- 1 The Effect of the 2013-2016 High Temperature Anomaly in the Subarctic Northeast Pacific
- 2 (The "Blob") on Net Community Production
- 3 Bo Yang^{1†}, Steven R. Emerson¹, M. Angelica Peña²
- ⁴ School of Oceanography, University of Washington, Seattle, WA 98195, USA
- ⁵ ² Institute of Ocean Sciences, Fisheries and Oceans Canada, PO Box 6000, Sidney, BC, Canada,
- 6 V8L 4B2
- ⁷ [†]Present Address: Department of Environmental Sciences, University of Virginia, Charlottesville,
- 8 VA 22904
- 9 Corresponding author: Bo Yang (by3jr@virginia.edu)
- 10 Email address: Steven R. Emerson (emerson@uw.edu), M. Angelica Peña (Angelica.Pena@dfo-
- 11 mpo.gc.ca)
- 12 Key words: The warm blob, net community production, Ocean Station Papa
- 13

14 Abstract

A large anomalously warm water patch (the "Blob") appeared in the NE Pacific Ocean in 15 the winter of 2013–14 and persisted through 2016 causing strong positive upper ocean 16 temperature anomalies at Ocean Station Papa (OSP, 50°N, 145°W). The effect of the 17 temperature anomalies on annual net community production (ANCP) was determined by upper 18 ocean chemical mass balances of O₂ and DIC using data from a profiling float and a surface 19 mooring. Year-round oxygen mass balance in the upper ocean (0 to 91-111 m) indicates that 20 ANCP decreased after the first year when warmer water invaded this area and then returned to 21 the "pre-blob" value (2.4, 0.8, 2.1, and 1.6 mol C m⁻² yr⁻¹ from 2012 to 2016, with a mean value 22 of 1.7 ± 0.7 mol C m⁻² yr⁻¹). ANCP determined from DIC mass balance has a mean value that is 23 similar within the errors as that from the O_2 mass balance but without significant trend (2.0, 2.1, 24 2.6, and 3.0 mol C m⁻² yr⁻¹ with a mean value of 2.4 ± 0.6 mol C m⁻² yr⁻¹). This is likely due to 25 differences in the air-sea gas exchange, which is a major term for both mass balances. Oxygen 26 has a residence time with respect to gas exchange of about one month while the CO_2 gas 27 exchange response time is more like a year. Therefore the biologically induced oxygen saturation 28 anomaly responds fast enough to record annual changes whereas that for CO_2 does not. 29 30 Phytoplankton pigment analysis from the upper ocean shows lower chlorophyll-a concentrations and changes in plankton community composition (greater relative abundance of picoplankton) in 31 the year after the warm water patch entered the area than in previous and subsequent years. Our 32 33 analysis of multiple physical and biological processes that may have caused the ANCP decrease after warm water entered the area suggests that it was most likely due to the temperature-induced 34 35 changes in biological processes.

36 **1 Introduction**

Net community production (NCP) in the upper ocean is defined as net organic carbon 37 production, which equals biological production minus respiration. At steady state when 38 integrated over a period of at least one year, the annual NCP (ANCP) is equivalent to the flux of 39 biologically-produced organic matter from the upper ocean to the interior. Both biological 40 41 production and respiration processes are temperature dependent, and heterotrophic activities such as community respiration and zooplankton grazing are usually considered to be more sensitive to 42 temperature change than autotrophic production (Allen et al., 2005; Brown et al., 2004; Gillooly 43 44 et al., 2001; López-Urrutia et al., 2006; Regaudie-De-Gioux and Duarte, 2012; Rose and Caron, 2007). This implies that rising temperature should lead to enhanced heterotrophy and lower NCP 45 (López-Urrutia et al., 2006). In contrast, it has also been suggested (e.g., Chen and Laws, 2017) 46 that the main effect of temperature on community metabolism is likely due to differences in 47 phytoplankton community composition (e.g. cyanobacteria dominate in warm, oligotrophic 48 49 waters, whereas diatoms dominate in cold, nutrient-rich areas) rather than to lower temperature 50 sensitivity of phytoplankton production.

From the winter of 2013, a large anomalously warm water patch (the "Blob") appeared in 51 52 the NE Pacific Ocean (Bond et al., 2015). The "Blob" had stretched from Alaska to Baja California by the end of 2015 (Di Lorenzo and Mantua, 2016) and caused widespread changes in 53 the marine ecosystem, such as geographical shifts of plankton species, harmful algal blooms, and 54 55 strandings of fishes, marine mammals, and seabirds (Cavole et al., 2016; Peña et al., 2018). Here we calculate the ANCP with upper ocean oxygen (O_2) and dissolved inorganic carbon (DIC) 56 mass balances using data from Ocean Station Papa in the NE Pacific (OSP, 50°N, 145°W, Figure 57 58 1), to determine if there were significant NCP changes during the anomalous warm event. The

monthly Sea Surface Temperature Anomaly (SSTA) at OSP from 2012 to 2016 (Figure 2) indicates that for most of the 1st year (starting from June 2012) sea surface temperature (SST) was lower than usual, but then transitioned to strong positive temperature anomaly from 2013 to 2014. The positive anomaly continued with a magnitude of ~ 2°C to June 2015, and then dropped back to "normal" in the summer of 2016.

Our field location is in the subarctic northeast Pacific Ocean at OSP, where repeat 64 hydrographic cruises have been carried out since 1981 by Fisheries and Oceans Canada with a 65 frequency of two to three times per year (Freeland, 2007). A NOAA surface mooring has been 66 67 deployed at OSP since 2007, for physical and biogeochemical measurements such as temperature, salinity, wind, ocean current, radiation, oxygen and total gas pressure, pH, and 68 carbon dioxide (CO₂) (Emerson et al., 2011; Cronin et al., 2015; Fassbender et al., 2016). In 69 addition, Argo profiling floats have been deployed near OSP since the 2000s (Freeland and 70 Cummins, 2005). The first floats measured only temperature, salinity, and pressure but then 71 measurements of oxygen and nitrate were added (Bushinsky and Emerson, 2015; Johnson et al., 72 2009). NCP at OSP has been determined using various approaches over the years, including 73 bottle incubations (Wong, 1995), ²³⁴Th methods (Charette et al., 1999), carbon/nutrient 74 75 drawdown (Fassbender et al., 2016; Plant et al., 2016; Takahashi et al., 1993; Wong et al., 2002a, 2002b), and oxygen mass balance (Bushinsky and Emerson, 2015; Emerson, 1987; Emerson et 76 al., 1991, 1993; Giesbrecht et al., 2012; Juranek et al., 2012; Plant et al., 2016). 77

78 **2 Methods**

79 2.1 Measurements of O₂, DIC, and phytoplankton biomass

Autonomous in situ oxygen measurements were made on a profiling float deployed by
the University of Washington (Special Oxygen Sensor Argo float, SOS-Argo F8397, WMO #

82 5903743, Figure 1). The complete dataset is available at

92

93

94

https://sites.google.com/a/uw.edu/sosargo/, and some of the data have been published previously 83 by Bushinsky and Emerson (2015) and Yang et al. (2017). Oxygen measurements on the SOS-84 Argo float were obtained using an Aanderaa optode oxygen sensor with air-calibration 85 mechanism (Bushinsky et al., 2016) capable of providing the air-sea difference in oxygen 86 87 concentration with an accuracy of about ± 0.2 % and a vertical resolution of 3-5 m in the top 200 m of water column. This float was operated at a cycle interval of ~ 5 days covering depths from 88 surface to 1800 m. 89 90 Partial pressure of seawater CO_2 (pCO_2), temperature, and salinity data were obtained from the NOAA mooring at OSP (WMO # 4800400). The complete dataset is available at 91

http://cdiac.ornl.gov/oceans/Moorings/Papa_145W_50N.html, and some of the data were published by Fassbender et al. (2016). DIC was calculated using the total alkalinity (TA)- pCO_2

pair in CO2sys program Version 1.1 (van Heuven et al., 2011), where TA was calculated using

the linear relationship with salinity developed in Fassbender et al. (2016) (TA = $37 \times S + 988$) 95

for the OSP vicinity. The calculation was performed on the total pH scale using the carbonate 96 dissociation constants (K_1 and K_2) of Lueker et al. (2000), the HSO₄ dissociation constant from 97 98 Dickson et al. (1990), and the B_T/S ratio from Lee et al. (2010). The DIC data were normalized to the annual mean salinity at OSP (32.5), to eliminate the influence from evaporation/dilution. 99

Water samples for phytoplankton abundance and community composition were collected 100 at OSP during 14 Line P repeat hydrographic cruises aboard the CCGS John P. Tully from 2012 101 102 to 2016 (February, June, and August for each year). Phytoplankton biomass, measured as total 103 chlorophyll a (chl-a) concentrations, and the contribution of the main taxonomic groups of phytoplankton to chl-a were determined from high performance liquid chromatography (HPLC) 104

measurements of phytoplankton pigment concentrations (chlorophylls and carotenoids, Zapata 105 106 et al. 2000) followed by CHEMTAX v1.95 analysis (Mackey et al., 1996). Eight algal groups were included in the chemotaxonomic analysis: diatoms, haptophytes, chlorophytes, 107 pelagophytes, prasinophytes, dinoflagellates, cryptophytes, and cyanobacteria. However, 108 cryptophytes were not found since their biomarker pigment, alloxanthin was not detected in any 109 110 of our samples. Pigment ratios for each algal group were obtained from Higgins et al. (2011) and used as 'seed' values for multiple trials (60 runs) from randomized starting points, as described 111 by Wright et al. (2009). The same initial pigment ratios (Table 1a) were used in all cruises but 112 113 each cruise was run separately to allow potential variations in the CHEMTAX optimization to be expressed. The range of final pigment ratios are given in Table 1b and the final ratios for each 114 cruise are given in Peña et al. (2018). The six best solutions (those with the lowest residuals) 115 were averaged for estimating the taxonomic abundances. 116

117 **2.2 Models used for NCP calculation**

118 2.2.1 Oxygen mass balance model

119 Oxygen, temperature, and salinity data from SOS-Argo F8397 and wind speed (U_{10}) data

120 from NOAA PMEL OSP mooring (https://www.pmel.noaa.gov/ocs/data/disdel/,

121 <u>https://www.pmel.noaa.gov/ocs/data/fluxdisdel/</u>) were used in a multi-layer upper ocean O₂

mass balance model to calculate NCP. This model frame (Figure 3) is similar to what was used

in Bushinsky and Emerson (2015), which compartmentalizes the upper ocean (0-150 m) into a

- 124 mixed layer box (with variable height) with one meter boxes below. This model assumes that
- horizontal processes are not important. Because horizontal gradients of oxygen are small, lateral

transport has much less influence on this property than fluxes from air-sea gas exchange, vertical

advection, and diapycnal eddy diffusion. A detailed assessment of this assumption is given in

Yang et al. (2017). Furthermore, the temperature time series measured by the SOS-Argo (Figure
S1) shows no significant intrusions of fronts/eddies, and the continuity of water mass during the
study period also allows us to use this simplified model that ignores horizontal processes.

We define ANCP as the flux of organic carbon that escapes the "upper ocean" after a 131 complete seasonal cycle. To be consistent with this definition NCP is integrated vertically from 132 133 the surface ocean to the winter mixed layer depth, which in this location is roughly equal to the pycnocline depth. Because internal waves cause a 10 to 20 meter variation in the depth of density 134 surfaces in this location, we used the annual mean pycnocline depth as the base of the modeled 135 136 "upper ocean" to conserve mass in the model. Fluxes across the base of the upper ocean are calculated using measured gradients in oxygen at the density of the pycnocline, independent of 137 its depth. 138

Oxygen concentration changes over time in the modeled "upper ocean" with depth of h (dh[O₂]/dt) are the sum of: gas exchange fluxes (F_{A-W}), vertical advection flux (F_V), diapycnal eddy diffusion (F_{Kz}), entrainment between the mixed layer and the water below (F_E), and net biological oxygen production (J_{NCP}).

$$\frac{dh[O_2]}{dt} = F_{A-W} + F_V + F_{Kz} + F_E + J_{NCP}$$
(1)

143

F_{A-W} is calculated only for the mixed layer box, using a gas exchange model that includes both diffusion and bubble processes (Emerson and Bushinsky, 2016; Liang et al., 2013). With the time step (3 h) used in our case, the mixed layer change between time steps is always smaller or equal to 1 m, so entrainment occurs only between the mixed layer box and the box below. The entrainment flux (F_E) that gets out of the mixed layer box ends up going into the box below and vice versa, so F_E for these two boxes have the same value but different signs and cancel each 150 other out. F_V is calculated from Ekman pumping rate (derived from wind speed) and oxygen gradient from SOS-Argo measurements. F_{Kz} is calculated with oxygen gradient and diapycnal 151 eddy diffusion coefficient from Cronin et al. (2015), which decreases with depth from the base of 152 the mixed layer to a background value of 10^{-5} m⁻² s⁻¹ (Whalen et al., 2012) with a 1/e scaling 153 described in Sun et al. (2013) (See also Bushinsky and Emerson, 2015). For the mixed layer 154 155 reservoir F_{kz} and F_V are considered only at the base of the box. For all the boxes below the mixed layer, F_{kz} and F_V are considered both on the top and at the base of each box. Biological oxygen 156 production, J_{NCP}, is the difference between the calculated fluxes and the measured time rate of 157 158 change (left hand side of Equation 1). This value is converted from oxygen to carbon production (i.e. ANCP) using a constant oxygen to carbon ratio of 1.45 (Hedges et al., 2002). 159

160 The uncertainty of ANCP was estimated using a Monte Carlo approach. Confidence 161 intervals for oxygen measurements and the gas exchange mass transfer coefficients used in the 162 oxygen mass balance model were assigned to the model, and varied randomly while ANCP was 163 calculated in two hundred runs for each calculation. Details of this approach are presented in the 164 supporting information and Yang et al. (2017).

165 **2.2.2 DIC mass balance model**

We used a similar mass balance model for DIC, in which the base of the modeled "upper ocean" is set to the annual mean pycnocline depth (the same as the oxygen mass balance model). This choice of the upper ocean depth distinguishes this model from the mixed layer model used in Fassbender et al. (2016). Fluxes at the base of the upper ocean in our model use DIC gradients, diapycnal eddy diffusion coefficients, and upwelling velocities determined at the mean pycnocline depth while Fassbender et al. (2016) used the values at the bottom of the mixed layer. Because the OSP surface mooring provided only the mixed layer DIC data, we assumed that

there is no annual net DIC change in the depth region between the mixed layer and the annual
mean pycnocline depth. The depth gradient of DIC used to calculate fluxes across the
pycnocline was calculated from measured oxygen gradients assuming dO₂/dz to dDIC/dz ratio of
1.45 (Hedges et al., 2002). Thus, we assume for this calculation that the DIC change at the
pycnocline depth is only due to degradation of organic matter, which ignores the change due to
CaCO₃ dissolution (Fassbender et al., 2016). For the DIC mass balance the multi-layer model is
equivalent to a one-layer model:

$$\frac{dh[DIC]}{dt} = F_{A-W} + F_V + F_{Kz} + F_E + J_{NCP}$$
(2)

180

where the DIC change (dh[DIC]/dt) for the modeled upper ocean (the air-sea interface to the 181 182 mean depth of the pycnocline) is due to air-water CO_2 exchange (F_{A-W}) at the air-sea interface, 183 vertical advection (F_V) and diapycnal eddy diffusion (F_{Kz}) at the base of the modeled "upper ocean", and net biological carbon production (J_{NCP}) in between. For this one-layer model, 184 entrainment occurred within the same layer (box) and therefore there is no net entrainment flux 185 $(F_E = 0)$. The air-sea gas-exchange mass transfer coefficient is calculated as a function of wind 186 speed using equations from Wanninkhof (2014). The DIC gradients used for F_V and F_{Kz} are 187 derived from oxygen gradients at the pycnocline depth as described above. 188

189 **2.3 Temperature dependence of NCP derived from the metabolic theory of ecology**

190 The correlation between NCP variation and environmental temperature could be 191 attributed to the temperature dependence of planktonic metabolism. Regaudie-De-Gioux and 192 Duarte (2012) derived the temperature dependences of gross primary production (GPP) and 193 community respiration (CR) using the metabolic theory of ecology and a large historical dataset 194 on volumetric planktonic metabolism in different seasons and ocean regimes (1156 estimates of

volumetric metabolic rates and the corresponding water temperature). Equations 3 & 4below are their linear regressions between the natural logarithm of the specific metabolic rates (*GPP/Chla* and *CR/Chla*) and the inverted water temperature (1/kT),

$$Ln\frac{GPP}{Chla} = a_p \frac{1}{kT} + b_p \tag{3}$$

$$Ln\frac{CR}{Chla} = a_r \frac{1}{kT} + b_r \tag{4}$$

198

where *Chla* is the chlorophyll-*a* concentration, *k* is the Boltzmann's constant, *T* is the environmental temperature in Kelvin, and a_p , b_p , a_r , b_r are slopes and intercepts for each linear regression. The temperature dependence of *GPP/CR* can be derived by combining Equations 3 & 4:

$$\frac{GPP}{CR} = EXP\left[(a_p - a_r)\frac{1}{kT} + (b_p - b_r)\right]$$
(5)

203

Since the community respiration (CR) includes the respiration of both autotrophs and

205 heterotrophs, NCP can be calculated as the difference between GPP and CR.

$$NCP = GPP - CR = GPP \left(1 - \frac{1}{\frac{GPP}{CR}}\right)$$
(6)

206 Combining Equations 5 and 6 gives us the NCP-temperature relationship.

$$NCP = GPP\left\{1 - \frac{1}{EXP[(a_p - a_r)\frac{1}{kT} + (b_p - b_r)]}\right\}$$
(7)

207

208 **3 Results**

3.1 Oxygen and DIC measurements

210 The evolutions of density, oxygen concentration, and the oxygen anomaly in percent supersaturation ($\Delta O_2 = ([O_2]/[O_2]_{sat}-1) \times 100$) determined by the profiling float at OSP from 2012 211 to 2016 are presented in Figure 4(a-c). The saturation concentration of oxygen ($[O_2]_{sat}$) was 212 213 calculated using equations from Garcia and Gordon (1992, 1993). The thin black line indicates the mixed layer depth, which is defined by a density offset from the value at 10 m using a 214 threshold of 0.03 kg m⁻³ (de Boyer Montégut, 2004). The thick blue line indicates the pycnocline 215 with a density of $\sigma_{\theta} = 25.8 \text{ kg m}^{-3}$, which follows [O₂] gradients well (Figure 4b). The white 216 boxes indicate the modeled "upper ocean" for each year, in which base of the modeled "upper 217 ocean" is the mean pychocline depth for each year. Oxygen in the mixed layer was 218 supersaturated from mid April to October/November, and near saturation or slightly 219 undersaturated for the rest of the year (Figure 4c). 220 The evolution of salinity normalized DIC in the mixed layer determined by the OSP 221 mooring is presented in Figure 4d. The pCO_2 sensor stopped working during two periods in 2013 222

and 2016 (indicated with dash line boxes), and therefore the data for these two periods is filled
with interpolated values. Strong summertime DIC drawdown was observed in each year with the
lowest DIC around September.

226 **3.2 Annual Net Community Production**

All the terms of the oxygen mass balance calculation in each year are presented in Table 2a. The ANCP results $(2.4 \pm 0.6, 0.8 \pm 0.4, 2.1 \pm 0.4 \text{ and } 1.6 \pm 0.4 \text{ mol C m}^{-2} \text{ yr}^{-1}$, with a mean value of $1.7 \pm 0.7 \text{ mol C m}^{-2} \text{ yr}^{-1}$) indicate that ANCP initially decreased after warmer water invaded this area (2013-14) and then returned to the "pre-blob" value of 2012-13 in subsequent years. Given the uncertainty in the estimate of ANCP in each year, the value during year 2013-14 is significantly different at the 95% confidence interval (as determined by t-test, Bethea et al.,

233 1975). With the exception of the unusually low value for 2013-14, ANCP values from oxygen 234 mass balance calculation are very close to the historical ANCP estimates at OSP (2.3 ± 0.6 mol 235 C m⁻² yr⁻¹, Emerson 2014).

If we integrate the ANCP from the ocean surface to the depth of the mixed layer (ANCP_{mixed layer} in Table 2a) instead of to the annual mean depth of the pycnocline, the results are higher (3.4, 1.3, 2.3 and 2.3 mol C m⁻² yr⁻¹, with a mean value of 2.4 ± 0.9 mol C m⁻² yr⁻¹). While the mean value is higher because it includes some organic carbon flux that is degraded between the mixed layer and pycnocline in summer, the annual trend, in which ANCP is significantly lower in year two (2013-14), is the same as that in which ANCP values were determined for the depth interval above the pycnocline.

In comparison, ANCP values determined from DIC mass balance are 2.0, 2.1, 2.6, 3.0 mol C m⁻² yr⁻¹, with a mean value of 2.4 ± 0.5 mol C m⁻² yr⁻¹ (Table 2b). The mean value is similar within the errors of the value determined from the oxygen mass balance (1.7 ± 0.7 mol C m⁻² yr⁻¹) but there is no significant change between the second year (2013-14) and those before and after. The somewhat higher value could be due to the assumption we made about DIC change below the mixed layer or because we neglected horizontal advection (See Discussion).

249 **3.3 Phytoplankton abundance and community composition**

250 Chl-*a* concentration, an indicator of phytoplankton biomass, was about 50% lower (0.22 251 mg m⁻³) during the period from August 2013 to June 2014 than during the rest of the 2012 to 252 2016 period (Figure 5a) and the historical annual average at OSP (Peña and Varela, 2007). Chl-*a* 253 resumed to the 2012-13 level in August 2014 and had a significant increase in the summer of 254 2016. 19'-hexanoyloxyfucoxanthin (Hex), which is mainly derived from prymnesiophytes, was 255 found to be the most abundant pigment after T-chla (Figure 5b). Fucoxanthin (Fuco), a pigment

256	associated with diatoms, haptophytes and pelagophytes, was also abundant and showed increased
257	concentration (0.54 mg m ⁻³) in June 2016, coinciding with increased T-chla. After Hex, and
258	Fuco, chlorophyll-b was the most abundant pigment (0.36 to 0.27 mg m ^{-3}), indicating the
259	presence of green algae. We also detected occasionally lutein (0-0.125 mg m ⁻³), violaxanthin (0-
260	0.012 mg m ⁻³) and, prasinoxanthin (0-0.005 mg m ⁻³), which are biomarkers for green algae.
261	The CHEMTAX analysis detected the presence of seven classes of phytoplankton
262	(Figure 5c) and showed an increase in the relative contribution of cyanobacteria and
263	chlorophytes during the "Blob" period with the highest proportion of the former group in June of
264	2014 and the latter in June 2015 (Figure 5c). There was also a decrease in the abundance of
265	diatoms from August 2013 to June 2015. The remainder of the phytoplankton community was
266	primarily composed of haptophytes and the contribution of the other phytoplankton groups was
267	variable and showed no consistent year-to-year variability. By August 2015 the phytoplankton
268	community had returned to a similar relative composition as observed in 2012-13, with
269	nanoplankton (mostly haptophytes) being dominant and with microplankton (diatoms and
270	dinoflagellates) increasing in abundance. The input matrix (Table 1a) appeared to describe the
271	environment well since the final pigment ratio matrix did not differ dramatically from the initial
272	input values.

273 **4 Discussion**

4.1 Comparisons of ANCP from oxygen and DIC mass balances

Although the ANCP are integrated to the same depth in our oxygen and DIC mass balance models, as mentioned in Section 3.2, the ANCP determined from DIC mass balance (4year mean: 2.4 ± 0.5 mol C m⁻² yr⁻¹) is somewhat higher than the value determined from oxygen mass balance (4-year mean: 1.7 ± 0.7 mol C m⁻² yr⁻¹), but still within the error of the model.

279 There are two possible reasons for such discrepancy. First of all, due to the lack of DIC data 280 below the mixed layer, for the DIC model we made an assumption that there is no annual net DIC change in the depth region between the mixed layer and the annual mean pycnocline depth. 281 282 With this assumption, the ANCP from DIC mass balance is higher because it includes the organic carbon that is degraded between the mixed layer and pycnocline in summer, so the 283 ANCP from DIC mass balance (4-year mean: 2.4 ± 0.5 mol C m⁻² yr⁻¹) is very similar to the 284 mixed layer ANCP determined from our oxygen mass balance model (4-year mean: 2.4 ± 0.9 285 mol C m⁻² yr⁻¹) and the mixed layer ANCP determined by Fassbender et al. (2016) (2 \pm 1 mol C 286 $m^{-2} yr^{-1}$). The second possible reason that the 4-year mean value of ANCP determined from the 287 288 DIC mass balance is higher than the value determined from the oxygen mass balance is horizontal advection. Because gas exchange resets the oxygen saturation anomaly for oxygen 289 290 about ten times faster than CO₂, the DIC mass balance is more vulnerable to horizontal fluxes than the O₂ mass balance. If we assumed that the difference in ANCP estimated from these two 291 tracers (0.7 mol C $m^{-2} yr^{-1}$) is due to horizontal advection, and calculate the horizontal DIC 292 gradient using the 4-year mean horizontal velocity at OSP of 0.08 m s^{-1} , we found that a 293 horizontal DIC gradient of 1×10^{-8} mol m⁻⁴ is required to cause the difference of 0.7 mol C m⁻² yr⁻ 294 ¹, which is possible at this location (horizontal DIC gradient along the 4-year mean horizontal 295 flow at OSP is about $2 \sim 3 \times 10^{-8}$ mol m⁻⁴ from GLODAP v1.1 gridded product, Key et al., 2004). 296 As for the inter-annual changes in ANCP, the oxygen mass balance calculation shows 297 that ANCP had a significant decrease in 2013-14 and then returned to the "pre-blob" level in the 298 following years whereas ANCP calculated from DIC mass balance does not show this trend. 299 Since air-sea exchange is a large part of the flux mass balance for both oxygen and CO_2 (Table 300 301 2), a likely reason for this discrepancy is due to the shorter residence time with respect to gas

302 exchange for the oxygen compared to the CO_2 saturation anomalies. An example of the residence 303 time calculation is included in the supporting information where it indicates that the gas exchange residence time in the upper ocean for oxygen is about one month and that for CO_2 is 304 about one year (See also Emerson and Hedges, 2008, Chapter 11). Thus, the biologically induced 305 306 saturation anomaly for oxygen responds fast enough to record annual changes whereas that for 307 pCO_2 and DIC does not. On the other hand, as discussed above, since DIC mass balance is more vulnerable to horizontal flux than oxygen mass balance, the DIC signal might already been 308 "smoothed" by the horizontal flux, which may also explain why the inter-annual ANCP changes 309 310 were not observed by using the DIC mass balance approach. Alternatively, the production ratio 311 of particulate organic carbon (POC) and particulate inorganic carbon (PIC) may cause the interannual variation of DIC mass balance. However, in our case since there was no significant bloom 312 of haptophytes (e.g. coccolithophore) during the study period (Figure 5c), it is unlikely that the 313 inter-annual change in POC/PIC ratio would affect the ANCP result calculated from DIC mass 314 balance. Hence, from this point forward we will focus on analyzing the factors that might 315 316 influence ANCP variations determined by the oxygen mass balance model.

4.2 Causes of ANCP decrease

In the following paragraphs, we analyze connections between ANCP decrease and the "Blob" temperature anomaly in the context of multiple physical and biological processes, including the choices of start time from which ANCP are calculated, the base depth of the modeled "upper ocean", planktonic metabolism, and changes in phytoplankton community composition.

Our observations began in June 2012, 10 – 12 months before the positive SST anomalies.
To determine whether the start date for determining the ANCP values affects the results, we

began the time series on four different months (Table 3). We are somewhat limited because
there is only about 12 "pre-blob" months before June 2012. However, as shown in Table 3, as
long as there are more "pre-blob" months than "Blob-affected" months in the 1st year, the
significant ANCP decrease from 1st to 2nd year is still observed and the trend of ANCP variation
for those 4 years remains.

To determine whether the annual mean pycnocline depth (the white rectangles in Figure 4a-4c) influences the ANCP trends we calculated ANCP using the 4-year mean depth of 100 m for the modeled "upper ocean". The ANCP results only change slightly (2.6, 1.0, 1.9, and 1.6 mol C m⁻² yr⁻¹) and the decrease in 2013-14 is still statistically significant, indicating that the different base depth used for the modeled "upper ocean" is not the key factor that causes ANCP changes.

To test if the temperature dependence of planktonic metabolism is strong enough to 336 cause the ANCP decline we observed (e.g. 1.6 mol C m^{-2} yr⁻¹ between 2012-13 and 2013-14), we 337 calculated the GPP from measured NCP of year 1 (2012-13) using Equation 7, and assumed GPP 338 339 was constant for all four years so we could then determine the effect of temperature on NCP based on the metabolic theory of ecology (Equation 7). Since the specific phytoplankton growth 340 341 rate increases with increasing temperature (e.g. Regaudie-De-Gioux and Duarte, 2012; Chen and Laws, 2017), if phytoplankton biomass would have remained the same during the "blob", GPP 342 would have increased. Thus, assuming a constant GPP in this calculation is somewhat 343 344 speculative, but it at least provides a first-order assessment of the metabolic temperature effect on ANCP. The parameterizations derived with datasets from the Arctic were used (Regaudie-De-345 Gioux and Duarte, 2012), because it gives the largest change in ANCP. The results (Table 4) 346 347 indicate that temperature dependence of planktonic metabolism is not strong enough to account

for the measured ANCP decrease in the 2^{nd} year (2013-14), suggesting that this is not the major reason for the observed ANCP decline.

Having ruled out the above likely candidates, we suggest that the observed ANCP 350 decrease is most likely linked to the changes in GPP (e.g. low phytoplankton biomass observed 351 in the 2nd year Figure 5a) and phytoplankton community composition (Figure 5c). In general, 352 larger phytoplankton (i.e. microplankton) are more efficient exporters than smaller nanoplankton 353 and picoplankton (e.g., Chen and Laws, 2016). Given the lower export rates of picoplankton 354 (e.g. cyanobacteria) than those of larger phytoplankton (e.g. diatoms) the observed changes in 355 356 phytoplankton community composition (Figure 5b) in 2013-14, which included a decrease in the relative abundance of diatoms, and an increase in the relative abundance of cyanobacteria and 357 green algae (chlorophytes), could have further contributed to the decrease in ANCP. After the 358 359 initial response to the temperature anomaly, chl-a concentration and the phytoplankton community composition returned to a level similar to those observed before the warming 360 occurred, suggesting that the plankton community rapidly adapted to the higher temperature and 361 362 prevailing environmental conditions. These changes in GPP and phytoplankton community composition could be ultimately in response to the lack of micronutrients like iron (due to 363 enhanced stratification from the "blob" that restricted the vertical supply), which has been shown 364 to regulate phytoplankton biomass and composition in this high-nutrient, low-chlorophyll region 365 (e.g. Hamme et al., 2010; Marchetti et al., 2006). Unfortunately, we do not have iron data 366 367 available to confirm that at this time.

368 **5** Conclusions

The annual net community production (ANCP) at Ocean Station Papa (OSP) in the
subarctic Northeast Pacific Ocean was determined from June 2012 to June 2016 to examine the

371 effect of the temperature anomaly on the efficiency of carbon export. The ANCP determined by oxygen mass balance had a four year mean value of 1.7 ± 0.7 mol C m⁻² yr⁻¹, whereas ANCP 372 determined by DIC mass balance gives a somewhat higher mean value $(2.4 \pm 0.5 \text{ mol C m}^{-2} \text{ vr}^{-1})$. 373 374 ANCP for individual years determined from O_2 mass balance showed a significant decrease in year 2 (2013-14) after the onset of the temperature anomaly, but no significant decrease in 375 ANCP was found when calculated with DIC mass balance. We believe that this indicates that the 376 DIC concentration and pCO_2 respond too slowly to capture annual changes in ANCP. Based on 377 our observations and historical ANCP estimates at OSP as reference, we found there was a 378 379 significant ANCP decrease in 2013-14 due to the warm anomaly, which is consistent with the 380 findings from concurrent phytoplankton data. Possible mechanisms for the observed decrease in ANCP by the oxygen mass balance in the second year were analyzed in the context of multiple 381 physical and biological processes that could be affected by temperature anomaly. Our analysis 382 showed that the ANCP decrease, as well as changes in phytoplankton abundance and community 383 composition, was most likely due to changes in GPP after the "Blob" entered the area. These 384 changes could be ultimately in response to the lack of micronutrients like iron during the "Blob" 385 period. However, the ultimate cause cannot be specified by our analysis at this time. 386 387

388 Data availability.

- Float data are available online (https://sites.google.com/a/uw.edu/sosargo/home). Mooring data
 is available online at: <u>http://cdiac.ornl.gov/oceans/Moorings/Papa_145W_50N.html</u>.
- 391 *Author contributions*.

- 392 BY and SRE designed the experiments. BY developed the model code and process the data. AP
- provided the data, analysis and interpretation of phytoplankton. BY and SRE prepared the 393
- manuscript with contributions from all co-authors. 394
- Competing interests. 395
- The authors declare that they have no conflict of interest. 396
- 397 Acknowledgements.
- We thank Dr. Stephen Riser and Dana Swift for their assistance in development of the SOS-Argo 398
- float, and scientists of NOAA PMEL and the Institute of Ocean Sciences (IOS) and crews of 399
- 400 CCGS John P. Tully, for their work on OSP mooring and Line P cruises. Special thanks are
- given to Dr. John Crusius for the constructive discussions and comments on this study. This 401
- work was supported by National Science Foundation grant OCE-1458888. 402

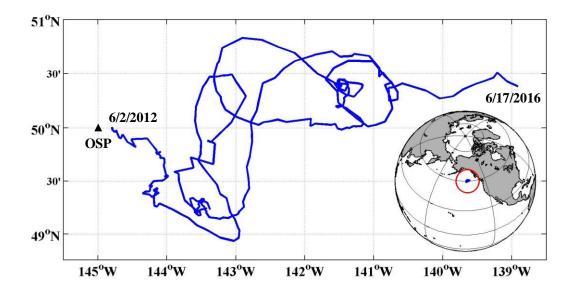
References 403

- 404 Allen, A. P., Gillooly, J. F. and Brown, J. H.: Linking the global carbon cycle to individual
- metabolism, Funct. Ecol., 19(2), 202–213, doi:10.1111/j.1365-2435.2005.00952.x, 2005. 405
- Bethea, R. M., Duran, B. S. and Boullion, T. L.: Statistical methods for engineers and scientists, 406
- 407 Marcel Dekker, Inc., New York., 1975.
- Bond, N. A., Cronin, M. F., Freeland, H. and Mantua, N.: Causes and impacts of the 2014 warm 408
- anomaly in the NE Pacific, Geophys. Res. Lett., 42(9), 3414–3420, doi:10.1002/2015GL063306, 409 2015.
- 410
- de Boyer Montégut, C.: Mixed layer depth over the global ocean: An examination of profile data 411
- and a profile-based climatology, J. Geophys. Res., 109(C12), C12003, 412
- 413 doi:10.1029/2004JC002378, 2004.
- Brown, J. H., Gillooly, J. F., Allen, A. P., Savage, V. M. and West, G. B.: TOWARD A 414
- METABOLIC THEORY OF ECOLOGY, Ecology, 85(7), 1771-1789, doi:10.1890/03-9000, 415
- 2004. 416
- 417 Bushinsky, S. M. and Emerson, S.: Marine biological production from in situ oxygen
- measurements on a profiling float in the subarctic Pacific Ocean, Global Biogeochem. Cycles, 418 29(12), 2050–2060, 2015. 419
- 420 Bushinsky, S. M., Emerson, S. R., Riser, S. C. and Swift, D. D.: Accurate oxygen measurements
- on modified Argo floats using in situ air calibrations, Limnol. Oceanogr. Methods, 2016. 421
- Cavole, L., Demko, A., Diner, R., Giddings, A., Koester, I., Pagniello, C., Paulsen, M.-L., 422
- Ramirez-Valdez, A., Schwenck, S., Yen, N., Zill, M. and Franks, P.: Biological Impacts of the 423
- 2013–2015 Warm-Water Anomaly in the Northeast Pacific: Winners, Losers, and the Future, 424
- Oceanography, 29(2), 273–285, doi:10.5670/oceanog.2016.32, 2016. 425

- 426 Charette, M. A., Bradley Moran, S. and Bishop, J. K. B.: as a tracer of particulate organic carbon
- 427 export in the subarctic northeast Pacific Ocean, Deep Sea Res. Part II Top. Stud. Oceanogr.,
- 428 46(11–12), 2833–2861, doi:10.1016/S0967-0645(99)00085-5, 1999.
- 429 Chen, B. and Laws, E. A.: Is there a difference of temperature sensitivity between marine
- 430 phytoplankton and heterotrophs?, Limnol. Oceanogr., doi:10.1002/lno.10462, 2016.
- 431 Cronin, M. F., Pelland, N. A., Emerson, S. R. and Crawford, W. R.: Estimating diffusivity from
- the mixed layer heat and salt balances in the North Pacific, J. Geophys. Res. Ocean., 120(11),
- 433 7346–7362, 2015.
- 434 Dickson, A. G., Wesolowski, D. J., Palmer, D. A. and Mesmer, R. E.: Dissociation constant of
- bisulfate ion in aqueous sodium chloride solutions to 250. degree. C, J. Phys. Chem., 94(20),
 7978–7985, 1990.
- Emerson, S.: Seasonal oxygen cycles and biological new production in surface waters of the
 subarctic Pacific Ocean, J. Geophys. Res. Ocean., 92(C6), 6535–6544, 1987.
- 439 Emerson, S. and Bushinsky, S.: The role of bubbles during air-sea gas exchange, J. Geophys.
- 440 Res. Ocean., 2016.
- Emerson, S. and Hedges, J.: Chemical oceanography and the marine carbon cycle., 2008.
- 442 Emerson, S. and Stump, C.: Net biological oxygen production in the ocean—II: Remote in situ
- 443 measurements of O 2 and N 2 in subarctic pacific surface waters, Deep Sea Res. Part I Oceanogr.
- 444 Res. Pap., 57(10), 1255–1265, 2010.
- Emerson, S., Quay, P., Stump, C., Wilbur, D. and Knox, M.: O2, Ar, N2, and 222Rn in surface
- waters of the subarctic Ocean: Net biological O2 production, Global Biogeochem. Cycles, 5(1),
 447 49–69, doi:10.1029/90GB02656, 1991.
- Emerson, S., Quay, P. and Wheeler, P. A.: Biological productivity determined from oxygen mass
- balance and incubation experiments, Deep Sea Res. Part I Oceanogr. Res. Pap., 40(11), 2351–
- 450 2358, 1993.
- 451 Emerson, S., Sabine, C., Cronin, M. F., Feely, R., Cullison Gray, S. E. and DeGrandpre, M.:
- 452 Quantifying the flux of CaCO 3 and organic carbon from the surface ocean using in situ
- measurements of O 2, N 2, pCO 2, and pH, Global Biogeochem. Cycles, 25(3), n/a-n/a,
 doi:10.1029/2010GB003924, 2011.
- 455 Fassbender, A. J., Sabine, C. L. and Cronin, M. F.: Net community production and calcification
- 456 from 7 years of NOAA Station Papa Mooring measurements, Global Biogeochem. Cycles, 30(2),
- 457 250–267, doi:10.1002/2015GB005205, 2016.
- 458 Freeland, H.: A short history of Ocean Station Papa and Line P, Prog. Oceanogr., 75(2), 120–
- 459 125, doi:10.1016/j.pocean.2007.08.005, 2007.
- 460 Freeland, H. J. and Cummins, P. F.: Argo: A new tool for environmental monitoring and
- 461 assessment of the world's oceans, an example from the N.E. Pacific, Prog. Oceanogr., 64(1), 31–
- 462 44, doi:10.1016/j.pocean.2004.11.002, 2005.
- 463 Garcia, H. E. and Gordon, L. I.: Oxygen solubility in seawater: Better fitting equations, Limnol.
- 464 Oceanogr., 37(6), 1307–1312, doi:10.4319/lo.1992.37.6.1307, 1992.
- 465 Garcia, H. E. and Gordon, L. I.: Erratum: Oxygen Solubility in Seawater: Better Fitting
- 466 Equations, Limnol. Ocean., 38(3), 656 [online] Available from:
- 467 http://www.jstor.org/stable/2838040?seq=1, 1993.
- 468 Giesbrecht, K. E., Hamme, R. C. and Emerson, S. R.: Biological productivity along Line P in the
- subarctic northeast Pacific: In situ versus incubation-based methods, Global Biogeochem.
- 470 Cycles, 26(3), doi:10.1029/2012GB004349, 2012.
- 471 Gillooly, J. F., Brown, J. H. and West, G. B.: Effects of Size and Temperature on Metabolic

- 472 Rate, Science (80-.)., 293(September), 2248–2252, doi:10.1126/science.1061967, 2001.
- 473 Hamme, R. C., Webley, P. W., Crawford, W. R., Whitney, F. A., Degrandpre, M. D., Emerson,
- 474 S. R., Eriksen, C. C., Giesbrecht, K. E., Gower, J. F. R., Kavanaugh, M. T., Pea, M. A., Sabine,
- 475 C. L., Batten, S. D., Coogan, L. A., Grundle, D. S. and Lockwood, D.: Volcanic ash fuels
- anomalous plankton bloom in subarctic northeast Pacific, Geophys. Res. Lett., 37(19),
- 477 doi:10.1029/2010GL044629, 2010.
- 478 Hedges, J. I., Baldock, J. A., G??linas, Y., Lee, C., Peterson, M. L. and Wakeham, S. G.: The
- biochemical and elemental compositions of marine plankton: A NMR perspective, Mar. Chem.,
- 480 78(1), 47–63, doi:10.1016/S0304-4203(02)00009-9, 2002.
- 481 van Heuven, S., Pierrot, D., Rae, J. W. B., Lewis, E. and Wallace., D. W. R.: MATLAB Program
- 482 Developed for CO2 System Calculations. ORNL/CDIAC-105b., ,
- 483 doi:10.3334/CDIAC/otg.CO2SYS_MATLAB_v1.1, 2011.
- 484 Johnson, K. S., Berelson, W. M., Boss, E. S., Claustre, H., Emerson, S. R., Gruber, N.,
- 485 Körtzinger, A., Perry, M. J. and Riser, S. C.: Observing Biogeochemical Cycles at Global Scales
- 486 with Profiling Floats and Gliders: Prospects for a Global Array, Oceanography, 22 [online]
- 487 Available from: http://dx.doi.org/10.5670/oceanog.2009.81, 2009.
- 488 Juranek, L. W., Quay, P. D., Feely, R. A., Lockwood, D., Karl, D. M. and Church, M. J.:
- 489 Biological production in the NE Pacific and its influence on air-sea CO2 flux: Evidence from
- 490 dissolved oxygen isotopes and O2/Ar, J. Geophys. Res. Ocean., 117(C5), n/a-n/a,
- doi:10.1029/2011jc007450, 2012.
- 492 Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R., Bullister, J. L., Feely, R. A.,
- 493 Millero, F. J., Mordy, C. and Peng, T. H.: A global ocean carbon climatology: Results from
- 494 Global Data Analysis Project (GLODAP), Global Biogeochem. Cycles, 18(4), 1–23,
- doi:10.1029/2004GB002247, 2004.
- Lee, K., Kim, T.-W., Byrne, R. H., Millero, F. J., Feely, R. A. and Liu, Y.-M.: The universal
- 497 ratio of boron to chlorinity for the North Pacific and North Atlantic oceans, Geochim.
- 498 Cosmochim. Acta, 74(6), 1801–1811, 2010.
- Liang, J. H., Deutsch, C., McWilliams, J. C., Baschek, B., Sullivan, P. P. and Chiba, D.:
- Parameterizing bubble-mediated air-sea gas exchange and its effect on ocean ventilation, Global
 Biogeochem. Cycles, 27(3), 894–905, doi:10.1002/gbc.20080, 2013.
- 502 López-Urrutia, A., San Martin, E., Harris, R. P. and Irigoien, X.: Scaling the metabolic balance
- 503 of the oceans., Proc. Natl. Acad. Sci. U. S. A., 103(23), 8739–44, doi:10.1073/pnas.0601137103, 2006.
- 505 Di Lorenzo, E. and Mantua, N.: Multi-year persistence of the 2014/15 North Pacific marine
- 506 heatwave, Nat. Clim. Chang., (July), 1–7, doi:10.1038/nclimate3082, 2016.
- 507 Lueker, T. J., Dickson, A. G. and Keeling, C. D.: Ocean pCO 2 calculated from dissolved
- 508 inorganic carbon, alkalinity, and equations for K 1 and K 2: validation based on laboratory
- 509 measurements of CO 2 in gas and seawater at equilibrium, Mar. Chem., 70(1), 105–119, 2000.
- 510 Mackey, M. D., Mackey, D. J., Higgins, H. W. and Wright, S. W.: CHEMTAX A program for
- 511 estimating class abundances from chemical markers: Application to HPLC measurements of
- 512 phytoplankton, Mar. Ecol. Prog. Ser., 144(1–3), 265–283, doi:10.3354/meps144265, 1996.
- 513 Marchetti, A., Juneau, P., Whitney, F. A., Wong, C. S. and Harrison, P. J.: Phytoplankton
- 514 processes during a mesoscale iron enrichment in the NE subarctic Pacific: Part II-Nutrient
- tilization, Deep. Res. Part II Top. Stud. Oceanogr., 53(20–22), 2114–2130,
- 516 doi:10.1016/j.dsr2.2006.05.031, 2006.
- 517 Peña, M. A. and Varela, D. E.: Seasonal and interannual variability in phytoplankton and nutrient

- dynamics along Line P in the NE subarctic Pacific, Prog. Oceanogr., 75(2), 200–222,
- 519 doi:10.1016/j.pocean.2007.08.009, 2007.
- 520 Peña, M. A., Nemcek, N. and Robert, M.: Phytoplankton responses to the 2014–2016 warming
- anomaly in the northeast subarctic Pacific Ocean, Limnol. Oceanogr., 0(0),
- 522 doi:10.1002/lno.11056, 2018.
- Plant, J. N., Johnson, K. S., Sakamoto, C. M., Jannasch, H. W., Coletti, L. J., Riser, S. C. and
- 524 Swift, D. D.: Net community production at Ocean Station Papa observed with nitrate and oxygen
- sensors on profiling floats, Global Biogeochem. Cycles, 30(6), 859–879,
- 526 doi:10.1002/2015GB005349, 2016.
- Regaudie-De-Gioux, A. and Duarte, C. M.: Temperature dependence of planktonic metabolism
 in the ocean, Global Biogeochem. Cycles, 26(1), doi:10.1029/2010GB003907, 2012.
- Rose, J. M. and Caron, D. A.: Does low temperature constrain the growth rates of heterotrophic
- protists? Evidence and implications for algal blooms in cold waters, Limnol. Oceanogr., 52(2),
- 531 886–895, doi:10.4319/lo.2007.52.2.0886, 2007.
- 532 Sun, O. M., Jayne, S. R., Polzin, K. L., Rahter, B. A. and St. Laurent, L. C.: Scaling Turbulent
- 533 Dissipation in the Transition Layer, J. Phys. Oceanogr., 43(11), 2475–2489, doi:10.1175/JPO-D-534 13-057.1, 2013.
- Takahashi, T., Olafsson, J., Goddard, J. G., Chipman, D. W. and Sutherland, S. C.: Seasonal
- variation of CO 2 and nutrients in the high-latitude surface oceans: A comparative study, Global
- 537 Biogeochem. Cycles, 7(4), 843–878, doi:10.1029/93GB02263, 1993.
- 538 Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean revisited,
- 539 Limnol. Oceanogr. Methods, 12(JUN), 351–362, doi:10.4319/lom.2014.12.351, 2014.
- 540 Whalen, C. B., Talley, L. D. and MacKinnon, J. A.: Spatial and temporal variability of global
- ocean mixing inferred from Argo profiles, Geophys. Res. Lett., 39(17),
- 542 doi:10.1029/2012GL053196, 2012.
- 543 Wong, C. ., Waser, N. A. ., Nojiri, Y., Whitney, F. ., Page, J. . and Zeng, J.: Seasonal cycles of
- nutrients and dissolved inorganic carbon at high and mid latitudes in the North Pacific Ocean
- during the Skaugran cruises: determination of new production and nutrient uptake ratios, Deep
- 546 Sea Res. Part II Top. Stud. Oceanogr., 49(24–25), 5317–5338, doi:10.1016/S0967-
- 547 0645(02)00193-5, 2002a.
- 548 Wong, C. S.: Analysis of trends in primary productivity and chlorophyll-a over two decades at
- 549 Ocean Station P (50°N, 145°W) in the subarctic northeast Pacific Ocean, Can. J. Fish. Aquat.
- Sci., 121, 107–117 [online] Available from: http://ci.nii.ac.jp/naid/10009665016/en/ (Accessed 4
 February 2017), 1995.
- 551 February 2017), 1995.
- 552 Wong, C. S., Waser, N. A. D., Nojiri, Y., Johnson, W. K., Whitney, F. A., Page, J. S. C. and
- 553Zeng, J.: Seasonal and Interannual Variability in the Distribution of Surface Nutrients and
- 554 Dissolved Inorganic Carbon in the Northern North Pacific: Influence of El Ni $\{\tilde{n}\}$ o, J. Oceanogr.,
- 555 58(2), 227–243, doi:10.1023/A:1015897323653, 2002b.
- 556 Yang, B., Emerson, S. R. and Bushinsky, S. M.: Annual net community production in the
- subtropical Pacific Ocean from in situ oxygen measurements on profiling floats, Global
- 558 Biogeochem. Cycles, 31(4), doi:10.1002/2016GB005545, 2017.
- 559Zapata, M., F. Rodrigues, and J. L. Garrido. 2000. Separation of chlorophylls and carotenoids
- 560 from marine phytoplankton: a new HPLC method using a reversed phase C-8 column and
- pyridine-containing mobile phases. Mar. Ecol. Prog. Ser. 195: 29–45. doi:10.3354/meps195029.





563 564 Figure 1 Study area and float path from 2012 to 2016. The black triangle indicates the position of Ocean Station Papa (OSP) Mooring, and the blue line indicates the trajectory of the SOS-Argo 565 float which was within roughly a 2° (N-S) $\times 6^{\circ}$ (E-W) box. 566

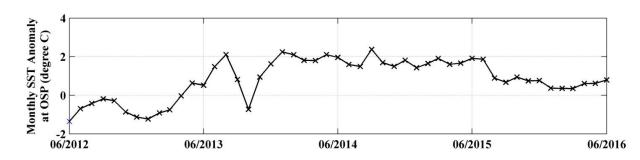
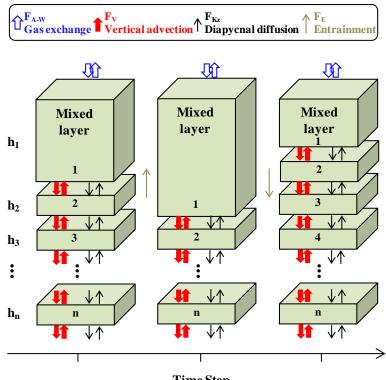




Figure 2 Monthly SST Anomaly at Ocean Station Papa (OSP). The anomaly is defined as the 569

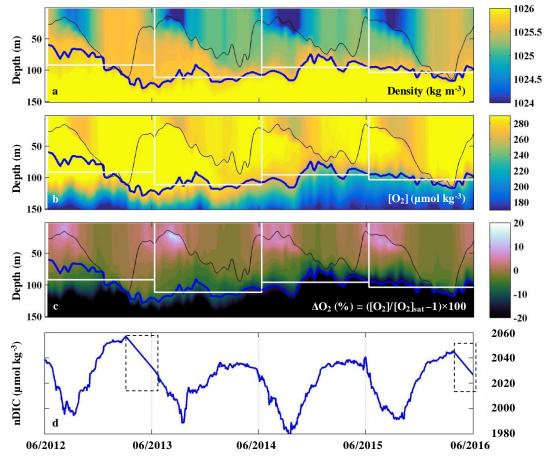
- difference between the measured SST and the mean of 1971-2000. Data are from: 570
- http://iridl.ldeo.columbia.edu/maproom/Global/Ocean_Temp/Anomaly.html 571
- 572



573

Time Step

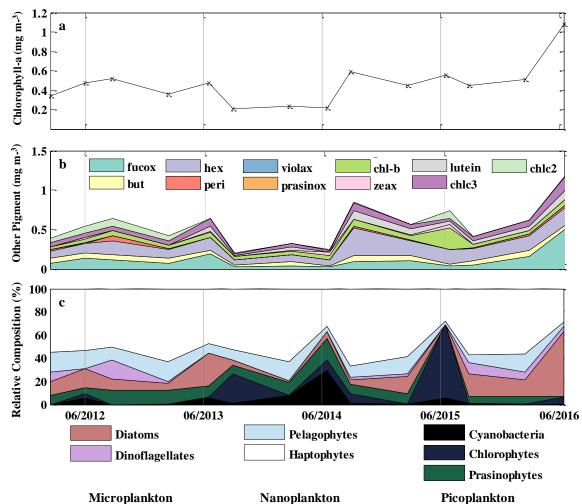
- Figure 3 Schematic of the multi-layer upper ocean oxygen mass balance model (adapted from 574
- Bushinsky and Emerson, 2015). Fluxes (F) are from air-sea gas exchange (F_{A-W}, including 575 diffusion and bubble processes), vertical advection (F_V), diapycnal eddy diffusion (F_{Kz}), and
- 576 entrainment (F_E). 577
- 578



579

Figure 4 (a-c) Upper ocean density, oxygen concentration, and oxygen supersaturation ΔO_2 (%) from the SOS-Argo float at OSP. The thin black line indicates the mixed layer depth, the thick blue line indicates the pycnocline depth, and the white rectangles indicate the modeled "upper ocean" for each of the four years that ANCP were calculated. (d) Mixed layer DIC normalized to a surface salinity at OSP (S= 32.5) from June 2012 to June 2016. Dash line boxes indicate

periods when the pCO2 data were not available and thus were filled with a straight line interpolation.



587 Microplankton Nanoplankton Picoplankton
588 Figure 5 Mixed layer mean (a) chl-*a* concentration (mg m⁻³), (b) other pigment concentration
589 (mg m⁻³), and (c) relative phytoplankton composition (%) at OSP. Values were determined from
590 HPLC pigment analysis of samples collected in February, June, and August for each year from
591 2012 to 2016.

	Chl c_3	Chl c_2	Peri	But	Fuco	Pras	Viola	Hex	Allo	Zea	Lut	Chl b	Chl a
(a)													
Cyano	0	0	0	0	0	0	0	0	0	0.64	0	0	1
Chloro	0	0	0	0	0	0	0.049	0	0	0.032	0.17	0.32	1
Prasino	0	0	0	0	0	0.25	0.054	0	0	0.058	0.021	0.73	1
Crypto	0	0.2	0	0	0	0	0	0	0.38	0	0	0	1
Diatoms	0.08	0.28	0	0	0.99	0	0	0	0	0	0	0	1
Dinofla	0	0.22	0.56	0	0	0	0	0	0	0	0	0	1
Pelago	0.22	0	0	0.64	0.772	0	0	0	0	0	0	0	1
Hapto	0.18	0.21	0	0.039	0.289	0	0	0.47	0	0	0	0	1
(b)													
Cyano	0	0	0	0	0	0	0	0	0	0.48-0.85	0	0	1
Chloro	0	0	0	0	0	0	0.02-0.15	0	0	0.03-0.04	0.06-0.21	0.26-0.45	1
Prasin	0	0	0	0	0	0.04-0.23	0.02-0.06	0	0	0.02-0.06	0.017-0.022	0.72-1.12	1
Crypto	0	0.15-0.23	0	0	0	0	0	0	0.34-0.44	0	0	0	1
Diatoms	0.05-0.09	0.21-0.3	0	0	0.8-1.15	0	0	0	0	0	0	0	1
Dinofla	0	0.19-0.26	0.45-0.64	0	0	0	0	0	0	0	0	0	1
Pelago	0.11-0.25	0	0	0.68-1.15	0.22-0.82	0	0	0	0	0	0	0	1
Hapto	0.05-0.22	0.16-0.26	0	0.037-0.068	0.07-0.25	0	0	0.58-0.81	0	0	0	0	1

Table 1. Pigment:Chl *a* ratios for eight algal groups: (a) CHEMTAX initial ratio matrix, and (b) ranges of final pigment ratios obtained by CHEMTAX on the pigment data.

Abbreviations: Cyano, cyanobacteria; Chloro, chlorophytes; Prasino, prasinophytes; Crypto, cryptophytes; Dinofla, dinoflagellates; Pelago, pelagophytes; Hapto, haptophytes; Chl c_3 , chlorophyll c_3 ; Chl c_2 , chlorophyll c_2 ; Peri, peridinin; But, 19'butanoyloxyfucoxanthin; Fuco, fucoxanthin; Pras, prasinoxanthin; Viola, violaxanthin; Hex, 19'-hexanoyloxyfucoxanthin; Allo, alloxanthin; Zea, zeaxanthin; Lut, lutein; Chl *b*, chlorophyll *b*; Chl *a*, chlorophyll. **Table 2** Annual net community production (ANCP) determined from (a) O_2 mass balance, and (b) DIC mass balance. The annually integrated fluxes for each of the important terms (columns 4-9) indicate that the air sea flux and biological production terms dominate for both tracers. Two ANCP values are given in (a): one integrated from the ocean surface to the depth of annual mean pycnocline (column 3), ANCP, and another value integrated over the depth of the mixed layer, ANCP_{mixed layer}. Only the former is a measure of the biological organic carbon that escapes the upper ocean on an annual basis (see text).

a											
Year	Time Period (June to June)	h (m)	Annual oxygen mass balance (mol $O_2 \text{ m}^{-2} \text{ yr}^{-1}$) dh[O_2]/dt = $F_{A-W} + F_E + F_{Kz} + F_v + J_{NCP}$						ANCP = $J_{NCP}/1.45$ (mol C m ⁻² yr ⁻¹)	ANCP _{mixed layer} (mol C m ⁻² yr ⁻¹)	
			dh[O ₂]/dt	$F_{a\text{-}w} = F_s + F_b$	$F_{\rm E}$	F_{Kz}	F_V	J _{NCP}	(more m yr)	(more m yr)	
1	2012-13	91	-0.7	-2.9	0	-0.6	-0.6	3.5	2.4 ± 0.6	3.4	
2	2013-14	111	-1.3	-1.5	0	-0.8	-0.2	1.2	0.8 ± 0.4	1.3	
3	2014-15	95	-0.6	-1.7	0	-0.9	-1.0	3.0	2.1 ± 0.4	2.3	
4	2015-16	103	0.8	-0.1	0	-0.7	-0.3	2.3	1.6 ± 0.4	2.3	
b											
	Time Period		Annual DIC mass balance (mol C m ⁻² yr ⁻¹)					$ANCP = - J_{NCP}$			
Year	(June to June)	h (m)	$dh[DIC]/dt = F_{A-W} + F_E + F_{Kz} + F_v + J_{NCP}$				$- (\text{mol C } \text{m}^{-2} \text{ yr}^{-1})$				
			dh[DIC]/dt	F _{a-w}	$F_{\rm E}$	F _{Kz}	F_V	J _{NCP}		i yi)	
1	2012-13	91	-0.2	1.0	0	0.7	0.1	-2.0	2.0		
2	2013-14	111	-0.1	1.5	0	0.4	0.1	-2.1	2.1		
3	2014-15	95	0.05	2.0	0	0.5	0.1	-2.6	2.6		
									3.0		

Table 3 ANCP calculated from O_2 mass balance with different start dates to determine if the chosen annual period affects the conclusions (see text).

Start Tir	Start Time					
	1 st year (2012-13)	2.4	2.3	2.4		
ANCP	2 nd year (2013-14) 3 rd year (2014-15)	0.8	0.9	0.7		
$(mol C m^{-2} yr^{-1})$	3 rd year (2014-15)	2.1	2.6	2.5		
	4 th year (2015-16)	1.6	-	-		

Table 4 Comparisons of ANCP measured with O_2 mass balance and ANCP predicted from the temperature dependence parameterization of planktonic metabolism using parameters from the Arctic Ocean [*Regaudie-De-Gioux and Duarte*, 2012]. Gross primary production (GPP) is calculated from ANCP in year 1 and Equation 7, and it is assumed to be the same through years 1 - 4. ANCP_{diff} = 2.4 (mol C m-2 yr⁻¹) – ANCP_{Predicted or Measured}

Year	Mean temperature	ANCP (mo	$1 \mathrm{C} \mathrm{m}^{-2} \mathrm{yr}^{-1}$	$\mathbf{ANCP}_{\mathbf{diff}} (\mathbf{mol} \ \mathbf{C} \ \mathbf{m}^{-2} \ \mathbf{yr}^{-1})$		
	(°C)	Predicted	Measured	Predicted	Measured	
1	8.4	-	2.4	-	-	
2	10.4	1.9	0.8	-0.5	-1.6	
3	10.8	1.9	2.1	-0.5	-0.3	
4	9.9	2.1	1.6	-0.3	-0.8	