**Table S1**Nutrient composition in nutrient-replete (HN) and nutrient-limited (LN) mediaused in *Chlorella sp.* batch cultures.

	HN Media	LN Media	
Nutrient	Concentration (mM)	Concentration (mM)	
NaNO <sub>3</sub>	17.6	0.23	
K <sub>2</sub> HPO <sub>4</sub>	0.23	0.045	
MgSO <sub>4</sub> .7H2O	0.30		
CaCl <sub>2</sub> .2H2O	0.24		
Citric acid	0.03		
Ammonium ferric citrate	~0.03		
green			
EDTANa <sub>2</sub>	$2.7 \times 10^{-3}$		
Na <sub>2</sub> CO <sub>3</sub>	0.19		
Trace metal solution <sup><math>\pm</math></sup>	1 mL L <sup>-1</sup>		

<sup>\*</sup>Contains per L: 2.86 g H<sub>3</sub>BO<sub>3</sub>; 1.81g MnCl<sub>2</sub>.4H<sub>2</sub>O; 0.22 g ZnSO<sub>4</sub>.7H<sub>2</sub>O; 0.39 g Na<sub>2</sub>MoO<sub>4</sub>.2H<sub>2</sub>O; 0.08 g

CuSO<sub>4</sub>.5H<sub>2</sub>O; 0.05 g Co(NO<sub>3</sub>)2.6H<sub>2</sub>O.

**Table S2**Diagnostic neutral loss or product ions in MS/MS spectra used to determineclass for lipid species analysed using LC-ESI-MS/MS in positive ionisation mode. Seematerials and methods section for description of MS conditions.

Lipid	Molecular	Neutral loss or product ion	Neutral loss or product ion
Class	ion	mass	description
MGDG	$[M+NH_4]^+$	179; 197	glycosyl; glycolsyl + H <sub>2</sub> 0
DGDG	$[M+NH_4]^+$	341; 359	glycosyl; glycolsyl + H <sub>2</sub> 0
SQDG	$\left[\mathrm{M+NH_4}\right]^+$	243; 261	glycosyl; glycolsyl + H <sub>2</sub> 0
PG	$[M+NH_4]^+$	189	phosphoglycerol
PE	$[M+H]^+$	141	phosphoethanolamine
PC	$[M+H]^+$	184	Phosphocholine
DGTS	$[M+H]^+$	236	Headgroup

Table S3 SIMPER analyses of polar lipid species contributing to the dissimilaritybetween lipid samples taken from *Chlorella sp.* grown in nutrient-limited (LN) media at day4 and day 9 and day 4 and 15 of batch cultures.

Species	LN Day 4	LN Day 9	Contribution	Cumulative
			%	contribution %
MGDG 34:7	78.4	11.1	43.94	43.94
PG 34:4	60.7	31.3	8.46	52.40
MGDG 34:5	0.6	29.9	8.34	60.75
MGDG 34:6	14.6	39.9	6.20	66.94
PC 36:6	36.1	15.1	4.35	71.30

Species	LN Day 4	LN Day 15	Contribution	Cumulative
			%	contribution %
MGDG 34:7	78.4	1.62	29.23	29.23
PG 34:1	7.8	76.8	23.74	52.97
PG 34:4	60.7	0	18.25	71.21





PC

НО

phosphatidylcholine



DGTS Diacylglyceryl-trimethyl-homoserine







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 $HO_{S\approx0} \rightarrow HO_{R_{1}} \rightarrow HO_{OH} \rightarrow$ 

sulfoquinovosyldiacylglycerol

SQDG

digalatosyldiacylglycerol



**PE** phosphatidylethanolamine

**Figure S1** Chemical structures of different polar lipid classes analysed in this study. R<sub>1</sub> and R<sub>2</sub> denote different acyl groups (different in carbon chain length and degree of unstauration) that give rise to different species within each class.





MS/MS fragmentation spectra for confirmation of acyl groups in polar lipid Figure S2 species using positive ionisation (a) MGDG  $34:6,18:3/16:3([M+NH_4]^+=764.5 m/z)$  (b) DGDG 36:6, 18:3/18:3  $([M+NH_4]^+=954.5m/z)$ (c) SQDG 34:3, 16:0/18:3  $([M+NH_4]^+=835.5m/z)$ , and negative ionisation (d) PE 34:0, 17:0/17:0  $([M-H]^-=719.5m/z)$  (e) PG 34:0,17:0/17:0 ([M-H]=750.5m/z) (f) PC 34:0, 17:0/17:0 ([M+acetate]=820.5m/z) and (g) DGTS 32:0, 16:0/16:0 ([M+acetate]<sup>=</sup>=770.5*m/z*). Note that MS<sup>2</sup> and MS<sup>3</sup> fragmentation (data independent acquisition) was required for PC and DGTS species, respectively, to yield acyl ions. Ions corresponding to acyl fragments indicated inset spectra.