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6	Vertically migrating phytoplankton drive seasonal formation of subsurface
7	negative preformed nitrate anomalies in the subtropical North Pacific and
8	North Atlantic
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## 24 Abstract

25	Summertime drawdown of dissolved inorganic carbon in the absence of measurable
26	nutrients from the mixed layer and subsurface negative preformed nitrate (preNO <sub>3</sub> ) anomalies
27	observed for the ocean's subtropical gyres are two biogeochemical phenomena that have thus far
28	eluded complete description. Many processes are thought to contribute including biological
29	nitrogen fixation, lateral nutrient transport, carbon overconsumption or non-Redfield C:N:P
30	organic matter cycling, heterotrophic nutrient uptake, and the actions of vertically migrating
31	phytoplankton. Here we investigate the seasonal formation rates and potential contributing
32	mechanisms for negative preformed nitrate anomalies (oxygen consumption without
33	stoichiometric nitrate release) in the subsurface and positive preformed nitrate anomalies
34	(oxygen production without stoichiometric nitrate drawdown) in the euphotic zone at the
35	subtropical ocean time series stations ALOHA in the North Pacific and BATS in the North
36	Atlantic. Non-Redfield -O2:N stoichiometry for dissolved organic matter (DOM)
37	remineralization is found to account for up to ~15 mmol N m <sup>-2</sup> yr <sup>-1</sup> of negative preNO <sub>3</sub> anomaly
38	formation at both stations. Residual negative preNO3 anomalies in excess of that which can be
39	accounted for by non-Redfield DOM cycling are found to accumulate at a rate of $\sim$ 32 – 46 mmol
40	N m <sup>-2</sup> yr <sup>-1</sup> at station ALOHA and $\sim 46 - 87$ mmol N m <sup>-2</sup> yr <sup>-1</sup> at the BATS station. These negative
41	anomaly formation rates are in approximate balance with positive preNO <sub>3</sub> anomaly formation
42	rates from the euphotic zone located immediately above the nutricline in the water column.
43	Cycling of transparent exopolymer particles (TEP) and heterotrophic nitrate uptake can
44	contribute to the formation of these preNO3 anomalies, however a significant fraction, estimated
45	at $\sim$ 50 – 95%, is unexplained by the sum of these processes. Vertically migrating phytoplankton
46	possess the necessary nutrient acquisition strategy and biogeochemical signature to quantitatively





47	explain both the residual negative and positive preNO3 anomalies as well as the mixed layer
48	dissolved inorganic carbon drawdown at stations ALOHA and BATS. TEP production by the
49	model Rhizosolenia mat system could provide accelerated vertical transport of TEP as well as
50	link the three processes together. Phytoplankton vertical migrators, although rare and easily
51	overlooked, may play a large role in subtropical ocean nutrient cycling and the biological pump.
52	
53	Introduction
54	Subtropical ocean gyre ecosystems exhibit low rates of primary productivity caused by
55	thermal stratification of the water column that acts as an impediment to sustained nutrient supply
56	to the surface ocean. Yet these regions exhibit significant annual net community production
57	(ANCP), estimated at $3 \pm 1 \text{ mol C m}^{-2} \text{ yr}^{-1}$ for station ALOHA in the North Pacific (Hawaii
58	Ocean Time-series) and the BATS station (Bermuda Atlantic Time-Series) in the North Atlantic
59	(Emerson, 2014), contributing about half of the global biological carbon pump (Emerson et al.,
60	1997). Observations at these two well-characterized time-series sites indicate a seasonal
61	drawdown of mixed layer dissolved inorganic carbon (DIC) occurs during the summer and early
62	autumn months that is attributed to net community production with minor contributions from
63	lateral mixing and air-sea CO <sub>2</sub> exchange (Gruber et al., 1998, 2002; Keeling et al., 2004;
64	Williams et al., 2013).
65	The nutrient sources supporting this seasonal DIC drawdown at the time-series sites have
66	eluded oceanographers since the phenomenon was first documented (Michaels et al., 1994;
67	Toggweiler, 1994; Gruber et al., 1998; Keeling et al., 2004). Numerous nutrient input
68	mechanisms have been investigated including vertical mixing, N2 fixation, atmospheric
69	deposition, and eddy movements with their sum still falling short of explaining the observed DIC





70	drawdown or a stoichiometric equivalent subsurface oxygen consumption (Jenkins and
71	Goldman, 1985; Jenkins and Doney, 2003) assuming Redfield stoichiometry between organic
72	matter production and remineralization. More recently, episodic vertical mixing events and
73	lateral advection are two physical mechanisms that have been proposed to supply the surface
74	subtropical gyres with the "missing" nutrients to explain observed ANCP (Johnson et al., 2010;
75	Letscher et al., 2016). However, in order to explain the observed summertime DIC drawdown
76	from the subtropical gyre mixed layer, these two physical mechanisms must supply nutrients,
77	carbon, and oxygen in non-Redfield stoichiometries. Letscher et al. (2016) reported C-deficient,
78	non-Redfieldian supply of inorganic carbon and nutrients within the lateral nutrient streams
79	reaching the subtropical gyres; however, this mechanism still falls short of explaining the
80	observed DIC drawdown at stations ALOHA and BATS, even after accounting for non-Redfield
81	C:N:P stoichiometry of organic matter production. Johnson et al. (2010) used profiling floats
82	equipped with biogeochemical sensors to observe episodic, near monthly, vertical mixing events
83	near station ALOHA that supply nitrate from the nitracline upwards into the euphotic zone to a
84	depth of $\sim$ 75-100 m. To explain the surface DIC drawdown, these authors suggested the non-
85	Redfieldian supply of nitrate into the mixed layer above ~50 m is carried out by large, non-
86	flagellated phytoplankton that migrate between the nutricline and the surface as part of their life-
87	history strategy for nutrient acquisition (Villareal et al., 1993; 2014).
88	In conjunction with the "missing" nutrient supply required to explain observed mixed
89	layer DIC drawdown, the subtropical gyre regions also exhibit a deficit of sub-euphotic zone
90	nitrate as expected from observed oxygen consumption and Redfield -O2:N organic matter
91	remineralization stoichiometry. This phenomenon is revealed when examining spatiotemporal
92	patterns of the preformed nitrate (preNO <sub>3</sub> ) tracer. preNO <sub>3</sub> is calculated as $preNO_3 = NO_{3meas} - NO_{3$





93	AOU/R- $_{O2:N}$ , where AOU is the apparent oxygen utilization and R- $_{O2:N}$ is the stoichiometric ratio
94	of oxygen consumed to N regenerated for the remineralization of Redfieldian organic matter, e.g.
95	150:16 (9.4). preNO <sub>3</sub> quantifies the fraction of measured nitrate in a water parcel not attributable
96	to remineralization of Redfieldian organic matter and was initially formulated as a conservative
97	tracer for examining the distribution of water masses involved in the global thermohaline
98	circulation (Broecker, 1974). However, observations of preNO3 within upper mesopelagic depths
99	(~100-300 m) of the subtropical ocean have revealed negative preNO <sub>3</sub> (NPN) anomalies,
100	suggesting non-Redfieldian processes impacting the in situ dissolved oxygen and nitrate pools
101	(Abell et al., 2005; Johnson et al., 2010). Abell et al. (2005) suggested production, export, and
102	remineralization of dissolved organic matter (DOM) with non-Redfield, elevated C:N
103	stoichiometry could quantitatively explain the preNO3 distribution in the subtropical North
104	Pacific. That is, the observed negative values were the result of oxygen consumption when high
105	C:N DOM was remineralized without concurrent Redfieldian nitrate accumulation. Working in
106	the same ecosystem, Johnson et al. (2010) suggested that the subsurface NPN anomaly
107	(calculated using a modified Redfield ratio) is sustained by vertical separation between nitrate
108	uptake in the nutricline and oxygen production near the surface that is mediated by combined 1)
109	vertical physical mixing and 2) vertically migrating phytoplankton transporting nitrate upwards
110	along a near-zero concentration gradient above the nutricline. These are not mutually exclusive
111	mechanisms, although to date no work has partitioned the contribution of the mechanisms to
112	formation of the negative preNO <sub>3</sub> anomaly.
113	In this work, we expand the examination of preNO3 anomalies to the BATS station in the

North Atlantic and revisit the missing nutrient and NPN anomaly problems at both stations
ALOHA and BATS. We update the calculation of preNO<sub>3</sub> to include the contribution of DOM





116	and its non-Redfield –O <sub>2</sub> :N remineralization stoichiometry to the subsurface tracer fields in a
117	manner analogous to Abell et al. (2005). Using this revised preNO3 calculation, we identify a
118	residual negative preNO <sub>3</sub> (rNPN) anomaly within the subsurface nutricline and a residual
119	positive preNO $_3$ (rPPN) anomaly within the euphotic zone not attributable to the non-Redfield –
120	O2:N, DOM remineralization stoichiometry mechanism. Seasonal formation of a sub-euphotic
121	zone rNPN anomaly at the BATS station and a persistent sub-euphotic zone rNPN anomaly at
122	station ALOHA is identified, similar to previous work in the subtropical North Pacific (Abell et
123	al., 2005; Johnson et al., 2010). rPPN anomalies are observed within the euphotic zone $(0 - 80)$
124	or $\sim 100$ m) at both sites, with rates of formation that are in approximate stoichiometric balance
125	with the rNPN anomalies located immediately below in the water column. These residual
126	anomalies account for the effects of both particulate organic matter (POM) and DOM
127	remineralization with elevated -O <sub>2</sub> :N stoichiometry and require additional mechanisms for their
128	formation. We then undertake a quantitative examination of other potential contributing
129	mechanisms to explain the subsurface rNPN anomalies, euphotic zone rPPN anomalies, and
130	mixed layer DIC drawdown including transparent exopolymer particle (TEP) cycling, subsurface
131	bacterial uptake of nitrate, and vertical migration by phytoplankton. We find that TEP cycling
132	may explain a fraction of both the rNPN and rPPN anomalies; bacterial nitrate uptake accounts
133	for only a small fraction of rNPN and none of the rPPN anomalies. Phytoplankton vertical
134	migration can, within the limits of available abundance data, fully explain both the rNPN and
135	rPPN anomalies at both stations ALOHA and BATS.
136	

137 Methods

138 **Data** 





139	Time-series biogeochemical data including concentrations of total dissolved nitrogen,
140	nitrate + nitrite, and oxygen for the years 1988-2016 were downloaded from http://bats.bios.edu
141	for the BATS station and http://hahana.soest.hawaii.edu/hot for station ALOHA. Dissolved
142	organic nitrogen was calculated as total dissolved nitrogen minus [nitrate + nitrite]. Global
143	annual climatologies for dissolved $O_2$ and $NO_3^-$ from the World Ocean Atlas 2013 (Garcia et al.,
144	2014a; 2014b) were downloaded from http://www.nodc.noaa.gov/OC5. The Global Ocean Data
145	Analysis Project (GLODAP) v2 dataset (Olsen et al. 2016) including dissolved O <sub>2</sub> , NO <sub>3</sub> <sup>-</sup> , CFC-
146	11, and CFC-12 was downloaded from http://www.nodc.noaa.gov/ocads/oceans/GLODAPv2.

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#### 148 **Tracer computations**

The preformed NO<sub>3</sub> tracer defined by Broeker (1974) separates the observationally 149 determined concentration of nitrate for a given water parcel into contributions from water mass 150 mixing (preformed) and regenerated from respiration of organic matter. Traditional formulations 151 of preNO<sub>3</sub> assign a uniform –O<sub>2</sub>:NO<sub>3</sub> stoichiometry of organic matter remineralization without 152 discriminating between particulate vs. dissolved organic matter (DOM) pools. However, Abell et 153 al. (2005) showed that DOM remineralization stoichiometry is significantly elevated with respect 154 to Redfield proportions in the subtropical North Pacific, with -O<sub>2</sub>:N stoichiometries of 23 to 30 155 within shallow mesopelagic density layers ( $\sigma_{\theta} = 24.4 - 26.1$ ) compared to Redfield values of 6.9 156 to 10.6 (Takahashi et al., 1985; Martin et al., 1987; Anderson and Sarmiento, 1994; Paulmier et 157 al., 2009). This required an additional term in the calculation of preNO<sub>3</sub>. Here we adopt the Abell 158 et al. (2005) analysis and estimate the  $-O_2$ :N stoichiometry of dissolved organic nitrogen (DON) 159 remineralization within upper mesopelagic density layers at stations ALOHA and BATS to test if 160 non-Redfield DOM –O<sub>2</sub>:N remineralization stoichiometry can fully explain the preNO<sub>3</sub> 161





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- anomalies observed by Johnson et al. (2010) from the subtropical North Pacific and those that we
- 163 document at stations ALOHA and BATS in this work.
- The subsurface neutral density layers  $\gamma^n = 24.2 24.7$  and  $\gamma^n = 24.7 25.2$  were chosen at 164 station ALOHA and  $\gamma^n = 25.8 - 26.3$  at the BATS station for subsequent calculation of DON – 165 O2:N remineralization stoichiometry. These density layers were chosen based on examination of 166 the depths exhibiting NPN anomalies using the traditional formulation of the preNO<sub>3</sub> tracer, i.e. 167 preNO<sub>3</sub> = NO<sub>3meas</sub> - AOU/R<sub>-02:N</sub>. NO<sub>3meas</sub> is the sum of dissolved nitrate + nitrite. Apparent 168 oxygen utilization (AOU) was calculated as AOU =  $O_{2sat} - O_{2meas}$ ; the difference between  $O_2$ 169 saturation at a given temperature, salinity, and pressure with the observationally determined  $O_2$ 170 171 concentration. The value of R-O2:N for the calculation of the traditional preNO3 tracer was selected as 150:16. For the updated calculation of the preNO<sub>3</sub> tracer that accounts for the 172 fractional contribution of DOM remineralization, the stoichiometric ratio of O<sub>2</sub> consumed per 173 174 mole of DON remineralized,  $r_{\rm DOM}$ , was determined empirically each year between 1989 – 2000 at station ALOHA and 1993 – 2016 at the BATS station by Model II linear regression (Ricker, 175 1973; Trujillo-Ortiz and Hernandez-Walls, 2010) of AOU vs. DON within the three neutral 176 177 density layers. Thus, the preNO<sub>3</sub> tracer formulation including the effects of DOM remineralization is: 178

$$preNO_{3} = NO_{3meas} - \left(f_{DOM} \cdot \frac{AOU}{rDOM}\right) - \left(f_{POM} \cdot \frac{AOU}{rPOM}\right) \tag{1}$$

The fraction of oxygen consumption attributable to DOM remineralization,  $f_{\text{DOM}}$ , is determined empirically for each density layer following the equation of Abell et al. (2000):

182 
$$f_{DOM} = \frac{\Delta DOM}{\Delta DOM + \Delta POM} = \frac{rPOM}{\frac{\Delta AOU}{\Delta DON}}$$
(2)

183 We determined the ratio  $\Delta AOU/\Delta DON$  (equivalent to  $r_{DOM}$ ) empirically each year from

regressions of AOU (computed) vs. DON (measured) within the respective density layers, with





185	the climatological average $r_{\text{DOM}}$ used in the calculation of preNO <sub>3</sub> . Years with a regression
186	correlation coefficient > 0.33 were included in the climatological average (~55% of years
187	investigated). Thus, our approach assumes $r_{\text{DOM}}$ in constant over time within each density
188	horizon investigated at each station. The stoichiometric ratio of O2 consumed per mole of
189	particulate organic nitrogen (PON) remineralized, $r_{POM}$ , is taken from the literature. We tested
190	the sensitivity of our computed preNO <sub>3</sub> to upper and lower bound values for $r_{POM}$ of 10.6 and 6.9
191	(Paulmier et al., 2009). The fraction of AOU attributable to POM remineralization, $f_{POM}$ , is
192	calculated as $1 - f_{\text{DOM}}$ .
193	The seasonal formation rate of rNPN/rPPN anomalies at each time-series site were
194	estimated by a linear regression of preNO <sub>3</sub> vs. time within each density layer for the years 1989-
195	2016 at station ALOHA and 1993-2016 at the BATS station. The slope of this regression yields
196	the volumetric rate of anomaly formation (negative or positive preNO3 not explained by high
197	C:N DOM remineralization) in units of µmol N m <sup>-3</sup> d <sup>-1</sup> . The volumetric rates were depth and
198	time integrated to provide annual rates of rNPN/rPPN anomaly formation in units of mmol N m <sup>-2</sup>
199	yr <sup>-1</sup> . Depth integration was performed by estimating the thickness, $H$ , each year of the neutral
200	density layers exhibiting rNPN anomalies at the BATS and ALOHA stations. Values of H varied
201	between 20 to 100 m. Depth integration of rPPN anomalies within the euphotic zone at each
202	time-series site were performed within the $0 - 100$ m layer at station ALOHA and within the 0
203	- 80 m layer at the BATS station. For the calculation of the preNO <sub>3</sub> tracer within the euphotic
204	zone, we made the assumption that the values of $f_{\text{DOM}}$ and $r_{\text{DOM}}$ were equivalent to those
205	empirically derived for the upper mesopelagic density layer present immediately below the
206	euphotic zone at each site. The time integration was calculated from the number of days elapsed
207	between the first observation of decreasing (or increasing) preNO3 values to the date when





- 208 preNO<sub>3</sub> ceased decreasing (or increasing) within the annual cycle. Seasonal rNPN anomaly
- formation duration ranged from a minimum of 2 months to a maximum of 10.5 months with a
- 210 median of 7.5 months. Seasonal rPPN anomaly formation duration ranged from a minimum of 4
- 211 months to a maximum of 10 months with a median of 6 months.
- 212
- 213 Results

## 214 DOM remineralization in the upper mesopelagic at the ALOHA and BATS stations

Empirically derived values of  $r_{\text{DOM}}$  at station ALOHA varied between 10.4 and 24.2 for

the  $\gamma^n = 24.2 - 24.7$  layer and between 12.7 and 23.5 for the  $\gamma^n = 24.7 - 25.2$  layer. Values of

 $r_{\text{DOM}}$  at the BATS station varied between 14.0 and 25.3 in the  $\gamma^{n} = 25.8 - 26.3$  layer.

218 Climatological average  $r_{\text{DOM}}$  were computed for each density layer, yielding ratios of 18.1 to

18.9 at station ALOHA and 21.1 at the BATS station (Table 1; standard errors on  $r_{\text{DOM}}$  are on the

220 order of 33%). These climatological values of  $r_{\rm DOM}$  were used in subsequent calculations of

preNO<sub>3</sub> and  $f_{\text{DOM}}$  from equations 1 and 2. The empirically derived values of  $r_{\text{DOM}}$  are consistently

larger than the literature estimates of  $r_{\text{POM}}$ , indicating that remineralization of DOM in the upper

223 mesopelagic returns less moles of nitrate per mole of O<sub>2</sub> respired at the two sites compared to

224 Redfield POM stoichiometry. Thus, DOM remineralization contributes to the NPN anomalies

estimated with the traditional preNO<sub>3</sub> formulation and needs to be accounted for in any study

that utilizes the preNO<sub>3</sub> tracer.

Empirically derived values of  $f_{\text{DOM}}$  varied between 0.38 and 0.59 for the  $\gamma^n = 24.2 - 24.7$ layer and between 0.36 and 0.6 for the  $\gamma^n = 24.7 - 25.2$  layer at station ALOHA. Values of  $f_{\text{DOM}}$ at the BATS station varied between 0.33 and 0.5 in the  $\gamma^n = 25.8 - 26.3$  layer. Climatological





- average  $f_{\text{DOM}}$  values of 0.5 for both density layers at station ALOHA and a value of 0.4 at the
- BATS station (Table 1) were used in subsequent calculation of preNO<sub>3</sub> from equation 1.
- 232

# 233 Upper ocean preNO<sub>3</sub> climatology at the ALOHA and BATS stations

234	Station ALOHA – The climatology of the residual preNO <sub>3</sub> [ $\mu$ M] tracer (the amount
235	remaining after accounting for DOM contributions to AOU) is presented for the upper 250 m at
236	station ALOHA in Figure 1a. preNO3 varies between -1 to 1 $\mu$ M in the upper ~200 m with
237	increasingly positive values below 200 m. The resulting rNPN anomaly is a persistent feature
238	within the $24.2 - 25.2$ neutral density layer at a depth of ~100 to 200 m. Seasonal rPPN
239	anomalies are observed immediately above the 24.2 neutral density horizon within the euphotic
240	zone, 0 to $\sim$ 100 m. Pulses of rPPN anomalies penetrating the bottom of the rNPN anomaly layer
241	are also observed that coincide with shoaling of the 25.2 neutral density horizon above 200 m.
242	A monthly averaged climatology of residual preNO <sub>3</sub> $[\mu M]$ at station ALOHA is
243	presented in Figure 1b. The subsurface rNPN anomaly is observed to grow in magnitude
244	between the months of May/June through Oct/Nov. There also exists an increase in the
245	magnitude of the rPPN anomaly within the euphotic zone $(0 - 100 \text{ m})$ , concomitant with the
246	rNPN anomaly formation at $\sim 100 - 200$ m depth in summer.
247	Volumetric rates of rNPN anomaly formation at station ALOHA are estimated at 2.8 $\pm$
248	1.4 and $3.0 \pm 1.5 \ \mu\text{mol N m}^{-3} \text{ d}^{-1}$ for the $\gamma^n = 24.2 - 24.7$ layer using $r_{\text{POM}}$ values of 6.9 and 10.6,
249	respectively (Table 1). Slightly lower rates of rNPN anomaly formation of 1.6 $\pm$ 0.8 and 2.5 $\pm$
250	1.4 $\mu$ mol N m <sup>-3</sup> d <sup>-1</sup> are estimated for the deeper $\gamma^n = 24.7 - 25.2$ layer at station ALOHA.
251	Combining the two density layers yields a total rNPN formation rate of $4.4 \pm 1.6$ ( $r_{POM} = 6.9$ )
252	and $5.5 \pm 2.1$ ( $r_{POM} = 10.6$ ) µmol N m <sup>-3</sup> d <sup>-1</sup> (Table 1). Depth and time integrated, the estimates of





253	rNPN anomaly formation become $28.3 \pm 9$	$6(r_{POM} = 6.9)$	) and $17.9 \pm 7.4$	$r_{\rm POM} = 10.6$	) mmol N
255	$1141$ 14 anomaly formation become $20.5 \pm 7$	0 (POM 0.)	j  und  1  1  .  .  .  +  .  .	(7 POM 10.0	, minor i

- 254  $\text{m}^{-2} \text{ yr}^{-1}$  for the  $\gamma^{n} = 24.2 24.7$  layer and  $18.1 \pm 8.8$  ( $r_{\text{POM}} = 6.9$ ) and  $13.7 \pm 7.8$  ( $r_{\text{POM}} = 10.6$ )
- 255 mmol N m<sup>-2</sup> yr<sup>-1</sup> for the deeper  $\gamma^n = 24.7 25.2$  layer. Total rNPN formation rate estimates for
- station ALOHA are between  $31.6 \pm 10.8$  to  $46.4 \pm 13.0$  mmol N m<sup>-2</sup> yr<sup>-1</sup> (Table 1).
- 257 The volumetric rate of rPPN anomaly formation within the euphotic zone at station
- 258 ALOHA is estimated at  $3.3 \pm 1.1$  and  $2.4 \pm 0.8 \mu$ mol N m<sup>-3</sup> d<sup>-1</sup> using  $r_{POM}$  values of 6.9 and 10.6,
- respectively (Table 1). These rates are in approximate balance within error of those estimated for
- rNPN formation rate within the  $\gamma^n = 24.2 24.7$  layer immediately below in the water column.
- 261 Depth and time integrated, the estimate of rPPN anomaly formation is  $61.2 \pm 20.2$  ( $r_{POM} = 6.9$ )
- and  $43.5 \pm 10.5$  ( $r_{POM} = 10.6$ ) mmol N m<sup>-2</sup> yr<sup>-1</sup> (Table 1). The euphotic zone integrated rPPN
- anomaly is approximately 33% higher than the estimated total integrated rNPN anomaly within the combined  $\gamma^n = 24.2 - 25.2$  layer.
- BATS The climatology of the residual preNO<sub>3</sub> [ $\mu$ M] tracer in the upper 200 m at BATS 265 is presented in Figure 2a. preNO<sub>3</sub> varies between -1 to 1  $\mu$ M in the upper ~200 m. Seasonal 266 subsurface rNPN anomalies at ~80 to 160 m depth are observed in most but not all years from 267 1993 to 2016. Similar to station ALOHA, seasonal pulses of rPPN anomalies are observed 268 immediately above the 25.8 neutral density horizon within the euphotic zone, 0 to  $\sim$ 80 m. Pulses 269 of rPPN anomalies penetrating from below the 26.3 neutral density horizon are present in a few 270 years but are much less frequent than observed in the station ALOHA climatology. rPPN 271 272 anomalies are observed immediately below the rNPN layer beginning at ~160 m. The monthly averaged climatology of residual preNO<sub>3</sub>  $[\mu M]$  at BATS is presented in 273 Figure 1b. The subsurface rNPN anomaly is observed to first appear beginning in Apr/May and 274
- 275 grow in magnitude through the end of the calendar year. The rNPN feature starts shallow at a





276	depth of ~60 to 100 m that deepens over the summer months to depths of ~80 to 160 m by years'
277	end. There also exists a layer of rPPN anomaly at $0 - 80$ m depth that increases in magnitude,
278	concomitant with the rNPN anomaly formation at $\sim 80 - 160$ m depth in summer and autumn.
279	Late winter convective overturn of the upper water column, which occurs in late Jan/Feb at the
280	BATS station (Hansell and Carlson, 2001) is likely responsible for resetting the subsurface rNPN
281	anomaly by mixing with the rPPN anomalous waters above and below the rNPN layer.
282	The volumetric rate of rNPN anomaly formation at the BATS station is estimated at 5.5 $\pm$
283	2.7 and $3.8 \pm 3.1 \mu \text{mol N m}^{-3} \text{ d}^{-1}$ for the $\gamma^n = 25.8 - 26.3$ layer using $r_{\text{POM}}$ values of 6.9 and 10.6,
284	respectively (Table 1). Depth and time integrated, the estimate of rNPN anomaly formation rate
285	at the BATS station is between $46.0 \pm 39.3$ to $87.1 \pm 41.0$ mmol N m <sup>-2</sup> yr <sup>-1</sup> (Table 1). The
286	volumetric rate of rPPN anomaly formation within the euphotic zone at the BATS station is
287	estimated at 5.8 $\pm$ 1.2 and 4.1 $\pm$ 0.8 $\mu$ mol N m <sup>-3</sup> d <sup>-1</sup> using $r_{POM}$ values of 6.9 and 10.6,
288	respectively (Table 1). These rates are in approximate balance within error of those estimated for
289	rNPN formation rate within the $\gamma^n = 25.8 - 26.3$ layer immediately below in the water column.
290	Depth and time integrated, the estimate of rPPN anomaly formation is $82.1 \pm 13.8$ ( $r_{POM} = 6.9$ )
291	and $61.8 \pm 12.2$ ( $r_{POM} = 10.6$ ) mmol N m <sup>-2</sup> yr <sup>-1</sup> (Table 1). The euphotic zone integrated rPPN
292	anomaly is approximately balanced ( $r_{POM} = 6.9$ ) or 33% higher ( $r_{POM} = 10.6$ ) than the estimated
293	integrated rNPN anomaly within the $\gamma^n = 25.8 - 26.3$ layer.
294	
295	Discussion
296	Both the ALOHA and BATS station climatologies of the residual preNO3 tracer exhibit

annual cycles of rPPN anomaly formation in the euphotic zone and rNPN anomaly formation
beginning at ~100 m (ALOHA) or ~80 m (BATS) that intensifies from early summer through to





299	mid-autumn (Fig. 1 and 2). This timeframe coincides with the period of thermal stratification of
300	the water column at the BATS station, separating the surface mixed layer, $\sim 0 - 30$ m, from the
301	deep chlorophyll max (DCM) present at ~100 - 120 m (Navarro and Ruiz, 2013). Station
302	ALOHA exhibits year-round stratification with the deep chlorophyll max present at $\sim 125$ m
303	(Navarro and Ruiz, 2013). The largest rPPN anomalies are observed in the vertical zone between
304	the surface mixed layer and the DCM at both sites, at a depth of $\sim 50 - 100$ m at station ALOHA
305	and a depth of $\sim 40 - 80$ m at the BATS station. This vertical zone of rPPN anomaly formation
306	coincides with the observed subsurface O <sub>2</sub> maximum that has historically been a conundrum to
307	biogeochemical explanation given the in situ <sup>14</sup> C-diagnosed net primary production estimates
308	(e.g. Jenkins and Goldman, 1985; Schulenberger and Reid, 1981; Platt et al., 1989). rNPN
309	anomalies begin to appear at a depth of ~100 m at station ALOHA and ~80 m at the BATS
310	station continuing down to depths of $\sim$ 200 m and $\sim$ 160 m, respectively. We estimated the depth
311	of the top of the nitracline by defining this as the depth where $[NO_3^- + NO_2^-] = 0.5 \ \mu M$ in the
312	monthly averaged climatologies. At station ALOHA, the top of the nitracline varies between 120
313	-130 m depth with a mean of ~126 m over the annual cycle. At the BATS station, the top of the
314	nitracline varies between $90 - 120$ m depth with an annual mean of ~102 m. Thus, the formation
315	of rNPN anomalies is concurrent with the depth in the water column where nitrate begins to
316	accumulate from remineralization processes at both sites and continues to form deeper into the
317	nitracline.
318	What is the role of physical mixing in creating the observed rPPN and rNPN anomalies?

To address this question, we turn to the World Ocean Atlas  $O_2$  and  $NO_3^-$  climatologies (Garcia et al., 2014a; 2014b) on the subsurface isopycnals present in the ~100 – 250 m depth layer at each site. We computed the residual preNO<sub>3</sub> tracer for the subtropical North Pacific using the values





322	of $f_{\text{DOM}}$ and $r_{\text{DOM}}$ for station ALOHA and for the subtropical North Atlantic using the values for
323	the BATS station in Table 1. Examination of the preNO <sub>3</sub> tracer on the $\gamma^n = 26.5$ density surface
324	(the surface approximately bisecting the 150 – 200 m layer near BATS exhibiting rPPN
325	anomalies) reveals that the BATS station is immediately surrounded by waters with a preNO <sub>3</sub>
326	value of ~1 $\mu$ M (Fig. S1). Waters with a preNO <sub>3</sub> content of ~2 – 3 $\mu$ M are present to the
327	southwest and to the northeast. The lack of a preNO <sub>3</sub> gradient on the $\gamma^n = 26.5$ density surface in
328	the immediate vicinity of the BATS station suggests the observed $\sim 1 \ \mu M \ preNO_3$ concentration
329	present at $\sim 150 - 200$ m depth in Figure 2 represents an advected signal with little mixing of
330	waters with different preNO3 content. Advective mixing of the higher preNO3 waters to the
331	southwest and northeast of the BATS station would increase the preNO <sub>3</sub> on $\gamma^n = 26.5$ to values
332	greater than 1 $\mu$ M at the BATS station, which is not observed. Plots of residual preNO <sub>3</sub> versus
333	the CFC-11 and CFC-12 age on $\gamma^n = 26.5$ in the North Atlantic reveal essentially no increasing or
334	decreasing preNO <sub>3</sub> age gradient (Fig. S1). In summation, this evidence suggests the BATS
335	station sits within the NW corner of a large region of the subtropical North Atlantic characterized
336	by a residual preNO <sub>3</sub> content of $\sim 1 \ \mu M$ on $\gamma^n = 26.5$ that is advected within the basin.
337	On the $\gamma^n = 26.0$ isopycnal which bisects the layer exhibiting the rNPN anomaly at the
338	BATS station, the site sits surrounded by waters with a preNO3 content of ${\sim}0~\mu M$ in the annual
339	climatology, with more distant waters exhibiting rNPN anomalies south of ~27 °N and waters
340	with rPPN anomalies north of ~37 °N (Fig. S2). Plots of residual preNO <sub>3</sub> versus CFC-11 and
341	CFC-12 age on $\gamma^n = 26.0$ again reveal essentially no preNO <sub>3</sub> gradient with increasing age (Fig.
342	S2). Given the lack of a preNO $_3$ tracer gradient with water mass age and the observation of a
343	repeating seasonal pattern of rNPN anomaly formation at the BATS station on $\gamma^n = 26.0$ (Fig. 2),
344	we conclude that lateral advective mixing cannot explain the observed seasonal rNPN anomalies,





instead suggestive of biological mechanisms supporting rNPN anomaly formation at the BATSstation.

- A similar pattern exists near station ALOHA that could potentially explain the rPPN 347 anomalies observed below ~200 m (Fig. 1). Examination of the residual preNO<sub>3</sub> tracer on the  $\gamma^n$ 348 = 25.4 density surface (the surface approximately bisecting the 200 - 250 m layer near ALOHA) 349 in the North Pacific within the World Ocean Atlas climatology reveals that station ALOHA sits 350 near the southern boundary of waters with a preNO<sub>3</sub> content of  $0 - 1.5 \,\mu\text{M}$  that extends as far 351 north as 40 °N and as far east as 130 °W (Fig. S3). Waters with higher preNO<sub>3</sub> content of 2-4352  $\mu$ M are located to the south of station ALOHA, beginning around the vicinity of the big island of 353 Hawaii (Fig. S3). Examination of plots of preNO<sub>3</sub> versus CFC-11 and CFC-12 age on  $\gamma^n = 25.4$ 354 in the North Pacific reveals that station ALOHA lies between younger, low preNO<sub>3</sub> content 355 waters to its north with older, higher preNO<sub>3</sub> content waters to its south (Fig. S3). Mixing of 356 these waters along  $\gamma^n = 25.4$  may explain the observed  $\sim 1 \ \mu M \text{ preNO}_3$  concentration present at 357 200 - 250 m depth in Figure 1. 358 On the  $\gamma^n = 24.7$  isopycnal which bisects the density layer exhibiting the rNPN anomaly 359 at station ALOHA, the site is surrounded by waters with rNPN anomalies on the order of -1 - 0360  $\mu$ M (Fig. S4). Plots of preNO<sub>3</sub> versus CFC-11 and CFC-12 age on  $\gamma^n = 24.7$  reveal essentially no 361 preNO<sub>3</sub> age gradient (Fig. S4). Similar to the BATS station, given the lack of a preNO<sub>3</sub> age 362 gradient on  $\gamma^n = 24.7$  and the observation of seasonal formation of rNPN anomalies, we conclude 363 364 that lateral advective mixing cannot explain the observed rNPN anomalies, suggestive of biological mechanisms. 365 Biological formation of rNPN anomalies requires either O<sub>2</sub> consumption without 366
- 367 concomitant stoichiometric nitrate accumulation or nitrate drawdown without concomitant





368	stoichiometric O <sub>2</sub> production. Formation of rPPN anomalies requires either O <sub>2</sub> production
369	without concomitant stoichiometric nitrate drawdown or nitrate accumulation without
370	concomitant stoichiometric O <sub>2</sub> consumption. Having ruled out lateral mixing and accounted for
371	the non-Redfield $-O_2/N$ DOM remineralization stoichiometry at each site (see Table 2 for the
372	rate of NPN/PPN anomaly formation attributable to N-poor DOM remineralization), we
373	hypothesize three other biological mechanisms to explain the observed seasonal formation rates
374	and integrated quantities of concurrent positive preNO3 accumulation in the euphotic zone and
375	negative preNO <sub>3</sub> accumulation in the upper mesopelagic at the ALOHA and BATS stations: 1)
376	biological production, export, and remineralization of N-deficient transparent exopolymer
377	particles (TEP); 2) heterotrophic bacterial uptake of nitrate to remineralize N-poor organic
378	matter; 3) vertical migration of autotrophic phytoplankton down to the nutricline to acquire
379	nitrate with subsequent photosynthetic oxygen production within the euphotic zone.
380	Transparent exopolymer particles (TEP) are the polysaccharide-rich exudate of
381	phytoplankton that accumulates in the size range <1 to >100 $\mu$ m in aquatic systems (Mari et al.,
382	2017). TEP is both sticky and positively buoyant in seawater (Azetsu-Scotte and Passow, 2004),
383	leading to aggregation and flotation towards the surface, with large enrichments of TEP present
384	in the sea surface microlayer (Wurl et al., 2009). Being comprised of nearly pure saccharide
385	material, TEP is a carbon rich and essentially N-deficient pool of non-sinking particulate organic
386	carbon formed within the euphotic zone of marine systems by phytoplankton production
387	(Alldredge et al., 1993). TEP production has been hypothesized to contribute to "carbon
388	overconsumption" in low nutrient oligotrophic marine ecosystems (Toggweiler, 1993) where
389	organic matter is produced in non-Redfield, C-rich/N-poor proportions. Due to its positive
390	buoyancy TEP has been viewed as a non-contributor to upper ocean carbon export; however,





391 more recent evidence suggests that a portion of the TEP pool is associated with sufficient ballasting particles (e.g. clays, biogenic minerals) to achieve negative buoyancy, and may 392 comprise a slowly sinking (a few meters per year) pool of organic carbon exported below the 393 euphotic zone (Mari et al., 2017). TEP production and remineralization stoichiometry has the 394 correct sense: O<sub>2</sub> production without Redfieldian nitrate drawdown within the euphotic zone, O<sub>2</sub> 395 396 consumption without Redfieldian nitrate accumulation within the mesopelagic, to contribute to both the observed rPPN anomalies within the euphotic zone and rNPN anomalies in the upper 397 mesopelagic at the ALOHA and BATS stations in our analysis. 398

We use field data of TEP concentrations near the BATS and ALOHA stations and a few 399 simplifying assumptions to test for the importance of this process as a contributor to the dual 400 rNPN/rPPN anomalies. Cisternas-Novoa et al. (2015) measured TEP concentration depth profiles 401 in the Sargasso Sea northeast of Bermuda on five separate occasions from February 2012 to June 402 2013. The profiles show a ~10  $\mu$ g XG eq L<sup>-1</sup> (xanthum gum equivalent) gradient between the 403 upper 100 m and the 100-200 m layer (Fig. 15 in Cisternas-Novoa et al., 2015). We take this 404 gradient to represent the fraction of the euphotic zone TEP pool that is exported annually to the 405 406 upper mesopelagic, 100-200 m depth layer. This assumption is supported by the observation that the euphotic zone to mesopelagic TEP concentration gradient is nearly erased in the winter 407 profile, presumably due to wintertime convective mixing, and reappears following the spring 408 409 bloom, remaining relatively unchanged throughout the late spring/summer month profiles. TEP in xanthum gum equivalents can be converted to  $\mu g C L^{-1}$  units using a 0.63 conversion factor 410 (Engel, 2004) and again into  $\mu$ M units, yielding a Sargasso Sea upper ocean gradient of ~0.5  $\mu$ M 411 412 TEP-C. Integrating over the surface to 80 m depth layer (the depth where rPPN anomalies switch to rNPN anomalies), we obtain a potential TEP production and export flux of 42 mmol TEP-C 413





414	m <sup>-2</sup> yr <sup>-1</sup> from the euphotic zone into the upper mesopelagic. We assume TEP is comprised of
415	pure carbohydrate with no N content such that TEP production/remineralization C:O2
416	stoichiometry can be assumed 1:1 (e.g. $CO_2 + H_2O \Leftrightarrow CH_2O + O_2$ ), meaning that an $O_2$
417	production flux in the absence of nitrate drawdown of 42 mmol $O_2 \text{ m}^{-2} \text{ yr}^{-1}$ can be ascribed to
418	TEP production within the euphotic zone, and the same flux can be ascribed to $O_2$ consumption
419	without concomitant nitrate accumulation from TEP remineralization in the mesopelagic. We can
420	convert this O <sub>2</sub> flux to a preNO <sub>3</sub> equivalent using Equation 1 and the values in Table 1, yielding
421	estimates of $3.2 - 4.5 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ preNO <sub>3</sub> anomaly formation rate equivalents, depending on
422	the choice of $r_{\text{POM}}$ . Thus, TEP formation within the euphotic zone of the Sargasso Sea has the
423	potential to explain $5.2 - 5.4\%$ of the estimated rPPN anomaly formation rate and $5.1 - 7.0\%$ of
424	the estimated rNPN anomaly formation rate within the $\gamma^n = 25.8 - 26.3$ layer (Table 2).
425	The potential contribution of TEP cycling to rPPN/rNPN anomaly formation near the
426	BATS station can be also be estimated using published sinking rates for negatively buoyant TEP.
427	Again, using the TEP profiles from the Sargasso Sea from Cisternas-Novoa et al. (2015), we
428	estimate a difference of ~5 $\mu g$ XG eq $L^{\text{-1}}$ between 100 m and 200 m depth (the approximate
429	depths exhibiting rNPN anomalies). Converting to molar carbon concentration yields a quantity
430	of ~0.26 $\mu$ M TEP-C that is apparently remineralized within the rNPN anomaly layer. We apply
431	the TEP sinking rate of 0.04 d <sup>-1</sup> from Hamanaka et al. (2002) to estimate the rate of delivery of
432	exported TEP from the euphotic zone into the upper mesopelagic, yielding a TEP supply and
433	remineralization flux of 10 $\mu$ mol C m <sup>-3</sup> d <sup>-1</sup> . Depth and time integrated to 15 meters and one year,
434	i.e. the depth slowly sinking TEP will sink after one year, this flux becomes 56.9 mmol C $m^{-2}$ yr <sup>-</sup>
435	<sup>1</sup> or O <sub>2</sub> units assuming 1:1 C:O <sub>2</sub> stoichiometry for TEP. Conversion of this O <sub>2</sub> flux into preNO <sub>3</sub>
436	equivalents yields an estimated $4.3 - 6.0 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ of the observed rPPN/rNPN anomaly





437	formation rate attributable to TEP cycling. Thus, computed using the sinking rate, TEP formation
438	within the euphotic zone has the potential to explain $7.0 - 7.3\%$ of the estimated rPPN anomaly
439	formation rate and $6.9 - 9.3\%$ of the estimated rNPN anomaly formation rate within the $\gamma^n = 25.8$
440	– 26.3 layer.

Seasonal depth profiles of TEP concentration are unavailable for the subtropical North 441 Pacific near station ALOHA. Wurl et al. (2011) measured TEP concentration profiles south of 442 the island of Hawaii during August/September 2009. We use the concentration gradient present 443 in these profiles with the TEP sinking rate of  $0.04 d^{-1}$  to estimate the TEP cycling contribution to 444 rPPN/rNPN anomaly formation rates near station ALOHA. The 100 to 200 m gradient in TEP-C 445 is  $\sim 1 \mu M$  yielding an export and supply flux of 40  $\mu$ mol C m<sup>-3</sup> d<sup>-1</sup>. Depth and time integrating for 446 15 m and one year, this flux becomes 220 mmol C  $m^{-2}$  yr<sup>-1</sup> (mmol O<sub>2</sub>  $m^{-2}$  yr<sup>-1</sup>). Conversion of 447 this O<sub>2</sub> flux to preNO<sub>3</sub> equivalents using Equation 1 and values in Table 1, yields an estimated 448  $16.2 - 21.8 \text{ mmol N m}^{-2} \text{ yr}^{-1}$  of the observed rPPN/rNPN anomaly formation rate potentially 449 attributable to TEP cycling at station ALOHA. Thus, TEP formation within the euphotic zone 450 has the potential to explain 35.6 - 37.2% of the estimated rPPN anomaly formation rate and 47.0451 -51.3% of the total estimated rNPN anomaly formation rate within the combined  $\gamma^n = 24.2 - 10^{-1}$ 452 25.2 layer (Table 2). 453 These estimates of the potential for TEP cycling to contribute to the observed euphotic 454 455 zone rPPN and mesopelagic rNPN anomaly formation rates assume 1) that TEP is pure

456 carbohydrate (CH<sub>2</sub>O); without any N content, and 2) that there exists a sufficiently large and

457 dense TEP pool to sink rapidly enough to contribute to annual carbon export and O<sub>2</sub>

remineralization budgets. Both assumptions, if incorrect, will overestimate the TEP contribution.

459 In conjunction with TEP cycling, Coomassie stainable particles are transparent protein-





460	containing particles (Long and Azam, 1996) that can reach similar concentrations within the
461	oligotrophic euphotic zone as TEP (Cisternas-Novoa et al., 2015). Thus, the assumption that
462	transparent exopolymer particle cycling delivers only C to the subsurface to drive rNPN anomaly
463	formation may not be entirely valid. Secondly, more information on the mass quantities of the
464	positively and negatively buoyant TEP within the euphotic zone and their C:N content is needed
465	to better constrain the role of this mechanism in rPPN/rNPN anomaly formation in the
466	subtropics.
467	Multiple studies have shown the uptake of nitrate and/or phosphate by heterotrophic
468	bacteria during the remineralization of organic matter or that inorganic nutrients can limit
469	bacterial OM consumption (e.g. Zweifel et al., 1993; Kirchman, 1994; Cotner et al., 1997;
470	Rivkin and Anderson, 1997; Caron et al., 2000; Letscher et al., 2015). Bacterial nitrate uptake to
471	remineralize OM has the effect of creating an NPN anomaly (O2 consumption without
472	concomitant nitrate accumulation) and thus can only contribute to the observed mesopelagic
473	rNPN anomaly formation. It cannot contribute to either the formation of the euphotic zone rPPN
474	anomaly or surface mixed layer drawdown of DIC. If TEP cycling is an important contributor to
475	oligotrophic ocean C export and shallow subsurface O2 consumption, heterotrophic bacterial
476	nitrate and/or phosphate uptake is a likely complementary biological process, since the nutrient
477	deficient content of TEP could require exogenous uptake of N and P from the seawater media for
478	bacterial production when growing on TEP organic matter. This would result in an imbalance
479	between rPPN and rNPN.
480	To assess the potential contribution of bacterial nitrate uptake to our observed rNPN
481	anomaly formation rates at the ALOHA and BATS stations, we examined the literature for

482 estimates of bacterial C production rates and bacterial biomass C:N ratios for the Sargasso Sea





483	and subtropical North Pacific. Carlson et al., (1996) measured bacterial production rates at the
484	BATS station using the <sup>3</sup> H-thymidine and <sup>3</sup> H-leucine uptake methods with average euphotic
485	zone rates of 23 pmol C L <sup>-1</sup> d <sup>-1</sup> by <sup>3</sup> H-thymidine and 0.41 nmol C L <sup>-1</sup> d <sup>-1</sup> by <sup>3</sup> H-leucine. Using a
486	bacterial biomass C:N of 5:1 for this region (Gunderson et al. 2002) and integrating for one year
487	and over the $\sim 80 - 160$ m thick layer exhibiting rNPN anomaly, yields an estimate of $0.17 - 3.0$
488	mmol N m <sup>-2</sup> yr <sup>-1</sup> bacterial N demand. If we assume that bacteria satisfy all of their N demand via
489	uptake of seawater nitrate in this shallow subsurface layer, bacterial nitrate uptake can explain at
490	most 0.2 – 6.5% of the estimated rNPN anomaly formation rate at the BATS station in the $\gamma^n$ =
491	25.8 – 26.3 layer.
492	We can make a similar calculation for station ALOHA using published <sup>3</sup> H-leucine
493	bacterial production rate measurements (Church et al., 2004). The mean bacterial C production
494	rate at 100 m is ~0.46 nmol C $L^{-1} d^{-1}$ . Using the same bacterial biomass C:N of 5:1 and
495	integrating for one year over the $\sim 100 - 200$ m thick layer exhibiting rNPN anomaly, yields an
496	estimated 3.4 mmol N m <sup>-2</sup> yr <sup>-1</sup> bacterial N demand. If we again assume that bacteria satisfy <i>all</i> of
497	their N demand from nitrate uptake, this process can explain at most $7.2 - 10.6\%$ of the
498	estimated rNPN anomaly formation rate at station ALOHA in the combined $\gamma^n = 24.2 - 25.2$
499	layer.
500	From our analyses, it is clear that neither remineralization of N-poor DOM and TEP or
501	heterotrophic bacterial nitrate uptake can quantitatively explain both the seasonal rPPN anomaly
502	formation within the euphotic zone and subsurface rNPN anomaly formation observed at the
503	ALOHA and BATS stations even with the generous assumptions made. Lastly, we examine the
504	vertical migration of phytoplankton down to the nitracline as a potential biological mechanism to
505	explain the dual rPPN/rNPN anomalies.





506	Flagellate motility and cyanobacteria buoyancy control has been recognized for decades
507	as a strategy to exploit spatially disjunct light and nutrient fields (Cullen, 1985; Eppley et al.,
508	1968, Ganf and Oliver, 1982; Hasle, 1950; Steemann Nielsen, 1939) and was first suggested for
509	non-flagellated marine species in Pyrocystis (Ballek and Swift, 1986; Rivkin et al., 1984). Fraga
510	et al. (1992, 1999) provided clear evidence that vertically migrating dinoflagellates
511	(Gymnodinium catenatum) in relaxed upwelling conditions transport nutrients to an extent that
512	modify geochemical properties and developed modifications to Broeker's (1974) NO tracer to
513	express this. Thus, the question in the open ocean is not whether it is occurring, but rather how
514	various taxa are overcoming the much greater distances (~50-100 m) required to access the two
515	resources fields (light and nutrients). Rhizosolenia mats (macroscopic, multi-species associations
516	of multiple Rhizosolenia spp.) have been the model for understanding this process. There is
517	consistent evidence of high $\delta^{15}$ N composition of <i>Rhizosolenia</i> biomass similar to sub-nutricline
518	N (Villareal et al., 1993, Villareal et al., 2014), internal millimolar nitrate pools that can only be
519	acquired by direct uptake at $\mu$ M concentrations (Villareal and Lipschultz, 1995; Villareal et al.,
520	1996; Woods and Villareal, 2008), buoyancy reversals linked to nutrient status (Richardson et
521	al., 1996), nitrate reductase activity (Joseph et al., 1997) induced only when nitrate is the primary
522	N source, ascent/descent rates of m hr <sup>-1</sup> (Villareal et al., 2014; Moore and Villareal 1996),
523	observation of Rhizosolenia mats from the surface to 305 m (Pilskaln et al., 2005), and
524	compositional difference in floating and sinking mats that mirror physiological changes
525	associated with nutrient depletion and carbohydrate ballasting (Villareal et al., 1996). The m hr <sup>-1</sup>
526	ascent/descent rates permit the necessary 50-100 m vertical excursions and when coupled with
527	the large vacuole of these giant phytoplankton, allow the necessary storage (mM concentrations
528	in vacuoles that are 90+% of total cell volume) for a multiple day migration and division cycle.





529	Giant phytoplankton are found throughout the warmer oceans of the world and the required
530	characteristics of buoyancy reversals, high internal nitrate pools and rapid ascent have been
531	found in multiple taxa from the Atlantic and Pacific Oceans (Villareal et al., 2014). Unlike the
532	more widely known zooplankton vertical migration, open ocean phytoplankton migration is a
533	multi-day cycle (Richardson et al., 1998; Villareal et al., 1996). It is asynchronous and not cued
534	to diel rhythms as in coastal dinoflagellates or vertically migrating zooplankton.
535	For rNPN and rPPN development, the unique characteristics of vertical migration are that
536	cells remove nitrate from depth, transport it into the euphotic zone, and then reduce it via
537	oxygenic photosynthesis. Nitrate transport calculations by vertical migration has a number of
538	assumptions and caveats including considerable uncertainty in abundance estimates (Villareal et
539	al., 2014). However, mid-range assumptions produced site-specific estimates of 6–444 $\mu$ mol N
540	m <sup>-2</sup> d <sup>-1</sup> for <i>Rhizosolenia</i> mats. Four other taxa yielded transport rates of 3.2 ( <i>Ethmodiscus</i> spp.),
541	9.2 (free living Rhizosolenia spp.), 17.0 (Pyrocystis spp.) and 33.2 (Halosphaera spp.) µmol N
542	m <sup>-2</sup> d <sup>-1</sup> . These taxa exhibit basin-specific abundance patterns (i.e. <i>Rhizosolenia</i> mats are rare in
543	the N. Atlantic; Carpenter et al., 1977, Halospheara viridis has an extensive vertical presence in
544	the deep Mediterranean in winter; Wiebe et al., 1974); however, it is clear that the generalized
545	rates are consistent with the required rNPN and rPPN rates at both the BATS station $(126 - 239)$
546	and 169 – 225 $\mu mol~N~m^{-2}~d^{-1},$ respectively) and station ALOHA (88 – 122 and 119 – 168 $\mu mol$
547	N m <sup>-2</sup> d <sup>-1</sup> , respectively). There are several implications of this. Lower abundance or turnover
548	times of this flora will still have substantial effects on rNPN and rPPN. Patchiness in abundance
549	(Villareal, 2007; et al., 2014) or concentration of buoyant particles by mesoscale fronts (Guidi,
550	2012) could lead to significant local perturbations on rNPN and rPPN.





551	We estimate the contribution of vertically migrating phytoplankton to the rNPN and
552	rPPN anomaly features at the two stations by subtracting our estimates of the contributions of
553	TEP cycling and bacterial nitrate uptake to rNPN and/or rPPN formation from the total observed
554	rNPN/rPPN anomaly formation rates (presented in Table 2). Phytoplankton vertical migration
555	potentially explains $16 - 21 \text{ mmol N m}^2 \text{ yr}^{-1}$ or $45 - 50\%$ of rNPN anomaly formation and $27 - 50\%$
556	36 mmol N m <sup>-2</sup> yr <sup>-1</sup> or 59 – 62% of rPPN anomaly formation at station ALOHA (Table 2). At the
557	BATS station, phytoplankton vertical migration potentially explains $43 - 78 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ or
558	90 - 93% of rNPN anomaly formation and $59 - 76$ mmol N m <sup>-2</sup> yr <sup>-1</sup> or $87 - 95%$ of rPPN
559	anomaly formation. These are likely underestimates because the bacterial nitrate uptake and TEP
560	contribution are maximum estimates.
561	Vertically migrating phytoplankton can also help explain the observed summertime DIC
562	drawdown in the absence of measurable nitrate from the mixed layer at both the ALOHA and
563	BATS stations. The concurrently operating migration cycles of different individuals would
564	continually bring intracellular nitrate-rich migrators into the surface mixed layer where their
565	oxygenic photosynthesis would draw down DIC and release dissolved O2, contributing to rPPN
566	anomaly formation within the mixed layer. High intracellular nitrate concentrations within
567	migrators can also lead to excretion of dissolved nitrate into the water column (Singler and
568	Villareal, 2005). Thus, mixed layer DIC drawdown need not be entirely supported by migrator
569	photosynthesis, instead their nitrate leakage could help explain the observation of a presumed
570	subsurface nitrate source supporting pico-eukaryotic phytoplankton in the mixed layer, even
571	during the stratified summer months at the BATS station (Fawcett et al., 2011). However, any
572	surface ocean taxa that are supported by this migrator-mediated nitrate supply, are required to





573 sink out of the mixed layer in some form in order to contribute to summertime net DIC

574 drawdown at these two sites.

575	We also investigated for the presence of subsurface negative preformed phosphate
576	(prePO <sub>4</sub> ) anomalies at the ALOHA and BATS stations. Dissolved organic phosphorus
577	concentration data density was not sufficient to allow for statistically significant regressions of
578	AOU versus DOP needed to empirically estimate $f_{\text{DOM}}$ and $r_{\text{DOM}}$ terms specific to DOP
579	remineralization at each site. To compute we prePO <sub>4</sub> for each station, we used the values of $f_{\text{DOM}}$
580	and $r_{\text{DOM}}$ from Table 1, calculated from regressions of AOU vs. DON. Station ALOHA does not
581	exhibit a subsurface negative prePO <sub>4</sub> anomaly (Fig. S5), with the exception of a small anomaly
582	present in years $2002 - 2004$ . There does exist a subsurface negative prePO <sub>4</sub> anomaly and
583	euphotic zone positive prePO <sub>4</sub> anomaly at the BATS station (Fig. S6), present throughout the
584	time series. Carbon to phosphorus ratios exhibit their global maxima in the subtropical North
585	Atlantic for phytoplankton biomass (Martiny et al., 2013), dissolved organic matter (Letscher
586	and Moore, 2015), and exported organic matter (Teng et al., 2014). The hypothesized
587	phosphorus limitation of this basin (Ammerman et al., 2003; Moore et al., 2004) may explain the
588	contrasting observations of the presence of a negative prePO <sub>4</sub> anomaly at the BATS station in the
589	North Atlantic while not at station ALOHA in the North Pacific. Because of the many
590	observations of elevated C:P across organic matter pools in the North Atlantic, we tested for the
591	theoretical value of R-O2:P, the stoichiometric ratio of O2 consumed to phosphate released during
592	the remineralization of organic matter, needed to eliminate the subsurface negative prePO <sub>4</sub>
593	anomaly at the BATS station. This theoretical value of $R_{-O2:P}$ was found to be ~1000:1 (Fig. S7),
594	which is $\sim 4x$ higher than the inferred R <sub>-O2:P</sub> for the North Atlantic from an inversion of
595	subsurface O <sub>2</sub> and phosphate data (DeVries and Deutsch, 2014). We hypothesize that P-limited





596	or P-stressed vertically migrating phytoplankton also take up phosphate at the nutricline in
597	combination with nitrate to contribute to both the observed rNPN/rPPN and the subsurface
598	negative prePO <sub>4</sub> anomaly present at the BATS station. Field data on intracellular phosphate
599	concentrations of vertically migrating phytoplankton are needed to confirm our hypothesis.
600	Subsurface rNPN anomalies cover a large portion of the subtropical ocean (Fig. 3); thus
601	vertically migrating phytoplankton may play a hitherto underappreciated large role in upper
602	ocean nutrient budgets and the biological pump. Our analyses have revised the preNO3
603	calculation and revealed a rNPN anomaly that is not accounted for by organic material
604	remineralization. Our consideration of three possible sources suggest that the dominant role (in
605	decreasing order of importance) is played by vertically migrating giant phytoplankton, TEP
606	formation/remineralization, and bacterial utilization of nitrate (Table 2). The analyses also
607	revealed a near-surface rPPN anomaly that is approximately balanced and concurrent with the
608	rNPN anomaly.
609	The role of vertically migrating flora was independently explored by Fraga (2001). This
610	work developed an independent assessment of the impact of vertical migration on the NO trace

work developed an independent assessment of the impact of vertical migration on the NO tracer (functionally related to our preNO<sub>3</sub> tracer) based on first principles of photosynthetic production and biosynthesis of biomass. For both coastal dinoflagellates and oceanic diatoms, a subsurface minimum in NO and a related tracer, NCO (NO corrected for the stoichiometry of carbohydrate synthesis) formed. For migrating *Rhizosolenia*, the NO and NCO minimum was at ~150 m with negative anomalies from ~80 to ~200 m (Fig. 6 in Fraga, 2001). The Fraga (2001) formulation also included an explicit term for release of soluble carbohydrate (functionally equivalent to TEP). Migrating phytoplankton can clearly provide a mechanistic linkage via upward nutrient





- transport to the observed NO anomalies. TEP may contribute as well, depending on the
- 619 stoichiometry of production/remineralization and shifts in buoyancy characteristics.
- 620 More observations of upper ocean, surface to  $\sim$ 200 m, abundance estimates of the
- 621 vertically migrating phytoplankton taxa, their intracellular nitrate and phosphate contents, and
- their migration timescales are needed to confirm the conclusion by multiple authors of this
- flora's important role in nutrient transport and rNPN/rPPN anomaly formation at the time-series
- stations and by extension to elsewhere in the subtropical gyres. In addition, the well-
- 625 characterized migrator, Rhizosolenia, has been shown to release TEP in the subtropical North
- Pacific (Pilskaln et al., 2005) so it may be that all three biological mechanisms we investigated
- are non-mutually exclusive with vertically migrating phytoplankton contributing to TEP
- 628 production/export, nitrate transport across the nitracline into the euphotic zone, and bacterial
- 629 nitrate uptake to remineralize N-deficient TEP.
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632

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# **Table 1.** Negative preNO<sub>3</sub> (NPN) and positive preNO<sub>3</sub> (PPN) anomaly formation rates at stations

# 941 ALOHA and BATS.

	Depth (m) or							
	Neutral Density	$f_{\text{DOM}}$	r <sub>DOM</sub>	r <sub>POM</sub>	rNPN		rPPN	
	$\gamma^{n}$				µmol N m <sup>-3</sup> d <sup>-1</sup>	mmol N m <sup>-2</sup> yr <sup>-1</sup>	µmol N m <sup>-3</sup> d <sup>-1</sup>	mmol N m <sup>-2</sup> yr <sup>-1</sup>
ALOHA	0 – 100 m	0.5	18.1	10.6			$2.4 \pm 0.8$	$43.5 \pm 10.5$
				6.9			$3.3 \pm 1.1$	$61.2 \pm 20.2$
	24.2 - 24.7	0.5	18.1	10.6	$3.0 \pm 1.5$	$17.9 \pm 7.4$		
				6.9	$2.8 \pm 1.4$	$28.3 \pm 9.6$		
	24.7 - 25.2	0.5	18.9	10.6	$2.5 \pm 1.4$	$13.7 \pm 7.8$		
				6.9	$1.6 \pm 0.8$	$18.1 \pm 8.8$		
Total	$r_{\rm POM} = 10.6$				$5.5 \pm 2.1$	$31.6 \pm 10.8$		
Total	$r_{\rm POM} = 6.9$				$4.4 \pm 1.6$	$46.4 \pm 13.0$		
DATO	000	0.4	01.1	10.6			4.1 + 0.0	(1.0.) 10.0
BATS	0 – 80 m	0.4	21.1	10.6			$4.1 \pm 0.8$	$61.8 \pm 12.2$
				6.9			$5.8 \pm 1.2$	$82.1 \pm 13.8$
	25.8 - 26.3	0.4	21.1	10.6	$3.8 \pm 3.1$	$46.0 \pm 39.3$		
				6.9	$5.5 \pm 2.7$	$87.1 \pm 41.0$		





			TEP production		Phytoplankton
		N-poor DOM	&	Bacterial nitrate	vertical
Station	Feature	remineralization	remineralization	uptake	migration
		1 – 16	16 – 22	0.0 - 3.4	16 – 21
ALOHA	NPN	mmol N m <sup>-2</sup> yr <sup>-1</sup>			
		2 - 21	16 – 22		27 - 36
	PPN	mmol N m <sup>-2</sup> yr <sup>-1</sup>	mmol N m <sup>-2</sup> yr <sup>-1</sup>		mmol N m <sup>-2</sup> yr <sup>-1</sup>
		1 - 14	3.2 - 6.0	0.2 - 3.0	43 - 78
BATS	NPN	mmol N m <sup>-2</sup> yr <sup>-1</sup>			
		2 - 17	3.2 - 6.0		59 - 76
	PPN	mmol N m <sup>-2</sup> yr <sup>-1</sup>	mmol N m <sup>-2</sup> yr <sup>-1</sup>		mmol N m <sup>-2</sup> yr <sup>-1</sup>

# **Table 2.** Contribution to NPN and PPN anomalies by presumed sources.





- 972 **Figure 1.** (a) Climatology of the residual preNO<sub>3</sub> tracer  $[\mu M]$  in the upper 250 m at station
- 973 ALOHA (22.75 °N 158 °W). Black contour lines show neutral density  $\gamma^n = 24.2, 24.7, \text{ and } 25.2.$









- Figure 2. (a) Climatology of the residual preNO<sub>3</sub> tracer  $[\mu M]$  in the upper 200 m at the BATS
- station (31.67 °N 64.17 °W). Black contour lines show neutral density  $\gamma^n = 25.8$  and 26.3. (b) The





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- **Figure 3.** Seasonal climatology of the residual preNO<sub>3</sub> tracer  $[\mu M]$  at 150 m depth from the
- 994 World Ocean Atlas, 2013, 1° climatologies of O<sub>2</sub> anomaly and nitrate. Residual preNO<sub>3</sub> is
- 995 calculated using values of  $f_{\text{DOM}} = 0.5$ ,  $r_{\text{DOM}} = 20.0$ , and  $r_{\text{POM}} = 8.75$ .

