

Biogeochemical characteristics of a long-lived anticyclonic eddy

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

M. Cornejo¹, L. Bravo², M. Ramos³, O. Pizarro⁴, J. Karstensen⁵, M. Gallegos⁶, M. Correa-Ramirez¹, N. Silva⁷, L. Farias⁸, and L. Karp-Boss⁹

¹Escuela de Ciencias del Mar, Pontificia Universidad Católica de Valparaíso, P.O. Box 1020, Valparaíso Chile and Instituto Milenio de Oceanografía (IMO), Valparaíso, Chile

²Centro de Estudios Avanzados en Zonas Áridas (CEAZA), Facultad de Ciencias del Mar, Universidad Católica del Norte & Millennium Nucleus for Ecology and Sustainable Management of Oceanic Islands (ESMOI), Coquimbo, Chile

³Departamento de Biología Marina, Facultad de Ciencias del Mar, Universidad Católica del Norte & Millennium Nucleus for Ecology and Sustainable Management of Oceanic Islands (ESMOI) and Centro de Estudios Avanzados en Zonas Áridas (CEAZA), Coquimbo, Chile

⁴Programa de Oceanografía Física y Clima, Universidad de Concepción, P.O. Box 160-C, Concepción, Chile and Instituto Milenio de Oceanografía (IMO), Concepción, Chile

⁵GEOMAR Helmholtz centre for Ocean Research Kiel, Kiel, Germany

⁶Departamento de Ecología, Pontificia Universidad Católica de Chile, Santiago, Chile

⁷Escuela de Ciencias del Mar, Pontificia Universidad Católica de Valparaíso, P.O. Box 1020, Valparaíso Chile

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⁸Departamento de Oceanografía, Centro ciencia de Clima y la Resielcia (CR2) and Instituto Milenio de Oceanografía (IMO), Concepción, Chile

⁹School of Marine Science, University of Maine, Orono, ME 04469, USA

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Correspondence to: M. Cornejo (marcela.cornejo@ucv.cl)

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Eastern boundary upwelling systems are characterized by high productivity that often leads to subsurface hypoxia on the shelf. Mesoscale eddies are important, frequent, and persistent features of circulation in these regions, transporting physical, chemical and biological properties from shelves to the open ocean. In austral fall of 2011, during the Tara Oceans expedition, a subsurface layer (200–400 m) in which the concentration of oxygen was very low ($< 2 \mu\text{mol kg}^{-1}$ of O_2) was observed in the eastern South Pacific, ~ 900 km offshore (30° S, 81° W). Satellite altimetry combined with CTD observations associated the local oxygen anomaly with an intrathermocline, anticyclonic, mesoscale eddy with a diameter of about 150 km. The eddy contained Equatorial Sub-surface Water (ESSW) that at this latitude is normally restricted near the coast. Undersaturation (44 %) of nitrous oxide (N_2O) and nitrite accumulation ($> 0.5 \mu\text{M}$) gave evidence for denitrification in this water mass. Based on satellite altimetry, we tracked the eddy back to its region of formation on the coast of central Chile (36.1° S, 74.6° W). We estimate that the eddy formed in April 2010. Field studies conducted on the Chilean shelf in June 2010 provided approximate information on initial O_2 and N_2O concentrations of “source water” in the region at the time of eddy formation. Concentrations of both O_2 and N_2O in the oxygen minimum zone (OMZ) of the offshore eddy were lower than its surroundings or “source water” on the shelf, suggesting that these chemical species were consumed as the eddy moved offshore. Estimates of apparent oxygen utilization rates at the OMZ of the eddy ranged from 0.29 to $44 \text{ nmol L}^{-1} \text{ d}^{-1}$ and the rate of N_2O consumption was $3.92 \text{ nmol L}^{-1} \text{ d}^{-1}$. Our results show that mesoscale eddies in the ESP not only transport physical properties of the ESSW from the coast to the ocean interior, but also export and transform biogeochemical properties, creating suboxic environments in the oligotrophic region of the eastern South Pacific. Suboxic water masses that are advected by eddies act as hotspots for denitrification and loss of fixed nitrogen from the system.

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1 Introduction

Mesoscale eddies play a major role in vertical and horizontal transport of heat, salts and other physical, chemical and biological constituents. In the eastern South Pacific (ESP) Ocean, mesoscale eddies frequently form in the coastal transition zone off central Chile due to instability of the alongshore currents in the coastal region (Hormazábal et al., 2013; Morales et al., 2010, 2012). These eddies transport water long distances over several months across biogeographic boundaries, from the productive Humboldt (Peru-Chile) Current to adjacent oligotrophic waters of the subtropical gyre (Pizarro et al., 2006). Although eddies have been considered a net loss of nutrients from the coastal zone (Gruber, 2011), they constitute a nutrient source in the open ocean that stimulates production in oligotrophic regions (McGillicuddy et al., 1998). In addition to transporting nutrients, eddies 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). Impacts of eddies on biogeochemical processes are of particular interest for coastal transition zones of eastern boundary currents, where oxygen minimum zones (OMZs) and eddies interact (Altabet et al., 2012; Stramma et al., 2013). Open-ocean eddies associated with subsurface hypoxic or suboxic conditions have been observed in both the eastern tropical Atlantic and eastern tropical Pacific (e.g., Lukas and Santiago-Mandujano, 2001; Stramma et al., 2014; Karstensen et al., 2015). High surface productivity and downward particle flux and oxygen respiration, combined with sluggish exchange between the eddy interior and surrounding waters, have been proposed as mechanisms leading to formation of “dead zones” observed within eddies (Karstensen et al., 2015). Oxygen consumption rates within an eddy can be 3 to 5 times higher than in the surrounding oligotrophic water (Karstensen et al., 2015). Eddies containing hypoxic or suboxic water can become hotspots for nitrogen cycling, including biogenic production of N_2 and loss of fixed nitrogen from the system (Altabet et al., 2012; Stramma et al., 2013). Recent observations on eddies formed in the eastern tropical Pacific Ocean, off Peru, suggest that coastal eddies are regions

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of active fixed nitrogen loss, whereas the contribution of eddies generated in the open ocean to nitrogen loss in this region is negligible (Stramma et al., 2013).

In upwelling zones with a pronounced subsurface OMZ, such as in the ESP, eddies may play an important role in transporting OMZ waters and their microbial communities to the open ocean. The OMZ in the upwelling region of the ESP is associated with Equatorial Subsurface Water (ESSW), originating in the Pacific Ocean equatorial belt and transported poleward along the coast with the Peru-Chile undercurrent. The ESSW is characterized by active, bacterially mediated nitrogen cycling, including production and consumption of the greenhouse gas nitrous oxide (N_2O). Intense nitrification, denitrification and nitrous oxide (N_2O) production (Codispoti and Christensen, 1985) associated with ESSW is generally confined to a narrow coastal band and contributes to net nitrogen loss in this region (Lam and Kuypers, 2011). Intriguing questions about the role of coastally generated eddies abound: what biogeochemical transformations occur as this volume of water is advected offshore? Do concentrations of dissolved oxygen decrease, increase or remain the same? If changes in dissolved oxygen concentrations occur during transport, what are other biogeochemical consequences? Here, we present results of the physical and chemical characteristics of a single eddy observed ~ 900 km offshore, off central Chile. We tracked it back to its region of formation and examined changes in concentration of oxygen and nitrogen species from the time it left the coast to the time it was sampled in the oligotrophic ocean.

2 Methods

2.1 Hydrography and nitrogen data

Hydrographic data and water samples for analyses of nutrients, N_2O and surface $\delta^{15}N$ -POM were collected along a transect from Valparaíso, Chile ($33^\circ S$, $71.6^\circ W$) to Easter Island ($28.2^\circ S$, $107.4^\circ W$) during the Tara Oceans Expedition (16–31 March 2011, Fig. 1; Karsenti et al., 2011). Sampling consisted of 11 vertical profiles using a Sea-

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Bird 911 equipped with an oxygen sensor (SBE43, sampling rate 24 Hz; Picheral et al., 2014). Unfortunately, the oxygen sensor could not be calibrated on 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 September 2011 (during a stopover in Papeete). The sensor showed mean drifts of 0.101 (August 2010) and 0.405 $\mu\text{mol kg}^{-1}$ (September 2011), respectively, between successive calibrations. Because oxygen calibrations could not be done routinely, post-cruise validation of oxygen data included comparison of raw oxygen measurements with WOA13 climatology (Garcia et al., 2014) as described by Roullier et al. (2014). For the ESP transect, absolute differences between measured dissolved oxygen (SBE 43) and climatology for the upper 500 m of the water column averaged 9.1 $\mu\text{mol kg}^{-1}$ (0.03–24.47 $\mu\text{mol kg}^{-1}$) for oceanic stations and 16.7 $\mu\text{mol kg}^{-1}$ (0.06–36.24 $\mu\text{mol kg}^{-1}$) for the coastal stations. Below 850 m, absolute differences between in situ measurements and climatology averaged 6.62 $\mu\text{mol kg}^{-1}$ (0.81–19.08 $\mu\text{mol kg}^{-1}$).

Discrete water samples for N_2O (in triplicate) and nutrient (in duplicate) analyses were obtained from a rosette equipped with 12 L Niskin bottles. Samples were collected at 0, 50, 100, 150, 200, 250, 300, 400, 500, and 900 m. N_2O samples (20 mL) were fixed with 50 μL of saturated mercuric chloride and stored in the dark. N_2O concentrations were determined onshore using a gas chromatograph equipped with an electron capture detector (ECD), following a headspace technique (McAullife, 1971). A four-point calibration curve was determined with air (0.32 ppm) and N_2O standards of 0.1, 0.5 and 1 ppm (Scotty gas mixture; Air Liquid Co.).

Nutrient samples (NO_3^- , NO_2^- and PO_4^{3-}) were collected by filtering seawater (GF/F 0.7 μm filters); filtrates were stored at -20°C until analysis onshore. Concentrations of NO_3^- , NO_2^- and PO_4^{3-} were measured using a Seal Analytical AA3 AutoAnalyzer (Grasshoff et al., 1983).

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 to station E03 were used in this analysis.

2.3 Glider information at the origin of the eddy

To characterize the properties of water close to the time 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. 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 equipped with an optical oxygen sensor (Aanderaa Data Instrument oxygen Optode model 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).

3 Results and discussion

3.1 Hydrography

A vertical section of temperature, salinity and oxygen, measured along the transect from Valparaíso (33.4° S, 71.6° W) to Easter Island (27.08° S, 109.3° W) in March 2011 provides regional context (Fig. 1). A subsurface oxygen minimum layer (with dissolved oxygen concentration as low as $1.17 \mu\text{mol O}_2 \text{ kg}^{-1}$) was detected at station E03, 922 km offshore (30° S, 81° W, Fig. 1d). Dissolved oxygen concentrations observed at E03 are anomalous given that the boundary of the OMZ (defined as $\text{O}_2 < 44.6 \mu\text{mol kg}^{-1}$) at this latitude is typically located closer to shore (~ 600 km from shoreline), while its core (defined as $\text{O}_2 < 22.3 \mu\text{mol kg}^{-1}$) is confined to a thin subsurface layer that does not

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normally stretch beyond 500 km from shore (Silva et al., 2009). Suboxic conditions ($O_2 < 10 \mu\text{mol kg}^{-1}$), are thought to be confined to the shelf region and were reported only in some bottom waters over the continental shelf (Farías, 2003). Climatological data indicate that the subsurface layer at station E03 region is typically oxygenated (Fig. 1e). According to this classification of dissolved oxygen concentrations, the OMZ observed at station E03 has its upper and lower boundaries at depths of 164 and 536 m, respectively, while suboxic conditions were observed between 174 and 421 m (66 % of the OMZ).

The low-oxygen water mass was associated with higher salinities (34.60–34.66) compared to background water (Fig. 1c) and climatology for this region (34.15–34.36, for the years 1965–2012). Historical data from previous cruises conducted along the P06-WOCE transect (32.5° S) or north of the study region (e.g., 28° S, Scorpio; Silva et al., 2009; 27° S, CIMAR 5 cruise; Fuenzalida et al., 2007) do not show such extreme physical and chemical conditions at this longitude (Fig. 2a and b). The presence of the anomalous salinity signature observed in this study is supported by an independent Argo float that profiled in the vicinity of E03 (33.86° S, 79.84° W) during the Tara Oceans' sampling period (Fig. 2).

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

Reconstruction of this mesoscale eddy suggests that it formed near Concepción (36.09° S, 74.21° W), in the coastal transition zone, approximately 315 d prior to our sampling and advected northwest at a mean velocity of 2.4 cm s^{-1} (Fig. 4). Reconstruc-

tion of the eddy's velocity and direction agrees well with previously reported trajectories of eddies in the area (Chaigneau, 2005).

3.2 OMZ evolution in the eddy

In the ESP, eddies could frequently transport suboxic water from the coastal OMZ to oceanic regions. Low-oxygen water masses ($O_2 < 44.6 \mu\text{M}$) have been detected in the middle of the South Pacific Ocean (2000 km offshore at 28°S ; Silva et al., 2009), but their association with mesoscale eddies has been speculative. In the North Pacific Ocean, low concentrations of dissolved oxygen in the subsurface open ocean have been previously described in association with anticyclonic mesoscale eddies (Altabet et al., 2012; Chaigneau et al., 2011; Johnson and McTaggart, 2010; Lukas and Santiago-Mandujano, 2001), and could result from low-oxygen source waters (Lukas and Santiago-Mandujano, 2001) or from local consumption as the eddy is being transported (Karstensen et al., 2015).

To approximate the evolution of dissolved oxygen in the subsurface layer of the sampled eddy, we used underwater glider measurements, collected at 36.5°S (120 km from shore) during June 2010. This is the estimated location of the eddy one month after its formation. The distribution of dissolved oxygen measured by the glider showed a well-developed OMZ ($O_2 < 44.6 \mu\text{M}$; Fig. 5) between 104 and 352 m, with a suboxic layer between 135 and 226 m. We refer to these values as the eddy's initial subsurface oxygen concentrations. Dissolved oxygen concentrations were then compared along isopycnals between the estimated location of the eddy's origin and its offshore location at station E03 (Fig. 6). By the time the eddy reached its offshore location, the OMZ in the eddy was deeper and thicker (located between 164 and 537 m) than the OMZ measured in the coastal transition zone, and the lowest dissolved oxygen concentration decreased from $7.34 \mu\text{mol kg}^{-1}$ at 173 m to $1.17 \mu\text{mol kg}^{-1}$ at a depth of 338 m. The suboxic layer in the open-ocean eddy was located between 174 and 422 m, a layer almost three times thicker than the suboxic layer of the "source water" (Fig. 6). This suggests that the observed offshore OMZ is a result of both the transport of low-oxygen

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coastal water by an eddy and continuing biological consumption as the eddy moved off-shore. Estimated oxygen consumption rate in the OMZ of the eddy ranged from 0.29 to 44 nmol O₂ L⁻¹ d⁻¹ (~ 0.1–15 μmol O₂ L⁻¹ yr⁻¹) in the core of the eddy (Fig. 6), which is quite high compared to previously reported oxygen consumption rates in other OMZs in this depth range (Karstensen et al., 2008). Considering the eddy's area (20 × 10³ km²), a thickness of the layer with dissolved oxygen concentrations < 44.6 μM (373 m), an oxygen deficit of 12.2 Tg of O₂ is expected in the whole subsurface eddy's layer. If the whole oxygen sub-saturated layer (from ~ 80 to 1000 m) of the eddy is considered, the oxygen deficit transported to the oceanic region is even larger. Although this crude, back-of-the-envelope calculation should be taken with a grain of salt, it highlights the significant influence of eddies on OMZs in the open ocean. When the eddy dissipates, the oxygen deficit in the subsurface layer will be redistributed and will contribute to the overall oxygen budget of the ESP OMZ region.

The area of the “birth” of the studied eddy (~ 36° S) has been identified as a hotspot of eddy generation (Hormazábal et al., 2013), with ~ 5–7 ITE eddies that can reach a diameter > 100 km formed every year. If the eddy studied here is representative of eddies generated in the OMZ between 31 and 36° S of the eastern boundary of the Pacific Ocean, advection of and continued respiration within oxygen-deficient waters could produce a deficit as high as 60–85 Tg O₂ yr⁻¹ within the oceanic region.

3.3 Subsurface biogeochemical implications of the eddy

OMZ regions of eastern boundary current systems are considered important with respect to the nitrogen cycle. They are areas where nitrogen is lost due to denitrification and anammox, and are often associated with buildup of nitrite (NO₂⁻; Lam and Kuypers, 2011). Much of these features can be advected and enhanced offshore as indicated by the observed accumulation of high subsurface NO₂⁻ in anticyclonic coastal eddies (Stramma et al., 2013). In the present study, initial oxygen concentrations in the OMZ of the eddy were low enough to support high denitrification and anammox and, consequently, the accumulation of NO₂⁻. Previous measurements from the area of the eddy's

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origin show that nitrite concentrations in hypoxic waters ($< 7 \mu\text{mol O}_2 \text{ kg}^{-1}$) are $< 0.1 \mu\text{M}$ (Cornejo and Farías, 2012b). As an eddy is transported offshore, oxygen is consumed and conditions become favorable for denitrification. In the coastal water off Chile, elevated NO_2^- concentrations are generally found in the core of the OMZ (Cornejo and Farías, 2012a; Silva et al., 2009). In this study, the vertical distribution of NO_2^- in station E03 (oligotrophic ocean) shows a buildup of this nitrogen species, forming a subsurface NO_2^- maximum (up to $0.56 \mu\text{M}$) at a depth of 250 m (Fig. 1f). The increase in NO_2^- concentration corresponds to a NO_3^- deficit of $-13.90 \mu\text{M}$ (Fig. 6) when compared to surrounding water (determined from the deviation of the $\text{NO}_3^- : \text{PO}_4^{3-}$ molar ratio from the Redfield ratio according with Deutsch 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 (conducted at 1969; 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.

Another indication of an anaerobic environment is the presence of a N_2O consumption layer. This greenhouse gas is produced by nitrification and denitrification under hypoxic conditions and consumed by denitrification under suboxic conditions ($< 8 \mu\text{M}$ of O_2 ; Bonin et al., 1989). The vertical distribution of N_2O in the eddy (station E03) shows a double peak with supersaturation at the upper and lower boundaries of the subsurface OMZ (up to 224 %) and subsaturation (44 %) in the upper region of the OMZ core (Fig. 1e), suggesting that both production and consumption of N_2O occurred in the eddy. Layers depleted in N_2O have been previously observed in different OMZs in coastal environments where denitrification takes place (Cornejo and Farías, 2012a). To our best 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 are often too high to support significant N_2O consumption (Cornejo and Farías, 2012b; Cornejo et al., 2014). Thus

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Table 1. Hydrographic information used during this study. The name, location, and distance of the nearest station from the station E03 are also reported (this profile corresponds to a cast done near station TARA_094, label TARA_20110316T1152Z_999).

Cruise	Year	Station	Latitude [° S]	Longitude [° W]	Distance to E03 [km]
P06E (WOCE) ^a	1992, 2003 2010	24	32.52	80.64	93.1
Biosope ^b	2004	STB19	33.04	81.18	23.8
TARA Oceans ^c	2011	E03	33.2471	81.1267	0
Float ARGO ^d	2011	–	33.86	79.84	137.3
WOA13 ^b	Climatology	13 604	33.50	81.50	44.2

^a <http://www.nodc.noaa.gov/woce>,

^b source: <http://www.nodc.noaa.gov/OC5/indprod.html>,

^c <http://doi.pangaea.de/10.1594/PANGAEA.836473>,

^d source: <http://www.coriolis.eu.org>.

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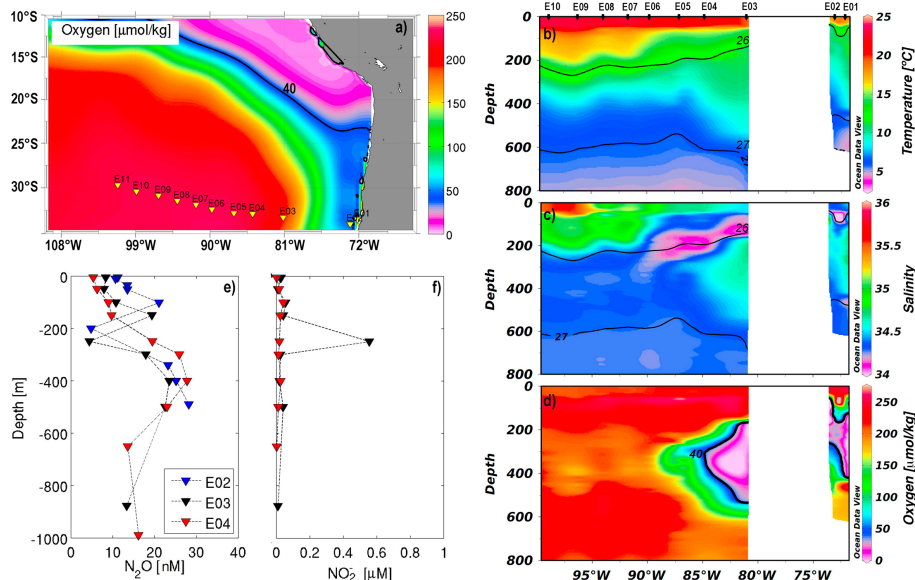


Figure 1. Top, left panel: **(a)** Climatology of dissolved oxygen distribution ($\mu\text{mol kg}^{-1}$) at a depth of 200 m in the eastern South Pacific Ocean. Yellow triangles indicate locations of stations during the Tara Oceans cruise. Right panel: Vertical distribution of **(b)** temperature ($^{\circ}\text{C}$) **(c)** salinity and **(d)** dissolved oxygen at the coast and on the ocean transect during the Tara Ocean cruise. Black lines in **(b)** and **(c)** indicate the 26.0 and 27.0 kg m^{-3} stisopycnals. Black line in **(d)** indicates the isoclines of 40 $\mu\text{mol kg}^{-1}$ of dissolved oxygen. **(e)** Vertical distribution of N_2O at stations E02 (34.0° S / 73.0° W, blue triangles; TARA_20110312T1637Z_093_EVENT_CAST), E03 (33.2° S / 81.1° W, black triangles; TARA_20110316T1152Z_999_EVENT_CAST) and E04 (32.8° S / 84.8° W, red triangles; TARA_20110317T1815Z_999_EVENT_CAST). **(f)** Vertical distribution of NO_2 – at stations, E03 (black triangles) and E04 (red triangles). For a complete detail of the Tara CTD cast please refer to Picheral et al. (2014).

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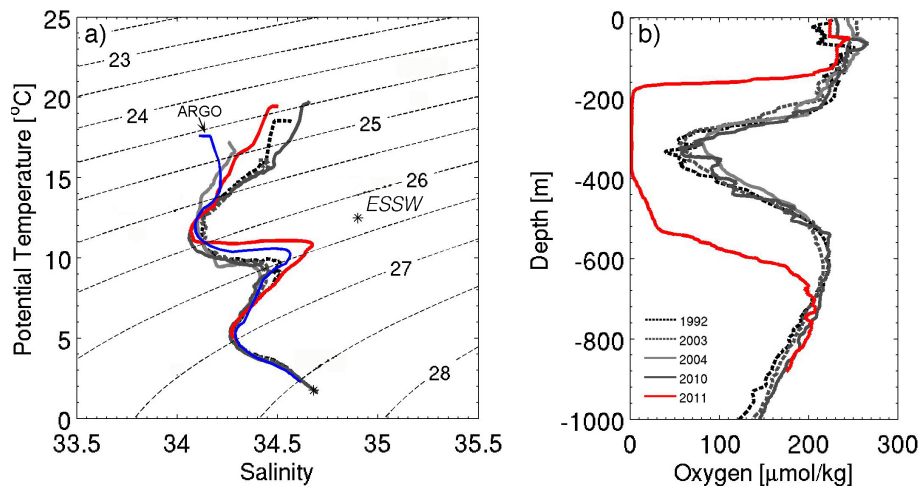


Figure 2. (a) T - S diagram from various sampling programs in the area of study; (b) Dissolved oxygen profiles at station E03 and its vicinity. The CTD data correspond to the Tara Oceans cruise (red line), P06; WOCE transect (1992, black dashed line; 2003, gray dashed line; 2010, thick gray line); Biosope cruise (2004; thin gray line); and from Argo buoys (blue line, without oxygen).

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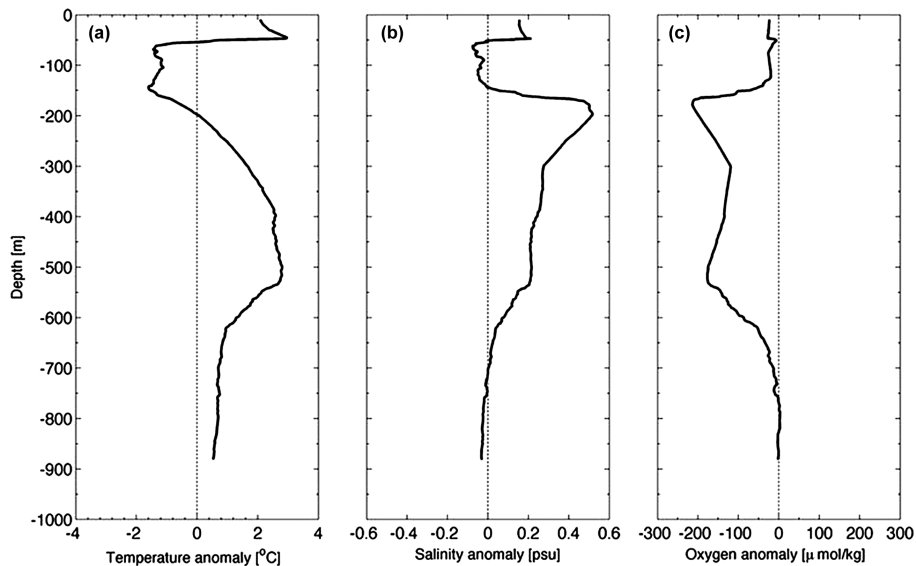


Figure 3. Vertical anomalies of: **(a)** temperature ($^{\circ}\text{C}$), **(b)** Salinity, **(c)** dissolved oxygen ($\mu\text{mol kg}^{-1}$) in station E03 compared with WOA 2009 climatology.

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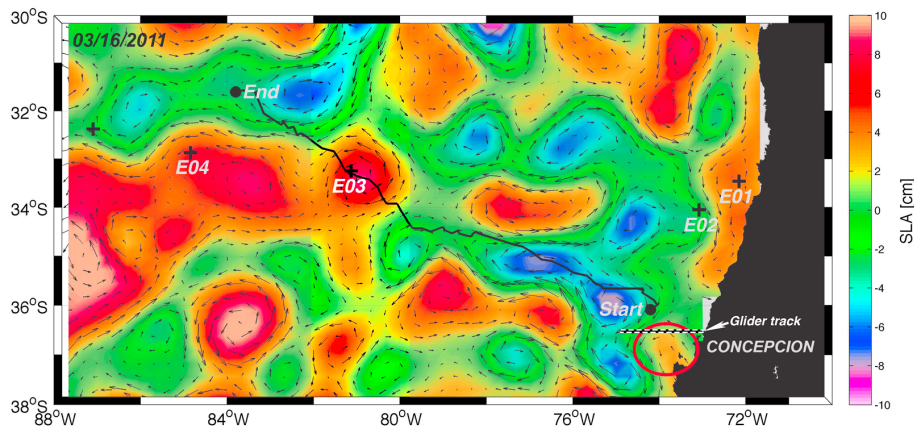


Figure 4. Sea level from satellite data during E03 sampling in March 2011. The position of the sampling stations (black crosses) and estimated eddy trajectory (black line) with start and end locations (black circles) of the trajectory are also indicated. The red circle off Concepción (36° S) shows the probable eddy generation zone.

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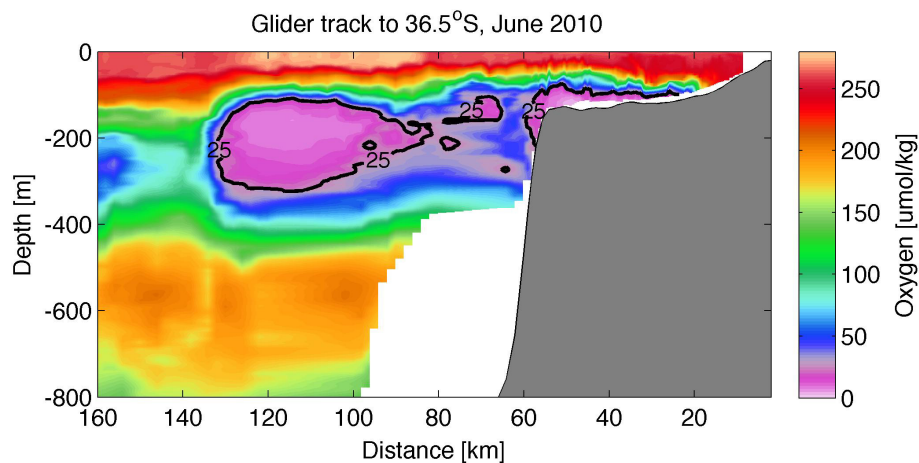


Figure 5. Vertical dissolved oxygen distribution ($\mu\text{mol kg}^{-1}$) in a cross-shore section at 36.5° S during the coastal eddy's generation in June 2010 (colors). Black line indicates the isocline of $25 \mu\text{mol kg}^{-1}$.

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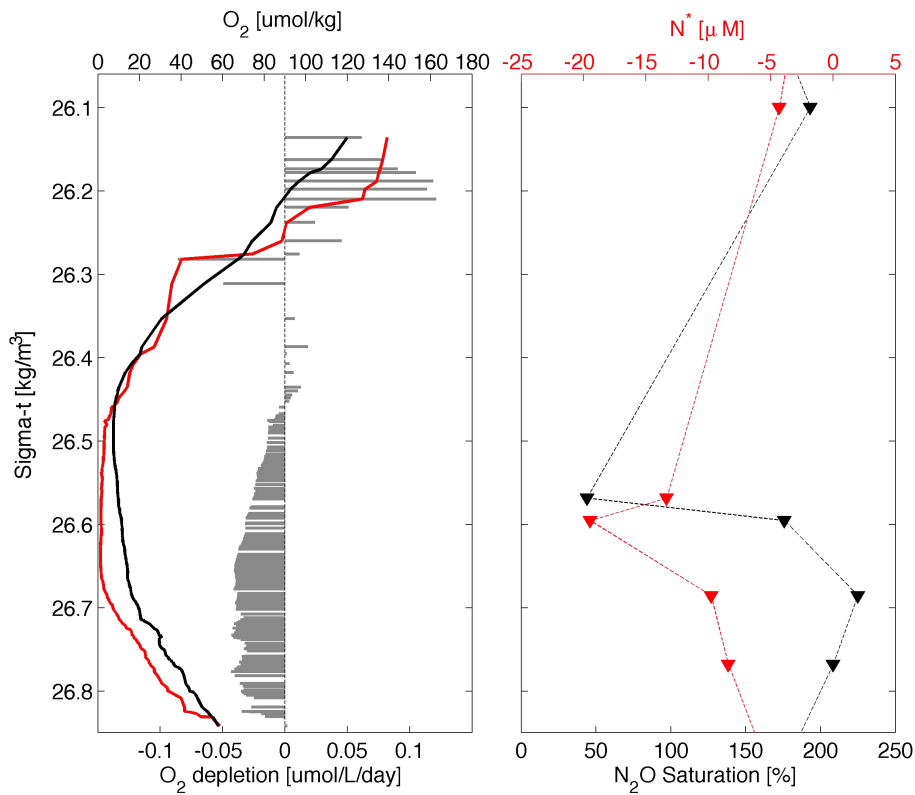


Figure 6. A plot of σ_t vs. oxygen concentration and depletion rate at station E03 in March 2011 (red line) and at the coast in June 2010 (black line). Estimated O_2 depletion rates are shown as gray bars, where the vertical dotted line marks zero O_2 consumption rate.

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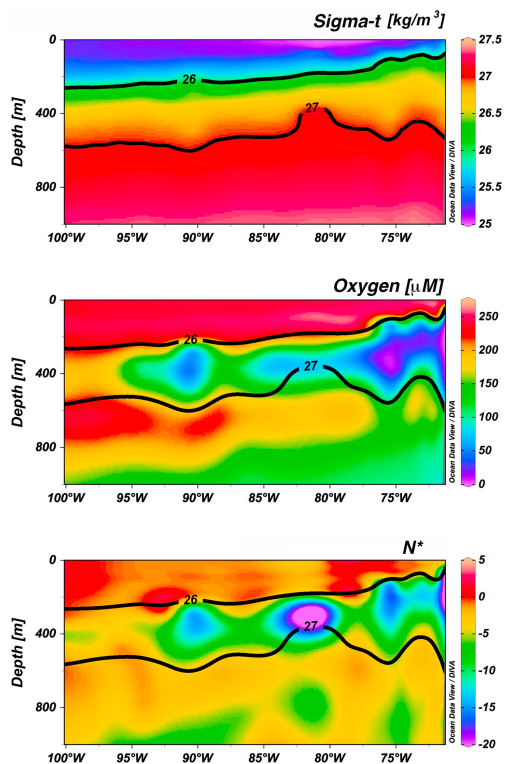


Figure 7. Vertical distribution of σ_t , dissolved oxygen and N^* (according to Deutsch et al., 2001) along 28° S in the Eastern Southern Pacific Ocean (72° to 100° S) during Scorpio cruise (June 1967). Black lines refer to σ_t of 26 and 27 kg m⁻³.

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