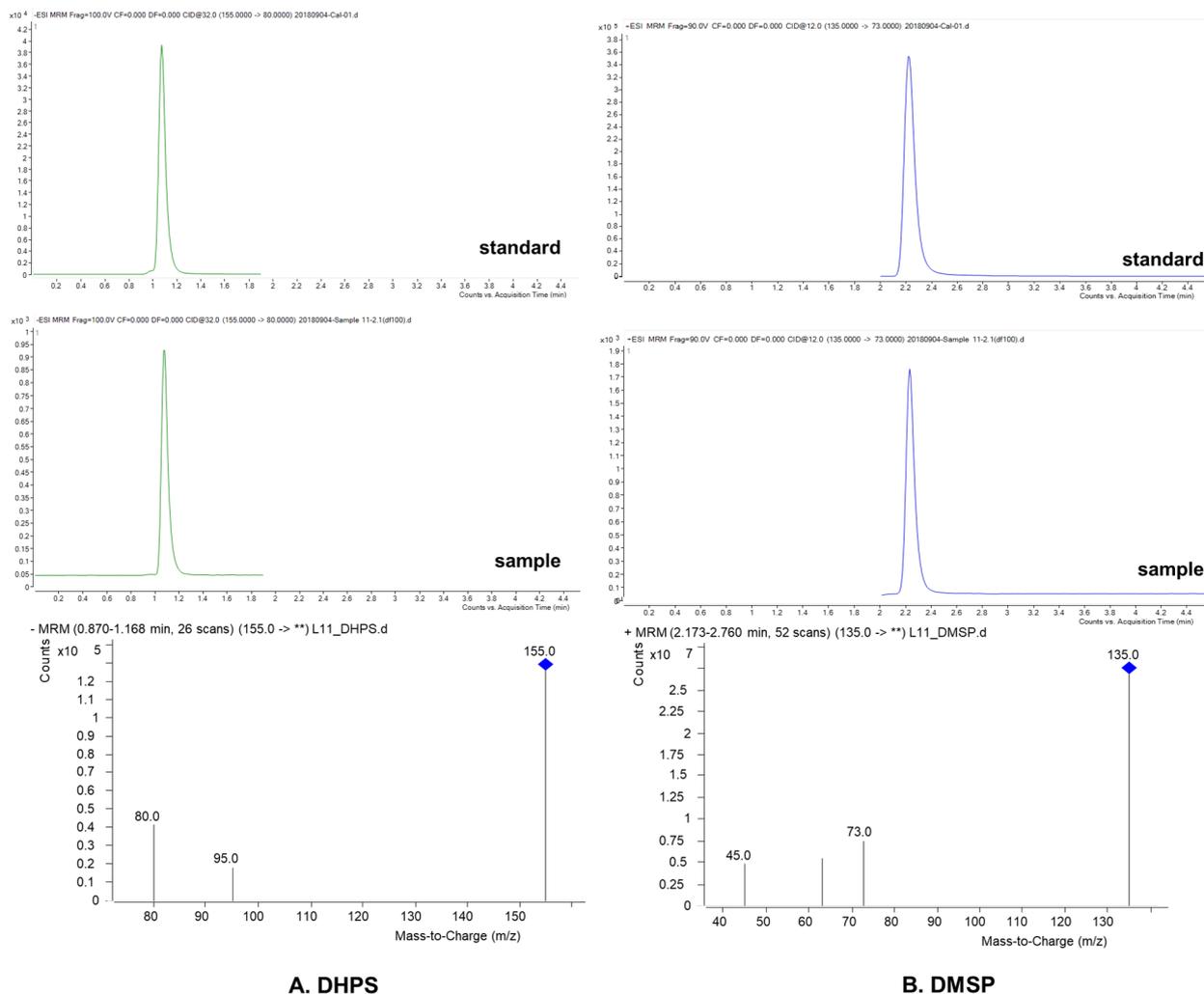
## Supplementary Materials

**Table S1.** MRM conditions for each metabolite.

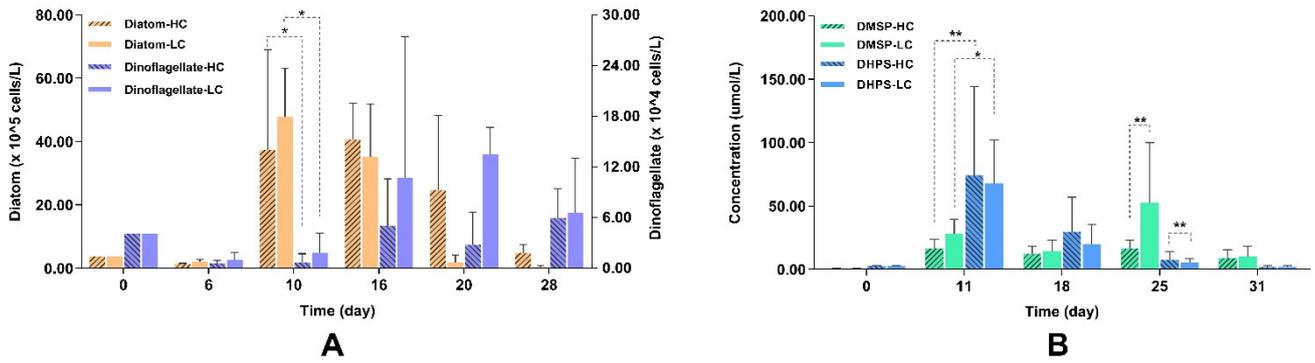
Metabolite	Parent ( <i>m/z</i> )	Product ( <i>m/z</i> )	CV (V)	CE (V)	Polarity	Quantifier/Qualifier
DHPS	155	95	2	14	Negative	Quantifier
		80	2	30	Negative	Qualifier
DMSP	135	73	2	12	Positive	Quantifier
		63	2	12	Positive	Qualifier
		45	2	23	Positive	Qualifier

CV, cone voltage.

CE, optimized collision energies.



**Figure S1.** Analysis of DHPS (A) and DMSP (B) via targeted LC-MS/MS. The extracted ion chromatograms (EICs) from standard solutions (upper figures) and samples (middle figures) of the targeted analytes under the optimal conditions. The MS/MS characteristics of DHPS and DMSP are also shown (lower figures).



**Figure S2.** Community succession of the predominate phytoplankton (A), and concentrations of DHPS and DMSP (B) during the mesoscale experiment. HC: high  $p\text{CO}_2$  treatment groups, 1000 ppmv; LC: low  $p\text{CO}_2$  treatment groups, ~410 ppmv. (A) Data were quoted from [24]; Error bars represent standard deviation of replicates for different treatments (HC,  $n = 4$ ; LC,  $n = 3$ ). (B) The metabolite concentrations were present as the mean values with standard deviation of triplicate samples for replicate cultured bags ((HC,  $n = 12$ ; LC,  $n = 9$ ) with the same treatment. Two-way ANOVA analysis, \*,  $p < 0.05$ ; \*\*,  $p < 0.01$ .