

Table S2. Annotation information for metabolites. Chemical shift values for candidate HSQC peaks are from Human Metabolome Databases (HMDB) except for DHPS, DMSP, homarine, and β -1,3-glucan (see Methods for details). Confirmed peaks are shown in bold. Peaks overlapping with those of other compound(s) are indicated by asterisks. For the annotation confidence levels, see Methods. Annotation confidence assignments are as follows: 1 = putative compounds with functional group information; 2 = partially matched to HSQC chemical shift information in the databases or literature; 3 = fully matched to HSQC chemical shift; 4 = fully matched to HSQC chemical shift and validated by HSQC-TOCSY; 5 = validated by a spiking experiment. Synthesis match indicates whether synthesis pathway genes were enriched in the diatom transcriptome, if known. Bacterial transporter match indicates whether uptake genes were enriched in the bacterial transcriptome at the same time point. Y = yes, N = no, nd = not determined due to no temporal difference/gene not known.

Compounds	¹ H (ppm)	¹³ C (ppm)	Confidence level	Synthesis match	Bacterial transporter match
2,3-dihydroxypropane-1-sulfonate (DHPS)	3.03, 3.11, 3.58, 3.69, 4.14	56.5, 56.5, 67.3, 67.3, 70.8	4	Y	N
Dimethylsulfoniopropionate (DMSP)	2.73, 2.91, 3.44	34.1, 27.8, 43.4	4	Y	Y
Glycine	3,55	44,3	3	N	Y
Proline	1.99, 2.07, 2.34, 3.32, 3.41, 4.13	26.5, 31.8, 31.7, 49, 49, 64	4	N	nd
Glutamate	2.09, 2.34, 3.74*	29.8, 36.4, 57.6*	4	Y	nd
Glutamine	2.12*, 2.44, 3.76*	29.3*, 33.9, 57.2*	4	nd	nd
Alanine	1.49, 3.78	19.0, 53.6	4	nd	nd
Isoleucine	0.93, 1, 1.25, 1.45, 1.96, 3.65*	13.9, 17.4, 27.2, 27, 38.7, 62.5*	4	nd	nd
Valine	0.98, 1.03, 2.26, 3.6	19.4, 20.8, 31.9, 63.3	4	Y	nd
Glycine betaine	3.25, 3.89*	55.9, 68.6*	3	Y	N
Lysine	1.43*, 1.49*, 1.72, 1.88*, 3.02, 3.75*	24*, 24*, 29.2, 32.7*, 42.1, 57.5*	4	Y	nd
β -1,3-glucan	3.51*, 3.51*, 3.56, 3.73*, 3.78, 3.92*, 4.79	70.9*, 78.4*, 76.0, 63.4*, 86.9, 63.4*, 105.4	4	nd	N
Arginine	1.68, 1.91, 3.24*, 3.76*	26.5, 30.5, 43.3*, 57.3*	4	N	nd
Leucine	0.94, 0.96, 1.7*, 1.71, 3.74*	23.6, 24.8, 42.6*, 26.8, 56.2*	4	nd	nd
Acetate	1,91	26,1	3	nd	nd

Glycerol 3-phosphate	3.61*, 3.68*, 3.78, 3.82, 3.86*	65*, 65*, 67.6, 67.6, 74*	4	nd	N
Guanosine	3.82*, 3.86*, 4.22*, 4.39*, 5.89, 7.98*	64.2*, 64.2*, 88.1*, 73.3*, 90.4, 140.6*	4	nd	nd
Uridine	3.8*, 3.91*, 4.12, 4.23*, 4.35, 5.89, 5.9, 7.86*	63.6*, 63.6*, 87.1, 72.1*, 76.5, 105.1, 92.1, 144.6*	4	nd	nd
Aspartate	2.71, 2.8, 3.91	39.3*, 39.5*, 55.1	4	nd	Y
Glucose	3.23, 3.4, 3.46, 3.52, 3.7, 3.72, 3.81, 3.82, 3.89, 4.63, 5.22	77, 72.5, 78.6, 74.3, 75.6, 63.5, 74.1, 63.3, 63.4, 98.7, 94.9	2	Y	Y
Homarine	4.37, 7.98, 8.04, 8.55, 8.72	49.3, 130.2, 129, 149.4, 148.6	4	nd	nd
Phosphorylcholine	3.2*, 3.57, 4.15	56.5*, 68.9, 60.6	4	nd	nd
