

Laboratorio Biogeoquímica de Gases de Efecto Invernadero Facultad de Ciencias del Mar y Geografía PONTIFICIA UNIVERSIDAD CATÓLICA DE VALPARAÍSO

Valparaíso-Chile, March 15, 2016

Editors of Biogeosciences

Dear Editors,

I am pleased to send the manuscript entitled "BIOGEOCHEMICAL CHARACTERISTICS OF A LONG-LIVED ANTICYCLONIC EDDY IN THE EASTERN SOUTH PACIFIC OCEAN" by Marcela Cornejo, Luis Bravo, Marcel Ramos, Oscar Pizarro, Johannes Karstensen, Mauricio Gallegos, Marco Correa-Ramirez, Nelson Silva, Laura Farias and Lee Karp-Boss. The manuscript was revised by two reviewers, who made several comments and suggestions about the presentation of results and figures, as well as about the English.

We have taken into account most of the suggestions from both reviewers and We included them in the manuscript. The English was re-reviewed by a native English colleague. All the changes we made in the paper have been included in a document below with a detailed point by point.

We are deeply grateful to the reviewers, who with their comments and suggestions have helped to strengthen and improve the manuscript.

I look forward to hearing from you.

Yours sincerely,

Marcela Cornejo-D'Ottone

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DETAILED CHANGES AT THE MANUSCRIPT

We thank the reviewers for their time and constructive comments. We carefully read each of the comments and addressed them as stated below:

About the comments made by Reviewer #2:

- The manuscript was re-reviewed and re-edited by a colleague, who is a native English speaker, Dr. John Dolan.
- 2. All the mistakes and non-scientific terms noticed by Reviewer #2 have been corrected in the text.
- 3. We revised the abstract and expanded it to improve the summary of the results.
- 4. The information about eddy polarities and their properties were included in the introduction and We are explicit about that our eddy was an anticyclonic eddy throughout the manuscript.
- 5. The characteristics of the waters transported by cyclonic eddies were included in the introduction.
- The name of the stations were changed from E03 to 094-A in order to uniform the name as the Tara Oceans stations.
- 7. The table and its caption was modified as suggested by the reviewer.



- 8. We put the label a) b) c), etc, in a white box, in order to make them easily to see.
- 9. The climatological mean was added to Figure 2.
- 10. We corrected the terms "stisopycnales" by "sigma-t isopicnals" and "isocline" by "isolines"
- 11. The caption in figure 6 was changed in order to be clearer.
- 12. In figure 7, the lines of isopicnals were reviewed and changed.
- 13. We defined ESP (Eastern South Pacific) in the abstract.
- 14. The asked references in the introduction were included.
- 15. The acknowledgement to AVISO was included in the corresponding section.
- 16. We corrected the citation of the mentioned figures in the text.
- 17. The information of the use of a $1^{\circ}x1^{\circ}$ grid was included in the method section.
- 18. We were more specific when we talk about the low oxygen concentrations detected in the middle of the ocean by Silva et al. (2009). We revised the phrase and re-written to better explain it.



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About the comments made by Reviewer#3:

- 1. About the hotspot of denitrification inside the eddy, the reviewer raises a valid concern. The proxies that we measured in it suggest the presence of active denitrification. However, as the reviewer says, is only one sampled profile in this eddy so We had the precaution to say that, and that this issue needs to have further studies. In the same sense, about the rates of change in biogeochemical properties we referred to the calculations as 'back of the envelope' type calculations and cautioned in the text that they should be taken with a grain of salt. We were very careful to specify that our calculations are rough and we need more studies in order to estimate more precisely these rates.
- 2. We added the standard deviation of replicate samples for nitrite and N_2O values. In the case of nitrite, the standard deviations are very low, so it is difficult to see them in the figure.
- We were more explicit about that with our data we can not include mixing in our calculations.



- 4. The first paragraph of the introduction was modified in order to separate the ideas.
- 5. We added information in the introduction about the description and characteristics of water masses in the region which is source of water for the mesoscale eddies.
- 6. We added a description of sample collection in the methods.
- 7. We included the reference about the glider track in the methods.
- 8. We included the data from E02 (now station 093) in the figure 1e.
- 9. We included the caption of figure 6b.

Definición de

Biogeochemical characteristics of a Long-lived anticyclonic eddy in the eastern South Pacific Ocean

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73 ABSTRACT

74	Eastern boundary upwelling systems are characterized by high productivity that often leads	
75	to subsurface hypoxia on the shelf. Mesoscale eddies are important, frequent, and	Con formato
76	persistent features of the circulation in these regions the eastern South Pacific (ESP) Ocean,	Con formato
77	transporting physical, chemical and biological properties from the productive shelves to the	
78	open ocean. In Some of these eddies exhibit subsurface hypoxic or suboxic conditions and	
79	may serve as important hotspots for nitrogen loss, but little is known about oxygen	
80	consumption rates and nitrogen transformation processes associated with these eddies. In	
81	the austral fall of 2011, during the Tara Oceans expedition, a subsurface layer (200-400 m)	
82	in which the concentration of oxygen was very low (<2 μ mol kg ⁻¹ of O ₂) was observed in the	
83	eastern South Pacific, ~900 km offshore (30°S, 81°W). Satellite altimetry combined with CTD	
84	observations associated the local oxygen anomaly with an intrathermocline, anticyclonic,	
85	mesoscale eddy with a diameter of about 150 km. suboxic (<2 μ mol kg ⁻¹ of O ₂), subsurface	
86	layer (200-400 m) was detected ~900 km off the Chilean shore (30°S, 81°W). The eddy	
87	containedcore of the eddy's suboxic layer had a temperature-salinity signature	
88	characteristic of Equatorial Subsurface Water (ESSW) that at this latitude is normally	
89	restricted to an area near the coast. Undersaturation Measurements of nitrogen species	
90	within the eddy revealed undersaturation (below 44%) of nitrous oxide (N_2O) and nitrite	
91	accumulation (> 0.5 μ M) gave evidence for), suggesting that active denitrification occurred	
92	in this water mass. Based on Using satellite altimetry, we tracked were able to track the eddy	
93	back to its region of formation on the coast of central Chile (36.1°S, 74.6°W). We estimate	
94	that the eddy formed in April 2010. Field studies conducted on thein Chilean shelf in June	

95 2010 waters close to the time of eddy formation provided approximate information on estimates of initial O₂ and N₂O concentrations of -the ESSW source water-water in the 96 97 region ateddy. By the time of eddy formation. Concentrationsits offshore sighting, 98 concentrations of both O₂ and N₂O in the subsurface oxygen minimum zone (OMZ) of the 99 offshore eddy were lower than its surroundings or concentrations in surrounding water 100 and 'source water' on the shelf, suggestingindicating that these chemical species were 101 consumed as the eddy moved offshore. Estimates of apparent oxygen utilization rates at the OMZ of the eddy ranged from 0.29 to 44 nmol L⁻¹ d⁻¹ and the rate of N₂O consumption 102 103 was 3.92 nmol L⁻¹ d⁻¹. OurThese results show that mesoscale eddies affect open-ocean 104 biogeochemistry in the ESP not only transport by transporting physical and chemical 105 properties of the ESSW-from the coast to the ocean interior, but also export and transform 106 biogeochemical properties, creating suboxic environments in the oligotrophic region of the 107 eastern South Pacific. Suboxic water masses that are advected by eddies act as hotspots forduring advection, local biological consumption of oxygen within an eddy further 108 109 generates conditions favorable to denitrification and loss of fixed nitrogen from the system.

132 INTRODUCTION

133

134 other physical, chemical and biological constituents- (Chelton et al., 2007; Chaigneau et al., 135 2008, 2009). In the eastern South Pacific (ESP) Ocean, mesoscale eddies frequently form in 136 the coastal transition zone off central Chile due to the instability of the alongshore currents 137 in the coastal region (Hormazábal et al., 2013; Morales et al., 2010, 2012). These eddies Con formato 138 transport water for long distances and over several months across biogeographic 139 boundaries, from the productive Humboldt (Peru-Chile) Current to adjacent oligotrophic 140 waters of the subtropical gyre (Pizarro et al., 2006). While cyclonic eddies transport surface Con formato waters and are seen as negative anomalies by altimetry data, anticyclonic eddies, including 141 142 the Intrathermocline eddies (ITE) are deeper and transport low oxygen and salty subsurface 143 waters from the Equatorial Subsurface Waters (ESSW) (Chaigneau et al., 2011). 144 Although eddies have been considered a net loss of nutrients from the coastal zone (Gruber, Con formato 145 2011), they constitute a nutrient source in the open ocean that stimulates production in 146 oligotrophic regions (McGillicuddy et al., 1998). In addition to transporting nutrients, eddies Con formato 147 introduce spatial heterogeneity in productivity, community structure and particle flux, as has been observed in the Sargasso Sea (McGillicuddy et al., 1998; Sweeney et al., 2003). 148 Con formato 149 Impacts of eddies on biogeochemical processes are of particular interest for coastal 150 transition zones of eastern boundary currents, where oxygen minimum zones (OMZs) and 151 eddies interact (Altabet et al., 2012; Stramma et al., 2013). Open-ocean eddies associated Con formato 152 with subsurface hypoxic or suboxic conditions have been observed in both the eastern

Mesoscale eddies play a major role in vertical and horizontal transport of heat, salts and

153 tropical Atlantic and eastern tropical Pacific (e.g., Lukas and Santiago-Mandujano 2001; Con formato

176	Stramma et al., 2014; Karstensen et al., 2015). High surface productivity-and, downward	
177	particle flux and oxygen respiration, combined with sluggish exchange between the eddy	
178	interior and surrounding waters, have been proposed as mechanisms leading to \underline{the}	
179	formation of "dead zones" observed within <u>anticyclonic-mode water</u> eddies (Karstensen et	Con formato
180	al., 2015). Oxygen consumption rates within an eddy can be 3 to 5 times higher than in the	
181	surrounding oligotrophic water (Karstensen et al., 2015). Eddies containing hypoxic or	Con formato
182	suboxic water can become hotspots for nitrogen cycling, including biogenic production of	
183	N_2 and loss of fixed nitrogen from the system (Altabet et al., 2012; Stramma et al., 2013).	Con formato
184	Recent observations on eddies formed Recently, Stramma et al. (2013) suggested that in	
185	the eastern tropical Pacific Ocean, off Peru, suggest that coastal mode water eddies are	
186	regionszones of active loss of fixed nitrogen loss, whereas the contribution of eddies	
187	generated in the open ocean to while nitrogen loss in this region associated with older, open	
188	ocean mode water eddies is negligible (Stramma et al., 2013).considerably lower.	
189	In <u>eastern boundary subtropical</u> upwelling zonessystems with a pronounced subsurface	
190	OMZ, such as in the ESP, eddies may play an important role in transporting OMZ waters and	
191	their microbial communities to the open ocean. The OMZ in the upwelling region of the ESP	
192	is associated with Equatorial Subsurface Water (ESSW), originating in) that has been	
193	transported poleward, from the Pacific Ocean equatorial belt-and transported poleward,	
194	along the coast with the Peru-Chile undercurrent. The ESSW is characterized by high salinity	
195	and nutrient concentrations, low oxygen concentrations and an active, bacterially mediated	
196	nitrogen cycling, including production and consumption of the greenhouse gas nitrous oxide	
197	(N ₂ O). Intense nitrification, denitrification and nitrous oxide (N ₂ O) production (Codispoti	

218 and Christensen, 1985)Intense nitrification, denitrification and nitrous oxide (N2O)

production associated with ESSW is generally confined to a narrow coastal band and
 contributes to net nitrogen loss in this region (Lam and Kuypers, 2011).

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Intriguing questions about the role of coastally generated eddies abound: What 221 222 biogeochemical transformations occur as this volume of water is advected offshore? Do 223 concentrations of dissolved oxygen decrease, increase or remain the same? If changes in 224 dissolved oxygen concentrations occur during transport, what are other biogeochemical 225 consequences in both surface and subsurface layers? Here, we present results offrom a 226 study on the physical and chemical characteristics of a single anticyclonic eddy observed 227 ~900 km offshore, off central Chile. We tracked it he eddy back to its region of formation and examined changes in concentration of oxygen and nitrogen species from the time it left 228 229 the coast to the time it was sampled in the oligotrophic ocean.

230 METHODS

231 Hydrography and nitrogen data

Hydrographic data and water samples for analyses of nutrients, N₂O and surface δ^{15} N-POM

- were collected along a transect from Valparaíso, Chile (33°S, 71.6° W) to Easter Island (28.2°
- S, 107.4° W) during the Tara Oceans Expedition (16<u>11</u> 31 March 2011, Fig. 1; Karsenti et Con formato
 al., 2011). Sampling consisted of 11 vertical profiles using a Sea-Bird <u>911equipped911</u>
- <u>equipped</u> with an oxygen sensor (SBE43, sampling rate 24 Hz; Picheral et al., 2014).
 <u>UnfortunatelyDue to logistical constraints</u>, the oxygen sensor could not be calibrated on

259 board. It was calibrated at the start of the expedition (July 2009) and a year later (August 2010 during a stopover in Cape Town, South Africa). A third calibration was conducted in 260 261 September 2011 (during a stopover in Papeete). The sensor showed mean drifts of 0.101 262 (August 2010) and 0.405 μmol kg⁻¹ (September 2011), respectively, between successive calibrations. Because oxygen calibrations could not be done routinely, post-cruise validation 263 264 of oxygen data included comparison of raw oxygen measurements with WOA13 climatology 265 (Garcia et al., 2014) as described by Roullier et al. (2014). For the ESP transect, absolute 266 differences between measured dissolved oxygen (SBE 43) and climatology for the upper 500 267 m of the water column averaged 9.1 μ mol kg⁻¹ (0.03 – 24.47 μ mol kg⁻¹) for oceanic stations 268 and 16.7 µmol kg⁻¹ (0.06 – 36.24 µmol kg⁻¹) for the coastal stations. Below 850m, absolute differences between in situ measurements and climatology averaged 6.62 μ mol kg⁻¹ (0.81 – 269 19.08 µmol kg⁻¹). 270

271 Discrete water samples for N₂O (in triplicate) and nutrient (in duplicate) analyses were 272 obtained from a rosette equipped with 1210 L Niskin bottles. Samples were collected at 0, 273 50, 100, 150, 200, 250, 300, 400, 500, and 900 m. N₂O samples (20mL)20 mL) were taken 274 after the inorganic carbon samples, using a tygon tubing to avoid bubble formation. 275 Samples were fixed with 50 μ L of saturated mercuric chloride and stored in the dark. N₂O 276 concentrations were determined onshore using a gas chromatograph equipped with an 277 electron capture detector (ECD), following a headspace technique (McAullife, 1971). A four-278 point calibration curve was determined with air (0.32 ppm) and N₂O standards of 0.1, 0.5 and 1 ppm (Scotty gas mixture; Air Liquid Co.). 279

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Nutrient samples (NO₃⁻, NO₂⁻ and PO₄⁻³) were collected by filtering seawater (GF/F 0.7 μ m 299 300 filters); filtrates were stored at -20°C until analysis onshore. Concentrations of NO₃⁻, NO₂⁻ and PO₄-³ were measured using a Seal Analytical AA3 AutoAnalyzer (Grasshoff et al., 1983). 301 Con formato 302 Eddy identification and tracking 303 Presence and position of mesoscale eddies in the region was determined by analyzing 304 weekly maps of anomalies in sea level and geostrophic velocities from the multi-satellite 305 **AVISO** product (Ssalto/Duacs, http://www.aviso.oceanobs.com/duacs/), http://www.aviso.oceanobs.com/duacs/), from B06 307 April 2010 to September 2011. This gridded, multi-satellite altimeter product provides 308 spatial resolution of $1/3^{\circ}$ and allows resolution of eddies with an e-folding scale > 40 km 309 (Chaigneau et al., 2011; Chelton et al., 2011). Detection of an eddy and subsequent tracking Con formato 310 back to its region of origin used the Okubo-Weiss (W) parameter For eddy tracking, we used 311 the Okubo-Weiss parameter method (W), which evaluates the relative dominance of strain 312 and vorticity (Chelton et al., 2007; Okubo, 1970; Sangrà et al., 2009; Weiss, 1991), which Con formato 313 evaluates the relative dominance of strain and vorticity:

- 314 $W = S_n^2 + S_s^2 \omega^2$ (1)
- 315 With
- 316 $S_n = \frac{\partial u}{\partial x} \frac{\partial v}{\partial y}$; (2)

317 $S_s = \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}$; (3)

338
$$\omega = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y};$$
 (4)

339 where, S_n and S_s are the normal and shear components of strain, respectively, and ω is the 340 relative vorticity.

This approach associated confirmed that the water mass sampled in station E03094-A (30°S,
81°W; TARA_20110316T1152Z_999_EVENT_CAST;
http://doi.pangaea.de/10.1594/PANGAEA.836473; Fig. 1)1a) was associated with an eddy.
The path of this eddy was reconstructed from its time of origin (28 April 2010) to the time
of its decay (29 June 2011) by tracing the eddy center (approximate position of i.e., the
center of the region with highest vorticity region) in successive geostrophic fields.

Vertical hydrographic profiles obtained from the E03-station (sampled <u>094-A</u> (within the identified eddy) were compared with <u>available</u> vertical profiles of temperature, salinity and dissolved oxygen concentration collected during other studies in the area and with nearby Argo buoy profiles and climatological information from WOA13 data (Garcia et al., 2014). Data available for the nearest grid (1° x 1°) to station E03094-A were used in this analysis.

352 Glider information at the origin of the eddy

To characterize the properties of water <u>close_tonear</u> the time<u>and location</u> of eddy formation we used temperature, salinity and oxygen data from a cross-shore transect (73.0 -74.8° W, 36.5° S) conducted with a Slocum glider (Teledyne Technologies) in June 2010-(<u>Pizarro et al., 2015</u>). The data covered an area that extended to within 160 km from the presumed starting point of the eddy based on satellite backtracking. The glider was **Con formato** fuente: Autom

equipped with an optical oxygen sensor (Aanderaa Data Instrument oxygen Optode model
380 3830). Oxygen sensor calibrations are routinely done at the Physical Oceanography
Laboratory, Universidad de Concepción, with a two-point calibration curve-(0% and 100%
of oxygen saturation). Details of the sensor and the physical principles involved in the
measurements are described in Körtzinger et al. (2005) and Uchida et al. (2008).

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384 **RESULTS AND DISCUSSION**

385 Hydrography

386 A vertical section of temperature, salinity and oxygen, measured along the transect from 387 Valparaíso (33.4° S, 71.6° W) to Easter Island (27.08° S, 109.3° W) in March 2011 provides 388 regional context (Fig. 1).1b, 1c, 1d, respectively). A subsurface oxygen minimum layer (with 389 dissolved oxygen concentration as low as 1.17 μ mol O₂ kg⁻¹) was detected at station EO3094-390 A, 922 km offshore (30°S, 81°W, Fig. 1d). Dissolved oxygen concentrations observed at 391 E03094-A are anomalous given that at this latitude the boundary of the OMZ (defined as 392 O₂< 44.6 µmol kg⁻¹) at this latitude is typically located closer to shore (~ 600 km from 393 shoreline), while and its core (defined as $O_2 < 22.3 \,\mu$ mol kg⁻¹) is confined to a thin subsurface 394 layer that doesdo not normally stretchtypically extend beyond <u>~600 km and ~</u>500 km from 395 shorethe shoreline, respectively (Silva et al., 2009). Suboxic conditions (O₂< 10 µmol kg⁻¹), 396 are thought to be confined to the shelf region and were reported only in some bottom 397 waters over the continental shelf (Farías, 2003). Climatological data indicate that the 398 subsurface layer at water in the vicinity of station E03 region 094-A is typically oxygenated 399 (Fig. 1e). According to this above classification of dissolved oxygen concentrations, the OMZ

observed at station E03094-A has its upper and lower boundaries at depths of 164 and 536
m, respectively, while suboxic conditions were observed between 174 m and 421 m (66%
of the OMZ).

403 The low-oxygen water mass was associated with higher salinities (34.60 – 34.66) compared 404 to backgroundsurrounding water (Fig. 1c) and climatology for this region (34.15 – 34.36, for 405 the years 1965 - 2012). Historical data from previous cruises conducted along the P06-406 WOCE transect (32.5° S) or north of the study region (e.g., 28°S, Scorpio; Silva et al., 407 2009Silva et al., 2009; 27°S, CIMAR 5 cruise Fuenzalida et al., 2006)Fuenzalida et al., 2006) 408 do not show such extremeanomalies in physical and chemical conditions at this longitude 409 (Fig. 2a and 2b). The presence of the anomalous salinity signature observed in this study is 410 supported by an independent Argo float that profiled in the vicinity of E03094-A (33.86° S, 411 79.84° W) during the Tara Oceans' sampling period (Fig. 2).

412 Vertical profiles of salinity and temperature anomalies at E03 show a warm and salty core 413 centered between 230 and 270 m, accompanied by the dome and bowl shapes of the upper 414 and lower thermocline, respectively (Fig. 3). This feature is characteristic of an 415 intrathermocline, anticyclonic eddy (ITE, Xiu and Chai 2011; Chaigneau et al., 2011; 416 Hormazábal et al., 2013). Positive sea level anomalies (SLA) and associated geostrophic 417 currents further indicate that station E03094-A show a warm and salty core centered 418 between 230 and 270 m, accompanied by the dome and bowl shapes of the upper and 419 lower thermocline, respectively (Fig. 3). This feature is characteristic of an intrathermocline, 420 anticyclonic eddy (ITE, Xiu and Chai 2011; Chaigneau et al., 2011; Hormazábal et al., 2013). 421 Positive sea-level anomalies (SLA) and associated geostrophic currents further indicate that 442 <u>station 094-A</u> was located close to the center of a mesoscale anticyclonic eddy (~ 150 km in
443 diameter), centered at 33.45°S, 80.85°W (Fig. 4).

444	Reconstruction of this mesoscale eddy suggests that it was formed nearin the coastal	
445	transition zone off Concepción (36.09° S, 74.21° W), in the coastal transition zone,	
446	approximately 315 d prior to our sampling at station 094-A, and advected northwest at a	
447	mean velocity of 2.4 cm s ⁻¹ , approx. 2 Km d ⁻¹ (Fig. 4). Reconstruction of the eddy's velocity	
448	and direction agrees well with previously reported trajectories of eddies in the area	
449	(Chaigneau, 2005).	Con formato
450	OMZ evolution in the eddy	
451	In the ESP, eddies could frequently transport suboxic water from the coastal OMZ to oceanic	
452	regions- <u>(Hormazábal et al., 2013).</u> Low-oxygen water masses ($O_2 < 44.6 \mu M$) have been	
453	detected in the middle of the South Pacific Ocean (2000 km offshore at 28°S; Silva et al.,	Con formato
454	2009), but their association at the time the authors did not associated these water masses	
455	with mesoscale eddies has been speculative In the North Pacific Ocean, low concentrations	
456	of dissolved oxygen in the subsurface open ocean have been previously described in	
457	association with anticyclonic mesoscale eddies (Altabet et al., 2012; Chaigneau et al., 2011;	Con formato
458	Johnson and McTaggart, 2010; Lukas and Santiago-Mandujano, 2001), and could-result	
459	from have been attributed to low-oxygen source waters (Lukas and Santiago-Mandujano,	Con formato
460	2001) or fromto local consumption asduring the transport of an eddy is being transported	
461	(Karstensen et al., 2015).	Con formato

462 To approximate the evolution estimate temporal changes in concentrations of dissolved 463 oxygen in the subsurface layer of theour sampled eddy, we used underwater glider 464 measurements, collected in June 2010, at 36.5°S / 74° W (120 km from shore) during June 465 2010.). This is the estimated location of the eddy one month after its formation. The 466 distribution and oxygen concentrations of source water are in agreement with those reported for other ITEs in the same region (Hormazábal et al. 2013). Glider measurements 467 468 of dissolved oxygen measured by the glider showed a well-developed OMZ (O_2 < 44.6 μ M; 469 Fig. 5) between 104 and 352 m, with a suboxic layer located between 135 and 226 m. We 470 refer to these values as the eddy's initial'initial' subsurface oxygen concentrations. 471 Dissolved oxygen concentrations were then compared along isopycnals between the 472 estimated location of the eddy's origin and its offshore location at station E03094-A (Fig. 6). 473 By the time the eddy reached its offshore location, the OMZ in the eddy was deeper and 474 thicker (located between 164 and 537 m) than the OMZ measured in the coastal transition 475 zone, and the lowest dissolved oxygen concentration decreased from 7.34 µmol kg⁻¹ at 173 476 m to 1.17 μ mol kg⁻¹ at a depth of 338 m. The suboxic layer of the eddy in the open-ocean 477 eddy was located between 174 and 422 m, a layer almost three times thicker than the 478 suboxic layer of the "source water" (Fig. 6). This suggests that the observed OMZ offshore 479 OMZ-is a result of both the transportadvection of low-oxygen coastal water by an eddy and 480 continuing biological consumption as the eddy moved offshoreduring its transport. Estimated oxygen consumption rate in the OMZ of the eddy ranged from 0.29 to 44 nmol 481 $O_2 L^{-1} d^{-1}$ (~0.1 - 15 µmol $O_2 L^{-1} yr^{-1}$) in the core of the eddy (Fig. 6), which is quite high 482 483 compared to previously reported oxygen consumption rates in other OMZs in this depth 505 range (Karstensen et al., 2008). Considering the eddy's area $(20 \times 10^3 \text{ km}^2)$, a; transport of Con formato 506 ESSW of \sim 1.38 Sv) and the thickness of the layer with dissolved oxygen concentrations < 507 44.6 μ M (373 m), an oxygen deficit of 12.2 Tg of Θ_2 -is expected in the whole-subsurface 508 eddy's layer. This calculation is likely to underestimate the oxygen deficit since mixing with 509 surrounding oxygen-rich water has not been taken into account here. If the whole oxygen 510 sub-saturated oxygen layer (from ~80 to 1000m) of the eddy is considered, (from ~80 to 511 1000m), the estimated oxygen deficit transported to the oceanic region is even larger. 512 AlthoughWhile this crude, back-of-the-envelope calculation of oxygen deficit should be 513 taken with a grain of salt, it highlights the significant influence of eddies on OMZs in the 514 open ocean. When the eddy dissipates, the oxygen deficit in the subsurface layer will be 515 redistributed and will contribute to the overall oxygen budget of the ESP OMZ region.

516 The area of the 'birth' of the studied eddy (~36°S) has been identified as a hotspot of eddy

517 generation (Hormazábal et al., 2013), with~ 5-7 ITE eddies ITEs that can reach a diameter >

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518 100 km being formed every year. If the eddy studied here is representative of eddies

519 generated in the OMZ between 31° and 36° S of the eastern boundary of the Pacific Ocean,

520 <u>between 31° and 36° S</u>, advection of and continued respiration within oxygen-deficient

waters could produce a deficit as high as $60 - 85 \text{ Tg } O_2 \text{ yr}^{-1}$ within the oceanic region.

522 Subsurface biogeochemical implications of the eddy

523 OMZ regions of eastern boundary current systems are considered important with respect 524 to the nitrogen cycle. They<u>These</u> are areas where nitrogen is lost due to denitrification and 525 anammox, and are often associated with buildup of nitrite (NO₂⁻; Lam and Kuypers, 2011).

548	Much of Water masses with these features can be advected and the processes enhanced	
549	offshore as indicated by the observed accumulation of high subsurface NO_2^- in anticyclonic	
550	coastal eddies (Stramma et al., 2013).	Con formato
551	Off the Chilean coast, elevated NO ₂ - concentrations are generally found within In the present	
552	study, initial oxygen concentrations in the OMZ of the eddy were low enough to support	
553	high denitrification and anammox and, consequently, the accumulation of NO2 - Previous	
554	measurements from the area of the eddy's origin show that nitrite concentrations in	
555	hypoxic waters (<7 μ mol O ₂ -kg ⁻¹) are <0.1 μ M (Cornejo and Farías, 2012b). As an eddy is	
556	transported offshore, oxygen is consumed and conditions become favorable for	
557	denitrification. In the coastal water off Chile, elevated NO2 ⁻ concentrations are generally	
558	found in the core of the OMZ (Cornejo and Farías, 2012a; Silva et al., 2009). Previous studies	Con formato
559	conducted in the region of the eddy's formation show that nitrite concentrations in hypoxic	
560	waters (< 7 μ mol O ₂ kg ⁻¹) are < 0.1 μ M (Cornejo and Farías, 2012b). In the present study,	
561	initial oxygen concentrations in the OMZ of the eddy were low enough to support high	
562	denitrification and anammox and, consequently, the accumulation of NO2 ⁻ . In this study,	
563	the vertical distribution of NO2 ⁻ in station EO3 (oligotrophic ocean) shows a buildup of this	
564	nitrogen species, forming a subsurface NO ₂ -maximum (up to 0.56 μ M) at a depth of 250 m	
565	(Fig. 1f). The increase in NO ₂ ⁻ concentration corresponds to a NO ₃ ⁻ deficit of -13.90 μ M (Fig.	
566	6) when compared The vertical distribution of NO ₂ ⁻ in station 094-A (oligotrophic ocean)	
567	shows a subsurface NO ₂ ⁻ maximum (up to 0.56 μ M) at a depth of 250 m (Fig. 1f). The	
568	apparent buildup of NO_2^- concentration within the eddy corresponds to a NO_3^- deficit (N*)	
569	of -13.90 μ M (Fig. 6) relative to surrounding water (determined from the deviation of the	
1		

NO₃⁻:PO₄⁻³ molar ratio from the Redfield ratio according with <u>Deutsch et al., 2001</u>)<u>Deutsch</u> et al., 2001), suggesting that conditions in the eddy's anoxic zone were favorable for denitrification. A subsurface water mass with low oxygen concentrations and marked nitrate deficit has been previously observed in the oligotrophic, oceanic water of the EPS, during the Scorpio cruise (Fig. 7, Silva et al., 2009), but other nitrogen species indicative of denitrification were not measured, and tools to link this water mass to eddy activity were not well developed at that time.

599 Another indication of anthe existence of anaerobic environment conditions within the OMZ 600 of the eddy is the presence of a N_2O consumption layer. This greenhouse gas is produced 601 by nitrification and denitrification under hypoxic conditions and consumed by 602 denitrification under suboxic conditions (< 8 μ M of O₂; Bonin et al., 1989). The vertical 603 distribution of N_2O in the eddy (station EO3094-A) shows a double peak with a 604 supersaturation at the upper and lower boundaries of the subsurface OMZ (up to 224%) 605 and subsaturation (44%) in the upper region of the OMZ core (Fig. 1e), suggesting that both 606 production and consumption of N₂O occurred in the eddy. Layers depleted in N₂O have been 607 previously observed in different OMZs in coastal environments where denitrification takes 608 place (Cornejo and Farías, 2012a). To our the best of our knowledge, this is the first reported

 N_2O consumption layer in oceanic subsurface waters of the South Pacific Ocean.

Oxygen concentrations in the eddy's generation region<u>area where the eddy was formed</u> are often too high to support significant N₂O consumption (Cornejo and Farías, 2012b; Cornejo et al., 2014). (Cornejo and Farías, 2012b; Cornejo et al., 2015). Thus N₂O is being accumulated alongshore in the coastal OMZ (up to 25 nM) and consumed only in bottom Con formato

636 waters associated with suboxic conditions. TakingIn the absence of direct measurements of 637 N_2O concentrations at the time of eddy formation, we use the mean coastal N_2O 638 concentrations (22.68 ± 2.99 nM) from three previous cruises (FIP; Cornejo et al., 2015) 639 observed at the isopycnal σ_t = 26.56 kg m⁻³, corresponding to (depth with N₂O 640 undersaturation, at station 094-A) as the starting point during the eddy's generation, we 641 'initial' concentration of N₂O in the eddy. We estimated a $\aleph_2\Theta$ -consumption rate of 3.92 nmol N₂O L⁻¹ d⁻¹ during the time the eddy was moving advected offshore. This N₂O 642 643 consumption rate is half of those reported from incubation experiments conducted at the 644 upper (shallower) boundary of the OMZ off Perú (8.16 nmol L⁻¹ d⁻¹; Dalsgaard et al., 2012). Con formato Higher rates might have occurred in the center of the eddy, where more active 645 646 denitrification should beis expected. Furthermore, unlike incubation experiments, 647 estimates of in situit is likely that we have underestimated N₂O consumption are affected Con formato by diffusion from the production since mixing with upper and lower layers with that are 648 649 supersaturated with respect to N₂O-supersaturation, resulting in underestimation of the 650 N₂O reduction., was not taken into account in our calculation.

Although N₂O was sampled from discrete depths, the thickness of the N₂O consumption layer can be estimated considering that N₂O consumption does not occur at dissolved oxygen concentrations > 8 μ M (Bonin et al., 1989). AtWithin the eddy, this layer was 60 m thick (210 – 270 m) meaning that net consumption was at least ~_0.15 Gg N₂O during the offshore transfer. This N₂O consumption represents only 14% of the N₂O accumulation estimated above and below the consumption layer, meaningsuggesting that the eddy provided a net supply of ~0.85 Gg of N₂O to the oceanic region. Regardless of the N₂O

Observing both production orand consumption <u>of N₂O</u> in the eddy, the occurrence of both
 means a signifies net nitrogen loss, with possible impacts on even global nitrogen and N₂O
 balances.

This study provides further indication<u>new evidence</u> that <u>anticyclonic</u> mesoscale eddies play important roles in the biogeochemistry of the ESP (Altabet et al., 2012; Stramma et al., 2013). Previous studies have shown that coastal mesoscale eddies provideact as hotspots for microbially mediated nitrogen loss via denitrification<u>in coastal water</u>; here we show that open-ocean<u>anticyclonic</u> eddies can play a similar role in parts of the ocean that are far removed from productive coastal waters and their associated OMZs.

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near station TARA_094, labelTARA_20110316T1152Z_999).							
CruiseName of	Year	Station	Latitude	Longitude	Distanceto	F	Tabla con fo
<u>the program</u>			[°S]Location	[°WDistance	E03		
				<u>to 094-A</u>	[km]Kind		
				<u>[km]</u>	<u>of data</u>		
P06E (WOCE) ¹	1992, 2003 2010	24	32.52 <u>°</u> <u>S/80.64°W</u>	<u>93.1</u> 80.64	Profile93.1		
Biosope ²	2004	STB19	33.04 <u>°</u> <u>S/81.18°W</u>	<u>23.8</u> 81.18	Profile23.8		
TARA Oceans ³	2011	E03	33.2471	81.1267	θ		
Float ARGO ⁴ <u>ARGO³</u>	2011		33.86 <u>°</u> <u>S/79.84°W</u>	<u>137.3</u> 79.84	<u>Float</u> 137.3 ·	▶	Tabla con fo
WOA13 ²	Climatology	13604<u>13237</u>	33.50 <u>°</u>	<u>81.5041.7</u>	44.2	+	Con formate
			<u>S/81.50°W</u>			· · · · · · · · · · · · · · · · · · ·	Con formato
¹ http://www.nodc.noaa.gov/woce						Con formato	

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Table 1.Hydrographic information Sources of hydrographic data used duringin this study. The name, location, and distance of between the nearest location of the measurements and station from the station E03094-A are also reported (this profile corresponds to a cast done

²source² source: http://www.nodc.noaa.gov/OC5/indprod.html

³ http://doi.pangaea.de/10.1594/PANGAEA.836473

⁴source: http://www.coriolis.eu.org

³source: http://www.coriolis.eu.org







Figure 2.a) T-S diagram from various sampling programs in the study area; b) Dissolved oxygen profiles at Tara station 094-A (red line) and stations in its vicinity from cruises conducted on 1992 (black dashed line), 2003 (gray dashed line), 2010 (thick gray line) and 2004 (thin gray line); from Argo buoys (blue line, without oxygen), and the WOA 2013 climatology (green line). More detail on data sources are provided in Table 1.







Figure 4. Sea surface hight from satellite data at the time of sampling in Tara station 094-A (March 2011). The position of the sampling stations (black crosses) and estimated eddy trajectory (black line) with start and end locations (black circles) of the trajectory are also indicated. The red circle off Concepción (36°S) shows the probable eddy generation zone



Figure 5.Vertical distributions of dissolved oxygen (μmol kg⁻¹) in a cross-shore section at 36.5°S near the time of eddy formation (June 2010). Black line indicates the isoline of 25 μmol kg⁻¹.



Figure 6. a) Vertical distribution of Oxygen as a function of sigma-t at Tara station 094-A (within the eddy) in March 2011 (red line) and at the coast in June 2010 (black line). Estimated O_2 depletion rates are shown as gray bars, where the vertical dotted line marks zero O_2 consumption rate. b) Vertical distributions of Nitrate deficit (N*) and Nitrous oxide saturation (black triangles and line) as a function of sigma-t within the eddy at station 094-A.



