Supplementary Figures

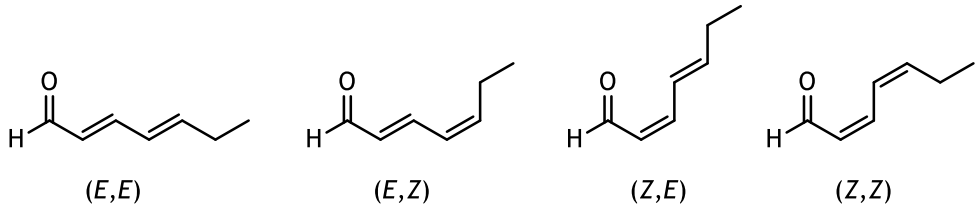

Figure S1: Molecular structure of isomers Type I using heptadienal as an example.

Supplementary tables

Table S1: Phytoplankton functional groups used for FLOW CAM quantification of large size phytoplankton (10-250 µm) cell abundance and biovolume. Grouping name for analysis is detailed.

Category	Size range 09 to 20 µm	Size range 20 to 100 µm	Size range 100 to 250 µm
Others	Spherical cells	Spherical cells	
	Elliptical cells	Elliptical cells	Elliptical cells
	Discoid cells	Discoid cells	
	Cylindrical cells		
	Filamentous chains	Filamentous chains	Filamentous chains
Coccolithophorids		Coccolithophores	
Silicoflagellates	Silicoflagellates	Silicoflagellates	Silicoflagellates
Dinoflagellates		*Protoperidinium*	*Protoperidinium*
		Ceratium	*Ceratium*
		Prorocentrum	*Prorocentrum*
		Gymnodiniales	*Gymnodiniales*
		Peridiniales	
		Unidentified dinoflagellates	Unidentified dinoflagellates
Tintinids		Extended-lorica tintinnids	Extended-lorica tintinnids
		Globular-lorica tintinnids	Globular-lorica tintinnids
Diatoms		Pennate diatoms	Pennate diatoms
		Needle-like diatoms	Needle-like diatoms
		Rhizosolenia & *Proboscia*	Proboscia
		Wide-chain diatoms	Pleurosigma
		Guinardia striata	
		Blavyanus flaccida	
		Leptocylindrus	
		Filamentous diatoms	
		Slightly-connected diatoms	
		Chaetoceros	*Chaetoceros*
		Skeletonema	*Skeletonema*
		Unidentified single centric diatoms	Unidentified single centric diatoms
		Unidentified short-chain diatoms	
		Unidentified long-chain diatoms	
		Thalassiosira	
		Asterionellopsis	*Asterionellopsis*
		Thalassionema	*Thalassionema*
Phaeocystis		*Phaeocystis*	

Table S2: Spearman rank correlation coefficients performed on particulate (pPUA) and dissolved PUA (dPUA) data and enviromental variables. d: dissolved; p: particulate; C7: 2*E*,4*E*/*Z*-heptadienal. C8: 2*E*,4*E*/*Z*-octadienal; C10: 2*E*,4*E*/*Z*-decadienal; T: Temperature (ºC); S: Salinity; PAR: Photosynthetic Active Radiation (mmolquanta m^{-2} s^{-1}); F: Fluorescence (f.u.); ε: coefficient of dissipation of turbulent kinetic energy (m^2 s^{-3}); Nitrate, phosphate and Silicate: µM. O_2: mg L^{-1}. * significant at level 0.05: ** significant at level 0.01.

Station depth	PUA	T	S	PAR	F	NO_3^-	PO_4^{3-}	SiO_4	ε	Oxygen
Jet 5 m	dPUA	0.206	-0.181	0.034	0.180	-0.140	-0.058	-0.186	**0.598****	0.198
	dC7	0.259	-0.169	0.08	0.136	-0.195	-0.028	-0.162	0.333	0.227
	dC8	0.182	-0.204	-0.022	0.200	-0.137	-0.074	-0.206	**0.660****	0.193
	dC10	0.169	-0.119	0.072	0.133	-0.094	-0.039	0.068	**0.522****	0.15
	pPUA	**0.55**	**0.67**	-0.458	**0.748**	-0.317	0.189	-0.335	0.099	-0.26
	pC7	**0.77**	**0.78**	-0.411	**0.755**	-0.267	-0.061	**-0.57**	0.13	-0.25
	pC8	0.13	0.32	**-0.505**	**0.631**	**-0.580**	**0.577**	0.131	0.03	-0.28
	pC10	0.41	**0.68**	-0.260	**0.575**	-0.164	0.103	-0.371	0.059	-0.08
Coast 5 m	dPUA	-0.041	0.056	0.287	-0.104	0.116	0.251	-0.425	-0.133	-0.0023
	dC7	0.26	-0.17	0.08	0.156	-0.060	0.218	-0.133	-0.085	0.188
	dC8	0.182	-0.204	-0.022	-0.128	-0.103	0.278	-0.041	-0.126	0.05
	dC10	-0.141	0.17	-0.12	0.073	0.346	0.083	0.105	-0.152	-0.34
	pPUA	**-0.955**	-0.219	**0.662**	-0.060	0.400	-0.322	**0.568**	**-0.94**	0.318
	pC7	**-0.917**	-0.173	**0.519**	-0.129	**0.569**	-0.480	0.463	**-0.89**	0.177
	pC8	**-0.917**	-0.226	**0.854**	0.016	0.102	-0.061	**0.655**	**-0.921**	0.484
	pC10	**-0.751**	-0.486	**0.821**	0.410	-0.406	0.476	**0.848**	**-0.791**	**0.827**
Gyre 5 m	dPUA	-0.148	0.125	0.0126	-0.05	0.132	0.044	0.113	0.359	-0.196
	dC7	-0.17	0.128	0.03	-0.04	0.141	0.076	0.101	0.454	-0.184
	dC8	-0.07	0.08	0.004	-0.06	0.081	-0.028	0.097	0.236	-0.173
	dC10	-0.278	0.217	-0.01	-0.05	0.223	0.168	0.160	0.283	-0.239
	pPUA	-0.012	0.01	**0.902**	0.227	-0.424	-0.455	-0.219	-0.109	-0.029
	pC7	**-0.852**	**-0.796**	0.287	-0.266	-0.497	**-0.730**	-0.158	0.75	0.816
	pC8	-0.194	-0.171	**0.897**	0.089	**-0.516**	**-0.529**	-0.202	0.046	0.14
	pC10	0.234	0.245	**0.892**	0.338	-0.310	-0.290	-0.199	-0.245	-0.267
Jet DCM	pPUA tot	**0.55**	**0.67**	-0.458	**0.748**	-0.317	0.189	-0.335	0.099	-0.26
	pC7	**0.77**	**0.78**	-0.411	**0.755**	-0.144	-0.061	**-0.570**	0.13	-0.25
	pC8	0.13	0.32	**-0.505**	**0.631**	**-0.580**	**0.577**	0.131	0.03	-0.28
	pC10	0.41	**0.68**	-0.26	**0.575**	-0.164	0.103	-0.371	0.059	-0.08
	dPUA	0.206	-0.181	0.034	0.18	-0.140	-0.058	-0.186	**0.598**	0.198
	dC7	0.259	-0.169	0.08	0.136	-0.195	-0.028	-0.162	0.333	0.227
	dC8	0.182	-0.204	-0.022	0.2	-0.137	-0.074	-0.206	**0.660**	0.193
	dC10	0.169	-0.119	0.072	0.133	-0.094	-0.039	-0.131	**0.522**	0.150
Coast DCM	pPUA	**-0.955**	-0.219	**0.662**	-0.06	0.400	-0.322	**0.568**	**-0.940**	0.318
	pC7	**-0.917**	-0.173	**0.519**	-0.129	**0.569**	-0.480	0.463	**-0.890**	0.177
	pC8	**-0.917**	-0.226	**0.854**	0.016	0.102	-0.061	**0.655**	**-0.921**	0.484
	pC10	**-0.751**	-0.486	**0.821**	0.41	-0.426	0.476	**0.848**	**-0.791**	**0.827**
	dPUA tot	-0.041	0.056	0.287	-0.104	0.116	0.251	-0.425	-0.133	-0.002
	HD	0.123	-0.131	0.128	0.156	-0.060	0.218	-0.133	-0.080	0.188
	OD	0.039	-0.003	**0.544**	-0.128	0.069	0.278	-0.041	-0.120	0.050
	DD	-0.36	0.362	-0.103	-0.339	0.346	0.083	0.105	-0.152	-0.340
Gyre DCM	pPUA tot	-0.012	0.01	**0.902**	0.227	-0.424	-0.455	-0.219	-0.109	-0.029
	HD	**-0.852**	**-0.796**	0.287	-0.266	-0.497	**-0.730**	-0.158	**0.750**	**0.816**
	OD	-0.194	-0.171	**0.897**	0.089	**-0.516**	**-0.529**	-0.202	0.046	0.140
	DD	0.234	0.245	**0.892**	0.338	-0.310	-0.290	-0.199	-0.245	-0.267
	dPUA tot	-0.148	0.125	0.0126	-0.05	0.132	0.044	0.113	0.359	-0.196
	HD	-0.17	0.128	0.03	-0.04	0.141	0.076	0.101	0.454	-0.184
	OD	-0.07	0.08	0.004	-0.06	0.081	-0.028	0.097	0.236	-0.173
	DD	-0.278	0.217	-0.01	-0.05	0.223	0.168	0.160	0.283	-0.239

Table S3: Sperman rank correlation coefficients performed on pPUA data and biological variables I (pigments) at the DCM of the different sites. High correlation are highlighted in grey. dPUA: dissolved PUA; pPUA: particulate PUA; dC7: 2*E*,4*E*/*Z*-heptadienal. dC8: 2*E*,4*E*/*Z*-octadienal; dC10: 2*E*,4*E*/*Z*-decadienal. Perid.: peridinin; Fx: Fucoxanthin; Viol.: violaxanthin; Prasin.; prasinoxanthin; Diadin.; diadinoxanthin; Allox.; alloxanthine; But-Fx:19'-butanoyloxyfucoxanthin. Hex-Fx: 19'-hexanoyloxyfucoxanthin. Significant values are highlighted in bold. "–" denotes undetected concentrations.

Station	pPUA	Chl*a*	$Chlc_1$	$Chlc_2$	$Chlc_3$	Perid.	But-Fx	Fx	Violax	Prasinox	Hex-Fx	Diadin.	Allox	Diatox.	Luteine
Jet	**pPUA**	0.91	-0.11	0.42	0.079	-0.256	0.003	0.918	0.441	0.977	0.964	0.901	0.842	-0.381	0.62
	pC7	0.946	-0.60	0.63	0.031	-0.023	-0.511	0.954	0.183	0.785	0.704	0.973	0.991	-0.414	0.502
	pC8	0.31	0.709	-0.07	0.217	-0.394	0.766	0.265	0.463	0.631	0.724	0.224	0.096	0.011	0.311
	pC10	0.51	-0.29	-0.21	-0.64	-0.432	-0.089	0.792	0.777	0.775	0.758	0.683	0.586	-0.896	0.991
Coast	**pPUA**	0.937	0.911	-0.982	0.783	0.03	0.587	0.851	0.65	0.533	0.984	0.803	0.99	0.908	
	pC7	0.988	0.809	-0.999	0.643	-0.171	0.413	0.728	0.485	0.352	0.929	0.668	0.986	0.806	
	pC8	0.769	0.996	-0.865	0.945	0.361	0.823	0.977	0.866	0.784	0.986	0.956	0.929	0.995	
	pC10	0.475	0.956	-0.616	0.998	0.683	0.975	0.986	0.99	0.959	0.854	0.996	0.725	0.958	
Gyre	**pPUA**	-0.214		-		-0.374	-0.456		-		-0.227	-0.351	-	-0.141	-
	pC7	0.494		-		-0.193	0.178		-		0.188	0.481	-	0.31	-
	pC8	-0.047		-		-0.33	-0.34		-		-0.107	-0.191	-	-0.004	-
	pC10	-0.385		-		-0.36	-0.554		-		-0.314	-0.527	-	-0.256	-

Table S4: Spearman rank correlation coefficients performed on pPUA data and biological variables II (biovolume of taxonomical categories of large size phytoplankton) at the DCM of the different sites. High correlation is highlighted in grey. Significance level *p< 0.05; **p<0.01. dPUA: pPUA: particulate PUA; dC7: 2*E*,4*E*/*Z*-heptadienal. dC8: 2*E*,4*E*/*Z*-octadienal; dC10: 2*E*,4*E*/*Z*-decadienal. Significant values are highlighted with grey area.

		Diatoms	Cocolitophorids	Silicoflagellates	Dinoflagellates	Others
Jet	**pPUA**	0.730	-0.425	0.881*	0.043	0.466
	pC7	0.831*	-0.326	0.897*	0.057	0.524
	pC8	0.463	-0.536	0.622	0.117	0.338
	pC10	0.568	-0.292	0.945**	-0.215	0.282
Coast	**pPUA**	-0.086	-0.157	0.244	-0.041	-0.116
	pC7	-0.174	-0.208	0.339	-0.189	-0.203
	pC8	0.021	-0.106	0.026	0.171	-0.009
	pC10	0.446	0.286	-0.029	0.645*	0.423
Gyre	**pPUA**	-0.559	-0.43	0.092	-0.483	-0.514
	pC7	-0.193	-0.429	0.106	-0.687	-0.544
	pC8	-0.591	-0.524	0.109	-0.611	-0.62
	pC10	-0.542	-0.33	0.068	-0.318	-0.392
Total	**pPUA**	0.338	-0.079	0.569*	-0.103	0.273
	pC7	0.503*	0.085	0.744*	-0.073	0.414
	pC8	0.333	-0.103	0.566*	-0.058	0.327
	pC10	0.578*	0.0109	0.746*	-0.065	0.509